Organic Pollutants in Wastewater I
Methods of Analysis, Removal and Treatment

Edited by
Inamuddin
Abdullah M. Asiri
Ali Mohammad
Wastewater represents an alternative to freshwater if it can be treated successfully for re-use applications. Promising techniques involve photocatalysis, adsorption, nanocomposites, and membranes. The book focuses on the following topics:


**Keywords:** Wastewater Treatment, Organic Pollutants, Organic Dyes, Photocatalysis, Nanocomposite Photocatalysts, Photocatalytic Degradation, Adsorption, Membrane Filtration, Fenton Processes, Biosorbents, Phenolic Compounds, Carbon Quantum Dots, Methylene Blue Degradation, ZnO Composites, TiO₂ Based Nanocomposites
Organic Pollutants in Wastewater I
Methods of Analysis, Removal and Treatment

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Preface

The demand for freshwater resources has been continuously increasing, mainly in arid and semi-arid regions. Wastewater has been considered as an alternative water resource if it has been treated to a level that permits for re-use applications. The presence of organics in wastewater streams poses a great challenge and hence several treatment technologies have been developed for the remediation of organics from treated effluent streams. The presence of organics in wastewater has been associated with mining and oilfields, municipal and industrial effluents, and runoff from agricultural farms.

In this first volume of a 2-volume set, topics such as photocatalysis, adsorption, nanocomposites, and membranes are covered. For example, the first chapter presents the potential application of agricultural solid wastes as adsorbents for dye removal via physical and chemical activation methods. In the second chapter, effluent detoxification and degradation kinetics of organic dyes were investigated using Fenton and photo-Fenton processes through which several process operating conditions were optimized. The third chapter presents an interesting topic and discusses the degradation of methylene blue using nanocomposites as a potential photocatalyst. Several characterization methods were used supported by experimental studies. Furthermore, the fourth chapter is another application of the agricultural and agro-industries based wastes as low-cost biosorbents through which raw, processed and charred biomass were investigated. In the fifth chapter, great attention is given to the use of carbon quantum dots (CQDs) for photocatalytic degradation of organic pollutants. Different synthesis methods such as hydrothermal treatment, a microwave method, electrochemical and synthetic route are also highlighted. Another important topic is highlighted in the sixth chapter; which is the removal of phenolic compounds from wastewater. Chemical and physical methods of determining phenolic presence as well as the degradation of phenols via biological processes are discussed in this chapter. The seventh chapter highlights the evolution of photocatalysis process and its future trends as a promising technology in wastewater treatment. More attention is given to the fundamentals of titanium dioxide (TiO₂) based photocatalysts, including basic mechanism of heterogeneous photocatalysis, advantages, and challenges of TiO₂ based photocatalysts. The eighth chapter discusses the decomposition of organic dyes via photocatalysis process. It includes a critical review of oxide-semiconductor nanomaterials towards photocatalytic wastewater purification. The structural aspects, nanostructure formation process and the various parameters affecting catalytic activity, photocatalytic applications of oxides based catalysts for efficient photocatalytic degradation of organic dyes are reviewed. The ninth chapter summarizes recent progress in the fabrication and photocatalytic efficiency of various types of zinc oxide (ZnO) composites for degradation of organic pollutants. In
the tenth chapter, TiO$_2$ based nanocomposites are thoroughly discussed. The eleventh chapter is dedicated to the membrane filtration process and its applicability in the removal of organics from industrial wastewater. It also focuses on different types of pollutants present in food and agro-alimentary industries and their membrane-based treatment methods.

We believe that this volume is a great source to a broad range of professionals such as industrial operators, professional engineers, academicians, undergraduate and graduate students, technicians, and many others.

Lastly, we extend our great appreciation to the contributing authors for their countless efforts towards the preparation of this book. We would like to thank all distributors, authors, and other who conceded consent to utilize their figures, tables, and schemes. However, every effort has been made to get the copyright approvals from the individual proprietors to join reference to the reproduced materials; we might need to offer our sincere articulations of disappointment to any copyright holder if unintentionally their benefit is being infringed.

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Chapter 1

Green Applications of Magnetic Sorbents for Environmental Remediation

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Abstract
Adsorption of both inorganic and organic xenobiotics by utilizing a variety of biomaterials signifies promising prospects for the reduction of environmental pollution. For the purpose of improving manipulation of the biosorbents, their potential magnetic derivatives have been investigated. These diamagnetic biomaterials of different origin (lignocellulosic material, prokaryotic and eukaryotic cells, food wastes, biopolymers etc.) can be magnetically modified in order to acquiring ‘smart’ biomaterial exhibiting a definite response to the external magnetic field. This chapter summarizes the synthesis procedures of magnetic modification and eco-friendly applications of these ‘smart’ biomaterials both in nano and micro-sized forms.

Keywords
Magnetic Separation, Magnetic Modification, Sorbents, Biomaterials, Carriers, Biocatalysts

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1. Introduction

The treatment of contaminated soil and industrial effluents is a challenging task in respect of controlling water pollution, purification and soil remediation [1]. Several land areas, streams, and rivers get contaminated by untreated disposal of heavy metals, organic compounds, and other hazardous substances. Presently, increasingly metals are being used in process industries. Therefore, waste streams from these industries contain metal ions which cause devastating and permanent contamination of the environment because of their non-biodegradable and persistent nature [2]. The water pollution due to heavy metals (chromium, lead, mercury, zinc, cadmium etc. has gained more and more attention, due to increasing applications of heavy metals in the chemical industry for chrome plating, dyes, and battery etc. [3]. Presently, the removal of toxic materials from soil and effluents has attracted the attention of many researchers [4, 5]. Of late, scientists have investigated a range of innovative processes for the effective removal of pollutants from contaminated water and soil. Remediation techniques for environmental cleanups can be categorized as biological, chemical and physical processes [6]. For instance, several mechanisms such as biodegradation, electron-beam irradiation, extraction, adsorption, air sparging and incineration are being applied to remove or reduce the pollutants [7]. Chiefly, the adsorption of pollutants is widely utilized in this field due to simple applicability, cost-effectiveness and eco-friendliness of this approach [8]. Moreover, the removal by adsorption is mainly decided by the properties of various materials that have been used as adsorbents, namely activated carbon [9,10], zeolites [11,12], iron oxides [13,14] and silica [15]. Much interest lies in the utilization of biological materials such as bacteria, algae, and fungi for the removal and recovery of
metals among these mechanisms [16-18]. The biomasses have revealed cost-effective and eco-friendly characteristics [19]. Bio sorbents are intrinsically broad sourced, low-cost, and rapidly useful for adsorption. In recent times, many reports are available regarding the correlative development on heavy metal remediation by immobilized microorganisms [20]. Magnetic separation has been a promising ways for an environmental remediation mechanism because of nonexistence of contaminants like flocculants production with an added advantage of large amount of waste removal within a short time span [1]. Magnetic particles have been used as an upcoming new sorbent to adsorb heavy metal ions where an external magnetic field is used to resolve the difficulty of separation [21]. The dual integrated techniques of bio-adsorption and magnetic separation has the advantage of being a green application, flexibility, eco-friendly features and economic viability. Hence the present chapter suggests the green application of magnetic sorbents for environmental cleanup.

2. Features of magnetic solid phase extraction (MSPE)

At present, the magnetic solid phase extraction (MSPE) with functionalized magnetic particles (FMPs) as adsorbents has created an innovative niche in the analytical community. During the 70s era, Robinson et al. (1973) first reported magnetic separation for biotechnological purpose [22]. Later, Wilkstrom et al. [23] reported magnetically susceptible additives like ferrofluids and external magnetic field for faster liquid-liquid phase extraction. In the 90s, Towler et al. [24] used for the first time manganese dioxide coated magnetite as an adsorbent for metal recovery from seawater, and in 1999, Safarikova et al. [25] first coined the term magnetic solid phase extraction for analytical purposes. For this purpose, an external magnetic field is employed to separate the target analyte from the aqueous solution by addition of FMPs into the sample solution and adsorption of the analyte onto the surface of magnetic beads. The FMPs can re-disperse in aqueous solution on the removal of the external magnetic field, which makes washing and desorption more convenient as depicted in Fig. 1. The FMPs can also facilitate mass transfer by increasing the interfacial area present between the analyte and sample solution [26]. Among the FMPs used, iron-oxides (Fe₃O₄ and Fe₂O₃) are the most common because of certain characteristics of simple and fast preparation for large-scale production; convenient modifications due to presence of abundant functional groups on the surface; easy mode of operation without centrifugation or filtration, due to their super-para-magnetic properties; appropriate recoverability and reusability as well as the excellent dispersibility in aqueous solution to reach rapid extraction equilibrium [26]. Unlike the conventional SPE; pretreatment of the sample is very convenient in MSPE, due to fast and easy phase separation by an external magnetic field [27]. The magnetic
sorbents have been widely utilized as optimized materials for applications in medical, biological and engineering fields; in addition to their progressively use for trace metal analysis as well. Recently, several exciting techniques have been applied for analysis and on-line pre-concentration of heavy metal ions present in contaminant samples using micro-or nanomagnetic particles.

2.1 Magnetic sorbent materials

Different types of sorbent materials like ion exchangers, octadecyl (C$_{18}$), polymers, carbon nanotubes, activated carbon and magnetic particles have been effectively used in solid phase extraction. Usually, FMPs constitute of magnetic elements namely Fe, Ni, Co or their oxides and alloys with added super-para-magnetic or ferromagnetic characteristics. Upon magnetization, the FMPs act as small permanent magnets, so that due to magnetic interaction they can form aggregates or lattice-like structure. Moreover, the ferromagnetic particles are known to be a permanent magnet, so they can easily form lattice structure on the removal of the magnetic field, whereas the super-paramagnetic particles preserve no residual magnetism upon removal of the magnetic field. The FMPs are obtainable in a large range of sizes from micro-sized to nanometer-sized (1 to 100 nm) particles, which have drawn attention in technological research for their high 

Figure 1. Schematic representation showing the technique applied for functionalized magnetic solid phase extraction (MSPE).
dispersibility, large surface area and significant surface to volume ratio resulting in inefficient adsorption capacity [28,29]. The nano-sized FMPs presently have a range of potential utilization in environmental, biological and food analysis due to their easiness for surface modifications, the simplicity of large-scale production and effective recycle [30]. A list of application of various magnetic sorbents for heavy metal removal has been provided in Table 1. The purely inorganic magnetic materials including Fe₃O₄ relatively intend to the formation of the lattice-like structure causing a change in their magnetic characters. Also, their possible low selectivity makes them un-adaptable for samples with composite matrices. Therefore, to overcome this limitation, an appropriate modification of the magnetic coating (core) with the attachment of specific active group is required. Such coatings onto the surface of FMPs are termed ‘shell’ as shown in Fig. 2. These are obtained by attachment of inorganic elements like silica and alumina or organic components like surfactant or any suitable polymer in order to increase their chemical stability, oxidation resistance and improving the uptake of specific ions [31-34]. These ‘shells’ which are attached to the FMPs are utilized for different analytical purposes [35-37] and environmental pollutant treatment [38-41]. For advanced environmental remediation through a fluidized bed which is magnetically stabilized, the FMPs can be fluidized and kept in a magnetic filter column while the waste effluent can be pumped through the column [42]. Complex FMPs like titano-magnetite have been often used as alternatives to fluidized magnetically stabilized beds possibly due to adequate retention of functionalized magnetic sorbents and free water flow for effective separation by its matrix [43]. Certain specialized microorganisms have the capability of forming inorganic FMPs like ferrous sulfate which has application for consuming heavy metals through metabolic processes, which makes removal of heavy metals simplified and eco-friendly [44]. Some other groups of naturally occurring magnetotactic bacteria have the ability to orient themselves in the direction of the magnetic field. These find an efficient application in organic contaminant removal from effluent by the enzymatic actions [45]. Surfactant covered magnetite particles have attracted the scientific community in the extraction of organic pollutants such as 2-hydroxyphenol [46]. Certain polymer coated floating magnetic sorbent materials having vermiculite iron oxide composite coating have been applied for fast and efficient separation of spilled oil pollutant in water [47].
Table 1: Applications of magnetic sorbents for toxic heavy metal removal.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Applications</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>For heavy metal uptake and magnetic separation, highly magnetic iron sulfide sorbent development</td>
<td>Certain microorganisms have the ability to produce magnetic iron sulfide. Likewise, it was for metal uptake.</td>
</tr>
<tr>
<td>2</td>
<td>A clay substituted layered double hydroxide (LDH) type sorbent with Fe and Ni ions developed for As removal and magnetic separation</td>
<td>Under very high gradient field of about 5T; layered double hydroxide (LDH) synthesized from Fe and Ni demonstrated better uptake potential for As.</td>
</tr>
<tr>
<td>3</td>
<td>Magnetic hydrogel synthesis for removal of heavy metal pollutants</td>
<td>Magnetic hydrogels with recycling features based on 2-acrylamide-2 methyl-1-propane sulfonic acid were employed for removal of heavy metal ions of Cd(II), Co(II), Fe(II), Ni(II), Cu(II), Cr(III) from liquid samples.</td>
</tr>
<tr>
<td>4</td>
<td>Bismuthioal-II-immobilized Functionalized magnetic particles (FMPs) for separation and preconcentration of heavy metals like Pb, Cu, Cr and their analysis using ICP-OES.</td>
<td>Bismuthioal-II-immobilized FMPs with recycling features demonstrated static sorption capacities of 8.6, 5.3 and 9.4 mg/g for Pb, Cu, and Cr, respectively. Specific sensitivity in detection and general advantage of utilizing magnetic assistance.</td>
</tr>
<tr>
<td>5</td>
<td>Magnetic Fe-Ni oxide synthesis from waste Ni liquid cause selective sorption of Cr (VI)</td>
<td>A magnetic Fe-Ni oxide with recycling features demonstrated maximum of 30 mg/g Cr (VI) uptake capacity.</td>
</tr>
<tr>
<td>6</td>
<td>Magnetic separation for magnetic ion and particle by magnetic chromatography with novel magnetic column.</td>
<td>Separation of magnetic materials or FMPs with varied susceptibilities Different fractionating column designed based on FMP size, susceptibility, material mobility and column height.</td>
</tr>
<tr>
<td>7</td>
<td>Synthesis and characterization of magnetic chelating resin made from chitosan for removal of Cu (II), Co (II) and Ni (II)</td>
<td>The magnetic carrier on the chitosan-based character.</td>
</tr>
</tbody>
</table>
2.2 Synthesis and characterization of magnetic sorbents

The synthesis of any magnetic particle generally involves three fundamental steps; namely, production of the magnetic material, coating formation of the magnet ore and the specific characterization of the magnetic core-shell structure. For the preparation of magnetite as a magnetic core, the chemical co-precipitation method of Fe$^{2+}$ and Fe$^{3+}$ ions in aqueous solution is commonly applied [31]. The synthesis process constitutes vigorous stirring of a solution mixture of FeCl$_3$.6H$_2$O and FeCl$_2$.4H$_2$O in ultrapure water at 70-85°C in the presence of atmospheric nitrogen and rapid addition of liquid ammonia, resulting in a dark precipitate, confirming the formation of nanoparticles of magnetite. Alternatively, magnetite can also be prepared by solvothermal reaction process in the presence of ethylene glycol, oleic acid and hexadecylamine [48]. Conversely, the maghemite FMPs are derived from monodispersive nano-sized Fe$_3$O$_4$ particles upon successive dissolution in acid medium and heating at 90 to 100 °C for 30 min so that the magnetite particles (Fe$_3$O$_4$) get oxidized entirely [49]. Alternatively, cation diffusion is also a way to complete oxidation of maghemite FMPs by long-term exposure to air resulting in γ-magnetite FMP formation [50]. Recently, a new innovative reactor system; the submerged circulative impinging steam reactor unit (SCISR) was introduced for the synthesis of γ-maghemite FMPs, which has a special flow configuration, causing a perfect sequential circulation of mixing flow and non-mixing-flow and micro-mixing.
effect in the impingement zone, thereby providing the unique advantage of preparing \( \gamma \)-maghemite FMPs ultrafine powders as well as nanoparticles [51]. The magnetic core coating can be done using silica, alumina or any other oxides of metal and organic polymers. The cores of FMPs coated with silica are generally synthesized by the Stober method through a sol-gel reaction involving the use of tetraethoxysilane (TEOS) in acidic or basic solution in the presence of nitrogen. There is no requirement of any primer to promote the adhesion and deposition of silica since the oxides of iron have strong bonding affinity toward silica. The silane coupling agents including amine, thiol, carboxylic and C18 are applied to introduce the functional groups onto the surface of the silica coated FMPs by silanation. Fig. 3 illustrates the schematic process for the preparation of silica coated FMPs modified with various functional groups. The generation of alumina coated FMPs are carried out by dissolving aluminum-isoproxide in a mixed solution of magnetite FMPs and ethanol with the help of ultrasonic, combined with the drop-wise mixing and vigorous shaking of water-ethanol into the suspension of the FMPs [37].

![Diagram](image.png)

**Figure 3.** The mechanism for the synthesis of Schiff base functionalized iron-oxide-silica hybrid magnetic nanoparticles for pre-concentration of heavy metals like Hg (II), Pb (II), Cu (II), Cd (II) etc.
The fundamental techniques for the identification and characterization of FMPs include transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Transmission electron microscopy is used for determining differences in electron density, allowing analysis of shape and size of the FMPs while scanning electron microscopy is used for morphological and structural characterization of the FMPs. For determination of the crystalline structure specifically, a technique known as selected-area electron diffraction (SAED) is generally applied [52]. For determination of the composition and structural analysis of maghemite or magnetite in the solid matrix, X-ray diffraction is used. The porosity and mean diameter measurement along with the observation of the surface area of modified or unmodified FMPs are carried out using nitrogen adsorption-desorption porosimetry following the Brunauer-Emmett-Teller (BET) process [53]. The investigation of the adsorption mechanism of the target heavy metals and detecting the surface functional groups of solids is performed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) [31]. Lately, the magnetic properties of the FMPs were studied using a Vibrating sample magnetometer (VSP) operating at large scale magnetic operations and maximum magnetic fields. These analytical techniques highlight important information regarding the FMPs. Also, certain innovative techniques like thermo-gravimetric analysis, Mossbauer spectrometry are applied for the estimation of thermal stability and magnetic behavioral properties of magnetic sorbents respectively [38]. Table 2 summarizes, in general, the magnetic solid phase extraction (MSPE) with inorganic and organic coating and detection techniques for removal of heavy metal ions from aqueous solutions.

Table 2: List of MSPE with inorganic and organic coating for removal of metal ions from water samples.

<table>
<thead>
<tr>
<th>Target metal ions</th>
<th>Coating material</th>
<th>Functional groups</th>
<th>Eluent</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd (II)</td>
<td>SiO₂</td>
<td>Metal-organic framework (Fe₃O₄-Py/MOF)</td>
<td>NaOH + K₂SO₄</td>
<td>Flame atomic absorption spectrometry (FAAS)</td>
</tr>
<tr>
<td>Cr (III), Al (III)</td>
<td>SiO₂</td>
<td>3-Mercapto-propionic acid (MPA)</td>
<td>HNO₃</td>
<td>Flame atomic absorption spectrometry and electrothermal atomic absorption spectrometry (FAAS, ETAAS)</td>
</tr>
</tbody>
</table>


### Organic Pollutants in Wastewater I

<table>
<thead>
<tr>
<th>Target metal ions</th>
<th>Core particles</th>
<th>Shell material</th>
<th>Functional groups</th>
<th>Maximum adsorption capacity $q_m$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>SiO$_2$</td>
<td>Zincon</td>
<td>HCl</td>
<td>ETAAS</td>
</tr>
<tr>
<td>Cu (II), Cd (II), Ni (II), Co (II), Pb (II)</td>
<td>SiO$_2$</td>
<td>Cetylpyridinium bromide</td>
<td>HNO$_3$ + Methanol</td>
<td>ETAAS</td>
</tr>
<tr>
<td>Cr (III), Cu (II), Pb (II)</td>
<td>SiO$_2$</td>
<td>Bismuthiol II</td>
<td>HNO$_3$</td>
<td>Inductively coupled plasma atomic emission spectrometry (ICP-AES)</td>
</tr>
<tr>
<td>Cr (III), Cu (II), Pb (II)</td>
<td>SiO$_2$</td>
<td>Dithizone</td>
<td>HNO$_3$</td>
<td>ICP-AES</td>
</tr>
<tr>
<td>Cd (II), Cr (III), Mn (II), Cu (II)</td>
<td>SiO$_2$</td>
<td>TiO$_2$</td>
<td>HNO$_3$</td>
<td>Inductively coupled plasma mass spectrometry (ICP-MS)</td>
</tr>
<tr>
<td>[UO$_2$]$^{2+}$</td>
<td>SiO$_2$</td>
<td>Quercetin</td>
<td>-</td>
<td>UV/Vis</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>Al$_2$O$_3$</td>
<td>Sodium dodecyl sulphate</td>
<td>HNO$_3$</td>
<td>FAAS</td>
</tr>
<tr>
<td>Cr (III)</td>
<td>ZrO$_3$</td>
<td>-</td>
<td>HNO$_3$</td>
<td>FAAS</td>
</tr>
</tbody>
</table>

### MSPE using organic coating material

<table>
<thead>
<tr>
<th>Target metal ions</th>
<th>Core particles</th>
<th>Shell material</th>
<th>Functional groups</th>
<th>Maximum adsorption capacity $q_m$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd (II)</td>
<td>Iron oxide (Fe$_3$O$_4$)</td>
<td>Ammonium cellulose</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>Cr (VI), As (V)</td>
<td>Fe$_3$O$_4$</td>
<td>Chitosan</td>
<td>Chitosan anthranilic acid glutaraldehyde (Schiff’s base)</td>
<td>58.48, 62.42</td>
</tr>
<tr>
<td>Cu (II), Cd (II), Ni (II)</td>
<td>Fe$_3$O$_4$</td>
<td>Chitosan</td>
<td>2-aminopyridine-glyoxal</td>
<td>124.23, 84.53, 67.35</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Fe$_3$O$_4$</td>
<td>Polypyrrole</td>
<td>-</td>
<td>169.49</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Fe$_3$O$_4$</td>
<td>Polyethylamine</td>
<td>Montmorillonite</td>
<td>8.8</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>Fe$_3$O$_4$</td>
<td>Calcium alginate</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>Cu (II), Co (II), Ni (II)</td>
<td>Fe$_3$O$_4$</td>
<td>Polymethylmethacrylate</td>
<td>Ethylene diamine</td>
<td>50.3, 51.7, 49.6</td>
</tr>
<tr>
<td>Cu (II), Co (II)</td>
<td>Fe$_3$O$_4$</td>
<td>Carbon</td>
<td>-</td>
<td>3.21, 1.23</td>
</tr>
<tr>
<td>Cd (II), Hg (II)</td>
<td>Fe$_3$O$_4$</td>
<td>Activated carbon</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co (II)</td>
<td>Fe$_3$O$_4$</td>
<td>Graphene oxide</td>
<td>-</td>
<td>12.98</td>
</tr>
</tbody>
</table>
3. Overview of magnetically responsive bio-sorbents

Biological compounds of various origins are essential sources of biologically active materials and other biomaterials derived substances and products. The magnetic nano-, as well as micro-particles (FMPs), have found several applications in different fields of medicine, biotechnology, biosciences and environmental technology. The varied responses of several sizes of FMPs enable different applications including targeting, localization and specific separation of these magnetically responsive FMPs. This is aided by an external magnetic field for uniform separation using a strong permanent magnet, generation of heat and rise in negative T2 contrast by magnetite FMPs. This is especially observed when there is a gradual increment in viscosity of the magneto rheological fluids upon exposure to an external magnetic field or in magnetic resonance imaging [54]. This is often applied for magnetic modification of diamagnetic materials including microbial cells and plant-derived substances. This is also used in case of biopolymers, magnetic labeling of bioactive substances and functional ligands such as enzymes, aptamers, and antibodies [54].

Several research groups are involved in applying the different processes leading to the synthesis of homogenous FMPs with uniform size, structure, composition, coating etc. [55]. Commercially several non-magnetic particulate compounds are available including adsorbents, chromatographic substances, catalysts, microbial cells etc. In most cases, the efficiency of such materials can be enhanced by their structural and functional modifications thereby causing the formation of functionalized magnetically responsive bio-sorbents. Such enhancement can significantly reduce the rigorous separation of magnetic complexes. Lately, it was observed that both functionalized magnetic nanoparticles as well as magneto-ferritin exhibit peroxidase-like activity [56].

There can be different possibilities for the separation of magnetic adsorbents and removal from treated aqueous solutions and suspensions, relating to the character of FMPs and volume of suspension.

In several cases, easily available and a cost-effective magnetic separator or a small piece of strong magnet is often utilized for separation of the micrometer-sized biological complexes.

The nanometer-sized magnetic compounds generally require more elaborate separation techniques like high gradient magnetic separator (HGMS). For large scale, magnetic separation processes using magnetic microparticles, the drum magnetic separators are utilized. Scientists are coming up with the strategy of new innovative and inexpensive magnetically responsive materials to improve the efficiency of magnetic separation processes for large-scale units. Therefore, magnetic modification of inexpensive bio-
sorbents and carriers can genuinely direct the required substances for large-scale biotechnological and environmental applications.

3.1 Mechanism of magnetic biomaterial modifications

In addition to the currently applied mechanism on the selective development of distinct magnetic structures, alternative processes causing the formation of effective magnetic responsive biomaterials have been developed. These methods based on the principle of ‘post-magnetization’ of the already existing natural or experimental FMPs (diamagnetic or paramagnetic). The entire mechanism of magnetic biomaterial modification of nonmagnetic components was deduced by Mosbach at the end of the 70’s and beginning of the 80’s in the 20th century when magnetic modification of gel particles for column chromatography was done using a suitable magnetic fluid (Ferrofluid) [54]. Such magnetic modification processes led to the development of uniformly bio-specific magnetic functionalized derivatives with general application in ligand binding affinity chromatography. The mechanism of post-magnetization generally aims for the synthesis of heavy magnetic composite substances, where the original FMP (diamagnetic or paramagnetic) is basically accountable for biological, bio-adsorptive, bio-catalytic or bio-carrier function of the formed material, whereas the magnetic labels (which are often formed of magnetite or maghemite nano and microparticles deposited on the pores, gels or surface of treated materials) are accountable for strong magnetic behavior of the formed complex material [54]. The commonest approach for magnetic modification is based on the alkali precipitation and heating of ferrous and ferric salts in presence of the treated material [57]. On the other hands, erbium ions can be used to modify the non-magnetic materials which defend their remarkably high atomic magnetic dipole moment in several chemical structures [58]. The post-magnetization mechanism can be followed for several inorganic substances including clays, activated charcoal, synthetic polymer particles, biopolymer materials, waste plant products, microbial cell units, entire algal and cyanobacterial cell units and several others [54].

3.1.1 Magnetic fluid modification

As already discussed, for magnetic modification, various ionically and sterically stabilized magnetic fluids nanoparticles are utilized. Following the easy mechanism of addition of perchloric acid stabilized ferrofluids with methanol suspension of an inorganic waste powder material to be modified (eg. sawdust), which caused precipitation of FMPs from the ferrofluids on the particles surface [54].

In general, perchloric acid stabilized ferrofluids are used for the post magnetization modification of living baker’s or brewer’s yeast cells after washing with acetate or
glycine-HCl buffer. Conversely, tetramethyl ammonium hydroxide stabilized ferrofluids are also applied for the modification of baker’s yeast after washing with glycine-NaOH buffer thereby leading to the precipitation of nano-sized FMPs on the cell surface [57]. Several magnetic modifications can be conducted in varied physiological states of yeast cells, likewise; surface modifications can be obtained only in dormant yeast cells, whereas for actively growing cells, the modification causes the accumulation of magnetic modifier in the periplasmic space [59].

Fig. 4 (1,2) showing SEM and TEM images of ferrofluid stabilized Saccharomyces cerevisiae cells attached to nano-sized functionalized magnetic particles (FMPs) and their aggregates on the surface of the cell as well as on the cell wall [59]. Effective and innovative post-magnetization mechanism is inclined on the application of water-based ferrofluid stabilized with perchloric acid, carefully mixed for proper modification and completely dried. This process has advantages due to its ease of application in various biological, inorganic and polymer materials to be converted to their magnetic components [60].

3.1.2 Microwave aided magnetic modification

Presently synthesis of FMPs from ferrous sulfate with the aid of microwave facility has been studied. Usually, such microwave irradiation can increase several chemical reaction phenomena in the production of organic and inorganic materials. Unlike conventional heating methods, chemical reactions assisted by microwave irradiate extremely rapidly and the products can be acquired within a short time span. The simple, one pot modification process includes treatment of iron (II) salt at high pH in the regular kitchen microwave oven (700-750 W, 2450 MHz) under specified time in presence of the treated substance. During the treatment process, several sub-micrometer FMPs in nano and micro sizes are deposited on the surface of the treated substances in the form of single units or aggregates [61]. For the modification of reasonably high pH and heat stable materials, direct microwave aided magnetization is followed. Nevertheless, for magnetic modifications of more sensitive and selective materials, an indirect microwave aided magnetization has been developed. The FMPs in nano and micro sizes (nano FMP ranges between 25 to 100 nm; which on synthesis form aggregates of size 20 µm) have been produced from ferrous sulfate at high pH in a microwave oven [62]. The substances to be magnetically modified were carefully added to the magnetite or maghemite particle suspension and completely dried at 70 °C which led to the deposition of functionalized magnetite or maghemite nanoparticle aggregates on the surface of the modified material as shown in Fig. 4 (10). The indirect post-magnetization mechanism applying microwave synthesized FMPs are used for the magnetic treatment of thermally sensitive substances
like powdered enzymes and biopolymers [107]. These enzyme powders are suspended in aqueous media which prevent their solubilization (like highly concentrated glycol solution, ammonium sulfate, ethanol, and methanol) and cause cross-linkage with glutaraldehyde. The post magnetization process using nano and micro-sized magnetite or maghemite particles produced using microwave technique was successfully studied at a very low temperature in the freezer (-20 °C). The magnetically synthesized enzymes can generally take several weeks to dry and form the powder enzyme state completely [57]. Application of lower temperature drying techniques has been followed for such magnetically synthesized enzymes, which were immobilized on non-magnetic carriers and also for other sensitive biomaterials like starch grains.

3.1.3 Mechano-chemical magnetic modification

Of late, mechanochemical techniques were used to produce functionalized magnetite or maghemite particles and ferrites nanoparticles. The field of mechano-chemistry characterizes one of the several ways of chemical activation. In solid state mechano-chemistry, certain non-thermal chemical reactions occur due to the deformation and factorization of solids, which are mechanically processed by milling or grinding of the substances. During such processes, the extremely high mechanical energy causes chemical reactions and phase transformations [63]. The simple standard mechanism for mechano-chemical production of magnetic bio-composite materials includes grinding of hydrated ferrous and ferric chlorides in a mortar at room temperature for 10 minutes and addition of an excess of sodium chloride to the precursors to prevent agglomeration. This was followed by addition and thorough mixing of a specific amount of target non-magnetic powder material with the magnetic mixture for a definite time. Powdered alkaline hydroxide was added as the last mixing ingredient, followed by further grinding for about 10 minutes. For completing the mechano-chemical process, the magnetically modified substance was carefully washed with distilled water. Several varieties of inorganic and biological materials including starch, pollen and maize grains, potato, powdered lignocellulosic compounds (as shown in Fig. 4 (3,9)) have successfully modified magnetic mechanism [64,102].
4. Application of magnetically responsive bio-sorbents

With the development of scientific techniques, different magnetic derivatives of biosorbents have been widely studied and applied as adsorbents, biocatalysts, and carriers etc. Some bio-composites which have been extensively studied are listed below:

- Individual biopolymer sorbents of diverse origin such as polysaccharides (chitin, alginate, cellulose, agar, chitosan, agarose, plant gums etc.) proteins (keratin, casein, ovalbumin, gelatin, albumin) and poly-hydroxy alkanoates (e.g. poly-hydroxybutyrate).

- Complex biopolymer sorbents of various origins such as lignocellulosic materials of plant origin like spent barley grain, sawdust, straw, peanut husks, spent coffee and tea residues etc.

- Microbial and microalgae cellular biomass such as baker’s yeast (*Saccharomyces cerevisiae*), fodder yeast (*Kluyveromyces marxianus*) and unicellular algae like *chlorella vulgaris*.

- Aquatic seagrass and macroalgae such as *Posidonia oceanic* (which forms Neptune balls) and various species of *Sargassum* [57].

- Inorganic biosorbents like egg shells, sheaths of *Leptothrix ochracea* or other different diatoms.

Table 3 lists the magnetically responsive bio-sorbent composites materials which have been applied for potential environmental sustainability. It is clear from Table 3 that several routes are available for the synthesis of different types of magnetic bio-sorbent composites. Both the nano and micro-sized bio-sorbent composites have been significantly utilized in model experiments. Presently, magnetic derivatives of chitosan open an attractive research area for scientists for inorganic as well as organic xenobiotics removal. Furthermore, magnetic derivatives from plant waste matter also pave a new pathway for green applications to magnetic biosorbent research.
Table 3: Magnetic responsive biocomposites for heavy metal removal.

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Composite type</th>
<th>Target metals</th>
<th>Matrix</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>Magnetically responsive chitosan resin</td>
<td>Au (II), Ag (I), Hg (II)</td>
<td>Aqueous solution</td>
<td>Reused with 0.1 M KI, glutaraldehyde cross-linking</td>
</tr>
<tr>
<td></td>
<td>Amine nano-sized FMP chitosan composite</td>
<td>Pb (II), Cu (II), Cd (II)</td>
<td>Aqueous solution</td>
<td>Reused with weak acid and ultrasound</td>
</tr>
<tr>
<td></td>
<td>Magnetic chitosan, quarternary amine resin</td>
<td>Cr (VI)</td>
<td>Alkaline aqueous solution</td>
<td>Have glutaraldehyde cross-linking</td>
</tr>
<tr>
<td></td>
<td>Cross-linked chitosan-diacetyl monoxime (Schiff’s base) resin</td>
<td>Co (II), Cu (II), Ni (II)</td>
<td>Aqueous solution</td>
<td>Have glyoxal cross-linking, reused with 0.01-0.1 M EDTA</td>
</tr>
<tr>
<td></td>
<td><em>Saccharomyces cerevisae</em> magnetically responsive chitosan particles</td>
<td>Cu (II)</td>
<td>Aqueous solution</td>
<td>The cells were immobilized on chitosan coated nano-sized FMP</td>
</tr>
<tr>
<td>Chitin</td>
<td>Magnetite particles immobilized on chitin</td>
<td>Cu (II)</td>
<td>Aqueous solution</td>
<td>Maximum adsorption potential 53.19 mg/g</td>
</tr>
<tr>
<td>Alginate</td>
<td>Calcium alginate encapsulated magnetic sorbent</td>
<td>AsO$_4^{3-}$</td>
<td>Aqueous solution</td>
<td>After biosorption, arsenate was reduced to arsenite</td>
</tr>
<tr>
<td></td>
<td>Magnetically responsive alginate beads</td>
<td>Co (II)</td>
<td>Aqueous solution</td>
<td>Beads having Cyanex 272, reused using HNO$_3$</td>
</tr>
<tr>
<td></td>
<td>Magnetically responsive alginate microcapsules</td>
<td>Ni (II)</td>
<td>Aqueous solution</td>
<td>Maximum adsorption potential 60.0 mg/g</td>
</tr>
<tr>
<td>Gum arabic</td>
<td>Biosorption of gum on surface of nanosized FMP</td>
<td>Cu (II)</td>
<td>Aqueous solution</td>
<td>Maximum adsorption potential 38.5 mg/g</td>
</tr>
<tr>
<td>Gellan gum</td>
<td>Magnetic nanosized particles with gel beads</td>
<td>Pb (II), Cr (III), Mn (II)</td>
<td>Aqueous solution</td>
<td>Reused with sodium citrate</td>
</tr>
</tbody>
</table>
4.1 Magnetically responsive biopolymer

The search for an effective sorbent that can be applied for environmental remediation has been obstructed by a preferred combination of simplicity to process, selectivity, and high affinity. Although, synthetic polymeric materials with these preferences have been developed from time to time; nevertheless the expense of ultrafiltration, toxicity of synthetic materials, generation of polymeric wastes and incompatibility of these materials with the environment have made them unsuitable for large-scale environmental application [65]. To resolve such difficulties, a plausible solution could be the mixtures of several types of natural biological substances. Thus, biopolymers which are a new generation of polymeric substances occurring that are still in the development stage have attracted attention for effective replacement of conventional synthetic materials due to a positive impact on sustainable development. One of the attractive biopolymers for the synthesis of non-magnetic as well as magnetic biocomposite adsorbents is chitosan. For proper biosorption of heavy metal ions, the amino and hydroxyl groups present in chitosan provide the main sorption sites. For the chelation process, nitrogen atoms of the amino chemically react with heavy metal cations under a neutral condition, whereas the protonated amino groups show a strong affinity with heavy metal anions by electrostatic forces under acidic conditions [66]. The technique for the uptake of certain metal ion may vary with respect to the pH and composition of the solution. The biosorption possibility of heavy metal ions increases with lower pH conditions (acidic) and on chitosan with decreasing rate of acetylation. For instance, chitosan has been reported to show higher sorption capacity than chitin for the heavy metal ions Pb(II), Hg(II), Cd(II), Cr(III) as well as for several dyes over a wide range of pH. Chitosan without post magnetization modification depicts reduced adsorptive capacity to alkaline and alkaline earth metal ions [67]. Generally, under acidic conditions, chemisorption plays an important role along with the main functional amino groups whereas, under alkaline conditions, physical-sorption dominates with chief functional hydroxyl groups. Fig. 4 (10) depicts optical microscopy image showing microwave stabilized magnetically responsive biopolymer chitosan microparticles [107]. Interactions of chitosan with organic dyes are through electrostatic attraction, hydrophobic forces and physic-adsorption but the molecular size and anionicity of dyes also affect the degree of biosorption [67]. Besides chitin and chitosan, other biopolymers like alginate and plant gums have also attracted attention in synthesis and application of magnetically responsive biosorbents for environmental remediation as listed in Table 3. Fig. 4 (4) depicts an image taken from an optical microscope showing magnetically responsive biopolymer derivative alginate microparticles [103]. In certain reported experiments, the functionalized magnetic biopolymers (FMBPs) have been used as a matrix to capture active sorbents for their
modifications. For instance, the hydrophobic octadecyl nano-sized functionalized magnetite or maghemite particles were captured into hydrophilic barium alginate materials to produce a novel type of magnetic solid phase extraction (SPE) bio-sorbent utilized for the pre-concentration of polycyclic aromatic hydrocarbons and phthalate ester contaminants from marine waste samples. Here, the hydrophilicity of barium alginate capturing agent improvises the dispersibility of sorbents in marine samples while the magnetic properties of functionalized magnetite or maghemite particles facilitate the magnetic separation [68]. In a recently reported article, sodium alginate based magnetic carbonaceous material (Fe-SA-X, where X is heating temperature) was caged by carbothermal reduction of ferric alginate, which was intended for efficient removal of heavy metal ion like Cr (VI) from wastewater sample. The authors have studied the optimization, kinetics, and adsorption isotherm modeling parameters for Cr (VI) onto the samples and characterized using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy, nitrogen sorption, and Raman spectrometry. On observing the whole biosorption mechanism, the results depicted that the newly developed magnetic biosorbent is promising enough for the removal of toxic metal ions like Cr (VI) from water [69].

4.2 Magnetically responsive plant derivatives

The magnetically modified substances derived from plants are potential sorbents for the removal of organic and inorganic contaminants. Recent research on magnetic bio-sorbents is concentrated on developing and describing the sorption properties of naturally occurring eco-friendly, cost-effective and compatible green biomaterials like agriculture and wood industry by-products and bio-wastes like sawdust, barley straw, tea bark, peanut skins etc. There are plenty of agricultural by-products and bio-waste materials needing to be disposed and are therefore ready to be utilized, cheap, and easily available in good quantities. The use of such bio-wastes for removal of contaminants would be favorable for both the environment and industries. Research articles describing the application of such magnetically modified agro wastes (sawdust, spent tea and coffee residues) in the treatment of undesirable materials have attracted the scientific society, although there are only a few examples of FMPs which are derived from plants applicable for xenobiotics removal. These materials have been tested in laboratory experiments and large-scale functions are yet to be obtained. Various modification mechanisms have been followed like ferrofluid treatment for sawdust, peanut husks, spent grain, spent tea and coffee residues etc. and microwave aided treatment include straw or spent rooibos (Aspalathus linearis) tea biomass [70-74]. Fig. 4 (3) depicts an experimental image of magnetically responsive plant derivative spent grain before and after magnetically treated separation [102]. For instance, the water-based ferrofluid
stabilized with perchloric acid has been utilized for laboratory scale magnetic modification of certain plant-derived substances which had the maximum adsorption capacity values reaching up to almost 100 mg/g. These biomaterials exhibit potential adsorption of not only heavy metal ions but also inorganic and complex water-soluble dyes, oils and various other undesirable pollutants from wastewater. Certain biomaterials (like wheat bran derived from wheat grain which was modified using a microwave magnetic procedure produced functionalized magnetite and maghemite particles or FMPs) have been applied for the sorption of uranium ions. These plant-derived magnetically responsive sorbent materials can also be used as cost-effective, biocompatible carriers for immobilization of different enzymes. For instance, spent grain which was magnetically modified by ferrofluids was used as cost-effective, magnetically responsive and compatible carrier for immobilization of *Candida rugosa* lipase. Another modification mechanism was also performed using native as well as poly (ethyleneimine) modified magnetic wheat grain. This material on post magnetization modification can be an effective low-cost magnetic carrier for immobilization of various enzymes which will find application in biotechnology and food and feed technology [75].

### 4.3 Magnetically responsive microalgae

The rising sources for biomass and metabolite production with substantial use in the fields of food, feed, marine, pharmaceutical, cosmetics and fuel industries are the prokaryotic blue-green algae and eukaryotic microalgae. The eukaryotic microalgae perform a pivotal part in several environmental applications by acting as potential nitrogen fixers, biocatalysts in biotransformation and degradation of organic contaminants, wastewater treatment material and also parts of biosensors for identification of polluting substances [76-78]. From a commercial point of view, the effectiveness of these eukaryotic organisms is based on their rich metabolic functions thereby producing valuable products. These are also easily cultivatable, adaptable to various natural conditions and rapidly growing organisms. The expense of industrial process can be decreased by their application due to their ability to use natural sunlight, flue gas or wastewater as energy and nutrient sources. In addition, they can grow all around the year in enormous productivity independent of weather situations and in non-arable or wasteland unlike conventional marine plants or agricultural crops with much less requirement of land area [79]. In general, frequently occurring algal cells are able to interact with various nano and microparticles including gold, silica, platinum, palladium, silver and carbon nanotubes. These modified organisms mainly sustain their viability by themselves although the presence of such foreign particles on their cell surfaces, in intracellular organelles or protoplasm can offer certain supplementary functionalities. The modification with nano and micro-sized FMPs is chiefly important and such magnetically
responsive microalgal cells have been considerably studied and applied in several applications [80]. The majority of microalgal cells exhibit diamagnetic characteristics. Fig. 4 (8) showing TEM image of a fine section of polyallylamine hydrochloride stabilized FMPs coated with microalgal cells of *Chlorella pyrenoidosa* [106]. The post magnetic modification of diamagnetic cells can be carried out by forming strong affinity of nano or micro-sized FMPs with the cell surface. The mechanism used here involves non-specific attachment of FMPs by ferrofluid treatment or magnetic microparticles binding onto cell surface, also polymer assisted FMP binding, covalent immobilization of FMPs onto microalgal cell surface or vice versa, selective interactions with immunomagnetic nano and micro-sized particles or entrapment onto biocompatible polymers [81-83]. The magnetic properties of the modifiers are basically due to the presence of nano or micro-sized functionalized magnetite or maghemite particles or their mixtures as well as ferrite particles. Generally, the phenotypic alteration or viable mutation of modified cells is not affected by bonding with the FMPs. In selective cases, the particles attached to the surface of the cell can be internalized by the treated cells and appears in the protoplasm. In most cases, the usual features of all magnetically modified or responsive cells are their definite interactions with external magnetic field.

The first discovered magnetotactic alga, from the coastal mangrove swamp near Fortaleza, Brazil, found in brackish mud and water samples were identified as *Anisonema platysomum*. The organism has cells enclosed with numerous, uniformly organized chains of bullet shaped magnetite crystal particles of sizes 80 to 180 nm in length and 40-50 nm in width. The coordinated structures of magnetosomes are so specifically arranged in this algae that this organism possibly bio-mineralizes and organizes endogenous magnetite crystal particles in a definite well-controlled fashion within the cell, where intracellular structural filaments play an important role in the production and functionalization of magnetosome chain as also shown by the magnetotactic bacteria [84].

Techniques for dewatering microalgae cultures, along with their advantages and disadvantages have been extensively reported in the literature. For instance, the harvesting of microalgae includes different solid-liquid separation techniques and steps such as centrifugation, gravity filtration, flocculation methods, sedimentation and flotation steps [85-87]. One of the critical bottlenecks in the large-scale production process is the biomass recovery since it claims almost 30-40% of biomass production expense. Generally, large microalgal biomass volumes are processed for concentrating the cells due to the fact of smaller size of microalgae (about 5-10 nm) so cell separation becomes difficult with low sedimentation velocity, also colloidal characteristics are present with repulsive negative surface charges and reduced biomass concentrations in culture broths (about 60.5 kg/m³ dry biomass in large-scale systems) [84]. Therefore, it is
very important to lower the volume of microalgal suspension after cultivation by a 2-step mechanism with concentration factors of 100-200 in the first and 2-10 in the second process to make the downstream processing cost effective. It is always essential to pre-concentrate the microalgal broth cultures using simple and low-cost techniques of flocculation before applying the rigorous cell separation techniques of centrifugation or filtration [84]. The different harvesting methods for microalgae are typically case dependent; likewise, the actual product price, selection of harvesting mechanisms can be varied per preferred moisture content in the product. Usually, a sludge formed due to gravity sedimentation has a higher amount of moisture content than the recovered microalgal biomass by centrifugation. This could significantly control the expense of product recovery when the related downstream processing step is an energy demanding (thermal-drying) process [88].

Nano and micro-sized FMPs have the capability of harvesting agents. The bio-separation processes employing such FMPs involve by the non-destructive feature of the magnetic field, the utility of simple techniques and instruments, biocompatibility of FMPs, effective manipulation and regeneration [84]. The magnetic harvesting process of microalgae using an external magnetic field after biosorption of a magnetic agent onto microalgal cells can also be a one-step synthesis process because flocculation and separation both occur simultaneously [87]. The preferred magnetic harvesting agents for various microalgal species are generally in the form of uncoated nano or micro-sized FMPs or as functionalized nanocomposites that constitute a magnetic core coated with silica. This silica coating can equally carry selective functional groups like polyethyleneimine (PEI) or cationic polyelectrolytes like chitosan (CS), polydiallyldimethyl ammonium chloride(PDDA) and cationic polyacrylamide (CPAM) [89].

The microalgal cells can be applied as a part of whole cell biosensors, also immobilized on transducers for different types of immobilization processes like physical-sorption, chemical cross-linking, matrix incorporation etc. Magnetic immobilization can overcome some important drawbacks of these processes including reduction of viability of algal cells. The magnetic immobilization technique constitutes of temporary attachment of FMPs on biosensor surface by a strong external magnetic field. The FMPs are held and manipulated on the electrode by minute magnets positioned under the electrode [90]. Presently, a whole cell amperometric herbicide biosensor on magnetically responsive microalgae and screen-printed electrodes has been studied. The microalgae cells coated with nano-sized FMPs were biocompatible and stabilized by polyallylamine hydrochloride with an average diameter of 15 nm. Suspension of algal cells was magnetized during vortexing after addition of FMP suspension. These modified cells
were employed for the construction of amperometric biosensors having a screen-printed electrode, which was connected with supporting tetrafluoroethylene plate with slotted 2 mm cylindrical NdFeB magnet in the space under the working area of electrode thereby producing strong magnetic field surrounding the surface of the electrode. A drop of a suspension containing a mixture of an electron mediator (K₃Fe (CN)₆) and electrolyte (Na₂SO₄) was kept around the working area of the electrode and the magnetized algal cells were instantly covered above the magnetic field area. This particular biosensor was employed for analysis and quantification of triazine herbicides. The biosensor was capable of quantifying other xenobiotics including atrazine of 0.9 to 74 mM and propazine of 0.6 to 120 Mm with limits of detection values of 0.7 and 0.4 mM respectively [91].

Magnetically responsive diatoms have been considered as an effective drug carrier for in-vivo functions. This material exhibits low cytotoxic potential, due to the presence of low toxic silica and protein-coated FMPs. Also, this material depicted very slow biodegradability in body fluids [92].

Typical non-magnetic immobilized algal cells have been used for the removal of various pollutants and xenobiotics. However, magnetically modified cells of *C. vulgaris* were employed as the latest low-cost magnetic sorbent for the removal of a variety of water-soluble toxic dyes. The dried microalgal cells were magnetically modified using ferrofluids concentrated with perchloric acid. The experimental data from a published dye sorption process were fitted to Langmuir isotherm and the highest adsorption capacities were in between 24.2 and 257.99 mg/g of dried magnetically responsive algal biosorbents for Saturn blue LBRR and aniline blue respectively [84].
Fig. 4 (1) SEM image of ferrofluid stabilized Saccharomyces cerevisiae cells showing attached functionalized magnetic particles (FMPs) and their aggregates on the surface of the cell [9]. (2) TEM image showing ferrofluid modified Saccharomyces cerevisiae with attached magnetite nanoparticles on the cell wall [59]. (3) Magnetically responsive plant derivatives including spent grain before and after magnetically treated separation [102]. (4) Image taken from optical microscope showing magnetically responsive biopolymer derivative alginate microparticles [103]. (5,6) Entrapment of Sachharomyces cerevisiae cells in magnetically responsive millimetre or micron-sized alginate bead particles and functionalized magnetic particles (FMPs). Scale bar showing the size of 50 µm [104]. (7) TEM image showing magnetically responsive microbial cells including dried fodder yeast (Kluveromyces fragilis) [105]. (8) TEM image showing a fine section of polyallylamine hydrochloride stabilized FMPs coated with microalgal cells of Chlorella pyrenoidosa [106]. (9) SEM image showing mechanochemically modified native potato starch [64]. (10) Image taken from optical microscope showing microwave stabilized magnetically responsive biopolymer chitosan microparticles [107]. (11) Image taken from optical microscope showing a fine section of polyallylamine hydrochloride stabilized FMPs attached to Caenorhabditis elegans nematode [108].
4.4 Magnetically responsive activated carbons

One of the important and versatile materials applied as an effective adsorbent, catalyst and supporting catalyst with large surface area, high porosity, wide range of surface chemistry and surface reactivity is activated carbons (ACs) or activated charcoal. AC is used for several applications including treatment of contaminants from aqueous or gaseous phases, purification as well as recovery of materials. AC sorption is an immensely attractive domain to many industrial, economic and agricultural areas as varied as food, chemical, cosmetics, petroleum, agro products, pharmaceuticals, nuclear or automobile, treatment of industrial effluent, drinking water, domestic and urban waste water etc. The only disadvantage of activated carbons is their high production cost in comparison to other adsorbents. Nowadays, preparation of AC from green sources or waste materials has been a primary perspective of several types of research. The production cost can be lowered by opting easily available, naturally occurring raw materials [93]. One of the important possible approaches for improving the sorption efficiency of AC is the magnetic modification of such green activated carbons which can be simply separated from complex systems or positioned to a definite place using a strong external magnetic field.

The magnetic modification of activated carbons (ACs) is generally occurred due to the presence of nano or micro-sized FMPs within the pores of carbon particles or on the surface of carbon particles or inside the gels having co-entrapped carbon particles. Such nano or micro-sized FMPs modifying AC are chiefly magnetite or maghemite or different types of ferrites, although at times metallic iron and nickel have also been prepared and used as magnetic labels. The simplest and the most frequently applied magnetic modification is the alkaline precipitation of ferrous and ferric salts in presence of AC along with heat treatment of the liquid suspension forming particles of magnetite or maghemite or different types of ferrites. Alternatively, the ACs are impregnated with salts of iron or nickel by heat treatment at high temperature and the resulting modified FMPs formed; depends on the types of salt used, heating and atmosphere conditions. Alternatively, magnetic ACs can be synthesized using standard precipitation process by continuous stirring of carbon powder and magnetite or maghemite suspension mixture followed by heat drying at 40°C. Interestingly ferrofluid stabilized triethanolamine oleate was employed for the rapid preparation of magnetically modified AC by step-by-step process of impregnation, washing and air drying at 90 °C [94]. Another reported mechanism showed treatment of AC and magnetite mixture in a high energy planetary ball mill. In another mechanism, the micro-sized FMPs were coated with a slim layer of epoxy resin which gradually enhanced the binding affinity of AC. Furthermore, the
encapsulation of AC with FMPs inside a selective and specific biopolymer or synthetic polymer is another perspective of magnetically responsive activated carbons.

ACs has been frequently applied as potential sorbents for several organic and inorganic xenobiotics, radionuclides and noble materials [95]. In general, magnetically modified AC derivatives exhibit similar sorption mechanism for target substances as the native non-magnetic ACs. Of late, several studies reported the utilization of magnetic activated carbon for site remediation and xenobiotic removal from polluted water areas. Magnetic AC is an additional supplement to magnetically responsive biocomposites applied for such purposes. For instance, a novel magnetically separable composite photocatalyst, (titania based magnetic AC) was synthesized by deposition of anatase titania onto a magnetic AC surface and the photocatalytic activity of the samples was analyzed by degradation of reactive brilliant red X-3B under UV irradiation. This particular biocomposite could be regenerated and reused with only slight reduction of its photocatalytic activity [96]. Modified AC with zero-valent Fe deposits demonstrated dehalogenation activity for chlorinated and brominated hydrocarbons. The contaminants were deposited and enriched at the surface of the magnetic AC and by reductive dechlorination, these contaminants were destroyed at the iron clusters. Regeneration studies of magnetically responsive ACs after adsorption processes have been performed to keeping the production expenses as low as possible. Recently, a magnetic CuFe2O4 AC composite was experimented by the chemical co-precipitation mechanism. The regeneration process was performed after adsorption of acid orange II by heating in an inert atmosphere. The results demonstrate that CuFe2O4 particles possibly catalyze thermal pyrolysis of the adsorbed dye material. The regeneration experiment predicted that full adsorption capacity of the composite sorbent was restored upon thermal treatment and could be reused for several cycles [95]. Alternatively, hydrogen peroxide has been widely used for such regeneration procedure and the magnetite or maghemite nano-sized particles were found effective for attaining high regeneration efficiency. Magnetic AC has been applied as a potential sorbent for dyes and heavy metal ions during the development of magnetic solid phase extraction (MSPE). About 460-fold enrichment of materials was obtained using magnetic AC as sorbent and water-soluble dyes and heavy metal ions as analytes. Moreover, magnetic AC can also become an exclusive easy to prepare the magnetic composite substance for smart innovative project materials in college or high school education. The simple laboratory experiment includes the preparation of magnetically responsive AC within 2 h using mostly easily available chemicals. Potential adsorption of dyes and metal ions by magnetic AC can be analyzed just by visual evaluation without the requirement of any spectrometer and the magnetic separation procedure can be easily performed using cheap, small NdFeB magnets [97].
4.5 **Magnetically responsive microbial cells**

The microbial cells in free or immobilized condition are applicable for the pre-concentration or treatment of metal ions, organic and inorganic dyes, xenobiotics or bioactive compounds. The adsorption of metal ions on microbial cells depends on the composition of their cell walls. Typical examples would be the cell walls of yeast constitute of numerous complex organic materials and their polymers including 28% of glucan, 31% of mannan, 13% of proteins, 8% of lipids and 2% of chitin and chitosan. The cell walls of brown algae constitute 10 to 40% of alginic acid, 5-20% of fucoidan and about 2-20% of cellulose; red algae constitutes agar, cellulose, pectin, carrageenan, and xylan while the cell wall of green algae constitutes pectin and cellulose. Such substances contain several functional groups participating in the heavy metal binding process [66]. Fig. 4 (5) and Fig. 4 (6) depicts the entrapment of *Saccharomyces cerevisiae* cells in magnetically responsive millimeter or micron-sized alginate bead particles and functionalized magnetic particles (FMPs) [104]. Research observation with fungal biomass and seaweeds showed a strong affinity for ion exchange metal binding to ionized amine, carboxyl and phosphate groups. For instance, the carboxyl groups of amino acids of peptidoglycan layer and the hydroxyl groups of polysaccharides present on the yeast cell walls form a strong attachment with the metal ion Au (III). The positively charged amino groups of yeasts are engaged in the adsorption of heavy metal like Cr (VI) while the imidazole groups of yeast histidine are engaged with As (V). The various physical and chemical treatment processes of microbial biomass reveal the metal attachment functional groups by disruption, modification and membrane permeability. Pre-concentration with HCl, NaOH, DMSO, ethanol or other organic solvents causes improved adsorption of certain heavy metal ions.

The magnetotactic bacteria are interesting microorganisms possessing the capability to produce intracellular biogenic magnetic functionalized nanoparticles, which allow a magnetic separation process. The other forms of prokaryotic and eukaryotic microbial cells are to be modified magnetically in laboratory conditions through complex formation with magnetite or maghemite. In general, the ferrofluids magnetic modification technique is frequently applied to induce strong attachment of magnetic nanoparticles on the surface of microbial cells through selective chemical interactions with immune-magnetic nano and micro-sized particles, biological-based precipitation of paramagnetic substances on the surface of the cell, covalent immobilization on magnetic carriers, cross-linking of the microbial cells or cell walls with bifunctional reagent in the presence of magnetic particles or by entrapment into biocomposite polymer [66]. Additionally, the magnetic modification can also be done by attachment of paramagnetic cations on acid groups present on the microbial cell surface. Of late, a novel mechanism for the synthesis of
magnetically responsive microbial cells is based on suspending the cells in methanol and gradual mixing with perchloric acid based ferrofluid. During the process, a definite precipitation of FMPs on the outer surface of the treated microbial cells was observed [66]. The magnetically modified microbial cells find efficient application in removal of heavy metal ions such as Hg(II), Cu(II), Pb(II), and Cr(VI) along with organic xenobiotics. Important ones are low-cost biomaterials of baker’s yeast like *Saccharomyces cerevisiae*, fodder yeast like *Kluyveromyces fragilis* and algae like *Chlorella Vulgaris* are of common interests [54]. Fig. 4 (7) shows a TEM image of magnetically responsive microbial cells of dried fodder yeast (*Kluyveromyces fragilis*) [105]. It is reported that the biosorption capacities of magnetically modified yeast cells and algae cells for xenobiotics removal can be up to a level of 430 mg of the pollutant per gram of magnetic sorbent [98]. One of the promising sorbents is magnetic fodder yeast which can be used to concentrate and separate Sr$^{2+}$ ions from effluents of spent fuel reprocessing in nuclear power plants [99]. The magnetic modification of living microbial cells can also form magnetically responsive whole-cell biocatalysts [100]. For this process, both direct and definite modifications of cell walls with ferrofluids and entrapment of cells into biocomposite polymers gels in presence of FMPs are carried out. Usually, the intracellular enzymatic reactions will not get reduced after the magnetic modification as seen in the case of hydrogen peroxide degradation and sucrose hydrolysis by the enzyme catalase and invertase which occurs inside magnetically responsive *Saccharomyces cerevisiae* cells [100]. The magnetically modified algal cells can be employed as part of interesting biosensor systems, both in microfluidics configuration and part of screen-printed electrodes. These are also used for measurement of genotoxic and cytotoxic potentials, quantifying the herbicides of atrazine and propazine [54]. Another frequently used technique for cell separation and magnetic modification is immunomagnetic separation. This mechanism is useful for the isolation of stem cells and cancer cells. Detection of disease-causing pathogenic microbes is essential in microbiological and parasitological fields, For example, *Salmonella* sp., *Listeria monocytogenes*, verocytotoxin producing *E. coli* and parasites including *Cryptosporidium* as well as *Giardia* sp. Fig. 4 (11) depict optical microscopy image showing a fine section of polyallylamine hydrochloride stabilized FMPs attached to *Caenorhabditis elegans* nematode [108]. These cells upon proper magnetic labeling with biocompatible nanosized functionalized magnetic particles enable *in vitro* detection through Fe staining by the production of ferric ferrocyanide (Prussian blue) or *in vivo* detection through MRI visualization due to a specific reduction of T$_2$ relaxation time, causing the formation of the hypo-intense dark signal. The MRI can be utilized to analyze the engraftment of cells, also their migration time course and survival in the targeted tissues [101]. Table 4
summarizes the varied magnetically responsive microbial cells for removal of heavy metal ions.

**Table 4: Magnetically responsive microbial cells for removal of heavy metal ions.**

<table>
<thead>
<tr>
<th>Microbial cells</th>
<th>Composite type</th>
<th>Target metals</th>
<th>Matrix</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pseudomonas putida</em></td>
<td>Magnetically responsive immobilized cells</td>
<td>Cu (II)</td>
<td>Waste effluent</td>
<td>Pretreatment of cells with HCl and regeneration with acid treatment</td>
</tr>
<tr>
<td><em>Pseudomonas putida</em></td>
<td>Magnetically responsive immobilized cells</td>
<td>Cu (II)</td>
<td>Industrial wastewater</td>
<td>Semi-continuous-adsorption; pretreatment of cells with HCl; and utilization with acid treatment</td>
</tr>
<tr>
<td><em>Stenotrophomonas sp.</em></td>
<td>Magnetotactic bacteria</td>
<td>Au (III)</td>
<td>Aqueous solution</td>
<td>Regeneration with thiourea</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em></td>
<td>Cells immobilized on chitosan coated nano-sized FMP</td>
<td>Cu (II)</td>
<td>Aqueous solution</td>
<td>Maximum adsorption potential 144.9 mg g⁻¹</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae Subsp. uvarum</em></td>
<td>Cells modified with water-based ferrofluids</td>
<td>Hg (II), Cu (II), Ni (II), Zn (II)</td>
<td>Simulated water solution</td>
<td>Desorption with 0.1 M HNO₃</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae Subsp. uvarum</em></td>
<td>Cells modified with water-based ferrofluids</td>
<td>Water-soluble organic dyes</td>
<td>Aqueous solution</td>
<td>About five dyes tested</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em></td>
<td>Cells modified with water-based ferrofluids</td>
<td>Water-soluble organic dyes</td>
<td>Aqueous solution</td>
<td>About six dyes tested</td>
</tr>
<tr>
<td><em>Kluveromyces fragilis</em></td>
<td>Cells modified with water-based ferrofluids</td>
<td>Sr (II)</td>
<td>Aqueous solution</td>
<td>Desorption with 0.1 M HNO₃</td>
</tr>
<tr>
<td><strong>Kluveromyces fragilis</strong></td>
<td>Cells modified with water-based ferrofluids</td>
<td>Water-soluble organic dyes</td>
<td>Aqueous solution</td>
<td>About seven dyes tested</td>
</tr>
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<tr>
<td><strong>Saccharomyces cerevisiae</strong></td>
<td>Cells modified with water-based ferrofluids</td>
<td>Water-soluble organic dyes</td>
<td>Aqueous solution</td>
<td>Five dyes tested</td>
</tr>
<tr>
<td><strong>Chlorella vulgaris</strong></td>
<td>Algal cells modified with water-based ferrofluids</td>
<td>Water-soluble organic dyes</td>
<td>Aqueous solution</td>
<td>Six dyes tested</td>
</tr>
</tbody>
</table>

5. **Conclusions and future outlook**

The variety of naturally occurring, low cost, easily available biomaterials including plant-derived substances, microbial cells, activated carbons, microalgal cells etc. can be efficiently used as green sorbents for environmental remediation and sustainability. To modify and improve their sorption efficiency, conversion of these green sorbents was made into ‘smart sorbents’, which exhibited a response to a strong magnetic field; thereby facilitating their specific and definite magnetic separation from waste effluents. These ‘smart’ materials have a huge perspective to influence different areas of medicine, engineering technology, biosciences, environmental prospects, biotechnology etc. where varied applications both *in vitro* and *in vivo* have been discussed in this chapter. It is seen here, that these ‘smart’ magnetically responsive green sorbents cannot only be beneficial as sorbents for several organic and inorganic pollutants like heavy metal ions, EDCs (endocrine disruptors), water-soluble dyes, radionuclide, drug metabolites which are potential toxicants of the total ecosystem but also as biological carriers for cells and intracellular enzyme immobilization or as biosensors. Because of the presence of functionalized magnetic particles (FMPs) in nano or microforms, these biomaterials can be effectively employed as contrast agents in MRI or for targeting of potential drugs metabolites. Progress is expected from biotechnological as well as environmental point of view on the preparation of more commercially effective biocompatible magnetic composites. The utilization of green magnetic sorbents for large-scale applications is necessary as these are reasonably inexpensive and free from generating unwanted by-products and toxic waste. Efficacy, biocompatibility and safety studies of these ‘smart’ materials have to be tested from time to time especially their long-term toxicity potentials. The collaboration of scientists from different fields with similar mindset are
utmost important to correlate the influence of green application of magnetic sorbents in the near future.

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Chapter 2

Photocatalytic Decomposition of Organic Dyes

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Abstract

Effluent detoxification and degradation kinetic of Acid Yellow 216 were investigated using Fenton and photo-Fenton processes. pH, contact time, Fe⁺² concentration, H₂O₂ concentration, dye initial concentration, and temperature were optimized. The decolorization (87%) was considerably higher under experimental conditions of 20 min irradiation, pH 3, 50 mg/L initial dye concentration, 1.5 mM Fe⁺², 5 mM H₂O₂ and 40°C temperature. However, in the photo-Fenton process dye degradation was achieved up to 98%. Among, first-order, second-order and Behnajady–Modirshahla–Ghanbery (BMG) kinetic models, BMG kinetic model fitted well to experimental data. Under optimized conditions, up to 83 and 94% degradation of textile effluents were achieved using Fenton and Photo-Fenton process along with 56 and 76% COD reduction, respectively.

Keywords

Fenton oxidation, Acid Yellow, Effluents, Dyes, Photo-Fenton, Textile effluents, Kinetics model, Detoxification

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1. Introduction

The effluents discharged from textiles and other related industries constitute hazardous organic and inorganic components, especially dyes, which are stable and cause environmental and aesthetic problems [1-7]. Besides, dyes and their intermediates are toxic and carcinogenic hereby posing serious threats to living organisms. The genotoxicity and mutagenicity cause genetic alteration that appeared in future generations [8-12]. Therefore, the remediation of dyes is important. As a result, different biological, physical and chemical processes have been applied for the treatment of waste and wastewaters containing dyes [13-18].

Among the treatment methods, an advanced oxidation process (AOP) has emerged as an efficient technology for the degradation and mineralization of organic pollutants [19, 20]. The AOP is a chemical oxidation method based on in situ generation of reactive radicals (i.e., hydroxyl radical, \( \cdot \text{OH} \)) and refers to a set of different methods like Fenton and Fenton-like reactions (\( \text{Fe}^{2+}/\text{H}_2\text{O}_2, \text{Fe}^{3+}/\text{H}_2\text{O}_2 \)), photo-Fenton and photo-Fenton-like reactions (\( \text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}, \text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{3+} \), \( \text{UV}/\text{H}_2\text{O}_2, \text{UV}/\text{TiO}_2 \)), and ionizing radiation which have been successfully employed for the removal of pollutants [20]. Among all investigated AOPs, the Fenton reaction is considered to be an important source of \( \cdot \text{OH} \) radicals since the catalytic breakdown of hydrogen peroxide yielded \( \cdot \text{OH} \) radicals in the presence of Fe ions as a catalyst [9] (Eqs. 1-2). The strong oxidizing species like \( \cdot \text{OH} \)...
radicals are produced in situ, which break down the complex organic molecule into harmless substances such as CO₂, H₂O, and inorganic ions through chain reactions [11].

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH} \quad \text{(Eq. 1)}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O} + \text{UV} \rightarrow \text{Fe}^{2+} + \cdot\text{OH} + \text{H}^+ \quad \text{(Eq. 2)}
\]

Fenton and photo-Fenton processes degrade AY 216 dye in aqueous solution and textile effluent were investigated. The effects of the solution pH, concentration levels of H₂O₂ and dye concentration, UV exposure duration and Fe²⁺ dose were examined comprehensively in a series of decolorization of AY 216 by batch experiments. The experimental data were also subjected to the first-order, second-order and Behnajady–Modirshahla–Ghanbery kinetic models.

2. Material and methods

2.1 Chemical and reagents

The chemical and reagents were purchased from Sigma-Aldrich and dye the sample was procured from the local textile market, Faisalabad, Pakistan. Dye 1M solution (1L) was prepared and working solutions of different concentrations (mg/L) were prepared by dilution method. An aqueous solution of NaOH (0.1 M) and H₂SO₄ (0.1 M) were used for pH adjustment (HI-8014 HANNA). Fenton's reagent (Fe²⁺ + H₂O₂) (100 mL) was prepared by adding FeSO₄·7H₂O (2 mM) and 35% H₂O₂ (5 mM). The quenching of the oxidation of reaction mixture was done by Na₂SO₃.

2.2 Treatment process

A water bath shaker (PA 9/250 U) with controlled temperature system was used in all the experiments for dye solution. The UV irradiation (UV- 4S/L lamp, 365 nm) was done at different shaking and intensities (261, 243, 212, 176 and 96 Counts/Sec) of UV radiation with the wavelength of 365 nm. For analysis, samples were drawn at regular intervals and dye residual concentration was monitored at \( \lambda_{\text{max}} = 440 \text{ nm} \) (CE Cecil 7200, UK) and percentage degradation was estimated using the relation shown in Eq. 3. Where Cᵢ and Cᵢ are initial and final concentrations of dye.

\[
\text{Degradation (\%)} = \left[ \frac{C_i - C_f}{C_i} \right] \times 100 \quad \text{(Eq. 3)}
\]
2.3 Analytical procedures

The kinetics of the decolorization process of dye was determined by 1st order, 2nd order and BMG models. The cytotoxicity, COD, and TOC were evaluated as reported previously [11, 20]

2.4 Statistical analysis

All experiments were performed in triplicate and data were averaged and reported as mean ±SD. The correlation coefficient R² values of kinetic models were determined by using statistical functions of Microsoft Excel, 2007 (Version Office XP, Microsoft Corporation, USA).

3. Results and discussion

3.1 Effect of pH

The key factor to examine the efficiency of Fenton’s reagent is based on the pH of the solution. The generation of ³OH radicals and the concentration of Fe²⁺ are mainly controlled by the pH of the solution. The pH range 3-8 for decolorization of AY 216 was premeditated with the experimental conditions of 50 mg/L dye initial concentration, 2 mM Fe²⁺, 5 mM H₂O₂, 30°C and duration 1 h at 100 rpm. The degradation pattern obtained is shown in Fig. 1(A) and UV-Vis spectrum can be seen in Fig. 2(A). Maximum dye removal of 84% was achieved at pH 3.0 and on further increasing the pH to 8.0, the percentage removal efficiency decreased to 69%. This decreasing trend might be due to the precipitation of Fe as hydroxide above pH 4. At lower pH (pH < 3), the dye removal was also less which can be attributed to the low activity of ³OH radical, probably due to the formation of hydronium ions (H₃O⁺) by solvating the proton and hydrogen peroxide. The hydronium ion enhances the stability of hydrogen peroxide and presumably reduced the reactivity with ferrous ion significantly [21]. Therefore, the ³OH radical reactivity decreased at low pH values and resultantly, the removal efficiency decreased. These findings are in consonance with previous studies i.e., the methyl violet dye degradation by Fenton’s reagent conducted at different pH values of 2-4. It was reported that the pH strongly affects the oxidation process of methyl violet and pH 3 was found favorable for dye degradation. The lower degradation of dyes at pH less than 3 is probably due to the formation of Fe complexes i.e., [Fe(H₂O)₆]²⁺,[Fe(H₂O)₅OH]²⁺ and [Fe(H₂O)₅OH]²⁺. The reaction slowed down in the presence of hydrogen peroxide concentration greater/less than optimized level because of hydroperoxyl radical (Eq. 4) instead of ³OH radical [22].

Fe³⁺ + H₂O₂ → Fe²⁺ + HO₂⁻ + H⁺  

(Eq. 4)
Figure 1 (A) Effect of pH on the decolorization of AY 216 (dye concentration—50 mg/L, time—60 min, Fe$^{+2}$ concentration—2 mM, H$_2$O$_2$—5 mM, temperature—30$^\circ$C, shaking speed—150 rpm) and (B) Effect of contact time (min.) on the decolorization of AY 216 (dye concentration—50 mg/L, pH—3, Fe$^{+2}$ concentration—2 mM, H$_2$O$_2$—5 mM), temperature—30$^\circ$C, shaking speed—150 rpm).
Figure 2 (A) UV–Vis absorption spectra of AY 216 untreated and treated at different initial pH values, (B) UV–Vis absorption spectra of AY 216 untreated and treated at different time intervals by \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) (C) UV–Vis absorption spectra of AY 216 untreated and treated at different time intervals by \( \text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV} \) (D) Decrease of the AY 216 as a function of time by Fenton and photo-Fenton processes.
3.2 Effect of contact time

The equilibrium time is one of the important parameters for a cost-effective wastewater treatment. In decolorization efficiency, the utmost dye removal was achieved within 20 min of reaction. The reaction was preceded at optimal pH 3, while keeping Fe\(^{2+}\) concentration, H\(_2\)O\(_2\) dose, initial dye concentration, temperature and shaking speed constant. The selected time ranges were 0, 5, 10, 20, 30, 40, 50 and 60 min (Figs. 1B) and Figs. (2B and 2C). Maximum percentage removal of 82\% of AY 216 was achieved within 20 min followed by no change up to 60 min. It was assumed that the direct reduction of \(^{'}\)OH radicals by metal ions was responsible for reducing the activity. The decolorization of RY 86 within 20 min was 96\% when the Fe\(^{2+}\) concentration was 5.0 \times 10^{-4} \text{ mol/L}. The initial concentration of H\(_2\)O\(_2\) also affects the decolorization of RY 86. When the sample was irradiated by UV radiation, the decolorization rate of RY 86 increased with increasing the concentration of H\(_2\)O\(_2\). It was noticed that RY 86 did not achieve 90\% decolorization within 20 min when the concentration of H\(_2\)O\(_2\) was less than 5.0\times10^{-2} \text{ mol/L} [23].

3.3 Effect of Fe\(^{+2}\) dose

The removal of dye enhanced as the concentration of ferrous ion increased to a certain extent. The optimal dosage of ferrous ion is characteristic of Fenton’s reagent for the dyes degradation. Decolorization of AY 216 varied on varying the concentration of Fe\(^{+2}\) ions. In the present study, the concentration range of 0.25, 0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 mM Fe\(^{+2}\) ions was examined at pH 3, contact time 20 min and 5 mM H\(_2\)O\(_2\) at 30\(^\circ\)C temperature with shaking speed 150 rpm. As evident from Fig. 3(A), a 85\% dye removal was possible with 1.5 mM Fe\(^{+2}\) ions. Starting from 72\% degradation at a lower concentration of Fe\(^{+2}\) ions, it reached a maximum at 1.5 mM of Fe\(^{+2}\) ions and then, decreased to 71\% at 4 mM concentration of Fe\(^{+2}\). The UV-Vis absorption spectrum of dye degradation is shown in Fig. 4(A). It has been reported that Fe\(^{2+}\) is efficient to a certain limit and beyond optimum concentration, the efficiency may decrease significantly. Previously, a similar effect of Fe\(^{2+}\) was reported. Based on TOC reduction, it was observed that 0.27 mM concentration of Fe\(^{+2}\) was better and further increase in Fe\(^{+2}\) concentration decreased the removal efficiency. An excessive dosage of Fe\(^{+2}\) leads to other competitive and undesirable reactions (produced less active species) which ultimately lower the quantity of available radicals required to oxidize organics (Eqs. 5a and 5b) [24, 25].

\[
\text{Fe}^{2+} + \text{HO}^{'\prime} \rightarrow \text{Fe}^{3+} + \text{OH}^{-} \quad \text{(Eq. 5a)}
\]
Fe^{2+} + HO_2^- \rightarrow Fe^{3+} + HO_2^- \quad \text{(Eq. 5b)}

Figure 3 (A) Effect of Fe^{2+} on the decolorization of AY 216 (dye concentration—50 mg/L, time—20 min, pH—3, H_2O_2—5 mM, temperature—30°C, shaking speed—150 rpm) and (B) Effect of H_2O_2 on the decolorization of AY 216 (dye concentration—50 mg/L, time—20 min, pH—3, Fe^{2+} concentration—1.5 mM, temperature—30°C, shaking speed—150 rpm).
Figure 4 (A) UV–Vis absorption spectra of AY 216 untreated and treated at different doses of Fe\(^{2+}\), (B) UV–Vis absorption spectra of AY 216 untreated and treated in the presence of different H\(_2\)O\(_2\) concentrations.
3.4 Effect of H$_2$O$_2$ concentration

The decolorization AY 216 was also checked by varying the H$_2$O$_2$ dose. The H$_2$O$_2$ doses of 1, 2, 3, 4, 5, 6, 7 and 8 mM were investigated, whereas other parameters were kept constant (i.e., pH 3, contact time 20 min, 1.5 mM of Fe$^{2+}$, 30°C temperature and shaking speed 150 rpm) and the results thus, obtained are shown in Fig. 3(B). It was observed that the maximum dye removal (83%) was achieved using 5 mM H$_2$O$_2$ concentration. At lower concentration, the dye removal was 64%, which increased to 83% at 5 mM of H$_2$O$_2$ and then, again decreased to 68% at 8 mM concentration of H$_2$O$_2$. Previously, methyl orange also showed similar behavior regarding H$_2$O$_2$ concentration effect in the range of 4.5-48 mmol/L.

3.5 Effect of initial dye concentration

The percentage removal of AY 216 was also investigated at different dye initial concentrations. The initial dye concentration was investigated in the range of 10, 20, 30, 40, 50, 60, 70 and 100 mg/L, whereas pH 3, 1.5 mM Fe$^{2+}$ concentration, 5 mM H$_2$O$_2$ concentration, 30°C and 150 rpm were kept constant. Degradation percentage and UV-Vis spectrum are shown in Fig. 5(A) and Fig. 6(A). It was observed that dye removal was 60% at a lower concentration that reached to 85% for 50 mg/L of dye initial concentration and finally, reduced to the 60% at 100 mg/L of dye initial concentration. It is reported that $^\cdot$OH radicals generation, which are responsible for dye degradation remained invariable at lower concentration and at higher concentration, the dye molecules increased but the $^\cdot$OH radical concentration remained constant and therefore, the removal efficiency decreased. In UV irradiation process at higher dye concentration photons, penetration into solution decreased facilitating the formation of $^\cdot$OH radicals [26].

3.6 Effect of temperature

Temperature is a significant parameter to understand the nature of the reaction. The effect of temperature on the dye removal was examined at 30, 40, 50, 60 and 70°C, whereas pH 3, 1.5 mM concentration of Fe$^{2+}$, 5 mM H$_2$O$_2$ concentration, 50 mg/L initial dye concentration and 150 rpm remained constant. The rate of reaction with Fenton’s reagent increased by increasing the temperature and reached to 87% at 40°C and then, decreased gradually to 64% at 70°C (Fig. 5(B) (degradation) and Fig. 6(B)) (UV-Vis spectra). It is known that the reaction between H$_2$O$_2$ and Fe$^{2+}$ is affected by temperature and therefore, the kinetics of dye degradation was also influenced by the temperature variation. In the Fenton process, the optimum temperature was around 50°C for maximum removal of methyl violet dye [27].
Figure 5 (A) Effect of initial dye concentration on the decolorization of AY 216 (reaction time—20 min, pH—3, Fe$^{+2}$ concentration—1.5 mM, $H_2O_2$—5 mM, temperature—30°C, shaking speed—150 rpm) and (B) Effect of temperature (°C) on the decolorization of AY 216 (dye concentration—50 mg/L, time—20 min, pH—3, Fe$^{+2}$ concentration—1.5 mM, $H_2O_2$—5 mM, shaking speed—150 rpm).
Figure 6 (A) UV–Vis absorption spectra of untreated and treated as a function of different initial dye concentration (B) UV–Vis absorption spectra of AY 216 untreated and treated at different temperatures.
Figure 7 (A) Effect of UV intensity on the decolorization of AY 216 (dye concentration—50 mg/L, time—20 min, pH—3, Fe$^{2+}$ concentration—1.5 mM, $H_2O_2$—5 mM, temperature—40°C, shaking speed—100 rpm), (B) UV–Vis absorption spectra of AY 216 untreated and treated at different UV intensities.
3.7 **Effect of UV radiation**

The dye degradation rate enhanced by UV radiation in combination with Fenton reagent and UV intensity also found to be effective in degrading dye since the dye degradation was different at different UV intensities i.e., 261, 243, 212, 176 and 96 counts/sec. The percent dye removal reached to 98% under the influence of UV radiation (Fig. 7(AB)) in combination with Fe$^{+2}$/H$_2$O$_2$. The degradation of AY 216 was considerably enhanced by increasing UV intensity. This was due to the fact that the •OH radicals generation is enhanced under irradiation. It is also evident that Photo-Fenton efficiency was considerably higher than Fenton treatment. The increase in •OH radical formation leads to enhancement in dye removal efficiency. The hydrolysis rate of H$_2$O$_2$ increased with UV irradiation and in Fenton reagent, the generation of hydroxyl radical was less under UV irradiation [28]. The Fenton oxidation process was studied by varying the intensity of UV radiation from 8.6 to 45.3 W/m$^2$. By increasing the UV intensity from 8.6 to 45.3 W/m$^2$, within 2 min the dye removal rate increased from 57.3 to 96%, which indicates that the dye degradation can be enhanced significantly by using UV radiation in a combination of Fenton process (Fig. 7(A)).
Figure 8 Kinetics models fit for AY 216 degradation (A) First-order, (B) second-order and (C) Behnajady–Modirshahla–Ghanbery.
4. Kinetic modeling

The data obtained from AY 216 oxidation degradation were tested using three kinetic models i.e., first order, second order and BMG models [29]. The linear forms of first-order, second-order and BMG models are given Eqs. 6-8. Where $C_0$ and $C_t$ are representing initial at “0” and time $t$, respectively, $m$ and $b$ are the constants, which represent the relation between oxidation capacity and reaction kinetics. A Higher value of $1/m$ is indicative of faster removal rate of dye. The maximum removal of a fraction of dye ($1/b$) is equal to the maximum oxidation capacity of Fenton process at the end of reaction when the time approaches to infinity [30].

\[
\ln \frac{c_0}{c_t} = K_1 \cdot t \tag{Eq. 6}
\]

\[
\ln \frac{1}{c_t} - \frac{1}{c_0} = K_2 \cdot t \tag{Eq. 7}
\]

\[
\frac{t}{1(c_t-c_0)} = m + b \cdot t \tag{Eq. 8}
\]

The kinetic model's parameters for the decolorization of AY 216 at different reaction conditions were calculated by applying for the first order, second order and BMG models. The calculated results for AY 216 are represented in Table 1 and Figs. 8 (ABC). The experimental data of Fenton process fitted well to the BMG kinetic model with a higher correlation coefficient ($R^2$) of 0.9986 as compared to first and second order models. Previously, acid red 66 and direct blue 71 have also shown similar kinetic behavior [29]. In another study, the kinetics of decolorization of dyes was also studied and it had been revealed that the experimental data of dyes degradation were best explained by BMG kinetic model [31]. The kinetic model's parameters for the decolorization of AY 216 at different UV intensities i.e., 96, 176, 212, 243, and 261 counts/sec were also calculated by employing these three models. The obtained results are shown in Table 2. The $R^2$ values for BMG model again are higher than those of the first-order and the second-order kinetic models. Therefore, BMG kinetic model is fitted well to the decolorization of AY 216 at different intensities of UV radiation.
Table 1 Comparison of first-order, second-order and Behnajady–Modirshahla–Ghanbery Kinetic models for AY 216 decolorization.

<table>
<thead>
<tr>
<th></th>
<th>First order Kinetic</th>
<th>Second order Kinetic</th>
<th>BMG Kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K₁ (1/min)</td>
<td>R²</td>
<td>K₂ (1/M. min)</td>
</tr>
<tr>
<td></td>
<td>0.026</td>
<td>0.553</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table 2 Comparison of first-order, second-order Behnajady–Modirshahla–Ghanbery (BMG) Kinetic models for Acid Yellow 216 decolorization at different intensities of UV radiation intensities.

<table>
<thead>
<tr>
<th>Intensity (counts/sec.)</th>
<th>First order Kinetic</th>
<th>Second order Kinetic</th>
<th>BMG Kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K₁ (1/min)</td>
<td>R²</td>
<td>K₂ (1/M. min)</td>
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<tr>
<td>96</td>
<td>0.071</td>
<td>0.903</td>
<td>0.006</td>
</tr>
<tr>
<td>176</td>
<td>0.075</td>
<td>0.839</td>
<td>0.008</td>
</tr>
<tr>
<td>212</td>
<td>0.081</td>
<td>0.823</td>
<td>0.009</td>
</tr>
<tr>
<td>243</td>
<td>0.093</td>
<td>0.837</td>
<td>0.014</td>
</tr>
<tr>
<td>261</td>
<td>0.129</td>
<td>0.893</td>
<td>0.039</td>
</tr>
</tbody>
</table>
5. Degradation, water quality and cytotoxicity of effluents

The treatment conditions optimized for the degradation of AY 216 were employed for the treatment of real samples textile effluents. The treatment conditions i.e., pH 3, 1.5 mM Fe\(^{2+}\), 5 mM H\(_2\)O\(_2\), 40 °C temperature, reaction time 30 min and UV radiation 261 counts/sec were applied for the treatment of textile effluents and treatment efficiency was evaluated on the basis of degradation, water quality parameters and reduction in cytotoxicity. Among water quality parameters, TOC and COD were selected and cytotoxicity was evaluated using bioassays such as haemolytic and brine shrimp lethality tests. The COD determines the oxygen required for the chemical oxidation of organic matter and non-biodegradable matter present in wastewater. COD is also an important pollution indicator which reflects the chemical quality of effluent [11], whereas TOC is suitable for determining organic matter content and provides more accurate evaluation of the total organic compounds present in a water/wastewater, which is estimated by measuring the CO\(_2\) generated when the organic compounds are oxidized [32]. Bioassays have been used to evaluate the toxicity of raw and treated industrial effluents i.e., brine shrimp and haemolytic tests [10, 11, 19, 20, 33]. The textile wastewater was treated by both Fenton and photo-Fenton processes which exhibited excellent efficiency for the degradation of dyes in textile effluents (Fig. 9AB). The degradation to the levels of 83% and 94% was achieved under optimized conditions by Fenton and photo-Fenton. Besides, the water quality improvement, the reduction in COD was observed up to 56.3 and 76% for Fe\(^{2+}/\)H\(_2\)O\(_2\) and Fe\(^{2+}/\)H\(_2\)O\(_2\)/UV, respectively. Similarly, the TOC was reduced up to 52.2 and 67.8% by Fenton and photo-Fenton processes, respectively. In view of considerable degradation as well as COD and TOC reduction, the cytotoxicity was also reduced significantly as a result of Fenton and Photo-Fenton treatments. The cytotoxicity reductions according to haemolytic test were 42 and 57% for Fe\(^{2+}/\)H\(_2\)O\(_2\) and Fe\(^{2+}/\)H\(_2\)O\(_2\)/UV, respectively, whereas up to 51 and 66% cytotoxicity reductions were observed in case of brine shrimp assay. Previously, the efficiencies of AOPs such as TiO\(_2/\)UV, O\(_3\), electro-Fenton, wet-air oxidation, UV/electro-Fenton, Photo-Fenton, sunlight irradiation, TiO\(_2\) based photocatalysis, H\(_2\)O\(_2/\)UV, O\(_3/\)UV, and TiO\(_2/\)H\(_2\)O\(_2/\)UV [34] were also evaluated for toxicity reduction. Present investigation revealed that both treatment processes are capable to degrade the mixed dyes in textile wastewaters and subsequently, the improvements in water quality and toxicity reduction. These findings are in line with previous studies that advanced oxidation processes are capable to detoxify the toxic compounds in simulated aqueous solution and in industrial wastewater as well i.e., the effect of gamma radiation treatment on detoxification of textile effluents was evaluated on the basis of *Allium cepa*, haemolytic, brine shrimp, and Ames tests. The microbial load was reduced to zero, and root length and root count were increased by
31.1 and 38.3%, respectively, at 5 kGy treatment. The reductions in cytotoxicity were recorded as 39.6, 49.7, and 79.6% in the case of human and sheep red blood cells and brine shrimp, respectively. Before treatment, the samples were mildly mutagenic and after treatment mutagenicity was not detected [35]. The cytotoxicity and mutagenicity of textile effluents, treated by gamma radiation in combination with hydrogen peroxide were investigated. The *Allium cepa*, heamolytic, brine shrimp bioassays were used for cytotoxicity evaluation, whereas mutagenicity was tested using Ames tests. Before treatment, textile effluents showed a significant cytotoxicity and mutagenicity signs which were and reduced significantly after treatment. *A. cepa* showed a reduction of 50% in cytotoxicity, whereas the reductions of 56–59% in case of heamolytic test and up 93% in cytotoxicity were recorded by brine shrimp assays. The mutagenicity of gamma radiation in the presence of hydrogen peroxide-treated effluents reduced up to 59% and 54% in case of TA98 and TA100, respectively [11]. Gamma radiation/H₂O₂ treatment of nonylphenol polyethoxylates was performed and treatment effect was evaluated on the basis of degradation, water quality and toxicity reduction. In response of 90% degradation of nonylphenol ethoxylates, up to 68.7, 77, and 94% reductions in cytotoxicity were observed in case of *A. cepa*, heamolytic and shrimp assays, respectively. The mutagenicity reduced up to 62, 74, and 79% (TA98) and 68, 78, and 82% (TA100), respectively of NPEO-6, NPEO-9, and NPEO-30 irradiated to the absorbed dose of 15 kGy/4.6% H₂O₂. Photo-catalytic detoxification of industrial wastewater also showed a significant reduction in toxicity along with water quality improvement [19]. Authors subjected wastewater to ultraviolet radiation in the presence of hydrogen peroxide and titanium dioxide and cytotoxicity, mutagenicity, microbial load reduction were measured. *allium cepa*, heamolytic and Ames tests showed considerable reductions in cytotoxicity and mutagenicity because of photo-catalytic and UV/H₂O₂/TiO₂ treatments of soap and detergent wastewaters. It was revealed that the advanced oxidation treatment could be used for removal of cytotoxicity and mutagenicity and treated wastewater could possibly be used for irrigation purposes [33]. Therefore, in view of water quality improvement and toxicity reduction, the present investigation, as well as previous reports, support the application of Fe³⁺/H₂O₂ and Fe²⁺/H₂O₂/UV for the treatment of industrial wastewater.
Figure 9 (A) Comparison of different treatment combinations for AY 216 degradation, (B) Degradation and effect of Fenton and Photo-Fenton treatment on TOC, COD and cytotoxicity reductions (pH 3, 1.5 mM Fe$^{2+}$ concentration, 5 mM H$_2$O$_2$, 40°C temperature and UV exposure time reaction time 30 min).
6. Conclusions

The Fenton and Photo-Fenton processes were investigated for decolorization of AY 216 and textile effluents. Results revealed that Fenton process was efficient for the decolorization of AY 216 dye in wastewater. About 85% decolorization of dye was achieved at pH 3, with dye initial concentration (50 mg/L), in the presence of 1.5 mM Fe^{2+} and 5 mM H_{2}O_{2}, at 40 °C with 20 min of reaction time. The decolourization enhanced to 98% if reaction carried out under UV irradiation instead of sun light. Under optimized conditions, up to 83 and 94% degradation along with significant reductions in TOC, COD and cytotoxicity were also achieved in response of Fe^{2+}/H_{2}O_{2}/UV treatment of textile effluent. The Behnajady–Modirshahla–Ghanbery kinetic model fitted well to experimental data for AY 216 degradation. The results indicated that Photo-Fenton process can be used for efficient degradation of dyes in textile effluents.

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Chapter 3

Effective Degradation of Methylene Blue using ZnO:Fe:Ni Nanocomposites

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Email: dhimanpooja85@gmail.com*

Abstract

This work supports the novelty of ZnO based semiconductor composites as a potential photocatalyst for the degradation of methylene blue (MB) dye. ZnO:Fe:Ni nanocomposites were prepared by solution combustion route. The prepared product was characterized for structural, morphological, optical and photocatalytic activities. The crystallinity and the structure of the samples were determined by X-Ray diffractometer and the relevant structural parameters were obtained using Rietveld fitting of the X-ray spectra. The X-ray photoelectron spectroscopy confirms the elemental presence and the valence state of the elements present in the sample. UV–visible absorption spectra have been utilized to calculate the band gap of the prepared samples. The prepared nanocomposite showed good photodegradation of MB dye. In general, many photocatalytic degradation studies have been reported using the man-made light source, however in the present chapter work on ZnO:Fe:Ni composite used in degradation of methylene blue in presence of direct sunlight is discussed.

Keywords

Rietveld Fitting, X-ray Photoelectron Spectroscopy, HRTEM, Photocatalysis

Contents

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1. Introduction

Our environment is getting degraded by polluting wastewater emerging from the industries. The organic dyes as the major component of the wastewater of the industries like textile, food, coloring, and leather etc. are continuously causing their harmful effects on human health [1-3]. The dyes have been broadly classified according to their usage and their chemical structures. Dyes consist of the group of atoms or chromophores which are responsible for their characteristic colors. The wastewater coming from the industries generally consists of residual stuff of dyes and which accounts for their colored nature and toxicity [4]. Dyes are also known as natural dyes, food dyes, synthetic dyes and other dyes etc. Among all, azo dyes are widely used in the pharmaceutical, textile, cosmetic and other coloring industries. It is still an important and less resolved issue on how the impact of the pollutants can be reduced. Since India is a developing country the issue becomes more important as we have limited number of techniques available for this purpose. Thus, the development of a simple and economic method for the efficient degradation of dyes has gained greater significance. However, nowadays, semiconductor-based photocatalysis is being widely used for the degradation of these dyes [5]. Photocatalysis is better and more acceptable approach for this problem as this method can mineralize the dyes into minerals (H₂O and CO₂) without pollution or health hazards. A lot of semiconductors which includes TiO₂, Fe₂O₃, Cu Fe₂O₄, ZnO, CdS, ZnS, or their composites have been tried as a photocatalyst. These materials are relatively cheap, easily available, and effective and are environment-friendly as well [6-14]. According to the recent reports, ZnO has emerged an effective photocatalyst for the degradation or decoloring of these organic dyes. ZnO has been utilized for the degradation of dyes like Methyl orange, methylene blue, malachite green, rhodamine B, congo red, and benzopurpurine 4B etc. In the present chapter, we are limiting ourselves to methylene blue.
(MB) which are a heterocyclic aromatic chemical compound having IUPAC name 3, 7-bis(dimethylamino)-phenothiazin-5-iium chloride with the molecular formula C₁₆H₁₈N₃SCl. In the recent studies, ZnO nanoparticles have been employed for the degradation of methylene blue with very promising results [15-20]. These reports differ in the synthesis route opted with different photocatalysis results. Some composites of ZnO have also been reported by researchers which are also potential photocatalyst for degradation of MB [21-23]. We have synthesized ZnO: Fe: Ni nanocomposites by an easy, fast and economic synthesis route of solution combustion for the effective degradation of MB.

2. Materials and methods

For the preparation of ZnO:Fe: Ninanocomposites, zinc, iron, and Ni nitrates were taken as raw materials. Glycine was used as fuel for the combustion process of aqueous solutions of metal nitrates. Oxidizer to fuel (O/F) ratio was kept unity using total oxidizing and reducing valencies of the oxidizer and the fuel [24-25]. The mixture was heated at 373K with constant stirring on a magnetic hot plates. Finally obtained powder was kept in a muffle furnace at a temperature of 773 K for 4 h. The prepared samples were named as ZNF1, ZNF3, and ZNF5 respectively with 1% Ni and Fe in the range of 1-5%. The resulting powder was ground to fine powder and characterized with various instrumental techniques.

Crystal structure changes and the relevant structural parameters were obtained using a XPERTPRO diffractometer using Cu Kα radiation. Transmission electron microscope has been used to analyze the particle size and the particle shape was determined using high-resolution transmission electron microscope (HRTEM) (JEOL, USA). The elemental composition and the valence state information were collected using X-ray photoelectron spectrometer.

The study of the optical properties was performed on SYSTRONICS double beam spectrophotometer 2202 by using suspension of 2 mg of prepared sample in distilled water.

The UV–Vis studies were performed using double beam spectrophotometer. The photocatalytic efficiency of the samples was examined for degradation of methylene blue (MB) (Merck, 98.9%) in presence of natural sunlight in a slurry type batch reactor. All experiments were repeated three times and average values were reported.
2.1 X-Ray diffraction

The Rietveld fitted X-ray diffraction spectra for the prepared samples have been presented in Fig.1. It can be seen from the spectra that the diffraction peaks exhibit a pure phase wurtzite structure having space group P\textsubscript{6\textsubscript{3}}mc (JCPDS#36-1451). No traces of impurity or secondary phase formation have been observed within the detection limit of the X-ray diffractometer. The possibility of cluster formation is rare because of the very small content of transition metals. Any cluster cannot be present in the sample because the annealing temperature of 500ºC is quite high which automatically converts the content of the cluster into vapors. The impurity phases can be like ZnFe\textsubscript{2}O\textsubscript{4}, NiO, Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4} etc. The position of the peak (0 0 2) which is the characteristic peak of hexagonal wurtzite structure changes with an increase in Fe content. The intensity of characteristic peaks decreases with increase in Fe percentage. In general, only two possibilities are there (a) transition metal can substitute Zn sites and (b) they can replace the interstitials. Since energy barrier required for the substitution of interstitials is smaller than that of forming interstitial atoms, therefore the probability of substituting atoms is higher than that of forming interstitial atoms [26]. With the higher iron content, the change in lattice parameters is attributed to the difference in the ionic radii of iron, nickel and zinc ions.

For the wurtzite structure of ZnO, different parameters can be calculated using the following equations:

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 +hk+k^2}{a^2} + \frac{l^2}{c^2} \tag{1}
\]

and Zn-O bond length is expressed as:

\[
L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \tag{2}
\]

and unit cell volume:

\[
V = 0.866 \times a^2 \times c \tag{3}
\]

The theoretically calculated and refined parameters are listed in Tables 1 and 2, respectively. The fitted parameters and the manually calculated parameters are almost same.
Table 1: Different structural parameters derived manually from XRD pattern using FWHM method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter a=b (Å)</th>
<th>Lattice parameter c (Å)</th>
<th>c/a ratio</th>
<th>u parameter</th>
<th>Crystallite volume V(Å³)</th>
<th>Bond length (Zn-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZNF1</td>
<td>3.2491</td>
<td>5.2062</td>
<td>1.603</td>
<td>0.3785</td>
<td>47.595</td>
<td>1.9796</td>
</tr>
<tr>
<td>ZNF3</td>
<td>3.2476</td>
<td>5.2029</td>
<td>1.602</td>
<td>0.3797</td>
<td>47.521</td>
<td>1.9767</td>
</tr>
<tr>
<td>ZNF5</td>
<td>3.2598</td>
<td>5.2209</td>
<td>1.601</td>
<td>0.3886</td>
<td>48.044</td>
<td>1.9698</td>
</tr>
</tbody>
</table>

Table 2: Structural parameters derived from Rietveld Fitting of XRD pattern.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter a=b (Å)</th>
<th>Lattice parameter c (Å)</th>
<th>c/a ratio</th>
<th>u parameter</th>
<th>Crystallite volume V(Å³)</th>
<th>Bond length (Zn-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZNF1</td>
<td>3.2498</td>
<td>5.2053</td>
<td>1.6020</td>
<td>0.3799</td>
<td>47.610</td>
<td>1.9776</td>
</tr>
<tr>
<td>ZNF3</td>
<td>3.2497</td>
<td>5.2053</td>
<td>1.6019</td>
<td>0.3799</td>
<td>47.608</td>
<td>1.9776</td>
</tr>
<tr>
<td>ZNF5</td>
<td>3.2477</td>
<td>5.2019</td>
<td>1.6017</td>
<td>0.3799</td>
<td>47.518</td>
<td>1.9763</td>
</tr>
</tbody>
</table>
Figure 1  X-Ray Diffraction spectra for prepared samples.
2.2 X-Ray photoelectron spectroscopy

X-ray photoelectron spectroscopy has been used for the quantitative analysis and the valence state determination of the transition metal ions. XPS spectra for ZNF1 and ZNF3 nanocomposite are presented in Fig. 2. The obtained spectrum reveals the presence of peaks which are assigned to Fe, Ni, C, Zn, and O peaks. However, this is an integral spectrum obtained but for more qualitative and detailed information, core level XPS scan has been done. After de-convoluting the peaks according to the shape symmetry of the peaks using XPS peak fit software, peak positions of the different elements are presented in Table 3. Fig. 3 presents the core level de-convoluted scan for O 1s peak containing three deconvoluted peaks in which the low binding energy side peak remains at the same position while the other two get slightly shifted indicating the variation of the oxygen environment in both samples. It can be clearly seen from the spectra of ZNF3 sample that the area under the medium binding energy curve slightly decreases for the ZNF3 in comparison to ZNF1 sample. This implies that the oxygen deficiency slightly decreases in the ZNF3 but the loosely bound oxygen or adsorbed oxygen increases in comparison to ZNF1. Fig. 4(a-b) presents the fitted narrow scan, Gaussian fitted XPS spectra for Fe of ZNF1 and ZNF3 respectively. From the earlier reports, peak position of metallic Fe occurs at 719.9 eV (Fe 2p1/2) and 706.5 eV (Fe 2p3/2) and that of Fe2+ occur at 709.30 eV for Fe 2p3/2, and 722.30 eV for Fe 2p1/2 respectively, meanwhile the peaks of Fe 2p3/2 and Fe 2p1/2 for Fe3+ in the Fe2O3 are located at 710.70 and 724.30 eV, respectively. The peaks of FeO occur at 722.3 eV and at 709.3 eV [27-28].

Fig. 5(a-b) presents the Ni 2p HR-XPS spectra of ZNF1 and ZNF3 respectively. To investigate the disturbing effects of Ni element, Gaussian fitting was performed on the Ni 2p spectrum. From the literature, the positions of Ni 2p3/2 peaks for metallic Ni occur at 852.7 eV, for NiO at 853.8 eV, and for Ni2O3 at 856.7 eV respectively [29-30]. The position of the satellite peak of 2p 3/2 occurs at 861.3 eV [31-32]. The energy difference for ZNF1 between Ni peaks is 18.42 eV which is greater than the mentioned value in the literature (17.49 eV). These results confirm that Ni ions are only present in the 2+ state and all other types of impurity phases related to Ni are absent in the samples. Therefore, it can be concluded from XPS analysis that the Fe, Zn, and Ni are in valance states of 3+, 2+, and 2+ respectively. XPS analysis also gives information regarding defects like oxygen vacancies and zinc interstitials present in the samples.
Figure 2 XPS survey spectra for ZNF1 and ZNF3 samples.

Figure 3 De-convoluted O 1s spectrum for ZNF1 and ZNF3 nano-composites.
Table 3 Various peak positions of de-convoluted Fe, O, and Ni XPS peaks.

<table>
<thead>
<tr>
<th></th>
<th>Sample</th>
<th>Peak 1 position (eV)</th>
<th>Peak 2 position (eV)</th>
<th>Peak 3 position (eV)</th>
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</thead>
<tbody>
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<td>ZNF1</td>
<td>530.15</td>
<td>531.64</td>
<td>532.62</td>
</tr>
<tr>
<td></td>
<td>ZNF3</td>
<td>530.15</td>
<td>531.46</td>
<td>532.33</td>
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<table>
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<tr>
<th>Fe 2p peak</th>
<th>Sample</th>
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<th>Peak 2 position (eV)</th>
<th>Satellites peaks (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZNF1</td>
<td>710.35</td>
<td>724.14</td>
<td>712.40 718.34</td>
</tr>
<tr>
<td></td>
<td>ZNF3</td>
<td>710.33</td>
<td>724.19</td>
<td>712.26 718.32</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Ni 2p peak</th>
<th>Sample</th>
<th>Peak 1 position (eV)</th>
<th>Peak 2 position (eV)</th>
<th>Satellites peaks (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZNF1</td>
<td>853.71</td>
<td>855.22</td>
<td>861.11</td>
</tr>
<tr>
<td></td>
<td>ZNF3</td>
<td>854.51</td>
<td>855.42</td>
<td>861.36</td>
</tr>
</tbody>
</table>

Figure 4 De-convoluted Fe 2p spectrum for ZNF1 and ZNF3 nanocomposites.
2.3 Transmission electron microscopy (TEM)

Fig. 6(a-c) represents the low-resolution TEM images for all prepared nanocomposite samples. The samples have been found to consist of roughly spherical particles with a wide range of particle size distribution. Particle ranges from 20 to 45 nm for all samples. A slight variation in the particle diameter can be observed from ZNF1 to ZNF5. However, a slight degradation in the crystallinity from ZNF1 to ZNF5 can also be seen from the high-resolution TEM presented in Fig. 7(a-c). The d spacings can be clearly seen from the inset image in the Fig. 7(a-c).
2.4 UV–Visible spectroscopy

The UV-Vis spectra of the samples ZNF1, ZNF3 and ZNF5 are presented in Fig. 8. It is observed from the absorption spectra that the absorption band edge slightly shifted to the higher wavelength side starting from ZNF1 to ZNF5 associating with the decrease in band gap [33]. This observed red shift in the absorption spectra is assigned to the formation of shallow levels inside the band gap due to the incorporation of transition metal in the structure. The increased absorption in the wavelength range from 400–600 nm, is attributed to the d-d transition [34]. The band gap value obtained by using Tauc’s plot was found to decrease with increase in iron content. The band gap value varies from
3.14 eV (ZNF1) to 3.08 (ZNF5) eV. The decrease in the band gap is attributed to the sp-d exchange interactions. Many authors have reported increase or decrease in band gap on doping Fe or Ni in ZnO. In the recent work, the band gap value for Fe$_{0.01}$Ni$_{0.01}$Zn$_{0.98}$O nanoparticles (~23nm) was found to be 3.17eV, which is very near to our calculated value for the band gap [35]. However the effect of increased Fe content in ZnO:Fe:Ni nanocomposites on the band gap is not reported anywhere.

Figure 8  UV-vis. Spectra for ZNF1, ZNF3, and ZNF5 samples at room temperature.

2.5 Photocatalytic activity

The photocatalytic activity of all prepared samples was tested under natural sunlight illumination using methylene blue as a target pollutant [36-37]. The optical absorption spectroscopy is a great tool for monitoring the degradation of dye. For photocatalytic efficiency and many other practical applications, it is required that any photocatalyst should absorb UV as well as visible light as visible radiation accounts for 45% of energy in the solar radiation while UV light less than 10% [38]. It is therefore of great significance to construct a material that can absorb both UV and visible light to increase the range of a photocatalyst. This can be done by creating surface defects in a material
which ultimately results in increase in the surface area and thereby increase in photodegradation efficiency. There have been several reports of increased photocatalytic activity of different morphologies of nanoparticles [39-40]. The defects present in any system can cause either improvement or worsen of the photocatalytic activity, depending on the type, nature, and location of native defects. In the mechanism of absorption of radiation, generation of electron-hole pairs takes place. These electron-hole pairs on reaction with water and dissolved oxygen create hydroxyl free radicals and superoxide ion radical which attack the conjugation in the dyes and thus degrades them. The photocatalytic efficiency of the samples was analyzed for degradation of methylene blue as a pollutant in presence of natural sunlight in a slurry type batch reactor. Photocatalytic efficiency of the samples has been checked in the slurry type batch reactor (Fig. 9). In this typical experiment, the slurry mixture consisting of dye and catalyst suspension was stirred magnetically.

Figure 9  Arrangement for studying the degradation of Dye on illumination to natural sunlight.
The observed absorption spectrum of MB in the presence of Fe, Ni@ ZnO nanocomposites is presented in Fig. 10. The sample ZNF1 has higher degradation capacity in comparison to ZNF3 and ZNF5. The percentage of photodegradation of MB was calculated from the following equation:

\[
\% \text{ Degradation} = \left[ 1 - \frac{C_t}{C_0} \right] \times 100
\]  

(4)

where \( C_t \) is the absorbance after time \( t \) and \( C_0 \) is the initial concentration of dye. The calculated value of percentage degradation of dye is plotted with experiment length and is shown in Fig. 11(a-c). After 5 hours 81% degradation was achieved for the ZNF1 sample. While for the ZNF3 sample as a photocatalyst the degradation was 89%. However, ZNF5 decolorizes 79% of the dye during 5 hours. This implies that ZNF3 is a better photocatalyst than ZNF1 and ZNF5 samples. Earlier, we have observed that the band gap decreases from ZNF1 to ZNF3. This variation in band gap explains the photocatalytic behavior of ZNF1 and ZNF3. But for ZNF5 sample, it doesn’t fit better. This can be explained in view of the fact, that the increase in iron in the form Fe\(^{3+}\) ions indicates the presence of more cation vacancies. The concentration of Ni\(^{2+}\) is fixed and it provides an almost equal number of charge carriers. The charge carries are sufficient for the recombination in the case of ZNF1 and ZNF3, but for ZNF5 it is no more possible which leads to decrease in photocatalytic efficiency. The bar depiction of dye degradation with time is presented in Fig. 11(d). The mechanism involved in the dye degradation is probably the interfacial electron transfer which takes place between donor states of oxygen vacancies and the Zn interstitials and dye. Since methylene blue (MB) is a cationic dye, it takes an electron from excited donor states and then decomposes into leucomethylene which is non-toxic, harmless and environment-friendly in nature.
Figure 10  Absorption spectra of MB in presence of ZNF1, ZNF3, and ZNF5 samples at various times (initial concentration of MB = $10^{-5}$M, pH=7, temperature = 30±0.5°C).
Figure 11  The extent of decomposition of MB with respect to time in presence of ZNF1, ZNF3 and ZNF5 samples (initial concentration of MB = $10^{-5}$M, pH=7, temperature = 30±0.5°C).

Figure 12  The depiction of dye removal by zinc oxide nanoparticles.
4. Conclusions

The solution combustion synthesized ZnO:Fe:Nanocomposites were found to be highly effective photocatalyst for the decomposition of methylene blue dye via interfacial electron transfer mechanism. X-ray diffraction and transmission electron micrographs showed the crystalline nature of the samples without any impurity phase formation. X-ray photoelectron microscopy confirms the elemental presence, valence state and the composition of the samples. UV-Visible spectrophotometry studies demonstrate the decrease in band gap with an increase in Fe content.

Acknowledgement

Dr. Pooja Dhiman gratefully acknowledges USIC Facility, Himachal Pradesh University, Shimla for XRD measurements.

References


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Chapter 4

Use of Agricultural Solid Wastes as Adsorbents

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Abstract

Biosorption through agricultural lignocellulosic wastes and by-products has been identified as a viable substitute to current technologies applied to remove toxic metal ion and organic pollutants from water and wastewater. The present study emphasizes the use of agricultural and agro-industries based residues as low-cost biosorbents. The study aims to revisit the status of biosorption and various recent advances made in this arena. Biomasses are the main focus of this study which requires substantial management. Further, this is supplemented with the physicochemical processing of such biomasses and their application in adsorption. The surge in biomass to energy applications in recent years has resulted in charred biomass production as a residual. These biochars have been used as adsorbents. The biosorbents have been divided into the following three groups: (i) raw biomass, (ii) processed biomass and (iii) charred biomass. The affinity of sorbents in the removal of organic and inorganic pollutants and their applications on water and wastewater have also been studied.

Keywords

Agricultural Waste, Heavy Metals, Organic Contaminants, Biomass, Biochar

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1. Introduction

Agriculture and akin sectors are pivotal to sustainable growth and development. Agriculture derives its prominence from the fact that it has vital supply and demand links with the manufacturing sector. During the past few decades, the production and productivity of food grains, commercial crops, oilseeds, fruits, and vegetables in India have witnessed remarkable growth [1]. The Indian economy is driven by the agricultural sector and since independence, an exponential growth has been encouraged in this particular sector. It has been primarily an outcome of multi-pronged, government-driven program known as ‘Green Revolution’ which aimed at ensuring availability and use of quality seeds, irrigation facilities, chemical fertilizers, pesticides, farm machinery, equipment, etc.

With the onset of the green revolution, the surplus crop residue generation increased proportionally in developing and developed countries. About 4000 Mt/yr crop residue is produced worldwide from food crops [2]. The widely available agricultural residue is one of the most abundant renewable resources in the world. About 25% of nitrogen, 25% phosphorus, 50% of sulfur and 75% of potassium uptake by cereal crops are retained in residues, thus serving as valuable sources of nutrients. These residues have little or no economic value and often create a disposal problem. Globally, open agricultural residue burning is practiced for farm management, resulting in the emission of particulate matter, polycyclic aromatic hydrocarbons (PAH), soot and greenhouse gasses [3,4]. A large proportion of the residues, about 140 Mt, is burned in open fields, to immediately clear straw after harvest of the previous crop [5]. Typically, the residue is burnt for rice, wheat, maize, sugarcane, cotton, jute, millet, rapeseed, and groundnut crops. Several endeavors have been started for the proper utilization of the waste viz: composting of residues for
manure, farmyard manure (FYM), energy from waste, bioethanol, biomethanation, gasification of residues and pyrolysis to produce biochar [6,7]. Particularly, biochar technology is investigated for its carbon sequestration characteristics and is suitable for multifaceted applications in conservation agriculture [2,8] to combat the climate change scenario. Alternatively, biomass, its composites, and biochar have been studied for the biosorption of various organic and inorganic pollutants in water and wastewater treatment [9,10,11].

Biomass-based biosorption is one of the prominent processes for removal of organic and inorganic pollutants from water and wastewater at lower concentrations. In the recent past, several studies have been carried out, where the plant materials constituting lignocellulosic content have proven efficient and effective biosorbents for heavy metal ion removal. Heavy metals are hazardous for the environment and humans due to their toxic nature and non-biodegradability [12,13]. Both natural and anthropogenic sources contribute to heavy metals present in the environment. Natural sources are generally geogenic in origin. Volcanic eruptions, weathering of rocks, and leaching to water bodies act as a mode of entry of these contaminants to air, water and soil. Anthropogenic sources can be classified as industrial, agricultural, domestic effluents, mining, motor vehicle emissions etc. many of the inorganic pollutants remain unaffected by water and wastewater treatment processes because of their conservative nature. These include heavy metals from metal finishing and plating operations, and other industrial discharges [14]. Heavy metals are regarded as trace elements, whose bioavailability is influenced by many physical, chemical and biological factors. Toxicity of non-essential metals like Hg(I, II), Cd(II) and Pb(II) etc. mainly occurs through displacement of trace metals from their binding sites or through ligand interactions [15,16]. Long-term exposure to these metals may lead to carcinogenicity (through arsenic); dysfunctional nervous system (through mercury); hypertension and heart ailments (through cadmium); and interference with hemoglobin formation (through lead). Organic contaminants can be broadly classified as pesticides, dyes, antibiotics and polycyclic aromatic hydrocarbons (PAH). These contaminants originate from industries, agriculture, landfills, household wastes and through accidental leakage or spills leading to their entry in environmental matrices. Such contaminants can pose danger to living organisms by entering into the food chain. Therefore, there is a need to adopt proper disposal methods or treatment technologies to remove these harmful chemicals from the environment.

Several methods have been adopted to treat water and wastewater, which include biological, chemical and physical techniques. In the past few decades, the commonly used techniques are ion-exchange [17], electrolysis [18], flotation [19], membrane filtration [20], coagulation [21] and adsorption [22]. Treatment technologies available for
removal of organic contaminants include ultrasound combined with photo-Fenton treatment [23], advanced oxidation processes [24], ozonation [25], electrodialysis membranes [26] etc. However, these methods have several shortcomings such as high operational and maintenance costs, generation of secondary pollutants etc. Compared to all these treatment techniques, adsorption has emerged to be an effective approach for the abatement of water and soil organic contaminants. The most commonly used adsorbent is activated carbon, which is used for removal of a variety of organics broadly classified as pesticides, dyes, drugs, pharmaceutical products, polycyclic aromatic hydrocarbons (PAH) etc. However, concerns related to its use include higher costs, regeneration capacity, and disposal.

Agro-wastes are energy efficient, low cost and effective substitute for activated carbon as an adsorbent. Agricultural wastes are lignocellulosic rich in organic content and contain many functional groups which help in binding the contaminants on the adsorbent surface. The basic components of the agricultural waste biomass include cellulose, hemicellulose, lignin, lipids, proteins, sugars, starch, polysaccharides, and pigments. These constituents have varied functional groups on their surface. In the present chapter, the physicochemical adsorption mechanism of the biomass, chemically modified biomass and thermochemical treated biomass has been explored for the removal of organic and inorganic pollutants.

1.1. Use of raw biomass as biosorbents

Agricultural based plant adsorbents are abundant, economical, and renewable and are mainly composed of cellulose and lignin, hence making them a viable option for wastewater treatment. The presence of structural-functional groups plays important role in efficacy of the biosorbents [27,28]. In the last few decades various researchers have explored the efficacy of agricultural wastes as biosorbents viz: husk [29,30], stalk [31,32], bagasse [33,34], shell [35,36] and straw etc. [37,38].
Table 1  Adsorption behavior and efficiency of raw biomass for heavy metal pollutants.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Agricultural Waste</th>
<th>Heavy metal</th>
<th>Adsorbent dose (g/L)</th>
<th>pH</th>
<th>Reaction time (min)</th>
<th>Amount adsorbed (qe) (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rice straw</td>
<td>Cd(II)</td>
<td>-</td>
<td>2-6</td>
<td>180</td>
<td>13.84</td>
<td>[39]</td>
</tr>
<tr>
<td>2.</td>
<td>Barley straw</td>
<td>Cu(II)</td>
<td>1</td>
<td>6-7</td>
<td>120</td>
<td>4.64</td>
<td>[37]</td>
</tr>
<tr>
<td>3.</td>
<td>Cashew nut shell straw</td>
<td>Ni(II)</td>
<td>3</td>
<td>5</td>
<td>30</td>
<td>18.86</td>
<td>[35]</td>
</tr>
<tr>
<td>4.</td>
<td>Rice shell</td>
<td>Cu(II)</td>
<td>10</td>
<td>6</td>
<td>180</td>
<td>2.95</td>
<td>[40]</td>
</tr>
<tr>
<td>5.</td>
<td>Wheat shell</td>
<td>Cu(II)</td>
<td>10</td>
<td>6</td>
<td>180</td>
<td>17.42</td>
<td>[40]</td>
</tr>
<tr>
<td>6.</td>
<td>Lentil shell</td>
<td>Cu(II)</td>
<td>10</td>
<td>6</td>
<td>180</td>
<td>9.59</td>
<td>[40]</td>
</tr>
<tr>
<td>7.</td>
<td>Wheat stem</td>
<td>Cd(II)</td>
<td>-</td>
<td>5</td>
<td>60</td>
<td>11.2</td>
<td>[41]</td>
</tr>
<tr>
<td>8.</td>
<td>Wheat bran</td>
<td>Cr(VI)</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>0.942</td>
<td>[42]</td>
</tr>
<tr>
<td>9.</td>
<td>Picea smithiana</td>
<td>Cr(VI)</td>
<td>2.0</td>
<td>4.5</td>
<td>1440</td>
<td>228</td>
<td>[43]</td>
</tr>
<tr>
<td>10.</td>
<td>Pinus sylvestris</td>
<td>Cr(VI)</td>
<td>1</td>
<td>7</td>
<td>120</td>
<td>0.201</td>
<td>[44]</td>
</tr>
<tr>
<td>11.</td>
<td>Sugarcane bagasse</td>
<td>Hg(II)</td>
<td>5</td>
<td>4</td>
<td>60</td>
<td>35.71</td>
<td>[45]</td>
</tr>
<tr>
<td>12.</td>
<td>Agave bagasse raw</td>
<td>Pb(II)</td>
<td>2</td>
<td>5</td>
<td>-</td>
<td>35.60</td>
<td>[34]</td>
</tr>
<tr>
<td>13.</td>
<td>Agave bagasse raw</td>
<td>Zn(II)</td>
<td>2</td>
<td>5</td>
<td>-</td>
<td>7.84</td>
<td>[34]</td>
</tr>
<tr>
<td>14.</td>
<td>Olive stone</td>
<td>Cu(II)</td>
<td>-</td>
<td>5.5-6</td>
<td>60</td>
<td>2.02</td>
<td>[46]</td>
</tr>
<tr>
<td>15.</td>
<td>Olive stone</td>
<td>Pb(II)</td>
<td>-</td>
<td>5.5-6</td>
<td>60</td>
<td>9.261</td>
<td>[46]</td>
</tr>
<tr>
<td>16.</td>
<td>Olive stone</td>
<td>Ni(II)</td>
<td>-</td>
<td>5.5-6</td>
<td>60</td>
<td>2.13</td>
<td>[46]</td>
</tr>
<tr>
<td>17.</td>
<td>Olive stone</td>
<td>Cd(II)</td>
<td>-</td>
<td>5.5-6</td>
<td>60</td>
<td>7.733</td>
<td>[46]</td>
</tr>
<tr>
<td>18.</td>
<td>Egyptian mandarin peel</td>
<td>Hg(II)</td>
<td>5</td>
<td>6.02</td>
<td>1440</td>
<td>19.01</td>
<td>[47]</td>
</tr>
<tr>
<td>19.</td>
<td>Sunflower hull</td>
<td>Cu(II)</td>
<td>2</td>
<td>5</td>
<td>180</td>
<td>57.14</td>
<td>[48]</td>
</tr>
</tbody>
</table>
Table 2 Agricultural wastes as adsorbent for organic pollutants.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Agro-waste</th>
<th>Organic contaminant</th>
<th>Particle size</th>
<th>Adsorption conditions</th>
<th>Adsorbent dose (g/L)</th>
<th>Amount adsorbed (q_e) (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><em>Phaseolus vulgaris</em> biomass</td>
<td>Reactive Red 198</td>
<td>&lt;300µm</td>
<td>pH=2, Contact time=20min at 20°C</td>
<td>1.6</td>
<td>80</td>
<td>[49]</td>
</tr>
<tr>
<td>2.</td>
<td>Rice husk ash</td>
<td>2, 4-Dichloro phenoxy acetic acid</td>
<td>-</td>
<td>Contact time=12h at 30°C</td>
<td>0.1</td>
<td>1.425</td>
<td>[50]</td>
</tr>
<tr>
<td>3.</td>
<td>Pine leaves</td>
<td>Acid yellow 220 dye</td>
<td>63–500 µm</td>
<td>pH=2, Contact time=90 min</td>
<td>1</td>
<td>32.26</td>
<td>[51]</td>
</tr>
<tr>
<td>4.</td>
<td>Coir pith</td>
<td>Crystal violet</td>
<td>600 µm</td>
<td>300K</td>
<td>0.1</td>
<td>65.53</td>
<td>[52]</td>
</tr>
<tr>
<td>5.</td>
<td>Coir pith</td>
<td>Rhodamine B (RB)</td>
<td>600 µm</td>
<td>300K</td>
<td>0.1</td>
<td>55.54</td>
<td>[52]</td>
</tr>
<tr>
<td>6.</td>
<td>Sugarcane fiber</td>
<td>Crystal violet</td>
<td>600 µm</td>
<td>300K</td>
<td>0.1</td>
<td>10.44</td>
<td>[52]</td>
</tr>
<tr>
<td>7.</td>
<td>Sugarcane fiber</td>
<td>rhodamine B (RB)</td>
<td>600 µm</td>
<td>300K</td>
<td>0.1</td>
<td>15.98</td>
<td>[52]</td>
</tr>
<tr>
<td>8.</td>
<td>Sugar beet pulp</td>
<td>Safranin</td>
<td>-</td>
<td>pH=10, Contact time=240 min</td>
<td>8</td>
<td>147.00</td>
<td>[53]</td>
</tr>
<tr>
<td>9.</td>
<td>Sugar beet pulp</td>
<td>Methylene blue</td>
<td>-</td>
<td>pH=10, Contact time=240 min</td>
<td>8</td>
<td>211</td>
<td>[53]</td>
</tr>
<tr>
<td>10.</td>
<td>Sunflower seed shells</td>
<td>Trifluralin</td>
<td>-</td>
<td>298K</td>
<td>12</td>
<td>2.29 ×10⁻²</td>
<td>[54]</td>
</tr>
<tr>
<td>11.</td>
<td>Sugarcane bagasse</td>
<td>Indosol turquoise FBL dye</td>
<td>300 µm</td>
<td>pH=3, Contact time=30 min</td>
<td>1</td>
<td>22.72</td>
<td>[55]</td>
</tr>
</tbody>
</table>
1.2 Mechanism of biosorption

Biosorption is a multifaceted process affected by several factors. Mechanisms involved in the biosorption process includes chemisorption, microprecipitation, ion-exchange, complexation, adsorption–complexation on surface and pores, heavy metal hydroxide condensation onto the surface and surface adsorption [57]. Functional groups present on the surface of adsorbent play a pivotal role in immobilizing the metal adsorbed onto biomass material. Plant cell walls are the sites where all the functional groups are present which are helpful in the binding process, cell walls are generally composed of cellulose molecules, organized in microfibrils, surrounded with hemicellulose (glucomannans, mannans, galactans, arabinogalactans, xylans), lignin and pectin [58]. The arrangement of cellulose, hemicelluloses, and lignin is depicted in Fig. 1. The inner core is made of crystalline cellulose, stacked one above another by interlayer hydrogen bonding with few of the sections carrying amorphous cellulose [59]. These amorphous regions are better known for the adsorption of heavy metals based on the available functional groups. The cellulose layers are intertwined with the amorphous hemicellulose followed by the covalent binding with lignin in the shell surface. Lignin is a polyphenolic polymer comprising of three main phenol derivatives namely, coniferyl alcohol, coumaryl alcohol and sinapyl alcohol. These three components primarily have hydroxyl and carboxyl components, which are responsible for heavy metals sorption, whereas the crystalline structure with hydrophobic pores is essentially responsible for the adsorption of various organic adsorbates. Thus, the behavior of the substrate is highly dependent upon the porosity, crystallinity, surface area and degree of polymerization of fibers. The additional features of high ash content i.e. silica, N, P, K etc. in the crop residues result in enhancing adsorption behavior of the crop residues vis-a-vis the woody biomass [60].

<table>
<thead>
<tr>
<th></th>
<th>Citrus sinensis</th>
<th>Reactive yellow 42</th>
<th>&lt;0.25</th>
<th>Contact time= 60min</th>
<th>20</th>
<th>13.99</th>
<th>[56]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.</td>
<td>Citrus sinensis</td>
<td>Reactive red 45</td>
<td>&lt;0.25</td>
<td>Contact time= 60min</td>
<td>20</td>
<td>15.21</td>
<td>[56]</td>
</tr>
<tr>
<td>13.</td>
<td>Citrus sinensis</td>
<td>Reactive blue 19</td>
<td>&lt;0.25</td>
<td>Contact time= 60min</td>
<td>20</td>
<td>14.80</td>
<td>[56]</td>
</tr>
<tr>
<td>14.</td>
<td>Citrus sinensis</td>
<td>Reactive blue 49</td>
<td>&lt;0.25</td>
<td>Contact time= 60min</td>
<td>20</td>
<td>27.41</td>
<td>[56]</td>
</tr>
</tbody>
</table>
Laszlo and Dintzis, [61] have shown that lignocellulosic have sorption capacity. Lignocellulosic are hygroscopic in nature, where water permeates the non-crystalline portion of cellulose, hemicellulose, and lignin. Cellulose can thus adsorb heavy metals from a solution [62]. The molecular structure and supramolecular structure of cellulose have a strong influence on sorption properties. Adsorption of an aqueous solution by fibres result in cellulose swelling. The more it swells, the higher is the amount of adsorption. Swelling also depends on the fibre structure, degree of crystallinity or amorphous and void regions [63].

Figure 1 Lignocellulosic biomass compositions, structural arrangement and chemical characteristics of the components of biomass [2].
2. Physicochemically treated biomass and their adsorption characteristics

As discussed earlier, agricultural solid waste materials are available in abundance and can be used as biosorbents due to their physicochemical characteristics. The utilization of agricultural solid wastes is of countless significance and can play a vital role in the national economy [63]. The major constituents of agricultural waste are lignin, hemicellulose, and cellulose that contain several functional groups such as aldehydes, alcohols, carboxylic acid, ketones, phenolic and ether linkages. These groups have resilient ability to bind with toxic metal ions by utilizing an electron pair to form different complexes in solution [64]. Recently, Zafar et al. [65] modified rice bran through various chemicals and utilized for the adsorption of nickel ions. Similarly, various results (Table 3) focus on using treated biomass for contaminant removal.

Table 3 Physicochemically processed agricultural residual biomass and their adsorption efficiency for metal ions.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Agri waste</th>
<th>Heavy metal</th>
<th>Adsorbent dose (g/L)</th>
<th>pH</th>
<th>Reaction time (min)</th>
<th>Amount adsorbed (q_e) (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Barley straw citric acid</td>
<td>Cu(II)</td>
<td>1</td>
<td>6-7</td>
<td>120</td>
<td>31.71</td>
<td>[37]</td>
</tr>
<tr>
<td>2.</td>
<td>Grapefruit ZnCl_2</td>
<td>Pb(II)</td>
<td>10</td>
<td>5.3-6.5</td>
<td>90</td>
<td>12.73</td>
<td>[66]</td>
</tr>
<tr>
<td>3.</td>
<td>Agave bagasse HCl</td>
<td>Cd(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>12.50</td>
<td>[34]</td>
</tr>
<tr>
<td>4.</td>
<td>Agave bagasse HCl</td>
<td>Pb(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>42.31</td>
<td>[34]</td>
</tr>
<tr>
<td>5.</td>
<td>Agave bagasse HCl</td>
<td>Zn(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>12.40</td>
<td>[34]</td>
</tr>
<tr>
<td>6.</td>
<td>Agave bagasse HNO_3</td>
<td>Cd(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>13.50</td>
<td>[34]</td>
</tr>
<tr>
<td>7.</td>
<td>Agave bagasse HNO_3</td>
<td>Pb(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>54.29</td>
<td>[34]</td>
</tr>
<tr>
<td>8.</td>
<td>Agave bagasse HNO_3</td>
<td>Zn(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>14.43</td>
<td>[34]</td>
</tr>
<tr>
<td>9.</td>
<td>Agave bagasse</td>
<td>Cd(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>18.32</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
<td>Pb(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>50.12</td>
<td>[34]</td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>--------</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>10.</td>
<td>Agave bagasse NaOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Agave bagasse NaOH</td>
<td>Zn(II)</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>20.54</td>
<td>[34]</td>
</tr>
<tr>
<td>12.</td>
<td>Orange peel citric acid</td>
<td>Cd(II)</td>
<td>4.3</td>
<td>6</td>
<td>120</td>
<td>0.90</td>
<td>[67]</td>
</tr>
<tr>
<td>13.</td>
<td>Egyptian mandarin peel NaOH</td>
<td>Hg(II)</td>
<td>5</td>
<td>6.02</td>
<td>1440</td>
<td>23.26</td>
<td>[68]</td>
</tr>
<tr>
<td>14.</td>
<td>Orange peel KCl</td>
<td>Cu(II)</td>
<td>5</td>
<td>5-5.5</td>
<td>120</td>
<td>59.77</td>
<td>[44]</td>
</tr>
<tr>
<td>15.</td>
<td>Orange peel KCl</td>
<td>Cd(II)</td>
<td>5</td>
<td>5-5.5</td>
<td>120</td>
<td>125.63</td>
<td>[44]</td>
</tr>
<tr>
<td>16.</td>
<td>Orange peel KCl</td>
<td>Pb(II)</td>
<td>5</td>
<td>5-5.5</td>
<td>120</td>
<td>142.94</td>
<td>[44]</td>
</tr>
<tr>
<td>17.</td>
<td>Orange peel KCl</td>
<td>Zn(II)</td>
<td>5</td>
<td>5-5.5</td>
<td>120</td>
<td>45.29</td>
<td>[44]</td>
</tr>
<tr>
<td>18.</td>
<td>Orange peel KCl</td>
<td>Ni(II)</td>
<td>5</td>
<td>5-5.5</td>
<td>120</td>
<td>49.14</td>
<td>[44]</td>
</tr>
<tr>
<td>19.</td>
<td>Orange peel K+</td>
<td>Cu(II)</td>
<td>5</td>
<td>5-5.5</td>
<td>120</td>
<td>59.77</td>
<td>[69]</td>
</tr>
<tr>
<td>20.</td>
<td>Orange peel Mg2+</td>
<td>Cu(II)</td>
<td>5</td>
<td>5-5.5</td>
<td>120</td>
<td>40.37</td>
<td>[69]</td>
</tr>
<tr>
<td>21.</td>
<td>Orange peel sulfured</td>
<td>Pb(II)</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>164.0</td>
<td>[70]</td>
</tr>
<tr>
<td>22.</td>
<td>Orange peel sulfured</td>
<td>Zn(II)</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>80.0</td>
<td>[70]</td>
</tr>
</tbody>
</table>

Various studies have reported the effect of pre-treatment on raw agricultural wastes (Table 4). Sadaf et al. [55] investigated the effect of chemical (acids, chelating agents, and organic solvents) and physical treatment (autoclaving and boiling) on sorption capacity of sugarcane bagasse and reported an increase in sorption capacity by these treatments. Treatment with HCl achieved the highest increase in the investigations. Increase in porosity, and high surface area, resulting in the availability of more active sites was the reason for higher sorption capacity.
Table 4  Physicochemically treated agricultural residual biomass and their adsorption characteristics for organic pollutants.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Agricultural waste biomass</th>
<th>Organic contaminant</th>
<th>Particle size</th>
<th>Kinetic conditions</th>
<th>Loading (g/L)</th>
<th>Amount Adsorbed (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rice husk Mechanical</td>
<td>2, 4-Dichlorophenoxyacetic acid</td>
<td>42.1 nm</td>
<td>pH=5 60min</td>
<td>1.5</td>
<td>76.92</td>
<td>[71]</td>
</tr>
<tr>
<td>2.</td>
<td>Rice hull Tartaric acid</td>
<td>Methylene blue</td>
<td>-</td>
<td>300min</td>
<td>5</td>
<td>25</td>
<td>[72]</td>
</tr>
<tr>
<td>3.</td>
<td>Sugarcane bagasse HCl</td>
<td>Indosol turquoise FBL dye</td>
<td>300 µm</td>
<td>pH=3 30 min</td>
<td>1</td>
<td>27.17</td>
<td>[55]</td>
</tr>
<tr>
<td>4.</td>
<td>Sugarcane bagasse Na-alginate-immobilized forms</td>
<td>Indosol turquoise FBL dye</td>
<td>300 µm</td>
<td>pH=3 1h</td>
<td>1</td>
<td>10.54</td>
<td>[55]</td>
</tr>
<tr>
<td>5.</td>
<td>Cotton stalks NaOH</td>
<td>Methylene blue</td>
<td>-</td>
<td>1440 min</td>
<td>2</td>
<td>-</td>
<td>[73]</td>
</tr>
<tr>
<td>6.</td>
<td>Palm shells H₂SO₄</td>
<td>Chloropyrophos</td>
<td>-</td>
<td>pH=6 240 min</td>
<td>-</td>
<td>52.63</td>
<td>[74]</td>
</tr>
<tr>
<td>7.</td>
<td>Palm shells H₂SO₄</td>
<td>Monocrotophos</td>
<td>-</td>
<td>pH=6 240 min</td>
<td>-</td>
<td>51.099</td>
<td>[74]</td>
</tr>
<tr>
<td>8.</td>
<td>Citrus sinensis Acetic acid</td>
<td>Reactive yellow 42</td>
<td>&lt;0.2 m &lt;0.2 5 mm</td>
<td>60 min</td>
<td>2</td>
<td>17.64</td>
<td>[56]</td>
</tr>
<tr>
<td>9.</td>
<td>Citrus sinensis Acetic acid</td>
<td>Reactive blue 19</td>
<td>&lt;0.2 5 mm</td>
<td>60 min</td>
<td>2</td>
<td>23.31</td>
<td>[56]</td>
</tr>
<tr>
<td>10.</td>
<td>Citrus sinensis Acetic acid</td>
<td>Reactive blue 49</td>
<td>&lt;0.2 5 mm</td>
<td>60 min</td>
<td>2</td>
<td>33.53</td>
<td>[56]</td>
</tr>
</tbody>
</table>
3. **Use of charred biomass**

While many adsorbents derived from agro-waste are widely available, but their adsorption capacity is low when compared with the processed forms. Many researchers have reported enhanced activity of pyrolyzed waste or activated char compared with the parent material in the raw form [75]. Biochar is gaining attention for its use as an adsorbent to remove organic compounds from water and soil environments. It's used as adsorbents environmental friendly, renewable and generates minimum waste production besides supporting, regeneration of adsorbent. Biochar is a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment. It is a source of renewable energy with the high potential to aid in environmental management. Biochar considered a form of black carbon is stable, recalcitrant organic, and produced from a variety of waste biomass materials such as crop residues, wood waste, garden waste, municipal solid waste, animal manure and food waste etc. under temperature and oxygen controlled conditions [76]. It has varied functional groups on its surface (Fig. 2). Slow pyrolysis leads to the generation of biochar and gas as major products. The key application of biochar is in sequestration of carbon and hence combating climate change. Beside this, when added to soil, biochar also acts as a soil conditioner which helps in holding carbon, improving microbial activity, increasing soil biodiversity by replenishing nutrient in deficient soil and thus enhance crop yield and food security. Biochar also helps in retaining nutrients and agrochemicals for a plant, hence resulting in reduced run-off and leaching into the underlying water. Due to all these functions, it has emerged as a very effective tool for environmental management [76]. Biochar was primarily introduced as a soil amendment, but the recent research has highlighted its ability to immobilize various organic contaminants in soil [75,77,78]. Biochar is known to enhance the sorption as well as the bioavailability of pesticide residues for biota. The two major processes governing the fate of organic contaminants in soil are sorption-desorption and degradation [79]. Biochar amended soils are reported to have high inorganic content, high cation exchange capacity (CEC), moisture content, adsorptive capacity, and pH. Biochar increases soil’s sorption capacity for pesticides. Wheat and rice residue biochars were found to be 2500 times more effective than soil in sorbing diuron [80]. Highly carbonaceous and aromatic structure and high surface area play an important role for such high sorption [79].
3.1 Production of biochar

Biochar is produced through thermochemical conversion of biomass at high temperatures, usually ranging from 200-900°C with limited or no oxygen, by the process known as pyrolysis. Pyrolysis can be fast or slow. Fast pyrolysis results in more liquid fuel (bio-oil), with the lesser solid product (biochar), whereas slow pyrolysis yields a high amount of biochar and lesser liquid fuel. Residence time is <2s in fast pyrolysis, which yields about 75% bio-oil, and for slow pyrolysis, it varies from few minutes to days, with biochar as the major product (25-35%) [82,83].

Biochar yield generally depends on the temperature of pyrolysis, residence time, heating rate and type of feedstock. Sohi et al. [84] reported that high biochar yield is obtained from biomass with high lignin content. Biochars produced from crop residues and wood biomass has low carbon content and high molar H/C and O/C ratios and thus higher surface areas than those produced from animal litter and solid wastes. The heating rate is found to be the least influencing factor in determining biochar yield [85]. Pyrolysis temperature is known to affect biochar characteristics significantly. The increase in pyrolysis temperature enhances carbonization and lowers O and H contents. The surface area of biochar also increases with increasing pyrolysis temperatures as it removes
volatile material which results in high micropore volume [86]. Keiluweit et al. [87] observed a decline in biochar yield at a temperature of less than 300°C due to initial dehydration reactions. With an increase in temperature, plant-based biomass undergoes dehydration and depolymerization into smaller dissociation products of lignin and cellulose. This change can be shown by Van krevelen diagram. McKendry et al. [88] compared biomass and fossil fuels in terms of their oxygen to carbon and hydrogen to carbon ratios and inferred that these ratios are inversely proportional to the energy content of material (Fig 3).

![Van Krevelen Diagram](image)

**Figure 3 Van krevelen diagram depicting fuel characteristics (Source: McKendry et al. (2002)).**

Use of biochar as an adsorbent can be limited because of its relatively low surface area and high residual volatile matter. However, these shortcomings can be overcome by various pre- and post-treatment technologies (Fig 4). These modified biochars have large surface area and high porosity, which leads to their use as an alternative for activated carbon. Activation is suggested for enhancing biochar properties. Biochar properties can be modified by physical activation (steam activation and heat treatment) and chemical activation (acidic or alkaline modification and impregnation methods) [89]. These two
methods are successfully used to enhance the surface area and porosity of biochar [90,91,92]. The biochars thus produced from these treatment types are called *activated biochars*. In physical activation by steam, biomass is subjected to steam at 800-900°C temperature after carbonization. Heat treatment involves heating of biochar at 800-900°C for 1-2 hours to provide more basic surface functional groups which are quite efficient for sorbing hydrocarbons [93,94]. Chemical activation, which yields better porous structure [95] involves impregnation of raw material with an activating agent under heat treatment in the inert atmosphere [96]. Different oxidants are used for acidic modification of biochars to increase their acidic property by removing mineral elements [94]. It is conducted by soaking biochars in acidic solutions at 120°C in biochar to acid ratio of 1:10 [96,97]. Alkaline modification helps to adsorb negatively charged species. It is carried out by soaking biochars in different basic concentrations at 25-100°C after which pyrolysis is done with limited or no oxygen [93,98]. In impregnation, biochars are mixed with metal salts or oxides to facilitate easy adsorption of metal ions. Application of these methodologies gives biochar different properties. Azargohar and Dalai [90] investigated the effects of steam and potassium hydroxide (KOH) as a means of physical and chemical activation of biochar. The BET surface area was found to have increased when the temperature for steam and chemical activation was increased. Biochars produced from fast pyrolysis were given steam treatment, which showed enhanced sorption capacity for the removal of contaminants by increasing the biochars’ surface area and porosity [91]. Wheat straw was used as a precursor for the production of activated biochar by activating it using phosphoric acid, acid treated char was heated afterward to acquire desired properties for the removal of heptachlor from aqueous solution [99].
Figure 4 Physical and chemical activation of biochar leading to the different surface phenomenon.

3.2 Characteristics of biochar for adsorption

The pyrogenic conversion of waste materials into biochar is beneficial as it adds considerable economic value; helps in the reduction of waste disposal cost, and is a potentially reasonable alternative to the present commercial activated carbons. These waste materials have high adsorption capacity, considerable mechanical strength, and low ash content [100]. Pyrogenic carbon is an amorphous carbon with a high degree of porosity, which governs the way in which it performs the purifying role, and the large surface area provides multiple sites upon which the adsorption takes place [101]. The
factors which favor selection of agricultural adsorbents include widespread presence, low cost, regenerability and organic composition.

Various mechanisms such as H-bonding, cation-bridging, covalent bonding, and hydrophobic interactions are involved in adsorption of anthropogenic organic compounds onto biochar [102]. Surface properties of biochar and characteristics of adsorbate play an important role in determining the reaction rate for adsorption. For various natural and synthetic organic compounds present in terrestrial environments, aromatic structures form the major components. Different adsorption mechanisms have been suggested for interactions between aromatic π-systems of organic compounds and sorption sites at the organic matter and biochar [87]. Aromatic π-systems have been considered to be involved in π-π electron donor-acceptor (EDA) interactions, and polar-π interactions between organic matter and biochar [103,104].

The surface activity of biochar particles may become attenuated with time as the external space available for adsorption reactions diminishes with the increasing presence of organic compounds at the surface [105]. Surface activity of biochar can be affected by aging process (like pore blockage, surface oxidation, swelling, surface coverage), which has been studied in the soil in detail [106-110]. Various studies on biochar from agro waste have manifested a good adsorption capacity for heavy metal contaminants such as Cu, [111-116], Zn [111,116], Pb [117, 118], and Cr [119].

Table 5 Biochar generated under various pyrolysis conditions and their adsorption characteristics for heavy metal ions.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Agri waste</th>
<th>Pyrolysis Temperature (°C)</th>
<th>Heavy metal</th>
<th>Adsorbent dose (g/L)</th>
<th>Optimum pH</th>
<th>Reaction time (h)</th>
<th>Amount Adsorbed (q_e) (mg/g)</th>
<th>Kinetics</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rice husk</td>
<td>300-400</td>
<td>Cu(II)</td>
<td>10</td>
<td>5</td>
<td>24</td>
<td>44.47</td>
<td></td>
<td>[120]</td>
</tr>
<tr>
<td>2.</td>
<td>Rice husk</td>
<td>300</td>
<td>Pb(II)</td>
<td>0.1</td>
<td>5</td>
<td>5</td>
<td>2.40</td>
<td>Pseudo second order</td>
<td>[117]</td>
</tr>
<tr>
<td>3.</td>
<td>Corn straw</td>
<td>600</td>
<td>Cu(II)</td>
<td>0.1</td>
<td>5</td>
<td>24</td>
<td>12.52</td>
<td>Pseudo-second order</td>
<td>[111]</td>
</tr>
<tr>
<td>4.</td>
<td>Corn straw</td>
<td>600</td>
<td>Zn(II)</td>
<td>0.1</td>
<td>5</td>
<td>24</td>
<td>11.0</td>
<td>Pseudo-second order</td>
<td>[111]</td>
</tr>
<tr>
<td>5.</td>
<td>Corn bran</td>
<td>600</td>
<td>Cr(VI)</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>86.49</td>
<td>-</td>
<td>[119]</td>
</tr>
</tbody>
</table>

### Various studies have shown the effect of agro-wastes on pesticides and other organic contaminants in an aqueous environment (Table 6). In a study by Cederlund et al. [123], heat treatment was found to enhance adsorption and decrease desorption of bentazone and 2-methyl-4-chlorophenoxyacetic acid (MCPA). Chemical treatment using magnetite increased the adsorption of glyphosate, decreasing desorption of chlorpyrifos. Chlorpyrifos and diuron were adsorbed on untreated biochar owing to their high octanol-
water partition coefficients, whereas glyphosate was least adsorbed. The adsorption capacity of biochar iron composite was found to be highest for all pesticides [123]. In another study, the efficiency of rice husk agro waste in nano-sorbent form for removal of 2,4 D was 96.87% removal of the contaminant at pH 5.0, temperature 30°C, the adsorbent dosage of 1.5 g/l attaining an equilibrium within an hour [71].

Sorption of pesticides was found to be more with biochar compared to soil or soil amended with raw material (straw) [78,79]. At intermediate and quasi-equilibrium conditions 48-55 and 66.6-72.4% sorptions were achieved respectively, for soil amended with biochar compared to control and straw for simazine [78].

Table 6 Selected reports on adsorption-desorption of contaminants with biochar amended media.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Biochar</th>
<th>Organic contaminant</th>
<th>Pyrolysis temperature (°C)</th>
<th>Surface area (m²/g)</th>
<th>Adsorption Conditions</th>
<th>Loading rate (g/L)</th>
<th>Amount adsorbed (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Soybean stover</td>
<td>Trichloroethylene</td>
<td>300</td>
<td>6</td>
<td>pH=7 2880 min</td>
<td>0.3</td>
<td>9.85</td>
<td>[101]</td>
</tr>
<tr>
<td>2.</td>
<td>Soybean stover</td>
<td>Trichloroethylene</td>
<td>700</td>
<td>420</td>
<td>pH=7 2880 min</td>
<td>0.3</td>
<td>25.38</td>
<td>[101]</td>
</tr>
<tr>
<td>3.</td>
<td>Peanut shells</td>
<td>Trichloroethylene</td>
<td>300</td>
<td>3</td>
<td>pH=7 2880 min</td>
<td>0.3</td>
<td>7.79</td>
<td>[101]</td>
</tr>
<tr>
<td>4.</td>
<td>Peanut shells</td>
<td>Trichloroethylene</td>
<td>700</td>
<td>448</td>
<td>pH=7 2880 min</td>
<td>0.3</td>
<td>30.74</td>
<td>[101]</td>
</tr>
<tr>
<td>5.</td>
<td>Switchgrass</td>
<td>Metribuzin</td>
<td>425</td>
<td>1.1</td>
<td>pH=2 1440 min</td>
<td>1</td>
<td>223</td>
<td>[124]</td>
</tr>
<tr>
<td>6.</td>
<td>Olive kernel (Physical activation under steam)</td>
<td>Bromopropylate</td>
<td>800</td>
<td>600</td>
<td>75 min</td>
<td>5</td>
<td>0.094</td>
<td>[125]</td>
</tr>
<tr>
<td>7.</td>
<td>Corn cobs</td>
<td>Bromopropylate</td>
<td>800</td>
<td>630</td>
<td>135 min</td>
<td>5</td>
<td>0.086</td>
<td>[125]</td>
</tr>
<tr>
<td></td>
<td>Physical (Physical activatio n under steam)</td>
<td>(Physical activatio n under steam)</td>
<td>Bromopropy late</td>
<td>800</td>
<td>490</td>
<td>135 min</td>
<td>5</td>
<td>0.0893</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>8.</td>
<td>Rapeseed stalks</td>
<td>Bromopropy late</td>
<td>800</td>
<td>570</td>
<td>135 min</td>
<td>5</td>
<td>0.078</td>
<td>[125]</td>
</tr>
<tr>
<td>9.</td>
<td>Soya stalks</td>
<td>Bromopropy late</td>
<td>800</td>
<td>570</td>
<td>135 min</td>
<td>5</td>
<td>0.078</td>
<td>[125]</td>
</tr>
<tr>
<td>10.</td>
<td>Corn cob</td>
<td>Atrazine (A) and imidacloprid (I)</td>
<td>600</td>
<td>242.1</td>
<td>1440 min</td>
<td>0.1</td>
<td>18.0–30.4%(A),(14.7–28.4%(I)</td>
<td>[126]</td>
</tr>
<tr>
<td>11.</td>
<td>Eucalyptus bark</td>
<td>Atrazine (A) and Imidacloprid (I)</td>
<td>600</td>
<td>188.2</td>
<td>Contact time= 1440 min, 27°C</td>
<td>0.1</td>
<td>23.4–40.1%(A),5.9–20.1%(I)</td>
<td>[126]</td>
</tr>
<tr>
<td>12.</td>
<td>Rice husk</td>
<td>Atrazine (A) and Imidacloprid (I)</td>
<td>600</td>
<td>159.1</td>
<td>1440 min</td>
<td>0.1</td>
<td>11.8–42.6%(A), 28.0–46.2%(I)</td>
<td>[126]</td>
</tr>
<tr>
<td>13.</td>
<td>Rice straw</td>
<td>Atrazine (A) and Imidacloprid (I)</td>
<td>600</td>
<td>220.2</td>
<td>1440 min</td>
<td>0.1</td>
<td>37.5–70.7%(A),</td>
<td>[126]</td>
</tr>
<tr>
<td>14.</td>
<td>Corncob</td>
<td>Methylene blue</td>
<td>400</td>
<td>700</td>
<td>45min</td>
<td>2</td>
<td>28.65</td>
<td>[127]</td>
</tr>
<tr>
<td>15.</td>
<td>Corncob</td>
<td>Methylene blue</td>
<td>500</td>
<td>633</td>
<td>120min</td>
<td>2</td>
<td>17.57</td>
<td>[127]</td>
</tr>
<tr>
<td>16.</td>
<td>Corncob</td>
<td>Methylene blue</td>
<td>600</td>
<td>600</td>
<td>120 min</td>
<td>2</td>
<td>0.809</td>
<td>[127]</td>
</tr>
<tr>
<td>17.</td>
<td>Korean cabbage</td>
<td>Congo red</td>
<td>500</td>
<td>11.44</td>
<td>pH=9.18, 1440</td>
<td>1</td>
<td>21.9</td>
<td>[128]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<tr>
<td>18.</td>
<td>Rice straw</td>
<td>Congo red</td>
<td>500</td>
<td>34.73</td>
<td>pH=8.6</td>
<td>1</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td>1440</td>
<td>min</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>Rice straw</td>
<td>Crystal violet</td>
<td>500</td>
<td>34.73</td>
<td>pH=8.6</td>
<td>1</td>
<td>261.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td>1440</td>
<td>min</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>Wood chips</td>
<td>Congo red</td>
<td>500</td>
<td>&lt;0.01</td>
<td>pH=4.</td>
<td>1</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>71</td>
<td>1440</td>
<td>min</td>
<td></td>
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<tr>
<td>21.</td>
<td>Wood chips</td>
<td>Crystal violet</td>
<td>500</td>
<td>&lt;0.01</td>
<td>pH=4.</td>
<td>1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>71</td>
<td>1440</td>
<td>min</td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td><em>Jatropha curca</em> pods</td>
<td>Remazol,brilliant blue R</td>
<td>600</td>
<td>pH=3</td>
<td>8</td>
<td>90%</td>
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<td>23.</td>
<td>Wheat straw</td>
<td>Heptachloro</td>
<td>500</td>
<td>176.4±</td>
<td>pH=7</td>
<td>2</td>
<td>2.218</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>0.631</td>
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<td></td>
<td></td>
<td></td>
<td>cm³g-μm</td>
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<tr>
<td>24.</td>
<td>Groundnut shell biochar</td>
<td>2, 4-dichlorophenoxyacetic acid</td>
<td>650</td>
<td>43</td>
<td>pH=8.5</td>
<td>40</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>25.</td>
<td>Groundnut shell activated carbon</td>
<td>2, 4-dichlorophenoxyacetic acid</td>
<td>800</td>
<td>709</td>
<td>pH=9.</td>
<td>0.6</td>
<td>250</td>
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<td>7</td>
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</tr>
<tr>
<td>26.</td>
<td>Rice straw</td>
<td>Phenol</td>
<td>550</td>
<td>71.35</td>
<td>1440</td>
<td>2</td>
<td>83.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>Rice straw</td>
<td>Phenol</td>
<td>550</td>
<td>143.3</td>
<td>KOH</td>
<td>2</td>
<td>93.5</td>
<td></td>
</tr>
<tr>
<td>28.</td>
<td>Rice straw</td>
<td>Phenol</td>
<td>550</td>
<td>87.2</td>
<td>HNO₃</td>
<td>2</td>
<td>66.8</td>
<td></td>
</tr>
<tr>
<td>29.</td>
<td>Rice straw</td>
<td>Phenol</td>
<td>550</td>
<td>56.9</td>
<td>H₂SO₄</td>
<td>2</td>
<td>65.6</td>
<td></td>
</tr>
<tr>
<td>30.</td>
<td>Rice straw</td>
<td>Phenol</td>
<td>550</td>
<td>110.9</td>
<td>H₂O₂</td>
<td>2</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>31.</td>
<td>Rice straw</td>
<td>Phenol</td>
<td>550</td>
<td>87.75</td>
<td>KMnO₄</td>
<td>2</td>
<td>64.2</td>
<td></td>
</tr>
</tbody>
</table>
Yavari et al. [131] found that biochars produced from oil palm empty fruit bunches were more efficient for the sorption of polar pesticides like imazapic and imazapyr. This sorption behavior is accounted to the elemental composition and surface functional groups on the oil palm biochar as compared to rice husk derived biochars. It was observed that low pyrolysis temperature retains organic functional groups on biochar’s surface, which leads to higher sorption of these polar pesticides.

The surface functional moieties on biochar had a significant influence on adsorption than the surface area of the biochar at elevated pyrolysis temperature. In contrast to this study, biochar obtained at high temperature was more effective at terbuthylazine (non-polar pesticide) adsorption than the one produced at lower temperature [132]. This affinity for non-polar molecules is accounted to the non-polar nature of surface as well as increased porosity of biochar produced at elevated pyrolysis temperature. Trivedi et al. [75] highlighted the effect of preparation conditions on adsorption of 2, 4-D on groundnut shell biochar prepared at 650 and 850°C. The surface area and organic carbon content increased with thermal activation of biomass, which enhanced the sorption capacity. Phosphorous treated and untreated rice husk biochar (RHBC) showed maximum herbicide sorption as compared with eucalyptus bark, corn cob, and bamboo chips, prepared under similar operating conditions. The cation exchange capacity, pore volume, and polarity of RHBC were highest among other biochars. The performance of RHBC was further enhanced by phosphoric acid treatment as it increased the functional groups on the surface of biochar pores. Apart from this, the surface area for RHBC was lowest. Pore size and pore volume show good correlation with adsorption onto biochar whereas no correlation was observed with a surface area of biochar [126]. Carbera et al. [133] related sorption of bentazone on the biochar-amended soil to surface area and dissolved organic carbon (DOC) content of biochar. Sorption was lesser on biochar with high DOC, as DOC has the tendency to get adsorbed to soil particles, hence competing with herbicides for adsorption sites. On the other hand, sorption of aminocyclopyrachlor increased in biochar with high surface area and low DOC due to the interactions between biochar DOC and mineral soil surfaces. Polar herbicides such as glyphosate and 2-methyl-4-chlorophenoxyacetic acid (MCPA) were weakly adsorbed on biochar owing to the negative charge on biochar surface which offered electrostatic repulsion [77]. soybean stover and peanut shells biochars produced at 700 and 300°C have studied for Trichloroethylene (TCE) adsorption [101]. Low adsorptive properties of the biochars produced at 300°C were attributed to high oxygen content or low carbon content at low temperature. Adsorption capacity was positively correlated with carbon content but negatively correlated with an oxygen content of biochars. This positive and negative correlation with C and O content of biochar, respectively, with adsorption of TCE, is
attributed to the hydrophobicity of biochar and to the removal of acidic functional groups. The surface functional moieties on the char result in increased polarity of biochar produced at low pyrolysis temperature. This results in reducing the adsorption of TCE, as polar sites are known to hinder the removal of TCE due to the formation of water clusters. Low oxygen content in high-temperature biochars hindered the formation of water clusters and enhanced adsorption of TCE. Another reason for high adsorption with rising temperature was the formation of micropores which increases surface area leading to greater diffusion of TCE.

4. Conclusion

Lignocellulosic biomass-based agricultural residues have been extensively studied for remediation of heavy metal and organic contaminants in water and wastewater. The basic approach involves raw biomass physicochemically treated biomass and pyrolyzed biomass (biochar) for use as surface active adsorbents for heavy metals and organic contaminants. Limited studies on the physicochemically treated biomasses and their applications in adsorption of heavy metal or organic contaminants are available. There is a substantial promise in the usage of biochar as an adsorbent for heavy metal and pesticides.

One of the major concerns about adsorption is the disposal of the waste generated in the process. It is believed that lignocellulosic can be used in further thermochemical processes (combustion & pyrolysis) whereby the ash liberated would carry the adsorbate and be concentrated significantly, up to 50 times in case of heavy metals. This would have the added advantage that the thermochemical processes are catalyzed by the heavy metal adsorbates leading to a variety of value-added biorefinery products. On the other hand, the organic impurities volatilize and yield more toxic products. The other alternatives of regeneration and reuse are cost and environmentally ineffective so far. However, efforts are required in the management of these adsorption based wastes for the effective use of industrial wastewater and water treatment technologies.

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Chapter 5

Carbon Quantum Dot Composites for Photocatalytic Degradation of Organic Pollutants

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Abstract

In the present chapter, basic chemistry of carbon quantum dots (CQDs) has been presented. CQDs actually represent a class of materials comprising of carbon atoms in the nanometric range. These are more important as compared to other quantum dots. The CQDs can be synthesized using different methods such as hydrothermal treatment, microwave method, electrochemical and synthetic route, etc. CQDs are of immense importance due to their eco-friendly nature, easy availability and cost-effectiveness. Different composites based on CQDs have been synthesized in the recent years and being used for a number of applications such as biosensing, bioimaging, photocatalysis and chemical sensing, etc. CQDs based composites have been used as catalysts due to their outstanding electrochemical catalytic activity.

Keywords

Carbon Quantum Dots, Photocatalytic Degradation, Hydrothermal Treatment, Quantum Dots, Fluorescence

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1. Introduction to carbon quantum dots

Quantum dots (QDs) are the minute fragments of matter; even so small that it can be concentrated into a single point. These are zero-dimensional particles. Due to their extremely small size, the particles carrying electricity get restricted and have well-defined energy levels according to the laws of quantum theory [1-4]. QDs are few nanometer wide crystals which can be made from semiconductors, organic materials as well as from conductors. In spite of the small size, these have the tendency of acting as individual atoms. And although QDs are crystals, they behave more like individual atoms that is why they are also known as artificial atoms [5]. Exceptional quantum size effect of QDs enhances their properties such as wide excitation spectrum, exceptional photostability, high quantum yield of fluorescence and maximum photobleaching.
Increasing environmental issues have made the researchers to discover some particles or materials that are not harmful to nature. Carbon is the skeleton of all living tissues and is also non-toxic in nature. Carbon-based quantum dots (CQDs, C-dots or CDs) offer an alternative to the traditionally used toxic materials. CQDs were first accidentally discovered during the purification of single-walled carbon nanotubes which were prepared through electrophoresis. Later on, these were also prepared through laser ablation of graphite powder and cement in 2006. CQDs have gained huge attention because of their chemical stability, biocompatibility, and low toxicity in comparison to other quantum dots [6-9]. In addition, CQDs are also abundant and inexpensive in nature which increases their utility range [10]. Carbon is basically a black material and normally deliberated to have low solubility in water and feeble fluorescence. Extensive consideration has been concentrated on CQDs due of their noble solubility and strong luminescence; that is why they are also referred to as carbon nano lights [11]. In the past few years, much progress has been achieved in the synthesis, properties, and applications of carbon-based quantum dots and much has been reported by Baker et al., Lee et al., and Zhu et al. Compared to traditional semiconductor quantum dots and organic dyes, photoluminescent CQDs are superior in terms of high (aqueous) solubility, robust chemical inertness, facile modification and high resistance to photobleaching [12-17]. The superior biological properties of carbon quantum dots, such as low toxicity and good biocompatibility, assign them with probable applications in bioimaging, biosensor and drug delivery [18,19]. The high electronic properties of CQDs as electron donor and acceptor, causing chemiluminescence and electrochemical luminescence, bestow them with extensive potentials in optronics, catalysis, and sensors.

2. **Structure of carbon quantum dots**

Carbon quantum dots are generally spherical in shape with a diameter of approximately 10 nm. CQDs comprise only a few molecules or atoms of nanostructured materials. Their molecular weight ranges from only a few thousand to tens of thousands. The presence of –COOH, -OH and –NH$_2$ groups in the structure, gave them the ability to attach to a number of organic, inorganic and biological molecules or groups [20-23]. These groups also make them an efficient tool for a number of applications such as targeted drug delivery, photoluminescence, and sensors, etc.

3. **Synthesis of carbon quantum dots**

A number of techniques have been proposed for the synthesis of carbon quantum dots. Basically, their synthesis techniques are categorized into two: top- down and bottom- up approaches [24-26]. The top-down approach includes cutting, oxidation and the bigger
molecules are broken down to the nanometer size particles. However, the bottom-up approach involves chemical reactions of the precursor molecules to form the nano range products [27,28].

3.1 Top-down approach

Top-down approaches for CQDs are the commonly used preparation measures which include arc-discharge approach [30], electrochemical method [31] and laser ablation [32]. In 2004, during the synthesis of single-walled carbon nanotubes by arc discharge method, Xu et al. accidentally discovered CQDs. They further introduced nitryl onto the CQDs by arc discharge fuming nitric acid so as to enhance its hydrophilicity [33,34]. After that, NaOH solution having pH 8.4 was utilized to extract the precipitate to address a black suspension. Three groups of fluorescent carbon nanoparticles with different molecular weights were obtained after further electrophoretic separation [35-37]. These three groups were known to exhibit a characteristic color of green, yellow and orange, respectively.

3.1.1 Electrochemical method

In the starting stage, electrochemical methodologies were employed mostly for the CQDs synthesis. S.T. Lee et al., utilized graphite electrodes as the carbon source [38]. Particularly, researchers employed graphite rods as both cathode and anode in an electrochemical setup, with NaOH/ethanol as the electrolyte solution. The flow of electric current in this electrochemical cell helps in the production of CQDs. These CQDs show different colors exhibiting their luminescence capacity. Fig. 1 shows the images of CQDs prepared from the electrochemical method. In spite of its high production ability, the electrochemical method still suffers from certain drawbacks such as CQDs produced do not have a uniform size distribution, same surface morphologies, and uniform crystallinity, etc.

3.2 Bottom-up approach

This approach includes the combination of atoms or molecules so as to form a nanoscale structure through chemical reactions and polymerization methods. It basically includes hydrothermal method [39-41], simple pyrolysis [42,43], microwave-based pyrolysis [44,45] and acid dehydration method [46]. Among these, hydrothermal and microwave-based pyrolysis methods are the most extensively used methods for CQD preparation.
Figure 1  CQDs produced through an electrochemical method. (a) TEM image of the CQDs (exhibiting small < 5 nm diameters); (b) photoluminescence images recorded upon excitation at different wavelengths; (c–h) high-resolution TEM images showing the crystalline graphite lattice planes. Scale bars correspond to 2 nm [38].

3.2.1 Hydrothermal method

Hydrothermal method is the most commonly used method for the synthesis of carbon quantum dots due to its simple mode of operation and versatile nature. It is actually a heterogeneous process which mineralizes under high pressure and temperature conditions. High temperature and pressure conditions help in dissolving the materials which are not under ordinary conditions and produce a nanomaterial with uniform size distribution, surface morphologies, and high purity content, etc. As compared to others, this method is quite eco-friendly and cost-effective w.r.t. instrumentation and maintenance cost [47]. It can be hybridized with many other processes such as microwave, ultrasound, and electrochemistry.

In 2007, the hydrothermal method was used for the first time for the preparation of carbon quantum dots by Liu and his coworkers. Candle ash was chosen as the carbon source mixed with nitric acid through heat reflux and produced a black solution. It was purified through a number of processes such as centrifugation, dialysis, and electrophoresis. This method resulted in fluorescent CQDs having uniform size distribution [48]. S.P. Lau and his colleagues also synthesized CQDs through hydrothermal treatment. They used glucose as the carbon precursor. In this experiment, the CQDs were accumulated by the nucleation process which leads to the development of “self-passivated” layers having different groups such as –OH, -COR and –CH [47] as shown in Fig. 2.
3.2.2 Microwave method

In addition to the hydrothermal method, microwave method for the synthesis of carbon quantum dots is also quite in usage due to its fast processing and easy mode of use. Zhu with his coworkers synthesized fluorescent CQDs using the simple microwave method. Carbohydrate and PEG200 was chosen as the carbon precursor and coating agent, respectively [49]. Under 500W microwave power radiation for 2-10 min, the reaction system progressively changed from colorless to a dark brown solution. The dark brown solution was further diluted with water and fluorescent CQDs were obtained. They also demonstrated how the particle size and yield of CQDs depend upon the reaction time. Wang et al. also used this method for the synthesis of CQDs. They used eggshells as the carbon source and converted them into ashes. These ashes were then thoroughly mixed with NaOH aqueous solution. The resultant solution was subjected to the microwave radiation for about 4-5 min. This radiation treatment yielded CQDs with high purity content. The fluorescent quantum yield was noted to be about 14% [50].

Another experiment which demonstrated the synthesis of CQDs was carried out by Chandra and his group [51]. They used sucrose as the carbon source in the presence of
phosphoric acid environment under the microwave radiation. The reaction time was adjusted between 3-4 min and the obtained fluorescent CQDs were bright green colored. Yang et al. also used microwave method for the CQD preparation using chitosan as the carbon source. They chemically modified them with amino groups and the resulting particles were used for the adenocarcinoma A549 cell imaging [52].

3.3 Synthetic methods

Researchers have suggested several synthetic methods for the assembly of carbon quantum dots having scarce luminescent properties. H. Lin with his coworkers chemically modified the carbon quantum dots with –N containing functional groups such as amines, amides, and other carbon-nitrogen units. These N- doped CQDs unveiled a fascinating properties as these showed strong emission around 600nm. This is one of the rare observations since a maximum of the CQDs showed luminescence properties at shorter wavelengths (green- blue).

One of the most interesting experiments was the use of waste frying oil for the production of CQDs which were doped with sulfur atoms to improve properties, as demonstrated by J.S. Yu and his colleagues [53]. These sulfur-doped carbon quantum dots were found to show a wide range of properties and were used mainly for the cell imaging. These properties were found to be dependent on the pH of the solution. Fig. 3 is the schematic representation of a synthetic method for the preparation of sulfur-doped carbon quantum dots using waste frying oil as the carbon precursor [53].

Figure 3 Preparation of sulfur-doped carbon- dots from waste frying oil [53].
The additional experiment includes the use of folic acid as the carbon precursor for the preparation of CQDs. The hydrothermal method was used for their preparation as synthesized CQDs showed high sensitivity towards the folate receptors. These receptors are mostly found in the cancerous cells in the large amount [54]. Fig. 4 shows general route for the synthesis of CQDs using folic acid as a carbon precursor.

![Folic Acid](image)

**Figure 4** Carbon- dot preparation from folic acid. Scheme of the thermal process for generation of the Carbon dots in basic aqueous solution [54].

**Table 1** Different synthesis methods of CQDs from different carbon precursors with their major applications.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Carbon source</th>
<th>Method</th>
<th>Application</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>Glucose</td>
<td>Hydrothermal method</td>
<td>Bioimaging</td>
<td>55</td>
</tr>
<tr>
<td>2.</td>
<td>Sucrose</td>
<td>Microwave method</td>
<td>Bioimaging</td>
<td>56</td>
</tr>
<tr>
<td>3.</td>
<td>Chitosan</td>
<td>Hydrothermal method</td>
<td>Bioimaging</td>
<td>57</td>
</tr>
<tr>
<td>4.</td>
<td>Citric acid and ethylenediamine</td>
<td>Hydrothermal treatment</td>
<td>Fe$^{3+}$ sensing</td>
<td>58</td>
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<tr>
<td>5.</td>
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<td>Hydrothermal method</td>
<td>Cu$^{2+}$ sensing</td>
<td>59</td>
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<tr>
<td>6.</td>
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<td>Hydrothermal method</td>
<td>pH sensing</td>
<td>60</td>
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<tr>
<td>7.</td>
<td>PEG and saccharide</td>
<td>Microwave method</td>
<td>-</td>
<td>61</td>
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<tr>
<td>8.</td>
<td>Watermelon peels</td>
<td>Carbonization</td>
<td>Bioimaging</td>
<td>62</td>
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<td>9.</td>
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<td>Printing</td>
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<tr>
<td>10.</td>
<td>Organogel</td>
<td>Topochemical polymerization</td>
<td>-</td>
<td>64</td>
</tr>
</tbody>
</table>
4. Properties of carbon quantum dots

4.1 Optical

CQDs have lucrative absorption in the ultraviolet range, which can also outspread to the visible range. Modification with the help of some passivating agents, the redshift region may be obtained unceasingly. Photoluminescence and electrochemical luminescence are the two main types of luminescence properties shown by CQDs. However, photoluminescence is the most important one [65]. As a pertinent role in all areas of fluorescent nanomaterials, the brilliant optical properties of CQDs chiefly include steep fluorescence durability, nonblinking, tunable excitation, and emission wavelengths. Nevertheless, the complete mechanism of emission of CQDs is still not clear. The intensive quantum study needs an aspiring establishment. Few researchers speculated that the emitting mechanisms of CQDs are complex due to quantum confinement, surface blockade, or exciton recombination radiation process [66].

4.2 Biologically compatible

Carbon quantum dots have quite lower toxicity value and extremely small size which make their smooth passage through the cell walls. Their easy penetrating nature makes them to be used in the biological field. In addition, the amount of CQDs contains a predestine functional groups and thus, can be modified mutually with organic, inorganic, polymer, and other substances endowing different pragmatic properties.

5. Applications of carbon quantum dots

5.1 Chemical sensing

Carbon quantum dots have been used for a number of applications such as chemical sensing, targeted drug delivery, and bioimaging, etc. Fluorescent CQDs have exceptional optical properties, chemical stability, and high water solubility. For this reason, they have been used for metal ions as well as anion recognition and biomolecule detection [67,68]. CQDs have the ability to alter the proficiency of recombination between the surfaces of electron-hole pairs by interaction with the analyte. This phenomenon occurred during the quenching treatment so as to acquire qualitative or quantitative analysis of the object. CQDs have been used for the detection of toxic heavy metals such as mercury, lead, and chromium, etc. Mercury is among the most toxic metal ions present in the environment having serious carcinogenic effects. Researchers have suggested many different methods for the removal of Hg$^{2+}$ from the environment by the use of CQDs [69-71].
Carbon quantum dots synthesized by the hydrothermal method using grapefruit peel as the carbon precursor has received much attention due to high detection ability towards Hg$^{2+}$. The detection limit was calculated to be about 0.23nM. Liu et al. acquired CQDs with exceptional luminous stability by the polyethylene glycol (PEG) refluxed with NaOH. They used these CQDs as a sensor that can precisely detect Hg$^{2+}$ in solution and the detection limit was calculated to be 1fM. This test method efficaciously detected Hg$^{2+}$ in the rivers, lakes, and tap water samples and the sensitivity noted was very high [72,73]. In addition, anion and smaller molecules can also be detected using carbon quantum dots based materials.

5.2 Photocatalysis

With the rising urge for low-carbon materials, more emphasis is laid on how to make the full use of solar energy and other relevant cheap energy sources [74]. The visualization of photocatalytic technology caused its expansion, involving solar energy, photovoltaic cells, self-cleaning materials, environmental atomic waste control and multiple other familiar fields. However, the commonly used photocatalytic materials such as TiO$_2$ and ZnO consistent with absorption range in ultraviolet region; visible light cannot be taken as a perfect advantage and have been greatly isolated in prudent applications [75-79]. Thus, formulating nanomaterials with high stability is of great significance in deciphering environmental problems and energy concerns.

TiO$_2$ is among the most commonly used photocatalysts. It has been used for the decomposition of organic pollutants and also to generate H$_2$ from H$_2$O. But, due to the marginal gap between the valence and conduction band, it shows absorption peaks in shorter wavelengths only (ultraviolet). Thus, to increase its absorption range to higher wavelengths, researchers formulated that the composites of TiO$_2$ nanoparticles and CQDs can meritoriously enlarge the range of the optical response of the composite structure and intensify the consumption of solar energy and transformation [80-85]. Fig. 5 shows a general mechanism of CQD sensitization. For instance, Zhang et al. utilized CQDs-TiO$_2$ composites to get H$_2$ from the water decomposition under visible light irradiation, wherein the introduction of CQDs obviously widens the light response range of TiO$_2$. Consequently, based on the upconversion property of CQDs and the synergistic effect between the CdSe QDs and CQDs, the CdSe quantum dots were aided to amend the TiO$_2$-CQD nanocomposites, and the photocatalytic efficiency was greatly enhanced [86].
5.3 Bioimaging

We know that the CQDs possess great advantages as compared to the traditionally used semiconductor QDs due to their exceptional optical and steady chemical properties. Moreover, CQDs are eco-friendly and low noxious nanomaterials [87]. These characteristics make the CQDs to replace the semiconductor quantum dots in bioimaging.

As an experiment, Yang et al. injected CQDs into the 1 mice body in three different ways: subcutaneous injection, intradermal injection, and intravenous injection. They got effective in-vivo imaging under light irradiation of 470 and 545nm. They found that CQDs subcutaneously injected into the mice of the forelimb migrate along the forearm to the axillary lymph nodes, while CQDs of intravenous injection in the systemic circulation concentrated at the bladder area. They also notified that fluorescence images of the urine can also be detected after 3h of injection. After 4h, the fluorescent CQDs exist mainly in the kidney of mice. They speculated that polyethylene glycol could diminish the effective surface of CQDs on the affinity to protein and makes CQDs more difficult in uptake by the liver [88]. Bioimaging applications of different CQDs having different carbon precursor with their method of preparation have been presented in Table 2.

Figure 5 Illustration of the sensitization mechanism of CQDs [86].
Table 2  Bioimaging applications of different CQDs having different carbon precursors with their method of synthesis.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Carbon precursor</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Phenol/formaldehyde resin</td>
<td>Carbonization</td>
<td>89</td>
</tr>
<tr>
<td>2.</td>
<td>Candle soot</td>
<td>HNO₃ oxidation</td>
<td>90</td>
</tr>
<tr>
<td>3.</td>
<td>Orange juice</td>
<td>Hydrothermal treatment</td>
<td>91</td>
</tr>
<tr>
<td>4.</td>
<td>Sugarcane juice</td>
<td>Hydrothermal method</td>
<td>92</td>
</tr>
<tr>
<td>5.</td>
<td>Gelatine</td>
<td>Hydrothermal treatment</td>
<td>93</td>
</tr>
<tr>
<td>6.</td>
<td>Hair fibre</td>
<td>H₂SO₄ treatment</td>
<td>94</td>
</tr>
<tr>
<td>7.</td>
<td>3-(3,4-Dihydroxyphenyl)-L-alanine, L-histidine, and L-arginine</td>
<td>Carbonization</td>
<td>95</td>
</tr>
<tr>
<td>8.</td>
<td>Acetic acid</td>
<td>Carbonization</td>
<td>96</td>
</tr>
<tr>
<td>9.</td>
<td>Carbohydrate</td>
<td>Amine passivation</td>
<td>97</td>
</tr>
<tr>
<td>10.</td>
<td>Chitosan</td>
<td>Microwave oven</td>
<td>98</td>
</tr>
</tbody>
</table>

5.4 Drug delivery

Traditionally used drug carrier materials do not offer the ability of their observability and traceability. Researchers have suggested the use of fluorescent nanomaterials to the drug carrier system due to their easy detectability [99]. Due to low toxicity, admirable biocompatibility, and modifiable surface functional groups, CQDs have become a center of attraction of the drug delivery research.

Lai et al. prepared CQDs by pyrolysis using glycerol as the carbon precursor. The synthesized CQDs were modified using polyethylene glycol (PEG) and the particle size was controlled through mesoporous nanoparticles to acquire a uniform and excellent optical properties of CQDs (CQDs @ mSiO₂-PEG). They used CQDs @ mSiO₂-PEG as an anticancer drug carrier, doxorubicin (DOX) and studied the release rate of DOX in HeLa cells. The results revealed that CQDs and DOX in the cytoplasm emitted blue fluorescence. However, red fluorescence was observed in the nucleus [100]. According to the proportions of the two fluorescent colors, this method acts as an active
pharmaceutical carrier. They also reported that these can act as a traceability agent in the amount of drug released in the cells.

Zheng et al. imprinted amino groups on CQDs surface with oxaliplatin through the chemical coupling reaction integrating the two substances as one. The reformed CQDs can enter into the interior of cancer cells via endocytosis. Due to the hasty changes in the interior environment of the cancer cells, the drug can be easily released from the surface of the CQDs. The results showed that by monitoring the fluorescent CQD signals in cancer cells, dispersal of oxaliplatin in the cancer cells can be easily detected, which will deliver great help to doctors to grasp the exact time and drug dose injection.

6. Degradation of organic pollutants using carbon quantum dot based composites

Rapid growth in industrialization has led to increasing of effluents in the water system. Industries are the major source for the addition of organic pollutants, dyes and pharmaceutical effluents, etc. to the water. These pollutants have many adverse effects including eutrophication and aquatic life degradation. For this reason, their removal is of immense importance. Researchers have suggested that solar energy can be used in this context due to its renewable, cheap and abundant nature. Degradation of pollutants in the presence of solar light has been proved to be a simple and the most effective method.

The probable utilization of CQDs in photocatalytic mechanisms has been extensively revealed, where they have the tendency to absorb both UV and visible light and directly help in transferring photoexcited electrons. CQDs are highly used for photodegradation processes due to their low cost, easy production, and non-toxicity.

A number of CQD based composites have been prepared and used for the photocatalytic degradation of the organic pollutants. Zhang with his coworkers synthesized CQDs using an electrochemical method which was further modified and CQDs/Ag$_3$SO$_4$ & CQDs/Ag/Ag$_3$SO$_4$ composite catalysts were prepared. They studied the ability of these composite catalysts for the photocatalytic degradation of methylene blue under visible light radiation. Their experimental results showed that the photocatalytic degradation capability of CDs/Ag/Ag$_3$SO$_4$ is about 5.5 times greater than that of CDs/Ag$_3$SO$_4$. B.Y. Yu with his co-workers synthesized carbon quantum dots embedded with mesoporous hematite nanospheres with the solvent-thermal process in aqueous solution. The mesoporous hematite nanospheres provide high surface area and the CQDs act as a catalyst, promoting the rate of photocatalytic degradation. Their results showed the high photocatalytic degradation ability having up to 97% retention capacity [101].
Figure 6 Photocatalytic degradation pathway of isoproturon [102].
For complete exploitation of solar energy, R. Xie, and his co-workers synthesized a novel carbon quantum dots (CQDs) modified Bi_{20}TiO_{32} photocatalysts with varying carbon quantum dot content. Results revealed the uniform distribution of CQDs on the surface of Bi_{20}TiO_{32}. Prepared photocatalyst was capable of absorbing light both under visible and near-infrared region due to the presence of CQDs which were acting as photosensitizers. As prepared CQDs/Bi_{20}TiO_{32} composite was used for the degradation of herbicide isoproturon and a maximum of 98.1% degradation was recorded with only 1% carbon quantum dot content. Active species in the photodegradation process were $h^+$ and $‘O_2^-$. The degradation rate was about 4.5 times greater than pure Bi_{20}TiO_{32} indicating the high catalytic ability of catalytic ability of CQDs. Fig. 6 shows the photocatalytic degradation pathway of isoproturon [102].

Rhodamine B is an organic dye used for the detection of rate of reaction and the direction of flow. It is a fluorescent dye so quite easily detectable but its presence in high amount in water is a serious matter of concern. M. Ji et al. [103], tried to remove it from the wastewater so to protect the aquatic life. They utilized (CQDs)/Bi_{4}O_{3}I_{2} which were synthesized by solvothermal method. The CQDs, imprinted successfully on the Bi_{4}O_{3}I_{2} acted as transfer sites for the electrons generated during photocatalysis and adsorption site for the organic pollutant. A multipurpose CQDs/ N-ZnO photocatalyst was capable of degrading three commercial dyes namely, malachite green, methylene blue, and fluorescein dyes, within 30–45 min of daylight irradiation. Due to the photo-corrosion property of the synthesized CQDs/N-ZnO photocatalyst, it was used up to four times without significant deactivation [103].

7. Conclusions

Fluorescent CQDs have excellent optical properties as well as good biocompatibility due to which they show a wide range of applications such as bioimaging, biosensing, chemical sensing, drug delivery and photocatalysis, etc. Hydrothermal and microwave methods have been proved to be the best preparative techniques of CQDs with high purity level and maximum yield. Modification helps in injecting a number of functional groups on CQDs which makes it a highly effective sensor and catalyst. The addition of functional groups helps in the generation of electron-hole pairs which further enhance the rate of degradation of the organic pollutants from the wastewater.

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Chapter 6

Methods for the Detection, Determination and Removal of Phenolic Compounds from Wastewater

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Abstract

Phenolic compounds are pollutants of main concern, which at very low concentration are highly toxic. In this chapter, we have discussed the comparison of the applicability and efficiency of conventional as well as advanced methods of treatment of wastewater for removal of phenols. Conventional treatments like extraction, adsorption, electrochemical as well as chemical oxidation, and distillation, have been effectively used for many phenolic compounds, but advanced treatments like ozonation, Fenton processes, photochemical treatment, and wet air oxidation have received little attention as compared to that of conventional treatment methods. Compared to physicochemical treatment, biological treatment is energy saving and environment-friendly as compared to that of physicochemical treatment. But it is not a very effective treatment method for pollutants with high concentration. Enzymatic treatment is the best treatment method for the removal of phenols with a number of enzymes such as peroxidases, laccases, and tyrosinases under gentle conditions.

Keywords

Wastewater Treatment, Phenol Toxicity, Degradation, Bioremediation

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1. Introduction

At present, the most crucial problem faced by humans is the environmental pollution. Groundwater and soil quality is affected by larger production/leakage of toxic compounds into the environment as an effluent [1, 2]. For the past 20 years, the immense increase in industrialization in the region of the world has a big role in environmental pollution. Moreover, the chlorinated phenolic compounds and derivatives are produced by the natural decomposition of plants by fungi e.g. tannins are produced within the plants as secondary metabolites. Different human activities are responsible for various sources of phenols such as phenolic herbicides and biocides such as 2, 4-dichlorophenoxyacetic acid (2, 4-D) and pentachlorophenol (PCP reside in the environment due to human activities [3]. Dissolved phenols and polycyclic aromatic
hydrocarbons (PAHs) are present in industrial effluents which may pollute the underground water table and cause severe drinking water pollution problems. These chemicals, when exposed to the human body, can affect the respiratory system, the central nervous system, blood system, and kidney [4, 5]. Phenols have been classified as the 45th top hazardous compounds of main concern by ATSDR (Agency for Toxic Substances and Disease Registry), USA, harmful compounds which must be treated on an urgent basis before their exposure to the environment [5, 6].

Chronic and acute exposure are the two types of phenol toxicity, the acute poisoning of phenol in humans can be seen through symptoms such as dryness in throat and mouth, and dark colors of urine excreted due to the occurring of lipid peroxidation [7]. Chronic exposure causes several symptoms such as anerxia, muscle pain, headache, gastrointestinal pain which will then lead to cancer [8]. Phenol is easy to be absorbed after being exposed via inhalation because it can be present in the atmosphere as a gaseous or particulate form or directly dermal contact. Phenol has the ability to irritate skin, and long-term of dermal contact can lead to severe skin damage [9]. Oral accidental exposure to phenol may cause severe damage to the liver and kidney due to accidental ingestion of 1 g phenol which is reported to cause fatality to human [10] (Table 1).

Toxicity of phenols is related with two causes i.e. Organic free radical species generation and hydrophobicity of the phenolic compound [3]. First, the logarithm of the partition coefficient (log P_{ow}) of phenolic compounds in water and n-octanol correlates with the hydrophobicity of solvent. The toxicity of phenols is influenced by the log P_{ow} value. The value between 1.5-4.0 is toxic to living cells especially microorganism. Log P_{ow} value of phenol solvent within that range has the ability to disturb the structure of membrane hence damaging its vital function [11]. Secondly, Different substitution and other chemical reactions of the reactive hydroxyl group of phenols enhance the toxicity of phenols like chlorination of phenols. Different chemical reactions can be carried out on the benzene ring of phenol such as nitrification, alkylation, and halogenations. For example, the presence of chlorine in phenolic structure because of water treatment brings about the increase of toxicity of phenolic compound and resistance in the atmosphere. The ability of chemical groups attached to phenol, their properties and position on a ring structure are the deciding factor for their residence in the environment [3].

Due to the toxic effects of phenol and derivatives to human and animals, it is necessary to remove such toxic compounds from wastewater. Therefore, it has become a challenging problem to remove such organic compounds to decrease their concentrations up to the permitted levels before releasing waters to the environment. For the removal of phenolics from wastewater, a number of methods have been introduced, which includes chemical coagulation [12], electrochemical oxidation [[13], membrane separation [14],
solvent extraction [15] biodegrading, photocatalytic degradation [9] bioremediation [16] and using many synthetic and natural adsorbents. For the remediation of organic compounds from wastewater, different techniques have been developed. Bioremediation of organic phenolic compounds is a most desirable technique due to its easy implementation but it is not very suitable for high molecular weight phenolic compounds having 5-6 aromatic rings [16].

This chapter is related to removal of phenol from wastewater, to ensure and provide a safe place for the next generation in future especially water sources. Literature included in this chapter is from 1983 to 2016.

Table 1 Harmful Effects of Phenols [17].

<table>
<thead>
<tr>
<th>HUMAN AND ANIMALS</th>
<th>AGRICULTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Short-term effects:</strong></td>
<td><strong>Effects on soil:</strong></td>
</tr>
<tr>
<td>Respiratory infection, headaches, burning eyes, skin rashes.</td>
<td>Porosity of soil decreases, flocculation</td>
</tr>
<tr>
<td><strong>Chronic effects (high exposure):</strong></td>
<td><strong>Effects on plants:</strong></td>
</tr>
<tr>
<td>Muscle pain, weakness, weight loss, anorexia, fatigue.</td>
<td>Reduced amount of germination of seeds</td>
</tr>
<tr>
<td><strong>Long-term effects (low exposure):</strong></td>
<td><strong>Effect on groundwater:</strong></td>
</tr>
<tr>
<td>Heart disease, respiratory cancer, immune system weakness.</td>
<td>Groundwater near hazardous site is contaminated by phenol which seeps through the soil.</td>
</tr>
</tbody>
</table>

2. Methods of determination of Phenols

Generally, a spectrophotometric method is used for the determination of phenolic contents in wastewater. For determination of specific phenolic compounds, at very low concentration, a gas chromatographic (GC) method with flame ionization detector or (FID) or electron capture detection (ECD) is used. A liquid-liquid extraction gas chromatographic/mass spectrometric (GC/MS) method can also be used for the determination of phenols at a little higher concentration.

A highly selective spectrophotometric method can be used for the determination of phenolic in industrial and municipal wastewater samples (Table 3). For this purpose, aminoantipyrine is an extensively used reagent. Another reagent N-hydroxyl-N, N’-diphenyl benzamidine (HODPBA) is used for determination of phenols by spectrophotometric method. In this method phenol reacts with HODPBA in the presence of vanadium and a complex of blue-colour is formed which is extractable into CHCl₃.
2.1 Physical methods

2.1.1 Solvent extraction
Solvent extraction is the widely used technique for the removal of phenols from different effluents in wastewater [15]. Main types of MSE (membrane solvent extraction) are non-porous MSE and porous MSE. A driving force like the potential difference is responsible for the transportation of solute across the membrane. With low mass transfer resistance due to its pore size range from 0.1-10 μ, the microfiltration membrane has been extensively used for MSE amongst porous membranes. For coal gasification wastewater treatment method methyl isobutyl ketone was used as extracting solvent. By this method, about 93% of phenol was recuperated as a by-product from wastewater, which was an additional economic advantage of this method [18].

2.1.2 Liquid-liquid extraction
It is the process in which components of a solution are separated on the basis of their relative solubility (Fig. 1). It is a very simple method for removal of phenols using different solvents. Piava et al worked on the batch removal of phenol by liquid-liquid extraction from methyl isobutyl ketone (14.4%) as a solvent, in a bench-scale mixed vessel [19]. The temperature range was 10 to 40 °C, along with NaOH concentration between 5.5 and 6.5% and the range of rotational speed was between 400 to 800 rpm. The removal efficiency was noted to be 94.0-97.6%. Different solvents used in the removal of phenol are summarized in Table 2.

![Continuous liquid-liquid extractors with solvent-dispersing frits](image)

Figure 1 Continuous liquid-liquid extractors with solvent-dispersing frits [20].
Table 2 Different solvents used for removal of phenol.

<table>
<thead>
<tr>
<th>Solvents used</th>
<th>%Removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amide and its compounds.</td>
<td>92%</td>
<td>[21]</td>
</tr>
<tr>
<td>Imidazole and its homolog compounds</td>
<td>90%</td>
<td>[21]</td>
</tr>
<tr>
<td><strong>Mixed solvents:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% TBP, 20% n-octanol and 60% Cyclohexane</td>
<td>99.3%</td>
<td>[21]</td>
</tr>
<tr>
<td><strong>Green based liquid organic solvent:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palm oil</td>
<td>83%</td>
<td>[22]</td>
</tr>
<tr>
<td>Methyl-ter-butyl ether (MTBE)</td>
<td>98%</td>
<td>[23]</td>
</tr>
<tr>
<td>1-decanol</td>
<td>98%</td>
<td>[24]</td>
</tr>
<tr>
<td>Methyl iso-butyl ketone</td>
<td>94-97%</td>
<td>[19]</td>
</tr>
<tr>
<td>Kerosene</td>
<td>95%</td>
<td>[25]</td>
</tr>
<tr>
<td>Aliquat-336</td>
<td>75-96%</td>
<td>[26]</td>
</tr>
</tbody>
</table>

Figure 2 Sketch structure of the proposed three-liquid-phase extractor: 1—three-phase mixer; 2—three-phase settler; 3—two-phase mixer; 4—liquid-flow control zone [27].

2.1.3 Three Phase Liquid System

The three phase liquid system is composed of organic extractant, high molecular polymer, and salt. Pinhua Yu et al [20] investigated separation of P-Nitro phenol and O-Nitro phenol by using a three-phase extraction system. O-nitrophenol was collected at top phase, p-nitrophenol in the middle and mixture of o & p nitrophenol was at the bottom
phase [Fig. 2& 3]. About 85% of ortho-nitro phenol and 90% of para-nitro phenol were recovered using this method at pH 4.

Figure 3 The partition of two phenols in three-layered liquid phases (Agitating at 300rmin⁻¹ for 15 min for the extraction reaches final equilibrium. O-NP: ortho-nitrophenol, p-NP: para-nitrophenol, t: top phase, m: middle phase, b: bottom phase. Vₜ: Vₘ: Vₜ (1: 2.1:1.7) [20]

Table 3 Various industries and its associated phenols [3].

<table>
<thead>
<tr>
<th>Industries</th>
<th>Type of Phenols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textile</td>
<td>Phenol, Chloro phenol, Alkyl phenols, Catechol, Chloro catechol, Nitro phenol.</td>
</tr>
<tr>
<td>Wood processing</td>
<td>Phenol, Chloro phenol, Alkyl phenols.</td>
</tr>
<tr>
<td>Pharmaceutical</td>
<td>Catechol, Chloro catechol, Chloro phenol, Methyl phenol, Buthyl hydroxyl toluene, Buthyl hydroxyanisole.</td>
</tr>
<tr>
<td>Rubber</td>
<td>Petrochemical Phenol, Methyl phenol.</td>
</tr>
<tr>
<td>Cosmetics</td>
<td>Chlorocetachols, Methyl phenol, Buthyl hydroxyl toluene, Buthyl hydroxyanisole.</td>
</tr>
<tr>
<td>Coal-tar production</td>
<td>Phenol, Nitrophenols, Methyl phenols.</td>
</tr>
</tbody>
</table>
2.1.4 Pervaporation

Pervaporation is a separation process wherein the compounds are separated from the solution by partial vaporization through a non-porous or porous membrane. The two steps involved in this process are permeation and evaporation. The membrane used acts as a selective barrier that allows the desired component of the liquid feed to pass through it by vaporization [Fig. 4]. Kujawski et al [23] worked on pervaporation and adsorption for phenol removal. Various membranes like poly (ether-block-amide) (PEBA), pervaporation 1060 (PERVAP1060) and PERVAP1070 were used. All the membranes were found to be selective for phenols. PEBA membranes showed the highest selectivity for phenol removal but, these are not commercially available, PERVAP1060 and PERVAP1070 membranes are commonly used.

![Figure 4. The schematic representation of laboratory scale of pervaporation setup [28].](image)

2.1.5 Membrane filtration

Subha, et al, [29] reported different membrane filtration methods for the removal of phenols from wastewater these are as follows.

2.1.5.1 Reverse osmosis separation methods

Reverse osmosis (RO) is a very effective method for the removal of phenols from wastewater. It can easily be operated at room temperature and this is an energy saving process. It has drawn attention due to its energy saving nature. This method is widely
used for the separation of organics from water. Depending on the mode of application, operating pressure remains in the range of 15-50 bars. RO rejects the organic molecules having a molecular weight of more than 50 along with monovalent ions. This method can be applied commonly to sea water and brackish water desalination. [30, 31]. For the characterization of reverse osmosis and nanofiltration membrane, two models: *the combined film theory-(Spiegler-Kedem) and combined film theory (solution diffusion)* were used. Both models used commercial polyamide composite thin-film reverse osmosis membrane for phenol rejection. In the phenol-water system, the combined film theory of Spiegler-Kedem model more accurately calculated rejection of phenols in water than the other model.

### 2.1.5.2 Ultrafiltration

The principle of ultrafiltration is alike to that of reverse osmosis, except that in ultrafiltration the pore size of the membrane (0.002-0.003 mm) is large and it can be operated at reduced pressure. The rejection of organic molecules with molecular weight more than 800 by ultrafiltration membranes frequently operated at pressures below 5 bar. The surfactant micelles i.e. charged particles containing these organic molecules are large enough so that they cannot passe through the pores of the membrane. This fact makes the ultrafiltration membrane more efficient for phenol removal from a stream of water [32-35].

### 2.1.5.3 Nanofiltration

Nanofiltration membranes have properties between the membranes of ultrafiltration and reverse osmosis with pore sizes ranging from 1-100 nm. Nanofiltration can be used for both, the removal of disinfectants from water and for water softening. Nanofiltration membranes permit the movement of monovalent ions through them, for instance, sodium/potassium. Organic molecules with molecular weight > 200 and high concentration of divalent ions like calcium & magnesium are rejected by the membranes. Normally the operating pressure is kept close to 5 bars. Nanofiltration may be effective for the removal of color and organic compounds [30]. For removal of phenol from its aqueous solution Bodalo *et al.* [30] used many nanofiltration membranes (NF- 99 DSS-HR98PP and NF-97) under different experimental conditions at operating pressures: 10, 15 and 20 x 105 N/m² with constant feed flow at 2.78 x 10-5 m³/s, T= 25°C and pH=8 with variation of concentration of phenol from 50 -200 x 10-3 x kg/m³. Different rejection percentages were obtained with a variation of concentration. It was concluded that molecular properties like solubility, hydrogen bonding and acidity etc., were responsible for a rejection rate of organic compounds in nanofiltration membranes [30].
Table 4 Phenol removal by adsorption using different plant sources.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Adsorbant dose (g/L)</th>
<th>Phenol removal</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date pit activated Carbon</td>
<td>7</td>
<td>24</td>
<td>25</td>
<td>4</td>
<td>The adsorption ability of low-cost date seed adsorbent was evaluated at elevated 2,4-dinitrophenol concentration</td>
<td>[36]</td>
</tr>
<tr>
<td>Mango peel</td>
<td>7</td>
<td>6</td>
<td>30</td>
<td>0.25</td>
<td>Mango peel and agricultural waste was used as adsorbent for the removal of chlorophenols from wastewater of paint industry</td>
<td>[37, 38]</td>
</tr>
<tr>
<td>Chestnut shells</td>
<td>2.5</td>
<td>8</td>
<td>50</td>
<td>-</td>
<td>Chestnut shell was used as adsorbent for removal of phenolics from wastewater of paint industry</td>
<td>[38]</td>
</tr>
<tr>
<td>Pineapple peel</td>
<td>7</td>
<td>48</td>
<td>25</td>
<td>-</td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td>Rice husk and sugarcane bagasse</td>
<td>5</td>
<td>5</td>
<td>25</td>
<td>1g</td>
<td>Activated carbon prepared from Rice husk and sugar -cane bagasse impregnated with ZnCl₂ used as adsorbent for the removal of arsenic, phenols and other landfill leachates from municipal wastewater and solid waste</td>
<td>[40]</td>
</tr>
<tr>
<td>Activated tea waste</td>
<td>2.4</td>
<td>5</td>
<td>25</td>
<td>1.5</td>
<td>Synthetic wastewater was treated with activated tea leaves at different concentrations, PH, pollutant dose etc.</td>
<td>[41]</td>
</tr>
<tr>
<td>Potato peel</td>
<td>1-2</td>
<td>1</td>
<td>55</td>
<td>-</td>
<td>Polyphenol oxidase from Potato peel waste was used for the degradation of phenols from olive mill wastewater</td>
<td>[42]</td>
</tr>
<tr>
<td>Olive mill waste</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>1</td>
<td>Onion solid byproduct was used to produce peroxidase for the removal of phenolic from olive mill wastewater</td>
<td>[43]</td>
</tr>
<tr>
<td>Tamarind bean</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td></td>
<td>[44]</td>
</tr>
</tbody>
</table>

2.1.6 Adsorption

It is a surface phenomenon. There are two types of adsorption physical-sorption (operated by van der Waals forces) and chemisorption (formation of covalent bonding), both of these depend on the forces between adsorbent and adsorbate. It can be normally
illustrated by an isotherm at constant pressure. A thin film of adsorbate formed on the surface of adsorbent is the function of concentration (in case of liquid)/ pressure (in case of gas). To explain this phenomenon a variety of isotherm models like Langmuir, Freundlich constant, Henry adsorption constant, adsorption enthalpy, BET theory etc are available. Adsorption is one of the most investigated techniques used for Phenol removal from wastewater of industries. Table 4 shows various synthetic sorbents and microbial, agricultural, synthetic and chemical sources for adsorption and respectively. They have been tested for their adsorption capacities of organic pollutants, including phenols. Due to diverse sources, adsorption can be performed in fluidized bed reactor, fixed bed reactor, trickle bed reactors and much more. Owing to its versatility and ease of operation, it is one of the most commonly used wastewater treatment methods for removal of phenols and phenolic compounds.

2.1.7 Cloud point extraction method

It is an advanced physical method for phenol extraction from wastewater. In this technique, the analyte gets partitioned itself between two isotropic phases i.e. aqueous phase and surfactant-rich phase. Surfactant solution (water-based solution without toxic organic solvents) is used as a solvent. This extraction technique is very efficient, low cost and less time consuming; environmentally benign separation approach frequently used as an alternative to conventional extraction systems. This technique has very good ability to concentrate the solutes with high recoveries, need very small amount of surfactant which is non-volatile and inflammable and the surfactants can be disposed of easily [45]. In this process, the aqueous solutions of some surfactants show the cloud point phenomenon. Due to a decrease in solubility of the surfactant in water, the surfactant solution becomes turbid suddenly. The clouding phenomenon is generated with an increase in temperature. Consequently, an isotropic layer is formed which further split into two isotropic phases discussed above [46].

It was concluded that the isotropic phase rich in surfactant which is separated under the cloud point condition is able to pre-concentrate a wide range of inorganic and organic compounds and to extract them from the aqueous phase. The solute present in the aqueous solution of the surfactant is distributed between the two phases above the cloud point temperature.
2.2 Chemical methods

2.2.1 Advanced oxidation process

Advanced oxidation process (AOP) can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species such as hydroxyl radicals in the mechanism leading to the destruction of the target pollutant. AOPs are gaining much importance in research and development due to their areas of prospective application and variety of technologies.

Over the past 30 years, AOPs has played a great part in research and development due to two main reasons namely the diversity of technologies involved. The key AOP processes include heterogeneous and homogeneous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, electrolysis, ozonation, the Fenton’s reagent, ultrasound and wet air oxidation. The processes like ionizing radiation, microwaves, pulsed plasma and the ferrate reagent are also emerging photodegradation processes, responsible for phenol removal. Depending on the properties of the waste stream to be treated and the treatment objective itself, AOPs can be employed either alone or coupled with other physicochemical and biological processes.

2.2.2 Air oxidation

For the estimation of phenol decomposition, byproduct accumulation, and final product accumulation, a new technique named as the differential neural network was introduced by Chairez and coworkers [47, 48]. The effect of raising pH on the dynamics of decomposition of phenol, 4-chlorophenol and 2, 4- Di chloroPhenol was very important. The total time for decomposition of phenol was reduced by the factor of ten. The presence of the chloro species in the phenol molecules reduces the degradation time during ozonation [37, 38].

2.2.3 Catalytic wet air oxidation of phenol

Wang et al. [49] used continuous packed bubble column reactor for wet air catalytic oxidation of phenol with pellets of catalyst (CeO\textsubscript{2}-Ru/ZrO\textsubscript{2}) ZrO\textsubscript{2} was introduced into Ru/CeO\textsubscript{2} to increase the adsorption capacity, specified surface area, and mechanical strength of this pelletized catalyst in this process, removal of phenol was stabilized about 100 % [39].

2.2.4 Photodecomposition

Photodegradation by UV radiations is used for the removal of phenol from wastewater. It is used by itself as well as with alternative adsorbents. In this process, UV radiation is
used to irradiate the sample for the removal of contaminants. The UV light is absorbed by contaminant compound which undergoes decomposition from its excited state. The UV photoreactors are highly efficient because the solution which is to be analyzed surround the photo reactor’s lamps. Generally, a medium pressure mercury lamp is used as a radiation source which has 400 W output. UV lamps radiate primarily UV radiation of 365 – 366 nm with radiations at 334, 313, 303, 297 and 265 nm in lesser amounts. The mechanism of phenol degradation is heterogeneous which follows zero-order kinetics. Heterogeneous degradation of phenols results in 70% conversion. Phenol degradation can be catalyzed in the presence of silver and TiO₂. In the presence of silver, degradation is carried out by direct electron transfer in the presence of TiO₂ in an aqueous medium at pH 5, phenol removal up to 99% has been observed after 4 hours at pH 5. Under the same conditions for 2 chloro phenol the percentage removal of other phenolic compounds was 92% and for 2, 4 dimethyl phenol was 83%. Phenol absorbs UV radiations from the light source and an electron is removed and taken up by the aqueous solvent solution which results in the formation of radicals OH & phenoxide radicals. The phenoxide radicals are being attacked by hydroxyl radical at ortho/para positions and after a further attack of OH convert this pyrocatechol to maleic acid followed by the formation of formic acid which decomposes to give CO₂ and H₂O (Fig. 5).

Figure 5 A schematic mechanism of photodegradation of phenol [50].
Udom and co-workers [51] worked on photodegradation of phenol using near UV radiation in the presence of aqueous FeO/TiO$_2$/red mud/Nickle mud mixture of Fe$_2$O$_3$ (31.80 wt. %), TiO$_2$ (22.60 wt. %), MgO (0.20 wt. %), Al$_2$O$_3$ (20.10 wt. %), CaO (4.78 wt. %), SiO$_2$ (6.10 wt. %), Na$_2$O (4.70 wt. %), K$_2$O (0.03 wt. %) annealed on a glass surface. The surface of the glass wool was covered by black or red nickel mud and annealed in a muffle furnace (at 300˚C) so as to reach the finest accessible rate for the adsorbent fixation, for the removal of possible organic impurities of adsorbent and increasing its adsorption capacity by converting the adsorbent particles into fiber through heating. These layers of glass wool containing catalysts were kept in a UV photoreactor in order to increase the phenol removal efficiency. The influence of catalysts was monitored.

![Diagram](image)

*Figure 6: A schematic mechanism of photodegradation of phenol by TiO$_2$ [52].*

Photodegradation of phenols in wastewater depends upon different parameters like light intensity, irradiation time, pH, the concentration of phenol and amount of TiO$_2$. Photodegradation process catalyzed by TiO$_2$ is a highly efficient method for the elimination of phenol from wastewaters. The effectiveness of this process is strongly dependent on the experimental reaction conditions. It depends mainly upon pH, TiO$_2$ concentration, and UV light intensity. By increasing intensity of UV light, the rate of phenol degradation can be increased. Optimum pH value for the quick OH radicals’ generation is 7. The generation of hydroxyl radicals produces a positive charge on the surface of TiO$_2$, which attracts the phenol having a negative charge. This results in efficient degradation of phenol into CO$_2$ and H$_2$O (Fig. 6) at loading range of TiO$_2$ 0 to 0.20 wt.%, the
degradation rate of phenol was observed to be increased with increased TiO$_2$ concentration. At loading rate of above 0.20 wt %, the phenol degradation was observed to remain constant with enhanced concentration of TiO$_2$. The degradation rate of phenol was best described by Pseudo-first order according to kinetic of reaction. The rate of degradation of phenol was more efficient as compared to sunlight under UV light.

2.2.5 Coupled ultrasound and Fenton’s reagent

Coupled Fenton’s reagent and sonochemistry technique has been used to study the phenol degradation in aqueous medium equilibrated with air for a variety of experimental conditions. Extra OH radicals produced by Fenton’s reagent through the reaction of Fe(II) with H$_2$O$_2$ contributes to the degradation of phenol in wastewater. This production of OH radicals by coupled ultrasound and Fenton’s reagent further enhance the rate of decomposition of phenols. In this technique, the rate of decomposition of aqueous phenol was extremely dependent upon the initial concentration and pH of reactants [53].

2.2.6 Three phase electrode system

The three-phase electrode system is an advanced method to remove phenol from wastewater. Ya Xiong and coworkers [54] worked on the performance of the three-phase three-dimensional electrode reactor which was highly effective for COD reduction in phenol-containing wastewater and its performance was compared with granulated activated carbon adsorption bed and 3D electrode system.

(v) Electrocoagulation

In this method, phenol is removed by electrocoagulation in which the sacrificed anodes form active coagulant that is then used to remove pollutant in situ by flotation and precipitation. Electrochemical cells containing an electrode arrangement in contact with polluted water are employed during electrocoagulation (Fig. 7). In 2013 Ashtoukhy and his team [55] worked on removal of phenolic compounds by electrocoagulation from petrochemical wastewater using a fixed bed reactor.

Parameters taken into consideration for electrocoagulation are pH, Retention time, initial phenol, current density, and NaCl, as well as alginic acid concentrations. For assessment of wastewater, the samples were taken up from reactors at different time periods and were centrifuged at 4000 rpm for 30 min. All analyses were carried out under conditions consistent with standard methods before analysis [44, 56]. The analysis of remaining wastewater was done for the concentration of phenols on the basis of color developed by the reaction of phenols with 4-aminoantipyrine. The phenol concentration was
determined by spectrophotometer at $\lambda_{\text{max}}$ 500 nm. Phenol removal was carried out by increasing concentration of NaCl and current density at pH 7.

Phenols are converted to phenoxide by removal of the electron under acidic conditions and these phenoxide ions combine with other phenol molecules present in solution under the effect of the electric field in an electrochemical cell. These aggregates thus formed and removed from water (Fig.7& 8).

![Figure 7. Schematic diagram for electrocoagulation [57].](image-url)
2.3 Biological Methods

Biodegradation of phenols is the process of breakdown of the phenols into simpler/non-toxic compounds by the action of microbes or enzymes. The two main types of biological degradation of phenols are enzymatic degradation and microbial degradation.

2.3.1 Enzymatic degradation

The enzymes, obtained from various sources are popularly being used for wastewater treatment. Among the many enzymes, polyphenol oxidases and peroxidases are widely used. According to Nagai and Suzuki [59], polyphenol oxidase is a copper-containing enzyme and the classification of polyphenol oxidase is as follows:

(a) Tyrosinase: Tyrosinase, also called catecholase, contains a binuclear copper active site that facilitates the degradation reaction of the phenols. It catalyzes the hydroxylation of mono-phenols to o-bi phenols, which is then degraded to form o-quinone by dehydrogenation reaction. The use of the tyrosinase enzyme can be coupled with various other techniques (integration into a biosensor, adsorption or immobilization) for better results.

Figure 8. Proposed mechanism of Electrodegradation of phenols [58].
(b) **Laccases**: Laccases are the enzymes that catalyze the degradation reaction by reduction of oxygen to water along with oxygenation of a phenolic molecule. These enzymes are also called blue copper oxidases or blue copper proteins. They contain four neighboring copper atoms at different binding sites, where two are concerned with transfer and electron capture, and two other with the binding of oxygen. On oxidation, the phenols are converted into o-bi phenols which may undergo further enzymatic degradation or may undergo polymerization reaction leading to the formation of the melanin-like dark brown accumulated product. Ulfat Jan with her team [60] worked on detoxification of phenols and aromatic amines in wastewater by using polyphenol oxidases. Sources of polyphenol oxidase were gooseberry, quince leaves, tea leaves, banana fruit/peel and potato etc. Jadhav [61] isolated and characterized the polyphenol oxidase (PPO) enzyme from banana peel. The PPO enzyme was used to treat industrial wastewater containing phenol. The parameters such as enzyme activity, optimum pH, optimum temperature, phenol degradation and phytotoxicity were examined. Complete degradation of phenols was seen within 24 hours for the smaller concentration of phenols, whereas 72 hours were required for higher phenol concentrations. The optimum temperature and pH for maximum enzyme activity were 35°C and 7, respectively. Peroxidases were found in various plants and microbes. Sources of peroxidase were radish, cabbage, tobacco etc. The different types of peroxidase enzymes were manganese peroxidase, lignin peroxidase, horse radish peroxidase, etc.

Enzyme peroxidase mechanism for phenol degradation was proposed by Chance-George. In this process, peroxidase catalyzed the one-electron oxidation of phenols. The mechanism is as follows:

\[
\begin{align*}
E + H_2O_2 & \rightarrow E_i + H_2O \\
E_i + AH_2 & \rightarrow E_{ii} + AH \\
E_{ii} + AH_2 & \rightarrow E + AH^{-} + H_2O \\
E_{ii} + H_2O_2 & \rightarrow E_{iii} + H_2O
\end{align*}
\]

Hydrogen peroxide (H$_2$O$_2$) oxidizes the subject enzyme (E) to form an active enzymatic intermediate named as E$_i$ (compound I). Oxidation of phenolic aromatic compound (AH$_2$) takes place at the active sites of E$_i$. Free radical (AH$^-$) produced and released in
solution as a result of oxidation of aromatic compound at \( E_i \). Hence \( E_i \) is converted to \( E_{ii} \) (Compound II). The oxidation of the second molecule of aromatic compound takes place on \( E_{ii} \) in the same way resulting in the production of free radical product again and the enzyme attains its original state \( E \), hence completion of the cycle takes place. The whole peroxidase reaction is composed of three reactions illustrated by Eqs. (1–3). If hydrogen peroxide is present in excess, the reaction of Eq. (4) becomes significant because \( E_{iii} \) (compound III) is an inactive form of the enzyme. This shows that presence of excess hydrogen peroxide inhibits the enzyme activity. Conversely, the rate of reaction during the second step is limited in limited supply of hydrogen peroxide. An optimum ratio of both enzyme and hydrogen peroxide would suppress the inhibition of this enzyme [44, 62]. During the process of enzyme reduction, phenol and its derivatives are transformed into phenolic-free radicals. The phenolic-free radicals are catalytically produced during the peroxidase reaction cycle. These phenolic–free radicals either produce phenolic polymers by combining with each other or produce other radical species by undergoing radical transfer reaction with phenolic polymers or monomers present in solution [63]. The Phenolic polymer radicals may be generated by the action of peroxidases enzymes with phenolic polymers. These radical species may react with other radical species to form larger polymers or may undergo radical transfer reaction which results in the production of polymers of different sizes in solution [64]. The phenolic polymers can be precipitated out from solution and can be removed by either filtration or gravity settling [65]. Different enzymes used for polymerization of phenol with their sources are given in Table 5. Potential advantages of enzyme-based treatment [65, 66] are given below.

- Removal of phenolic compounds and similar one is carried out by selective treatment.
- Possibilities of speeding up reaction velocity minimize stay time.
- Degradation of toxic compound lethal for microbes.
- Wider operation range of concentrations of substrate.
- Operational possibility over a wide range of pH, temperature, and salinity.
- No effects of shock loading.
- The control of the process, predictable, simpler and reliable.
**Table 5 Various microbial and plant enzymes and their sources involved in biodegradation of phenol [67].**

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Source</th>
<th>Work done</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol hydroxylase</td>
<td><em>Bacillus stearothermophilus</em></td>
<td>This bacterium isolated from river sediment and its enzyme used for phenol degradation at level 15 mM.</td>
<td>[68]</td>
</tr>
<tr>
<td>Polyphenol oxidase</td>
<td>Mushroom</td>
<td>Mushroom phenol oxidase activity on organic system under optimized conditions of temperature, pH, and concentration.</td>
<td>[69]</td>
</tr>
<tr>
<td>Polyphenol oxidase</td>
<td><em>Trametes trogii</em></td>
<td>The enzyme extracted from a white-rot fungus <em>Trametes trogii</em> for oxidation of wide range of phenolic compounds.</td>
<td>[70]</td>
</tr>
<tr>
<td>Polyphenol oxidase</td>
<td>Transgenic tomato</td>
<td>Polyphenol oxidase isolated from tomato plant for the oxidation of phenolics into quinones.</td>
<td>[71]</td>
</tr>
<tr>
<td>Polyphenol oxidase</td>
<td>Potato</td>
<td>Immobilized enzyme isolated from potato for the removal of chlorinated phenols.</td>
<td>[72]</td>
</tr>
<tr>
<td>Phenol oxidase</td>
<td><em>Lentinula edodes LE2</em></td>
<td>Soil contaminated with pentachlorophenol was treated with <em>Lentinula edodes LE2</em> and quick removal phenol was observed up to 99%.</td>
<td>[73]</td>
</tr>
<tr>
<td>Catechol 2,3-dioxygenase</td>
<td><em>Bacillus</em> sp.</td>
<td>Thermophilic bacteria isolated from sewage effluent. Its enzyme catalyze the phenol degradation by meta-cleavage pathway.</td>
<td>[74]</td>
</tr>
<tr>
<td>Laccase</td>
<td><em>Rhizoctonia praticola</em></td>
<td>Detoxification of phenolic pollutants was examined by laccase of fungal strain <em>Rhizoctonia praticola</em>.</td>
<td>[75]</td>
</tr>
<tr>
<td>Laccase</td>
<td></td>
<td>Characterization and purification of laccase from <em>Aspergillus oryzae</em>.</td>
<td>[76]</td>
</tr>
<tr>
<td>Laccase</td>
<td><em>Pleurotus ostreatus</em></td>
<td>Characterization and immobilization of laccase from <em>Pleurotus ostreatus</em> and its use for the continuous elimination of phenolic pollutants.</td>
<td>[77]</td>
</tr>
<tr>
<td>Laccase</td>
<td><em>Chalara paradoxa</em></td>
<td>Phenol-oxidase (laccase) activity in strains of the hyphomycete <em>Chalara paradoxa</em> isolated from olive mill wastewater disposal ponds.</td>
<td>[78, 79]</td>
</tr>
</tbody>
</table>
2.3.2 Microbial degradation

Van Schie [62] have described the utility of micro-organisms in biodegradation of Phenol. The degradation of phenol by this method is amenable due to its ease of manipulation of strains and scaling up of the process. The phenol is converted to catechol by oxygenation, which is further broken down and the compounds enter the metabolic cycle in order to produce carbon dioxide, water or other inorganic simple compounds. The degradation can be either aerobic or anaerobic condition. In aerobic degradation, the phenol is oxidized to catechol by the microbial enzyme (phenol hydrolase) in the presence of nicotinamide-adenine dinucleotide (NADH₂) (Fig. 9 and 10). Depending on the enzymes in the organism used, it is degraded into either 2-hydroxymuconic semialdehyde or cis muconic acid, that may enter the Krebs cycle and get degraded to carbon-dioxide and water. The various organisms involved in aerobic degradation are *Acinetobacter calcoaceticus, Pseudomonas, Streptomyces setonii* a *Trichosporon cutaneum* and *Candida tropicalis* etc (Table 6).
Figure 9 Schematic representation of aerobic degradation of phenol.

Aerobic Degradation Pathways

Pentachlorophenol

Anaerobic Degradation Pathway

Figure 10 Aerobic and anaerobic pathway of pentachlorophenol biodegradation [92].
In anaerobic degradation, the degradation of phenols occurs in the absence of oxygen. Anaerobic degradation usually occurs under reducing conditions. The mechanism, however, varies from one organism to another. In a nitrogen reducing bacteria called *Thauera aromatic*, the phenol ring is carboxylated into 4-hydroxybenzoate which is further degraded. For anaerobic degradation, the organisms involved are *Thauera aromatica* strain K172, *Geobacter metallireducens* (iron- reducing conditions), the sulfate-reducing organism *Desulfobacterium phenolicum, Desulfotomaculum* sp. Strain Groll (in presence of bi-carbonate) and *Desulfovibrio* species. Agarry [39] worked on strains of *Pseudomonas fluorescens* at different concentrations of phenol. A comparative study of the performance of *Pseudomonas fluorescens* and other microorganisms was carried out and complete degradation of phenol was by the action of the bacteria. The degradation time was increased from 84 to 354 hours with the increase in the concentration of phenols.

*Table 6* Microorganisms used for phenol degradation under various conditions.

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Conditions for phenol degradation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudomonas putida</td>
<td>Aerobic conditions</td>
<td>[93]</td>
</tr>
<tr>
<td>Corynebacterium sp. S. aureus, B. subtilis Proteus sp Staphylococcus sp</td>
<td>Resistant to 15mM of phenol</td>
<td>[94]</td>
</tr>
<tr>
<td>Kelibsiella Shigella Citrobacter</td>
<td>These bacteria have very good ability to degrade phenol in 0.2-0.9 g/L concentration range isolated from parshan lake</td>
<td>[95]</td>
</tr>
</tbody>
</table>
| Pseudomonas aeruginosa  
Pseudomonas fluorescens | In reaction vessel with soil, these bacteria degraded the phenols efficiently                                                                                                                                                                                                                  | [96, 97] |
| Acinetobacter baumannii              | Efficiently degrade phenols at high concentration range                                                                                                                                                                                                                                   | [98] |
| Alcaligenes faecalis                 | Capable to degrade phenol at concentration range up to 600 mg/L under anoxic conditions                                                                                                                                                                                                     | [99] |
| Candida species                      | Degradation of phenol on activated carbon by this sp. at phenol conc. Range up to 2 g/L                                                                                                                                                                                                       | [100, 101] |
| Aspergillus sp                       | This fungal strain degraded different concentration of phenols                                                                                                                                                                                                                              | [102, 103] |
Rhodococcus erythropolis | Usage of its catabolic gene for phenol degradation | [103, 104]
---|---|---
Pseudomonas stutzeri | optimal conditions of continuous bioconversion this bacterium showed the very good efficiency | [105]
Bacillus brevis | Degraded phenols at different environmental conditions | [106]

3. Conclusions

Together with the development of industrialization especially in developing countries, people have become more aware of phenol exposure effects on living organisms. Due to wide range usage of phenol in many industries, as the main chemical, the phenol is still one of the most omnipresent pollutants in the environment. The risk of phenol pollution cannot be avoided and hence the study on phenol degradation is still relevant. Among all methods available, the biological method seems to have the potential for phenol degradation in either anaerobic or aerobic condition that makes it the choice for researcher compared to other physical or chemical method. Many researchers found *Pseudomonas* sp. and *Rhodococcus* sp. to have higher potential ability to degrade phenol effectively. Toxicities of phenol and its derivatives have been associated with the ability to alter the structure of the membrane and its barrier. It leads to the imbalance of cell environment which results in the cells’ death. The action of toxicity due to environmental stress causes it to be happening in microorganisms. The transition of saturation degree in membrane phospholipids cis-fatty acid into trans-fatty acid depends on the hydrophobicity of solution and its location of the group on the aromatic ring where benzene ring itself can also undergo several chemical reactions such as halogenations or substitutions. The needs to isolate and characterise microorganism, capable to tolerate laboratory and real field conditions for the efficient phenol removal will become crucial in the near future where the organism can survive under stress conditions such as high salinity, low oxygen supply, or low pH, and many other xenobiotics presences in the mixed effluent discharge in water sources. Much more studies need to be done in the future regarding to the mechanism of phenol degradation in the presence of microorganisms.

References


Chapter 7

Photocatalysis: Present, past and future

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Abstract

As one of the most attractive technologies, photocatalysis has been emerging nowadays to harvesting the solar energy for producing green fuels and a wide range of environmental applications. Due to their unique physicochemical and optical properties, a wide variety of TiO2 based photocatalysts have emerged to drive various organic transformations and degradation reactions under light irradiation. In this chapter, we have systematically summarized the fundamentals of TiO2 based photocatalysts, including basic mechanism of heterogeneous photocatalysis, advantages, and challenges of g-TiO2 based photocatalysts. Through reviewing the important state-of-the-art advances on this topic, it may provide new opportunities for designing and constructing highly effective TiO2 and various bismuth-based photocatalysts for various applications in photocatalysis and other related fields, such as solar cells and photoelectrocatalysis.

Keywords

Semiconductors, Photocatalyst, Degradation, TiO2, Bismuth Materials
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1. Introduction

Semiconductor photocatalysis has received much attention during past few decades as a promising solution for both energy and environmental problems. Since the discovery of Fujishima and Honda effect that water can be split into hydrogen and oxygen using a semiconductor (TiO₂) electrode, a lot of work has been carried out to produce hydrogen from water splitting using a variety of semiconductor photocatalysts. Nowadays, the scientific interest in heterogeneous photocatalysis has also been focused on environmental applications such as effluent treatments and air purification. Various metal oxides have been investigated and evaluated as potential photocatalysts. The most prominent examples have been TiO₂, ZnO, and SnO₂. The great interest in the development of active photocatalysts is evidenced by many research publications appeared during the last few years. The purpose of this chapter is to summarize significant developments in the field of TiO₂ and alternative bismuth-based materials for degradation of pollutants. Following a brief outline of the structural properties of TiO₂, this section is devoted to the discussion of possible modifications to improve the
efficiency of the TiO$_2$ photocatalyst, followed by a summary of major parameters which are responsible for the degradation of organic pollutants.

1.1 Advanced oxidation processes (AOPs)

Advanced oxidation processes such as semiconductor photocatalysis, UV/H$_2$O$_2$, Photo-Fenton process and ozonation are widely used for the treatment of intractable compounds in industrial effluents. These processes involve the generation of (•OH) radicals. Generally Hydroxyl radical is considered to be a most powerful oxidizing agent with the oxidation potential of 2.8 eV and it reacts with organic compounds rapidly, the reaction leads to complete destruction of the targeted organic pollutants.

1.2 Principle of heterogeneous photocatalysis

A semiconductor can act as a photocatalyst in the photo mineralization process, due to its unique electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB). The photocatalytic effect of the semiconductor was first reported by Fujishima and Honda [1] for water splitting using TiO$_2$ semiconductor. When a semiconductor is illuminated with UV or Visible light, electrons are promoted from the VB to the CB leaving a hole as shown in Fig. 1 [2].

The effective generation of an electron-hole pair in a semiconductor particle depends on the intensity of the incident light as well as electronic characteristics of the matter. The threshold wavelength required for excitation of a semiconductor is governed by the following equation:

$$E_{bg} (eV) = \frac{1240}{\lambda_{bg} (nm)} \tag{1}$$

In the absence of electron-hole scavengers, the photogenerated electron-hole pairs may recombine and dissipate the input energy as a heat within a fraction of seconds. Thus for a photocatalytic process to be efficient, the electron must be removed by an electron acceptor. So, the electron acceptors are necessary for the photocatalytic process to prevent the recombination.
Oxygen is commonly used as electron acceptor. It may react with a photogenerated electron at the surface of semiconductors. The photogenerated holes, having an affinity for electrons, are very strong oxidizing agents. After migrating to the surface of the semiconductor, they oxidize the adsorbed water molecule or hydroxide ion to form hydroxyl radicals. The photogenerated (•OH) radicals with an unpaired electron are very reactive species. Due to its very high oxidation potential, it can oxidize most of the organic pollutants into CO₂ and their mineral acids. Therefore, the overall photocatalytic process can be summarized by the following reaction.

\[
\text{Organic pollutants} + \text{O}_2 \xrightarrow{\text{Semiconductor} \atop \text{UV/solar light}} \text{CO}_2 \uparrow + \text{H}_2\text{O} + \text{mineral acids}
\]  

(2)

Photogenerated electron and hole can also be used for reduction and oxidation before recombination. This makes the semiconductor as a combined redox catalyst in organic reactions.

1.3 Semiconductor photocatalysts for water splitting

Photocatalytic, water splitting and degradation of organic pollutants using semiconductor materials have attracted considerable interest. The development of clean and renewable
energy sources is a great technological challenge in near future. One of the most attractive options is the large-scale utilization of hydrogen (H₂) as a source for electricity. However, industrial H₂ production consumes huge amounts of fossil fuels resulting in large CO₂ emission which causes atmospheric pollution. Water splitting for hydrogen production has been the main goal of semiconductor materials in photoelectrochemistry for the past few decades. H₂ is considered to be a future fuel due to its high-energy capacity per unit volume as compared to oil and petroleum [3].

The most important requirements of semiconductor photoelectrodes for water splitting process are high stability, sufficient light assimilation, favorable band gaps with respect to water oxidation potential, slow recombination rate and low cost. Among the various semiconductor materials, metal sulfides and spinel ferrites have been considered to be the most promising photocatalytic materials, due to their good photochemical stability, non-toxicity, high photostability and low band gap energy.

There are many semiconductors that are commercially available for photocatalytic application. But, only a few of them are efficiently used for the photodegradation of a wide range of organic pollutants. Table 1 summarizes the semiconducting photocatalysts commonly used with their band gap energies and corresponding absorbance values. For a semiconductor to be a photochemically active catalyst, the redox potential of the photogenerated VB hole must be positive to generate •OH radicals and the redox potential of the photogenerated CB electron must be negative to be able to reduce adsorbed oxygen to superoxide radicals.

Table 1  Some common semiconductors, their band gap energies and corresponding threshold wavelengths.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band gap (eV)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>3.9</td>
<td>320</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>BiVO₄</td>
<td>2.4</td>
<td>516</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
<td>516</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>2.5</td>
<td>496</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.8</td>
<td>443</td>
</tr>
</tbody>
</table>
Among various semiconductors, TiO$_2$ has become the prominent catalyst against which the photocatalytic activity of other semiconductors is measured, because of its high photocatalytic activity and stability [4]. ZnO is found to be an alternative material to TiO$_2$. ZnO has proved to be more efficient than TiO$_2$ in various applications [5,6]. CdS is not as photoactive as TiO$_2$ but it has been studied extensively due to its good response to wavelengths of the visible light region [7]. CdS suffer from photo-corrosion induced by self-oxidation and release of some cadmium ions into solution to cause toxicity [8,9].

\[
\text{CdS} + 2\text{H}^+ \rightarrow \text{Cd}^{2+} + \text{S} \quad (3)
\]

Other semiconductors such as WO$_3$, BiVO$_4$, SnO$_2$, In$_2$O$_3$ and SrTiO$_3$ have also been used widely for photooxidation reactions [10]. The $E_g$ band gap of the ZnO and TiO$_2$ is 3.2 eV, which requires excitation wavelength in the UV region. It is found that unmodified TiO$_2$ has limited use in the degradation of toxic pollutants, because of its low efficiency and inability to utilize the visible light portion of the solar spectrum. Hence, the current research is focused on the tuning of physio-chemical factors of TiO$_2$ by various methods like doping with metals and non-metals, etc.

1.4 Applications of semiconductor photocatalysts

Qu et al. [11] studied the photocatalytic degradation (PCD) of rhodamine B in a TiO$_2$ solution using both UV and visible radiation. Photodegradation of a series of dyes (rhodamine B, sulforhodamine B, fluorescein, alizarin red and eosin) using TiO$_2$ catalyst under visible light illumination was studied by Wu et al. [12]. Wang et al. [13] reported the PCD of eight different commercial dyes containing various substitute groups using TiO$_2$ catalyst under solar irradiation. Arslan et al. [14] reported PCD of two different simulating textile wastewater from an integrated plant and a dyehouse mill using TiO$_2$ under ambient conditions.

PCD of reactive dyes (brilliant blue R, remazol black B and reactive blue) using TiO$_2$ and ZnO was reported by Gouvea et al. [15]. Galindo et al. [16] studied the PCD of acid orange 20 dye in the presence of TiO$_2$-P25 (Degussa) under UV light. CO$_2$ and aliphatic acids were identified as final degraded products. Decomposition of non-biodegradable methylene blue was examined using TiO$_2$ dispersions under UV illumination (Zhang et al. [17]). The PCD of eosin Y has been investigated by Poulios et al. [18] in aqueous solutions containing TiO$_2$-P25 (Degussa) and ZnO as photocatalysts. Yang et al. [19] reported the PCD of various dyes under visible light irradiation using TiO$_2$ electrodes. Wang et al. [20] prepared ZnO powders with various size (nanometric size: 10, 50, 200 and 1000 nm)
by thermal evaporation and chemical deposition methods, and examined their photocatalytic ability under UV light for degradation of methyl orange. Ren et al. [21] reported the large-scale synthesis of hexagonal ZnO nanoparticles by the esterification process using zinc acetate and alcohol. Furthermore, the prepared ZnO particles exhibit high PCD of rhodamine B, indicating that the nanostructured ZnO is promising as a semiconductor photocatalyst. Mohapatra et al. [22] synthesized the vertically oriented TiO$_2$ nanotube arrays by the sono electrochemical anodization technique which was found to be an excellent photocatalyst for the decomposition of non-biodegradable various azo dyes under simulated sunlight.

Wang et al. [23] synthesized ZnO nanoflowers by a simple low-temperature method in the absence of surfactants. Systematic studies were carried out to investigate the factors affecting the morphology of the samples. It was found that the ZnO with flower shape morphology exhibited improved activity towards the degradation of chlorophenols under UV radiation. Pardeshi and Patil [24] synthesized ZnO crystallites by solution free mechanochemical method. Photocatalytic activity of ZnO was checked by means of oxidative PCD of resorcinol, a potent endocrine disrupting material in water using solar light. The degradation efficiency was found to be dependent on crystallite growing rate and morphology of ZnO. Lu et al. [25] examined ZnO photocatalytic effectiveness to successfully degrade basic blue 11 under visible light irradiation. Rao et al. [26] investigated the PCD of direct yellow12 by a simple batch process using ZnO under irradiation with UV light. Sun et al. [27] developed a novel dumb-bell shaped ZnO photocatalyst by the simple hydrothermal method. The results indicated that the prepared dumbbell-shaped ZnO microcrystal photocatalyst exhibited good photocatalytic activity and it could be considered as a promising photocatalyst for dye effluent degradation.

Tong et al. [28] synthesized quasi-sphere-like ZnO using an ice-water bath. This hierarchically nanostructured ZnO showed significantly improved photocatalytic activity than ZnO nanopowder. The ZnO nanostructures synthesized in the shape of particles, rods, flower-like and micro-sphere using a facile hydrothermal method has been found very useful for decolorization of acid red dye solutions under sunlight [29]. Wu et al. reported that CdS showed the highly efficient photocatalytic performance on reducing 4-nitroaniline [30]. Luo et al. synthesized CdS hollow spheres which exhibited excellent photocatalytic activity towards the degradation of rhodamine B under UV irradiation [31].

Chen et al. [32] synthesized CdS nanoparticles which showed excellent photocatalytic activity, cyclic stability and higher photocatalytic efficiency than that of TiO$_2$. Shi et al. [33] and Liu et al. [34] reported that the combination of CdS with ZnS significantly improved photocatalytic activity and minimize the usage of toxic Cd. Zhang et al. [35]
studied the PCD of methyl orange using CoFe$_2$O$_4$/ZnO composite prepared by collosol technique. The results showed that the composite photocatalyst was able to degrade the dye substrate up to 93.9%. In addition, this magnetic photocatalyst also showed good magnetic property and could be completely recovered using an external magnet. Zhang et al. used NiS supported CdS for water splitting application with a high quantum efficiency of 51.3% [36]. Hou et al. [37] studied the PCD of 4-chlorophenol by ZnFe$_2$O$_4$ nanotube array electrode. Habibi et al. [38] reported the PCD of an azo textile dye effluents using ZnFe$_2$O$_4$-ZnO nanocomposite. Satsangi et al. [39] prepared a series of $\alpha$-Fe$_2$O$_3$ samples with a number of (Cu and Zn) dopants and reported that 5.0 at. % Zn doped $\alpha$-Fe$_2$O$_3$ film prepared by the spray pyrolysis method showed the best photoresponse as compared to other films.

1.5 Modified TiO$_2$ photocatalysts

TiO$_2$ has been a widely studied photocatalyst material for dye containing waste-water treatment, due to its ability to generate a strong oxidant hydroxyl radical, good chemical stability and non-toxicity. TiO$_2$ naturally occurs in three common crystalline polymorphs: anatase, rutile, and brookite. Although the anatase phase is considered as the most photocatalytically active phase, rutile is the most thermodynamically stable phase [40]. The wide energy band gap ($E_g > 3.2$ eV) in anatase may limit its potential application because only UV light can initiate the electron-hole generation process [41].

In general, by loading of co-catalyst to trap the photogenerated electrons or holes, the photocatalytic activity can be dramatically improved. It is a great challenge to activate TiO$_2$ under the sunlight, which consists of about 5% UV light and 45% visible light. Reduction of $E_g$ makes the catalyst solar light active. Photocatalytic activity can be improved by reducing electron-hole recombination and improving the adsorption rate of the pollutant.

A number of methods have been reported for the modification of TiO$_2$.

I. Addition of a low percentage of metal: The metal was introduced through different ways.

- Doping process (molecular combination of metal oxide in the lattice of TiO$_2$)
- Metallization process (deposition of noble metal on the photocatalyst crystallites)
- Impregnation method (deposition of a small amount of salt on photocatalyst surface).

However, recently transition metals (Cr, Mn, Fe, Co, Ni, Cu, and Zn) have been used to dope on TiO$_2$ surface and thus, to reduce the overall catalyst
production cost. The incorporation of transition metal ions into the TiO$_2$ lattice was found to lower the band gap ($E_g$) and shift the catalyst absorbance edge to the visible light region.

II. Addition of low concentrated transition metal ion (Ag$^+$, Zn$^{2+}$, Cd$^{2+}$, Ce$^{3+}$, Co$^{3+}$, Fe$^{3+}$ or W$^{6+}$) into the solution of substrate. [42-44]

III. Addition of low percentage of non-metal: The non-metals such as S, N, C, Cl, O, P and F are introduced on TiO$_2$ lattice by condensation and impregnation methods.

IV. Doping by anions such as SO$_4^{2-}$, PO$_4^{3-}$.

V. Supporting the photocatalyst on porous materials of larger particle size using silica [45], alumina [46], zeolites [47] and activated carbon[48].

VI. Loading of metal halides such as AgCl, AgBr etc.,

VII. Incorporation of dyes on TiO$_2$ to produce a dye-sensitized catalyst for harvesting visible light [49-51].

1.6 Application of modified TiO$_2$ photocatalysts

As a potential answer to the World’s collective environmental pollution problem, the application of hydrogen energy has attracted great attention. Extensive work has been devoted to the efficient production of hydrogen at low cost. The photocatalytic water splitting has been considered as a promising strategy for converting solar energy into hydrogen energy. The photocatalytic H$_2$ generation offers high energy consumption. The researchers have made enormous efforts to improve the efficiency of H$_2$ production by modifying TiO$_2$ nanostructures [52], as well as developing novel photocatalysts [53-55]. Due to the suitable energy band gap that matches to visible light absorption, chalcogenide semiconductors are regarded as good candidates for water splitting.

1.6.1 Metal loaded TiO$_2$

Sclafani et al. [56] reported the use of Ag$^+$ ions as redox reagent for the photocatalytic degradation of phenol using TiO$_2$ semiconductor. Prairie et al. [57] evaluated the photodegradation of salicylic acid using Pt$^{4+}$, Hg$^{2+}$, Au$^{3+}$ and Ag$^+$ ions loaded TiO$_2$ as photocatalyst [58]. Sclafani and Herrmann [59] studied the influence of Ag and Pt-Ag bimetallic deposits on the photocatalytic activity of TiO$_2$ (anatase and rutile phases) in dye degradation. The degradation products and a reduction in total organic carbon on the photodecomposition of phenol was reported by Ilisz et al. [60] Gouvea et al. [61] illustrated that the toxicity of lignin and Kraft E$_1$ effluent due to E. coli can be completely removed with the use of Ag-TiO$_2$ photocatalyst. By using Ag-TiO$_2$, by photocatalyst the formation of transient toxic species for the remazol brilliant blue R dye were observed by the Chen et al. Chen et al. [62] studied the effect of metal ions (Cu$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Al$^{3+}$, and Cd$^{2+}$) doping in TiO$_2$ towards the photodegradation of sulforhodamine B
(SRB), alizarin red (AR), and malachite green (MG) dyes. UV active Ag-TiO$_2$ with high surface area films for efficient photodegradation of methyl orange was examined by Arabatzis et al. [63].

Li et al. [64] investigated the mechanism of photosensitization and recombination of excited electron-hole pairs by depositing Pt on TiO$_2$. Arabatzis et al. [65] studied the effect of surface modification of rough, nanocrystalline TiO$_2$ thin-films by gold deposition using electron beam evaporation technique towards the degradation of industrial water pollutants.

Iliev et al. [66] studied the degradation of xylenol orange effluent by TiO$_2$, modified with Pd particles. TM/TiO$_2$/SiO$_2$ photocatalysts were prepared by the photodeposition method using transition metal salts (TM = Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$) for the photodegradation of reactive brilliant red dye. The TiO$_2$ catalysts modified by Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$ showed improved photocatalytic performance [67]. Xie et al. and Yuan et al. [68] developed the Nd$^{3+}$ ion modified TiO$_2$ by chemical co-precipitation technique. Photocatalytic reactivity of Nd$^{3+}$-TiO$_2$ sol was evaluated by PCD of phenol under visible light irradiation.

Sahoo et al. [69] investigated the PCD of crystal violet in dye solutions with Ag$^+$ modified TiO$_2$ under UV and simulated solar light. It was found that Ag$^+$ doped TiO$_2$ was more efficient than undoped TiO$_2$. Sobana et al. [70] reported Ag NPs doped TiO$_2$ for the degradation of direct red 23 and direct blue 53. The improved photocatalytic activity of Ag-TiO$_2$ was due to efficient electron trapping by Ag particle. Wang et al. [71] synthesized Fe$^{3+}$-TiO$_2$ nanopowders by plasma oxidative pyrolysis for use in effluent treatment. Vinu et al. [72] prepared the palladium substituted anatase TiO$_2$. The PCD of various dyes such as methylene blue, rhodamine B, and phenol was investigated under UV light. Ravichandran et al. [73] investigated the degradation of pentafluorobenzoic acid using Pt-doped TiO$_2$. Dozzi et al. [74] studied the effects of gold dopants on titanium dioxide towards the oxidative degradation of formic acid and acid red 1 dye under visible light irradiation.

### 1.6.2 Non-metal loaded TiO$_2$

Matos et al. [75] studied the synergetic effect for PCD of phenol by TiO$_2$/activated carbon composite. Herrmann et al. [76] reported solar PCD of chlorophenols using the synergistic effect between TiO$_2$ activated carbon composite in the aqueous dye solution. Da Silva et al. and Faria et al. [77] reported the PCD of solophenyl green dye using TiO$_2$/activated carbon composite. The mechanism of degradation was attributed to synergetic effect between activated carbon and TiO$_2$. 
Samantaray et al. [78] prepared the sulfate-modified TiO$_2$ with different crystal structures. Sulfated TiO$_2$ was used for the degradation of 4-nitrophenol. PCD of 4-nitrophenol depends on the surface area and the crystal form as well as the particle size of TiO$_2$. The photocatalytic activity of the advanced materials towards the degradation of some typical pollutants in water and air using the artificial and natural light was studied by Sakthivel et al. and Kisch et al. [79]. Tryba et al. [80] investigated the PCD activities of TiO$_2$ particles anatase phase covered by thin layer of carbon towards various dye effluents. Ohno et al. [81] synthesized chemically sulfur modified TiO$_2$ photocatalysts for the degradation of methylene blue and 2-propanol in aqueous solution under irradiation at visible light.

Li et al. [82] reported the photocatalytic activity of carbon-doped TiO$_2$ for gas-phase oxidation of benzene under solar light irradiation. The photocatalytic activity in the visible region is attributed to the presence of oxygen vacancy states between the valence band and conduction band in the TiO$_2$ band structure. Youji et al. [83] prepared TiO$_2$-decorated activated carbon (TiO$_2$/AC) composite by hydrolytic precipitation method and used for degradation of commercial dyes.

Yang et al. [84] reported the doping of nitrogen and carbon in TiO$_2$ films by sol-gel technique. Nitrogen and carbon doping into substitutional sites of TiO$_2$ lattice greatly reduces the band gap and shows improvement in the photocatalytic activity. Sun et al. [85] synthesized carbon-sulfur-co-doped TiO$_2$ composite by the hydrolysis of tetrabutyl titanate in a mixed aqueous solution containing thiourea and urea. The photocatalytic activity was evaluated by the PCD of 4-chloro phenols under both UV and visible light irradiation.

Chen et al. [86] reported the utilization of visible light more efficiently in photocatalytic reactions with carbon-doped TiO$_2$, nitrogen doped TiO$_2$ and the carbon and nitrogen co-doped TiO$_2$ nanoparticles. The photocatalytic activities of C-TiO$_2$, N-TiO$_2$, and C-N-TiO$_2$ samples with different C and N contents were evaluated by degradation of methylene blue under visible light irradiation. Xiao et al. [87] reported the preparation of carbon-doped TiO$_2$ nanoparticles by sol-gel method. The visible light photocatalytic activity of carbon-doped TiO$_2$ was attributed to the presence of oxygen vacancy between the valence bands and the conduction bands.

Jiang et al. [88] reported the visible light active N-doped TiO$_2$ nanomaterials by a solvothermal technique. The obtained nitrogen-doped TiO$_2$ were thermally stable and robust for photodegradation of methylene blue under visible light Irradiation. Hu et al. [89] fabricated the TiO$_2$ nanotube (TN) arrays by an anodic oxidation process. The experiments demonstrated that the TiO$_2$ Nanotube arrays displayed an excellent
photocatalytic activity under sunlight irradiation towards the degradation of methylene blue.

Parida et al. [90] prepared the sulfated TiO$_2$ by incipient wetness impregnation method. It was found that sulfate modification could reduce the crystallinity size and increase the specific surface area of the catalysts. The degradation of methyl orange under solar light radiation was investigated to evaluate the photocatalytic activity of the sulfated TiO$_2$ catalyst. Yu et al. [91] reported F-doped TiO$_2$ nanotubes by impregnation method. Compared to pure TiO$_2$ nanotubes, fluoride doped TiO$_2$ nanotubes showed enhanced photocatalytic efficiency. Vijayabalan et al. [92] reported the photocatalytic activity of fluorinated TiO$_2$ in the degradation of a chlorotriazine dye under ambient conditions. Surface fluorination of TiO$_2$ enhanced the adsorption of chlorotriazine dye while improving the overall degradation rate. Ang et al. [93] have prepared a series of nitrogen-doped TiO$_2$-SiO$_2$ mixed oxide catalysts by a sol-gel method. The N doped TiO$_2$-SiO$_2$ catalysts exhibited superior photocatalytic activity in degradation of methylene blue under visible light compared to the pure TiO$_2$ catalysts. Livraghi et al. [94,95] reported the nitrogen-doped TiO$_2$, a photocatalytic material active in visible light. These results provide a characterization of the electronic states associated with N impurities in TiO$_2$ particles for the effective degradation of dyes under irradiation with visible light.

### 1.6.3 Metal halide loaded TiO$_2$

Hu et al.[96] prepared Ag/AgBr/TiO$_2$ composite by the precipitation approach for photocatalytic application. The results indicated that AgBr was the main photoactive species for the destruction of azo dyes and bacteria under visible light irradiation. Wang et al. [97] prepared the TiO$_2$/BaF$_2$ ceramic powder using the TiCl$_4$ as a precursor. Experimental results indicated that the loading of BaF$_2$ enhanced the photoactivity of TiO$_2$. Elahifard et al. [98,99] prepared and used Ag/AgBr/TiO$_2$ deposited hydroxyapatite as adsorption bioceramic photosensitive material. The prepared Ag/AgBr/TiO$_2$-deposited hydroxyapatite has high ability to adsorb bacteria in the dark and also possesses high photocatalytic activity under the visible light.

Li et al. [100] synthesized the AgI/TiO$_2$ photocatalyst by a feasible approach and used for dye degradation. The highly efficient visible-light-induced photocatalytic activity of the nanostructured AgI/TiO$_2$ was attributed to its strong absorption in the visible region and low recombination rate and the synergetic effect between the components of AgI and TiO$_2$ in the nanostructured AgI/TiO$_2$. Zang and Farnood [101] investigated the photocatalytic activity of AgBr/TiO$_2$ under simulated solar light irradiation for the degradation of methyl orange. Yu et al. [102] studied a new visible-light-driven plasmonic photocatalyst Ag/AgCl/TiO$_2$ nanotube arrays. The prepared metal-
semiconductor nanocomposite plasmonic photocatalyst exhibited a highly PCD of methyl orange in the visible region.

1.7 Bismuth-based photocatalysts:

Bismuth-based composites attracted much interest among researchers in terms of synthesis, characterization and visible light photocatalytic activities. Many bismuth-based materials such as Bi$_2$S$_3$ and BiOX etc., classified as sulfides and oxyhalides. Most of these bismuth catalysts are active in the visible light region with a bandgap of less than 3.0 eV. The band gap of Bi$_2$S$_3$ and BiOI are less than 2.0eV, indicating their ability to absorb the visible light of longer wavelength. Therefore, the synthesis and photocatalytic activity of various bismuth-based compounds have been studied extensively [101].

1.7.1 BiOBr Semiconductors

Among the various BiOX (X= Cl, F, Br, I) BiOBr is a vital ternary compound, with a band gap of 2.64 eV. The unique tetragonal structure of BiOBr consists of the layered structure of [Bi$_2$O$_2$]$^{2+}$ sandwiched between the Br atoms. It has PbFCl type crystal structure is and D4h space group, which brings about an effective separation of the photoinduced electrons, and the holes for enhanced photocatalytic activity. However, the photocatalytic performance of BiOBr has been quite limited due to its high recombination rate which originated from its electron-hole pairs. According to previous reports, synergistic modifications in BiOBr brought through coupling with BiOCl and ZnFe$_2$O$_4$ or doping with noble metals such as Ag, Au, Pt have improved the photocatalytic activity [102].

1.7.2 Bi$_2$S$_3$ semiconductors

In recent years, there has been increasing interest among researchers in metal chalcogenides semiconductors owing to their unique properties and potential applications in various fields. Among these, Bi$_2$S$_3$ has been the most studied semiconductor which mostly exists in the orthorhombic phase. In particular, Bi$_2$S$_3$ nanomaterials have potential applications in various fields including, lithium-ion batteries, photovoltaic cells, photocatalysts and thermoelectric cooling devices, etc. Bi$_2$S$_3$ nanomaterials in the form of nanowires, nanoribbons, and nanorods have been synthesized by various techniques such as hydrothermal, solvothermal, physical vapor deposition (PVD), microwave synthesis and wet chemical synthesis methods. However, the participation of thiourea, thioacetamide and sodium sulfide as sulfur source induces various health and environmental risks. Such issues can be overcome by using various biomolecules assisted synthesis methods. The photocatalytic properties of different types of Bi$_2$S$_3$
nanostructures have been reported earlier. For example, though Bi$_2$S$_3$ is a good visible light active photocatalytic material but its electron-hole recombination rate is much faster that limits its practical application. Therefore, many efforts have been taken to improve the photocatalytic efficiency of Bi$_2$S$_3$ by combining with other semiconductors such as ZnO, BiOCl, CuS, CdS and other carbon materials [102].

Conclusions

Recently, many efforts have been put into the development of novel semiconductor materials for the degradation of organic pollutants and water purification by the photocatalytic process. The photocatalytic process has gained much attention from the researchers as the basic idea behind this process is quite simple. In this chapter, we have discussed in detail about various semiconductor photocatalysts that are already available and to provide an overview of recent developments that have emerged in this field to develop novel materials as a photocatalyst under visible light. We also encourage further research on this hot topic as there is a lot of space to be explored in this fascinating field of the photocatalyst.

References


Chapter 8

Photocatalytic Decomposition of Organic Dyes

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Abstract
In ecological and environmental protection, photocatalytic degradation of toxic organic dyes is a challenging task. Oxide-semiconductor is a special category of materials with a nanostructure that has obtained more attention in recent times owing to their fascinating properties and an extensive choice of applications in photocatalysis. This chapter includes a critical review of oxide-semiconductor nanomaterials towards photocatalytic wastewater purification. The structural aspects, nanostructure formation process and the various parameters affecting catalytic activity, photocatalytic applications of ZnO, TiO₂, Fe₃O₄, and CeO₂ based catalysts for efficient photocatalytic degradation of organic dyes are reviewed. It also includes a brief discussion on the mechanism of photocatalysis. In this regard, various oxide-semiconductor and their composite nanostructures for degradation of various organic dyes are sketched.

Keywords
Organic Dyes, Photocatalysis, Oxide-Semiconductor, Nanomaterials

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1. Introduction

Industry development is extensively connected with the disposal of a large number of various toxic pollutants, which are harmful to the environment, hazardous to human health, and difficult to degrade by natural means. Some organic compounds are major contaminators in industrial wastewater [1,2]. Discharges of chemical process industries such as pulp and paper, pharmaceutical agrochemical, dyestuff, food processing, petrochemical, tanning, steel, fiber wood, preservatives of foodstuffs, coal gasification, polymeric resin production, oil refining, coking plants etc. are the main sources of these organic pollutants [3-5]. Environmental problems caused by hardly-degradable and harmful organic pollutants have risen to be a grave menace to human growth and well-being. Organic pollutants once released into the aquatic ecosystem, they can cause various environmental problems, such as increasing biochemical oxygen, clogging sewage treatment plants and adversely affecting aquatic biota [6,7]. Therefore, before discharging the wastewater into the aquatic environment an effective and economical technique needs to be developed to lessen the concentration of organic pollutants.

Dyes are one group of organic pollutants used widely in textile, paper, dye houses and printing industries. The dye industry discharges one of the most problematic wastewaters to be considered not only for their high chemical and biological oxygen demands, content in toxic compounds and suspended solids but also for color, which is the first contaminant to be recognized by the human eye. Dyes may considerably influence photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life [8,9]. Dyeing of textiles requires high amounts of water and some harmful chemical substances too. Over 10,000 types of dyes are used for dyeing or printing of fabrics. These harmful chemicals in the form of dyes can be acquired by human beings through the skin, bronchially or through digestion. Textile materials can cause allergic reactions, or even can be carcinogenic and mutagenic [10]. Dyes commonly have complex aromatic molecular structures and synthetic origin, which make them more stable non-biodegradable, so these harmful dyes that affect human and environmental health should be taken into consideration [11]. Presently, various technologies such as coagulation and adsorption slightly concentrate or separate these
pollutants from water, but cannot completely remove or demolish them into biodegradable or less toxic organic compounds. Photocatalysis has endorsed a lot of changes over the past two decades [12]. For the photodegradation of organic pollutant and generation of energy, important advancements are being made in the synthesis of nanostructured and novel materials [13]. The improvement of a simple recyclable photocatalyst and also the recovery of the deactivated photocatalyst required for reducing the total cost, and lowering overall usage of the photocatalytic material [14]. Organic contaminants have become of more interest, due to the inability of traditional water-treatment technologies to completely decompose these contaminants in aqueous media. The presence of organic contaminants in groundwater, drinking water, sewage effluents, and sludge poses a serious threat to human and aquatic organisms [15,16]. Conventional analysis methods only transfer pollutants from one medium to another but the semiconductor photocatalyst converts contaminants to harmless products such as CO₂ and H₂O [17,18]. In addition, the reaction conditions are mild, the reaction time is moderate and can be used to gaseous, aqueous and solid phase treatments. So, to degrade organic pollutant the use of semiconductor nanomaterials-based photocatalysts perceived as one of the most hopeful areas of research and application. These materials include treatment of environmental pollution, pharmaceutical industries, and medicine (destruction of cancer and viruses) [19]. Accordingly, oxide semiconductor photocatalyst has the advantage of not only minimizing running costs but also producing the desired product in the most profitable and adequate way. Many semiconductor materials such as CdS [20], ZnS [21], Ag₃PO₄ [22] TiO₂ [23], ZnWO₄ [24], CeO₂ [25] and Fe₂O₃ [26] etc. can be used as photocatalysts for the degradation of organic pollutants. Consequently, to establish an advanced and stable system with high efficiency, particularly sunlight utilization, it still remains an urgent challenge. The significant characteristics of the photocatalytic system are the desired band gap, high surface area, suitable morphology reusability, and stability. Among the various photocatalyst, metal oxides have wide applications as photocatalyst and the oxides of vanadium, chromium, zinc, titanium cerium and tin having the aforementioned characteristics follow similar primary photocatalytic processes such as light absorption, which induces a charge separation process with the formation of positive holes which are capable of oxidizing organic substrates [27]. In this chapter, we have mainly focused on the contribution and aspects of oxide semiconductor nanoparticles for photodegradation of dyes.

2. **Features of oxide semiconductors for photocatalysis**

The dominant benefits of semiconductor photocatalysis are that they offer a satisfying substitute for the energy-intensive treatment methods and have the capacity to use
pollution-free and renewable solar energy. As visible light constitute a large fraction of the solar energy, one of the big dispute of photocatalyst study is to dream up new catalyst that can display high activity under illumination by visible light. Generally, the catalyst can be photoactivated by a photon with irradiation energy equal to or higher than its band gap energy ($E_g$). An electron moves from the valence band to the conduction band at the photocatalytic surface which accelerates the generation of holes ($h^+$) in the valence band (see equation i). Then an $O_2$ molecule is reduced to $\cdot O_2^-$ by the combination with an electron ($e^-$), which further turns into hydroxyl radical ($\cdot OH$) (described in Eqs. 2, 3, 4 and 5). In the intervening time, the interaction of holes ($h^+$) with hydroxyl ($OH^-$) may produce a hydroxyl radical ($\cdot OH$) (Eqs. 6 and 7). The resulting $\cdot OH$ radical acts as a strong oxidizing agent and converts organic substances into carbon dioxide ($CO_2$), water ($H_2O$) and other less hazardous molecules than the original substances (Eq. 8) [28,29].

\[
\text{Photocatalyst} + hv \rightarrow h^+ + e^- 
\]

\[
e^- + O_2 \rightarrow \cdot O_2^- \tag{2}
\]

\[
\cdot O_2^- + H^+ \rightarrow \cdot OOH \tag{3}
\]

\[
2\cdot OOH \rightarrow O_2 + H_2O_2 \tag{4}
\]

\[
H_2O_2 + hv \rightarrow 2\cdot OH \tag{5}
\]

\[
h^+ + OH^- \rightarrow \cdot OH \tag{6}
\]

\[
h^+ + H_2O \rightarrow \cdot OH + H^+ \tag{7}
\]

\[
\text{Pollutant} + \cdot OH \rightarrow CO_2 + H_2O + \text{degradation product} \tag{8}
\]

The photo induced electron/hole in oxide semiconductors precedes catalytic oxidation or reduction of the species on the surface, though the electron/hole recombination determines the extent of photocatalytic activity. Slower the rate of electron-hole recombination, higher is the photodegradation of the organic pollutants. The band gap of oxide semiconductors effectively fulfills requirement essential for excellent
photocatalyst. The charge transport developed due to quantum confinement effect in oxide-semiconductor particles drive at the nanoscale is promisingly contributes towards their photocatalytic activity. Moreover, other aspects such as ease of fabrication, non-toxic nature, stability under harsh environmental conditions, higher reproducibility are encouraging features that make the reliable candidate for photocatalysis applications.

3. Zinc oxide nanomaterials as photocatalyst

Currently, due to the excellent properties of the II-VI semiconductor zinc oxide (ZnO) is considered as one of the most flexible and functional materials which can be used for various high-technological applications. Many approaches have been developed to fabricate ZnO nanoparticles with different shapes and sizes including hydrothermal method [30], template synthesis [31], solvothermal method [32], chemical vapor deposition [33] and biosynthesis method [34] etc. Because of the non-toxicity, easy fabrication, high electrochemical, photocatalytic and adsorptive properties, ZnO is treated as one of the effective adsorbents for the removal of various toxic and hazardous chemicals and dyes. In addition, their composites have also been discussed. ZnO nanoparticles, nanorods, and nanoflowers synthesized through the hydrothermal process have been investigated for the photodegradation of methyl orange dye (Fig. 1).

Upon irradiation, the color of methyl orange solution was rapidly degraded with the addition of ZnO nanorods. Methyl orange decomposition efficiency of ZnO nanorods and nanoflowers after 4 cycles was 91.5 and 90% respectively [35]. In another study, ZnO/SnO₂ hetero-nanofibres of about 250 nm in diameter and several micrometers in length synthesized via electrospinning method. They have been thoroughly investigated for recycling ability. The photodegradation abilities of ZnO/SnO₂ nanostructures for various dyes (methylene blue, congo red, eosin red and methyl orange) were studied and were found useful for fast photodegradation of dyes (Fig. 2).
Figure 1(a and b) SEM images of the ZnO nanorod grown on the Cu substrate, (c and d) collected at the bottom of the autoclave. (e) Photographs of methyl orange solutions upon photodegradation catalyzed by ZnO nanorods. (f) Spectral changes of methyl orange solutions upon photodegradation catalyzed by ZnO nanorod. (g) Comparison of decomposition efficiency of different ZnO samples for the degradation of methyl orange as well as that only induced by UV irradiation in the absence of any ZnO samples. (h) SEM image of the commercial ZnO particles. (i) Photodegradation kinetics of MO in the presence of ZnO micro/nanostructures [35].
Figure 2(a-b)  SEM images of ZnO/SnO₂. (c) Photocatalysis degradation rate of the four dyes [36].

The enhanced photocatalytic ability of ZnO/SnO₂ hetero-nanofibres were attributed to the effective separation of the photogenerated electron/hole and high adsorption capacity. Photocatalytic degradation towards methylene blue, congo red, eosin red and methyl orange were 97.3, 96.8, 98.9 and 97.7% respectively. Based on this investigation, ZnO/SnO₂ hetero-nanofibers possess functional potential applications for wastewater purification with excellent recycling ability [36]. A green synthesis route was used to synthesize pure ZnO and ZnO/starch quantum dots with size range of 5-10 nm. Further, the solar photocatalytic activity for rhodamine B (RhB) dye of both the ZnO quantum dots was examined at the end of 30, 60, 90 and 120 minutes. In this, ZnO/starch quantum dots show more decomposition of RhB than pure ZnO quantum dots under the solar light environment (Fig. 3) [37].
ZnO@ZnS core-shell nanoparticles were synthesized via co-precipitation method. The photocatalytic activity of these core-shell nanoparticles was investigated for degradation of the congo red dye. Congo red dye degradation experiments indicate that the ZnO@ZnScore-shell nanoparticles degraded 70% dye after illumination for the nanoparticles [38]. Thus, ZnO nanomaterials exhibit wonderful photocatalytic activity and also show same effectiveness in the photodegradation of other environmentally hazardous organic pollutants under the natural solar light. A summary of the ZnO for the degradation of various dyes is summarized in Table 1.
Table 1  Summary of organic dyes removal by ZnO based nanomaterials.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Dye</th>
<th>Photocatalytic Degradation Time (min)</th>
<th>Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO CNTs</td>
<td>RhB</td>
<td>60</td>
<td>49</td>
<td>[39]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MO, MB</td>
<td>180</td>
<td>98.3</td>
<td>[40]</td>
</tr>
<tr>
<td>ZnO</td>
<td>RhB, MO</td>
<td>60</td>
<td>59.06, 56.66, 71.40, 78.60, 62.50, 61.60</td>
<td>[41]</td>
</tr>
<tr>
<td>ZnO</td>
<td>DR 81, VB, Rh 6G, FG, EBT, AO</td>
<td>90</td>
<td>71.40, 78.60, 62.50, 61.60</td>
<td>[42]</td>
</tr>
<tr>
<td>ZnO@ZnS</td>
<td>CR</td>
<td>120</td>
<td>70</td>
<td>[38]</td>
</tr>
<tr>
<td>Core-shell</td>
<td>MO</td>
<td>120</td>
<td>44.5</td>
<td>[43]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MO</td>
<td>120</td>
<td>83.99</td>
<td>[44]</td>
</tr>
<tr>
<td>ZnO/CuO</td>
<td>MB, MO</td>
<td>120</td>
<td>90</td>
<td>[45]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MO</td>
<td>90</td>
<td>90.5</td>
<td>[35]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MO</td>
<td>150</td>
<td>94.3</td>
<td>[46]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MO</td>
<td>160</td>
<td>97</td>
<td>[47]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MB</td>
<td>90</td>
<td>90.8</td>
<td>[48]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MG</td>
<td>120</td>
<td>93.09</td>
<td>[49]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MR</td>
<td>180</td>
<td>92.45</td>
<td>[50]</td>
</tr>
<tr>
<td>ZnO</td>
<td>RhB</td>
<td>45</td>
<td>40</td>
<td>[51]</td>
</tr>
<tr>
<td>ZnO NWs</td>
<td>MR</td>
<td>80</td>
<td>90</td>
<td>[52]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MO</td>
<td>60</td>
<td>100</td>
<td>[53]</td>
</tr>
<tr>
<td>ZnO</td>
<td>RhB</td>
<td>120</td>
<td>11</td>
<td>[37]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MB</td>
<td>125</td>
<td>70-75</td>
<td>[54]</td>
</tr>
<tr>
<td>ZnO/SnO₂ NFs</td>
<td>MB, CR, ER, MO</td>
<td>20</td>
<td>95.5</td>
<td>[36]</td>
</tr>
<tr>
<td>ZnO</td>
<td>MO</td>
<td>210</td>
<td>92</td>
<td>[55]</td>
</tr>
</tbody>
</table>

CR=Congo red, ER=Eosin red, RhB=Rhodamine B, MO=Methyl orange, DR81=Direct Red 81, VB=Victoria blue, Rh6G=Rhodamine 6G, FG=Fast green, EBT=Eriochrome black T, AO=Acridine orange, MB=Methylene blue, MR=Methyl red, MG=Malachite green. CNTs=Carbon nanotubes, NWs=Nanowires, NFs=Nanofibres

4. Titanium oxide nanomaterials as photocatalyst

Among the nano photocatalysis used in the treatment of environmental wastewater, titanium oxide nanostructures have been extensively studied [56]. Since the discovery of the phenomenon of the photocatalytic splitting of water on a TiO₂ electrode under UV light, enormous attempts committed to titania research have led to most promising applications in the fields of photovoltaics, photo electrochromic's, ceramics, sensors, and photocatalysis. As most advantageous semiconductor photocatalysts, TiO₂-based
materials are accordingly expected to play a major role to check serious environmental and pollution challenges and ease the energy crisis through the use of renewable solar energy [57-59]. For the synthesis of titanium oxide nanoparticles, a number of techniques are available and these include hydrothermal [60], solvothermal [61], sol-gel [62], simple chemical method [63] and chemical vapor deposition [64] etc. and have been successfully utilized for the photocatalytic degradation of dyes.

In another study, the carbon-coated TiO$_2$ nanocrystals synthesized were formed about 10 times lithium rate improvement and 4 times the photocatalytic performance compared to Li-based photocatalysts. To reveal the photocatalytic activity of TiO$_2$ and C-coated TiO$_2$,
photocatalytic decomposition of methylene blue (MB) and rhodamine B (RhB) solution was conducted. After the start of the reaction, the UV-Visible absorption spectra of MB and RB were monitored. The result showed that C-coated TiO₂ nanocrystals have an about four-time better photocatalytic activity than the pristine TiO₂ nanocrystals in decomposing of MB, and for RB it took around 40 min for C-coated TiO₂ nanocrystals to decolorize the RB, while a large amount of RB still remained after 60 min irradiation with pristine TiO₂ nanocrystals (Fig. 4).

The adding of a fine layer of amorphous carbon on crystalline materials may be used as a different approach for improving the photocatalytic performance of TiO₂ and other materials as well [65]. In another work, the 1D CdS nanowires@TiO₂ nanoparticles with very high photocatalytic activity for organic dye degradation was reported [66]. The 1D CdS nanowires @TiO₂ nanoparticles were reported with improved photocatalytic activity in comparison to the 1D CdS nanowires, for degradation of organic dyes (methyl orange, methylene blue, and rhodamine B) under visible light radiation due to the longer lifetime of photogenerated electron-hole pairs of ID CdS nanowires@TiO₂ nanoparticles, in contrast to the original 1D CdS nanowires (Scheme 1).

![Scheme 1](image_url)  
*Scheme 1  Illustration of the proposed reaction mechanism for degradation of dye pollutants over the 1D CdS NWs@TiO₂ NPs photocatalyst [66].*

Thus, the formation of a heterostructure between ID CdS nanowires and TiO₂ nanoparticles improved the charge separation efficiency. In another study, bifunctional TiO₂/Ag₃PO₄/graphene composites have been successfully synthesized by a combination of ion-exchange and hydrothermal methods. The improved photocatalytic activity of composites is attributed to the effective separation of photoexcited electron-hole pairs.
and fast charge transfer between components in the composites. Removal of the majority of Rhodamine B and methyl orange under visible light irradiation was obtained in 6 and 12 min, achieving a photocatalytic efficiency of around 60 and 100% respectively [67]. Overall, this discussion brings to attention the advancements of titanium oxide nanoparticles in their use for water-treatment processes. Further, since TiO$_2$ NPs can degrade organic pollutants and at the same time can oxidize heavy metal species [64]. A summary of the TiO$_2$ based photocatalyst for the degradation of various dyes is summarized in Table 2.

Table 2  Summary of organic dyes removal by TiO$_2$ based nanomaterials.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Dye</th>
<th>Photocatalytic degradation time (min)</th>
<th>Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-TiO$_2$ NCs</td>
<td>RhB</td>
<td>48 hours</td>
<td>15.8</td>
<td>[68]</td>
</tr>
<tr>
<td>TiO$_2$/ZrO$_2$ NCs</td>
<td>MO</td>
<td>105</td>
<td>59</td>
<td>[69]</td>
</tr>
<tr>
<td>CdS NWs@TiO$_2$</td>
<td>MO, MB, RB</td>
<td>2, 2, 3</td>
<td>99.7</td>
<td>[66]</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>MO, MB, RhB</td>
<td>2,</td>
<td>98.2</td>
<td>[65]</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>RhB</td>
<td>40</td>
<td>93</td>
<td>[70]</td>
</tr>
<tr>
<td>TiO$_2$/Ag$_3$PO$_4$/graphene composites</td>
<td>RhB, MB</td>
<td>6, 12</td>
<td>60, 100</td>
<td>[67]</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>RB5</td>
<td>5</td>
<td>13.2-15.3</td>
<td>[71]</td>
</tr>
<tr>
<td>Fe-doped TiO$_2$</td>
<td>MB</td>
<td>5 h</td>
<td>92</td>
<td>[72]</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>MO</td>
<td>100</td>
<td>90</td>
<td>[73]</td>
</tr>
<tr>
<td>TiO$_2$/s-PS aerogels</td>
<td>MB</td>
<td>180</td>
<td>30</td>
<td>[74]</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>MO, MB</td>
<td>60</td>
<td>80</td>
<td>[75]</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$-TiO$_2$-Ag NCs</td>
<td>RhB, MB</td>
<td>60</td>
<td>90</td>
<td>[76]</td>
</tr>
<tr>
<td>TiO$_2$ NFs</td>
<td>MB</td>
<td>120</td>
<td>70</td>
<td>[77]</td>
</tr>
<tr>
<td>TiO$_2$ NRs</td>
<td>MO</td>
<td>240</td>
<td>80</td>
<td>[78]</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>RB</td>
<td>150</td>
<td>30.12</td>
<td>[79]</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>MO</td>
<td>300</td>
<td>90</td>
<td>[80]</td>
</tr>
</tbody>
</table>

RhB=Rhodamine B, MO=Methyl orange, MB=Methylene blue, RB5=reactive black 5, RB=Remazol brown. NCs=Nano composites, NWs=Nanowires, NFs=Nanofibers, NRs=Nanorods, NPs=Nanoparticles

5. **Iron oxide nanomaterials as photocatalyst**

Iron oxide, as an ordinary compound is broadly distributed in nature and can be synthesized on large scale. Over the past few decades, magnetic iron oxide nanoparticles because of their significance in basic research were extensively synthesized with various morphologies and structures [81]. In addition, due to a wide range of applications including pigments, magnetic fluids, catalysis, magnetic resonance imaging (MRI),
biosensors, targeted drug delivery, data storage and the environmental remediation, magnetic iron oxides are of immense interest to researchers[82,83]. The different crystalline iron oxides have unique magnetic, catalytic, biochemical and other properties that make them suitable for specific technical and biomedical applications [84,85,86].

One of the specific morphology, three-dimensional (3D) cauliflower-like α-Fe₂O₃ based nanostructure was prepared by one-step toluene-water biphasic interfacial reaction route. The prepared microstructures were found to exhibit exceptional water treatment performance with high removal capacities for organic dyes. The 3D cauliflower-like α-Fe₂O₃ nanostructures with high surface area and porous structure showed better removal capacities for organic dye in wastewater and structurally enhanced visible-light photocatalytic activity in the presence of H₂O₂ when compared with the commercial α-Fe₂O₃ powders (Fig. 5) [87].

![FESEM images of microstructures prepared at different temperatures](image1)

**Figure 5** (a and b) FESEM images of the microstructures prepared at different temperatures, (c) UV–visible absorption spectra of congo red solutions in the presence of cauliflower-likeα-Fe₂O₃ at different time intervals and (d) adsorption rates of the congo red on newly prepared cauliflower-like α-Fe₂O₃ [87].

The higher surface area provided by the porous structure as well as 3D features probably the reason for the promoted catalytic activity of the 3D cauliflower-like α-Fe₂O₃ nanostructures. On the other hand, the combination of graphene oxide (GO) and Fe₂O₃ has been found effective for degradation of organic contaminants. The GO-Fe₂O₃ hybrid material found eminently effective for the degradation of Rhodamine B (RhB) in aqueous
solution with H₂O₂ under wide pH range of 2.09-10.09 and showed high photocatalytic activity after seven reaction cycles. The GO-Fe₂O₃ catalyst was also found efficient for the degradation of 4-nitrophenol (4-NP) [88]. On the other and photocatalytic degradation performance for congo red (CR), eosin red (ER) and methylene blue (MB) dyes was studied under visible light for α-Fe₂O₃. The order of degradation rate for the dyes was as MB (80%), ER (84%) and CR (98%) [89]. A summary of the iron oxide-based photocatalyst for the degradation of various dyes is summarized in Table 3.

**Table 3  Summary of organic dyes removal by iron oxide-based nanomaterials.**

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Dye</th>
<th>Photocatalytic degradation time (min)</th>
<th>Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄@SiO₂@TiO₂ NPs</td>
<td>RhB</td>
<td>120</td>
<td>92.03</td>
<td>[90]</td>
</tr>
<tr>
<td>Fe₃O₄–Ag₃PO₄</td>
<td>MB</td>
<td>30</td>
<td>79.3</td>
<td>[91]</td>
</tr>
<tr>
<td>Fe₃O₄@His@Ag NPs</td>
<td>MO, MB</td>
<td>8, 4</td>
<td>85</td>
<td>[92]</td>
</tr>
<tr>
<td>Fe₂O₃–BiVO₄ NPs</td>
<td>RhB</td>
<td>80</td>
<td>100</td>
<td>[93]</td>
</tr>
<tr>
<td>α-Fe₂O₃ NPs</td>
<td>RhB</td>
<td>120</td>
<td>40</td>
<td>[87]</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Orange II</td>
<td>90</td>
<td>75</td>
<td>[94]</td>
</tr>
<tr>
<td>Graphene oxide-Fe₂O₃</td>
<td>RhB</td>
<td>80</td>
<td>60</td>
<td>[88]</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>CR</td>
<td>120</td>
<td>55.5</td>
<td>[95]</td>
</tr>
<tr>
<td>γ-Fe₂O₃/α-</td>
<td>CR, ER, MB, 25, 50, 45</td>
<td>98, 84, 80</td>
<td>[89]</td>
<td></td>
</tr>
<tr>
<td>g-C₃N₄–Fe₃O₄</td>
<td>RhB</td>
<td>6 cycles</td>
<td>90</td>
<td>[96]</td>
</tr>
<tr>
<td>Diatomite-Fe₂O₃</td>
<td>RhB</td>
<td>5 cycles</td>
<td>90</td>
<td>[97]</td>
</tr>
<tr>
<td>Fe₂O₃/Carbon aerogel</td>
<td>RhB</td>
<td>3 cycles</td>
<td>98</td>
<td>[98]</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>RhB</td>
<td>160</td>
<td>98</td>
<td>[99]</td>
</tr>
<tr>
<td>Graphene-Fe₂O₄</td>
<td>MB</td>
<td>120</td>
<td>98</td>
<td>[100]</td>
</tr>
<tr>
<td>Fe₂O₃–TiO₂</td>
<td>MB</td>
<td>100</td>
<td>81</td>
<td>[101]</td>
</tr>
<tr>
<td>α-Fe₂O₃ NPs</td>
<td>MO</td>
<td>210</td>
<td>80</td>
<td>[102]</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>RhB</td>
<td>360</td>
<td>82</td>
<td>[103]</td>
</tr>
<tr>
<td>Fe₂O₃ pillared clay</td>
<td>MB</td>
<td>150</td>
<td>41</td>
<td>[104]</td>
</tr>
<tr>
<td>α-Fe₂O₃ NPs</td>
<td>RhB</td>
<td>140</td>
<td>79</td>
<td>[105]</td>
</tr>
<tr>
<td>α-Fe₂O₃/NiTiO₃NFs</td>
<td>RhB</td>
<td>180</td>
<td>90.4</td>
<td>[106]</td>
</tr>
<tr>
<td>α-Fe₂O₃ NPs</td>
<td>MB, ER, CR</td>
<td>50</td>
<td>57, 63, 93</td>
<td>[107]</td>
</tr>
</tbody>
</table>

CR=Congo red, ER=Eosin red, RhB=Rhodamine B, MO=Methyl orange, MB=Methylene blue, NPs=Nanoparticles, NFs=Nanofibres

Various major issues have to be addressed before recommending photocatalysts for large-scale industrial applications. Apart from offering easy separation of the photocatalyst from the reaction system, the magnetic iron oxide semiconductor system has obtained an exclusive place in the progress of heterogeneous photocatalysis.
6. Cerium oxide nanomaterials as photocatalyst

Cerium (CeO₂), as one of the most valuable rare earth metal oxides, has redox properties, metal-support interactions, and high oxygen storage capacity [108]. These uncommon properties make a CeO₂ an auspicious contender for using as catalysts, adsorbents [109], luminescence, polishing powder, UV blocking, and shielding materials [110,111], etc. Different nanostructures of CeO₂ and its based composites such as nanoparticles, microspheres [112], nanofibers, nanosheets, nanotubes, thin films [113] have been received much attention for their many exclusive and superior advantages, such as the small size and the high surface-to-volume ratio [114].

Undoped CeO₂ and Fe-doped CeO₂ nanoparticles were synthesized by a homogeneous/impregnation method. The superior photocatalytic performance of the Fe-doped CeO₂ films, compared with undoped CeO₂ films, was ascribed mainly to the decrease in band gap energy and an increase in the specific surface area of the material. The presence of Fe as found from XPS analysis was supposed to act as an electron acceptor and/or hole donor (Fig. 6), facilitating longer lived charge carrier separation in Fe-doped CeO₂ film as confirmed by photoluminescence spectroscopy.

![Figure 6: Proposed mechanism for the photoexcited electron-hole separation and transport processes at the Fe-doped CeO₂ interface under visible light irradiation [115].](image)

The 1.50 mol% Fe-doped CeO₂ film was found to be optimal iron doping concentration for methyl orange degradation by D. Channei et al. [115]. Zhang et al. successfully
synthesized porous CeO$_2$ nanofibers. The absorption performance of nanofibers showed that the CeO$_2$ nanofibers can remove the methyl orange in very short time i.e. the methyl orange removal was 50% in 5 min (Fig. 7). The accelerated adsorption is favorable for the water treatment [116].

![Figure 7](image)

**Figure 7** (a) SEM images of CeO$_2$ nanofibers and (b) absorption spectra of methyl orange solutions [116].

Photocatalytic degradation behavior of orange 16 reactive dye was successfully studied using cerium oxide nanoparticles. For CeO$_2$ nanoparticles, no color of reactive orange dye was observed after 120 min [117]. Photodegradation process by CeO$_2$ has attracted increasing attention during the past decades. However, its application is limited due to some main practical challenges such as low adsorption capacity for hydrophobic contaminants, post-recovery of the CeO$_2$ particles after water treatment and the uniform dispersion in aqueous suspension. The recently developed counter measures for improving the performance of CeO$_2$-based photocatalytic degradation of organic pollutants with respect to the above limitations have been reported [118-120]. A summary of the CeO$_2$ based photocatalysts for the degradation of various dyes is summarized in Table 4.
Table 4  Summary of organic dyes removal by CeO$_2$ based nanomaterials.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Dye</th>
<th>Photocatalytic Degradation time (min)</th>
<th>Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$-ZnO</td>
<td>MB</td>
<td>300</td>
<td>30</td>
<td>[121]</td>
</tr>
<tr>
<td>CeO$_2$/TiO$_2$ NCs</td>
<td>Bph-dye</td>
<td>3 h</td>
<td>72</td>
<td>[122]</td>
</tr>
<tr>
<td>CeO$_2$ NPs</td>
<td>Orange 16</td>
<td>2h</td>
<td>100</td>
<td>[117]</td>
</tr>
<tr>
<td>CuBi$_2$O$_4$/CeO$_2$ NCs</td>
<td>CR</td>
<td>100</td>
<td>83.05</td>
<td>[118]</td>
</tr>
<tr>
<td>CuBi$_2$O$_4$/CeO$_2$</td>
<td>CR</td>
<td>100</td>
<td>83.05</td>
<td>[119]</td>
</tr>
<tr>
<td>Fe$^{3+}$ Doped</td>
<td>RhB</td>
<td>12h</td>
<td>85</td>
<td>[120]</td>
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<tr>
<td>Mesoporous CeO$_2$</td>
<td>RhB</td>
<td>90</td>
<td>74.9</td>
<td>[121]</td>
</tr>
<tr>
<td>Micro/Nanostructure</td>
<td>RhB</td>
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<td>90</td>
<td>[122]</td>
</tr>
<tr>
<td>CeO$_2$</td>
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<td>10</td>
<td>78</td>
<td>[123]</td>
</tr>
<tr>
<td>CeO$_2$ NPs</td>
<td>Rh 6G</td>
<td>18 cycles</td>
<td>80</td>
<td>[124]</td>
</tr>
<tr>
<td>CeO$_2$ NPs</td>
<td>CR</td>
<td>240</td>
<td>90</td>
<td>[125]</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>RhB</td>
<td>100</td>
<td>50</td>
<td>[126]</td>
</tr>
<tr>
<td>CeO$_2$ SiO$_2$ NPs</td>
<td>MB</td>
<td>180</td>
<td>85</td>
<td>[127]</td>
</tr>
<tr>
<td>ZnS decorated CeO$_2$</td>
<td>RhB</td>
<td>120</td>
<td>92</td>
<td>[128]</td>
</tr>
<tr>
<td>Co-doped CeO$_2$ NPs</td>
<td>MB</td>
<td>420</td>
<td>98</td>
<td>[129]</td>
</tr>
<tr>
<td>CeO$_2$ nanostructure</td>
<td>MB</td>
<td>50</td>
<td>61.6</td>
<td>[130]</td>
</tr>
<tr>
<td>Fe–doped CeO$_2$</td>
<td>MO</td>
<td>120</td>
<td>10</td>
<td>[115]</td>
</tr>
<tr>
<td>CeO$_2$ NFs</td>
<td>MO</td>
<td>5</td>
<td>50</td>
<td>[116]</td>
</tr>
</tbody>
</table>

7. Conclusions

Recent efforts in photocatalytic degradation of organic dyes using different types of oxide-semiconductor nanomaterials have been encapsulated in the present chapter. It is concluded that above-discussed materials are very good photocatalysts and the addition of dopants to some of the pure nanomaterials can consider embellishing catalyst performance. Various dopants do not have the same effect on the interaction with electrons and holes due to the different position of the dopants in the host lattice. The search for new photocatalysts having desired characteristics to induce the oxidation of organic pollutants under visible light irradiation is encouraging. The metal oxides should be ecologically affable and preparation via inexpensive routes should be the main attention. These are the major concerns from the synthetic and industrial points of view which should be the primary focus of the researchers involved.
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Chapter 9

Photocatalytic Degradation of Organic Pollutants by Zinc Oxide Composite

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Abstract

Photocatalysis has been proved to be a promising approach for the degradation of organic pollutants. Oxide semiconductors have shown their recognition in the area of catalysis. Particularly, oxide semiconductor based composites have shown improved photodegradation of organic pollutants by modification of their electronic and structural properties than their single counterparts. ZnO has an advantage of being non-toxic, cost-effective and environmentally friendly to become an efficient photocatalyst that can be utilized for preparing different kinds of composites. This chapter summarizes the recent progress in the fabrication and photocatalytic efficiency of various types of ZnO composites for degradation of organic pollutants.

Keywords

Catalysis, Semiconductor, Composites, Organic Pollutants, Oxides

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1. **Introduction**

We are exposed to various organic pollutants (surfactants, pesticides, dyes, phenols, chloro compounds, nitrogen-containing compounds etc.) instigating from different industries (leather, paper, pharmaceutical and steel plant) and agricultural wastes (usage of pesticides, herbicides). These pollutants contaminate water resources and cause a hazardous effect on the human health, aquatic life as well as environment [1-5]. For the removal of various organic pollutants, various methods have been so far adopted such as physical, chemical and biological methods [6, 7]. Amongst these, photocatalytic degradation and physical adsorption are considered to be efficient because of their high efficiency, economic suitability, and easy fabrication. The processes have attracted much attention for degradation of organic pollutants [8-11].

In the past two decades, several semiconductor-based photocatalysts; ZnO, TiO$_2$, CuO, SnO$_2$, WO$_3$, Fe$_2$O$_3$ and Bi$_2$O$_3$ etc. have widely been preferred for degradation of organic pollutants due to their superior photocatalytic properties [12-18]. Among these materials, ZnO exhibits promising properties such as cost-effectiveness, non-toxic nature, biologically and chemically inert, photo and thermal stability as well as high quantum yield [19]. Pure ZnO based photocatalysts have a band gap (3.2 eV) at room temperature and high electron mobility (200-300 cm$^2$ V$^{-1}$s$^{-1}$) that promotes electron transfer efficiency [20]. To broaden the absorption range i.e. to improve the photoactivity of the
The extending of bandgap corresponds to the visible region can be achieved by improving various aspects such as structural modifications, the addition of foreign element, introducing metal doping, carbon-based composites and achieving quantum confinement effect by means of controlling size up to nano level [21]. Particularly, the superior charge transport ability of semiconductor-based materials due to their better electronic structure having adequate band gap separation between valence and conduction bands compared to other class of materials is effective for photocatalytic activity. The electrons present in the valence band jumped to the conduction band and leave a hole behind when the energy of an incident photon is equal to or exceeds the band gap energy of metal-oxide semiconductors. The photogenerated electron/hole induces reduction and oxidation respectively, at the surface. The ability of metal-oxide-semiconductors mainly depends upon their ability to generate electron/hole pair under illumination of incident light photons and their recombination. However, faster recombination of electrons and holes hampers the photocatalytic efficiency by trapping the photo-induced charge carriers [22]. The most efficient way to improve the separation of charge carrier is to couple ZnO with other semiconductor-based oxide or sulphide [23,24] as well as with high mesoporous materials (zeolite, clay, alumina, silica) [25-28] and carbon-based materials (graphene and its derivatives, CNT) [29-31], Doping with metal or non-metal [32,33], fabrication of composite with polymeric materials [34], dye sensitization [35] and metal oxide with hierarchical architectures are another possible method [36]. In this chapter, we aimed to cover the different kinds of ZnO composites investigated to degrade organic pollutants in the last five years.

2. Photocatalytic ZnO/graphene composites

It has been found that the combination of semiconductor material and carbon-based materials may enhance the photocatalytic efficiency of photocatalysts because the existence of semiconductor particles on the graphene surface avoids the aggregation of graphene sheets and preserves the surface area at a high level. It provides unique pore structure, electronic properties, adsorptive capacity, and acidity. These materials include activated carbon [37], CNT [31] and graphene and its derivatives [29,30].

Graphene, a 2D material has excellent electrical, thermal, optical and mechanical properties due to its unique structure. It consists of sp²-bonded carbon atoms that are connected in hexagonal shapes with each carbon atom covalently bonded to three other carbon atoms. Graphene not only provides reaction active sites due to the higher specific surface area but also possesses very high charge carrier mobility that can be effective to
enhance the charge separation in order to improve the photocatalytic process [38]. The reduced graphene oxide also improves charge separation by initializing hetero junction induced electric files at the interface with oxide semiconductors. The difference in Fermi level between reduced graphene oxide and oxide semiconductor promptly transfer an electron to the surface of graphene and stimulates faster reduction reaction, thereby contributes towards photocatalytic efficiency by enhancing separation competence of photogenerated electron-hole pairs [39]. The π-π stacking between aromatic rings of graphene and incoming moiety also significantly accelerates their adsorption on the oxide semiconductors [40]. This section covers the recent progress and work done on organic pollutant degradation using various forms of ZnO composites prepared using graphene and graphene oxides.

2.1 ZnO/graphene composites

A number of ZnO/graphene composites used for photocatalytic degradation of azo dyes. The ZnO/graphene composites prepared via chemical precipitation method showed 2.4 times enhancement in their photocatalytic degradation efficiency towards methylene blue (MB) compared to the bare ZnO [41]. The ZnO/graphene composites processed through simple chemical precipitation method followed by the heat treatment led to the formation of multilayer graphene accompany by the loss of 2D sheet-like structure with reduced surface area, thereby lowers photocatalytic activity of synthesized composite. The graphene loaded in ZnO nanofibers were prepared by electrospinning with 0.5% of graphene showed excellent photocatalytic activity towards degradation of MB under UV irradiation. The better electron transport due to the superior electrical conductivity of graphene [42] and strong interaction between ZnO and defect sites of graphene were attributed to the improved photocatalytic activity of ZnO/graphene composites [41]. The higher adsorption of MB on graphene is through π-π conjugation between aromatic regions of graphene and their oxidation by the charge transfer from ZnO to graphene under irradiation of light. Another study proposed graphene-ZnO composite with the quasi-shell-core structure for photocatalytic degradation of rhodamine B (RhB) [43]. According to this study, the electric field established between core ZnO and shell graphene layer has been responsible to decrease charge transfer resistance to the photogenerated electrons and for improved photocatalytic dye degradation capability. The studies concluded that the optimal ratio of ZnO and graphene is necessary to achieve higher photocatalytic degradation efficiency. The graphdiyne-ZnO nanohybrids used for degradation of two azo dyes (MB and RhB) showed better results than bare ZnO [44]. The electron acceptor nature of the graphdiyne nanosheets was similar to that of graphene which was confirmed the photoluminescent analysis. In another study, photocatalytic degradation of reactive black 5 (RB5) under visible light was accomplished using solvent
exfoliated graphene/ZnO photocatalysts [45] with remarkable RB5 degradation of 97.0% with a rate constant of 0.0199 min\(^{-1}\) under a low-power 15 W energy saving light bulb for 3 h. The optimum ZnO content was 69.0 wt\%, which demonstrated a 10-fold photocatalytic degradation enhancement after graphene hybridization.

An organic pollutant, 4-nitrophenol was degraded using ZnO/graphene composites and the reduction of nitrobenzene to aniline with a yield of 97.8 % was achieved using graphene-ZnO-Au nanocomposites [46, 47]. The photo performance of the catalysts depends on the amount of graphene present in the composite. The contribution of graphene and Au towards the photocatalytic activity of ZnO was also studied where graphene acted as an inhibitor towards the electron/hole recombination, due to excellent electron transport properties, and the Au-assisted inefficient charge separation.

2.2 ZnO/reduced graphene oxide composites

Hierarchical ZnO and reduced graphene oxide synthesized via hydrothermal method have been used as photocatalyst for the photodegradation of azure B dye [48], and effect of reduced graphene oxide content on photodegradation of azure B dye was also investigated. It was suggested that the optimum content of reduced graphene oxide effectively improved the photocatalytic activity of the catalyst. In another case, degradation of RhB from water was investigated using similar photocatalyst [49]. The composite showed an excellent cycling performance for RhB removal up to 99% recovery over several cycles via simulated sunlight irradiation. The composite structure was further modified by coating ZnO nanospheres with reduced graphene oxide, which was established by electrostatic attraction between positively charged ZnO nanospheres and negatively charged reduced graphene oxide [49]. About 10% reduced graphene oxide exhibits a 5-fold enhancement of photoactivity compared to bare ZnO nanospheres which are attributed to the decreased recombination of the electron/hole pairs and the improved absorption capacity of ultraviolet light. The photocatalytic degradation efficiency was closely related to the fate and transfer of photogenerated electrons. The highly enhanced photoactivity could be attributed to the fact that sufficient interfacial contact between ZnO nanospheres and RGO nanosheets greatly improves the fate and transfer of photogenerated electron-hole pairs from ZnO.

In another study, Ag-Ag\(_2\)O-ZnO/graphene oxide nanocomposites were used as a photocatalyst to degrade acid blue 74 dye under visible light irradiation in synthetic wastewater containing the dye [50]. The results indicated that Ag-Ag\(_2\)O-ZnO/ graphene oxide nanocomposite has a higher photocatalytic activity (90% removal) compared to Ag-Ag\(_2\)O-ZnO (85% removal) and ZnO (75% removal). The high visible light photocatalytic performance of the Ag-Ag-Ag\(_2\)O-ZnO/ graphene oxide nanocomposite
was due to: (i) the surface plasmon resonance of Ag, (ii) minimized electron-hole pair recombination by enhanced interfacial electron transport due to the $p-n$ heterojunction between Ag$_2$O and ZnO (iii) the outstanding electron mobility of graphene which enhances the transfer of photogenerated electrons and holes from ZnO to the graphene, thus, minimizing the rate of recombination of the electron-hole pairs.

Table 1 Photocatalytic ZnO/graphene and ZnO/reduced graphene oxide-based composites used for the photodegradation of organic pollutants.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Organic pollutants</th>
<th>Photocatalytic efficiency w.r.t. time &amp; light source</th>
<th>Content</th>
<th>Concentration of photocatalyst &amp; organic pollutant</th>
<th>Synthesis method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/GCs</td>
<td>MB</td>
<td>100%, 100 min UV-visible light irradiation (xenonarc lamp 300 W)</td>
<td>600 mg Zn(O$_2$CCH$_3$)$_2$</td>
<td>50 mg/100 mL &amp; (1×10$^{-5}$ M)</td>
<td>Precipitation method</td>
<td>[41]</td>
</tr>
<tr>
<td>ZnO/GNFs</td>
<td>MB</td>
<td>80%, 4 h UV light irradiation</td>
<td>0.5 wt.% G</td>
<td>0.1 &amp; 0.1 wt.%</td>
<td>Electro-spinning method</td>
<td>[42]</td>
</tr>
<tr>
<td>ZnO/GQSCCs</td>
<td>RhB</td>
<td>100%, 20 min UV-visible light irradiation (xenon arc lamp 300 W)</td>
<td>10 mg G</td>
<td>0.1 g/100 mL &amp; 10 mg/L</td>
<td>Wet-chemical method</td>
<td>[43]</td>
</tr>
<tr>
<td>ZnO/GY Cs</td>
<td>MB&amp;RhB</td>
<td>68 &amp; 55% UV light irradiation</td>
<td>0.5% GY</td>
<td>5 mg/L &amp; 1×10$^{-3}$ M</td>
<td>Hydrothermal method</td>
<td>[44]</td>
</tr>
<tr>
<td>ZnO/SEGCs</td>
<td>RB-5</td>
<td>97.0%, 3 h visible light irradiation (energy saving light bulb 15 W)</td>
<td>69.0 wt% ZnO</td>
<td>30 mg &amp; 20 mg/L (50 ml)</td>
<td>Chemical deposition-calcination method</td>
<td>[45]</td>
</tr>
<tr>
<td>ZnO/GCs</td>
<td>NB</td>
<td>95% UV light irradiation</td>
<td>weight ratio, RGO:Zn(O$_2$CCH$_3$)$_2$ : 1.4 %</td>
<td>100 mg &amp; 6×10$^{-5}$ M/100 mL</td>
<td>Hydrothermal method</td>
<td>[46]</td>
</tr>
<tr>
<td>Au/ZnO/GCs</td>
<td>NB</td>
<td>97.8%, 140 min UV light</td>
<td>4 mg/mL &amp; 5 mM (50 mL)</td>
<td></td>
<td>Hydrothermal method</td>
<td>[47]</td>
</tr>
<tr>
<td>Material</td>
<td>Method</td>
<td>Initial Concentration</td>
<td>Irradiation Conditions</td>
<td>Product</td>
<td>References</td>
<td></td>
</tr>
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<td>-------------------</td>
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<td></td>
</tr>
<tr>
<td>ZnOHC/ RGOCs</td>
<td>Hydrothermal method</td>
<td>10% RGO</td>
<td>UV light irradiation (mercury vapour lamp 125W)</td>
<td>AB</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>ZnONS/ RGOCs</td>
<td>Hydrothermal reduction</td>
<td>10% RGO</td>
<td>UV light irradiation (xenon arc lamp 300 W)</td>
<td>RhB</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>Ag-Ag2O/ ZnO/ GCS</td>
<td>Co-precipitation method</td>
<td>--</td>
<td>UV light irradiation (ozone free xenon lamp 150 W)</td>
<td>AB-74</td>
<td>[50]</td>
<td></td>
</tr>
<tr>
<td>ZnO/ GCS</td>
<td>Solvothermal method</td>
<td>--</td>
<td>UV light irradiation (xenon arc lamp 150 W)</td>
<td>MB</td>
<td>[51]</td>
<td></td>
</tr>
<tr>
<td>ZnO/ RGOCs</td>
<td>Photoreduction method</td>
<td>--</td>
<td>UV light irradiation (metal halogen lamp)</td>
<td>RhB</td>
<td>[52]</td>
<td></td>
</tr>
<tr>
<td>ZnO/ RGOCs</td>
<td>Chemical method</td>
<td>--</td>
<td>UV-visible light irradiation</td>
<td>CV</td>
<td>[53]</td>
<td></td>
</tr>
<tr>
<td>ZnOQD/ GCs</td>
<td>Chemical method</td>
<td>5% G</td>
<td>UV-visible light irradiation</td>
<td>MO</td>
<td>[54]</td>
<td></td>
</tr>
</tbody>
</table>
### 3. Photocatalytic ZnO/carbon nanotube based semiconductor composites

Carbon nanotubes (CNT), another class in the carbon family has shown their recognition and promising aspects in the photocatalysis application because of their good catalytic activity on verge of their large surface area, chemical stability, high mechanical strength and extraordinary electronic properties [60]. The mesoporous character of CNT provides channels or supports for diffusion of reactive species for the photocatalytic activity [61]. In recent years, a lot of publications have been reported on CNT-ZnO composites for photocatalytic degradation of various organic pollutants. ZnO/CNTs hierarchical microsphere composites synthesized via a facile chemical deposition route were used for...
photodegradation of methylene blue [62]. ZnO/CNTs hierarchical microsphere composites with 1.1 wt% CNTs showed the optimized photocatalytic activity and decrease for higher concentrations of CNT. The two major reasons were proposed for better photocatalysis; (1) light harvesting competition between CNTs and ZnO appears with an increase of CNTs amount (2) the excessive CNTs can act as a kind of recombination center instead of providing an electron pathway.

In another study, 1-D ZnO nanowire/multi-walled CNT composites synthesized by one-step hydrothermal method were used for photocatalytic degradation performances on methylene blue and rhodamine 6 Gunder UV irradiation. These materials showed 3 times higher photocatalytic efficiency than that of pure ZnO nanowires. Furthermore, when ZnO nanoparticles decorated on multi-walled CNT were used for photocatalytic degradation of RhB and methyl orange (MO), showed better photocatalytic activity than bare ZnO [63, 64]. The enhanced photocatalytic activity was attributed to the fast transfer of photogenerated electrons from ZnO to CNTs, leading to low recombination rate of photoinduced electron-hole pairs.

Recently, few publications have appeared on metal-doped ZnO/ multi-walled carbon nanotubes (MWCNTs) nanocomposites. Ahmad et al., [63] successfully synthesized Cu-doped ZnO nanoparticles embedded on MWCNTs via non-toxic sol method which exhibited extended light absorption in visible light region and possessed better charge separation capability, respectively as compared to Cu-doped ZnO, pure ZnO, and ZnO/CNTs composite. The photocatalytic activity was tested by degradation of MO dye under visible light irradiation. In another study, multi-walled CNT/ metal-doped ZnO nanohybrid materials (metal: Mn, Mg, and Co) were developed, where, the MWNT/Mg-doped ZnO hybrids showed the high photocatalytic ability for MO, in which the degraded rate for MO reached 100% in 60 min. It was concluded that the enhancement in photocatalytic activity was because of the superb electrical property of MWNTs and the formation of many defects in the ZnO crystals by Mg-doping. The synergic effect between MWCNT and ZnO hinders the recombination of electron-hole pairs, whereas the doped Mg replaces Zn site or join interstitial site in the ZnO lattice and generates intermediate energy gap between valence band and conduction band of ZnO that likely to promote the absorption of photons by generating the large number of electron-hole pairs, thereby improved overall photoactivity [65].
<table>
<thead>
<tr>
<th>Photo-catalyst</th>
<th>Organic pollutants</th>
<th>Photocatalytic efficiency w.r.t. time &amp; light source</th>
<th>Content</th>
<th>Concentration of photocatalyst &amp; organic pollutant</th>
<th>Synthesis method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/CNTs HMSCs</td>
<td>MB</td>
<td>92.3%, 60 min UV-visible light irradiation (mercury lamp 500 W) &amp; (xenon lamp 500 W)</td>
<td>1.1 wt% CNTs</td>
<td>0.17 g/L &amp; 30 mg/L</td>
<td>Chemical deposition method</td>
<td>[62]</td>
</tr>
<tr>
<td>ZnO/MC NTs</td>
<td>Rh B</td>
<td>~61%, 30 min sunlight irradiation (ultrasound natural and low power)</td>
<td>20 wt.% MCNTs</td>
<td>30 mg/ 30 mL &amp; 20 mg/L</td>
<td>Sol method</td>
<td>[63]</td>
</tr>
<tr>
<td>ZnO/MC NTs</td>
<td>MO</td>
<td>94.12%, 30 min UV light irradiation (high pressure mercury lamp 150 W)</td>
<td>--</td>
<td>0.5% wt &amp; 10 mg/L (70 mL)</td>
<td>--</td>
<td>[64]</td>
</tr>
<tr>
<td>Mn, Mg, Co/ZnO/MCNTs NH</td>
<td>MO</td>
<td>100 %, 60 min UV light irradiation (high pressure osram ultra-vitalux lamp 100 W)</td>
<td>--</td>
<td>0.25 g/L &amp; 20 mg/L</td>
<td>Co-deposition method</td>
<td>[65]</td>
</tr>
<tr>
<td>ZnONW/ MCNTs Cs</td>
<td>MB &amp; Rh6G</td>
<td>100%, 30 min UV light irradiation</td>
<td>10 wt.% MCNTs</td>
<td>10 mg &amp; 10 mg/L (50 mL)</td>
<td>Hydrothermal method</td>
<td>[66]</td>
</tr>
<tr>
<td>ZnO/MC NTsCs</td>
<td>Rh B</td>
<td>80%, 60 min UV light irradiation (high-pressure mercury lamp 300 W)</td>
<td>--</td>
<td>50 mg &amp; 1.0x10^-5 mol/L (50 mL)</td>
<td>Ammonia method</td>
<td>[67]</td>
</tr>
<tr>
<td>Cu/ZnO/ MCNTs</td>
<td>MO</td>
<td>120 min visible light irradiation (metal halogen lamp 400 W)</td>
<td>Cu: 3 wt.% CNTs: 10 wt.%</td>
<td>30 mg &amp; 20 ppm (30 mL)</td>
<td>Sol method</td>
<td>[68]</td>
</tr>
</tbody>
</table>

Rhodamine-B=RhB, Rhodamine-6G=Rh6G, Methyl orange=MO, MB=Methylene blue, Cs=Composites or nanocomposites, Carbon nanotubes=CNTs, Multiwalled carbon nanotubes=MCNTs, Nanohybrid=NH, Hierarchical microsphere=HMS, Nanowires=NW.
4. Photocatalytic ZnO-silica, alumina, zeolite and clay based composites

A number of attempts have also been made to resist the recombination of electron-hole pair counts which is a negative process and responsible for the lower photocatalytic efficiency. Mesoporous materials (zeolite, clay, alumina and silica etc.) and their modified forms used as support for semiconductors and coupling of two or more semiconductors are the well-known strategies that have been used to decrease the recombination process [25-28]. These mesoporous materials are eco-friendly in nature, thermally stable and cost-effective. For example, zeolites with uniform nanoscale pore size, superior cation exchange capacity, high adsorption capacity and extensive surface area have been applied in the designing of effective photocatalytic systems [26,69,70]. Moreover, they have the capacity to extending self life and reusability of the photocatalysts. Due to high adsorption capacity, they carry molecules of organic pollutants near the catalyst surface, where hydroxyl and superoxide radicals generated, and for this reason, photodegradation efficiency tends to increase [71].

Moreover, porous nature is significant in terms of obtaining less agglomerated semiconductor material, thereby helping to improve the surface area or active sites required to enhance photocatalytic degradation of organic pollutants. On the other hand, zeolites tend to produce a strong electric field, effectively distribute photogenerated electrons in the zeolitic network are supportive for reducing electron-hole pair recombination [72].

ZnO/mordenite zeolite nanoparticles were prepared via precipitation process using ultrasonic irradiation and hydrothermal methods [73]. Mordenite, a zeolite, is a mineral with an ideal composition (Na₈) [Al₈Si₄₀O₉₆]·nH₂O. Due to high thermal and catalytic activity, mordenite actively performs photocatalytic oxidation of AB92 under UV irradiation. The photocatalytic efficiencies of ZnO/mordenite with ZnO, ZnO/activated carbon and ZnO/Al₂O₃ nanocomposites were compared and results revealed that the insertion of ZnO on different supports results in the decrease of the particle size, increase in the surface area and reduction in electron-hole recombination rate in comparison to pure ZnO. Photocatalytic activity of catalysts was investigated by degradation of AB92 in water. Mass ratios 0.25:1 of ZnO and mordenite showed the highest photocatalytic activity [73].

The photodegradation of trichloroethylene (chlorinated hydrocarbons) was performed using heterogeneous nano-ZnO/laponite composites. A direct comparison of the photocatalytic degradation rates of trichloroethylene between TiO₂ powder and ZnO/laponite composites balls suggested ZnO/laponite composites as a valid alternative to suspended TiO₂ powder for mineralizing trichloroethylene [74]. In another study,
Metaldehyde (molluscicide) was removed through photocatalytic reactions using nano-sized ZnO/laponite composite. Statistical results showed that linear effects of time, quadratic/linear effects of nano-ZnO/laponite composites mass and the interaction of pH and nano-ZnO/laponite composites mass proved to be the most significant variables for degrading metaldehyde [75].

The degradation of humic acid was investigated using nano-sized ZnO/laponite composite. The photocatalytic degradation of humic acid was found to depend on pH and catalyst concentration. Experimental results showed that the photocatalytic efficiency was higher in an acidic medium which was ascribed to the protonation of functional groups at low pH and the creation of the less negatively charged humic acid reduces the intermolecular repulsion between the humic acid and the catalyst surfaces. Humic acid decomposition increased as the dose of catalyst increased up to an optimum value of 20 mg/L. Moreover, the effect of H2O2 was also studied through homogeneous and heterogeneous photocatalysis, in which heterogeneous photocatalysis showed better removal because of the combined effects of both the catalyst and added H2O2 [76].

A remarkable performance regarding photodecolorization of methylene blue (97.6%), malachite green (89.5%), congo red (85.6%), and MO (80.1%) by an electrogenerated ZrO2 and ZnO supported aluminosilicate protonated Y zeolite prepared by the facile synthesis has been reported for the first time. In addition, the catalyst remained stable even after five cycling runs and the leaching test showed negligible leaching effects [77].

Reactorite is a kind of layered silicate, the structure and characteristics are much similar to those of montmorillonite. It is referred to as an interstratified clay mineral which can adsorb organic substance both on its external surfaces and within its interlaminar spaces by interaction or substitution. For these reasons, many efforts have been focused on the use of reactorite-based materials to adsorb or catalyze organic pollutants. The nanometer ZnO/reactorite composites prepared by hydrothermal intercalation method have been subjected to examine their photocatalytic activity for photocatalytic decolorization of methylene blue under simulated sunlight irradiation. The suggested catalyst is stable low cost and reusable which requires sunlight only and does not need the addition of H2O2 [78].

The photocatalytic activity of ZnO/CuO supported on clinoptilolite nanoparticles regarding degradation of benzophenone has been reported. Experimental results illustrated that both supporting and coupling of two semiconductors played important role in enhancing their photocatalytic activity with respect to monocomponent catalysts and unsupported one. Also, the types of semiconductors in the coupled system affect the
photocatalytic activity; therefore the supported ZnO-CuO had better activity than the ZnS-CuS/clinoptilolite nanoparticles [79].

Table 3  Silica, alumina, zeolite, and clay based ZnO composites used for the photodegradation of organic pollutants.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Organic Pollutants</th>
<th>Photocatalytic Efficiency w.r.t time &amp; light source</th>
<th>Content</th>
<th>Concentration of photocatalyst &amp; organic pollutant</th>
<th>Synthesis method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/MDT</td>
<td>AB-92</td>
<td>88%, 2 h UV light irradiation (pyrex reactor equipped UV lamp)</td>
<td>Mass ratio, 0.25:1 ZnO:MDT</td>
<td>100 ppm &amp; 20 ppm</td>
<td>Precipitation method &amp; hydrothermal method</td>
<td>[73]</td>
</tr>
<tr>
<td>ZnO/LPTCs</td>
<td>TCE</td>
<td>100%, 60 min UV light irradiation (photocatalytic reactor, PVC plastic, 4 UV-C lamps 8 W)</td>
<td>--</td>
<td>20 g/L &amp; 10 mg/L</td>
<td>--</td>
<td>[74]</td>
</tr>
<tr>
<td>ZnO/LPTCs</td>
<td>MA</td>
<td>UV light irradiation (photocatalytic reactor, PVC plastic, 4 UV-C lamps 8 W)</td>
<td>--</td>
<td>28 g &amp; 278 μg/dm³</td>
<td>--</td>
<td>[75]</td>
</tr>
<tr>
<td>ZnO/ZrO/ASPY</td>
<td>MB</td>
<td>97.6%, 1 h visible light irradiation</td>
<td>1 wt.% ZrO₂–1 wt.% ZnO/ASPY</td>
<td>0.12 g &amp; 10 mg/L (200 mL)</td>
<td>Electrochemical method</td>
<td>[77]</td>
</tr>
<tr>
<td>ZnO/RRTC</td>
<td>MB</td>
<td>99%, 2 h simulated solar light</td>
<td>0.9 g/L &amp; 15 mg/L</td>
<td>Hydrothermal intercalation method</td>
<td>[78]</td>
<td></td>
</tr>
<tr>
<td>ZnO/CuO/CPTCs</td>
<td>BP</td>
<td>UV light irradiation (medium-pressure mercury-vapor lamp 35 W)</td>
<td>0.12 g/L &amp; 30 mg/L</td>
<td>Calcination method</td>
<td>[79]</td>
<td></td>
</tr>
</tbody>
</table>
5. Photocatalytic ZnO-luminescent agent based composites

In order to overcome the limited availability of ultraviolet light which is only 4% of solar light, researchers have doped upconversion luminescence agents such as Er$^{3+}$:Y$_3$Al$_5$O$_{12}$, Er$^{3+}$:YAlO$_3$, NaYF$_4$:Yb, NaYF$_4$:Tm, YF$_3$:Yb$^{3+}$ and YF$_3$:Tm$^{3+}$ etc. with semiconductors to enhance their photocatalytic efficiency [84-88]. These materials have the capability to transforming visible light and near-infrared (NIR) light to the ultraviolet light. Under solar light irradiation, the upconversion luminescence process can take place readily for the continuous irradiation under desired wavelengths. In that case, the luminescence agents can create full use of solar energy and supply the rich ultraviolet light for satisfying the actual requirement of semiconductor photocatalyst [88].

Comparative studies of photocatalytic activities were performed between Er$^{3+}$:Y$_3$Al$_5$O$_{12}$/TiO$_2$-ZnO and Er$^{3+}$:Y$_3$Al$_5$O$_{12}$/TiO$_2$ under solar light irradiation. Results revealed that Er$^{3+}$:Y$_3$Al$_5$O$_{12}$/TiO$_2$-ZnO have superior photocatalytic activities, the degree of degradation of azo fuchsine dyes was 96.65% within 60 min after irradiation [89].
NaYF$_4$:Yb$^{3+}$ and Tm$^{3+}$/ZnO composites were prepared via high-temperature thermolysis method and their NIR photocatalytic behavior was studied for the degradation of RhB. β-NaYF$_4$:Yb$^{3+}$, Tm$^{3+}$ materials as luminescence agents have potential to upconversion of NIR-to-UV which provided UV light to the ZnO semiconductor. Comparative studies of energy transfer in the composites and the mixtures of β-NaYF$_4$:Yb$^{3+}$, β-NaYF$_4$:Tm$^{3+}$ prepared with ZnO revealed that the β-NaYF$_4$:Yb$^{3+}$, Tm$^{3+}$/ZnO composites have higher photocatalytic activity than the mixture of β-NaYF$_4$:Yb$^{3+}$, Tm$^{3+}$ and ZnO. The activation of ZnO by energy transfer from upconverting β-NaYF$_4$:Yb$^{3+}$, Tm$^{3+}$ to ZnO was attributed to the NIR photocatalysis. Moreover, the energy transfer processes determine the overall photoactivity and were found different from that of the physical mixture of β-NaYF$_4$:Yb$^{3+}$, Tm$^{3+}$ and ZnO nanocomposites [90].

Interestingly, an attempt was made to utilize ultrasonic source conversion to UV light by using Er$^{3+}$:YAlO$_3$ having the capability to absorb the visible light from the ultrasonic source. The sonocatalytic activity of Er$^{3+}$:YAlO$_3$/TiO$_2$-ZnO composite was investigated to degrade acid red B dye by means of transfer of electron and hole between conduction and valence bands of ZnO and TiO$_2$, respectively, which counts slow electron/hole recombination and increases the sonocatalytic activity of Er$^{3+}$:YAlO$_3$/TiO$_2$-ZnO composite [91]. Another efficient material systems that can convert the visible solar light into ultraviolet light are Er$^{3+}$:YAlO$_3$ coated Co and Fe-doped TiO$_2$-ZnO films prepared via sol-gel process have been tested for degradation of azo fuchsine. Moreover, the photocatalytic efficiency of Er$^{3+}$:YAlO$_3$/Co-doped TiO$_2$-ZnO-doped was superior to that of Er$^{3+}$:YAlO$_3$/Fe-doped TiO$_2$-ZnO [92].
### Table 4 ZnO/ Luminescent based composites used for the photodegradation of organic pollutants.

<table>
<thead>
<tr>
<th>Photo-catalyst</th>
<th>Organic pollutants</th>
<th>Photocatalytic efficiency w.r.t time &amp; light source</th>
<th>Content</th>
<th>Concentration of photocatalyst &amp; organic pollutant</th>
<th>Synthesis method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;:Y&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;/TiO&lt;sub&gt;2&lt;/sub&gt;/ZnOCs</td>
<td>AF</td>
<td>96.65 %, 60 min solar light irradiation</td>
<td>10 wt % Er&lt;sup&gt;3+&lt;/sup&gt;:Y&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;</td>
<td>1.0 g/L &amp; 10 mg/L (100 mL)</td>
<td>Nitrates-citrate acid &amp; heat-treated method</td>
<td>[89]</td>
</tr>
<tr>
<td>β- NaYF&lt;sub&gt;4&lt;/sub&gt;:Yb&lt;sup&gt;3+&lt;/sup&gt;,Tm&lt;sup&gt;3+&lt;/sup&gt;/ZnOCs</td>
<td>RhB</td>
<td>65%, 30 min Near infrared irradiation</td>
<td>β- NaYF&lt;sub&gt;4&lt;/sub&gt;:20 % Yb,Tm:0.5%</td>
<td>0.5 mg &amp; 20 mg/L (0.5 mL)</td>
<td>High temperature thermolysis method</td>
<td>[90]</td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;:YAlO&lt;sub&gt;3&lt;/sub&gt;/TiO&lt;sub&gt;2&lt;/sub&gt;/ZnOCs</td>
<td>ARB</td>
<td>76.54%, 150 min ultrasonic irradiation</td>
<td>--</td>
<td>1.0 g/L &amp; 10 mg/L (100 mL)</td>
<td>Sol-gel &amp; auto-combustion method</td>
<td>[91]</td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;:YAlO&lt;sub&gt;3&lt;/sub&gt;/Fe,Co/TiO&lt;sub&gt;2&lt;/sub&gt;/ZnOCs</td>
<td>AF</td>
<td>93.5 &amp; 95.53 %, 60 min visible light irradiation (Xenon lamp 300W)</td>
<td>15 wt.% Er&lt;sup&gt;3+&lt;/sup&gt;:YAlO&lt;sub&gt;3&lt;/sub&gt;/Fe &amp; Co TiO&lt;sub&gt;2&lt;/sub&gt;/ZnO</td>
<td>10 mg/L &amp; 1000 mg/L (100 mL)</td>
<td>Nitrates-citric acid method</td>
<td>[92]</td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;:Y&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;/ZnOCs</td>
<td>AF</td>
<td>84.27%, 120 min solar light irradiation</td>
<td>12 wt % Er&lt;sup&gt;3+&lt;/sup&gt;:Y&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;</td>
<td>1.0 g/L &amp; 10 mg/L</td>
<td>Nitrates-citric acid method</td>
<td>[93]</td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;:YAlO&lt;sub&gt;3&lt;/sub&gt;/Co,Fe/ZnOCs</td>
<td>AF</td>
<td>89.8 and 99.2%, 80 min solar light irradiation</td>
<td>15.0 &amp; 25.0 wt.% Er&lt;sup&gt;3+&lt;/sup&gt;:YAlO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1000 mg/L &amp; 10 mg/L</td>
<td>Sol-gel method</td>
<td>[94]</td>
</tr>
</tbody>
</table>

Azo fuchsine=AF, Acid red-B=ARB, Rhodamine-B=RhB, Cs=Composites or nanocomposites.
6. Photocatalytic ZnO-transition metals, rare earth metals, and non-metals based composites

6.1 Transition metals-doped ZnO composites

Doping of transition metals including noble metals (such as, Mn, Fe, Cu, Cd, Pt, Hf, Ag and Au) in semiconductors is an effective approach to enhance the visible light absorption by generating energy states within the bandgap, which act as intermediate steps for electrons in their transitions between the valence and conduction bands due to photoexcitation [95-102]. The capability of a metal to trap photogenerated electrons within semiconductor during photochemical reactions allows the holes to interact with radical or species bound to the surface and promotes degradation of organic pollutants [103]. Photoactive surfaces such as oxygen vacancies, crystal interfaces and higher light scattering of metal are responsible for the enhancement of the photocatalytic activity of semiconductors [104,105]. In addition, the metal-doped semiconductors experience local electrical fields that enhance the surface plasmon activity, indeed is significant for photocatalytic applications [106].

Photocatalytic activities of the Ag-doped ZnO nanoparticles and undoped ZnO prepared through precipitation method were studied and compared for degradation of MO. The results revealed that Ag-doped ZnO nanoparticles containing 1 and 8% Ag content showed enhanced photocatalytic activity than the undoped ZnO nanoparticles and the time for the complete decomposition decreased to only 60 min [107]. Multivalent Cu-doped ZnO nanoparticles synthesized by green-chemical approaches with a yield of ∼100% showed superior photocatalytic activity for degradation of indigo carmine, orange G, rhodamine 6G and MB [108]. On the other hand, 94% of acid red 1 dye degraded (at optimized conditions) using Fe-doped ZnO as a photocatalyst which was prepared by solution combustion synthesis method. Various parameters such as the amount of Fe-doped, calcination temperature, calcination time, pH of the dye solution, catalyst dose, hydrogen peroxide concentration, reaction temperature and initial concentration of the dye solution were optimized for obtaining superior photocatalytic activity [109]. In another study, the Au-ZnO nanopyramids with controlled morphologies exhibited admirable photocatalytic activity for the photodegradation of RhB which was associated with the exposed crystal facets, crystallinity, and the creation of hybrid nanostructure. The most exposed polar {001} facts better crystallinity as well as the formation of a hybrid structure with the well-defined interface was ascribed for better photocatalytic activities [110].
<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Organic pollutants</th>
<th>Photocatalytic efficiency w.r.t time &amp; light source</th>
<th>Content</th>
<th>Concentration of photocatalyst &amp; organic pollutant</th>
<th>Synthesis method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/ZnOCs MB</td>
<td>MB</td>
<td>99%, 30 min UV-visible light irradiation (UV lamp &amp; tungsten lamp 60 W)</td>
<td>--</td>
<td>50 mg/16 mL &amp; 5x10⁻⁵ M (4.0 mL)</td>
<td>Surfactant mediated method</td>
<td>[102]</td>
</tr>
<tr>
<td>Ag/ZnOCs MO</td>
<td>MO</td>
<td>100%, 60 min UV light irradiation (UV lamp 100 W)</td>
<td>1 and 8 % Ag</td>
<td>50 mg &amp; 50 mg/50 mL</td>
<td>Precipitation method</td>
<td>[107]</td>
</tr>
<tr>
<td>Cu/ZnOCs IC, O-G, RbB-6G &amp; MB</td>
<td>UV-visible light irradiation (high-pressure mercury vapor lamp 125 W &amp; metal halide lamp 400 W)</td>
<td>1.5 M % Cu:Zn O</td>
<td>0.6 g/L &amp; 7.8x10⁻² M &amp; 5.3x10⁻² M &amp; 5.2x10⁻² &amp; 5.5x10⁻² mM</td>
<td>Green-chemical method</td>
<td>[108]</td>
<td></td>
</tr>
<tr>
<td>Fe/ZnO Cs AR-1</td>
<td>UV light irradiation (UV bulb 125 W)</td>
<td>2.5 wt.% Fe/ZnO</td>
<td>1.25 g/L &amp; 50 mg/L (250 mL)</td>
<td>Solution combustion synthesis method</td>
<td>[109]</td>
<td></td>
</tr>
<tr>
<td>Au/ZnOCs RhB</td>
<td>~100%, 30 min UV light irradiation (UV lamp 175 W)</td>
<td>---</td>
<td>10 mg &amp; 1 mg/L (100 mL)</td>
<td>--</td>
<td>[110]</td>
<td></td>
</tr>
<tr>
<td>Mn/ZnOCs O-II</td>
<td>100%, 210 min Solar light irradiation (Sylvania LuxLine FHO T5 neon tubes)</td>
<td>3%</td>
<td>60 mg &amp; 10 mg/L (30 mL)</td>
<td>Solvo-thermal method</td>
<td>[111]</td>
<td></td>
</tr>
<tr>
<td>Fe/ZnO Cs MO&amp;MB</td>
<td>UV light irradiation (Two UV lamps 20 W)</td>
<td>Fe conc. 21 %</td>
<td>0.6 g/L &amp; 20 mg/100 mL</td>
<td>co-precipitation method</td>
<td>[112]</td>
<td></td>
</tr>
<tr>
<td>Fe/ZnO Cs RhB</td>
<td>89%, 180 min UV-visible light (high-pressure mercury lamp 500 W &amp; Xenon lamp 500 W)</td>
<td>2% Fe</td>
<td>20 mg &amp; 10 mg/L (20 mL)</td>
<td>Hydro-thermal process</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>Cd/ZnOCs MB&amp;M</td>
<td>65 &amp; 45%, 300 min O</td>
<td>3%</td>
<td>(0.5 g/L) &amp; 10⁻⁵ M (100 mL)</td>
<td>Sono-chemical method</td>
<td>[114]</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Dye</td>
<td>Degradation Efficiency</td>
<td>Reaction Conditions</td>
<td>Concentration</td>
<td>Other Conditions</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------</td>
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<td>------------------------</td>
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<td>---------------</td>
<td>-----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Ag/Zn OCs</td>
<td>MO, MB&amp;4-NP</td>
<td>~100 %, 5, 4 &amp; 6 h</td>
<td>Visible light</td>
<td>2 mg &amp; 10 mg/L (20 mL), 10 mg/L (20 mL), 5 mg/L (20 mL)</td>
<td>--</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 mg &amp; 10 mg/L (20 mL)</td>
<td></td>
</tr>
<tr>
<td>Ag/Zn O/CdO Cs</td>
<td>AB-1 &amp; AV-7</td>
<td>~100 %, 45 &amp; 50 min</td>
<td>Sunlight irradiation</td>
<td>3×10^{-4} M, 5×10^{-4} M &amp; 3 g/L</td>
<td>Co-precipitation method</td>
<td>[116]</td>
</tr>
<tr>
<td>Pt/ZnO Cs</td>
<td>AO-II</td>
<td>86%, 5 h</td>
<td>UV light irradiation (UV lamp)</td>
<td>0.05 g/100 mL &amp; 0.020 g/L</td>
<td>Pt/ZnO</td>
<td>Solvo-thermal method</td>
</tr>
<tr>
<td>Hf/ZnO Cs</td>
<td>MB</td>
<td>85%, 120 min</td>
<td>Sunlight irradiation</td>
<td>2M %</td>
<td>Hf/ZnO</td>
<td>Sol-gel method</td>
</tr>
</tbody>
</table>

Acid black-1=AB-1, Acid violet 7=AV-7, Acid orange II=AO-II, 4-Nitrophenol=4-NP, Acid red 1=AR-1, Indigo carmine=IC, Orange-G=O-G, Orange-II=O-II, Rhodamine-B=RhB, Rhodamine-6G=RhB-6G, Cs=Composites or nanocomposites.

### 6.2 Rare earth metals-doped ZnO composites

Many researchers have proposed that rare earth metals are efficient dopant for ZnO nanoparticles for photocatalytic activity because of their luminescence properties delay time, and band edge emission with respect to particle size variation. The rare earth metals (Sm, Gd, Dy)-doped ZnO nanoparticles and their photocatalytic degradation efficiencies for acid blue 92, acid orange 7 and acid red 17 have been investigated [118-120]. In another study, La-doped ZnO nanorods synthesized by using different La contents via a microwave-assisted method showed that degradation efficiency of metasystox (pesticide) over La-doped ZnO increases up to 0.5 mol% doping then decreases for higher doping levels [121]. Whereas, Nd-doped ZnO showed highest photocatalytic activity for degradation of phenol with the optimal Nd content was 2.0% under visible light irradiation [122].
Table 6  ZnO/rare earth metal-doped composites used for the photodegradation of organic pollutants.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Organic pollutants</th>
<th>Photocatalytic Efficiency w.r.t time &amp; light source</th>
<th>Content</th>
<th>Concentration of photocatalyst &amp; organic pollutant</th>
<th>Synthesis method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm/ZnO-Cs</td>
<td>AB-92</td>
<td>90.10%, 150 min ultrasonic irradiation</td>
<td>6% Sm</td>
<td>1 g/L &amp; 10 mg/L</td>
<td>Sonochemical method</td>
<td>[118]</td>
</tr>
<tr>
<td>Gd/ZnO-Cs</td>
<td>AO-7</td>
<td>90%, 90 min ultrasonic irradiation</td>
<td>5% Gd</td>
<td>100 mg &amp; 5 mg/L (100 mL)</td>
<td>Sonochemical method</td>
<td>[119]</td>
</tr>
<tr>
<td>Dy/ZnO-Cs</td>
<td>AR-17</td>
<td>100%, 180 min ultrasonic irradiation</td>
<td>3% Dy</td>
<td>1 g/L &amp; 5 mg/L</td>
<td>Sonochemical method</td>
<td>[120]</td>
</tr>
<tr>
<td>La/ZnO-Cs</td>
<td>M</td>
<td>90 %, 150 min UV and sunlight irradiation (high pressure mercury lamp)</td>
<td>0.5 mol % La</td>
<td>100 mg &amp; 1.4×10^{-3} M (100 mL)</td>
<td>Microwave assisted method</td>
<td>[121]</td>
</tr>
<tr>
<td>Nd/ZnO-Cs</td>
<td>P</td>
<td>visible light irradiation</td>
<td>2.0%</td>
<td>100 mg &amp; 20 mg/L (100 mL)</td>
<td>Chemical precipitation method</td>
<td>[122]</td>
</tr>
<tr>
<td>Ce/ZnO-Cs</td>
<td>MO</td>
<td>100%, 80 min UV-visible light irradiation</td>
<td>0.2 M</td>
<td>10 ppm MO</td>
<td>Hydrothermal process</td>
<td>[123]</td>
</tr>
</tbody>
</table>

Acid blue-92=AB-92, Acid orange-7=AO-7, Acid red-17=AR-17, Methyl orange=MO, Metasystox=M, Phenol=P, Cs=Composites or nanocomposites.

6.3 Non-metals-doped ZnO composites

Doping with nonmetallic elements such as C, S, and N has also been considered to reduce the band gap of semiconductors [124]. The photocatalytic activities of C-ZnO nanocrystals obtained with different morphologies and carbon contents were evaluated for degradation of methylene blue under visible light irradiation [125]. Results showed that incorporation of carbon decreases the energy band gap of ZnO, improves the separation efficiency of its electron-hole pairs, and considerably enhances the visible light photocatalytic activity. On the other hand, nitrogen has been widely used as a dopant to modify the electronic structures of oxide semiconductors due to its comparable size to oxygen and small formation energy required for the substitution of O. Therefore, N doping has been applied to ZnO with the expectation of improving the light absorption property of ZnO in the visible region. In another study, N-doped mesoporous ZnO
nanospheres obtained via solvothermal method were found to exhibit higher photocatalytic activity for degradation of RhB compared to pure ZnO nanoparticles [126].

Recently, coupling of nonmetal-doped semiconductor and soft polymeric semiconductor (graphitic carbon nitride g-C3N4) materials and the generation of several kinds of g-C3N4 composite photocatalysts (semiconductor/g-C3N4 coupled with graphene oxide or CNTs etc.) have attracted a great deal of scientific interest in photocatalytic water splitting [127,128] and degradation of environmental pollutants under visible light irradiation due to their suitable band gap to absorb the visible-light and unique properties. This soft polymeric semiconductor can be easily coated on the surface of other materials in comparison to inorganic π-conjugative materials such as CNTs and graphenes [129]. Moreover, it has a well crystallized lamellar structure that assists improved charge transfer than organic π-conjugative materials. Later N-doped ZnO/g-C3N4 hybrid core-shell nanoplates were utilized for RhB degradation. The direct Z-scheme mechanism is proposed for the prolonged lifetime of charge carrier transfer at the interface of N-doped ZnO/g-C3N4 by trapping photoinduced electrons and holes under visible-light irradiation [130].

7. Conclusion

This chapter summarizes the potential aspects of ZnO based composites for degradation of various organic pollutants. The potential feature of different kinds of ZnO composites including carbon-based composites (graphene, reduced graphene oxides, CNT and MWCNT), mesoporous materials (silica, alumina, zeolite, and clay), luminescent agents, transition metals and rare earth metals and non-metals have been discussed thoroughly. It has been revealed that the combination of various materials with ZnO semiconductor improved overall photocatalytic efficiency of ZnO based composites by means of various aspects: bandgap modification, enhance charge transfer, reduction in the recombination of photogenerated electrons and holes, efficient use of sunlight and availability of active sites for the adsorption of organic pollutants by providing a high surface area.

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Chapter 10

**TiO₂ Based Nanocomposite for Photocatalytic Degradation of Organic Pollutants**

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**Abstract**

Organic contaminants such as synthetic dyes, phenols, pesticides, fertilizers, herbicides, and surfactants, etc. present in aqueous streams are of foremost concern with respect to the health of the general public. Titania based heterogeneous photocatalytic oxidation has received the attention of researchers for many years as an alternative method for purification of both air and water systems. The major issues of immense importance from industrial viewpoint have been the recovery and recycling of the photocatalyst. The present chapter discusses the utility of TiO₂ based nanocomposite materials in photocatalytic degradation of organic pollutants.

**Keywords**

Nanocomposites, Titania, Photocatalysis, Organic Pollutants, Wastewater

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1. Introduction

Organic contaminants such as synthetic dyes, phenols, pesticides, fertilizers, herbicides, and surfactants, etc. found in wastewater are of major concern with respect to the health of general public. A number of physicochemical methods, based on precipitation, coagulation, adsorption and membrane filtration, have been applied for the removal of the organic impurities from the waste streams, however, each process has its own limitations. Chemical oxidation technologies seem to have the most potential for the future. Therefore, the elimination of these pollutants from the environment has become a prime concern for researchers.

**Synthetic dyes:** Synthetic dyes are frequently used in various sections of the textile industry, leather tanning industry, paper production industry, food technology and in agricultural research, light-harvesting arrays, photoelectrochemical cells and also in hair colorings. Discharges from various industries usually contain considerable quantities of synthetic organic dyes and due to their large-scale production and extensive application, synthetic dyes can cause considerable non-aesthetic pollution and serious health-risk factors. Dyes contain chromophores such as -C=C-, -C=N-, -C=O, -N=N-, -NO$_2$, quinoid rings, and the auxochromes are -NH$_3$, -COOH, -SO$_3$H and -OH groups which cause or intensify the color.

Dyes are classified on the basis of the chemical structure or according to the methods of their application onto the substrate. Based on chemical structures, the dyes are classified into 20-30 different classes such as the azo, anthraquinone, sulfur, indigoid,
triphenylmethyl (trityl), and phthalocyanine derivatives. Azo dyes include the largest class of organic colorants recorded in the Colour Index (60-70% of the total) and constitute the majority of the dyes used by the textile-processing industries. Anthraquinone dyes are the second largest class (~15%), followed by triarylmethanes (~3%) and phthalocyanines (~2%) of the entries in the Colour Index.

**Pesticides:** Pesticides are the synthetic compounds or mixtures aimed for preventing, destroying, controlling, pest causing human or animal disease, unwanted species of plants, and animals causing harm during or otherwise interfering with the production, storage, processing, and transportation, or marketing of food or agricultural commodities. Pesticides are classified according to their biological activity as fungicides, herbicides, bactericides, rodenticides, insecticides, nematicides, and molluscicides. Some of the widely used pesticides are organophosphate pesticides, organochlorine pesticides, carbamates, urea, anilides, pyrethroid, and miscellaneous compounds [1].

**Phenols and their derivatives:** Phenols and their derivatives are the most important organic contaminants found in wastewater, released from industries such as petroleum refining, steel, dyestuff, synthetic resins, byproducts of agricultural chemicals, paper and pulp mills, tanning and fiberboard product to the environment. These compounds are also used as fungicides, bactericides, antiseptics, disinfectants, and wood and glue preservatives.

**Pharmaceutical compounds:** The emerging environmental problem is the presence of pharmaceutical residues in municipal, surface, ground- and even drinking water and has a potential impact on human health and the environment even at very low concentrations. Pharmaceutical residues usually detected in the environment at low concentration (ng/L) can induce toxic effects. Mostly, pharmaceutical residues are not toxic but may have some unwanted side effects. A well-known example is the identification of disruption of the endocrine system in the feminization of male sex organs in fish and snails [2]. Based on the manufacturing processes, pharmaceutical industries can be subdivided into the following five major subcategories [3]: (1) fermentation plants; (2) synthesized organic chemicals plants; (3) fermentation/synthesized organic chemicals plants (generally moderate to large plants); (4) natural/biological product extractions (antibiotics/vitamins/enzymes, etc.) and (5) drug mixing, formulation, and preparation plants (tablets, capsules, and solutions, etc.).

2. **Heterogeneous photocatalysis**

Heterogeneous photocatalysis has emerged as a potent destructive technology for the degradation of organic pollutants in a slurry or immobilized mode using semiconductors
as a photocatalyst in the presence of ultraviolet (UV) /solar light. The heterogeneous photocatalytic systems are found to be more efficient than the homogeneous systems [4]. The heterogeneous photocatalytic oxidation leads to the complete removal of organic compounds [5,6] and also undergoes partial decomposition of non-biodegradable contaminants to biodegradable intermediates [7]. Titania assisted heterogeneous photocatalytic oxidation has received the attention of researchers for many years as an alternative method for purification of both air and water systems.

2.1 Titanium dioxide as photocatalyst

TiO₂ is preferred as photocatalyst due to its biologically and chemically inertness, chemical and photo-corrosion resistance, non-toxicity, hydrophilicity and cost-effectiveness. Additionally, it is more stable than other photocatalysts in ambient conditions and can be reused again [8,9]. Furthermore, the favorable energy band gap facilitates the extensive applications of TiO₂ in the area photocatalysis, batteries, photovoltaics, UV blocker, the coating material in textile, paints, cosmetics, paper and biomedical sciences.

2.2 Electronic structure of TiO₂

Molecular orbitals are formed by contribution of atomic orbitals involved. This led to the formation of conduction bands by overlapping of the lowest unoccupied molecular orbitals (LUMO) and valence band by overlapping the highest occupied molecular orbital (HOMO). The energy difference in these bands is known as the band gap (Eg). The energy band gap of TiO₂ of anatase form is 3.2 eV and that of rutile is 3.0 eV corresponding to an absorbance maxima at, λ= 388 and 415 nm respectively. Titanium dioxide is regarded as an n-type semiconductor due to the presence of oxygen vacancies in the lattice. These vacancies are formed upon the release of two electrons and molecular oxygen leaving a positive (+2) oxide ion vacancy. When electrons of energy lower than the conduction band are present, the result is an n-type semiconductor. On the other hand, if a material is added with fewer electrons than the host, positive holes are added above the valence band resulting in a p-type semiconductor.

2.3 Physical properties of TiO₂

Titania is known as the world’s fourth most abundant metal and ninth most abundant element. It does not exist in its elemental state, but is mainly found in mineral form like rutile, ilmenite, leucoxene, anatase, brookite, perovskite and spene; titanates and as ores. The primary source and the most stable form of titanium dioxide is rutile ore. Rutile is found as one of the known polymorphs of titanium dioxide (TiO₂) and the other
polymorphs are anatase and brookite. All three prominent forms (brookite, rutile, and anatase) contain TiO$_6$ octahedra, where six oxygen (O$^{2-}$) atoms are coordinated to titanium (Ti$^{4+}$) atom (Fig. 1). The anatase form has a tetragonal structure formed by the sharing of the corner (vertices) of octahedra. In rutile, the TiO$_6$ octahedra share two edges to form linear chains with tetragonal structure and are slightly distorted. In case of the brookite form, both edges and corners are shared to form an orthorhombic structure [10-13]. The distortion of anatase TiO$_6$ is slightly larger than rutile phase. The density of anatase (3.79) is less as compared to the rutile phase (4.23).

Figure 1  Crystalline structures of titanium dioxide (a)-rutile, (b)-anatase and (c)-brookite [10].

The rutile phase is the thermodynamically favorable at all temperatures and pressures because of its linear chains than the zig-zag anatase form (ca. 1.2–2.8 kcal mol$^{-1}$). Phase transformation (anatase to rutile) occurs at higher temperature 700–1000°C depending on the crystallite size and impurity content. At lower temperature, anatase is the more stable form.

Table 1  Physical and chemical properties of anatase and rutile phases.

<table>
<thead>
<tr>
<th>Property</th>
<th>Anatase</th>
<th>Rutile</th>
<th>Brookite</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>79.88</td>
<td>79.88</td>
<td>79.88</td>
<td></td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1843</td>
<td>1843</td>
<td>1843</td>
<td></td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>2500 ~ 3000</td>
<td>2500 ~ 3000</td>
<td>2,972</td>
<td></td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
<td>[14]</td>
</tr>
<tr>
<td>Light absorption (nm)</td>
<td>&lt; 390</td>
<td>&lt; 415</td>
<td>&lt; 415</td>
<td>[15-17]</td>
</tr>
<tr>
<td>Atoms per unit cell (Z)</td>
<td>4</td>
<td>2</td>
<td>8</td>
<td>[18-19]</td>
</tr>
<tr>
<td>Lattice parameters (nm)</td>
<td>a = 0.3785, c = 0.9514</td>
<td>a = 0.4594, c = 0.29589</td>
<td>a = 9.184</td>
<td>[18-19]</td>
</tr>
<tr>
<td>Solubility in H$_2$O</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>[14]</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.79</td>
<td>4.23</td>
<td>3.99</td>
<td>[18-19]</td>
</tr>
<tr>
<td>Ti–O bond length (Å)</td>
<td>1.94 (4), 1.97 (2)</td>
<td>1.95 (4), 1.98 (2)</td>
<td>1.87-2.04</td>
<td></td>
</tr>
<tr>
<td>Volume/molecule (g cm$^3$)</td>
<td>34.061</td>
<td>31.2160</td>
<td>32.172</td>
<td></td>
</tr>
<tr>
<td>Density (kg/m$^3$)</td>
<td>3894</td>
<td>4250</td>
<td>3990</td>
<td>[18-19]</td>
</tr>
</tbody>
</table>
Band gap energies for anatase and rutile have been estimated and found to be 3.2 and 3.0 eV, respectively. The valence band of TiO$_2$ consists of 2p orbital of hybridized oxygen with a 3d orbital of titanium, while the conduction band consists of 3d orbital of titanium. The smaller bandgap of rutile, however, implies that a higher fraction of the solar radiation can induce band gap excitation (threefold increase in photocurrents). The structural, physical and chemical properties of anatase and rutile forms are given in Table 1.

2.4 Mechanism of TiO$_2$ assisted heterogeneous photocatalysis

The basic principle of heterogeneous photocatalysis involves the photoinduced reactions which are accelerated by the presence of semiconductor catalysts [20]. The detailed mechanism of the process as discussed by various scientists [21-23] is summarized in the preceding section.

(i) Photoexcitation of the semiconductor

When a photon energy is higher or equal to the threshold energy is absorbed by a semiconductor, an electron gets promoted from the valence band (VB) to the conduction band (CB) with the immediate creation of a hole in the valance band (hVB+). The conduction band energy level is known as the reduction potential of photoelectrons and the valance band energy level is helpful in determining the oxidizing ability of photo holes, and reflects the capability to promote reduction and oxidation reactions [24-26].

\[
\text{TiO}_2 + \text{hv (UV)} \rightarrow \text{TiO}_2 (e_{CB}^- + h_{VB}^+) \quad (1)
\]

where h$v$ is photon of energy required to excite the electron from the valence band (VB) region to the conduction band (CB) region.

(ii) Formation of hydroxyl radical

The $e_{CB}^-$ and $h_{VB}^+$ can migrate to the catalyst surface and undergo redox reaction on the surface of the catalyst. The photogenerated holes helps to oxidize the organic molecule or react with OH$^-$ or H$_2$O to generate hydroxyl (OH$^\bullet$) radicals as:

\[
\text{TiO}_2 (h_{VB}^+) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^\bullet \quad (2)
\]

\[
\text{TiO}_2 (h_{VB}^+) + \text{OH}^- \rightarrow \text{TiO}_2 + \text{OH}^\bullet \quad (3)
\]
The photogenerated electrons react with the oxygen to generate superoxide radical anion ($O_2^{−}$) which further lead to the additional formation of $\text{OH}^•$ radical [27-29].

$$\text{TiO}_2 (\text{e}^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{TiO}_2 + \text{O}_2^{−}$$ (4)

$$\text{O}_2^{−} + \text{H}^+ \rightarrow \text{HO}_2^•$$ (5)

$$\text{HO}_2^• + \text{H}^+ + \text{TiO}_2 (\text{e}^-_{\text{CB}}) \rightarrow \text{H}_2\text{O}_2 + \text{TiO}_2$$ (6)

$$\text{H}_2\text{O}_2 \rightarrow 2\text{''OH}$$ (7)

(iii) Recombination reaction

The recombination of $\text{e}^-_{\text{CB}}$ and the $\text{h}^+_{\text{VB}}$ on the surface or in the bulk of the catalyst in a few nanoseconds results in the dissipation of energy as heat which must be prevented to have favorable photocatalysed reactions [30-31].

$$\text{e}^-_{\text{CB}} + \text{h}^+_{\text{VB}} \rightarrow \text{e}^+_{\text{CB}} + \text{heat}$$ (8)

(iv) Degradation of organic pollutants

Organic pollutants adsorbed on TiO$_2$ catalyst surface undergo oxidation by an $\text{OH}$ radical, which is a very strong oxidizing agent (standard redox potential $+2.8$V) can oxidize organic pollutant to the mineralized products (Fig. 2).

$$\text{Organic pollutant} + \text{h}^+_{\text{VB}} \rightarrow \text{oxidation products}$$ (9)

$$\text{Organic pollutant} + \text{e}^-_{\text{CB}} \rightarrow \text{reduction products}$$ (10)

$$\text{Organic pollutant} + \text{OH}^• \rightarrow \text{degradation products}$$ (11)
Titanium dioxide (TiO$_2$) has been extensively used as a most efficient photocatalyst in widespread environmental applications [32-33].

2.5 Modification of TiO$_2$ photocatalysts

The titanium dioxide has the desirable properties of being chemically stable, readily available and widely used as photocatalyst as it absorbs the UV light because of its larger band gap (3.2 eV) [34].

The major disadvantage of the wide band gap is that it hinders the practical application of titanium dioxide in the visible light. Different strategies such as surface sensitization, bandgap modification by creating oxygen vacancies and doping of photocatalyst metals and nonmetals have been discovered for the synthesis of visible light responsive TiO$_2$ [35-39].

Other major issues to address are to control recombination reaction and the recovery as well as recycling of the catalyst.
2.6 Nanocomposites and their classification

The word “composite” means “made of two or more different parts”. A composite is a combination of two or more different materials that are mixed in an effort to obtain better characteristic properties than that of an individual component. Mostly composite materials consist of various discontinuous phases distributed in single continuous phase. The continuous phase is known as “matrix” whereas the discontinuous phase is known to be a “reinforcement, or reinforcing the material.

A nanocomposite is a composite material, in which one of the components is in nano the range i.e. around $10^{-9}$ m. The matrix comprised of resin and filler, which is used to improve the characteristic properties of the resin as well as the production cost. The filler-resin system acts as a homogeneous material, whereas the composites are made of a matrix and reinforcing the material. The reinforcement induces greater mechanical performance to composite material thereby external mechanical load is increased by the matrix and this protects the fibers against external attack. The type of the reinforcement matrix association depends upon desired characteristic properties of the product such as high mechanical characteristics, good thermal stability, and resistance to corrosion, etc. Most developed nanocomposites with demonstrable technological importance are composed of two phases, and can be microstructurally classified into three principal types:

(a) Nanolayered composite composed of alternating layers of nanoscale dimension

(b) Nanofilamentary composites composed of a matrix with embedded (and generally aligned) nanoscale diameter filaments

(c) Nanoparticulates composites composed of a matrix with embedded nanoscale particles.

3. TiO$_2$ based nanocomposites for photocatalytic degradation of organic pollutants

3.1 Organic Polymer based TiO$_2$ nanocomposites for degradation of organic pollutants

Poly(vinyl alcohol)(PVA)/poly(acrylic acid)(PAAC)/TiO$_2$/graphene oxide nanocomposite hydrogels were prepared by using radical polymerization and condensation reaction for the photocatalytic treatment of wastewater [40]. Graphene oxide (GO) was used as an additive to increase photocatalytic activity as PVA/PAAC/TiO$_2$ nanocomposite hydrogels. Both TiO$_2$ and graphene oxide were immobilized in PVA/PAAC hydrogel matrix for an easier recovery after the wastewater
treatment. The photocatalytic activities of PVA/PAAC/TiO2/GO nanocomposite hydrogels were assessed by degradation of pollutants. The improved removal of pollutants was due to the two-step mechanism based on the adsorption of pollutants by nanocomposite hydrogel and the effective decomposition of pollutants by TiO2 and GO. The highest swelling of nanocomposite hydrogel was observed at pH 10 indicating that poly(vinyl alcohol)/poly(acrylic acid)/TiO2/GO nanocomposite hydrogels were suitable as a promising system for the treatment of alkaline wastewater. The highest efficiency of dye decomposition (i.e. 88% of Coomassie brilliant blue R-250 (CBB) and 95% of methylene blue (MB) was observed at pH 10 due to the pH-sensitive swelling behavior of the PVA/PAAc/TiO2/GO nanocomposite hydrogels. The combination of TiO2 and GO strongly contributed to the efficient electron transfer between TiO2 and GO. GO strongly prevented TiO2 photocatalyst from the recombination of electron-hole formed under UV irradiation resulting in the improvement of photocatalytic activity. The synergetic contributions of pH-sensitive swelling characteristics of PVA/PAAc hydrogel matrix and GO having functional groups were beneficial for the efficient photocatalytic decomposition of basic water pollutants with PVA/PAAc/TiO2/GO nanocomposite hydrogels.

The pH-sensitive PVA/PAAc hydrogels containing TiO2 photocatalyst were prepared by radical polymerization and electrospinning methods [41]. The anatase phase of TiO2 was maintained in the TiO2/PVA/PAAc composite hydrogels without any change in structure during the preparation process. The TiO2/PVA/PAAc nanofibers showed faster and higher swelling property due to the larger surface area when the pH of the medium was changed from acidic to alkaline condition. The swelling property of pH-sensitive hydrogels was attributed to the ionization of PAAc component in the PVA/PAAc hydrogel without hindrance even in the presence of PVA. The photodegradation of dye was effectively improved by adding TiO2 photocatalyst in PVA/PAAc hydrogel nanofiber supports. Thus both hydrogel matrix and fibers help in the absorption of dye without their decomposition activity. The enhancement in decomposition efficiency of dye can be explained by the equal distribution of TiO2 and with the much higher surface to volume ratio of nano-sized fibrous supports. The faster and larger swelling properties of nanocomposite hydrogel nanofibers played an important role in the improved photo degradation ability of TiO2.

TiO2/hydrogel nanocomposites were synthesized in order to estimate their capacity to photodegrade different textile azo dyes: acid dyes C.I. acid red 18, C.I. acid blue 113, reactive dyes C.I. reactive yellow 17, C.I. reactive black 5 and direct dye C.I. direct blue 78 from aqueous solution [42]. Two different types of TiO2 nanoparticles were immobilized: colloidal TiO2 nanoparticles synthesized by acidic hydrolysis of TiCl4 and
the commercial Degussa P25 TiO₂ nanoparticles. SEM analysis, swelling and rheology studies revealed the dependency on pore size, swelling behavior and mechanical properties of the immobilized TiO₂ nanoparticles. Under illumination, nanocomposite with immobilized colloidal TiO₂ nanoparticles successfully removed and degraded the dyes (AR18, AB113, RB5 and DB78) with the highest removal (55%) of RY17 dye. Reproducibility study was performed for the dye AR18 and after four cycles of illumination, the removal rate was 75%, indicating that prepared TiO₂/hydrogel nanocomposites could be reused without reduction in photocatalytic efficiency.

3.2 Inorganic Polymer based TiO2 nanocomposites for degradation of organic pollutants

TiO₂–Montmorillonite(Mt)/polythiophene (PTP) 20%-sodium dodecyl sulfate (SDS) was prepared by in-situ chemical oxidative polymerization to show improved visible light absorption. The synthesized product was analyzed by FTIR, XRF, XRD, and FESEM, and the results indicated that the montmorillonite was successfully modified by TiO₂, followed by PTP, in the presence of surfactant (SDS) [43]. The sonocatalytic, photocatalytic, and sonophotocatalytic degradation processes of R6G were examined in the presence of heterogeneous photocatalysts (TiO₂–Mt/PTP20%-SDS, TiO₂–Mt and TiO₂-P25). The removal of the rhodamine 6G (R6G) from solution was observed and the results confirmed pseudo-first-order kinetics in the presence of all prepared catalysts which were examined by using three processes. The TiO₂–Mt/PTP20%-SDS was a most useful catalyst for R6G degradation. The incorporation of PTP and SDS surfactant into the TiO₂–Mt surface promoted the ease of electron transfer from excited polythiophene polymer to the conduction band of TiO₂. This results from the synergistic effect of the anion surfactant present in the nanocomposite.

TiO₂/clay nanocomposites were synthesized by dispersion of TiO₂ on the surfaces of a natural montmorillonite and a synthetic hectorite with increased sorption ability of TiO₂. This synthetic procedure allowed the formation of delaminated layers for hectorite–TiO₂ samples, whereas in case of montmorillonite–TiO₂ composites, the formation of a more lamellar-like aggregation occurred [44]. The photocatalytic efficiency of the nanocomposites was evaluated by using chloroacetanilide herbicide (dimethachlor) in water as a model compound. Nanocomposites exhibited good photodegradation efficiency and the overall removal efficiency of TiO₂ was better than that of bare TiO₂ produced by the sol-gel method. Because of good sedimentation ability, the nanocomposites could be studied as a hopeful alternative for the removal of organic water contaminants.
TiO₂/montmorillonite composites with intercalation structures containing anatase phase of TiO₂ was prepared [45]. The catalytic properties of TiO₂/montmorillonite composites were tested in the photooxidation of phenol. The total organic carbon (TOC) data showed that the photocatalytic efficiency of TiO₂ can be significantly enhanced by intercalation in montmorillonite support.

3.3 Metal oxide-based TiO₂ nanocomposites for degradation of organic pollutants

The TiO₂/SiO₂@Fe₃O₄ microspheres were synthesized by two sol-gel steps [46]. The as-prepared 9%TiO₂/6%SiO₂@Fe₃O₄ microspheres showed a core-shell structure which was composed of a SiO₂@Fe₃O₄ core of 205 nm in diameter and a porous TiO₂ layer of 5-6 nm in thickness. The anatase form of a TiO₂ layer is composed of primary anatase TiO₂ nanocrystals with a mean size of 3-5 nm and irregular pores with pore sizes of 2-3 nm with highest BET surface area of 373.5 m²/g. The samples showed a high degree of superparamagnetism and the maximum saturation magnetization (Ms) value of 9%TiO₂/6%SiO₂@Fe₃O₄ microspheres was about 66.4 A·m²/kg. The UV-vis diffuse reflection spectra of synthesized microspheres exhibited redshift towards visible region. The photocatalytic activity for the degradation of methyl orange and methylene blue in the presence of 9%TiO₂/6%SiO₂@Fe₃O₄ was studied. The results confirmed that these two dyes were completely decolorized in 60 min under the irradiation of high-pressure mercury lamp and can be reused for 6 times with maintained high photocatalytic performance.

The novel superparamagnetic Bi₂O₄/Fe₃O₄ nanocomposite was prepared by an in-situ growth method and utilized for photocatalytic removal of Ibuprofen [47]. Ibuprofen (IBU) is one of the persistent organic pollutants (POPs) which can cause adverse effects in humans and wildlife. The effective removal of IBU from water is a worldwide necessity. The structural characterization of the Bi₂O₄/Fe₃O₄ nanocomposite confirms the formation of the diameter of 10 nm with highly assembled nanorods of diameter 120 nm. Under visible light irradiation, the synthesized nanocomposites resulted in a complete photocatalytic degradation of IBU within 2 h, which is 1.7 times higher efficiency than pure Bi₂O₄, and complete mineralization of IBU with an irradiation time of 4 h. The photocatalytic mechanisms of Bi₂O₄/Fe₃O₄ (1:2.5) revealed that the enhanced photocatalytic performance was mainly due to the separation of electron-hole pairs after surface modification of Fe₃O₄, and photogenerated photocatalytic removal of IBU. Additionally, these can be magnetically recycled and shows good reusability without loss of their photocatalytic activity or structural change even after reusing over five cycles.

High-thermostability ordered mesoporous TiO₂/SiO₂ nanocomposites were successfully prepared through evaporation-induced self-assembly method combined with
ethylenediamine bounding strategy and subsequent high-temperature calcinations (700°C) [48]. The prepared samples were characterized by thermo gravimetric-differential scanning calorimetry, X-ray diffraction, Raman, transmission electron microscopy and N₂ adsorption. The results indicated that the samples were in the form of ordered mesostructure and SiO₂ inhibited the anatase-to-rutile phase transformation at high temperature. Significantly, the experimental results showed that the high-thermostable ordered mesoporous TiO₂/SiO₂ nanocomposites played bifunctional roles on effectively adsorbing As (III) and completely oxidizing higher toxic As (III) to lower toxic As (V) under various pH values. Moreover, after recycling for ten times the composites kept wonderful photocatalytic and adsorption performances.

Novel heterostructured ZnO/TiO₂ nanocomposites photocatalyst (Z9T) was prepared by sol-gel method and characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and UV–vis diffuse reflectance spectroscopy. The degradation efficiency with metal oxide nanocomposite for degradation of pesticides (quinalphos and monocrotophos) was found comparable to TiO₂ [49]. Mesoporous WO₃–TiO₂ nanocomposites at different WO₃ contents (0–5 wt%) have been used for photocatalytic degradation of the herbicide under visible light and UV illumination [50]. Under UV illumination, the overall photocatalytic efficiencies of the 3% WO₃–TiO₂ nanocomposite were 3.5 and 6.6 times higher than that of mesoporous TiO₂ and commercial UV-100 photocatalyst, respectively.

Magnetic recoverable CoFe₂O₄@TiO₂ decorated reduced graphene oxide nanocomposite was prepared and used for investigating the photodegradation of chlorpyrifos [51]. The photocatalytic degradation of chlorpyrifos followed the pseudo-first-order kinetic model. The results indicated that the nanocomposite exhibited a high efficient photocatalytic activity for the photodegradation of chlorpyrifos. The nanocomposite was separated from the solution by a magnet and reused after the photodegradation of chlorpyrifos. The recyclable of the nanocomposite was economically significant in the industry.

Heterostructured nanoporous Bi₂O₃-TiO₂ (BTO) was synthesized by a greener approach using ultrasonication technique and was calcinated at different temperatures. Doping with Bi₂O₃ led to the lowering of the band gap of TiO₂ from 3.25 eV to 2.5 eV. The kinetic study data of the degradation of quinalphos showed pseudo first order path with a rate constant of 0.01267 1/min. The synthesized BTO mixed oxide nanocomposites showed profound improvement in photocatalytic activity in the visible region as compared to TiO₂ [52].
3.4 Noble metal/ carbon-based TiO₂ nanocomposites for degradation of organic pollutants

The Ag-TiO₂/reduced graphene oxide (r-GO) (ATG) nanocomposite was synthesized by a one-pot solvothermal method[53]. All the ATG samples acquired a large surface area, which can provide more active sites to adsorb more reactant molecules. The excellent properties of r-GO and strong ability to absorb photogenerated electron of Ag nanoparticle enhanced the longer lifetime of an electron-hole pair, which is essential for photocatalytic activity. The photocatalytic activities of all ATG samples were superior to pure TiO₂ both for degrading Rh B dye and the reduction of CO₂ under visible light. The possible mechanism of the photocatalytic process has been discussed. The dyes can be oxidized by strong oxidizing power radical. This study paved a way for one-pot synthesis of graphene-based noble metal-doped semiconductor nanocomposite, which may be used in environmental fields.

An efficient, simple, cost-effective and environmentally benign method was developed for the preparation of the Ag/RGO/TiO₂ nanocomposite using leaf extract of E. helioscopia L. as a stabilizing and reducing agent [54]. The main advantages of this method include the elimination of toxic, expensive and harmful chemicals, the use of water as a solvent, easy-synthesis of the Ag/RGO/TiO₂ nanocomposite under environmental-friendly conditions, easy separation of the catalyst and experimental ease. The photocatalytic activity of the Ag/RGO/TiO₂ nanocomposite was checked by examining the reduction of aqueous solutions of 4-nitrophenol (NP), congo red (CR) and methylene blue (MB) dyes in the presence of NaBH₄ at room temperature. The progress of the reaction was monitored by using UV–visible measurements at regular intervals of time. The catalyst was recovered and reused for several times with no significant loss of photocatalytic activity. Table 2 summarizes the research work carried out using TiO₂ based nanocomposites for photocatalytic degradation of organic pollutants.

Conclusions

Chemical oxidation technology is the most potential technology for future applications in the field of environmental remediation i.e. the elimination of pollutants from the environment matrix. Titania based heterogeneous photocatalytic oxidation has received the attention of researchers for many years as an alternative method for purification of both air and water system. The major disadvantages that limit the practical application of titanium dioxide include low absorption in the visible region, the efficiency of the process and the recovery as well as recycling of the catalyst. TiO₂ based nanocomposites offer the potential to overcome these bottlenecks. The synthesis and applications of TiO₂ based nanocomposite materials for photocatalytic degradation of organic pollutants has been
discussed in the chapter. The environmental applications of TiO$_2$ based nanocomposites are interesting and endless. However, further insights into the interactions among the hybrid materials need to be revealed using modern analytical techniques. Further, the interplay among the nanocomposites and the targeted pollutants or the substrates needs to be investigated for understanding mechanism and potential applications in wastewater treatment.

Table 2  Summary of the research work using TiO$_2$ based nanocomposites for photocatalytic degradation of organic pollutants.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of catalyst</th>
<th>Method of preparation</th>
<th>Photocatalytic activity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly(Vinyl alcohol)/poly(acrylic acid)/TiO$_2$/graphene oxide nanocomposites</td>
<td>Radical polymerization and condensation reaction</td>
<td>CBB and MB</td>
<td>[40]</td>
</tr>
<tr>
<td>2</td>
<td>PVA/PAAn hydrogels TiO$_2$ photocatalyst</td>
<td>Radical polymerization and electro-spinning method</td>
<td>Dye</td>
<td>[41]</td>
</tr>
<tr>
<td>3</td>
<td>TiO$_2$/hydrogel nanocomposites</td>
<td>-</td>
<td>Textile azo dyes</td>
<td>[42]</td>
</tr>
<tr>
<td>4</td>
<td>TiO$_2$/MT/PTP/SDS nanocomposites</td>
<td>Chemical oxidative polymerization</td>
<td>Rhodamine 6G</td>
<td>[43]</td>
</tr>
<tr>
<td>5</td>
<td>TiO$_2$/clay nanocomposites</td>
<td>Precipitation method</td>
<td>Herbicides (dimethachlor)</td>
<td>[44]</td>
</tr>
<tr>
<td>6</td>
<td>TiO$_2$/Montmorillonite nanocomposites</td>
<td>sol-gel method</td>
<td>phenol</td>
<td>[45]</td>
</tr>
<tr>
<td>7</td>
<td>TiO$_2$/SiO$_2$/Fe$_3$O$_4$ microsphere hybrid nanocomposites</td>
<td>Solvothermal method</td>
<td>Methyl orange and methylene blue</td>
<td>[46]</td>
</tr>
<tr>
<td>8</td>
<td>TiO$_2$/SiO$_2$ nanocomposites</td>
<td>Insitu growth method</td>
<td>Ibuprofen removal</td>
<td>[47]</td>
</tr>
<tr>
<td>9</td>
<td>TiO$_2$/SiO$_2$ nanocomposites</td>
<td>Evaporation-induced self-assembly method</td>
<td>Removal of arsenic contaminants</td>
<td>[48]</td>
</tr>
<tr>
<td>10</td>
<td>Heterostructured TiO$_2$</td>
<td>-</td>
<td>Removal of organophosphate pesticides</td>
<td>[49]</td>
</tr>
<tr>
<td>11</td>
<td>Mesoporous WO$_3$-TiO$_2$ nanocomposites</td>
<td>Sol-gel method</td>
<td>Herbicides (Imazapyr)</td>
<td>[50]</td>
</tr>
<tr>
<td>12</td>
<td>CoFe$_2$O$_4$/TiO$_2$ decorated reduced graphene oxide nanocomposites</td>
<td>Coprecipitation method</td>
<td>Chlorpyrifos</td>
<td>[51]</td>
</tr>
<tr>
<td>13</td>
<td>Bi$_2$O$_3$/TiO$_2$</td>
<td>Ultrasonication method</td>
<td>Removal of Quinalphos pesticide</td>
<td>[52]</td>
</tr>
<tr>
<td>14</td>
<td>Ag/RGO/TiO$_2$ nanocomposites</td>
<td>Modified hummer method and ultrasonication</td>
<td>4-NP, Congo red and methyl blue</td>
<td>[53]</td>
</tr>
<tr>
<td>15</td>
<td>Ag-TiO$_2$/G-GO nanocomposites</td>
<td>Solvothermal method</td>
<td>RhB dye and reduction of CO$_2$</td>
<td>[54]</td>
</tr>
</tbody>
</table>

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Chapter 11

**Industrial Water Pollution and Treatment - Can Membranes be a Solution?**

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**Abstract**

Industry is one of the main sources of water pollution since a long time and currently increasing day by day. Industries produces pollutants that are not only extremely harmful to people but also to the aquatic environment. Many industrial facilities use freshwater to carry away waste from the industrial plants into rivers, lakes and oceans. During the last century a huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas. This resulted in serious pollution problems in the water bodies and caused negative effects to the eco-system and human’s life. There are many types of industrial wastewater pollutants based on different industries and each sector produces its own particular combination of pollutants from the processes. The technology for the treatment of industrial wastewater must be designed more specifically for the particular type of pollutants produced. Membrane has made important contributions to the welfare of people with positive quality of life more than the majority of all other disciplines. In this chapter most of the industrial pollutants and their membrane based treatment mechanisms are described.

**Keywords**

Membrane, Bioreactor, Industrial Wastewater, Water Pollution, Environmental Impact, Membrane Materials

**Contents**

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2. **Industrial pollutants and their impact on water** .........................................................297
1. Introduction

Wastewaters from agro-industries are characterized by high levels of chemical oxygen demand (COD), together with the presence of nitrogen and phosphorus.

The classic technologies used for the treatment of industrial wastewater are insufficient to meet current demand. Advanced technologies in wastewater treatment include membrane processes, ion-exchange processes, adsorption processes, ozonation, UV/ozone/H₂O₂ combinations, Fenton’s process, and nitrogen and phosphorus removal technologies. Membrane separation processes associated with a number of advantages, including appreciable energy savings, clean and easy operation, higher effectiveness, and greater flexibility in system design have been preferred. Membrane processes have recently become a great topic of research due to their applicability in wastewater treatment. Decreasing costs of installation and operation of membranes favored the use of membrane processes. Of the membrane processes, microfiltration and ultrafiltration are used mainly for primary treatment purposes while nanofiltration and reverse osmosis are used for final treatment. Specifically, reverse osmosis membranes offer such a high treatment efficiencies that they are used in a wide range of applications including recovery of materials from industrial wastewaters and treatment of sea water for drinking purposes.

The present chapter focuses on the various kinds of pollution present in food and agro alimentary industries. The remediation of the pollutants by application of membrane is
also discussed in this chapter. An overview about the different pollutants and treatment technologies including membrane is presented. The use of different membranes in the remediation of agro food pollutants is described with more attention to downstream purification. A large volume of wastewater in the form of either oil-in-water (o/w) or water-in-oil (w/o) emulsions is generated from various process industries such as metallurgical, transportation, food processing and petrochemical as well as petroleum refineries. In the following sections, we will focus on oil-in-water emulsions derived from vegetable oil processing.

2. Industrial pollutants and their impact on water

Agro-industries are major contributors to worldwide industrial pollution. Effluents from many agro-food industries are hazardous to the environment and require appropriate and a comprehensive management approach [1]. The quantity, composition and concentration of different agro-food wastewaters depend on the final products, production processes, equipment used, and composition variations [2].

<table>
<thead>
<tr>
<th>Industry</th>
<th>COD mg/L</th>
<th>BOD mg/L</th>
<th>pH</th>
<th>TS mg/L</th>
<th>TN mg/L</th>
<th>TP mg/L</th>
<th>Temperature ºC</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillery</td>
<td>85,000 - 1,000,000</td>
<td>42,000 - 51,000</td>
<td>3.1 - 4.7</td>
<td>70,000-95,000</td>
<td>800-1,200</td>
<td>180-350</td>
<td>85-95</td>
<td>[3]</td>
</tr>
<tr>
<td>Sugar factories</td>
<td>8,339-9,033</td>
<td>1,010-5,103</td>
<td>4.4 - 9.5</td>
<td>1,344</td>
<td>44-53</td>
<td>1 - 5</td>
<td>29.1</td>
<td>[2,4]</td>
</tr>
<tr>
<td>Dairies</td>
<td>346</td>
<td>50</td>
<td>7.3</td>
<td>250 - 2,750</td>
<td>42</td>
<td>3.3</td>
<td>--</td>
<td>[1,5]</td>
</tr>
<tr>
<td>Winery</td>
<td>1,800 – 21,000</td>
<td>--</td>
<td>--</td>
<td>150-200</td>
<td>310-410</td>
<td>40-60</td>
<td>--</td>
<td>[1]</td>
</tr>
<tr>
<td>Food processinga</td>
<td>1,000-8,000</td>
<td>600-4,000</td>
<td>--</td>
<td>--</td>
<td>50</td>
<td>3</td>
<td>--</td>
<td>[1]</td>
</tr>
<tr>
<td>Olive mil</td>
<td>130,100</td>
<td>--</td>
<td>4.9</td>
<td>9,090</td>
<td>270</td>
<td>110</td>
<td>--</td>
<td>[1,6]</td>
</tr>
</tbody>
</table>

Notes: a contains flour, soybean, tomato, pepper, and salt.
TS: Total solids; TN: Total nitrogen; TP: Total phosphorus; BOD: Biochemical oxygen demand; COD: Chemical oxygen demand.
Table 1 summarizes the physicochemical characteristics of agro-food industrial wastewater reported by various authors.

As evident from the data presented in Table 1, there is significant variation in COD (346 – 1,000,000 mg/L) and BOD (50–51,000 mg/L). The pH and total solids (TS) concentration varies in the range of 3,1 – 9,5 and 6,150 – 95,000 mg/L, respectively; and significant amount of nutrients, 42 – 1,200 mg/L of total nitrogen (TN) and 1 – 350 mg/L of total phosphorous are also found in agro-food industry wastewater. The wastewaters impact colour and unpleasant odor in water bodies but some of wastewaters exhibit good biodegradability [7].

One of the main characteristics of agro-food wastewater is the amount of water consumption. The high amount of effluent produced, raises specific problems for the treatment process. These relate to the volume and composition of the wastewater produced and consequently treatment plants must be versatile in relation to the loading regime and at the same time be able to cope with a succession of start-ups and closedowns, including periods of inactivity [8].

The untreated wastewater issued by agro-food industries can cause water and soil pollution and therefore permanent risk of environmental pollution (Fig. 1) [5,9]. Due to high organic loading, the oxygen depleting potential of agro-food wastewater is 100 times that of domestic sewage [10]. The conductivity of the agro-food wastewater exceeds 1,500 μS/cm, which proves excessive mineralization of the wastewater. For turbidity, the value is greater than 50 NTU, proving that the analyzed water is cloudy [5] and its dark color obstructs photosynthesis and causes adverse effect on aquatic life [3].

Wastewaters also alter the physico-chemical characteristics of the receiving aquatic bodies and affect aquatic flora and fauna. When discharged into the environment, wastewaters create serious health hazards to the rural and semi-urban populations. Agro-food effluent has an obnoxious odour and unpleasant colour when released into the environment without proper treatment. Contaminants, such as chloride, sulphate, phosphate, magnesium and nitrate, are discharged with the effluent of various industries, which create a nuisance due to physical appearance, odour and taste. Such harmful water is injurious to plants, animals and human beings [2,4].
The major chemical pollutants in agro-food wastewater are nitrogen and phosphorus. The presence of nitrogen in discharged wastewater is undesirable because its ecological impacts and adverse effect on public health. A major problem in some plants is a low pH (pH = 6) which arises due to extensive nitrification and low wastewater alkalinity. Nitrogen in the form of ammonia is toxic to fish and exerts an oxygen demand on receiving water by nitrifiers [11].

Surface waters may also contain phosphorus in various compounds, which is an essential constituent of living organisms. In natural conditions, phosphorus concentration in waters is balanced; however, when phosphorus input to waters is higher than that can be assimilated by a population of living organisms, the problem of excess phosphorus content occurs. Since phosphate is the limiting component for growth in most ecosystems and the emission of phosphate in surface waters lead to eutrophication and algae bloom, thus having negative impacts on nature conservation, recreation, and drinking water production [11]. Algal blooms are esthetically undesirable and they alter the native composition and species diversity of aquatic communities, in addition to impair recreational values of surface waters, impede commercial fishing, and pose problems for water treatment. When deprived of oxygen, fishes and other aquatic organisms die, emitting foul odors [12].

Agro-food effluents contain carbohydrate organics, dissolved and suspended solids. The immediate oxygen demands by these effluents cause rapid depletion of dissolved oxygen in receiving streams and produce anaerobic conditions. High solids level would have an
adverse impact on aquatic life, render the receiving water unfit for drinking and domestic purposes, reduce crop yields if used for irrigation, and exacerbate corrosion in water systems and pipes [13].

Agro-food wastewaters also affect the soil. The bacteria and fungi which maintain the soil fertility are affected by the release of highly toxic chemicals, causing concerns about the sustainability of continued reuse of treated wastewater in agriculture. The risks posed for human health represent another question at the heart of any discussion on wastewater reuse. These risks cannot be accurately estimated at the moment, but cannot be ignored. The evidences reported in the literature, as well as the critical analyses on the limitations of some experimental approaches highlight the importance of the accumulation and propagation of biological contaminants in soils due to wastewater irrigation. Human and animal pathogens, phytopathogens and antibiotic resistant bacteria and their genes are important biological contaminants that can be transported by wastewater and/or be enriched in soil. Also, numerous other chemical contaminants, such as xenobiotics, pharmaceuticals and metals, can threaten the environmental and human health. The mixture of these contaminants may have unpredictable consequences on both environment and human health [14].

3. Treatment technologies

The summary of opportunities and limitations of anaerobic, aerobic, physico-chemical and membrane treatment methods for agro-food wastewater is presented in Table 2.

*Table 2* Opportunities and limitations of anaerobic, aerobic, physicochemical and membrane treatment methods for agro-food wastewater.

<table>
<thead>
<tr>
<th>Treatment method</th>
<th>Opportunities</th>
<th>Limitations</th>
</tr>
</thead>
</table>
| Anaerobic        | *Energy production is possible due to the generation of methane during degradation of organic matters.  
*Less sludge production.  
*Effluent quality in terms of COD is good but nitrogen removal is low. | *Oil and grease are not easily degraded.  
*Post-treatment of effluent is often required. |
| Aerobic          | *Excellent effluent quality in terms of COD, BOD and nutrient removal.  
*Aerobic-SBOR has been reported to give high percentage of organics removal. | *Excess sludge produced is high.  
*Require larger area.  
*Complete removal of organics is not possible. |
In the case of aerobic SBR, smaller area is needed as compared to other aerobic activated sludge processes.

Aerobic SBR treatment systems offer better controlling.

Physico-chemical

Coagulation/flocculation, adsorption and electrochemical methods are the various physicochemical methods. Electro-oxidation was better treatment option in comparison to electro-coagulation.

No generation of secondary pollutants take place in electro-oxidation method.

Chemical coagulation/flocculation process generates secondary pollutants.

In the case of electrocoagulation, treated effluent may be contaminated with electrode material.

Membranes

Membrane assisted treatments methods such as RO, MF, NF, UF are most suitable to produce high-quality effluents to reuse directly.

Membrane separation can be used in dilute streams.

Effective in removal of recalcitrant contaminants.

Product recovery is possible.

Smaller footprint.

Improve nitrification and denitrification processes.

Volumes pumped are very high comparing to other food industry branches, the solutions exhibit high viscosity and high osmotic pressure.

Membrane fouling might be severe at the later stage of treatment.

Notes: Reverse osmosis (RO), microfiltration (MF), nanofiltration (NF), ultrafiltration (UF). Adapted from [2,15,16]

Depending on the characteristics of the wastewater and the preferred final disposal routes, wastewater treatment methods can involve a simple single operation or a series of separate operations, involving multiple units. Anaerobic treatment method for concentrated wastewater, in terms of pollutants is a widely used method in the industries. It has several advantages over aerobic processes, which include lesser energy requirement; methane (a source of energy) production due to the degradation of organic; and lesser sludge production, which indirectly reduces the sludge disposal cost [2,17].

In case of aerobic treatment process (Table 2), aerated lagoons, aerated submerged fixed-film culture, and mixed culture activated sludge process have been used for the treatment of agro-food wastewater. However, future studies are hoped to focus on aerobic
sequential batch reactor (SBR) treatment, a mixed culture activated sludge process. In the
case of aerobic SBR, smaller area is needed as compared to other aerobic activated
sludge processes. Both technologies, anaerobic and aerobic are complementary to one
another in respect of removing organics and nitrogen completely from agro-food industry
wastewater [17].

As agro-food wastewaters have high loading of dissolved solids and suspended solids,
physicochemical methods like adsorption and coagulation are well suited for their
treatment. Khan et al [18] reported coagulation with lime and subsequent adsorption with
activated charcoal. BOD and COD removal efficiencies were reported to be 96 and 95%,
respectively.

Membrane assisted treatment methods are very capable to produce high-quality effluent
to reuse directly. Future research in MBR is likely to focus on reduction in energy
demand and membrane fouling during the operation. Therefore, in view of producing
good quality treated wastewater for reuse, hybrid system comprising of membranes with
aerobic/anaerobic treatment methods and/or physicochemical methods may be promising
[2].

4. Agro industrial wastewater

4.1 Olive mill wastewater

Olive oil production is an important agricultural and economic activity in Mediterranean
countries. Olive oil processing (traditional press method or the most used three phase
continuous process) produces large amounts of olive oil mill wastewaters (OOMW).
OOMW are composed of olive pulpwater containing vegetable components and minerals,
plus water components used for the olive washing, plant cleaning, olive paste dilution in
the continuous process, and the residual olive pulp oil. The organic fraction contains
sugars, tannins, polyphenols, polyalcohols, pectins, lipids, proteins and organic acids
such as acetic, malic, fumaric, lactic, malonic, citric, tartaric, ossalic and succinic [19].
The composition of OOMW is not constant and exhibits great variability because it
depends on a lot of parameters such as kind of olive and ripeness, oil extraction
technology, and duration of aging.

OOMW from olive mills represent one of the greatest environmental problems in the
Mediterranean area, where olives cultivation is widespread and large volumes of effluents
are produced in a concentrated period of a few months. The polluting load depends on the
high COD values and the presence of phyto-toxic and antibacterial polyphenolic
components. Indeed, in these effluents, the presence of phytotoxic recalcitrant pollutants
makes them resistant to biological degradation and thus inhibits the efficiency of biological and conventional processes [20].

OOMW are often illegally discharged or widespread in agricultural fields, with adverse consequences on the field fertility. Straight discharge of OOMW has been reported by several authors to cause strong odor nuisance, soil contamination, plants growth inhibition, underground leaks, water body pollution and hindrance of self-purification processes, as well as severe impacts on the aquatic fauna and ecological status, due to the presence of bio-refractory contaminants, including a wide variety of phenolic compounds, tannins, fatty acids and organohalogenated pollutants. Inorganic compounds including chloride, sulfate and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper and traces of other elements are also common traits of OOMW [20].

Flexible and efficient treatment plants should assure not only a significant reduction of BOD and COD values but also the possibility of selectively recovering some valuable compounds that could be used in the same production cycle or as raw materials for other processes.

Scientific studies on OOMW treatment principally concentrated on the removal of the polluting load [21]. Physical and physico-chemical processes include thermal processes (evaporation, gasification, combustion) [22], thermochemical processes [23], electro-coagulation [7,24], flocculation/clarification, adsorption, extraction [25], and ozonation [26]. Nevertheless, these conventional treatments are not capable to abate the high concentration of dissolved monovalent and divalent ions present in OOMW, which present hazardous salinity levels according to the guidelines established by the Food and Agricultural Organization (F.A.O.) for irrigation uses [20]. Generally, physico-chemical processes need an integrative biological treatment for the complete degradation of the organic substances [27]. Biological treatments can be divided into aerobic and anaerobic. Anaerobic processes have greater efficiency in the pull down of the pollutant load and produce biogas reusable as energetic resource [28]. Anyway, both in the aerobic and in the anaerobic processes, microorganism growth is particularly difficult for the antibacterial action of polyphenols. Although the efficiency of the coupled physico-chemical and biological treatment of OOMW is better, from an environmental point of view, the discharge of the great amount of sludge produced, with volumes comparable to that of the OOMW treated, is a great problem [29].

Recently, researches have began to consider the recovering of polyphenols, as high value compounds with biological activities [30], the antioxidant, anti-inflammatory activities and radicalic elimination [31], and the antimicrobic activity [32], transforming OOMW from effluents to raw material with high potential economic value [33,34].
In this case, technologies offer high efficiency and moderate investment and maintenance expenses [21,35], even if final treatment of OOMW by membrane processes has not been widely accepted, yet, and limited research papers have been published up to date. Recently, Pulido [20] discussed the state of the art of the different pretreatment methods and integral membrane processes proposed up to 2016 for the reclamation and disposal of the effluents generated in olive mills operating with batch-press and two-phase as well as three-phase processes, comprising microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), along with membrane bioreactors (MBRs) [36], with an insight into the problem of fouling. MF and UF have been used mainly for primary treatment purposes, while NF and RO have been used for final treatment [37,38].

Several novel treatment approaches (Table 3) based on tangential flow membrane filtrations for the selective separation and total recovery of hydroxytyrosol, water and organic substances have been patented by ENEA and Verdiana Company [39]. MF and UF of OOMW without preliminary centrifugation step, operating with pilot plants with fixed process parameters were investigated by [38]. MF/UF permeates can be concentrated in RO. MF and UF permeates or RO concentrate can be used as functional integrators or in pharmacologic compositions. RO permeate can be used as base for the beverage industry. MF and UF concentrates can be used as fertilizers or in the production of biogas.

Membrane distillation (MD) is a non-isothermal process that has attracted the interest of academic and scientific communities during the last few years. It can be used successfully for OOMW with the objective to obtain pure water – which can be useful for irrigation or industrial uses – and a concentrate containing high amounts of polyphenols, which can be extracted later. Compared to other separation processes, MD has many advantages. It exhibits a complete rejection of dissolved, non-volatile species, lower operating pressure than the pressure-driven membrane processes, reduced vapor space, etc. The obtained concentrate of OOMW may represent a source of high added value compounds like sugar and polyphenols and the residue can be utilized in agriculture as a fertilizing agent through its high load of organic compounds [40].

One common problem of membrane filtration of OOMW is the membrane fouling that drastically reduces the efficiency of permeate and also changes its selectivity. Therefore, a pretreatment step is necessary to decrease membrane fouling and to increase filtration efficiency. The centrifuging process was found to be a promising pretreatment method [37]. Several MD processes have been identified (Figs. 2-4).

Hybrid processes, combining biological treatments, chemical processes and membrane technology, were developed too [41,42] in order to reach high removal efficiencies of
COD and mono-phenolic compounds. The important treatments processes based on membrane filtration are listed in Table 3.

Table 3  Several novel treatment approaches based on membrane filtration.

<table>
<thead>
<tr>
<th>Filtration System</th>
<th>Membranes (manufacturer)</th>
<th>Material</th>
<th>Cut-off</th>
<th>Feed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF Tangential flow</td>
<td>Ceramic Tami</td>
<td>Zirconium oxide</td>
<td>0.8 μm 0.45 μm</td>
<td>Acidified OOMW</td>
<td>[38]</td>
</tr>
<tr>
<td>Tangential flow</td>
<td>Ceramic Tami isoflux</td>
<td>Zirconium oxide</td>
<td>0.45 μm</td>
<td>Acidified OOMW</td>
<td>[38]</td>
</tr>
<tr>
<td>Tangential flow</td>
<td>Polymeric Nadir</td>
<td>Spiral-wound PES</td>
<td>500 Kd</td>
<td>Acidified OOMW</td>
<td>[38]</td>
</tr>
<tr>
<td>/</td>
<td>(Inopor GmbH)</td>
<td>Al₂O₃</td>
<td>/</td>
<td>Pre-filtered OOMW</td>
<td>[43]</td>
</tr>
<tr>
<td>/</td>
<td>Osmonics JX</td>
<td>/</td>
<td>/</td>
<td>Pre-treated OOMW</td>
<td>[44]</td>
</tr>
<tr>
<td>MBR</td>
<td>Carbosep (Novasep Orelis)</td>
<td>Carbon with ZrO₂–TiO₂</td>
<td>0.14 μm</td>
<td>Diluted OOMW</td>
<td>[36]</td>
</tr>
<tr>
<td>UF Tangential flow</td>
<td>Polymeric Osmonics</td>
<td>Spiral-wound PS</td>
<td>80 Kd 20 Kd 6 Kd</td>
<td>MF permeates</td>
<td>[38]</td>
</tr>
<tr>
<td>Tangential flow</td>
<td>Ceramic Tami</td>
<td>Zirconium oxide</td>
<td>1 Kd</td>
<td>MF permeates</td>
<td>[38]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>JW Osmonics</td>
<td>PVDF</td>
<td>30 kDa</td>
<td>Pre-treated OOMW</td>
<td>[45]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>MW Osmonics</td>
<td>Ultrafilic</td>
<td>100 kDa</td>
<td>Pre-treated OOMW</td>
<td>[45]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>Membralox-Ceraver</td>
<td>Ultrafine porous ZrO₂ / coarse porous alumina</td>
<td>0.05 μm</td>
<td>Olive mill solid wastewater</td>
<td>[42]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>UF-PES-004H (Macrodyn-Nadir)</td>
<td>Permanently hydrophilic PES</td>
<td>4 kDa</td>
<td>Pre-filtered OOMW</td>
<td>[19]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>C005F (Macrodyn-Nadir)</td>
<td>Regenerated cellulose</td>
<td>5 kDa</td>
<td>Pre-filtered</td>
<td>[19]</td>
</tr>
<tr>
<td>Process</td>
<td>Membrane Type</td>
<td>Description</td>
<td>MWCO</td>
<td>Application</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>---------------</td>
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<td></td>
</tr>
<tr>
<td>Cross-flow</td>
<td>C010F (Macrodyn-Nadir)</td>
<td>Regenerated cellulose</td>
<td>10 kDa</td>
<td>Pre-filtered OOMW [19]</td>
<td></td>
</tr>
<tr>
<td>Cross-flow</td>
<td>P010F (Macrodyn-Nadir)</td>
<td>Permanently hydrophilic PES</td>
<td>10 kDa</td>
<td>Pre-filtered OOMW [19]</td>
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<tr>
<td>Cross-flow</td>
<td>Etna 01PP (Alfa Laval)</td>
<td>Composite fluoropolymer</td>
<td>1 kDa</td>
<td>UF permeates [46]</td>
<td></td>
</tr>
<tr>
<td>Cross-flow</td>
<td>/</td>
<td>Ceramic (zirconia)</td>
<td>/</td>
<td>Pre-filtered OOMW [47]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>HFS (Toray)</td>
<td>PVDF</td>
<td>/</td>
<td>Pre-filtered OOMW [46]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>UC010 (Macrodyn® Nadir)</td>
<td>Cellulose</td>
<td>10 kDa</td>
<td>Centrifuged OOMW [37]</td>
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<tr>
<td>/</td>
<td>Osmonics GM</td>
<td>/</td>
<td>/</td>
<td>MF permeates [44]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>Desal-5 – GM4040F (Osmonics)</td>
<td>Composite</td>
<td>/</td>
<td>Pre-treated OOMW [48]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>PCI France</td>
<td>/</td>
<td>2-25-100 kDa</td>
<td>Pre-treated OOMW [41]</td>
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</tr>
<tr>
<td>Micellar enhanced</td>
<td>/</td>
<td>PVDF</td>
<td>/</td>
<td>OOMW [49]</td>
<td></td>
</tr>
<tr>
<td>NF</td>
<td>/</td>
<td>NF90 (DOW-Filmtec)</td>
<td>Thin-film</td>
<td>UF permeates [46]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>NP010 (Macrodyn® Nadir)</td>
<td>PES</td>
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<td>UF permeates [37]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>NP030 (Macrodyn® Nadir)</td>
<td>Permanently PES</td>
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<td>UF permeates [37]</td>
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<tr>
<td>/</td>
<td>NF270 (DOW Filmtec™)</td>
<td>PA</td>
<td>200-300 kDa</td>
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<td></td>
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<tr>
<td>Process</td>
<td>Membrane Type</td>
<td>Membrane Type</td>
<td>Permeate</td>
<td>Source</td>
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<tr>
<td>/</td>
<td>DK2540F</td>
<td>/</td>
<td>0.5 nm</td>
<td>Pre-treated OOMW [50]</td>
<td></td>
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<tr>
<td>/</td>
<td>/</td>
<td>Polymeric</td>
<td>200</td>
<td>UF permeates [47]</td>
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<tr>
<td>/</td>
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<td>/</td>
<td>/</td>
<td>MF permeates [44]</td>
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<td>/</td>
<td>Desal-5 DK4040F (Osmonics)</td>
<td>Composite</td>
<td>/</td>
<td>UF permeates [48]</td>
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</tr>
<tr>
<td>RO</td>
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<td>Polymeric hydronautics</td>
<td>Composite PA</td>
<td>/</td>
<td>UF permeates [38]</td>
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<tr>
<td>/</td>
<td>XLE (DOW Filmtec™) BW30 (DOW Filmtec™)</td>
<td>PA</td>
<td>/</td>
<td>UF permeates [37]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>/</td>
<td>Polymeric</td>
<td>100</td>
<td>UF permeates [47]</td>
<td></td>
</tr>
<tr>
<td>/</td>
<td>Osmonics SC</td>
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<td>/</td>
<td>NF permeates [44]</td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>Direct contact MD</td>
<td>GVHP (Millipore)</td>
<td>PVDF</td>
<td>/</td>
<td>OOMW [40]</td>
</tr>
<tr>
<td>Direct contact MD</td>
<td>TF200 (Gelman)</td>
<td>PTFE</td>
<td>/</td>
<td>OOMW [40]</td>
<td></td>
</tr>
<tr>
<td>Direct contact MD</td>
<td>TF200 (Gelman)</td>
<td>PTFE</td>
<td>/</td>
<td>Pre-treated OOMW [51]</td>
<td></td>
</tr>
<tr>
<td>Direct contact MD</td>
<td>TF200 (Gelman) TF450 (Gelman) TF1000 (Gelman)</td>
<td>PTFE/PP</td>
<td>/</td>
<td>Micro-filtered OOMW [52]</td>
<td></td>
</tr>
<tr>
<td>Osmotic distillation</td>
<td>TF200 (Gelman) TF450 (Gelman) TF1000 (Gelman)</td>
<td>PTFE/PP</td>
<td>/</td>
<td>OOMW [53]</td>
<td></td>
</tr>
<tr>
<td>Osmotic distillation</td>
<td>/</td>
<td>PP</td>
<td>/</td>
<td>NF permeates [43]</td>
<td></td>
</tr>
<tr>
<td>Vacuum MD</td>
<td>TF200 (Gelman)</td>
<td>TF450 (Gelman)</td>
<td>TF1000 (Gelman)</td>
<td>PTFE/PP</td>
<td>/</td>
</tr>
<tr>
<td>-----------</td>
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<td>----------------</td>
<td>---------</td>
<td>---</td>
</tr>
<tr>
<td>Vacuum MD</td>
<td>/</td>
<td>PP or PVDF</td>
<td>/</td>
<td>NF</td>
<td>permeates</td>
</tr>
</tbody>
</table>

Note: PA: polyamide; PES: polyethersulfone; PP: polypropylene; PS: polysulfone; PTFE: polytetrafluoroethylene; PVDF: polyvinylidene difluoride.

Figure 2  Direct contact membrane distillation system: (1) distilled water reservoir, (2) three-way valve, (3) cold unit, (4) flat sheet membrane module, (5) warm unit, (6) magnetic stirrer, (7) feed reservoir, (8) feed tank to keep the feed volume constant, (9) temperature sensor, (10) permeate outlet, (11) jacket connected to cold thermostat and (12) jacket connected to hot thermostat [40].

Figure 3  Hypothetical vegetation waters (VW) industrial treatment process [38].
Several integrated membrane processes (a sequence of two UF processes followed by a final NF step or one step of UF followed by NF and RO, or MF followed by NF and osmotic distillation or vacuum membrane distillation) have been also proposed to achieve high levels of purification of OOMWs and a water fraction which can be discharged in aquatic systems or to be reused in the olive oil extraction process [43,46,47,54]. Experimental results confirm that the future direction of the processes for the recovery of antioxidants from OOMW will be toward the utilization of membranes in a sequential design.

Micellar enhanced ultrafiltration (MEUF) treatment method for removal and concentration of polyphenols was developed, using an anionic surfactant (sodium dodecyl sulfate salt) and a hydrophobic poly(vinylidene fluoride) (PVDF) membrane [49]. Some of the schemes of the single or hybrid membrane processes are illustrated below in the form of Figs. 5-8.

Figure 4 Schematic flow diagram of the experimental set-up [45].
**Figure 5** Ultrafiltration process. T: feed tank, PC: Recycling pump, PA: Feed Pump, M: Ultrafiltration module adapted from reference [42].

**Figure 6** Proposed process scheme for the recovery of water and phenolic compounds from OOMWs [46].
Figure 7  Schematic representation of membrane bioreactor used for OOMW treatment [36].

Figure 8  Schematic flow diagram of pilot plant for OOMW treatment [41].
In the above flowchart (Fig. 9), the activities carried out for the recovery, purification and concentration of polyphenols from olive mill wastewater are illustrated [43].

### 3.2 Palm oil mill wastewater

Palm oil is one of the world’s most rapidly expanding equatorial crops. Indonesia and Malaysia are the two largest oil palm producing countries, but its by-product—palm oil mill effluent (POME), posed a great threat to the water environment. Palm oil processing, similar to other agricultural and industrial activities, raised environmental issues particularly water pollution, which adversely affects aquatic life and domestic water supply [55]. About half of the water used in the extraction process from the fresh fruit bunch results in highly polluting palm oil mill effluent wastewater (POMW) as evident from Fig. 10. POMW is a colloidal suspension of water (95-96%), oil (0.6-0.7%) and total solids (4-5%). It is non-toxic as no chemicals are added during oil extraction but has an unpleasant odor. It is highly polluting and characterized by low pH (average pH: 3.5–4.2), enhanced biological and chemical oxygen demands (BOD$_{3d, 30°C}$: 10–44 g/L, COD$_{cr}$: 16–100 g/L), increased salt content, and high suspended solids (SS: 5–54 g/L) [56]. The typical POMW characteristics are reported in the following Table 4 [57].
Table 4 Characteristics of palm oil mill effluent [57].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonical Nitrogen</td>
<td>35</td>
</tr>
<tr>
<td>BOD</td>
<td>25000</td>
</tr>
<tr>
<td>Boron</td>
<td>7.6</td>
</tr>
<tr>
<td>Calcium</td>
<td>439</td>
</tr>
<tr>
<td>COD</td>
<td>50000</td>
</tr>
<tr>
<td>Copper</td>
<td>0.89</td>
</tr>
<tr>
<td>Elements</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>46.5</td>
</tr>
<tr>
<td>Magnesium</td>
<td>615</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2</td>
</tr>
<tr>
<td>Oil &amp; Grease</td>
<td>4000</td>
</tr>
<tr>
<td>pH</td>
<td>4.7</td>
</tr>
<tr>
<td>Phosphate</td>
<td>180</td>
</tr>
<tr>
<td>Potassium</td>
<td>2270</td>
</tr>
<tr>
<td>SS</td>
<td>18000</td>
</tr>
<tr>
<td>TDS</td>
<td>40500</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>750</td>
</tr>
<tr>
<td>Total volatile solids</td>
<td>34000</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Figure 10 Flowchart of POME treatment using membrane technology [57].
Figure 11 Sustainable development of palm oil mill with zero discharge using membrane technology [57].

The high content of suspended solids and organic matter in the effluent discharge can cause severe pollution of waterways due to oxygen-depletion and other related effects. POMW contains high concentrations of protein, carbohydrate, nitrogenous compounds, lipids and minerals that may be converted into useful materials using microbial processes [58].

There is an urgent need to find a compromising way that will enable the balance between environmental protection and sustainable reuse of the nutrient sources found in the POMW (Fig. 11).

Currently, POMWs are treated by conventional biological processes of anaerobic [59] or aerobic digestion [60]. Several researchers have proposed other biological treatment systems which include aerated lagoon system, conventional anaerobic digester, anaerobic contact process, up-flow anaerobic sludge blanket (UASB) reactor, close tank digester, trickling filter, aerobic lagoon system, aerobic rotating biological contactor and evaporation processes [55,61–63]. However, the proposed biological treatment systems are only confined to lab scale analysis. Moreover, the nutrient sources available in the
POMW cannot be effectively reused as a substrate in fermentation after the conventional treatment process has been adopted.

Membrane separation technology is recognized as an efficient, economical, sustainable and reliable technology that exhibits high potential to be applied in POMW treatment. In the last decade, very few membrane processes were investigated. Ultrafiltration (UF) has been successfully developed from a useful laboratory tool to an industrial process. The main bottleneck of membrane separation is membrane fouling. Therefore, effective techniques of membrane cleaning need to be studied to mitigate membrane fouling.

A two-stage pilot-scale plant was investigated for POMW treatment. Biodegradation constituted the first biological stage, while ultrafiltration (UF) and reverse osmosis (RO) membrane units were combined as the second membrane separation stage [56,61].

![Schematic diagram of a pilot plant for palm oil mill effluent treatment](image)

Figure 12  Schematic diagram of a pilot plant for palm oil mill effluent treatment [56].

The investigation on the feasibility and suitability of the membrane separation technology in POME treatment was carried out extensively in a pilot plant (Fig. 12) with the capacity of 450 L/h [64,65]. Three designs of industrial scale membrane based POMW treatment plant were investigated and optimized for evaluation of performance and cost, in order to develop and design an industrial scale membrane plant suitable for a typical palm oil mill in Malaysia [61] (Fig. 13).
Recently membrane bioreactors (MBRs) have been developed. However, high loading of MBR system was affected due to biofouling on the membrane surface. A treatment process is necessary to remove the high content of organics in POMW that would otherwise severely resulted in fouling of the membrane and to a shorter membrane life-span (Table 5). Powdered activated carbon, zeolite, and *Moringa oleifera* were used as biofouling reducers (BFRs) and added into aerobic MBR [66].

A membrane anaerobic system (MAS) as depicted in Fig. 14 was investigated in order to treat POMW [67].
Table 5  Membrane filtration systems used for pretreatment of POMW.

<table>
<thead>
<tr>
<th>Filtration System</th>
<th>Membranes (manufacturer)</th>
<th>Material</th>
<th>Cut-off</th>
<th>Feed</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>UF</td>
<td>Dead-end</td>
<td>DSS-GR61PP (Alfa Laval)</td>
<td>PS</td>
<td>20000 g/mol</td>
<td>Pre-treated POMW</td>
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<td></td>
<td>Dead-end</td>
<td>DSS-GR70PP (Alfa Laval)</td>
<td>PS</td>
<td>20000 g/mol</td>
<td>Pre-treated POMW</td>
</tr>
<tr>
<td></td>
<td>Dead-end</td>
<td>DSS-GR81PP (Alfa Laval)</td>
<td>PES</td>
<td>10000 g/mol</td>
<td>Pre-treated POMW</td>
</tr>
<tr>
<td></td>
<td>Dead-end</td>
<td>DSS-GR95PP (Alfa Laval)</td>
<td>PES</td>
<td>2000 g/mol</td>
<td>Pre-treated POMW</td>
</tr>
<tr>
<td></td>
<td>Cross-flow</td>
<td>(PCI-Memtech)</td>
<td>Ceramic Polymeric</td>
<td>/</td>
<td>Pre-treated POMW</td>
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<tr>
<td></td>
<td>Cross-flow</td>
<td>/</td>
<td>/</td>
<td>200000 g/mol</td>
<td>/</td>
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<tr>
<td></td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>100000 g/mol</td>
<td>Pre-treated POMW</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>/</td>
<td>PVDF</td>
<td>200000 g/mol</td>
<td>Pre-treated POMW</td>
</tr>
<tr>
<td>RO</td>
<td>Cross-flow</td>
<td>(PCI-Memtech)</td>
<td>Polymeric</td>
<td>/</td>
<td>UF permeates</td>
</tr>
<tr>
<td></td>
<td>Cross-flow</td>
<td>(PCI-Memtech)</td>
<td>PVDF</td>
<td>Pre-treated POMW</td>
<td>[69]</td>
</tr>
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<td></td>
<td>/</td>
<td>ESPA-2 (Hydranautics)</td>
<td>/</td>
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<td>/</td>
<td>TFC</td>
<td>/</td>
<td>/</td>
<td>UF permeates</td>
</tr>
</tbody>
</table>

Note: PES: polyethersulfone; PS: polysulfone; PVDF: polyvinylidene difluoride; TFC: thin-film composite.

3.3 Dairy industry

The dairy industry involves processing raw milk into products such as milk, butter, cheese, yogurt, condensed milk, dried milk (milk powder), and ice cream, using methods such as chilling, pasteurization, and homogenization. Water is used in all of the activities of the dairy industry, including cleaning, sanitization, heating, cooling, and floor washing. Consequently, nowadays, the dairy industry is considered the major source of
food processing wastewater in regard to its large water consumption [70]. The effluent is characterized by variable volumes, flow rates and organic matter content. Dairy wastewater (DW) is distinguished by the higher BOD and COD values along with high levels of dissolved or suspended organic components (whey proteins, lactose, fats, oils, grease and minerals), nutrients (ammonia or minerals and phosphates), and cleaning chemicals (acids, alkalis and detergents) [71,72]. DWs, therefore, require specialized treatments to meet effluent discharge standards and to reduce the risk of environmental problems such as eutrophication in rivers, lakes and coastal waters.

![Membrane anaerobic system](image)

**Figure 14 Membrane anaerobic system [67].**

The highly variable nature of dairy wastewaters in terms of volume and flow rates as well as in terms of the pH and suspended solids content makes it difficult to choose an effective wastewater treatment regime. Conventional dairy wastewater treatment plants mainly based on activated sludge processes that involve the aerobic microbial metabolism of fats, lactose and proteins [73], anaerobic treatments [74–77], coagulation [78,79], and ecological treatment system [80]. Recently, there is an emerging interest focused on the energy recovery from wastes; in this field, microbial fuel cells (MFC) are gaining promising interest and a bio-electrochemical treatment system along with bioelectricity generation was used with real field dairy based wastewater as substrate [81].

Membrane technologies applied in the dairy industry since the early 1970s have been considered promising to treat DWs in order to produce reusable water [82]. Ultrafiltration (UF) of dairy wastewater yields a high permeate flux at low transmembrane pressure, but
its permeate water is not reusable as it contains too much lactose [83]. Instead, nanofiltration (NF) and reverse osmosis (RO) permit the recovery of lactose and milk proteins for non-human consumption. In fact, the concentrate retentate could be precipitated by coagulation and reutilized as feed supplement for animals, or could be treated by anaerobic digestion to collect renewable energy sources (H₂ and CH₄). Thus, it is regarded as an economical and environment-friendly process for treatment of dairy wastewater. Permeate water obtained from NF/RO treatment of dairy wastewater can be discharged into river or reused, but with the increase of organic solutes and inorganic salts in retentate during a concentration process; concentration polarization and osmotic pressure increase rapidly, leading to a large flux decline. Consequently, the advantages of membrane filtration in wastewater treatment are adversely affected by concentration polarization and subsequent membrane fouling as these factors cause flux decline and permeate quality deterioration. One of the principal limitations on the optimal performance of membrane processes is membrane fouling, which leads to a decrease in membrane flux with time.

Milk proteins, lactose and mineral salts present in DW are the possible ingredients of fouling layer on/in NF membranes [84]. In particular, available data on the electrophoretic mobility of α-lactalbumin and β-lactoglobulin allowed to suggest that serum proteins would also participate in the flux variations with a possible specific impact of α-lactalbumin as an internal foulant in UF [85].

Membrane selection and operating conditions have been important issues in minimizing membrane fouling. To control the fouling and to improve the productivity and life of membranes, use of coagulant and adsorbent before membrane application were done in primary and secondary effluent treatments [72]. Frappart et al. [86] confirmed the high potential of high shear dynamic filtration in reverse osmosis due to a minimization of concentration polarization, resulting in higher permeate fluxes and better solute rejection than with cross-flow filtration modules equipped with the same membrane.

Another problem related to NF/RO treatment of dairy wastewater is the difficulty of nutrient recovery. That is, because cleaning chemicals contained in dairy wastewater, are all retained by NF/RO membranes, contaminate the nutrients (lipids, proteins and lactose), and lipids have a negative impact on anaerobic digestion because these are difficult to degrade and thus plug the sludge bed [87]. A two-stage UF/NF process was proposed for utilization of whey protein and lactose, as proteins were retained by UF membrane and lactose in UF permeate was concentrated by NF [88]. For dairy wastewater treatment, a similar approach was also applied [89,90]. This approach could simultaneously eliminate pollution, produce reusable water, and recycle waste.
In the dairy industry, the use of acid, alkaline cleaners and sanitizers affects wastewater characteristics and typically results in a highly variable pH, which will bring an impact on the wastewater on-line treatment (Fig. 15). The effect of pH on the treatment of dairy wastewater by nanofiltration was investigated by Luo & Ding [91] using a rotating disk membrane module. The role of calcium and inorganic phosphate over the wide pH range was discussed by taking calculated salt equilibrium of milk as a function of acidic pH [85].

There is a growing interest in combining membranes with biological wastewater treatment. The membrane bioreactors (MBR) offer distinct advantages over traditional biological processes: higher biodegradation efficiency, smaller footprint, better quality of treated water, the absolute control of solids and hydraulic retention time, retention of all microorganisms and viruses, and easy control of operating conditions [92]. In Table 6, the membrane treatments used for dairy wastewater are summarized.

**Table 6 Membrane treatment used for dairy wastewater.**

<table>
<thead>
<tr>
<th>Filtration System</th>
<th>Membrane (manufacturer)</th>
<th>Material</th>
<th>Cut-off</th>
<th>Feed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>Cross-flow (Orelis)</td>
<td>Ceramic</td>
<td>0.45 μm</td>
<td>Pre-treated DW</td>
<td>[72]</td>
</tr>
<tr>
<td>UF</td>
<td>Dead-end (Millipore Corporation)</td>
<td>Cellulose acetate</td>
<td>1 kDa 10 kDa</td>
<td>Pre-treated DW</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>Dead-end UP005P (Microdyn-Nadir)</td>
<td>PES</td>
<td>5 kDa</td>
<td>Model DW</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>Dead-end UH030P (Microdyn-Nadir)</td>
<td>PES</td>
<td>30 kDa</td>
<td>Model DW</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>Dead-end Ultracel PLGC (Millipore)</td>
<td>Regenerated cellulose</td>
<td>10 kDa</td>
<td>Model DW</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>Cross-flow HFK-131 (Koch)</td>
<td>PES</td>
<td>150-300 g·mol⁻¹</td>
<td>Skim milk</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>Cross-flow (integrated into a Jet Loop MBR) (Jiuwu Hitech, Chinese)</td>
<td>Ceramic (Al₂O₃/ZrO₂)</td>
<td>50 nm</td>
<td>DW</td>
<td>[92]</td>
</tr>
<tr>
<td></td>
<td>Rotating disk membrane UP005P (Microdyn-Nadir)</td>
<td>PES</td>
<td>5 kDa</td>
<td>Model DW</td>
<td>[93]</td>
</tr>
<tr>
<td>Membrane Type</td>
<td>Type</td>
<td>Material</td>
<td>MWCO</td>
<td>Model</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-----------------------------</td>
<td>----------</td>
<td>-------</td>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>Rotating disk membrane</td>
<td>P010F (Microdyn-Nadir)</td>
<td>PES</td>
<td>10 kDa</td>
<td>Model DW</td>
<td>[93]</td>
</tr>
<tr>
<td>Rotating disk membrane</td>
<td>P020F (Microdyn-Nadir)</td>
<td>PES</td>
<td>20 kDa</td>
<td>Model DW</td>
<td>[93]</td>
</tr>
<tr>
<td>Rotating disk membrane</td>
<td>UH030P (Microdyn-Nadir)</td>
<td>Permanently hydrophilic PES</td>
<td>30 kDa</td>
<td>Model DW</td>
<td>[93]</td>
</tr>
<tr>
<td>Rotating disk membrane</td>
<td>UH050P (Microdyn-Nadir)</td>
<td>Permanently hydrophilic PES</td>
<td>50 kDa</td>
<td>Model DW</td>
<td>[93]</td>
</tr>
<tr>
<td>Rotating disk membrane</td>
<td>PES50 (Microdyn-Nadir)</td>
<td>PES</td>
<td>50 kDa</td>
<td>Model DW</td>
<td>[93]</td>
</tr>
<tr>
<td>Rotating disk membrane</td>
<td>US100P (Microdyn-Nadir)</td>
<td>Permanently hydrophilic PS</td>
<td>100 kDa</td>
<td>Model DW</td>
<td>[93]</td>
</tr>
<tr>
<td>NF Dead-end (Permionics Pvt.)</td>
<td>PA/PE</td>
<td>PA/PE</td>
<td>300 Da</td>
<td>Pre-treated DW</td>
<td>[72]</td>
</tr>
<tr>
<td>Dead-end NF 270 (DOW-Filmtec)</td>
<td>PA</td>
<td>PA</td>
<td>150 Da</td>
<td>UF permeates</td>
<td>[89]</td>
</tr>
<tr>
<td>Dead-end NF 90 (DOW-Filmtec)</td>
<td>PA</td>
<td>PA</td>
<td>90 Da</td>
<td>UF permeates</td>
<td>[89]</td>
</tr>
<tr>
<td>Dead-end Nanomax 50 (Millipore)</td>
<td>PA</td>
<td>PA</td>
<td>400 Da</td>
<td>UF permeates</td>
<td>[89]</td>
</tr>
<tr>
<td>Dead-end Desal-5 DL (GE Osmonics)</td>
<td>PA</td>
<td>PA</td>
<td>327 Da</td>
<td>UF permeates</td>
<td>[89]</td>
</tr>
<tr>
<td>Dead-end Desal-5 DK (GE Osmonics)</td>
<td>PA</td>
<td>PA</td>
<td>225 Da</td>
<td>UF permeates</td>
<td>[89]</td>
</tr>
<tr>
<td>Cross-flow Desal-5 DL (Osmonics)</td>
<td>PA</td>
<td>PA</td>
<td>5-10 kg·mol⁻¹</td>
<td>Skim milk</td>
<td>[85]</td>
</tr>
<tr>
<td>Cross-flow TFC-SR3 (Koch)</td>
<td>PA</td>
<td>PA</td>
<td>200 Da</td>
<td>Skim milk UF permeates</td>
<td>[94]</td>
</tr>
<tr>
<td>Cross-flow NF 90 (DOW-Filmtec)</td>
<td>PA</td>
<td>PA</td>
<td>100 Da</td>
<td>Biologically pre-treated DW</td>
<td>[95]</td>
</tr>
<tr>
<td>Cross-flow Desal-5 DL (GE Osmonics)</td>
<td>PA</td>
<td>PA</td>
<td>150-300 Da</td>
<td>Biologically pre-treated</td>
<td>[95]</td>
</tr>
<tr>
<td>Configuration</td>
<td>Membrane Type</td>
<td>Material</td>
<td>MWCO</td>
<td>Source</td>
<td>Code</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------------------------------</td>
<td>-----------------------------------</td>
<td>------</td>
<td>---------------------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>FM NP010 (Mycrodin-Nadir GmbH)</td>
<td>PES</td>
<td>1000 Da</td>
<td>Biologically pre-treated DW</td>
<td>[95]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>NF 270 (DOW-Filmtec)</td>
<td>Semiaromatic piperazine-based PA</td>
<td>200-300 Da</td>
<td>Biologically pre-treated DW</td>
<td>[95]</td>
</tr>
<tr>
<td>Rotating disk membrane</td>
<td>NF270 (DOW-Filmtec)</td>
<td>PA/PS</td>
<td>~ 270 Da</td>
<td>Model DW</td>
<td>[84,9 1,96, 97]</td>
</tr>
<tr>
<td>RO</td>
<td>Duratherm HF (GE Water &amp; Process Technologies)</td>
<td>Composite</td>
<td>/</td>
<td>Pre-filtered low-pollutant DW</td>
<td>[98]</td>
</tr>
<tr>
<td>Dead-end</td>
<td>(Permionics PVt.)</td>
<td>PA/PE</td>
<td>/</td>
<td>Pre-treated DW</td>
<td>[72]</td>
</tr>
<tr>
<td>Dead-end</td>
<td>(Osmonics)</td>
<td>Spiral-wound cellulose acetate</td>
<td>/</td>
<td>MF permeates</td>
<td>[72]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>TFC HR SW 2540</td>
<td>Spiral-wound composite (TFC)/PA</td>
<td>/</td>
<td>DW</td>
<td>[99]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>TFC HR (Koch)</td>
<td>Spiral-wound composite (TFC)/PA</td>
<td>/</td>
<td>Skim milk</td>
<td>[85]</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>TFC (GE Osmonics)</td>
<td>Aromatic PA-urea</td>
<td>/</td>
<td>NF permeates</td>
<td>[95]</td>
</tr>
<tr>
<td>Shear-enhanced</td>
<td>Desal AG (Osmonics)</td>
<td>PA/PS</td>
<td>/</td>
<td>Model DW</td>
<td>[86]</td>
</tr>
</tbody>
</table>

Note: PA: polyamide; PE: polyester; PES: polyethersulfone; PS: polysulfone; TFC: thin-film composite.
Figure 15  Schematic diagram of a two-step UF/NF process for dairy wastewater treatment and utilization for biorefinery processes [89].

3.4 Tomato-processing wastewater

The tomato industry produces huge amounts of wastewater effluents during tomato manufacturing. Tomato-processing wastewaters generally contain high organic content along with sufficient particulate and colloidal fractions that are not only slowly biodegradable but also exhibit very poor settling characteristics [100]. The wastewater stream produced during tomato manufacturing is characterized by dark color, bad smell, and high content of organics, as well as suspended solids particles. The concentration of pollutants in the effluent can vary considerably with time and space due to the changes in the harvested fruit composition and season. A discharge in the municipal sewage system of these streams is not directly possible because of the high organic contents exceeding the legally tolerated limits [101].

Recently, a process consisting of a biological pretreatment step and a batch nanofiltration process step was developed [101]. The spiral-wound module used for the separation step was a thin-film composite Desal-5 membrane (model DK2540) produced and supplied by Osmonics. Results showed that membrane processes can be successfully used to purify wastewater streams when operated at pressures far away from fouling conditions.

3.5 Fish-processing wastewater

Fish processing requires large amounts of water, primarily for washing and cleaning purposes, but also as media for storage and refrigeration of fish products before and
during processing. In addition, water is an important lubricant and transport medium in the various handling and processing steps of bulk fish processing. Consequently, fish processing operations produce wastewater, which contains organic contaminants in soluble, colloidal and particulate forms. Depending on the particular operation, the degree of contamination may be small (e.g., washing operations), mild (e.g., fish filleting), or heavy (e.g., bloodwater drained from fish storage tanks). In fishery wastewater the contaminants present are undefined mixtures of mostly organic substances. Moreover, it is difficult to generalize the extent of the problem created by this wastewater as it depends on the effluent strength, wastewater discharge rate and the absorbing capacity of the receiving water body [102]. Generally fish-processing and seafood-processing units release food waste with high content of organic nitrogen which is easily biodegradable [103].

Fish processing wastewaters have been treated using physical-chemical methods and biological treatments where microorganisms are involved in degradation of organic matter or a combination of both biological and chemical techniques [102,104–107].

A limiting factor for reuse of treated fish canning wastewater in industrial plants and other purposes is the high salt content, which persists even after conventional treatment. So, for the reuse of fish canning industrial wastewater, it was treated by combining conventional treatments, such as sedimentation, chemical coagulation-flocculation and aerobic biological degradation (activated sludge process) followed by a polishing step by reverse osmosis (RO) and ultraviolet (UV) disinfection. The final clarified effluent was found to have the quality requirements to be recycled or reused in the industrial plant, allowing the reduction of the effluent to be discharged, the water use and the costs of tap water for industrial use [104].

It is clear that the modern trend is to remove the polluting species from processing waters by various pressure-driven membrane techniques either integrated or not with other processes. Cross-flow MF is used in pre-treatment step for removal of suspended matter and during UF step, the proteins are concentrated. However, for complete recovery of proteins, NF step is required [108,109].

Also, the MBR technology is an attractive option for the treatment of such industrial wastewaters [110,111]. The experimental results have strongly confirmed the efficiency of the MBR, with good removal efficiencies in terms of BOD₅ and COD [103]. A new pilot-scale hybrid biofilm-suspended biomass membrane bioreactor was used to treat two wastewater streams generated in a fish canning factory [111].
3.6 Distillery wastewater

Distillery spent wash is the unwanted residual liquid waste generated during alcohol production in distilleries and the pollution caused by it is one of the most critical environmental issue. There are a number of large-scale distilleries integrated with sugar mills. The waste products from sugar mill comprise bagasse (residue from the sugarcane crushing), pressmud (mud and dirt residue from juice clarification) and molasses (final residue from sugar crystallization section). Bagasse is used in paper manufacturing and as fuel in boilers; molasses as raw material in distillery for alcohol production while pressmud has no direct industrial application. The major sugar producing countries are listed in Table 7.

<table>
<thead>
<tr>
<th>Period</th>
<th>Production (MT)</th>
<th>Export in (MT)</th>
<th>Population (millions)</th>
<th>Per capita consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>34</td>
<td>21.95</td>
<td>190</td>
<td>58</td>
</tr>
<tr>
<td>Australia</td>
<td>6.83</td>
<td>4.750</td>
<td>20</td>
<td>47</td>
</tr>
<tr>
<td>China</td>
<td>16.79</td>
<td>-</td>
<td>1 314</td>
<td>11</td>
</tr>
<tr>
<td>EU</td>
<td>21,567</td>
<td>2.400</td>
<td>490</td>
<td>34</td>
</tr>
<tr>
<td>India</td>
<td>30.8</td>
<td>3.298</td>
<td>1 117</td>
<td>20</td>
</tr>
<tr>
<td>Mexico</td>
<td>5.978</td>
<td>1</td>
<td>107</td>
<td>52</td>
</tr>
<tr>
<td>Pakistan</td>
<td>4.891</td>
<td>-</td>
<td>165</td>
<td>25</td>
</tr>
<tr>
<td>SADC</td>
<td>5.834</td>
<td>2.8</td>
<td>157</td>
<td>22</td>
</tr>
<tr>
<td>Thailand</td>
<td>8.033</td>
<td>6.25</td>
<td>65</td>
<td>36</td>
</tr>
<tr>
<td>United States</td>
<td>8.701</td>
<td>-</td>
<td>301</td>
<td>29</td>
</tr>
</tbody>
</table>

Note: MT: metric tonn; SADC: Southern African Development Community

3.7 Molasses spent wash

The effluents from molasses based distilleries contain large amounts of molasses spent wash (MSW) leading to extensive soil and water pollution. MSW is one of the most difficult waste products to dispose of because of low pH, elevated temperature, high concentrations of organic and inorganic substances, colorants (melanoidin, phenolics,
caramel and melanin), polymers with relatively low biodegradability [112], and high ash content. The BOD and COD values typically ranged between 35000–50000 and 100000–150000 mg/L, respectively [113]. The production and characteristics of spentwash are highly variable and dependent on feedstocks and various aspects of the ethanol production process. Together with its pollution and toxic profile, MSW has been widely reviewed [113–115]. The MSW is a potential water pollutant in two ways. First, the highly coloured nature of MSW can block out sunlight from rivers and streams, thus reducing oxygenation of the water by photosynthesis and hence becomes detrimental to aquatic life. Secondly, it has a high pollution load which would result in eutrophication of contaminated water bodies. Moreover, undiluted effluent has shown toxic effect on fishes and other aquatic organisms. MSW also leads to significant levels of soil pollution and acidification in the cases of inappropriate land discharge.

Elimination of pollutants and color from distillery effluent is becoming increasingly important from environmental and aesthetic point of view. Stillage, fermenter and condenser cooling water and fermenter wastewater are the primary polluting streams of a typical distillery. Due to the large volumes of effluent and presence of certain recalcitrant compounds, the treatment of this stream is rather challenging by conventional methods. Therefore, to supplement the existing treatments, a number of studies encompassing physicochemical and biological advanced treatment processes have been conducted [113–116].

Membrane processes can result in significant color removal thereby permitting reuse of the treated effluent [117,118]. MSW can be pre-treated with ceramic membranes prior to anaerobic digestion to reduce COD and improve the efficiency of the anaerobic process possibly due to the removal of inhibiting substances (Fig. 16). Reverse osmosis (RO) has also been employed for distillery wastewater treatment. Since spent wash is a complex, multicomponent stream that is known to cause considerable fouling, an understanding of the components those are primarily responsible for this phenomenon would assist in appropriate feed pre-treatment, for the efficient operation of the membrane system. For this reason, some of the membrane processes developed in last decade are summarized in Table 8.
<table>
<thead>
<tr>
<th>Filtration System</th>
<th>Membranes (manufacturer)</th>
<th>Material</th>
<th>Cut-off</th>
<th>Feed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>TFC-PA (Permionics)</td>
<td>/</td>
<td>/</td>
<td>Distillery effluent</td>
<td>[119]</td>
</tr>
<tr>
<td>NF</td>
<td></td>
<td>Composite polyamide</td>
<td>/</td>
<td>Pre-treated distillery effluent</td>
<td>[120]</td>
</tr>
<tr>
<td>RO</td>
<td>(Permionics)</td>
<td>/</td>
<td>/</td>
<td>UF permeates</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>ESPA2 (Hydranautics)</td>
<td>/</td>
<td>/</td>
<td>Pre-treated distillery effluent</td>
<td>[121]</td>
</tr>
<tr>
<td></td>
<td>LFC3 (Hydranautics)</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CPA2 (Hydranautics)</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BW30 (Filmtec)</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BW30LE (Filmtec)</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SG (Osmonics)</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SE (Osmonics)</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CE (Osmonics)</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBR</td>
<td></td>
<td>Polymeric</td>
<td>/</td>
<td>Synthetic wastewater</td>
<td>[112]</td>
</tr>
<tr>
<td>MBR equipped with filters prepared from waste fly ash</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Pre-treated distillery effluent</td>
<td>[122]</td>
</tr>
<tr>
<td>MBR equipped with a mesh filter</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Distillery effluent</td>
<td>[123]</td>
</tr>
</tbody>
</table>
3.8 Winery wastewater

Winery wastewater is important distillery industries. These industries generate large volumes of wastewater annually [124]. Wine distillery wastewater, or vinasse, is produced by the distillation of wine, wine lees, or fermented grape juice to extract ethanol or flavor compounds. The winery wastewaters mainly originate from various washing operations during the crushing and pressing of grapes, as well as rinsing of fermentation tanks, barrels, and other equipment as illustrated in Fig. 17 [125]. Winery wastewater contains various pollutants such as sugars, ethanol, esters, glycerol, organic acids, polyphenolic compounds, and numerous population of bacteria and yeasts [126]. The chemical analysis of winery wastewater has indicated that sugars constituted large portion of the COD, whereas organic acids played a more prominent role in the acidity of the wastewater. Due to the acidity, color, and high COD, this wastewater is treated prior to discharge, in order to avoid eutrophication of the receiving environment. Cleaning agents (NaOH, KOH) could be present in winery wastewaters. Numerous phenolic compounds are present in wines as a result of their extraction from the skin, flesh, and seeds of grapes. Phenolic compounds, though form a relatively small portion of the wastewater, offer great negative effects upon treatment systems as well as environmental damage if released untreated. The inhibitory effects of wine distillery
wastewater on plant growth can be attributed to the high percentage of organic compounds and salts, and thus high electrical conductivity of winery wastewater makes water uptake by seeds difficult and causes retardation of germination. Consequently, winery effluents are environmentally undesirable and require appropriate treatment. On the other hand, such effluents are valuable source for the recovery of polyphenols. As a result, numerous methods have been reported to treat or dispose of the phenolic-rich wastes that originate from wineries and distilleries. Among treatment methods, physical and chemical processes (such as filtration, oxidation by ozone, chlorine dioxide, hydrogen peroxide, and radiation as well as adsorption) and biological treatment techniques (including aerobic or anaerobic digestion) have been most popular \[8,124-129\].

**Figure 17 Schematic of process used in winery wastewater treatment [125].**
Table 9 Membrane processes applied in winery wastewater treatment.

<table>
<thead>
<tr>
<th>Filtration System</th>
<th>Membranes (manufacturer)</th>
<th>Material</th>
<th>Cut-off</th>
<th>Feed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF (Total recirculation mode)</td>
<td>V0.2 (Synder Filtration)</td>
<td>PVDF</td>
<td>/</td>
<td>Winery effluents from second racking</td>
<td>[132]</td>
</tr>
<tr>
<td>MF (Total recirculation mode)</td>
<td>MFP5 (Alfa Laval)</td>
<td>Fluoro polymer</td>
<td>/</td>
<td>Winery effluents from second racking</td>
<td>[132]</td>
</tr>
<tr>
<td>MF (Concentration mode)</td>
<td>(PAM Membranas Seletivas)</td>
<td>PI</td>
<td>/</td>
<td>Winery effluents from second racking</td>
<td>[132]</td>
</tr>
<tr>
<td>UF (Total recirculation mode)</td>
<td>GR95PP (Alfa Laval)</td>
<td>/</td>
<td>7600 Da</td>
<td>Winery effluents from second racking</td>
<td>[133]</td>
</tr>
<tr>
<td>UF (Total recirculation mode)</td>
<td>CA 400-22, CA 400-26, CA 400-28 (Laboratory made)</td>
<td>Cellulose acetate</td>
<td>/</td>
<td>UF permeates</td>
<td>[134]</td>
</tr>
<tr>
<td>NF (Total recirculation mode)</td>
<td>NF270 (Filmtec Corp.)</td>
<td>/</td>
<td>/</td>
<td>UF permeates</td>
<td>[134]</td>
</tr>
<tr>
<td>NF (Total recirculation mode)</td>
<td>ETNA01PP (Alpha Laval)</td>
<td>/</td>
<td>/</td>
<td>UF permeates</td>
<td>[134]</td>
</tr>
<tr>
<td>RO</td>
<td>AG2521TF (Desal)</td>
<td>PA</td>
<td>/</td>
<td>Pre-treated winery wastewater</td>
<td>[130]</td>
</tr>
</tbody>
</table>

Note: PA: polyamide; PI: polyimide; PVDF: polyvinylidene difluoride.
Biological treatment is particularly well suited to the treatment of winery wastewater, because the majority of the organic components present in the waste stream are readily biodegradable. Nevertheless, pollutants in winery wastewater like various recalcitrant high molecular weight compounds (e.g. polyphenols, tannins and lignins) are not mineralized by the biological treatment [130].

Consequently, other technologies for more exhaustive winery wastewater treatment must be applied to reach effluent quality standards for discharge in the environment. Membrane separation processes are becoming quite popular in wastewater treatment and reclamation since these combine process stability and excellent effluent quality.

Since winery effluents are rich in phenolic compounds, membrane treatments were applied with the aim of both reducing polluting compounds and recovering high-added values phenols. Beyond the application of UF for the fractionation of phenolic compounds and their separation from other co-extracted components in winery sludge [131], membrane processes as shown in Table 9 have been applied to winery wastewaters. Among these, reverse osmosis (Fig. 18) followed by solar photo-Fenton oxidation of the RO concentrate proved to be most successful combined process for the integrated treatment of winery effluents [130].

![Figure 18. Flow diagram of RO unit [130].]
Another important enzymatic activity in wine making and especially in wine clarification process is pectinases. Free enzyme membrane reactor (FEMR) is the main membrane bioreactor configuration used in wine clarification. The soluble enzyme is confined to the retentate side of the membranes where it is in contact with the substrate. In the following Table 10 some examples and membrane materials applied for the hydrolysis using
pectinases are reported. These applications are referred both to the wine and fruit juice treatments as described in Fig. 19(a,b).

Table 10  List of biocatalysts and membrane materials used in wine production.

<table>
<thead>
<tr>
<th>Biocatalyst</th>
<th>Membrane</th>
<th>Bioreactor configuration</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>pectin lyase from <em>Penicillium italicum</em></td>
<td></td>
<td>STR with an ultrafiltration unit</td>
<td>--</td>
<td>[144]</td>
</tr>
<tr>
<td>polygalacturonase from <em>A. niger</em></td>
<td>30 kDa flat regenerated cellulose membrane</td>
<td>STR with an ultrafiltration unit</td>
<td>--</td>
<td>[145]</td>
</tr>
<tr>
<td>Polygalacturonase and pectin lyase from <em>A. niger</em></td>
<td>Spiral wound polysulfone membrane (10 kDa)</td>
<td>STR with an ultrafiltration unit</td>
<td>--</td>
<td>[146]</td>
</tr>
<tr>
<td>Endo-polygalacturonase from <em>Aspergillus pulverulentus</em></td>
<td>Amicon 10 kDa</td>
<td>STR with an ultrafiltration unit</td>
<td>Production of pectic oligosaccharides</td>
<td>[147]</td>
</tr>
<tr>
<td>Polygalacturonase from <em>A. niger</em></td>
<td>Titania microfiltration</td>
<td>Biocatalytic membrane reactor</td>
<td>Pre-treatment of fruit juice</td>
<td>([148]</td>
</tr>
<tr>
<td>Amylase and pectinase</td>
<td>Polysulfone single-hollow fiber</td>
<td>Biocatalytic membrane reactor</td>
<td>Fruit juice processing</td>
<td>[149]</td>
</tr>
<tr>
<td>Commerical pectinase</td>
<td>Hollow fiber ultrafiltration</td>
<td>Biocatalytic membrane reactor</td>
<td>Fruit juice processing</td>
<td>[150]</td>
</tr>
<tr>
<td>Endopeptidase from <em>A. niger</em></td>
<td>10 kDa Spiral wound polysulfone</td>
<td>STR with an ultrafiltration unit</td>
<td>Apple pectin hydrolysis</td>
<td>[146]</td>
</tr>
</tbody>
</table>

Membrane treatment methods have been investigated to remove heavy metals. Indeed, in most cases of winery effluent, the heavy metals, especially zinc and copper, did not meet
the limits for the discharge as imposed by the most restrictive regulations at international level [135].

Winery wastewaters have different compositions and hence are difficult to treat by means of the conventional activated sludge processes because of the high organic loading associated with their production. To face this situation, membrane bioreactors (MBR) have been widely applied to treat winery wastewaters since 2007 [129,136–143]. MBR offers several benefits, such as rapid start-up, good effluent quality, low footprint area, and absence of voluminous secondary settler. Additionally, its operation is not affected by the settling properties of the sludge.

Cell immobilization is rapidly expanding research area. The main purpose to use this technique is to improve wine production. Many supports (inorganic, organic and natural materials) have been used for cell immobilization in this field. Some of the supports and their main applications have been listed in Table 11.

Table 11 Porous supports used in wine production processes.

<table>
<thead>
<tr>
<th>Support</th>
<th>Immobilized cell</th>
<th>Application</th>
<th>System configuration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic support</td>
<td>Mineral kissis</td>
<td><em>Saccaromices</em></td>
<td>Aroma improvement</td>
<td>[151]</td>
</tr>
<tr>
<td></td>
<td>γ-aluminium</td>
<td><em>Saccaromices</em></td>
<td>Continuous wine-making</td>
<td>[152]</td>
</tr>
<tr>
<td>Organic support</td>
<td>Cellulose covered with Ca-alginate</td>
<td><em>Saccaromices and Candida</em></td>
<td>Enhance glycerol formation in wine</td>
<td>[153]</td>
</tr>
<tr>
<td></td>
<td>Ca-alginate beds</td>
<td><em>Saccaromices</em></td>
<td>Must fermentation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Immobilized cell-recycle batch process</td>
<td>[154]</td>
</tr>
<tr>
<td>Natural support</td>
<td>Delignified cellulose Gluten pellets</td>
<td><em>Saccaromices</em></td>
<td>Fermentation Production of wine with less alcohol content</td>
<td>[155,156]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[153,157]</td>
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Compared with organic supports, inorganic supports have been more advantageous, because of providing improved fermentation productivity and in most cases better wine aroma [158]

**Conclusions**

Membrane applications for the treatment of agro-industrial wastewater focus on separating water from contaminants, using semi-permeable membranes under applied driving forces. Pressure is applied to reverse the natural equilibrium between the clean water and wastewater. The basic principle of natural equilibrium is that the clean water tends to migrate to the wastewater side to equalize the concentrations across the membrane. Mechanical pressure is used to force water molecules from the wastewater side to the clean water side and, thus, a "high-tech" filtration of the wastewater occurs. In this way, the pollutants can be separated in terms of process intensification strategies. In the past, the energy needed to apply the pressure and the fragility of the membrane surface made use of these alternatives economically unjustifiable. But due to stringent regulation before waste discharge forcing the industry to opt for the advanced treatment mechanism. Various industries have opted as discussed but still there are gaps between fundamental research and application in real life of membrane application in pollution remediation. Also problems with membrane applications include fouling and fragility of the membrane surface. Toxic synthetic compounds can oxidize the surface of the membrane and thus are injurious to membranes. Innovations in membrane technology have advanced the "cleanability" and research on reuse of membranes. The suitability of stainless steel and ceramic materials for membranes has greatly improved the use of these materials in developing advanced wastewater treatment techniques.

**References**


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