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Ultrathin FeOCl Nanosheet as a Robust Fenton-Like Catalyst for Enhanced Sulfamethoxazole Degradation

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Abstract: The widespread use of antibiotics has raised significant environmental concerns due to their potential ecological risks. Advanced oxidation processes (AOPs), particularly Fenton-like reactions, offer promising pathways for pollutant degradation. However, their large-scale application is often limited by the narrow pH window and iron sludge formation. In this study, nanosheet FeOCl catalyst was synthesized by exfoliating bulk FeOCl, and its performance in activating H_2O_2 to degrade SMX under various pH conditions was evaluated. Structural characterization confirmed that nanosheet FeOCl features a highly exfoliated morphology with reduced layer thickness and smaller crystalline domains compared to its bulk counterpart. The synthesized nanosheet FeOCl exhibited significantly enhanced catalytic performance, removing up to 95% of SMX within 30 minutes over a broad pH range (3–9), significantly outperforming the efficiency of bulk FeOCl. Radical quenching experiments further elucidated that hydroxyl radicals (•OH) served as the primary active species, with additional contributions from other reactive oxygen species. These findings demonstrate that nanosheet FeOCl is a highly efficient heterogeneous Fenton-like catalyst, providing a promising and practical strategy for antibiotic wastewater treatment.

1. Introduction

The widespread use of antibiotics in both human medicine and animal husbandry has resulted in their continuous release into aquatic environments, posing serious risks to ecosystems and human health.[1-3] As a typical sulfonamide antibiotic, sulfamethoxazole (SMX) is frequently detected in aqueous environments due to its incomplete removal during conventional wastewater treatment processes. Its potential to induce antibiotic resistance genes has made it a pollutant of growing concern.[4] Therefore, developing efficient, economical, and environmental-friendly advanced treatment technologies for its effective removal is of significant practical importance.

Advanced oxidation processes (AOPs) based on reactive oxygen species (ROS) have emerged as promising solutions for degrading recalcitrant organic pollutants. Among them, Fenton and Fenton-like reactions, which rely on the catalytic activation of hydrogen peroxide (H_2O_2) to produce hydroxyl radicals (•OH), are considered particularly promising due to their strong oxidizing capability and operational simplicity.[5-7] However, the widespread application of the conventional Fenton system is severely hampered by its inherent drawbacks, primarily the narrow optimal pH range (around 2-3), which significantly increases the operational costs associated with pH adjustment in real wastewater

treatment, and the generation of substantial iron-containing sludge, which increases the difficulty and risk of subsequent disposal. These challenges significantly limit the large-scale application of this technology.[8,9]

To address these limitations, researchers are increasingly focusing on heterogeneous Fenton-like systems. Developing stable, efficient heterogeneous catalysts capable of operating under near-neutral pH conditions has become a research hotspot.[10-12] Among numerous candidate materials, iron oxychloride (FeOCl) has emerged as a promising option due to its unique layered structure, cost-effectiveness, and environmental compatibility.[13,14] However, bulk FeOCl often suffers from limitations, such as limited specific surface area, poor accessibility of active sites, and significant mass transfer resistance, which consequently restrict its catalytic efficiency.[15] Recent advances in nanotechnology suggest that morphological control and structural design, such as constructing two-dimensional nanosheet structures, could greatly enhance the specific surface area, expose more active sites, and shorten mass transfer pathways, thereby offering the potential to enhance its intrinsic catalytic activity.

Based on this, this study proposes a simple physical exfoliation method to convert bulk FeOCl into two-dimensional nanosheet FeOCl. We hypothesize that this nanosheet structure will expose richer active sites, thereby significantly enhancing its ability to activate hydrogen peroxide (H_2O_2) and broadening the effective pH range for reaction. This research systematically characterizes the structural and morphological differences between the nanosheet and bulk FeOCl. Using SMX as the target pollutant, it thoroughly evaluates the catalytic degradation performance across a wide pH range. This work provides new material design ideas for solving the pH limitation problem of traditional Fenton technology, contributing positively to promoting the application of Fenton-like technology in practical wastewater treatment.

2. Materials and methods

Chemicals and materials. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), hydrochloric acid (HCl), and sodium hydroxide (NaOH) of analytical grade were obtained from Sigma-Aldrich and used without further purification. Ultrapure water (18.2 MΩ·cm) was supplied by a Milli-Q ultrapure water purification system.

Synthesis of bulk FeOCl and nanosheet FeOCl. Bulk FeOCl was synthesized via a facile thermal decomposition method.[16] Briefly, 2g of $FeCl_3 \cdot 6H_2O$ was thoroughly ground into powder using an agate mortar and pestle. The powder was then transferred into a quartz boat and calcined in a muffle furnace under static air at 220 °C for 2 hours with an increasing temperature rate of 10°C/min. After natural cooling to room temperature, the resulting reddish-brown product was gently ground again. The as-prepared composite was labeled as “bulk FeOCl”.

Nanosheet FeOCl was subsequently prepared from the bulk FeOCl through a liquid-phase exfoliation strategy. In a typical procedure, a certain amount of bulk FeOCl was dispersed in ultrapure water and subjected to ultrasonication for 6 hours to facilitate layer separation. The resulting suspension was then subjected to multiple cycles of centrifugation and rinsing with ultrapure water to remove unexfoliated fragments and collect the exfoliated nanosheets. Finally, the collected nanosheet FeOCl was dried to obtain a powder for further use.

Catalytic performance experiments. The catalytic performance of the FeOCl catalysts was evaluated through batch degradation experiments using sulfamethoxazole (SMX) as the target pollutant. Each reaction was conducted in an aqueous suspension containing 0.1 g/L of catalyst and 10 mg/L of SMX, stirred at 250 rpm under ambient conditions. Prior to reaction, the suspension was sonicated for 5 minutes to ensure catalyst dispersion, and the pH was adjusted using dilute NaOH or HCl solutions. The degradation process was initiated by adding a predetermined amount of H_2O_2 (30

wt%) solution. At given time intervals, the samples were taken with a syringe and immediately quenched with methanol to terminate the reaction for subsequent analysis. Prior to analysis, liquid samples were first filtered through a 0.22 μm poly(ether sulfone) membrane syringe filter to remove catalysts. The concentration of SMX was quantified by high-performance liquid chromatography (HPLC, Agilent 1260 system) equipped with a C18 column and a variable wavelength detector (VWD) set at 280 nm. The mobile phase employed was a water/acetonitrile mixture (60:40, v/v) running at a flow rate of 0.3 mL/min.

Material Characterization. The crystalline phases of the prepared FeOCl catalysts were identified by a powder X-ray diffraction (XRD) using an X′Pert Pro diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). Data were acquired in the 2θ range of 5–80° with a scanning speed of 2° min^{-1}. The surface morphology and microstructure of the catalysts were investigated by transmission electron microscopy (TEM) on a JEOL 2100F microscope.

3. Results and discussion

Morphological and Structural Characterization. The morphological structures of the bulk FeOCl and nanosheet FeOCl catalysts were investigated by transmission electron microscopy (TEM). As shown in Figure 1a, the bulk FeOCl exhibits a dense, thick layered architecture with low optical transparency, indicative of its stacked multilayer nature. In contrast, the nanosheet FeOCl (Figure 1b) displays a distinctly thinner and more transparent sheet-like morphology, which is characteristic of successfully exfoliated nanosheets. The significant reduction in both thickness and layer stacking number observed in nanosheet FeOCl provides direct visual evidence that the ultrasonication treatment effectively delaminated the bulk precursor into few-layer nanostructures. This morphological transformation is expected to greatly increase the specific surface area and expose more active sites, which is crucial for enhancing catalytic performance in subsequent Fenton-like reactions.

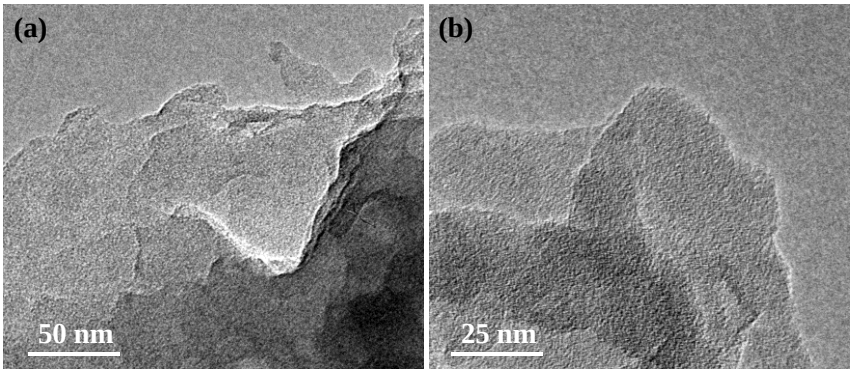

Figure 1 TEM image of (a) bulk FeOCl and (b) nanosheet FeOCl.

The crystal structures of the as-synthesized bulk FeOCl and nanosheet FeOCl were characterized by X-ray powder diffraction (XRD). As illustrated in Figure 2, both samples exhibit the characteristic diffraction patterns of crystalline FeOCl, with prominent peaks observed at 2θ values of approximately 11.05 °, 26.03 °, and 35.45 °, which correspond well to the standard reference (JCPDS No. 72-0619).[17] The presence of these distinctive peaks confirms the successful synthesis of the FeOCl phase in both materials. Notably, no significant peak shift is observed between the two samples, indicating that the exfoliation process did not alter the fundamental crystal structure of FeOCl. However, a clear difference is evident in the peak broadening. The diffraction peaks of nanosheet FeOCl are noticeably broader than those of the bulk counterpart, as quantified by an increase in the full width at half maximum.[18] According to the Scherrer equation, this peak broadening suggests a reduction in the average crystallite size within the nanosheets, which is a typical consequence of the

exfoliation process that breaks down larger crystalline domains into smaller nanoscale grains. This structural refinement is consistent with the morphological changes observed by TEM and is expected to contribute positively to the catalytic activity by increasing the density of surface-active sites.

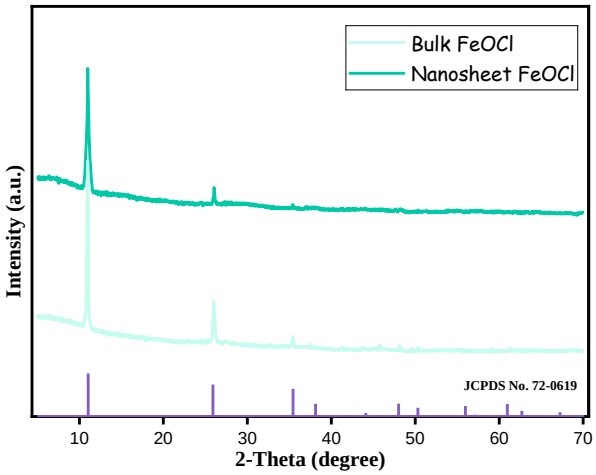

Figure 2 XRD patterns of bulk FeOCl and FeOCl nanosheet catalysts.

Catalytic degradation performances of nanosheet FeOCl. The Fenton-like catalytic activities of the as-prepared bulk FeOCl and nanosheet FeOCl were evaluated by degrading sulfamethoxazole (SMX) as a model organic pollutant. To elucidate the respective roles of the catalyst and the oxidant, control experiments were also conducted. As summarized in Figure 3, the degradation of SMX was negligible when only H_2O_2 was present, achieving ~10% removal after 30 minutes, which confirms the limited oxidative capacity of H_2O_2 without catalytic activation. Similarly, adsorption by the catalysts alone (without H_2O_2) resulted in only approximately 20% SMX removal, indicating that physical adsorption plays a minor role. When both FeOCl and H_2O_2 were present, a substantial improvement in SMX degradation was observed. Notably, nanosheet FeOCl exhibited superior catalytic performance compared to its bulk counterpart. Within just 5 minutes, nanosheet FeOCl achieved over 90% SMX degradation, ultimately reaching 95% within 30 minutes. In comparison, bulk FeOCl attained only about 60% removal after 5 minutes, with no significant further improvement. This remarkable activity of nanosheet FeOCl can be attributed to its larger specific surface area and higher density of exposed active sites, as evidenced by the TEM and XRD analyses, which facilitate more efficient activation of H_2O_2 and generation of reactive oxygen species. These results demonstrate that nanosheet FeOCl is a highly effective heterogeneous Fenton-like catalyst, with significantly enhanced activity under neutral pH conditions.

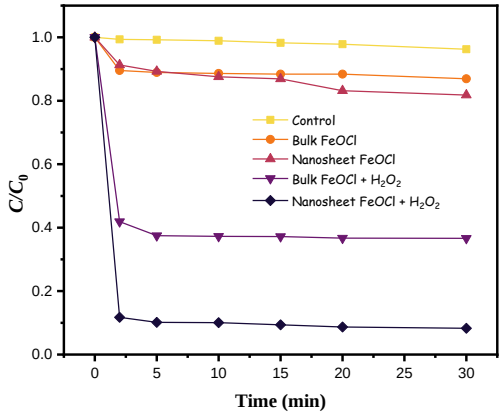

Figure 3 Catalytic SMX degradation performance of FeOCl/ H_2O_2 Fenton-like system under various conditions.

To assess the practical applicability of the catalysts, the influence of solution pH on SMX degradation efficiency was systematically investigated over a range of pH 3 to 9, as presented in Figure 4. Both bulk FeOCl (Figure 4a) and nanosheet FeOCl (Figure 4b) exhibited a general trend of decreasing degradation performance with increasing pH, consistent with conventional Fenton-like mechanisms where acidic conditions favor iron solubility and •OH generation. Notably, nanosheet FeOCl demonstrated significantly superior activity and broader pH adaptability compared to the bulk material. Under strongly acidic conditions (pH 3–4), nanosheet FeOCl achieved nearly complete SMX removal (>99%), whereas bulk FeOCl reached only about 70% under the same conditions. More importantly, nanosheet FeOCl maintained high degradation efficiency (~80%) even at pH 9. In contrast, bulk FeOCl exhibited a more pronounced activity loss, declining to approximately 60% efficiency at pH 9. The broad operational pH range (3–9) of the nanosheet FeOCl system, which significantly surpasses that of both homogeneous Fenton (pH 2.5–3.5) and typical heterogeneous Fe-based systems (pH 3.0–5.0), underscores its strong potential for practical wastewater treatment.[19,20]

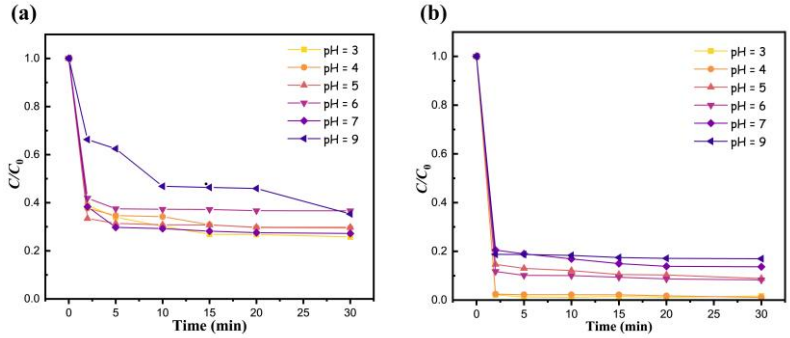

Figure 4 Effect of initial pH values on SMX degradation in the (a) bulk FeOCl/H_2O_2 and (b) nanosheet FeOCl/H_2O_2 Fenton-like system.

Reaction Mechanism of the FeOCl/H_2O_2 System. To elucidate the catalytic mechanism of the FeOCl/H_2O_2 Fenton-like system, radical quenching experiments were conducted to identify the primary reactive oxygen species (ROS) involved in SMX degradation. Methanol (MeOH), a potent scavenger of hydroxyl radicals (•OH), was employed to assess the contribution of •OH.[9] As illustrated in Figure 5, the addition of methanol resulted in a partial but significant suppression of SMX degradation, indicating that •OH radicals indeed play a major role in the oxidation process. However, the degradation was not completely inhibited, with a considerable portion of SMX still being removed even in the presence of excess methanol. This observation clearly suggests the involvement of additional ROS beyond •OH. Non-radical pathways or other radicals less susceptible to methanol quenching, such as surface-bound radicals or singlet oxygen ($^1O_2$), may also contribute to the overall degradation efficiency.

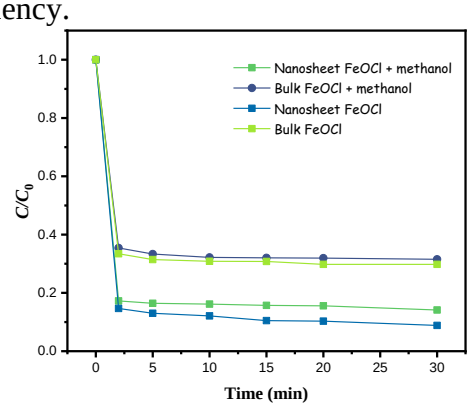

Figure 5 Effect of radical scavengers on SMX degradation in the FeOCl/H_2O_2 Fenton-like system.

Based on the possible intermediate products and the known reactivity of hydroxyl radicals, a proposed degradation pathway for SMX in the FeOCl/H_2O_2 Fenton-like system is proposed, as illustrated in Figure 6. The initial attack is primarily mediated by the highly reactive hydroxyl radicals (•OH) generated from the catalytic activation of H_2O_2 on the FeOCl surface. This pathway involves the oxidation of aniline on SMX to nitrobenzene, leading to the formation of SMX derivative, N-(5-methylisoxazol-3-yl)-4-nitrobenzene sulfonamide.[21] Concurrently, •OH attack on the sulfonamide moiety likely results in the cleavage of the S-N bond, (4,5-dihydroxy-4,5-dihydroisoxazol-3-yl) sulfamic acid and 6-aminocyclohexa-3,5-diene-1,3-diol.[22] Subsequent oxidation steps involve further hydroxylation and opening of the isoxazole ring, ultimately yielding smaller, less organic acids. These small-molecule organic acids are finally mineralized into CO_2, H_2O, and inorganic ions (e.g., NH_4^+, SO_4^{2-}).

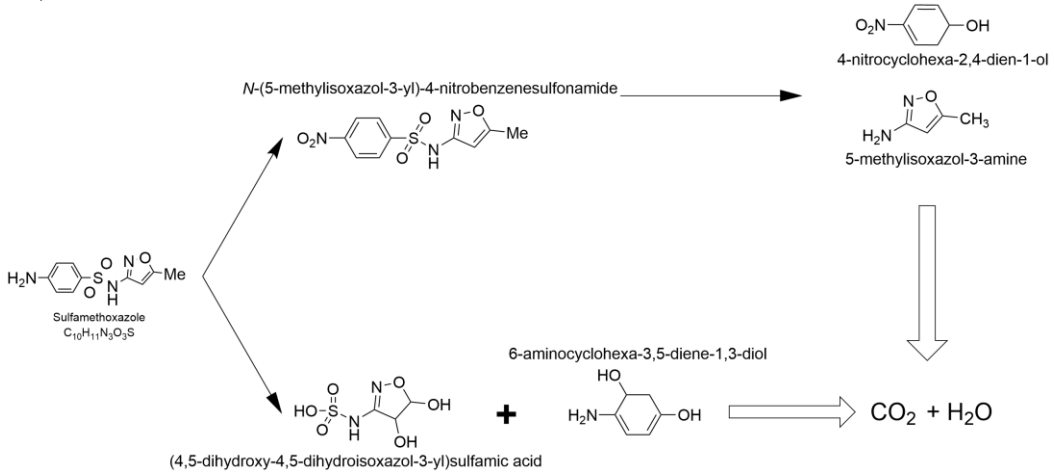

Figure 6 Proposed degradation pathways of SMX degradation by the FeOCl/H_2O_2 Fenton-like system.

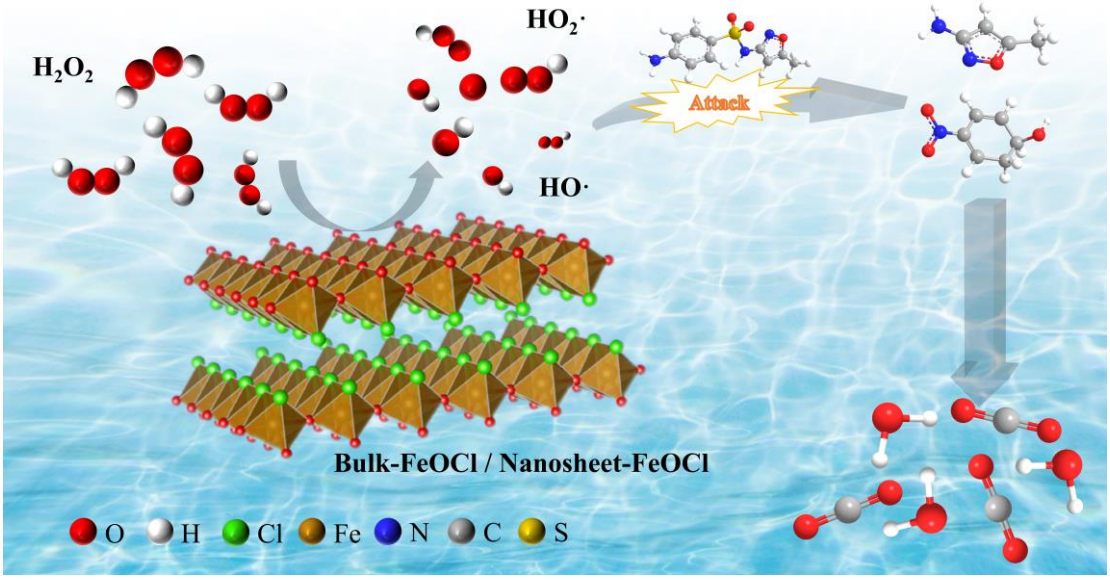

Figure 7 Proposed Fenton-like reaction mechanism for SMX degradation on the FeOCl/H_2O_2 surface.

Based on the experimental results, a Fenton-like reaction mechanism for SMX degradation on the nanosheet FeOCl surface is proposed, as depicted in Figure 7. The process is initiated by the

adsorption and activation of H_2O_2 on the Fe(III) sites of the FeOCl catalyst, facilitating the generation of hydroxyl radicals (•OH) and the reduction of surface Fe(III) to Fe(II). The surface Fe(II) species subsequently participate in a cyclic catalytic process by reacting with additional H_2O_2 molecules, regenerating Fe(III) sites while producing more •OH radicals.[23] This efficient redox cycling between Fe(III)/Fe(II) is significantly enhanced on the nanosheet FeOCl due to its larger surface area and superior electron transfer capability compared to the bulk material. The generated •OH radicals, either on the catalyst surface or released into the solution, then non-selectively attack the SMX molecules, leading to their decomposition through pathways involving hydroxylation, bond cleavage, and ultimately, mineralization.

4. Conclusion

In summary, this study successfully demonstrated that nanosheet FeOCl, synthesized via a simple exfoliation method, serves as a highly effective heterogeneous Fenton-like catalyst for the degradation of SMX. Nanosheet FeOCl exhibited significantly enhanced catalytic performance compared to its bulk counterpart, achieving high SMX removal efficiency over a broad pH range (3–9). The superior activity is attributed to its unique structural characteristics, including thinner multilayered morphology and reduced crystallite size, which collectively promote greater active site exposure and improved mass transfer. The distinctive properties of the FeOCl nanosheets represent a promising strategy for the development of advanced heterogeneous Fenton systems for pollutant degradation.

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