The Degradation of Tetracycline Hydrochloride by Iron Sludge-Based Catalyst/Persulfate System

Chen Fu [1], Lihua Huang [1], Kai Zhu [1, *], Qing Sun [2]

[1] Shandong Provincial Key Laboratory of Water and Soil Conservation and Environmental Protection, College of resources and environment, Linyi University, Linyi, China

[2] Linyi architectural design & research institute Co., Ltd, Linyi, China

Abstract. Advanced oxidation processes are one of the effective means for degrading tetracycline hydrochloride (TCH) in water. Using pickling iron sludge as the raw material, an iron sludge-based catalyst was prepared through a two-step hydrothermal method, and an iron sludge-based catalyst/persulfate system was established to degrade TCH in water. Experimental data show that the iron sludge-based catalyst/persulfate system exhibits high efficiency in TCH degradation. This experiment demonstrates that simple modification of pickling iron sludge can be transformed into a low-cost, high-efficiency catalyst.

Keywords: Advanced oxidation; Tetracycline hydrochloride; Pickling iron sludge.

1. Introduction

Emerging pollutants primarily composed of antibiotics are difficult to be degraded by microorganisms in the natural environment, prone to bioaccumulation in ecosystems, and can persist in the environment and within organisms for extended periods. They can acclimatize environmental microorganisms to produce antibiotic resistance genes, posing threats to ecological safety and human health. The average detection concentration of antibiotics in the effluent of wastewater treatment plants worldwide ranges from 2.0 to 580 $mg\cdot L^{-1}$, and in surface water bodies, it reaches 5.0 to 1300 $ng\cdot L^{-1}$ [1].,

Therefore, it is urgent to seek efficient and pollution-free methods for degrading antibiotics, and advanced oxidation processes (AOPs) are one of the effective methods for this purpose. Peroxomonosulfate (PMS) and peroxodisulfate (PDS) are commonly used oxidants in AOPs. Compared to the symmetric structure of PDS, PMS's non-symmetric structure makes it easier to be activated [2], which makes PMS a key direction for development in AOPs. PMS can be activated through methods such as ultrasound, light, heat, transition metals, and their compounds, generating hydroxyl radicals (•OH) and sulfate radicals ($\bullet SO_4^-$) to degrade pollutants [3]. Among these, cobalt ferrite ($CoFe_2O_4$) composite materials have attracted much attention due to their simple preparation, low cost, abundant resources, and excellent activation performance. Therefore, a simple synthesis method can be developed, and large-scale renewable resources can be sought to prepare $CoFe_2O_4$ for the degradation of antibiotics.

Pickling sludge is a byproduct in the steel production process, containing a large number of metals such as iron, nickel, and zinc, and is classified as hazardous waste of HW17 category. China is the world's largest producer, processor, and consumer of steel, with the generation of pickling sludge accounting for about 1% of the total steel production. In 2022, China's steel production was 1.013 billion tons, which corresponds to the generation of about 10 million tons of pickling sludge [4]. The main treatment methods for pickling sludge are landfilling, sintering ceramsite, and cement production, which not only pollute the environment but also cause a great waste of metal resources. Therefore, it is possible to study the use of the rich metal resources in pickling sludge to achieve the degradation of antibiotics, with the aim of treating pollution with waste.

2. Materials and Methods

2.1. Materials

Cobalt acetate, ethylene glycol, sodium acetate, ammonium molybdate, thiourea, and potassium persulfate are all of analytical purity and were purchased from the National Pharmaceutical Group Chemical Reagent Co., Ltd. Sodium chloride, sodium nitrate, sodium sulfate, etc., were purchased from Tianjin Hengxing Company, and tetracycline hydrochloride (TCH) is from Hefei Qiansheng Biotechnology Co., Ltd.

The main instruments used in the experiment include the DR6000 UV-V is spectrophotometer: Hach Company, USA, PHS-3C pH meter: Shanghai Lais Company, and overhead stirrer: Shanghai Yetuo Company.

2.2. Preparation of the Catalysts

A two-step solvothermal process was employed to synthesize the magnetic iron sludge-based catalyst $MoS_2@CoFe_2O_4$ structure using steel pickling sludge as an iron source. Initially, 1000 mg of thiourea and 500 mg of ammonium molybdate tetrahydrate were dissolved in 50 mL of ultrapure water and stirred for 10 minutes. This mixture was then subjected to solvothermal treatment at 220 °C for 720 minutes in a 100 mL Teflon-lined stainless-steel autoclave. The resulting MoS_2 precipitate was collected by filtration after cooling overnight and washed multiple times with ultrapure water before being dried at 60 °C for 300 minutes in a vacuum oven.

For the second step, 100 mg of the synthesized MoS_2 was combined with 120 mg cobalt acetate, 200 mg sodium acetate, and 200 mg treated steel pickling sludge in 40 mL of ethylene glycol. The mixtures were stirred mechanically for 30 minutes before being heated in a sealed Teflon-lined stainless-steel autoclave at 200 °C for 600 minutes, with a heating rate of 5°C per minute. The final product, $MoS_2@CoFe_2O_4$, was collected by filtration after cooling, washed with methanol and ultrapure water, and then dried at 60°C for 300 minutes in a vacuum oven.

3. Results and Discussion

3.1. SEM Image of the Prepared Catalyst

The SEM images reveal a rough surface with a large number of uneven granular structures. As shown in Figure 1, the prepared catalyst appears as irregular spherical bodies with a layered structure on the surface, which increases the specific surface area of the catalyst. The surface of the $MoS_2@CoFe_2O_4$ catalyst exhibits a multitude of elongated rod-like $CoFe_2O_4$ structures, densely attached to the surface of the spherical bodies, indicating that $CoFe_2O_4$ has successfully combined with MoS_2 through a solvothermal reaction.

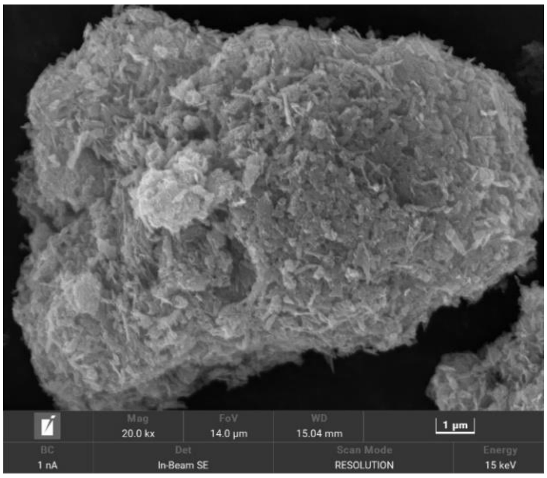

Figure 1. SEM image of the prepared catalyst

3.2. Effects of Operational Parameters on Degradation Efficiency

The dosage of persulfate (PMS) is a pivotal factor in the oxidation process of wastewater treatment, as it directly influences the production of reactive oxidizing species, which are essential for the breakdown of contaminants. Figure 2(a) demonstrates the correlation between PMS dosage and the degradation efficiency of TCH removal. As the PMS concentration escalates from 200 mg·L^{-1} to 800 mg·L^{-1}, there is a corresponding increase in the removal efficiency, which peaks at 76.2% when the dosage is at 600 mg·L^{-1} after a 20-minute reaction time. This trend indicates that the higher the PMS dosage, the more reactive oxidants are available to react with and remove TCHs from the wastewater.

However, this relationship does not continue indefinitely. At a dosage of 800 mg·L^{-1}, the TCH removal efficiency slightly decreases to 75.8%. This decline in efficiency at high PMS concentrations is hypothesized to be due to the recombination of excessive active free radicals, which neutralize each other and reduce their overall effectiveness in oxidizing TCHs. This phenomenon is supported by Equations (1) to (3), which describe the self-deactivation pathways of radicals [5].

Furthermore, an elevated PMS dosage can lead to an increased radical quenching effect, where the high concentration of PMS competes with TCHs for the reactive radicals, thereby reducing the radicals' availability for TCH oxidation. This quenching effect is detailed in Equations (1) to (7), which outline the side reactions that consume radicals without contributing to the oxidation of TCHs. The balance between the generation of reactive radicals and their subsequent consumption through quenching becomes critical in determining the overall efficiency of the oxidation process [6].

In summary, while increasing the PMS dosage can enhance the generation of reactive oxidants and improve TCH removal efficiency up to a certain point, there is an optimal dosage beyond which the efficiency plateaus or even declines due to radical recombination and quenching. This highlights the importance of finding the sweet spot in PMS dosage to achieve the most effective TCH removal without incurring unnecessary costs or operational inefficiencies. Understanding these dynamics is crucial for optimizing the treatment process and achieving the best possible outcomes in wastewater oxidation.

$$\cdot SO_4^- + \cdot SO_4^- \rightarrow S_2O_8^{2-} \tag{1}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{2}$$

$$\cdot SO_4^- + \cdot OH \rightarrow HSO_5^- \tag{3}$$

$$\cdot SO_4^- + HSO_5^- \rightarrow \cdot SO_5^- + SO_4^{2-} + H^+ \tag{4}$$

$$\cdot OH + HSO_5^- \rightarrow \cdot SO_5^- + H_2O \tag{5}$$

$$\cdot SO_4^- + HSO_5^- + H_2O \rightarrow \cdot HO_2^- + 2SO_4^{2-} + H^+ \tag{6}$$

$$\cdot OH + HSO_5^- \rightarrow \cdot HO_2^- + 2SO_4^{2-} + H^+ \tag{7}$$

The relationship between catalyst dosage and the degradation of contaminants in wastewater, as illustrated in Figure 2(b), is a critical aspect of optimizing advanced oxidation processes (AOPs). The figure shows a clear trend where the efficiency of TCH degradation increases with the catalyst dosage up to a certain point. Specifically, at catalyst dosages of 100 mg·L^{-1}, 200 mg·L^{-1}, and 300 mg·L^{-1}, the TCH removal efficiencies at a 20-minute reaction time are 62.8%, 76.2%, and 82.7%, respectively. This indicates that the catalyst plays a significant role in enhancing the degradation process, likely by providing more active sites for the reaction to occur.

However, the data also reveal a diminishing return when the catalyst dosage is increased beyond 300 mg·L^{-1}. The improvement in TCH removal efficiency plateaus as the dosage reaches 400 mg·L^{-1} and above, suggesting that there is an optimal catalyst dosage beyond which additional increments do not significantly improve the degradation process. This phenomenon is consistent with findings from other studies that have shown an upper limit to the effectiveness of catalyst dosages in AOPs [7].

The initial increase in efficiency with higher catalyst dosages can be attributed to the increased availability of active sites on the catalyst surface, which facilitates the adsorption and subsequent degradation of TCH molecules. However, when the catalyst dosage is too high, the system becomes limited by the concentration of PMS and TCH available in the solution. This limitation reduces the adsorption efficiency, as there are more catalyst sites than there are contaminants to react with, leading to a saturation point where further increases in catalyst dosage do not yield proportional improvements in TCH removal [8].

This observation underscores the importance of finding the optimal catalyst dosage to achieve the highest TCH removal efficiency without wasting resources. An overabundance of catalyst not only fails to enhance the degradation process but can also lead to operational inefficiencies and increased costs. Therefore, understanding the dosage-response relationship is essential for the practical application of AOPs in wastewater treatment. It allows operators to balance the need for effective contaminant removal with the economic and environmental considerations of catalyst use, ensuring that the treatment process is both efficient and sustainable. Examining the influence of initial pH on the oxidation process is crucial for determining the best operational parameters.

Understanding the initial pH's influence on the oxidation process is vital for fine-tuning the operational parameters to achieve optimal TCH removal. Figure 2(c) demonstrates the relationship between the initial pH range of 3.7 to 10.2 and the corresponding TCH removal efficiency. Interestingly, the pH level appears to have a negligible effect on the degradation of TCH, suggesting that other factors may be more influential in this process.

The dominance of HSO_5^- in acidic and neutral conditions, as indicated by the pKa values of PMS, is a critical consideration. HSO_5^-, being the predominant species, forms hydrogen bonds with O-O groups and H+ ions, which can stabilize the HSO_5^- ions and enhance their reactivity. This stabilization can potentially interfere with the electrostatic interactions between HSO_5^- and the positively charged bimetallic catalysts, affecting the catalyst's efficiency in promoting TCH degradation.

Moreover, the presence of an excess of hydrogen ions can lead to the neutralization of oxidative radicals, which are crucial for the oxidation process. This neutralization can reduce the overall effectiveness of the radicals in breaking down TCH, as described by Equations (8) to (9) [9]. This highlights the importance of maintaining a balanced pH level to ensure that the radicals remain active and effective in the degradation process.

In addition to the direct effects on HSO_5^- and oxidative radicals, the initial pH can also influence the speciation of other reactive species in the solution, which may further affect the oxidation process. For instance, the pH can affect the formation and stability of other reactive oxygen species (ROS), such as hydroxyl radicals (·OH), which are known to be highly reactive and effective in degrading organic pollutants like TCH.

Furthermore, the pH can impact the solubility and bioavailability of the contaminants themselves, potentially altering their susceptibility to oxidation. Some contaminants may be more soluble or reactive at certain pH levels, which could affect their removal efficiency.

In conclusion, while the initial pH may not have a significant direct impact on TCH degradation, it plays a crucial role in modulating the behavior of the oxidizing agents and the contaminants, which in turn can influence the overall efficiency of the oxidation process. Therefore, it is essential to consider the initial pH as a key parameter when designing and optimizing AOPs for effective TCH removal.

$$\cdot SO_4^- + H^+ + e^- \rightarrow \cdot HSO_4^- \tag{8}$$

$$\cdot OH + H^+ + e^- \rightarrow H_2O \tag{9}$$

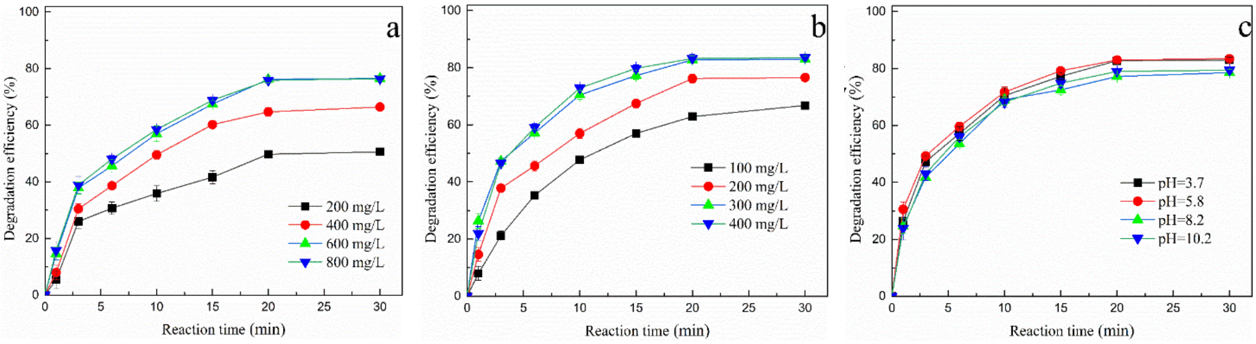

Figure 2. Effects of operational parameters on degradation efficiency: (a) effect of PMS dosage (TCH 200 mg·L^{-1}, initial pH 6.2, and catalyst dosage 200 mg·L^{-1}); (b) effect of catalyst dosage (TCH 200 mg·L^{-1}, initial pH 6.2 and PMS dosage of 600 mg·L^{-1}); (c) the effect of initial pH value (TCH 200 mg·L^{-1}, PMS 600 mg·L^{-1}, and catalyst dosage 300 mg·L^{-1}).

4. Conclusion

Using widely available pickling iron sludge as the raw material, a superior catalyst with MoS2 as the carrier and $CoFe_2O_4$ as the active component was successfully prepared through a two-step hydrothermal method, which can efficiently activate PMS to degrade TCH. Single-factor experiments determined the optimal experimental conditions for the iron sludge-based catalyst/persulfate system. The iron sludge-based catalyst shows strong TCH degradation effects under various conditions. In summary, this paper provides a strategy for degrading antibiotic wastewater using pickling iron sludge, offering new ideas for the reuse of pickling iron sludge and the degradation of TCH.

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