Degradation of Organic Compounds in Aqueous Media using Semiconductor Nanomaterials

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Received: 18 January 2024; Revised: 10 April 2024; Accepted: 30 May 2024

Abstract: Today, environmental pollution stemming from organic pollutants poses a significant challenge. Various categories of organic compounds, including dyes, pharmaceuticals, aromatics, volatile organic compounds, and more, contribute to contamination of water, soil, and air. The presence of these organics in water not only harms aquatic life but also poses health risks to humans. Thus, it is imperative to eliminate these organic pollutants from the environment. Different methods, such as absorption, adsorption, filtration, biodegradation, chlorination, ozonation have been developed to remove organics from waste water. Photodegradation is one of the important methods to remove organic compounds from aqueous media. Different catalysts have been used by different researchers for photocatalytic degradation of organics. Uses of nanomaterials as photocatalysts have been seen to be a potential approach of remediation of toxic organic compounds from environment. In this approach heterogeneous catalysts using semiconductor nanomaterials have shown to be good photocatalysts. These catalysts have been discovered to exhibit greater efficacy in advanced oxidation processes for eliminating organic contaminants from wastewater. Way of improving photodegradation efficiencies was also discussed. Metal and non-metal doping to regular materials has been seen to be a good approach of enhancing degradation efficiencies of normal photocatalysts. This discussion delves into the sources of these organic compounds, their detrimental effects on the environment, and a comprehensive exploration of conventional degradation methods available for combating these compounds.

Keywords: Organic compounds; Water pollution; Degradation; Nanomaterials; Semiconductor.

1. Introduction

In recent decades, semiconductor nanomaterials have garnered significant attention as photocatalysts for the degradation of organic pollutants in polluted water. The primary aim of this process is to transform toxic compounds into non-toxic or beneficial products. Effective photocatalysts should possess specific characteristics, including a high surface area, activity under visible light, increased generation of electrons and holes, minimal recombination rate, reusability, and more [1,2]. Among various semiconductor nanomaterials, TiO$_2$, CdS, ZnS, ZnO, and CuO are widely acknowledged as photocatalysts due to their robust oxidizing capabilities, chemical stability, and affordability [3–5]. Pure semiconductor nanomaterials typically encounter issues with electron-hole recombination and primarily exhibit activity under UV-light irradiation due to their high band gap. In addition to semiconductor materials, nanoparticles of gold, silver, and iron are also utilized for the degradation of organic pollutants in wastewater [6]. Given that only a minor portion (approximately 3–5%) of solar light falls within the UV region, it is anticipated that merely 3–5% of the entire solar radiant energy is beneficial for photocatalysis purposes. Consequently, for a specific photocatalyst, doping is employed to attain particular properties. For example, doping can alter the band gap of the host material, thereby enhancing the photocatalytic activity by increasing the presence of photo-generated electrons and holes [7]. Doping nanomaterials serves to decrease the band gap of the material, establishing an intermediate energy state within its energy levels. This reduction in band gap facilitates applications in photocatalysis under visible light irradiation. Moreover, the intermediate energy
state enables control over the emission properties of the base material. For instance, doping noble metals like silver into TiO₂ enhances anatase crystallinity, surface area, and lowers the band gap, thereby rendering TiO₂ an environmentally sustainable and efficient photocatalyst for degrading persistent organic pollutants [8,9]. The introduction of samarium ions into TiO₂ enhances specific surface area, improves the efficiency of electron-hole pair separation, and mitigates the recombination tendency of photoinduced electrons and holes. Consequently, the overall photocatalytic activity of TiO₂ for degrading methylene blue dye experiences a significant improvement [10]. The incorporation of iron (Fe) into TiO₂ results in the attainment of high specific surface areas, reduced crystal sizes, a mesoporous structure, and an abundance of surface-adsorbed water and hydroxyl groups. These characteristics collectively enhance the photocatalytic activity of Fe-doped TiO₂ for the degradation of XRG dye [11]. Doping TiO₂ powders with fluorine enhances surface acidity, promotes the creation of oxygen vacancies, increases the number of active sites, ultimately leading to the achievement of visible light photocatalytic activity for TiO₂ powders [12]. The incorporation of other materials like Sn [13], Si [14], and tri-doping of F–B–S [15] into TiO₂ nanoparticles enhances various properties such as UV-induced photodecomposition activities, visible light photocatalytic activity, significantly larger specific surface area, shorter duration of photocatalytic cleaning reactions, and suppression of the recombination of photogenerated electrons and holes. Additionally, beyond TiO₂, other photocatalysts such as ZnO, CdS, ZnS, Nb₂O₅, among others, have been investigated with different doping elements to enhance their photocatalytic performances [16–18]. Among various semiconductor nanoparticles, TiO₂, CdS, and ZnS hold significance due to their potential applications across diverse fields such as catalysis, biomedicine, sensors, and electrical and electronics industries [19–21]. The photocatalytic efficacy of these nanoparticles under visible light primarily hinges on factors such as their band gap, electron-hole recombination rate, specific surface area, and crystalline structure [22,23]. Therefore, the pursuit of creating a cost-effective and highly efficient photocatalyst remains a promising endeavor, both from fundamental research and industrial perspectives.

In this study photodegradation of different organic compounds such as pharmaceutical products, organic dyes, and aromatic compounds has been studied in aqueous medium. Different removal or degradation techniques for these organic compounds have been discussed. Advantages and disadvantages of each technique along with its efficiency have also been discussed. Effects of different photocatalysts along with its dose have been explored. Other reaction parameters such as in initial organic concentration, light source, time, and temperature have also been discussed.

2. Degradation of Pharmaceutical Products

Pharmaceutical compounds represent a significant class of toxic organic pollutants, primarily contributing to soil and water pollution. Certain categories of pharmaceuticals, such as antibiotics and antipyretics, are utilized extensively, with excess quantities discharged into the environment. Similar to other pharmaceutical compounds, antibiotics are incompletely metabolized within the body and are consequently released into the environment. The primary sources of pharmaceutical contaminants include sewage treatment plants from pharmaceutical industries and municipal wastewater. Extensive use of pharmaceutical products such as paracetamol, naproxen, amoxicillin, metronidazole, ibuprofen, etc creates environmental problem. Especially, excess quantity presence of antibiotics in environment causes soil and water pollution [24–26]. Hence, the thorough elimination of these organic pollutants from the environment is imperative. Various conventional methods, such as advanced oxidation processes (AOP), including electrochemical oxidation, ultrasonic radiation, and ozonation, have already been employed for the degradation of these pharmaceutical compounds. Reported studies on photocatalytic degradation of different pharmaceutical compounds by different researchers are shown in Table 1. Commonly used pharmaceutical compounds, such as paracetamol, metronidazole, naproxen, ibuprofen, amoxicillin, etc were used for photodegradation studies, photodegradation was conducted under visible and UV-light. Different nanocatalyst such as AgBr–α-NiMoO₄, ZnO, ZnSnO₃, Zn₃GeO₈, etc. were used as photocatalysts. From the reported studies (as shown in table 1) it has been seen that temperature for photodegradation was in the range of 25°C–450°C with initial organic concentrations were found to be in the range of 0.998 to 15 mg/L. Time taken for photodegradation was found to be in the range of 24–600 min. Photodegradation efficiencies were found to be around 80–100%. However, the existing methods are having some limitations such as more time consuming, UV-light dependent, requirement of high catalyst dose, catalyst regeneration problem, etc. Because of these reasons 100% removal of pharmaceutical compounds from environment is still a challenging job.
Table 1. Photodegradation of pharmaceutical compounds utilizing various nanoparticles as photocatalysts.

<table>
<thead>
<tr>
<th>Catalyst dose (g/L)</th>
<th>Pharmaceutical Compound</th>
<th>Initial organic conc. (mg/L)</th>
<th>Chemical Structure</th>
<th>Light source</th>
<th>Parameter (s)</th>
<th>Time (min)</th>
<th>% Deg.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug-CN₄</td>
<td>Paracetamol</td>
<td>-</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Visible Light (365 nm)</td>
<td>Temp. 25°C</td>
<td>24</td>
<td>100</td>
<td>[27]</td>
</tr>
<tr>
<td>AgBr-α-NiMoO₄</td>
<td>Naproxen</td>
<td>-</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Visible Light (420 nm)</td>
<td>Temp. 30°C</td>
<td>100</td>
<td>84</td>
<td>[28]</td>
</tr>
<tr>
<td>Ag-ZnO</td>
<td>Paracetamol</td>
<td>4.994</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Visible Light (420 nm)</td>
<td>Temp. 45°C</td>
<td>240</td>
<td>92</td>
<td>[29]</td>
</tr>
<tr>
<td>CO-GCN</td>
<td>Paracetamol</td>
<td>1</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Sunlight</td>
<td>Temp. 30°C</td>
<td>120</td>
<td>82.6</td>
<td>[30]</td>
</tr>
<tr>
<td>Ag-TiO₂, CdS, ZnS</td>
<td>Metronidazole</td>
<td>15</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>125 W, visible light (435.8 nm)</td>
<td>-</td>
<td>120</td>
<td>94-95</td>
<td>[25]</td>
</tr>
<tr>
<td>ZnO/Se p-</td>
<td>Ibuprofen</td>
<td>-</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>UV-Visible Light (320 nm)</td>
<td>Temp. 39°C</td>
<td>600</td>
<td>80</td>
<td>[31]</td>
</tr>
<tr>
<td>ZnSnO₃/RGO</td>
<td>Metronidazole</td>
<td>5</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>500 W visible lamp</td>
<td>-</td>
<td>180</td>
<td>72.5</td>
<td>[32]</td>
</tr>
<tr>
<td>H₂O₂, Fe⁺</td>
<td>Paracetamol</td>
<td>0.998</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Sunlight</td>
<td>Temp. 30°C</td>
<td>240</td>
<td>90</td>
<td>[33]</td>
</tr>
<tr>
<td>Zn₂GeO₄</td>
<td>Metronidazole</td>
<td>10</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>UV light (253.7 nm)</td>
<td>-</td>
<td>80</td>
<td>-100</td>
<td>[34]</td>
</tr>
</tbody>
</table>

3. Degradation of dyes

Contamination of dyes in environment is another issue. Especially synthetic dyes are more concern in this regards. Different sources of synthetic dyes in waste water are textile industries, pulp and paper industries, petroleum industries, etc [35,36]. In textile industries almost 15% of synthetic dyes are unutilized. This unutilized synthetic dyes are released into the waste water stream and ultimately coming to natural stream and river [37]. Regular discharge of synthetic dyes causes severe toxic effect to aquatic life, human beings and animals. Use of
dye contaminated water promotes mutagenicity and carcinogenicity effect. Presence of excess quantity of synthetic dyes in water increases biochemical oxygen demand (BOD) and chemical oxygen demand (COD), which ultimately lower the water quality [38]. So, removal of dyes from waste water is highly essential. Various methods have been developed for this purpose, including adsorption, absorption, filtration, and more. Each and every methods are having some limitations, such as lower dye removal efficiency, high cost, complicated method, etc. In recent years, there has been considerable interest in nanoparticle-based dye degradation due to their high efficiency in completely removing organics from contaminated water. These methods are characterized by their simplicity, low cost, time efficiency, and environmental friendliness [39–41]. Nevertheless, semiconductor-based nano-photocatalysts for dye degradation have garnered significant attention in the fields of environmental remediation and solar energy utilization. Over the past few decades, heterogeneous photocatalysis employing semiconductor nanomaterials has emerged as an advanced oxidation process for effectively removing dye pollutants from wastewater. [42]. Modification of semiconductor nanomaterials in the presence of doping helps to improve advanced oxidation process further. Different doped nanoparticles such as Fe-TiO$_2$ [43] and Ce-, Cu-, Mn-, Sn-TiO$_2$ [44] were used as photocatalysts for the degradation of dyes under UV light irradiation. Some other doped materials, such as Fe-CdS [43], Si-, Fe-TiO$_2$ [44], C-TiO$_2$ [45], Cu-ZnS [40], N-, S-TiO$_2$ [46], and Pt-TiO$_2$ [47] were utilized as photocatalyst for degradation of dyes under visible light. Some reported studies on photocatalytic degradation of different dyes by different researchers are shown in Table 2. Different dyes such as Malachite Green, methylene blue dye, etc. have been degraded under visible and UV light. Photocatalysts such as TiO$_2$, modified TiO$_2$, ZnO, SiO$_2$ were employed to degrade the dyes. The literature review (as depicted in table 2) reveals that initial organic concentrations typically ranged from 5 to 100 mg/L. Photodegradation times varied between 30 min and 14 h. Degradation efficiencies were found to be 90–95%. In recent years, there has been a growing research interest in the visible light-induced photodegradation of dyes using nanoparticles, aiming to enhance the process effectiveness, environmental friendliness, and cost-efficiency. Much of this research focuses on improving photocatalytic efficiency through the utilization of various doped nanoparticle, mesoporous materials with high surface areas, and similar strategies.

Table 2. Photo-degradation of dyes in the presence of different nanoparticles as the photocatalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst dose (g/L)</th>
<th>Name of dyes</th>
<th>Initial dye conc. (mg/L)</th>
<th>Chemical Structure</th>
<th>Light sources</th>
<th>Parameter(s)</th>
<th>Time (min)</th>
<th>% Deg</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.015</td>
<td>Malachite Green</td>
<td>15</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV–Visible</td>
<td>Temp. 30°C</td>
<td>140</td>
<td>96.1</td>
<td>[48]</td>
</tr>
<tr>
<td>Ag-ZnO</td>
<td>0.02</td>
<td>Methylene blue dye</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV-Visible</td>
<td>Temp. 30°C</td>
<td>−</td>
<td></td>
<td>82.15-98.38</td>
<td>[49]</td>
</tr>
<tr>
<td>Ag-TiO$_2$</td>
<td>0.25</td>
<td>Methylene blue dye</td>
<td>25</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV-Visible</td>
<td>Temp. 30°C</td>
<td>180</td>
<td>94.99-95.9</td>
<td>[3]</td>
</tr>
<tr>
<td>Mn, Ni, Cu-</td>
<td>0.15</td>
<td>Methylene blue dye</td>
<td>5</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV-Visible</td>
<td>Temp. 30°C</td>
<td>30</td>
<td>87.3-95.6</td>
<td>[50]</td>
</tr>
<tr>
<td>Sm-TiO$_2$</td>
<td>1.0</td>
<td>Methylene blue dye</td>
<td>100</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV-Visible</td>
<td>Temp. 30°C</td>
<td>120</td>
<td>95</td>
<td>[51]</td>
</tr>
<tr>
<td>N, S- TiO$_2$</td>
<td>0.2</td>
<td>Methylene blue dye</td>
<td>9</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV-Visible</td>
<td>Temp. 30°C</td>
<td>240</td>
<td>90.61</td>
<td>[52]</td>
</tr>
<tr>
<td>Ce, Cu, Mn, Sn-TiO$_2$</td>
<td>0.0375</td>
<td>Methylene blue dye</td>
<td>10</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV-Visible</td>
<td>Temp. 30°C</td>
<td>90</td>
<td>–97</td>
<td>[53]</td>
</tr>
<tr>
<td>Fe-ZnO</td>
<td>0.448</td>
<td>Methylene blue dye</td>
<td>32</td>
<td><img src="Image" alt="Chemical Structure" /></td>
<td>UV-sun light</td>
<td>Temp. 30°C</td>
<td>105/75</td>
<td>41/91</td>
<td>[54]</td>
</tr>
</tbody>
</table>
4. Degradation of aromatic compounds

Apart from pharmaceutical compounds and dyes presence of aromatic compounds in water causes environmental problems. Presence of aromatic compounds, such as phenolic compounds, benzo compounds, naphthalene, etc in water directly affect on the aquatic life and indirectly affect to animals and human beings. Aromatic compounds find utility in various industrial productions including paper and pulp, pesticides, dyes, explosives, cosmetics, pharmaceuticals, and more [58–60]. Unused aromatics from those industries are coming to effluent water and are mixing with natural water stream. Direct use of this water causes risks to human, animals and other living things. The contamination of water with aromatic compounds through regular usage can lead to severe health issues such as liver or kidney damage, lung irritation, increased heart rate, and skin problems. Consequently, the removal of aromatic compounds from water has become a significant concern today. However, conventional chemical or biological methods face challenges in effectively removing or degrading aromatics in effluent water due to their complex structure and their toxic and mutagenic effects on biological systems [61]. Over the last few years photodegradation of aromatic compounds are attracted a lot because of its easy and efficient techniques. Different heterogeneous catalyst have been employed for this purpose. Some reported studies on photocatalytic degradation of different aromatic compounds by different researchers are shown in Table 3. Aromatic compound such as benzene, chlorobenzene, nitrobenzene, etc. have been degraded in the presence of different photocatalysts. Photodegradation studied was conducted under visible and UV light. Based on the literature findings (as outlined in table 3), the temperature for photodegradation typically fell within the range of 20°C to 30°C, while initial organic concentrations varied from 6.153 to 400 mg/L. The duration of photodegradation ranged from 10 to 480 min. Percent degradation efficiencies were found to be around 53–98%.

Table 3. Photodegradation of aromatic compounds using various nanoparticles as photocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst dose</th>
<th>Aromatic compound</th>
<th>Initial organic conc. (mg/L)</th>
<th>Chemical Structure</th>
<th>Light source</th>
<th>Time (min)</th>
<th>Parameters</th>
<th>% Deg.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiPO₄</td>
<td>0.2 g/L</td>
<td>Benzene</td>
<td>250</td>
<td><img src="image" alt="Benzene" /></td>
<td>UV lamps</td>
<td>100</td>
<td>Temp. 30°C</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.2 g/L</td>
<td>Nitrobenzene</td>
<td>50.1</td>
<td><img src="image" alt="Nitrobenzene" /></td>
<td>UV lamp, 254 nm</td>
<td>180</td>
<td>air feeding of 150 mL/min</td>
<td>90</td>
<td>[63]</td>
</tr>
<tr>
<td>TiO₂/bentonite</td>
<td>0.1 g/L</td>
<td>Chlorobenzene</td>
<td>400</td>
<td><img src="image" alt="Chlorobenzene" /></td>
<td>UV light &amp; 65 W CFL lamp</td>
<td>10</td>
<td>Temp. 20°C</td>
<td>98%</td>
<td>[64]</td>
</tr>
<tr>
<td>N-Ce-TiO₂</td>
<td>1 g/L</td>
<td>Nitrobenzene</td>
<td>50</td>
<td><img src="image" alt="Nitrobenzene" /></td>
<td>visible lamp, 300 W</td>
<td>240</td>
<td>Temp. 30°C</td>
<td>53</td>
<td>[65]</td>
</tr>
</tbody>
</table>

Universal Journal of Green Chemistry
5. Conclusions

Organic compounds such as pharmaceutical compounds, dyes, aromatic compounds, etc are the major pollutants present in water. For the degradation or removal of these organics different methods have been developed such as filtration, absorption, adsorption, Photodegradation, etc. Photodegradation of organic compounds is considered as one of the most important methods for this purpose. Especially nanomaterials based photodegradation is considered as an efficient technique for the degradation of organic compounds. In this approach different semiconductor material, such as TiO$_2$, ZnS, CdS, ZnO, CdO, SiO$_2$, etc has been used in organic compound degradation in different methods. TiO$_2$, especially nano TiO$_2$ are preferred for photocatalytic degradation of organics because of its low toxic levels, photocatalytic nature, cost effectiveness, stability, and easy availability. To enhance the efficiency of the nanoparticles as photocatalyst, different modifications have been developed further. Metal impregnation along with semiconductor nanoparticles further improved the degradation efficiency of host materials. Metal doping is also a process to enhance the degradation efficiency of semiconductor nanomaterials. Developing semiconductor nanomaterials with enhanced selectivity and specificity for target organic compounds is a crucial focus. The future of organic compound degradation in aqueous media using semiconductor nanomaterials shows promise in tackling water pollution challenges. Additionally, future research could investigate synergies between semiconductor photocatalysis and processes like filtration, absorption, adsorption, and biological treatment. Nonetheless, ongoing research and innovation are imperative to translate these possibilities into practical solutions.

Conflict of interest

There is no conflict of interest for this study.

References


