

## Advanced oxidation processes (AOPs) coupled with nanocatalysts for wastewater remediation in Jodhpur, Rajasthan: Optimization and kinetic modeling

Shalini Bhatnagar<sup>1</sup>, Arun Sharma<sup>2</sup>

<sup>1</sup> Research Scholar, Department of Chemistry, School of Basic and Applied Sciences, Career Point University Kota, Rajasthan, India

<sup>2</sup> Research Supervisor, Department of Chemistry, School of Basic and Applied Sciences, Career Point University Kota, Rajasthan, India

### Abstract

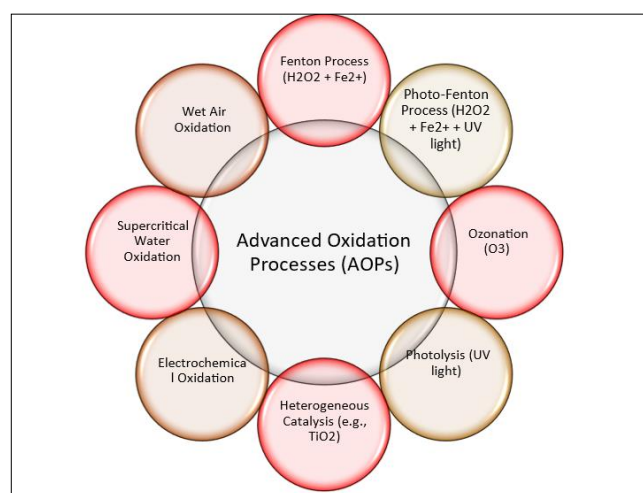
Wastewater remediation is a critical environmental challenge, particularly in arid regions like Jodhpur, Rajasthan, in which industrial and domestic effluents heavily impact on water quality. Advanced Oxidation Processes (AOPs), particularly Fenton and photo-Fenton processes enhanced with titanium dioxide (TiO<sub>2</sub>), were employed to optimize the treatment of wastewater. COD and TOC were analyzed to evaluate treatment performance. Results showed that solar TiO<sub>2</sub> photocatalysis achieved COD and TOC removal efficiencies of 45.5% and 50.1%, respectively, while the photo-Fenton process demonstrated higher removal efficiencies of 51.2% for COD and 55.3% for TOC. The study highlighted the superior performance of photo-assisted processes compared to dark mechanisms, particularly for TiO<sub>2</sub>-based catalysis, due to the enhanced generation of reactive hydroxyl radicals under light irradiation. Furthermore, acidic conditions in the pH range of 3 to 5.5 were found to significantly improve pollutant degradation for both photocatalysis and photo-Fenton processes. Kinetic analysis confirmed that COD and TOC degradation followed a pseudo-first-order model, indicating that the degradation rate is dependent on pollutant concentration and decreases exponentially over time. Overall, the photo-Fenton process emerged as the most effective treatment method, showcasing its potential as a sustainable and efficient approach for addressing complex wastewater challenges in regions like Jodhpur.

**Keywords:** Advanced Oxidation Processes (AOPs), nano catalysts, Kinetic modeling, fenton process, photocatalysis, Titanium dioxide (TiO<sub>2</sub>) and Graphene oxide (GO)

### Introduction

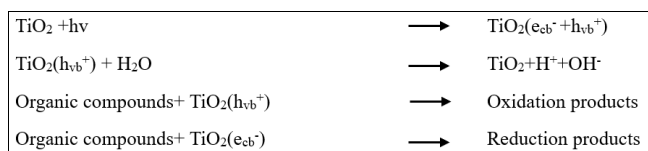
Industrial civilization represents a significant milestone in human development, but it has led to the generation of substantial amounts of industrial wastewater during production processes (Ai *et al.*, 2018) [1]. The rapid pace of industrialization has caused severe environmental harm, posing threats to human health and sustainable development. This issue is particularly acute in developing countries, which bear the brunt of processing and producing primary raw materials. These regions often face higher pollution levels due to the greater discharge and intensity of pollutants from raw material production compared to refined chemical processes (Hegab *et al.*, 2015) [16]. However, the lack of advanced treatment technologies and adequate funding exacerbates the problem. Industrial production not only consumes vast quantities of fresh water but also discharges wastewater containing high concentrations of refractory organic contaminants, salts, and toxic substances. While conventional treatment methods like evaporation, advanced oxidation, adsorption, and aerobic biochemical treatment are effective, they are often associated with significant energy consumption, carbon emissions, high costs, and the generation of hazardous waste. Moreover, these methods lack environmental sustainability and fail to address the pressing need for eco-friendly wastewater management solutions (Xu *et al.*, 2014) [11]. The focus now shifts to advanced oxidation processes (AOPs) as a sustainable and efficient solution for wastewater treatment. It has been garnered increasing attention in wastewater treatment research over the past two decades. Techniques

such as cavitation, photocatalytic oxidation, Fenton, and ozonation have successfully degraded recalcitrant organic pollutants at the laboratory scale. Both homogeneous and heterogeneous AOPs have been well-studied; however, the activation of these processes using ultraviolet (UV) light or concentrated oxidants can pose risks to aquatic life. Efficient AOPs aim for complete mineralization of organic dyes, yet some photocatalytic reactions may produce colorless intermediates that are more toxic than the original compounds (Fig-1).

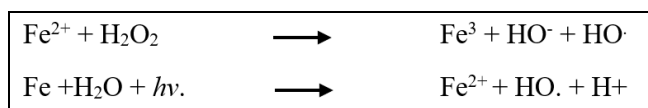


**Fig 1:** Numerous studies have employed microsized catalysts for organic degradation, only a limited number have explored nanomaterials as nanophotocatalysts in AOPs

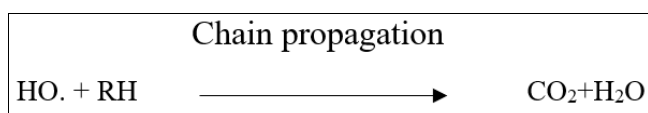
Membrane filtration, adsorption, flocculation/coagulation, and advanced oxidation processes (AOPs), are widely used for treating industrial and petroleum refinery wastewater. Among these, AOPs such as photo-Fenton and photocatalytic degradation have emerged as effective methods due to their ability to mineralize organic compounds, breaking them down into harmless byproducts (Singh & Kumar 2020) [10]. The use of natural solar light or artificial UV light enhances the efficiency of these processes, particularly in the removal of chemical oxygen demand (COD), dyes, and other targeted contaminants (Leong and Bashah 2012) [7]. Different metal oxides, including TiO<sub>2</sub>, ZnO, MgO<sub>3</sub>, ZnS, and CdS, serve as photocatalysts in these processes. Among these, TiO<sub>2</sub> is the most commonly used semiconductor due to its excellent properties, such as safety, resistance to photo-corrosion, high catalytic efficiency, and reliable absorption of light, making it a highly effective photocatalyst for degrading organic pollutants in aqueous solutions (Ali *et al.*, 2020).



With h<sub>vb</sub><sup>+</sup> and e<sub>cb</sub><sup>-</sup> are the charge carrier of valance band hole and conduction band electron (e<sub>CB</sub><sup>-</sup>), respectively. Furthermore, the mechanism of generating the hydroxyl radicals in photo Fenton can be generalized as follow:



In the presence of organic matter, the hydroxyl radicals will react with it, giving the rise to further oxidize harmless products as follows:



Although some research has been devoted to pollutant degradation using oxidation processes, the treatment of raw PRW using photo-Fenton and photocatalysis considering their comparison under specific operating conditions still need to be further investigated.

### Material and Methods

Wastewater samples were collected from the industrial and domestic area of Jodhpur. Sample were collected in sampling bottle and placed in icebox to preserve the properties of wastewater and were analyzed Environmental Analytical research solution Pvt Ltd Gulmohar Colony, Bhopal Madya Predesh. Water sample was filtered through a sieve to remove solid particles greater than a millimeter in size. After analysis, the filtered sample was then placed in the laboratory fridge at a temperature of less than 40C to minimize deterioration. pH, TOC, COD and turbidity was analyzed (Table-1).

**Table 1**

Optimization Parameters	Value
pH	9.5
Turbidity	7.6
COD (mg/L)	859
TOC (mg/L)	150



**Fig 2:** Wastewater of Domestic area

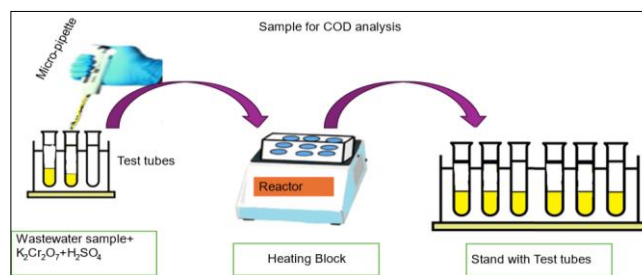


**Fig 3:** Wastewater of Industry area

### Chemicals and Instruments:

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)- 30%  
 Hydrochloric acid (HCl)- 32%  
 Ferrous sulfate hydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O)- 99%  
 TiO<sub>2</sub>-P25-99.7%

COD concentration was measured using a HACH DRB200 reactor, a DR890 colorimeter, and HACH COD reagent vials (HR range: 0-1500 mg/L) supplied by Rowe, following the guidelines outlined in the standard method 5220 D procedure handbook (Zulaikha *et al.*, 2014) [12]. The TOC concentration was analyzed using a Shimadzu TOC-V CPH analyzer, ensuring precise measurement of total organic carbon levels.



**Fig 4:** Chemical oxygen demand (COD) major organic compounds in water. It indicates the oxygen demand required to oxidize organic matter present in wastewater, which is critical for understanding the level of pollution

### Batch experiment

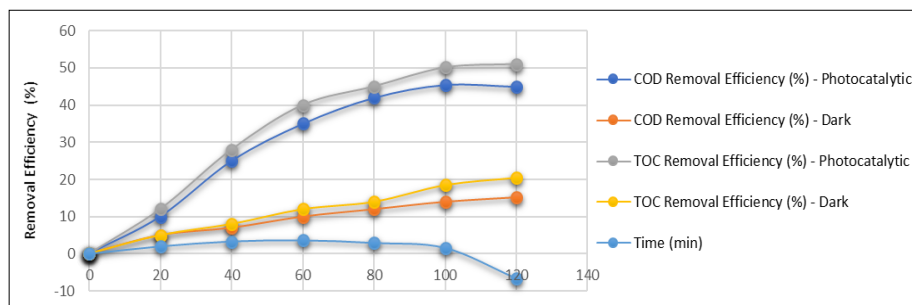
All experiments were conducted in a 300 mL glass beaker, functioning as a batch-mode reactor equipped with a magnetic stirrer. A solar simulator with a light intensity of 1000 mW/cm<sup>2</sup> served as the irradiation light source. Samples were withdrawn from the batch reactor at specific intervals using a gas-tight syringe and filtered through a 0.50 μm PVDF membrane syringe prior to TOC and COD

analysis. TOC and COD concentrations were employed as standard parameters to evaluate treatment efficiency.

## Result and Discussion

**Irradiation and reaction time:** The results show that light irradiation significantly enhances the photocatalytic efficiency of TiO<sub>2</sub>, achieving COD and TOC removal efficiencies of 45.5% and 50.1%, respectively, within 100 minutes. In comparison, the dark catalytic reaction under

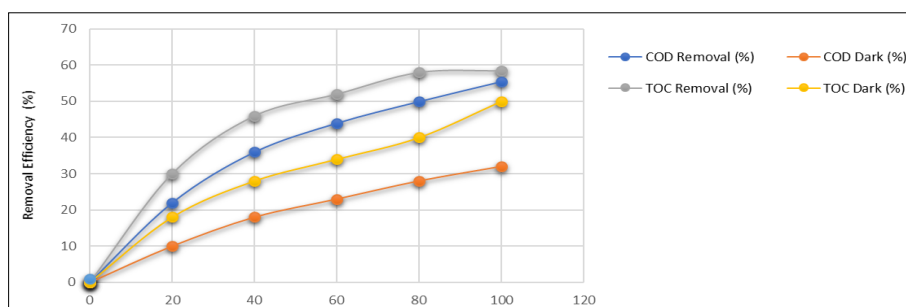
identical conditions reached only 14% COD and 18.5% TOC removal. The removal efficiency increased rapidly during the first 60 minutes before plateauing. Solar irradiation plays a vital role as an energy source, facilitating the breakdown of organic and inorganic pollutants through photogenerated holes on TiO<sub>2</sub> nanoparticles. These holes interact with OH<sup>-</sup> or H<sub>2</sub>O to produce OH radicals, which are key agents in degrading organic compounds and reducing COD and TOC levels (Figure-5).



**Fig 5:** Illustrates the impact of irradiation and reaction time on COD and TOC removal efficiencies for dark and photocatalytic treatments under optimized conditions (pH = 3.5, TiO<sub>2</sub> = 1 g/L)

Aljoubury *et al.*, 2020 optimized the ZnO/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> photocatalytic process under visible light, achieving 36.5% TOC removal from petroleum wastewater at pH 5.5, reducing the treatment period by 200%. The process is cost-effective, sustainable, and compliant with effluent standards. While Martini *et al.*, 2021 observed that solar TiO<sub>2</sub>

photocatalysis, Fenton, and photo-Fenton for PRW treatment, achieving maximum COD and TOC removal efficiencies of 54.1% and 59.1% with photo-Fenton. Acidic conditions (pH 3–5) and photo-assisted processes significantly enhanced degradation, following a pseudo-first-order kinetic model.



**Fig 6:** Effect of irradiation and reaction time on removal efficiency for Fenton and photo-Fenton processes (pH = 3.5, H<sub>2</sub>O<sub>2</sub> = 1 g/L, FeSO<sub>4</sub>·7H<sub>2</sub>O = 1 g/L)

In photo-Fenton process, involves light irradiation, achieves significantly higher removal efficiencies compared to the dark Fenton process. Specifically, the photo-Fenton process reaches a COD removal efficiency of 50.5% and a TOC removal efficiency of 58.5%, whereas the dark Fenton process achieves only 32% and 50%, respectively. This highlights the critical role of light irradiation in enhancing the generation of reactive hydroxyl radicals (•OH), which accelerate the degradation of pollutants. Both COD and TOC removal efficiencies increase rapidly during the initial 60 minutes of the reaction, indicating a higher reaction rate in the early phase. However, the rate of pollutant removal slows down after 60 minutes, likely due to the reduction in pollutant concentration over time. Additionally, TOC removal efficiency remains consistently higher than COD, suggesting a more effective breakdown and mineralization of organic matter. Overall, the graph emphasizes the superiority of the photo-Fenton process over the dark Fenton process, as light irradiation significantly enhances pollutant degradation. This makes the photo-Fenton process

a more efficient and sustainable option for wastewater treatment (Rao & Shrivastava, 2020).

## pH

The study explored the impact of pH on the performance of TiO<sub>2</sub> photocatalysis and Fenton processes, with and without solar light, for removing COD and TOC. It was found that acidic conditions were more favorable for the oxidation process, enhancing the mineralization of both organic and inorganic contaminants. For TiO<sub>2</sub> photocatalysis, the best performance occurred at pH 4, with COD and TOC removal efficiencies of 25% and 22%, respectively. Slightly lower efficiencies were observed at pH 8. In contrast, the photo-Fenton process performed best at pH 3, achieving COD removal of 48% and TOC removal of 44%. At the initial pH 9, both processes showed significantly lower removal efficiencies. The study suggested that the electrostatic interaction between the active sites of the semiconductor and the pollutant molecules, which influences the interaction between hydroxyl radicals and contaminants, contributed to the better performance at lower pH for TiO<sub>2</sub>

photocatalysis. Overall, the results demonstrated that pH 3 is optimal for both Fenton and photo-Fenton processes, while pH 5 is better suited for solar TiO<sub>2</sub> photocatalysis. In contrast, at an initial pH of 9, the removal efficiency of both COD and TOC was notably reduced. This decline in

efficiency during the photocatalytic reaction may be attributed to unfavorable surface interactions between the semiconductor material and pollutant molecules, which hinder the effective generation and interaction of hydroxyl radicals with contaminants (Elmolla and Chauduri 2010) [4].

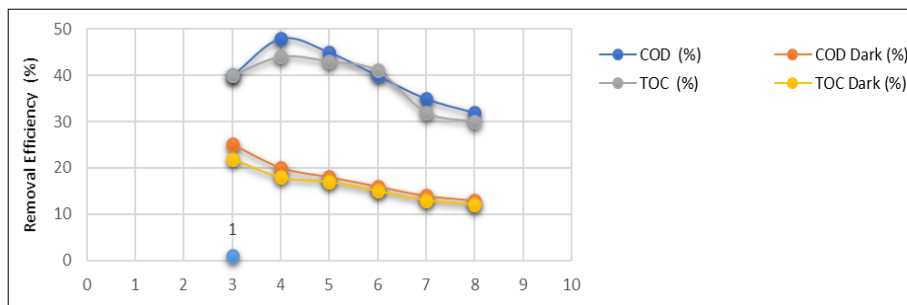


Fig 7: Effect of pH on removal efficiency for dark and photo catalytic treatment (t = 60 min, TiO<sub>2</sub> = 1 g/L)

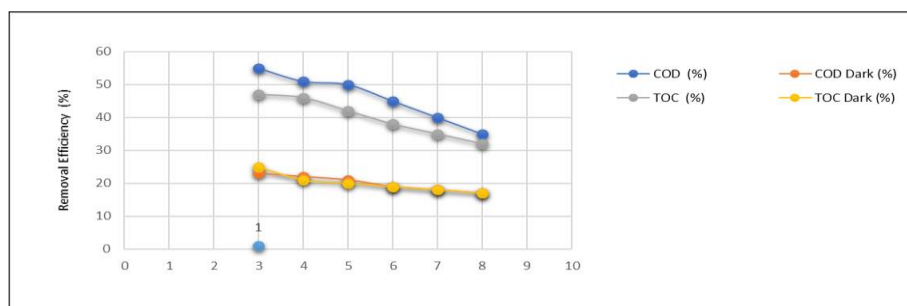


Fig 8: Effect of pH on removal efficiency for fenton and photo fenton (t=60 min, H<sub>2</sub>O<sub>2</sub>=1 g/L, FeSO<sub>4</sub>.7H<sub>2</sub>O=1 g/L)

**Kinetics Degradation:** For a pseudo-first-order reaction, the rate equation is:

$$\left(\frac{C_0}{C_t}\right) = k \cdot t$$

Where:

- C<sub>0</sub> is the initial concentration at t = 0,
- C<sub>t</sub> is the concentration at time t,
- k is the first-order rate constant (in min<sup>-1</sup>),
- t is the time in minutes.

From the experimental data in the figure, the relationship between time and the natural logarithm of the concentration ratio (ln(C<sub>0</sub>/C<sub>t</sub>)) is plotted (Fenoll, *et al.*, 2012 [5]; Oller, *et al.*, 2006) [9].

After plotting the data points for COD and TOC removal, the slope of the linear regression line for COD removal (photo-Fenton) comes out to be 0.051 min<sup>-1</sup>, and for TOC removal (photo-Fenton), it is 0.040 min<sup>-1</sup>.

For pseudo-second-order kinetics, the rate equation is:

$$\frac{1}{C_1} = \frac{1}{C_0} + k \cdot t$$

Where:

- C<sub>t</sub> is the concentration at time t,
- C<sub>0</sub> is the initial concentration,
- k is the second-order rate constant (in L/min·mg),
- t is the time.
- From the second-order plot of 1/C<sub>t</sub> vs time, the slope represents the second-order rate constant k. For the given data:

- The slope of the plot for COD removal (photo-Fenton) comes out to be 0.0098 L/min·mg,
- The slope for TOC removal (photo-Fenton) is 0.011 L/min·mg.

#### Rate Constants Calculation from the Graphs:

1. For Pseudo-First-Order Kinetics:

COD (photo-Fenton) rate constant k COD = 0.051 min<sup>-1</sup>

TOC (photo-Fenton) rate constant k TOC = 0.040 min<sup>-1</sup>

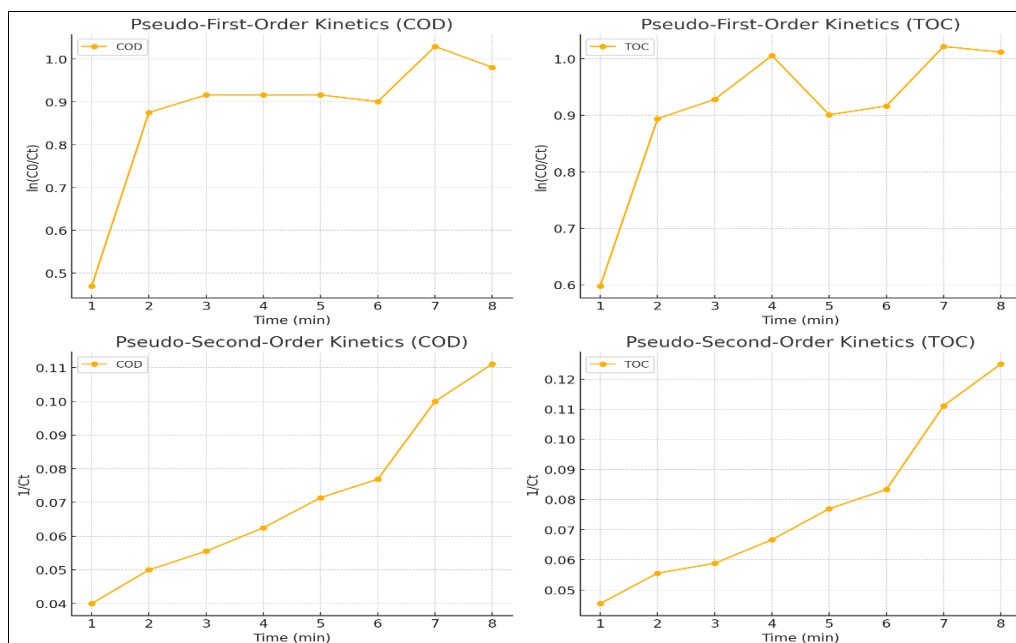
2. For Pseudo-Second-Order Kinetics:

COD (photo-Fenton) rate constant k COD = 0.0098 L/min·mg

TOC (photo-Fenton) rate constant k TOC = 0.011 L/min·mg

#### Interpretation of the Data

The first-order rate constant for COD removal is higher than that for TOC, suggesting that COD is degraded at a faster rate than TOC under photo-Fenton conditions. The pseudo-second-order model provides a better fit in many cases, especially when the reaction depends on the concentration of the contaminant. The second-order rate constants for COD and TOC show a lower reaction rate in comparison to the first-order model, indicating a different reaction mechanism, potentially influenced by concentration-dependent interactions. These rate constants and model fits help in understanding the dynamics of the degradation process and are crucial for optimizing operational parameters in practical applications like wastewater treatment.



**Fig 9:** The pseudo-first-order model shows an exponential decay in concentration, and the rate constant  $k$  reflects the speed of the degradation process

These findings confirm the potential of advanced oxidation processes (AOPs) coupled with nanocatalysts for the effective remediation of complex wastewater, contributing to sustainable water management solutions in urban and industrial areas like Jodhpur, Rajasthan.

### Conclusion

This study demonstrates that Advanced Oxidation Processes (AOPs) coupled with nanocatalysts, such as  $\text{TiO}_2$ , are highly effective for treating industrial and domestic wastewater, particularly in removing heavy metals. The initial characterization of wastewater from Jodhpur, Rajasthan, showed high levels of pollution, necessitating robust treatment methods. AOPs, including Fenton and photo-Fenton processes, were optimized to achieve high degradation efficiencies, with kinetic modeling and parameter adjustments enhancing performance. The results suggest that light irradiation has a more significant impact on the removal efficiency of COD and TOC in  $\text{TiO}_2$  photocatalysis compared to the Fenton/photo-Fenton processes. However, light irradiation also enhances the efficiency of the photo-Fenton reaction by promoting hydroxyl radical formation. Furthermore, acidic conditions, particularly within the pH range of 3 to 4, were identified as optimal for generating hydroxyl radicals, which play a crucial role in mineralizing organic and inorganic contaminants in the raw industrial solution. Despite these challenges, the study underscores the environmental benefits of AOPs in reducing pollution and supporting water reuse, particularly in water-scarce areas like Rajasthan. Future research should focus on scaling up these processes and integrating them with sustainable, cost-effective technologies for broader application.

### Reference

1. Ai J, Yang L, Liao G, Xia H, Xiao F. Applications of graphene oxide blended poly (vinylidene fluoride) membranes for the treatment of organic matters and its membrane fouling investigation. *Appl Surf Sci*,2018;455:502-12. doi:10.1016/j.apsusc.2018.05.162
2. Ali A, Shoeb M, Li Y, Li B, Khan MA. Enhanced photocatalytic degradation of antibiotic drug and dye pollutants by graphene-ordered mesoporous silica (SBA 15)/ $\text{TiO}_2$  nanocomposite under visible-light irradiation. *J Mol Liq*,2021;324:114696. doi:10.1016/j.molliq.2020.114696
3. Aljuboury DA al deen A, Shaik F. Assessment of  $\text{TiO}_2/\text{ZnO}/\text{H}_2\text{O}_2$  photocatalyst to treat wastewater from oil refinery within visible light circumstances. *S Afr J Chem Eng*,2021;35:69-77. doi:10.1016/j.sajce.2020.11.004
4. Elmolla ES, Chaudhuri M. Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/ $\text{TiO}_2$  and UV/ $\text{H}_2\text{O}_2/\text{TiO}_2$  photocatalysis. *Desalination*,2010;252(1-3):46-52.
5. Fenoll J, Flores P, Hellín P, Martínez CM, Navarro S. Photodegradation of eight miscellaneous pesticides in drinking water after treatment with semiconductor materials under sunlight at pilot plant scale. *Chem Eng J*,2012;204-206:54-64. doi:10.1016/j.cej.2012.07.077
6. Hegab HM, Wimalasiri Y, Ginic-Markovic M, Zou L. Improving the fouling resistance of brackish water membranes via surface modification with graphene oxide functionalized chitosan. *Desalination*,2015;365:99-107. doi:10.1016/j.desal.2015.02.029
7. Leong SK, Bashah NAA. Kinetic Study on COD Removal of Palm Oil Refinery Effluent by UV-Fenton. *APCBEE Procedia*,2012;3:6-10. doi:10.1016/j.apcbee.2012.06.037
8. Manna M, Sen S. Advanced oxidation process: a sustainable technology for treating refractory organic compounds present in industrial wastewater. *Environ Sci Pollut Res*,2022;30(10):25477-505. doi:10.1007/s11356-022-19435-0
9. Oller I, Gernjak W, Maldonado MI, Pérez-Estrada LA, Sánchez-Pérez JA, Malato S. Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale. *J Hazard Mater*,2006;138(3):507-17. doi:10.1016/j.jhazmat.2006.05.075

10. Singh B, Kumar P. Pre-treatment of petroleum refinery wastewater by coagulation and flocculation using mixed coagulant: Optimization of process parameters using response surface methodology (RSM). *J Water Process Eng*,2020;36:101317. doi:10.1016/j.jwpe.2020.101317
11. Xu X, Zhang Y, Yekeen TA, Li Y, Zhuang B, Huo X. Erratum to: Increase male genital diseases morbidity linked to informal electronic waste recycling in Guiyu, China. *Environ Sci Pollut Res*,2014;21(19):11610-10. doi:10.1007/s11356-014-3114-2
12. Zulaikha S, Lau WJ, Ismail AF, Jaafar J. Treatment of restaurant wastewater using ultrafiltration and nanofiltration membranes. *J Water Process Eng*,2014;2:58-62. doi:10.1016/j.jwpe.2014.05.001