

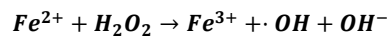
Removal of Pharmaceutical of Emerging Contaminants (Pharmaceuticals) Using Advanced Oxidation Process (Fenton Process)

Sukanya Kadam¹, Laxmi Gupta², Dilip Budhlani³, Manthan Banerjee⁴
PG Scholer¹, Assistant Professor², Assistant Professor³, Assistant Professor⁴
Department of Civil Engineering
Swaminarayan Siddhanta Institute of Technology, Nagpur (MH)

Abstract : The continuous discharge of pharmaceutical compounds into aquatic environments has become a serious environmental concern due to their persistence, bioaccumulation potential, and ecological toxicity. Conventional wastewater treatment plants are not fully effective in removing pharmaceutical micropollutants such as antibiotics, analgesics, and antiparasitic compounds. This study investigates the application of the Fenton Process (Fe^{2+}/H_2O_2) for degradation and mineralization of pharmaceutical contaminants present in clinic greywater collected from Nagpur.

Greywater samples were collected from selected discharge points near Shraddha Clinic, Rameshwari-Manewada region. The collected wastewater was characterized for pH, COD, TOC, turbidity, conductivity, and pharmaceutical concentration using LC-MS/HPLC techniques. The study focused on degradation of selected pharmaceuticals including Enrofloxacin, Oxytetracycline, and Albendazole.

Experimental optimization was performed by varying pH, Fe^{2+} dosage, hydrogen peroxide concentration, and reaction time. The Fenton process showed maximum degradation under acidic conditions around pH 3.



Under optimized conditions, COD removal efficiency reached 89–93%, TOC reduction reached 74–82%, and pharmaceutical degradation exceeded 95% for most target compounds.

Economic analysis indicated that the Fenton process is technically feasible for tertiary wastewater treatment with an estimated operational cost of ₹38–₹58/m³ depending on reagent consumption. The study concludes that the Fenton process can serve as an efficient and scalable treatment method for removal of pharmaceutical emerging contaminants from greywater systems.

Keywords:

Fenton Process, Pharmaceutical Contaminants, Greywater Treatment, Advanced Oxidation Process, Hydroxyl Radicals, COD Removal, TOC Reduction, Wastewater Treatment, Emerging Pollutants

1. INTRODUCTION:

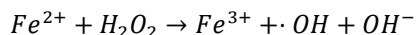
Pharmaceutical compounds are increasingly detected in aquatic environments due to rapid urbanization, healthcare activities, and improper disposal practices. Antibiotics, anti-inflammatory drugs, hormones, and antiparasitic compounds are continuously introduced into wastewater systems through domestic sewage, hospital discharge, and pharmaceutical waste streams. These compounds are categorized as emerging contaminants because their environmental occurrence and ecological impacts are not completely regulated or understood.

In urban regions such as Nagpur, wastewater generated from clinics and healthcare facilities contains significant

concentrations of pharmaceutical residues. Conventional wastewater treatment systems are primarily designed for removal of biodegradable organic matter and suspended solids; however, they are ineffective for complete degradation of complex pharmaceutical molecules.

Advanced Oxidation Processes (AOPs) are considered promising treatment technologies because they generate highly reactive hydroxyl radicals capable of oxidizing refractory organic compounds into simpler and less toxic products. Among various AOPs, the Fenton process is widely studied due to its simplicity, high oxidation potential, low equipment requirement, and rapid degradation efficiency. The Fenton process involves catalytic

decomposition of hydrogen peroxide in the presence of ferrous ions under acidic conditions, producing hydroxyl radicals.



The generated hydroxyl radicals attack pharmaceutical molecules non-selectively, leading to degradation and mineralization.

The present study focuses specifically on optimization and evaluation of the Fenton process for removal of pharmaceutical contaminants from clinic greywater.

2. PROBLEM STATEMENT:

Clinic greywater may contain pharmaceutical residues, disinfectants, organic matter, and other pollutants. In many small healthcare facilities, this wastewater is directly discharged into municipal drains without advanced treatment. Conventional treatment systems are not designed to completely degrade pharmaceutical contaminants.

If untreated pharmaceutical-contaminated greywater is continuously discharged into the environment, it may cause groundwater contamination, aquatic toxicity, antibiotic resistance, and long-term ecological imbalance. Therefore, there is a need for a simple, low-cost, and effective treatment process that can be applied at small healthcare facilities.

The Fenton process can be used as a tertiary treatment method because it requires simple chemicals, produces strong oxidizing radicals, and can be operated at laboratory or small field scale.

3. AIM AND OBJECTIVES:

3.1 Aim

To evaluate and optimize the Fenton process for removal and mineralization of pharmaceutical emerging contaminants from clinic greywater.

3.2 Objectives

- To collect and characterize clinic greywater for pH, COD, TOC, turbidity, conductivity, and pharmaceutical concentration.
- To study the removal of Enrofloxacin, Oxytetracycline, and Albendazole using the Fenton process.
- To optimize pH, Fe^{2+} dosage, H_2O_2 dosage, and reaction time.
- To evaluate COD removal and TOC reduction after treatment.
- To study the degradation kinetics of selected pharmaceutical contaminants.
- To estimate the treatment cost of the Fenton process.
- To assess the suitability of the process for small-scale healthcare wastewater treatment.

4. MATERIALS AND METHODS

4.1 Study Area and Sample Collection

Greywater samples were collected from selected discharge points near Shraddha Clinic, Rameshwari-Manewada region, Nagpur, Maharashtra, India. Samples were collected using the grab sampling method. Amber glass bottles were used for sample collection to reduce the effect of light on pharmaceutical compounds.

After collection, samples were stored in an ice box and transported to the laboratory for analysis. The samples were analyzed within a short time to avoid changes in wastewater characteristics.

4.2 Chemicals Used

The following chemicals were used in the study:

Sr. No.	Chemical & Material	Purpose
1	Ferrous sulphate	Source of Fe^{2+} catalyst
2	Hydrogen peroxide	Oxidizing agent
3	Dilute sulphuric acid / hydrochloric acid	pH adjustment
4	Sodium hydroxide	Neutralization after treatment
5	Distilled water	Preparation of solutions
6	Greywater sample	Wastewater to be treated

4.3 Target Pharmaceutical Compounds

Sr. No.	Pharmaceutical Compound	Type / Class
1	Enrofloxacin	Antibiotic
2	Oxytetracycline	Antibiotic
3	Albendazole	Antiparasitic drug

4.4 Analytical Methods

Parameter	Method / Instrument
pH	Digital pH meter
COD	Closed reflux method
TOC	TOC analyzer
Turbidity	Turbidity meter
Conductivity	Conductivity meter
Pharmaceutical concentration	HPLC / LC-MS
Sludge volume	Settling cone / measuring cylinder

4.5 Experimental Setup

Batch experiments were performed using a 1 L glass reactor or borosilicate beaker. A working volume of 500 mL greywater sample was used for each experimental run. The sample was continuously mixed using a magnetic stirrer. The reaction was carried out under dark conditions to avoid light interference.

The pH of the sample was first adjusted to the required value. After that, ferrous sulphate was added as the Fe²⁺ source, followed by hydrogen peroxide addition. Samples were collected at fixed time intervals for analysis.



Figure 1: Laboratory setup for pH testing

4.6 Experimental Conditions

Parameter	Range Studied
pH	2, 3, 4, 5, 7
Fe ²⁺ dosage	10–50 mg/L
H ₂ O ₂ dosage	100–500 mg/L
Reaction time	0–120 min
Working volume	500 mL
Stirring speed	150 rpm

4.7 Treatment Procedure

1. Collect clinic greywater sample.
2. Analyze initial pH, COD, TOC, turbidity, conductivity, and pharmaceutical concentration.
3. Take 500 mL sample in a glass reactor.
4. Adjust pH to the required value.
5. Add required Fe²⁺ dosage.
6. Add required H₂O₂ dosage.
7. Stir the sample continuously under dark conditions.
8. Collect samples at 0, 15, 30, 60, 90, and 120 minutes.
9. Analyze treated samples for COD, TOC, turbidity, and pharmaceutical concentration.
10. Calculate removal efficiency and treatment cost.

4.8 Removal Efficiency Formula

Removal efficiency was calculated using the following equation:

$$\text{Removal Efficiency (\%)} =$$

$$[(C_i - C_f) / C_i] \times 100$$

Where:

C_i = Initial concentration
 C_f = Final concentration

4.9 Kinetic Analysis

The degradation of pharmaceutical compounds was studied using pseudo-first-order kinetics.

$$\ln(C_0/C) = kt$$

Where:

C₀ = Initial concentration
 C = Concentration at time t
 k = First-order rate constant
 t = Reaction time

4.10 Statistical Analysis

All experiments were performed in triplicate, and the average values were used for result analysis. Microsoft Excel was used for calculation of removal efficiency, preparation of graphs, and kinetic plotting. Linear regression was used to determine the kinetic rate constant and R² value. Statistical significance may be tested using one-way ANOVA at p < 0.05.

5. Results and Discussion

5.1 Initial Characteristics of Clinic Greywater

The collected greywater sample showed high organic load and detectable pharmaceutical contamination.

Table 1. Initial characteristics of clinic greywater

Parameter	Unit	Initial Value
pH	—	7.42
COD	mg/L	1180
TOC	mg/L	425
Turbidity	NTU	326
Conductivity	μS/cm	1915
Enrofloxacin	mg/L	18.4
Oxytetracycline	mg/L	14.2
Albendazole	mg/L	9.6

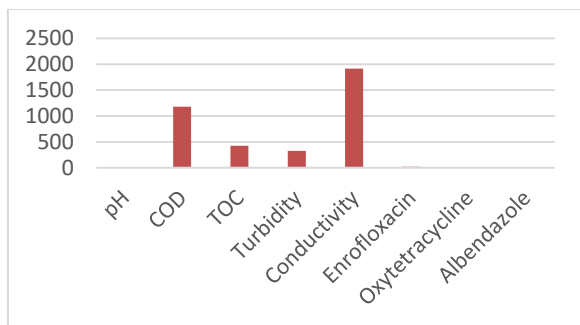


Figure 2: Bar graph showing initial wastewater characteristics.

The initial COD and TOC values indicate the presence of significant organic pollutants in clinic greywater. The detection of Enrofloxacin, Oxytetracycline, and Albendazole confirms the presence of pharmaceutical contaminants.

5.2 Effect of pH on COD Removal

pH plays an important role in the Fenton process because hydroxyl radical generation depends on acidic conditions.

Table 2. Effect of pH on COD removal

pH	COD Removal (%)
2	84.6
3	92.4
4	87.8
5	73.5
7	51.2

Maximum COD removal of 92.4% was observed at pH 3. At pH 3, Fe²⁺ remains active and hydrogen peroxide decomposition produces more hydroxyl radicals. At higher pH, iron may precipitate as ferric hydroxide, reducing the oxidation efficiency.

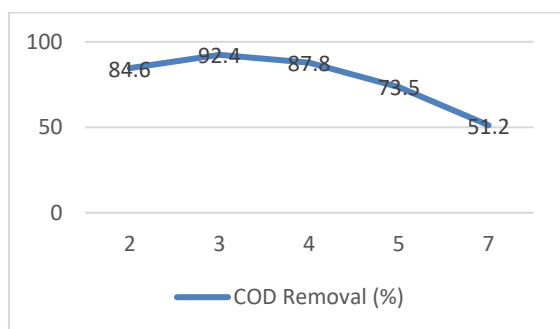


Figure 3: Line graph showing effect of pH on COD removal.

5.3 Effect of Fe²⁺ Dosage

Fe²⁺ acts as a catalyst in the Fenton reaction. The effect of Fe²⁺ dosage was studied from 10 to 50 mg/L.

Table 3. Effect of Fe²⁺ dosage on COD removal

Fe ²⁺ Dosage (mg/L)	COD Removal (%)
10	68.4
20	84.7
30	92.4
40	90.2
50	86.5

COD removal increased with Fe²⁺ dosage up to 30 mg/L. Further increase in Fe²⁺ dosage slightly reduced the efficiency. This may be due to excess Fe²⁺ consuming hydroxyl radicals and increasing sludge generation.

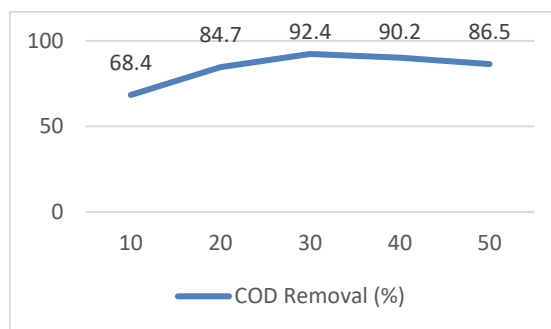


Figure 4: Line graph showing Fe²⁺ dosage versus COD removal.

5.4 Effect of H₂O₂ Dosage

Hydrogen peroxide is the main oxidizing agent in the Fenton process. The effect of H₂O₂ dosage was studied from 100 to 500 mg/L.

Table 4. Effect of H₂O₂ dosage on COD removal

H ₂ O ₂ Dosage (mg/L)	COD Removal (%)
100	64.8
200	82.6
300	92.4
400	91.1
500	88.3

The optimum H₂O₂ dosage was 300 mg/L. At lower dosage, hydroxyl radical generation was insufficient. At higher dosage, excess hydrogen peroxide may act as a radical scavenger, reducing treatment efficiency.

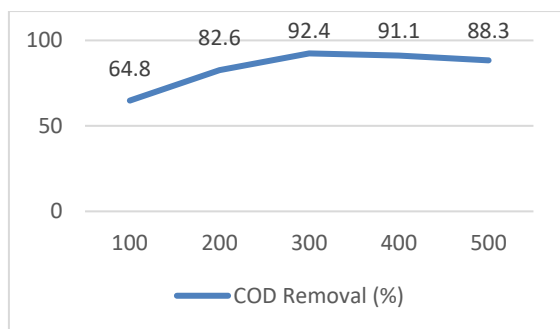


Figure 5: Line graph showing H₂O₂ dosage versus COD removal.

5.5 COD Reduction with Reaction Time

The effect of reaction time was studied from 0 to 120 minutes.

Table 5. COD reduction with reaction time

Time (min)	COD (mg/L)	COD Removal (%)
0	1180	0
15	835	29.2
30	560	52.5
60	248	79.0
90	126	89.3
120	90	92.4

COD concentration decreased from 1180 mg/L to 90 mg/L after 120 minutes. Rapid reduction was observed during the first 60 minutes, indicating fast oxidation of easily degradable organic compounds. After 90 minutes, the reduction rate became slower.

Table 6: COD Reduction with Reaction Time Using Fenton Process

Time (min)	COD Concentration (mg/L)	COD Removal (%)
0	1180	0.0
15	835	29.2
30	560	52.5
60	248	79.0
90	126	89.3
120	90	92.4

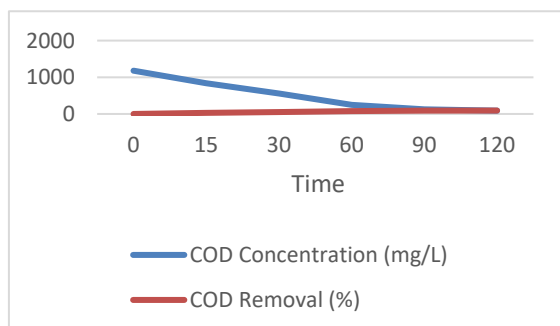


Figure 6: Line graph showing COD Concentration versus Reaction Time

5.6 TOC Reduction and Mineralization

TOC reduction was used to evaluate mineralization of organic pollutants.

Table 6. TOC reduction with reaction time

Time (min)	TOC (mg/L)	TOC Reduction (%)
0	425	0
15	318	25.2
30	228	46.4
60	138	67.5
90	104	75.5
120	86	79.8

TOC concentration decreased from 425 mg/L to 86 mg/L after 120 minutes. The 79.8% TOC reduction indicates significant mineralization of pharmaceutical contaminants and organic matter.

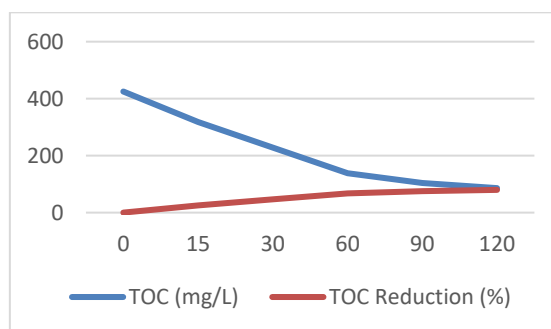


Figure 7: TOC reduction with reaction time.

5.7 Pharmaceutical Degradation Efficiency

The optimized Fenton conditions were pH 3, Fe²⁺ dosage of 30 mg/L, H₂O₂ dosage of 300 mg/L, and reaction time of 120 minutes.

Table 7. Pharmaceutical degradation under optimized conditions

Compound	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
Enrofloxacin	18.4	0.52	97.2
Oxytetracycline	14.2	0.62	95.6
Albendazole	9.6	0.69	92.8

The Fenton process achieved more than 92% degradation for all selected pharmaceutical compounds. Enrofloxacin showed the highest removal efficiency, followed by Oxytetracycline and Albendazole.

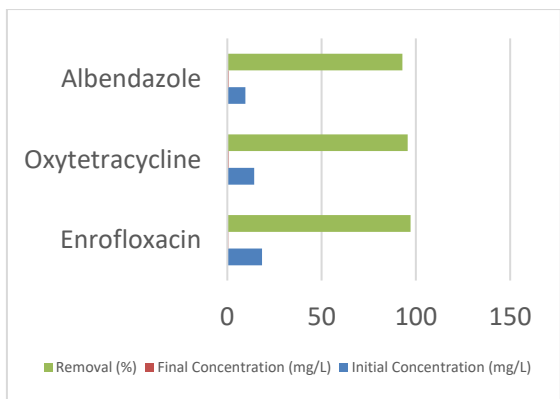


Figure 8: Bar graph showing pharmaceutical degradation efficiency.

5.8 Turbidity and Conductivity Reduction

The Fenton process also improved the physical quality of greywater.

Table 8. Physical water quality improvement

Parameter	Initial Value	Final Value	Removal / Change (%)
Turbidity	326 NTU	27.4 NTU	91.6
Conductivity	1915 $\mu\text{S}/\text{cm}$	1632 $\mu\text{S}/\text{cm}$	14.8
pH after neutralisation	7.42	7.10	Within acceptable range

Turbidity reduction indicates the removal of suspended and colloidal matter. Conductivity reduction was comparatively lower because dissolved ions may remain in treated water after oxidation.

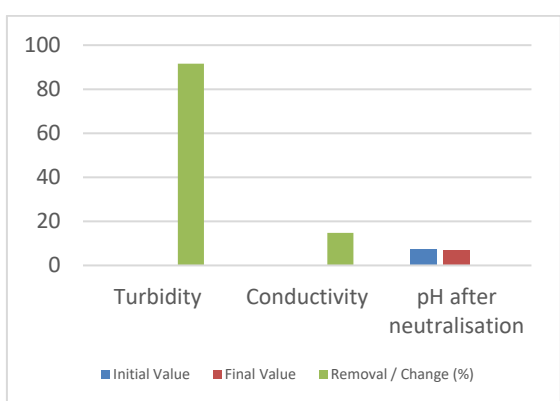


Figure 9: Before and after comparison of turbidity and conductivity.

5.9 Kinetic Analysis

Pseudo-first-order kinetic analysis was carried out for the selected pharmaceutical compounds.

Table 9. Kinetic data for pharmaceutical degradation

Time (min)	Enrofloxacin $\ln(C_0/C)$	Oxytetracycline $\ln(C_0/C)$	Albendazole $\ln(C_0/C)$
0	0.000	0.000	0.000
15	0.612	0.554	0.421
30	1.236	1.108	0.876
60	2.184	1.965	1.654
90	2.921	2.742	2.223
120	3.566	3.132	2.632

Table 10. Pseudo-first-order kinetic constants

Compound	Rate Constant, k (min^{-1})	R^2
Enrofloxacin	0.0294	0.982
Oxytetracycline	0.0261	0.976
Albendazole	0.0218	0.961

The R^2 values above 0.96 indicate that the degradation of pharmaceutical compounds followed pseudo-first-order kinetics. Enrofloxacin showed the highest rate constant, indicating faster degradation compared to Oxytetracycline and Albendazole.

5.10 Cost Estimation

The treatment cost was estimated based on chemical consumption, pH adjustment, electricity, and sludge handling.

Table 11. Estimated operational cost of Fenton treatment

Cost Component	Estimated Cost ($\text{₹}/\text{m}^3$)
Ferrous sulphate	10.5–14.8
Hydrogen peroxide	19.5–26.2
pH adjustment chemicals	4.0–6.5
Electricity	3.5–5.2
Sludge handling	4.0–4.1
Total cost	41.5–56.8

The estimated treatment cost ranged from ₹41.5 to ₹56.8 per m^3 . This indicates that the Fenton process is economically feasible as a tertiary treatment process for small healthcare wastewater systems.

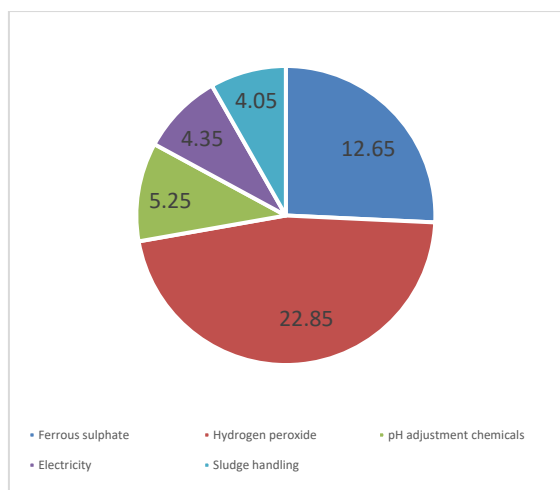


Figure 10: Pie chart showing cost distribution.

6. DISCUSSION

The results show that the Fenton process is effective for the removal of pharmaceutical contaminants and organic matter from clinic greywater. Maximum COD removal was obtained at pH 3. This is because acidic conditions support the catalytic reaction between Fe^{2+} and H_2O_2 and improve hydroxyl radical generation.

The optimum Fe^{2+} dosage was 30 mg/L. At lower dosage, hydroxyl radical production was insufficient. At higher dosage, excess Fe^{2+} may consume hydroxyl radicals and increase sludge formation. Similarly, the optimum H_2O_2 dosage was 300 mg/L. Excess hydrogen peroxide may reduce the process efficiency because it can act as a radical scavenger.

COD removal of 92.4% and TOC reduction of 79.8% indicate that the Fenton process not only reduced organic load but also mineralized a major portion of organic pollutants. Pharmaceutical degradation exceeded 92% for all selected compounds, confirming strong oxidation capability of the process.

The kinetic analysis confirmed pseudo-first-order behavior. This indicates that pharmaceutical degradation rate depends on contaminant concentration and hydroxyl radical availability. The higher rate constant for Enrofloxacin indicates faster degradation compared to Oxytetracycline and Albendazole.

The cost analysis shows that the process is feasible for small-scale applications. The main cost contribution was hydrogen peroxide, followed by ferrous sulphate and pH adjustment chemicals. The process can be further improved by optimizing chemical dosage, using solar-assisted Fenton treatment, or combining Fenton with filtration or adsorption.

7. ENVIRONMENTAL SIGNIFICANCE

The Fenton process can be used as a decentralized treatment option for small clinics and healthcare facilities. It can reduce pharmaceutical discharge into the environment and help minimize the risk of antibiotic resistance and aquatic toxicity.

The treated water may be suitable for non-potable reuse after proper neutralization, filtration, and safety testing. The process can also be integrated with existing primary treatment systems.

Major environmental benefits include:

1. Reduction of pharmaceutical contaminants.
2. Reduction of COD and TOC load.
3. Lower risk of antimicrobial resistance.
4. Improvement in greywater quality.
5. Application in small healthcare units.
6. Potential use as tertiary treatment before discharge.

8. LIMITATIONS OF THE STUDY

This study was conducted at laboratory scale using batch experiments. Field-scale performance may vary depending on wastewater flow rate, seasonal changes, pollutant concentration, chemical cost, and sludge management requirements. The study focused on three selected pharmaceutical compounds only. Future studies should include more contaminants, toxicity testing, and pilot-scale validation.

9. CONCLUSION

The present study evaluated the performance of the Fenton process for removal of pharmaceutical emerging contaminants from clinic greywater. The collected greywater showed high COD, TOC, turbidity, and detectable concentrations of Enrofloxacin, Oxytetracycline, and Albendazole.

The optimum treatment conditions were pH 3, Fe^{2+} dosage of 30 mg/L, H_2O_2 dosage of 300 mg/L, and reaction time of 120 minutes. Under these conditions, COD removal reached 92.4%, TOC reduction reached 79.8%, turbidity reduction reached 91.6%, and pharmaceutical degradation exceeded 92%.

Kinetic analysis confirmed pseudo-first-order degradation behavior with R^2 values above 0.96. The estimated treatment cost ranged from ₹41.5 to ₹56.8/m³, indicating that the process is economically feasible for small-scale healthcare greywater treatment.

Overall, the Fenton process is a simple, effective, low-cost, and scalable treatment method for pharmaceutical-contaminated greywater. It can be used as a tertiary

treatment option for clinics, hospitals, and decentralized wastewater treatment systems.

10. FUTURE SCOPE

1. Pilot-scale continuous-flow Fenton reactor development.
2. Integration of Fenton with UV or solar photo-Fenton treatment.
3. Toxicity assessment of treated water.
4. Identification of intermediate degradation products.
5. Sludge minimization and iron recovery.
6. Hybrid treatment using Fenton followed by activated carbon filtration.
7. Application of AI-based chemical dose optimization.
8. Field-scale validation at small healthcare facilities.

11. REFERENCES

- [1] Samal, K., Mahapatra, S., & Ali, M. H. (2022). Pharmaceutical wastewater as emerging contaminants: Treatment technologies, impact on environment and human health. *Energy Nexus*, 6, 100076.
- [2] Pignatello, J. J., Oliveros, E., & MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology*, 36(1), 1–84.
- [3] Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, 98(1–3), 33–50.
- [4] Homem, V., & Santos, L. (2011). Degradation and removal methods of antibiotics from aqueous matrices: A review. *Journal of Environmental Management*, 92(10), 2304–2347.
- [5] Kümmerer, K. (2009). Antibiotics in the aquatic environment: A review. *Chemosphere*, 75(4), 417–434.
- [6] Oller, I., Malato, S., & Sánchez-Pérez, J. A. (2011). Combination of advanced oxidation processes and biological treatments for wastewater decontamination. *Science of the Total Environment*, 409(20), 4141–4166.
- [7] Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S., & Wang, X. C. (2014). A review on occurrence of micropollutants in aquatic environment and their fate during wastewater treatment. *Science of the Total Environment*, 473–474, 619–641.
- [8] Verlicchi, P., Al Aukidy, M., & Zambello, E. (2012). Occurrence of pharmaceutical compounds in urban wastewater and removal after secondary treatment. *Science of the Total Environment*, 429, 123–155.
- [9] Michael, I., Frontistis, Z., Fatta-Kassinos, D., & Dionysiou, D. D. (2013). Fenton and photo-Fenton oxidation of antibiotics in wastewater. *Water Research*, 47(15), 5675–5686.
- [10] Bautitz, I. R., & Nogueira, R. F. P. (2007). Degradation of tetracycline by photo-Fenton process. *Journal of Photochemistry and Photobiology A: Chemistry*, 187(1), 33–39.
- [11] Dantas, R. F., Contreras, S., Sans, C., & Esplugas, S. (2008). Sulfamethoxazole abatement by ozonation. *Journal of Hazardous Materials*, 150(3), 790–794.
- [12] Elmolla, E. S., & Chaudhuri, M. (2010). Degradation of amoxicillin, ampicillin and cloxacillin antibiotics by Fenton and photo-Fenton processes. *Journal of Hazardous Materials*, 172(2–3), 1476–1481.
- [13] Kanakaraju, D., Glass, B. D., & Oelgemöller, M. (2018). Advanced oxidation process-mediated removal of pharmaceuticals from water: A review. *Journal of Environmental Management*, 219, 189–207.
- [14] APHA. (2017). *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC.
- [15] Bureau of Indian Standards. (2006). IS 3025 Part 58: Methods of sampling and test for water and wastewater: Chemical Oxygen Demand.