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Heterogeneous Photo-Fenton-like Degradation of Oxytetracycline Containing Wastewater

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Research Article

Abstract − Oxytetracycline (OTC) is a commonly used antibiotic. It can be absorbed to a limited extent by both humans and animals, so it can be detected at various levels in different water sources. Its presence in rivers or water and wastewater streams can pose serious problems for human and environmental health, and therefore, it needs to be treated. OTC degradation was studied using iron-doped g-C_3N_4 through a photo-Fenton-like oxidation process under simulated sunlight. In this study, the effects of key reaction parameters such as pH (3, 6, 9), catalyst amount (0-0.8 g/L), initial hydrogen peroxide concentration (HP, 0-20 mM) on the degradation of oxytetracycline were studied. The optimal reaction conditions for OTC degradation were found to be pH=6, catalyst amount of 0.4 g/L, and HP of 10 mM. Subsequently, the temperature effect was examined at the optimum reaction conditions. Based on the results, at 25, 35, and 45 °C, OTC degradation was found to be 51.1%, 60.8%, and 76.7%, respectively. The kinetic study conducted revealed that the observed reaction follows a second-order reaction kinetic model. In addition, the activation energy of observed reaction was found to be 86.96 kJ/mol.

Keywords − *Oxytetracycline, Fe doped g-C_3N_4, photocatalysis, kinetic study*

1. Introduction

Due to the common use of oxytetracycline (OTC) in veterinary medicine, agriculture, aquaculture, and horticulture, residues of OTC have been detected in various water flows, including natural surface waters (up to 200 ppb with a detection frequency of up to 90%) and wastewater treatment effluents (ranging from 0.061 to 23.6 ppb). Additionally, it has been found in vegetable farm soils and livestock, with concentrations reaching up to 2.98 mg/kg. OTC is acutely toxic, posing a threat to ecosystems and human health. Its limited absorption by animals and humans allows it to be excreted into the environment. Therefore, its widespread existence in the environment and its harmful effects on human and environmental health have led to the search for various ways to remove this harmful compound [1-3].

Advanced Oxidation Processes (AOPs) offer an alternative approach for breaking down recalcitrant compounds into biologically degradable compounds. Considering the studies in the literature, heterogeneous systems are found to be highly efficient in degrading organic compounds. Solar-Fenton-like oxidation, subset of AOPs, offers several advantages, including low-cost, high removal rate, easy operation, and capability to stimulate complete mineralization [4,5]. Thanks to these noteworthy properties, it has garnered interest, and it could be used to degrade oxytetracycline. Graphitic carbon nitride (CN) is sensitive to visible light owing to its narrow bandgap energy (~2.7 eV) and possesses some prominent features such as non-toxicity, low cost,

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and chemical stability. Bandgap tuning can be achieved through metal doping, thereby enhancing the removal efficiency [6-9]. Therefore, metal-doped CN has become a promising photocatalyst to remove recalcitrant compounds under sunlight.

In this study, the aim was to remove OTC-containing wastewater in the presence of iron-doped graphitic carbon nitride (FeCN) containing 5% Fe under simulated sunlight. Within this scope, the impact of pH, catalyst amount, initial hydrogen peroxide concentration, and temperature on degradation efficiency was examined, and optimum reaction conditions were determined. Additionally, a kinetic study was conducted.

2. Materials and Methods

The chemicals, namely, urea, iron (III) chloride, NaOH, HCl, and H_2O_2 (HP), utilized during the experimental study were purchased from Sigma Aldrich. Oxytetracycline hydrochloride (OTC) was purchased from Doğa İlaç.

Catalyst preparation: Metal-doped CN (Fe/g-C_3N_4) was synthesized based on the following procedure: To synthesize 5w.% iron containing Fe/g-C_3N_4 (5FeCN), urea (20 g) and the needed amount of iron (III) chloride to obtain 5FeCN were put in a ceramic pot and then, it placed into a muffle oven. Then, N_2 atmosphere was created by feeding N_2 into the oven. Then, the mixture underwent heating to 550 °C at 30-minute intervals. Upon reaching 550 °C, it was maintained at 550 °C for a duration of 3 hours. Subsequently, it was gradually cooled to 25 °C. Following this, the solid residue underwent a washing process using ultrapure water. Then, it was filtered to separate the final residue and dried at 25 °C [10]. A characterization study was carried out by SEM (FEI QUANTA 250 FEG model) with 1000x magnification and BET (Micromeritics ASAP 2010) analyses. The catalysts (CN and 5FeCN) were coated with Au/Pd before SEM analysis, and they were degassed at 300 °C for 2 h before BET analysis. BET surface areas were determined at 77 K using a multipoint BET method.

The experimental study was performed using 10 ppm OTC solution (100 mL) for a duration of 1 h under simulated solar light illumination. In this context, a typical experiment was carried out as follows: 10 ppm OTC solution (100 mL) was placed into the beaker without any pH adjustment and then, the desired amount (i.e., 0.1 g/L) of 5FeCN and the desired amount of HP (i.e., 10 mM) were added. After that, the solar light was turned on to start the reaction. Every ten minutes throughout the reaction, liquid samples (2 mL) were collected by taking from the beaker. In the experimental study, the impact of reaction parameters such as pH (3-9), HP (0-20 mM), and catalyst amount (0-0.8 g/L) was investigated to find the optimum reaction conditions for OTC removal %. A spectrophotometer (Spectroquant® NOVA 400 spectrophotometer) was used to analyze the liquid samples.

The removal of OTC was assessed by monitoring the reduction in its distinctive absorption band, situated at 275 nm. The diminishing intensity of this band suggests the opening of rings containing N-groups during the course of the reaction.

$$\%\ \text{Degradation of OTC} = \frac{A_{0_{at\ 275\ nm}} - A_{t_{at\ 275\ nm}}}{A_{t_{at\ 275\ nm}}} \times 100$$

The investigation into the kinetics was conducted under optimal reaction conditions at temperatures of 25, 35, and 45 °C. The gathered data was then scrutinized using both first and second-order reaction kinetic models.

3. Results and Discussion

SEM analysis was employed to determine morphological changes and SEM diagrams of pristine CN and 5FeCN are given in Figure 1. Whereas CN exhibited a substantial layered structure, 5Fe-CN exhibited a sheet-like structure reminiscent of CN, indicating that the incorporation of iron did not induce any alteration in the CN structure. This observation aligns with similar morphologies reported in the literature [11-13]. BET surface area of 5FeCN was found as 3.01 m^2/g. Comparatively, literature sources have reported BET areas for FeCN (0-1 wt.% Fe) ranging between 3.404 and 5.4 m^2/g for various iron concentrations [14]. Thus, it could be deduced that 5FeCN was successfully synthesized.

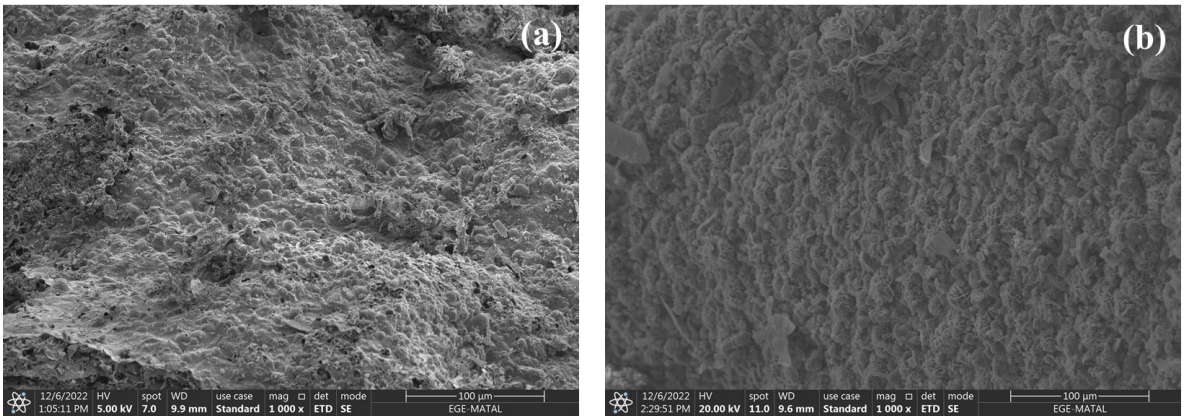

Figure 1. SEM diagrams of CN (a) and 5FeCN (b)

After the characterization study, the effect of reaction parameters was investigated to determine the optimum reaction conditions for OTC removal under simulated solar light illumination. Firstly, the effect of catalyst amount was investigated at different amounts of 5FeCN varied between 0 and 0.8 g/L, and the results are given in Figure 2. OTC degradation efficiency enhanced by increasing the amount of catalyst up to 0.4 g/L and almost the same degradation efficiency was achieved for 0.4 and 0.8 g/L of catalyst amounts. The highest degradation (51.1%) was obtained using 0.4 g/L of 5FeCN and therefore, the optimum catalyst loading was selected as 0.4 g/L and then, the effect of HP was investigated using 0, 5, 10 and 20 mM of HP, and the results are given in Figure 3.

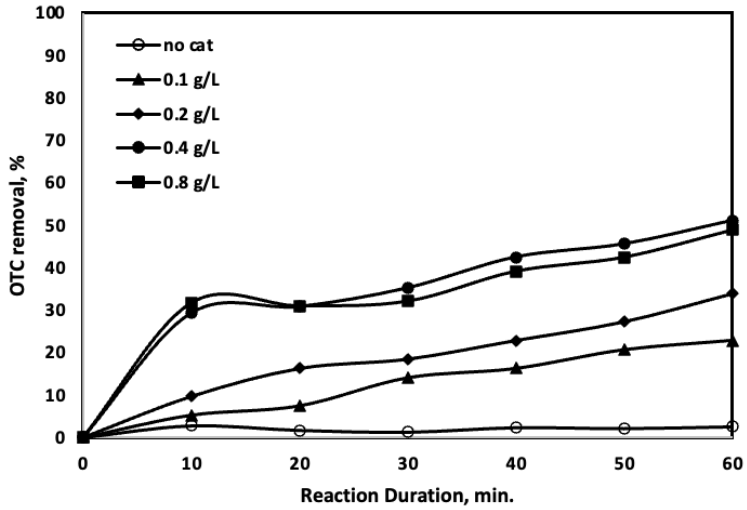

Figure 2. Effect of catalyst amount (Reaction conditions: 10 ppm OTC, pH=6, HP=10 mM)

Based on the results, the lowest efficiency (~12%) was achieved in the absence of HP on the other hand the highest efficiency was observed as 51.1% using 10 mM of HP. HP is an electron acceptor and it is better than

the molecular oxygen. It led to a decrease in the rate of electron-hole recombination and hence, an increase in degradation efficiency might be achieved. Furthermore, depending on the wavelength of the incident radiation, HP has the potential to generate hydroxyl radicals through photolytic splitting. It may help prevent oxygen starvation in the wastewater, which could otherwise occur due to insufficient oxygenation or limitations in mass transfer. In addition, the direct reaction of HP with photogenerated holes, along with its adsorption onto the photocatalyst, has the potential to enhance charge transfer rates on the semiconductor surface [15-17]. However, the excess usage of HP (20 mM) caused the scavenging effect and thus, the removal efficiency decreased. Considering the results, the optimum HP concentration was selected as 10 mM.

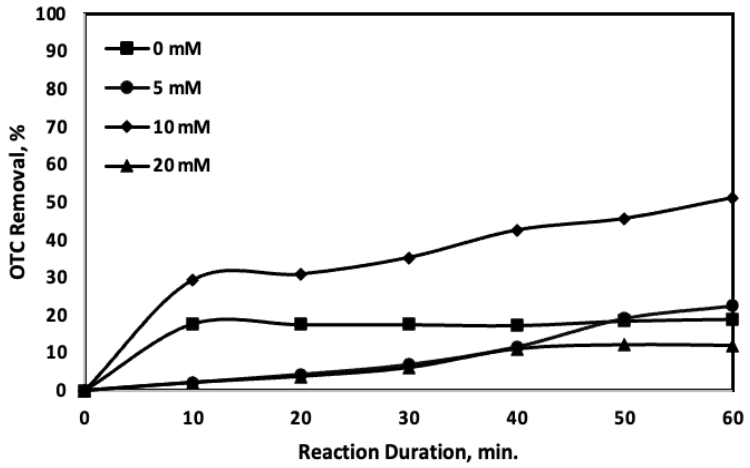

Figure 3. Effect of HP (Reaction conditions: 10 ppm OTC, pH=6, 0.4 g/L 5FeCN)

In photocatalytic degradation of organic pollutants, pH is a key parameter since it might change the ion (H^+ and OH^-) concentration. The change in ion concentration has an impact on the formation of reactive species (i.e., superoxide and hydroxyl radicals, etc.) and it is directly linked to the degradation efficiency of organic pollutants [18]. Therefore, the effect of pH was investigated at pH of 3, 6, and 9, and the results are given in Figure 4. Almost 41% and 51.1% of degradation were achieved at pH=3 and pH=6, respectively. However, 21.7% of OTC degraded at pH=9. pH_{zpc} of 5FeCN was determined as 7.2 and hence, higher degradation efficiency was observed under this value. At pH 6, there is an attraction between negatively charged 5FeCN and positively charged OTC, and thus, the degradation efficiency was high. Consequently, the optimum pH value was chosen as 6.

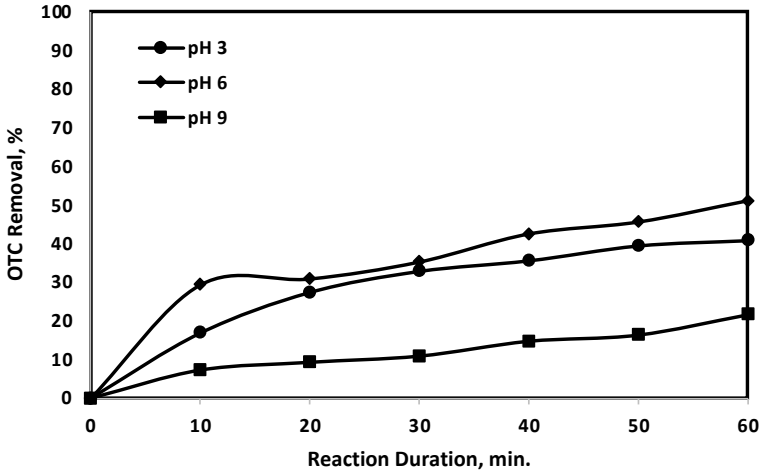

Figure 4. Effect of pH (Reaction conditions: 10 ppm OTC, 0.4 g/L 5FeCN, HP=10 mM)

Following the determination of optimal reaction conditions (pH=6, catalyst amount=0.4 g/L, and HP=10 mM), the kinetic study was conducted at varying reaction temperatures (25, 35, and 45 °C) over a 20-minute reaction duration. To comprehend the nature of OTC degradation, both first and second-order reaction kinetic models were applied. The experimental data show a strong alignment with the second-order reaction kinetic model considering the R^2 values. The linearized form of experimental data is given in Figure 5 and from this figure, the reaction kinetic rate constants of the observed reaction were found as 0.0004, 0.002, and 0.0036 (mg/L/min) for 25, 35, and 45 °C, respectively. From Figure 6, the activation energy of the observed reaction was found as 86.96 kJ/mol. (Figure 6, the gas constant R=8.3145 J/K mol). To understand the impact of temperature on OTC degradation, the reactions lasted for 1 hour, and based on the results, at the end of the 1 hour of reaction duration, 51.1, 60.8%, and 76.7 % of OTC was degraded at 25, 35, and 45 °C, respectively.

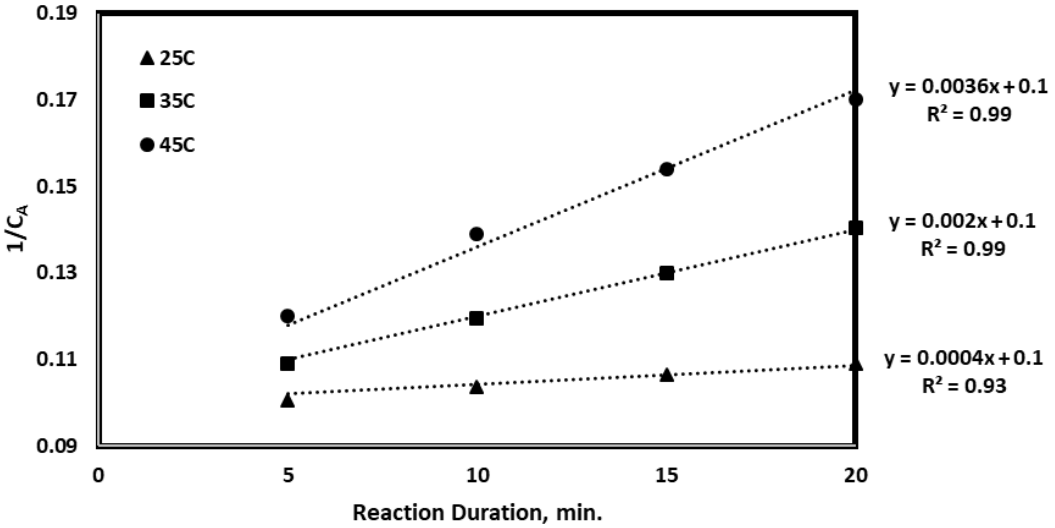

Figure 5. Linearized second-order kinetic plot (Reaction conditions: 10 ppm OTC, 0.4 g/L of 5FeCN, pH 6, 10 mM of HP)

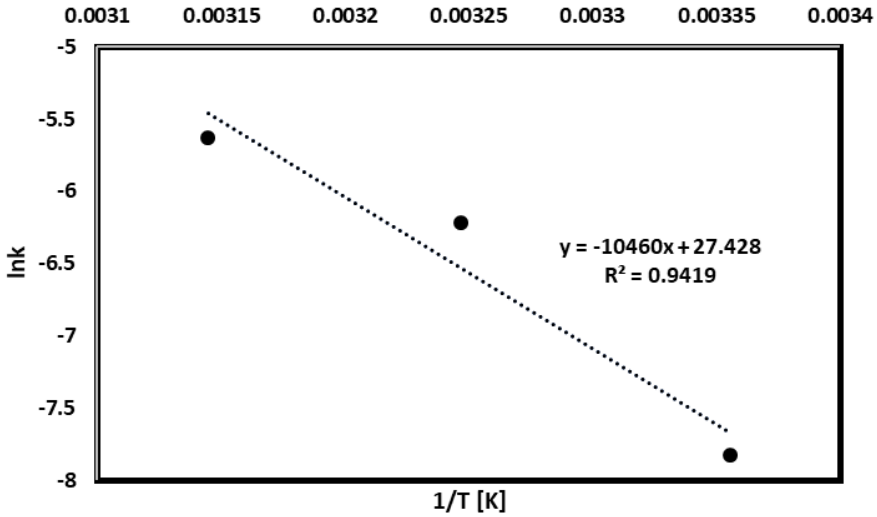

Figure 6. Arrhenius plot

In the literature, various photocatalysts were used to treat OTC. In particular, TiO_2 and TiO_2-based photocatalysts as well as semiconductor oxides were tested. A brief summary is given in Table 1.

Table 1. A brief summary of OTC degradation using various photocatalysts

Photocatalysts	OTC concentration (ppm)	Catalyst amount (g/L)	Degradation (%)	References
TiO_2 nanoflowers	0.5	5	80	[19]
Brown TiO_2 spheres	5	5	~50	[20]
BiOCl/TiO_2 hollow tubes	20	0.5	51	[21]
CdS/TiO_2	40	1	81	[22]
Fe_3O_4	46	0.5	42	[23]
$LaFeO_3$	40	0.5	~50	[24]
ZnO	46	0.5	41	[25]
$NiFe_2O_4$	46	0.5	65	[7]
$MnFe_2O_4$	46	0.5	<50	[26]
CN/$LaFeO_3$ (2%)	40	0.5	90	[24]
CN/$NiFe_2O_4$	46	10	97	[7]
N-ZnO/CdS/GO	20	0.5	50	[27]
Ag(8%)/CN	20	1	81	[28]
Fe(5%)/CN	20	0.4	51.1	This study

In this study, almost the same degradation efficiency was achieved using a relatively lower catalyst amount compared to the used amounts in the literature. For example, almost %50 of OTC degradation was achieved using 5 g/L of brown TiO_2 spheres [20] while 0.4 g/L FeCN was used to obtain almost the same degradation efficiency in this study. %41 of OTC was degraded using 0.5 g/L of ZnO [25] while relatively higher degradation efficiency was obtained in this study. 1 g/L of Ag(%8)/CN was used to treat OTC and %81 of OTC degradation was achieved [28]. However, Ag is an expensive metal so usage of a cheaper metal (iron) could be an alternative solution to treat OTC. Therefore, FeCN could be considered a promising photocatalyst for OTC degradation.

4. Conclusion

OTC is an antibiotic and due to its common usage, the unabsorbed OTC by humans and animals might be detected in different water sources and could threaten human and environmental health. Therefore, it should be treated, and in this study, OTC was degraded via photo-Fenton-like oxidation using 5FeCN under solar light irradiation, and optimum reaction conditions were selected as 6 of pH, 0.4 g/L of catalyst amount (5FeCN), and 10 mM of HP. Then, a kinetic study was conducted at the optimal reaction conditions and the observed reaction followed the second order-reaction kinetic model. In addition, the activation energy for this observed reaction was calculated to be 86.96 kJ/mol. Therefore, FeCN is a promising photocatalyst for the degradation of oxytetracycline.

Author Contributions

The first author performed the experiment and wrote the manuscript. The second author reviewed and edited the paper. All authors read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

References

[1] P. Raizada, P. Shandilya, P. Singh, P. Thakur, *Solar light-facilitated oxytetracycline removal from the aqueous phase utilizing a H2O2/ZnWO4/CaO catalytic system*, Journal of Taibah University for Science 11 (5) (2017) 689–699.

[2] H. Wang, M. Zhang, X. He, T. Du, Y. Wang, Y. Li, T. Hao, *Facile prepared ball-like TiO2 at GO composites for oxytetracycline removal under solar and visible lights*, Water Research 160 (2019) 197–205.

[3] Y. Wang, J. Zhou, W. Bi, J. Qin, G. Wang, Z. Wang, P. Fu, F. Liu, *Schwertmannite catalyze persulfate to remove oxytetracycline from wastewater under solar light or UV-254*, Journal of Cleaner Production 364 (2022) 132572 10 pages.

[4] Y. Jiang, J. Ran, K. Mao, X. Yang, L. Zhong, C. Yang, X. Feng, H. Zhang, *Recent progress in Fenton/Fenton-like reactions for the removal of antibiotics in aqueous environments*, Ecotoxicology and Environmental Safety 236 (2022) 113464 20 pages.

[5] J. Lin, W. Tian, Z. Guan, H. Zhang, X. Duan, H. Wang, H. Sun, Y. Fang, Y. Huang, S. Wang, *Functional carbon nitride materials in photo-fenton-like catalysis for environmental remediation*, Advanced Functional Materials 32 (24) (2022) 2201743 31 pages.

[6] J. Jiang, S. Cao, C. Hu, C. Chen, *A comparison study of alkali metal-doped g-C3N4 for visible-light photocatalytic hydrogen evolution*, Cuihua Xuebao/Chinese Journal of Catalysis 38 (12) (2017) 1981–1989.

[7] A. Sudhaik, P. Raizada, P. Shandilya, P. Singh, *Magnetically recoverable graphitic carbon nitride and NiFe2O4 based magnetic photocatalyst for degradation of oxytetracycline antibiotic in simulated wastewater under solar light*, Journal of Environmental Chemical Engineering 6 (4) (2018) 3874–3883.

[8] E. Fernandes, J. Gomes, R. C., Martins, *Semiconductors application forms and doping benefits to wastewater treatment: A comparison of TiO2, WO3, and g-C3N4*, Catalysts 12 (10) (2022) 1218 42 pages.

[9] Q. Wang, Z. Fang, W. Zhang, D. Zhang, *High-efficiency g-C3N4 based photocatalysts for CO2 reduction: modification methods*, Advanced Fiber Materials 4 (3) (2022) 342–360.

[10] Z. Li, C. Kong, G. Lu, *Visible photocatalytic water splitting and photocatalytic two-electron oxygen formation over Cu- and Fe-doped g-C3N4*, Journal of Physical Chemistry C 120 (1) (2016) 56–63.

[11] J. Hu, P. Zhang, W. An, L. Liu, Y. Liang, W. Cui, *In-situ Fe-doped g-C_3N_4 heterogeneous catalyst via photocatalysis-Fenton reaction with enriched photocatalytic performance for removal of complex wastewater*, Applied Catalysis B: Environmental 245 (2019) 130–142.

[12] T. Ma, Q. Shen, B. Z. J. Xue, R. Guan, X. Liu, H. Jia, B. Xu, *Facile synthesis of Fe-doped g-C3N4 for enhanced visible-light photocatalytic activity*, Inorganic Chemistry Communications 107 (2019) 107451 9 pages.

[13] M. N. Van, O. L. T. Mai, C. P. Do, H. L. Thi, C. P. Manh, H. N. Manh, D. P. Thi, B. D. Danh, *Fe-doped g-c3n4: High-performance photocatalysts in rhodamine b decomposition*, Polymers 12 (9) (2020) 1963 13 pages.

[14] G. Liu, G. Dong, Y. Zeng, C. Wang, *The photocatalytic performance and active sites of g-C 3 N 4 effected by the coordination doping of Fe(III)*, Chinese Journal of Catalysis 41 (10) (2020) 1564–1572.

[15] N. S. Abbood, N. S. Ali, E. H. Khader, H. S. Majdi, T. M. Albayati, N. M. C. Saady, *Photocatalytic degradation of cefotaxime pharmaceutical compounds onto a modified nanocatalyst*, Research on Chemical Intermediates 49 (1) (2023) 43–56.

[16] D. D. Dionysiou, M. T. Suidan, E. Bekou, I. Baudin, J.-M. L. Laîné, *Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water*, Applied Catalysis B: Environmental 26 (3) (2000) 153–171.

[17] R. Ullah, F. Khitab, H. Gul, R. Khattak, J. Ihsan, M. Khan, A. Khan, Z. Vincevica-Gaile, H. A. Aouissi, *Superparamagnetic zinc ferrite nanoparticles as visible-light active photocatalyst for efficient degradation of selected textile dye in water*, Catalysts 13 (7) (2023) 1061 19 pages.

[18] Z. Ur Rahman, U. Shah, A. Alam, Z. Shah, K. Shaheen, S. Bahadar Khan, S. Ali Khan, *Photocatalytic degradation of cefixime using CuO-NiO nanocomposite photocatalyst*, Inorganic Chemistry Communications 148 (2023) 110312 9 pages.

[19] J. Singh, R. K. Soni, *Fabrication of hydroxyl group-enriched mixed-phase TiO2 nanoflowers consisting of nanoflakes for efficient photocatalytic activity*, Journal of Materials Science: Materials in Electronics 31 (15) (2020) 12546–12560.

[20] J. Singh, S. Palsaniya, R. K. Soni, *Mesoporous dark brown TiO2 spheres for pollutant removal and energy storage applications*, Applied Surface Science 527 (15) (2020) 146796 10 pages.

[21] S. Bao, H. Liang, C. Li, J. Bai, *A heterostructure BiOCl nanosheets/TiO2 hollow-tubes composite for visible light-driven efficient photodegradation antibiotic*, Journal of Photochemistry and Photobiology A: Chemistry 397 (2020) 112590 10 pages.

[22] Y. B. Du, L. Zhang, M. Ruan, C. G. Niu, X. J. Wen, C. Liang, X. G. Zhang, G. M. Zeng, *Template-free synthesis of three-dimensional porous CdS/TiO2 with high stability and excellent visible photocatalytic activity*, Materials Chemistry and Physics 212 (2018) 69–77.

[23] P. Raizada, J. Kumari, P. Shandilya, R. Dhiman, V. Pratap Singh, P. Singh, *Magnetically retrievable Bi2WO6/Fe3O4 immobilized on graphene sand composite for investigation of photocatalytic mineralization of oxytetracycline and ampicillin*, Process Safety Environmental Protection 106 (2017) 104–116.

[24] K. Xu, X. Yang, L. Ruan, S. Qi, J. Liu, K. Liu, S. Pan, G. Feng, Z. Dai, X. Yang, R. Li, J. Feng, *Superior adsorption and photocatalytic degradation capability of mesoporous LaFeO3 /g-C3 N4 for removal of oxytetracycline*, Catalysts 10 (3) (2020) 301 18 pages.

[25] P. Raizada, J. Kumari, P. Shandilya, P. Singh, *Kinetics of photocatalytic mineralization of oxytetracycline and ampicillin using activated carbon supported ZnO/ZnWO4 nanocomposite in simulated wastewater*, Desalination and Water Treatment 79 (2017) 204–213.

[26] S. Gautam, P. Shandilya, B. Priya, V. P. Singh, P. Raizada, R. Rai, M. A. Valente, P. Singh, *Superparamagnetic MnFe2O4 dispersed over graphitic carbon sand composite and bentonite as magnetically recoverable photocatalyst for antibiotic mineralization*, Separation and Purification Technology 172 (2017) 498–511.

[27] P. Huo, M. Zhou, Y. Tang, X. Liu, C. Ma, L. Yu, Y. Yan, *Incorporation of N–ZnO/CdS/Graphene oxide composite photocatalyst for enhanced photocatalytic activity under visible light*, Journal of Alloys and Compounds 670 (2016) 198–209.

[28] Z. Ren, F. Chen, K. Wen, J. Lu, *Enhanced photocatalytic activity for tetracyclines degradation with Ag modified g-C3N4 composite under visible light*, Journal of Photochemistry and Photobiology A: Chemistry 389 (2020) 112217 12 pages.