

## Review

# Degradation of Organic Compounds in Aqueous Media using Semiconductor Nanomaterials

Siddhartha Sankar Boxi\* 

Department of Chemical Engineering, Haldia Institute of Technology, Haldia 721657, West Bengal, India  
E-mail: [ssboxich@gmail.com](mailto:ssboxich@gmail.com)

**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<sup>1,2</sup>. Among various semiconductor nanomaterials, TiO<sub>2</sub>, CdS, ZnS, ZnO, and CuO are widely acknowledged as photocatalysts due to their robust oxidizing capabilities, chemical stability, and affordability<sup>3-5</sup>. 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<sup>6</sup>. 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<sup>7</sup>. 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 TiO<sub>2</sub> enhances anatase crystallinity, surface area, and lowers the band gap, thereby rendering TiO<sub>2</sub> an environmentally sustainable and efficient photocatalyst for degrading persistent organic pollutants<sup>8,9</sup>. The introduction of samarium ions into TiO<sub>2</sub> 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 TiO<sub>2</sub> for degrading methylene blue dye experiences a significant improvement<sup>10</sup>. The incorporation of iron (Fe) into TiO<sub>2</sub> 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 TiO<sub>2</sub> for the degradation of XRG dye<sup>11</sup>. Doping TiO<sub>2</sub> 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 TiO<sub>2</sub> powders<sup>12</sup>. The incorporation of other materials like Sn<sup>13</sup>, Si<sup>14</sup>, and tri-doping of F–B–S<sup>15</sup> into TiO<sub>2</sub> 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 TiO<sub>2</sub>, other photocatalysts such as ZnO, CdS, ZnS, Nb<sub>2</sub>O<sub>3</sub>, among others, have been investigated with different doping elements to enhance their photocatalytic performances<sup>16–18</sup>. Among various semiconductor nanoparticles, TiO<sub>2</sub>, CdS, and ZnS hold significance due to their potential applications across diverse fields such as catalysis, biomedicine, sensors, and electrical and electronics industries<sup>19–21</sup>. 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<sup>22,23</sup>. Therefore, the pursuit of creating a cost-effective and highly efficient photocatalyst remains a promising endeavor, both from fundamental research and industrial perspectives.

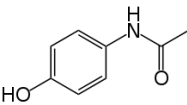
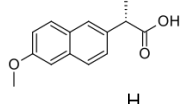
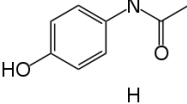
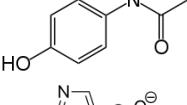
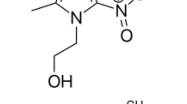
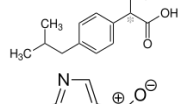
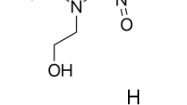
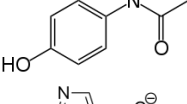
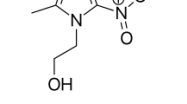
In this study photodegradation of different organic compounds such as pharmaceutical products, organic dyes, and aromatic compounds has been studied in aqueous medium. Different removal or degradation techniques for these organic compounds have been discussed. Advantages and disadvantages of each technique 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<sup>24–26</sup>. 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- $\alpha$ -NiMoO<sub>4</sub>, ZnO, ZnSnO<sub>3</sub>, Zn<sub>2</sub>GeO<sub>4</sub>, 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.

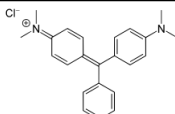
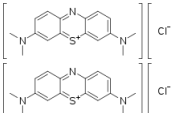
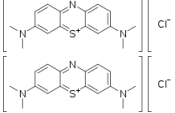
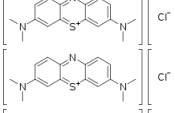
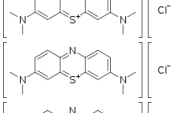
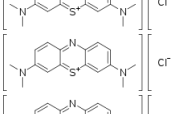
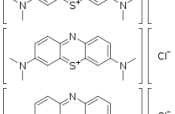
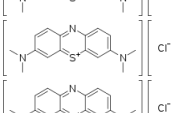
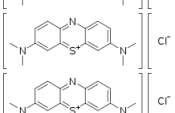
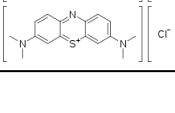

Catalyst	Catalyst Dose (g/L)	Pharmaceutical Compound	Initial Organic conc. (mg/L)	Chemical Structure	Light Source	Parameters	Time (min)	% Deg.	Ref.
Ag-C <sub>3</sub> N <sub>4</sub>	0.0003	Paracetamol	-		Visible Light (365 nm)	Temp. 25°C	24	100	27
AgBr- $\alpha$ -NiMoO <sub>4</sub>	-	Naproxen	-		Visible Light (420 nm)	Temp. 30°C	100	84	28
Ag-ZnO	-	Paracetamol	4.994		Visible Light (420 nm)	Temp. 450 °C	240	92	29
CO-GCN	0.01	Paracetamol	1		Sunlight	Temp. 30°C	120	82.6	30
Ag-TiO <sub>2</sub> , CdS, ZnS	0.5	Metronidazole	15		125 W, visible light (435.8 nm)	-	120	94-95	25
ZnO/Sep.	-	Ibuprofen	-		UV-Visible (320 nm)	Temp. 39°C	600	80	31
ZnSnO <sub>3</sub> /RGO	1	Metronidazole	5		500 W visible lamp	-	180	72.5	32
H <sub>2</sub> O <sub>2</sub> , Fe <sup>3+</sup>	0.00274, 0.00299	Paracetamol	0.998		Sunlight	Temp. 30°C	240	90	33
Zn <sub>2</sub> GeO <sub>4</sub>	1	Metronidazole	10		UV light (253.7 nm)	-	80	~100	34

### 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.<sup>35,36</sup>. 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<sup>37</sup>. 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<sup>38</sup>. 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<sup>39-41</sup>. 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<sup>42</sup>. Modification of semiconductor nanomaterials in the presence of doping helps to improve advanced oxidation process further. Different doped nanoparticles such as Fe-TiO<sub>2</sub><sup>43</sup> and Ce-, Cu-, Mn-, Sn-TiO<sub>2</sub><sup>44</sup> were used as photocatalysts for the degradation of dyes under UV light irradiation. Some other doped materials, such as Fe-CdS<sup>43</sup>, Si-, Fe-TiO<sub>2</sub><sup>44</sup>, C-TiO<sub>2</sub><sup>45</sup>, Cu-ZnS<sup>40</sup>, N-, S- TiO<sub>2</sub><sup>46</sup>, and Pt-TiO<sub>2</sub><sup>47</sup> 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<sub>2</sub>, modified TiO<sub>2</sub>, ZnO, SiO<sub>2</sub> 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 nanoparticles, mesoporous materials with high surface areas, and similar strategies.







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

Catalyst	Catalyst Dose (g/L)	Name of Dyes	Initial Dye conc. (mg/L)	Chemical Structure	Light Sources	Parameters	Time (min)	% Deg	Ref.
La Doped ZnO-SiO <sub>2</sub>	0.015	Malachite Green	15		UV-Visible	Temp. 30 °C	140	96.1	48
Ag-ZnO	0.02	Methylene blue dye	-		UV Visible Light	Temp. 30 °C	-	82.15-98.38	49
Ag-TiO <sub>2</sub>	0.25	Methylene blue dye	25		125 W, visible light (435.8 nm)	-	180	94.99-95.9	3
Mn, Ni, Cu-ZnS	0.15	Methylene blue dye	5		500 W HL	pH = 11	30	87.3-95.6	50
Sm-TiO <sub>2</sub>	1.0	Methylene blue dye	100		160 W HPMVL (UV)	-	120	95	51
N, S- TiO <sub>2</sub>	0.2	Methylene blue dye	9		500 W ML	pH = 3	240	90.61	52
Ce, Cu, Mn, Sn-TiO <sub>2</sub>	0.0375	Methylene blue dye	10		UV light, 254 nm	-	90	~97	53
Fe-ZnO	0.448	Methylene blue dye	32		UV/sun light	-	105/75	41/91	54
Pt/TiO <sub>2</sub>	1	Methylene blue dye	10		300 W XL	-	50	~95	55
Si, Fe, TiO <sub>2</sub>	1.0	Methylene blue dye	20		500 W LAXL	-	180	82.51	56
NaYF <sub>4</sub> :Yb,Tm/TiO <sub>2</sub>	1.0	Methylene blue dye	15		DL (980 nm)	-	14 h	65	57

## 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<sup>58-60</sup>. 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<sup>61</sup>. 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.

Catalyst	Catalyst Dose	Aromatic Compound	Initial Organic conc. (mg/L)	Chemical Structure	Light Source	Time (min)	Parameters	% Deg.	Ref.
BiPO <sub>4</sub>	0.2 g/L	Benzene	250		UV lamps (254 nm)	100	Temp. 30 °C	-	62
TiO <sub>2</sub>	0.2 g/L	Nitro benzene	50.1		UV lamp, 254 nm	180	air feeding of 150 mL/min	90	63
TiO <sub>2</sub> /bentonite	0.1 g/L	chlorobenzene	400		UV light & 65 W CFL lamp	10	Temp. 20 °C	98%	64
N-Ce-TiO <sub>2</sub>	1 g/L	Nitro benzene	50		visible lamp, 300 W	240	Temp. 30 °C	53	65
TiO <sub>2</sub>	0.2 g/L	Nitro benzene	49.94		mercury vapour lamp	480	air purging	98%	66
TSA-MIP-TiO <sub>2</sub>	0.1 g/L	Nitro benzene	6.153		UV lamp, 253.7 nm	90	-	>95	67

## 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<sub>2</sub>, ZnS, CdS, ZnO, CdO, SiO<sub>2</sub>, etc has been used in organic compound degradation in different methods. TiO<sub>2</sub>, especially nano TiO<sub>2</sub> 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

- [1] Foroutan, R.; Peighambaroust, S. J.; Boffito, D. C.; Ramavandi, B. Sono-Photocatalytic Activity of Cloisite 30B/ZnO/Ag<sub>2</sub>O Nanocomposite for the Simultaneous Degradation of Crystal Violet and Methylene Blue Dyes in Aqueous Media. *Nanomaterials* **2022**, *12*, 3103. <https://doi.org/10.3390/nano12183103>.
- [2] Meena, P. L.; Surela, A. K.; Poswal, K.; Saini, J. K.; Chhachhia, L. K. Biogenic synthesis of Bi<sub>2</sub>O<sub>3</sub> nanoparticles using Cassia fistula plant pod extract for the effective degradation of organic dyes in aqueous medium. *Biomass Convers. Biorefin.* **2022**, *14*, 3793-3809. <https://doi.org/10.1007/s13399-022-02605-y>.

- [3] Carneiro, J. O.; Samantilleke, A. P.; Parpot, P.; Fernandes, F.; Pastor, M.; Correia, A.; Luís, E. A.; Chivanga Barros, A. A.; Teixeira, V. Visible Light Induced Enhanced Photocatalytic Degradation of Industrial Effluents (Rhodamine B) in Aqueous Media Using TiO<sub>2</sub> Nanoparticles. *J. Nanomater.* **2016**. <https://doi.org/10.1155/2016/4396175>.
- [4] Dehghani, M. H.; Karamitabar, Y.; Changani, F.; Heidarinejad, Z. High performance degradation of phenol from aqueous media using ozonation process and zinc oxide nanoparticles as a semiconductor photo catalyst in the presence of ultraviolet radiation. *Desalin. Water Treat.* **2019**, *166*, 105–114. <https://doi.org/10.5004/dwt.2019.24607>.
- [5] Nazim, M.; Khan, A. A. P.; Asiri, A. M.; Kim, J. H. Exploring Rapid Photocatalytic Degradation of Organic Pollutants with Porous CuO Nanosheets: Synthesis, Dye Removal, and Kinetic Studies at Room Temperature. *ACS Omega* **2021**, *6*, 2601–2612. <https://doi.org/10.1021/acsomega.0c04747>.
- [6] Kumar, B. Green Synthesis of Gold, Silver, and Iron Nanoparticles for the Degradation of Organic Pollutants in Wastewater. *J. Composites Sci.* **2021**, *5*, 219. <https://doi.org/10.3390/jcs5080219>.
- [7] Mollick, S.; Mandal, T. N.; Jana, A.; Fajal, S.; Desai, A. V.; Ghosh, S. K. Ultrastable Luminescent Hybrid Bromide Perovskite@MOF Nanocomposites for the Degradation of Organic Pollutants in Water. *ACS Appl. Nano Mater.* **2019**, *2*, 1333–1340. <https://doi.org/10.1021/acsanm.8b02214>.
- [8] Li, Y.; Ma, M.; Chen, W.; Li, L.; Zen, M. Preparation of Ag-doped TiO<sub>2</sub> Nanoparticles by a Miniemulsion Method and their Photoactivity in Visible Light Illuminations. *Mater. Chem. Phys.* **2011**, *129*, 501–505. <https://doi.org/10.1016/j.matchemphys.2011.04.055>.
- [9] Hamal, D. B.; Klabunde, K. J. Synthesis, Characterization, and Visible Light Activity of New Nanoparticle Photocatalysts Based on Silver, Carbon, and Sulfur-Doped TiO<sub>2</sub>. *J. Colloid Interface Sci.* **2007**, *311*, 514–522. <https://doi.org/10.1016/j.matchemphys.2011.04.055>.
- [10] Xiao, Q.; Si, Z.; Yu, Z.; Qiu, G. Sol–Gel Auto–Combustion Synthesis of Samarium-Doped TiO<sub>2</sub> Nanoparticles and their Photocatalytic Activity under Visible Light Irradiation. *Mater. Sci. Eng. B.* **2007**, *137*, 189–194. <https://doi.org/10.1016/j.mseb.2006.11.011>.
- [11] Zhu, J.; Chen, F.; Zhang, J.; Chen, H.; Anpo, M. Fe<sup>3+</sup>-TiO<sub>2</sub> Photocatalysts Prepared by Combining Sol–Gel Method with Hydrothermal Treatment and their Characterization. *J. Photochem. Photobiol. A.* **2006**, *180*, 196–204. <https://doi.org/10.1016/j.jphotochem.2005.10.017>.
- [12] Li, D.; Haneda, H.; Hishita, S.; Ohashi, N.; Labhsetwar, N. Fluorine-Doped TiO<sub>2</sub> Powders Prepared by Spray Pyrolysis and Their Improved Photocatalytic Activity for Decomposition of Gas-Phase Acetaldehyde. *J. Fluor. Chem.* **2005**, *126*, 69–77. <https://doi.org/10.1016/j.jfluchem.2004.10.044>.
- [13] Kiraz, N.; Burunkaya, E.; Kesmez, Ö.; Çamurlu, H. E.; Asiltürk, M.; Yeşil, Z.; Arpaç, E. Preparation of Sn Doped Nanometric TiO<sub>2</sub> Powders by Reflux and Hydrothermal Syntheses and their Characterization. *J. Sol-Gel Sci. Technol.* **2011**, *59*, 381–386. <https://doi.org/10.1007/s10971-011-2515-7>.
- [14] Bui, D. -N.; Kang, S. -Z.; Li, X.; Mu, J. Effect of Si Doping on the Photocatalytic Activity and Photoelectrochemical Property of TiO<sub>2</sub> Nanoparticles. *Catal. Commun.* **2011**, *13*, 14–17. <https://doi.org/10.1007/s10971-011-2515-7>.
- [15] Li, F.; Yin, X.; Yao, M. -m.; Li, J. Investigation on F–B–S Tri-Doped Nano-TiO<sub>2</sub> Films for the Photocatalytic Degradation of Organic Dyes. *J. Nanoparticle Res.* **2011**, *13*, 4839–4846. <https://link.springer.com/article/10.1007/s11051-011-0461-5>.
- [16] Thakur, P.; Joshi, S. S.; Kapoor, S.; Mukherjee, T. Fluorescence Behavior of Cysteine-Mediated Ag@CdS Nanocolloids. *Langmuir* **2009**, *25*, 6377–6384. <https://doi.org/10.1021/la8042507>.
- [17] Habibi, M. H.; Mokhtari, R. Novel Sulfur-Doped Niobium Pentoxide Nanoparticles: Fabrication, Characterization, Visible Light Sensitization and Redox Charge Transfer Study. *J. Sol-Gel Sci. Technol.* **2011**, *59*, 352–357. <https://doi.org/10.1007/s10971-011-2510-z>.
- [18] Lu, X.; Liu, Z.; Zhu, Y.; Jiang, L. Sonochemical Synthesis and Photocatalytic Property of Zinc Oxide Nanoparticles Doped with Magnesium(II). *Mater. Res. Bulletin.* **2011**, *46*, 1638–1641. <https://doi.org/10.1016/j.materresbull.2011.06.015>.
- [19] Paumo, H. K.; Dalhatou, S.; Katata-Seru, L. M.; Kamdem, B. P.; Tijani, J. O.; Vishwanathan, V.; Kane, A.; Bahadur, I. TiO<sub>2</sub> assisted photocatalysts for degradation of emerging organic pollutants in water and wastewater. *J. Mol. Liq.* **2021**, *331*, 115458. <https://doi.org/10.1016/j.molliq.2021.115458>.
- [20] Sharma, S.; Dutta, V.; Singh, P.; Raizadaa, P.; RahmaniSanic, A.; Hosseini-Bandegharaeic, A.; Thakure, V. K. Carbon quantum dot supported semiconductor photocatalysts for efficient degradation of organic pollutants in water: A review. *J. Clean. Prod.* **2019**, *228*, 755–769. <https://doi.org/10.1016/j.jclepro.2019.04.292>.

- [21] Ramalingam, G.; Perumal, N.; Priya, A. K.; Rajendran, S. A review of graphene-based semiconductors for photocatalytic degradation of pollutants in wastewater. *Chemosphere* **2022**, *300*, 134391. <https://doi.org/10.1016/j.chemosphere.2022.134391>.
- [22] Imperato, C.; Bifulco, A.; Silvestri, B.; Vitiello, G. Recent Advances in Endocrine Disrupting Compounds Degradation through Metal Oxide-Based Nanomaterials. *Catalysts* **2022**, *12*, 289. <https://doi.org/10.3390/catal12030289>.
- [23] Natarajan, V.; Sathiyamoorthy, K.; Kumar, R. T.; Navaneethan, M.; Harish, S. Sunlight-driven photocatalytic degradation of organic pollutant in an aqueous medium by Gd-doped CuO nanocatalyst. *J. Mater. Sci. Mater. Electron.* **2024**, *35*, 25. <https://doi.org/10.1007/s10854-023-11715-w>.
- [24] Elmolla, E. S.; Chaudhuri, M. Degradation of the Antibiotics Amoxicillin, Ampicillin and Cloxacillin in Aqueous Solution by the Photo-Fenton Process. *J. Hazardous Mater.* **2009**, *172*, 1476–1481. <https://doi.org/10.1007/s10854-023-11715-w>.
- [25] Rysz, M.; Alvarez, P. J. J. Amplification and Attenuation of Tetracycline Resistance in Soil Bacteria: Aquifer Column Experiments. *Water Res.* **2004**, *38*, 3705–3712. <https://doi.org/10.1016/j.watres.2004.06.015>.
- [26] Gilliver, M. A.; Bennett, M.; Begon, M.; Hazel, S. M.; Hart, C. A. Enterobacteria: Antibiotic Resistance Found in Wild Rodents. *Nature* **1999**, *401*, 233–234. <https://doi.org/10.1038/45724>.
- [27] Salcedo, M. J.; Monge, M.; Tena, M. T. An organometallic approach for the preparation of Au-TiO<sub>2</sub> and Au-g-C<sub>3</sub>N<sub>4</sub> nanohybrids: Improving the depletion of paracetamol under visible light. *Photochem. Photobiol. Sci.* **2022**, *21*, 337–347. <https://doi.org/10.1007/s43630-022-00172-9>.
- [28] Ray, S. K.; Dhakal, D.; Lee, S. W. Rapid degradation of naproxen by AgBr- $\alpha$ -NiMoO<sub>4</sub> composite photocatalyst in visible light: Mechanism and pathways. *Chem. Eng. J.* **2018**, *347*, 836–848. <https://doi.org/10.1016/j.cej.2018.04.165>.
- [29] Al-Gharibi, M. A.; Kyaw, H. H.; Al-Sabahi, J. N.; Myint, M. T. Z.; Al-Sharji, Z. A.; Al-Abri, M. Z. Silver nanoparticles decorated zinc oxide nanorods supported catalyst for photocatalytic degradation of paracetamol. *Mater. Sci. Semicond. Process.* **2021**, *134*, 105994. <https://doi.org/10.1016/j.mssp.2021.105994>.
- [30] Pham, T. H.; Park, J. W.; Kim, T. Enhanced photodegradation of paracetamol from water by cobalt doped graphitic carbon nitride. *Solar Energy* **2021**, *215*, 151–156. <https://doi.org/10.1016/j.solener.2020.12.034>.
- [31] Akkaria, M.; Arandaa, P.; Belverc, C.; Bediac, J.; Haj Amarab, A. B.; Hitzkya, E. R. ZnO/sepiolite heterostructured materials for solar photocatalytic degradation of pharmaceuticals in wastewater. *Appl. Clay Sci.* **2018**, *156*, 104–109. <https://doi.org/10.1016/j.clay.2018.01.021>.
- [32] Dong, S.; Sun, J.; Li, Y.; Yu, C.; Li, Y.; Sun, J. ZnSnO<sub>3</sub> Hollow Nanospheres/Reduced Graphene Oxide Nanocomposites as High-Performance Photocatalysts for Degradation of Metronidazole. *Appl. Catal. B: Environ.* **2014**, *144*, 386–393. <https://doi.org/10.1016/j.apcatb.2013.07.043>.
- [33] Guerra, M. M. H.; Alberola, I. O.; Rodriguez, S. M.; Lopez, A. A.; Merino, A. A.; Alonso, J. M. Q. Oxidation mechanisms of amoxicillin and paracetamol in the Photo-Fenton solar process. *Water Res.* **2019**, *156*, 232–240. <https://doi.org/10.1016/j.watres.2019.02.055>.
- [34] Liu, J.; Zhang, G.; Jimmy, C.; Yu, J. C.; Guo, Y. In Situ Synthesis of Zn<sub>2</sub>GeO<sub>4</sub> Hollow Spheres and their Enhanced Photocatalytic Activity for the Degradation of Antibiotic Metronidazole. *Dalton Trans.* **2013**, *42*, 5092–5099. <https://doi.org/10.1039/c2dt32623j>.
- [35] Muruganandham, M.; Shobana, N.; Swaminathan, M. Optimization of Solar Photocatalytic Degradation Conditions of Reactive Yellow 14 Azo Dye in Aqueous TiO<sub>2</sub>. *J. Molecular Catal. A.* **2006**, *246*, 154–161. <https://doi.org/10.1016/j.molcata.2005.09.052>.
- [36] Chun, H.; Yizhong, W. Decolorization and Biodegradability of Photocatalytic Treated Azo Dyes and Wool Textile Wastewater. *Chemosphere* **1999**, *39*, 2107–2115. [https://doi.org/10.1016/s0045-6535\(99\)00118-6](https://doi.org/10.1016/s0045-6535(99)00118-6).
- [37] Ehrampoush, M. H.; Moussavi, G. R.; Ghanian, M. T.; Rahimi, S.; Ahmadian, M. Removal of Methylene Blue Dye from Textile Simulated Sample using Tubular Reactor and TiO<sub>2</sub> /UV-C Photocatalytic Process. *Iranian J. Environ. Health Sci. Eng.* **2011**, *8*, 35–40.
- [38] Lellis, B.; Zani, C.; Polonio, F.; Pamphile, J. A.; Polonio, J. C. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnol. Res. Innov.* **2019**, *3*, 275–290. <https://doi.org/10.1016/j.biori.2019.09.001>.
- [39] Ni, Y.; Zhu, Y.; Ma, X. A Simple Solution Combustion Route for the Preparation of Metal-Doped TiO<sub>2</sub> Nanoparticles and their Photocatalytic Degradation Properties. *Dalton Trans.* **2011**, *40*, 3689–3694. <https://doi.org/10.1039/c0dt01534b>.



- [40] Chauhan, R.; Kumar, A.; Chaudhary, R. P. Photocatalytic Degradation of Methylene Blue with Cu Doped ZnS Nanoparticles. *J. Lumin.* **2014**, *145*, 6–12. <https://doi.org/10.1039/c0dt01534b>.
- [41] Ghosh Chaudhuri, R.; Paria, S. Visible Light Induced Photocatalytic Activity of Sulfur Doped hollow TiO<sub>2</sub> Nanoparticles, Synthesized Via a Novel Route. *Dalton Trans.* **2014**, *43*, 5526–5534. <https://doi.org/10.1039/c3dt53311e>.
- [42] Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahneman, D. W. Environmental Applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96. <https://doi.org/10.1021/cr00033a004>.
- [43] Chauhan, R.; Kumar, A.; Chaudhary, R. P. Visible-light photocatalytic degradation of methylene blue with Fe doped CdS nanoparticles. *Appl. Surf. Sci.* **2013**, *270*, 655–660. <https://doi.org/10.1016/j.apsusc.2013.01.110>.
- [44] Lin, Y.; Jiang, Z.; Zhu, C.; Hu, X.; Zhang, X.; Zhu, H.; Fan, J.; Lin, S. H. Electronic and optical performances of Si and Fe-codoped TiO<sub>2</sub> nanoparticles: A photocatalyst for the degradation of methylene blue. *Appl. Catal. B Environ.* **2013**, *142–143*, 38–44. <https://doi.org/10.1016/j.apcatb.2013.04.061>.
- [45] Xiao, Q.; Zhang, J.; Xiao, C.; Si, Z.; Tan, X. Solar photocatalytic degradation of methylene blue in carbon-doped TiO<sub>2</sub> nanoparticles suspension. *Sol. Energy* **2008**, *82*, 706–713. <https://doi.org/10.1016/j.solener.2008.02.006>.
- [46] Lv, Y.; Ding, Y.; Zhou, J.; Xiao, W.; Feng, Y. Preparation, Characterization, and Photocatalytic Activity of N, S-Codoped TiO<sub>2</sub> Nanoparticles. *J. Am. Ceram. Soc.* **2009**, *92*, 938–941. <https://doi.org/10.1111/j.1551-2916.2009.02951.x>.
- [47] Di, L.; Xu, Z.; Wang, K.; Zhang, X. A facile method for preparing Pt/TiO<sub>2</sub> photocatalyst with enhanced activity using dielectric barrier discharge. *Catal. Today* **2013**, *211*, 109–113. <https://doi.org/10.1016/j.cattod.2013.03.025>.
- [48] Wang, S.; Chen, Z.; Zhao, Y.; Sun, C.; Li, J. High photocatalytic activity over starfish-like La-doped ZnO/SiO<sub>2</sub> photocatalyst for malachite green degradation under visible light. *J. Rare Earths* **2021**, *39*, 772–780. <https://doi.org/10.1016/j.jre.2020.04.009>.
- [49] Diantariani, N. P.; Wahyuni, E. T.; Kartini, I. Ag/ZnO photocatalyst for photodegradation of methylene blue, IOP Conference Series: *Mater. Sci. Eng.* **2019**, *509*, 012099. <https://doi.org/10.1088/1757-899x/509/1/012099>.
- [50] Pouretedal, H. R.; Norozi, A.; Keshavarz, M. H.; Semnani, A. Nanoparticles of Zinc Sulfide Doped with Manganese, Nickel and Copper as Nanophotocatalyst in the Degradation of Organic Dyes. *J. Hazard. Mater.* **2009**, *162*, 674–681. <https://doi.org/10.1016/j.jhazmat.2008.05.128>.
- [51] Xiao, Q.; Si, Z.; Zhang, J.; Xiao, C.; Tan, X. Photoinduced Hydroxyl Radical and Photocatalytic Activity of Samarium-Doped TiO<sub>2</sub> Nanocrystalline. *J. Hazard. Mater.* **2008**, *150*, 62–67. <https://doi.org/10.1016/j.jhazmat.2007.04.045>.
- [52] Lv, Y.; Ding, Y.; Zhou, J.; Xiao, W.; Feng, Y. Preparation, Characterization, and Photocatalytic Activity of N, S-Codoped TiO<sub>2</sub> Nanoparticles. *J. Am. Ceram. Soc.* **2009**, *92*, 938–941. <https://doi.org/10.1111/j.1551-2916.2009.02951.x>.
- [53] Ni, Y.; Zhu, Y.; Ma, X. A Simple Solution Combustion Route for the Preparation of Metal-Doped TiO<sub>2</sub> Nanoparticles and their Photocatalytic Degradation Properties. *Dalton Trans.* **2011**, *40*, 3689–3694. <https://doi.org/10.1039/c0dt01534b>.
- [54] Chauhan, R.; Kumar, A.; Chaudhary, R. P. Photocatalytic Degradation of Methylene Blue with Cu Doped ZnS Nanoparticles. *J. Lumin.* **2014**, *145*, 6–12. <https://doi.org/10.1016/j.jlumin.2013.07.005>.
- [55] Kumar, K.; Chitkara, M.; Sandhu, I. S.; Mehta, D.; Kumar, S. Photocatalytic, Optical and Magnetic Properties of Fe-Doped ZnO Nanoparticles Prepared by Chemical Route. *J. Alloys Comp.* **2014**, *588*, 681–689. <https://doi.org/10.1016/j.jlumin.2013.07.005>.
- [56] Esparza, P.; Hernández, T.; Borges, M. E.; Álvarez-Galván, M. C.; Ruiz-Morales, J. C.; Fierro, J. L. G. TiO<sub>2</sub> Modifications by Hydrothermal Treatment and Doping to Improve its Photocatalytic Behaviour Under Visible Light. *Catal. Today* **2013**, *210*, 135–141. <https://doi.org/10.1016/j.cattod.2012.12.011>.
- [57] Bayal, N.; Jeevanandam, P. Sol–Gel Synthesis of SnO<sub>2</sub>–MgO Nanoparticles and Their Photocatalytic Activity towards Methylene Blue Degradation. *Mater. Res. Bulletin.* **2013**, *48*, 3790–3799. <https://doi.org/10.1016/j.materresbull.2013.05.092>.
- [58] Piccinini, P.; Minero, C.; Vincenti, M.; Pelizzetti, E. Photocatalytic Mineralization of Nitrogen-Containing Benzene Derivatives. *Catal. Today* **1997**, *39*, 187–195. [https://doi.org/10.1016/s0920-5861\(97\)00100-4](https://doi.org/10.1016/s0920-5861(97)00100-4).
- [59] Bhatkhande, D. S.; Pangarkar, V. G.; Beenackers, A. A. C. M. Photocatalytic Degradation of Nitrobenzene using Titanium Dioxide and Concentrated Solar Radiation: Chemical Effects and Scaleup. *Water Res.* **2003**, *37*, 1223–1230. [https://doi.org/10.1016/s0043-1354\(02\)00490-6](https://doi.org/10.1016/s0043-1354(02)00490-6).

- [60] ElShafei, G. M. S.; Yehia, F. Z.; Dimitry, O. I. H.; Badawi, A. M.; Eshaq, G. Degradation of Nitrobenzene at Near Neutral pH using  $\text{Fe}^{2+}$ –Glutamate Complex as a Homogeneous Fenton Catalyst. *Appl. Catal. B* **2010**, *99*, 242–247. <https://doi.org/10.1016/j.apcatb.2010.06.026>.
- [61] O'connor, O. A.; Young, L. Y. Toxicity and Anaerobic Biodegradability of Substituted Phenols under Methanogenic Conditions. *Environ. Toxicol. Chem.* **1989**, *8*, 853–862. <https://doi.org/10.1016/j.apcatb.2010.06.026>.
- [62] Zheng, X.; Wang, J.; Liu, J.; Wang, Z.; Chen, S.; Fu, X. Photocatalytic degradation of benzene over different morphology  $\text{BiPO}_4$ : Revealing the significant contribution of high–energy facets and oxygen vacancies. *Appl. Catal. B: Environ.* **2019**, *243*, 780–789. <https://doi.org/10.1016/j.apcatb.2018.11.029>.
- [63] Whang, T. -J.; Hsieh, M. -T.; Shi, T. -E.; Kuei, C. -H. UV-Irradiated Photo catalytic Degradation of Nitrobenzene by Titania Binding on Quartz Tube. *Inter. J. Photoenergy* **2012**, 1–8. <https://doi.org/10.1155/2012/681941>.
- [64] Mishra, A.; Mehta, A.; Sharma, M.; Basu, S. Impact of Ag nanoparticles on photomineralization of chlorobenzene by  $\text{TiO}_2$ /bentonite nanocomposite. *J. Environ. Chem. Eng.* **2017**, *5*, 644–651. <https://doi.org/10.1016/J.JECE.2016.12.042>.
- [65] Shen, X. -Z.; Liu, Z. -C.; Xie, S. -M.; Guo, J. Degradation of Nitrobenzene using Titania Photocatalyst Co-doped with Nitrogen and Cerium under Visible Light Illumination. *J. Hazard. Mater.* **2009**, *162*, 1193–1198. <https://doi.org/10.1016/j.jhazmat.2008.06.004>.
- [66] Tayade, R. J.; Kulkarni, R. G.; Jasra, R. V. Photocatalytic Degradation of Aqueous Nitrobenzene by Nanocrystalline  $\text{TiO}_2$ . *Ind. Eng. Chem. Res.* **2006**, *45*, 922–927. <https://doi.org/10.1021/ie051060m>.
- [67] Shen, X.; Zhu, L.; Wang, N.; Zhang, T.; Tang, H. Selective Photocatalytic Degradation of Nitrobenzene Facilitated by Molecular Imprinting with a Transition State Analog. *Catal. Today.* **2014**, *225*, 164–170. <https://doi.org/10.1016/j.cattod.2013.07.011>.