

Article

Influence of Seawater Characteristics on Antibiotic Pollutant Removal via Fe(II)-Peroxymonosulfate-Modified Clay

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Abstract: Antibiotics have been identified as emerging pollutants, and they increasingly threaten the safety of mariculture; thus, effective treatment methods are urgently needed. In this study, Fe(II)-peroxymonosulfate-modified clay (Fe-PMS-MC), an effective mineral complex for harmful algal bloom control, was tested for sulfamethoxazole (SMX) removal from seawater. The results showed that SMX removal efficiency increased gradually from 42.3% to 100% in seawater in 6 h as the Fe-PMS-MC dose increased from 0.1 g/L to 1.0 g/L; this removal was more efficient than that in freshwater. Both an increase in temperature and the addition of inorganic anions such as Cl^- , HCO_3^- , and SO_4^{2-} improved the SMX removal efficiency; in contrast, there was no noticeable influence of a pH change from 3.0 to 9.0 or of *Heterosigma akashiwo* biomass addition from 10^3 cells/mL to 10^5 cells/mL. Oxidation was the main mechanism for the removal of SMX by Fe-PMS-MC treatment, and the mechanisms included radical oxidation and non-radical oxidation. PMS was the key component in Fe-PMS-MC for the production of radicals, which increased with temperature. Similarly, both radical oxidation and non-radical oxidation increased when PMS was attacked by Cl^- , HCO_3^- , and SO_4^{2-} in seawater.

Keywords: antibiotic pollutant; environmental factor; modified clay; oxidation; seawater

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1. Introduction

In recent years, mariculture has developed quickly and has increasingly become an essential source of high-quality protein to supplement the population's diet and improve people's quality of life [1]. However, with mariculture increasing in intensity and scope and the excessive use of antibiotics growing, antibiotic pollution has become increasingly severe in aquaculture seawaters [2–5]. Antibiotic pollutants have evident toxic effects on the ecosystem and even on humans [6]; furthermore, antibiotic resistance genes (ARGs) are propagated among different organisms, and an increasing number of superbugs are created [7,8]. It has been found that antibiotic pollutants can promote the growth of microalgae and the synthesis of algal organic matter at concentrations of 60–300 ng/L [9]. The long-term presence of trace levels of antibiotic contaminants can cause harmful algal blooms (HABs) [10]. Therefore, antibiotics were added to urgently strengthen treatment by the Ministry of Ecology and Environment of China as one of the four types of new pollutants.

Due to the risks associated with antibiotics in water resources, multiple methods, such as physical adsorption, biological treatment and advanced oxidation processes (AOPs), have been extensively studied to control antibiotic pollution in municipal water and wastewater [11–14]. Physical adsorption is easy to apply but can lead to the generation

of secondary pollution [11,12]. Biological treatments rely on active species generated by microbial metabolism to remove antibiotics such as sulfamethoxazole (SMX) under suitable conditions [14]. AOPs can degrade SMX via strongly oxidizing active species such as $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ [15]. Peroxymonosulfate (PMS) has been extensively applied as an effective supplemental oxidizing agent for antibiotic pollutant treatment in wastewater [15–17]. Many studies have suggested that PMS can be activated using transition metal ions (such as Fe^{2+} and Mn^{2+}), heat, ultraviolet light, and so on to generate reactive radicals capable of removing most antibiotic contaminants. Transition metals are often used for the activation of PMS because of their certain reducing capacity. PMS can be activated by transition metals to produce a lot of reactive radicals such as $\text{SO}_4^{\bullet-}$. Although Co(II) has a great activation effect among various transition metal elements, it is poisonous and not suitable for large-scale practical application. In comparison, Fe(II) has been found to be the most commonly used transition metal ion with limited environmental impact, lower cost of use, and effective activation of PMS. And Fe(II) can effectively improve the removal efficiency of PMS for organic pollutants at lower dosages. It has been found that the SMX removal efficiency of the Fe(II)/PMS system was higher than that of the PMS system alone, and it has been clarified that Fe(II) had a significant contribution to the radical oxidation of PMS [18–20].

Although many methods have been successfully used to mitigate antibiotic pollution in wastewater, no efficient methods have been put forth for seawater treatment to date; furthermore, there is a lack of knowledge on the influences of seawater characteristics on the antibiotic treatment efficiency of methods applied to freshwater.

Seawater has some distinguishing characteristics, such as high salinity and abundance of various ions and microorganisms, which often form HABs under eutrophic mariculture conditions [21,22]. Therefore, HABs and antibiotic pollution have become the most typical environmental problems in mariculture. In the context of complex pollution conditions, there is an urgent need for fast and effective methods to ensure the sustainable development of aquaculture. In recent years, modified clays (MCs) have been developed into a series of HAB removal agents with unique effects, some of which were successfully applied in more than one coastal seawater [21,22]. But there is a lack of focused research on its effectiveness in controlling antibiotic pollutants. PMS is a common modifier for modified clays, and multiple PMS-modified MCs have been shown to be efficient in HAB control [23,24]. They can also effectively remove nutrients [25] and algal toxins [26] and have demonstrated a good capacity to remove organic pollutants in seawater [24,27,28].

In order to ensure the healthy and sustainable development of mariculture, safe and effective synergistic treatment methods are urgently needed for the frequent occurrence of HABs and antibiotic pollution in mariculture. How can antibiotics and algal blooms be simultaneously treated in complex seawater matrices with the modified clay method? What are the critical factors limiting antibiotic pollutant treatment in seawater? In this paper, we aim to provide an effective method for controlling antibiotic contamination in seawater. We investigated the efficiency of SMX removal by Fe-PMS-MC and the influence of several marine environmental factors on Fe-PMS-MC treatment. The SMX oxidation mechanism of Fe-PMS-MC was analyzed to demonstrate its excellent potential in the practical remediation of marine antibiotic pollution. This study is the first to demonstrate the treatment of antibiotic pollution in seawater with a modified clay method and shows that a modified clay complex could efficiently reduce SMX concentrations in seawater.

2. Materials and Methods

2.1. Materials

Kaolin and SMX (>98%) were purchased from Aladdin company. Potassium peroxymonosulfate sulfate ($2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$) was purchased from Macklin Co., Ltd. (Shanghai, China). Ferrous sulfate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$), aluminum sulfate (AS), NaCl , $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, NaHCO_3 , tert-butanol (TBA), and L-histidine (L-His) certified reagents

were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol (MeOH) of chromatography-grade purity was purchased from Merck company.

2.2. Experimental

2.2.1. Preparation of the Modified Clay

The raw clay material was kaolin [29], the clay:AS weight ratio of the modified clay (MC) was 5:1.879 wt/v%, the oxidizer was PMS, Fe(II) was obtained from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and the specific method of surface modification treatment of clay was described by Yu et al. [30].

2.2.2. Preparation of the SMX Solution and Artificial Seawater

SMX (100 mg) was precisely weighed, dissolved in 700 mL of ultrapure water, sonicated at 25 °C for 30 min, transferred to a brown volumetric flask (1 L) with ultrapure water to adjust the volume and prepared as a stock solution with a concentration of 100 mg/L. The stock solution (100 mL) was added to a 1 L volumetric flask and diluted with ultrapure water to obtain a 10 mg/L SMX solution. Simulated seawater was prepared by dissolving in $\text{NaCl}:\text{MgSO}_4 \cdot 7\text{H}_2\text{O}:\text{NaHCO}_3$ at a weight ratio of 31:10:0.5 wt/v% in ultrapure water (1 L) [31].

2.2.3. Cultivation of the Microalgae

Heterosigma akashiwo was used as the red tide algal species, and was obtained from the Key Laboratory of Marine Ecology and Environmental Science, Chinese Academy of Sciences. The experimental algal species were cultured in L1 media with a light-dark ratio of 1:1 at 20 ± 1 °C; the algal solution was shaken regularly during the culturing process, and the algal solution was removed at certain target algal density stages for the experiment [32].

2.2.4. SMX Removal Experiments

A measured aliquot of the 10 mg/L SMX solution (prepared in Section 2.2.2) was taken and transferred to a 100 mL colorimetric tube at 25 ± 0.5 °C. An MC stock solution (25 g/L) was added to adjust the solution to the target MC concentration in the reaction solution. After the reaction, the solution was filtered by a 0.22 µm needle filter membrane, and then the solution was quenched with methanol and placed in a brown chromatography bottle stored at −20 °C. All experiments were conducted in triplicate. The quenching agents were MeOH, TBA, and L-His. Algae organic matter (AOM) was obtained from the filtered algal solution, and its concentration was measured via a TOC analyzer. The salinity of the reaction solution was regulated by a salinometer.

2.3. Analysis Methods

2.3.1. Analysis of SMX

The SMX concentration was determined via high-performance liquid chromatography (HPLC, Waters e2695) coupled with a diode array detector (Waters 996), and the SMX concentration was quantified by using the external standard method. The mobile phase ratio was 0.1% formic acid: methanol (60:40 (v/v)), and the column temperature was 30 ± 1 °C. The detection wavelength was 270 nm, and the flow rate was 1 mL/min.

2.3.2. Analysis of the PMS Concentration

The PMS concentration was tested via the iodometric-UV photometric method [33]. NaHCO_3 and KI were accurately weighed and added to ultrapure water to obtain the PMS chromogenic agent. PMS chromogenic agent and filtered solution were added to a cuvette. The absorbance was measured at 400 nm using a UV-visible spectrophotometer (Beijing, China).

2.3.3. Analysis of the Fe(II) Concentration

Fe(II) concentrations were detected via phenazine-UV spectrophotometry [34]. In an acetic acid-sodium acetate buffered medium at pH 4.5, a complex purple compound of

Fe(II) and PDT disulfonate was formed, whose maximum absorption peak was at 562 nm. Acetic acid and sodium acetate were added to ultrapure water to obtain a buffer at pH 4.5. PDT disulfonate was added to the buffer to obtain the Fe(II) chromogenic agent. The filtered solution and chromogenic agent were sequentially added to a cuvette, and the absorbance was measured at 562 nm.

2.3.4. Statistical Analysis

SPSS Statistics (version 26.0) was used for a 1-way ANOVA, and statistics were considered significant at $p < 0.05$. All graphs were plotted in Origin 2018.

3. Results and Discussion

3.1. SMX Removal Efficiency of Fe-PMS-MC

In this study, Fe-PMS-MC was selected as the modified clay and tested for SMX removal in seawater. As shown in Figure 1, the experimental results of the SMX solution treated with the Fe-PMS-MC in different environments indicated that the removal rate of the 10 mg/L SMX solution steadily increased from 42.3% to 100% in seawater as the dosage of the Fe-PMS-MC increased from 0.1 to 1.0 g/L. By further analyzing the SMX removal curve by Fe-PMS-MC treatment in seawater, we found that SMX removal followed a two-phase kinetic model with the first 5 min as the fast stage and the range from 5 to 360 min as the slow stage. In a few similar studies, it was found that SMX removal by the UV/PS system was inhibited by inorganic anions in seawater, which resulted in lower SMX removal efficiency than in freshwater [18]. In this study, Fe-PMS-MC had efficient SMX removal in both seawater and freshwater, and the SMX removal rate in seawater was higher than that in freshwater. This result is exciting, but seawater features are very complex. The SMX removal efficiency by the Fe-PMS-MC could be affected by complex environmental factors in seawater.

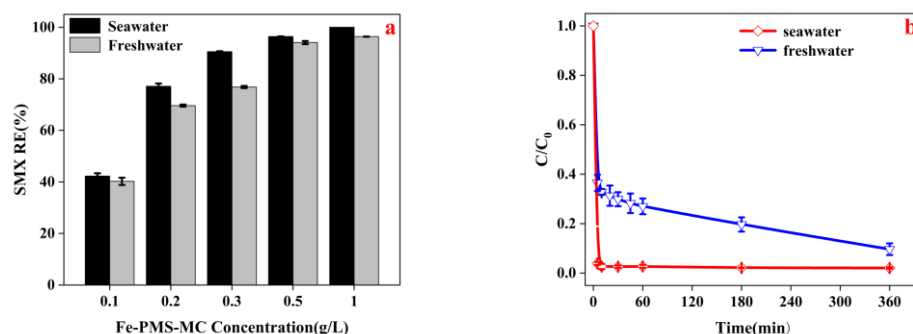


Figure 1. SMX removal rates (a) and curves (b) by Fe-PMS-MC treatment in seawater and freshwater.

3.2. Influences of Various Seawater Features

Seawater has unique characteristics, such as high salinity and abundance of various ions and microorganisms; therefore, the effect of various marine features, such as water temperature, pH, salinity, inorganic anions, microalgae, and AOM, on the SMX removal efficiency was investigated.

As shown in Figure 2a, the experimental results of the temperature effect on the SMX removal efficiency indicated that the removal rate of 10 mg/L SMX increased steadily from 28.6% to 77.9% within 6 h as the water temperature was increased from 25 to 55 °C with a 0.2 g/L dose of the Fe-PMS-MC. The rise in temperature mainly boosted the SMX removal efficiency in the first 5 min of the reaction. Similarly, it has been found that an increase in temperature improved the removal efficiency of PMS for other pollutants [19,35]. However, excessive temperature could cause a decrease in the oxidation efficiency of PMS in Fe-PMS-MC [36]; hence the temperature should be kept within an appropriate range. In addition, as shown in Figure 2b, the results of the influence of pH varied from 3.0 to 11.0, indicating that the SMX removal rate was not significantly increased or reduced in

a pH range of 3.0–9.0 ($p > 0.05$). However, when the pH was elevated from 9.0 to 11.0, the removal rate of SMX was reduced from 41.2% to 26.5% within 6 h and slowed in the first 5 min at pH 11. In contrast, some researchers have believed that alkaline conditions could promote PMS oxidation capacity [15,36]. We discuss the reasons limiting Fe-PMS-MC under peralkaline conditions in Section 3.3.

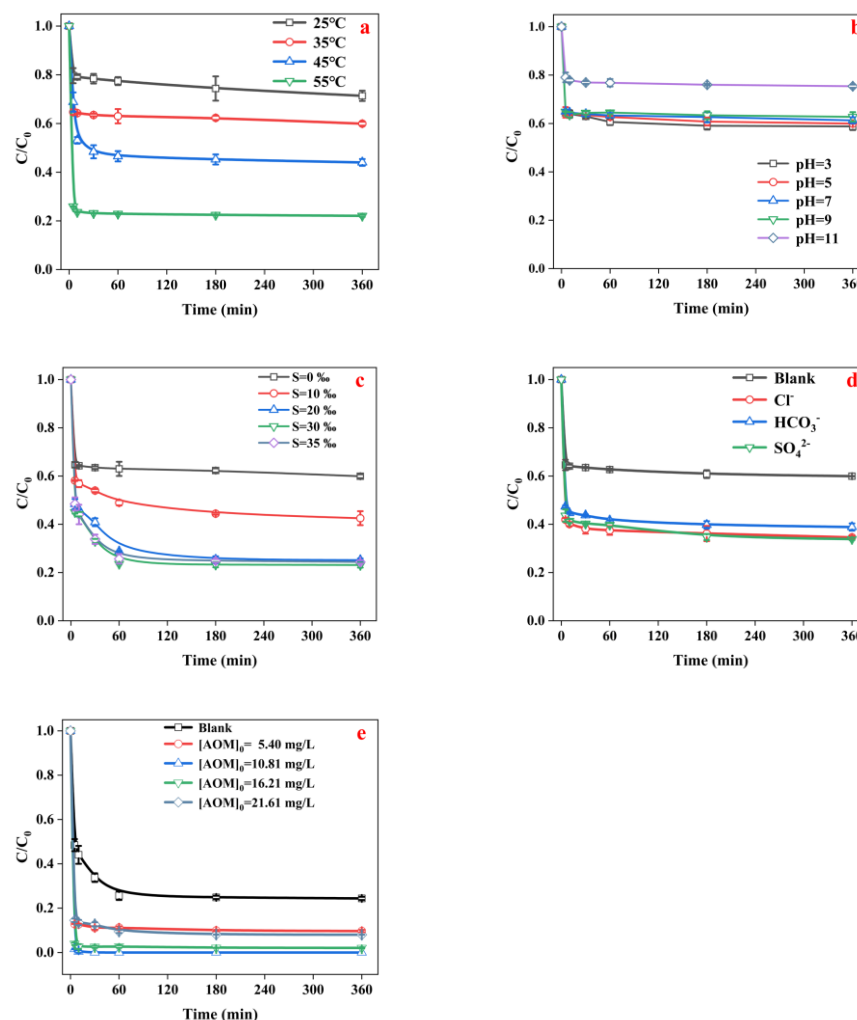


Figure 2. Effect of the marine environmental factors on the SMX removal efficiency by the Fe-PMS-MC (temperature (a), initial pH (b), salinity (c), inorganic anion (d), AOM (e); $[SMX]_0 = 10$ mg/L; $[Fe-PMS-MC]_0 = 0.2$ g/L; $Fe(II):PMS:MC = 0.135:0.15:1.0$ wt/v%).

High salinity is the main characteristic that distinguishes seawater from common freshwater systems. The SMX removal rate increased considerably from 40.1% to 74.8% as the salinity increased from 0‰ to 20‰ ($p < 0.05$). However, as shown in Figure 2c, there was no significant improvement in the SMX removal rate by the Fe-PMS-MC after the salinity was above 20‰ ($p > 0.05$). The abundance of inorganic anions is one of the main reasons for the high salinity of seawater [37,38], and Cl^- , HCO_3^- , and SO_4^{2-} are the most abundant anion species. Therefore, concentrations of Cl^- , HCO_3^- , and SO_4^{2-} were adjusted to 0.53 M, 40.6 mM, and 6.0 mM, respectively, to analyze their impact on SMX removal efficiency by Fe-PMS-MC in our study. As shown in Figure 2d, within 6 h of the reaction, Cl^- , HCO_3^- , and SO_4^{2-} increased the SMX removal rate by the Fe-PMS-MC from 28.3% to 65.4%, 61.1%, and 66.1%, respectively, and their effects were primarily concentrated in the first 5-min fast stage. Cl^- is the most abundant inorganic anion in seawater, which promoted the SMX removal efficiency of Fe-PMS-MC. It has been suggested that, at high concentrations, Cl^- could promote SMX removal by PMS at Fe-PMS-MC; in contrast, low

concentrations of Cl^- would inhibit Fe-PMS-MC-driven oxidation [39]. However, some studies found that HCO_3^- and SO_4^{2-} had no influence or had an inhibitory effect in PMS-dominated oxidation systems [39,40]; these results are opposite to those presented in this paper. On the basis of the mechanism presented in part 3.3, we inferred the reason why HCO_3^- and SO_4^{2-} promoted SMX removal, but more in-depth studies are needed to elucidate it.

Heterosigma akashiwo is extensively distributed in offshore water bodies and is one of the most damaging red tide species to aquaculture seawater [21,22]. Therefore, two typical algal densities (10^3 cells/mL and 10^5 cells/mL) of a red tide outbreak were simulated in our study. The comparative results from Figure 3a,b showed that Fe-PMS-MC could effectively remove SMX at the two algal densities, and there was almost no difference in the removal effect. The SMX removal rate was effectively improved by increasing the Fe-PMS-MC dosage at different algae densities in seawater. The specific experimental results showed that the removal rate with 10 mg/L SMX was more than 90% at 0.4 g/L Fe-PMS-MC. However, it has been found that microalgae have SMX removal effects when they are active [41,42]. In this work, the analysis suggested that the reason for the difference was based on the efficient microalgae removal capability of the modified clay [22]. Oxidation by the composite-modified clay mainly relied on the two mechanisms of flocculation and oxidation to obtain an efficient algal removal effect [24]. Therefore, a large amount of *Heterosigma akashiwo* was removed and killed in the reaction system, so the algae had almost no influence on SMX removal. Moreover, AOM is the main factor in the indirect photodegradation of antibiotics by microalgae, and microalgae create substantial amounts of AOM in offshore waters that could influence the migration and transformation of antibiotics in seawater [43]. As shown in Figure 2e, AOM improved the SMX removal efficiency by the Fe-PMS-MC in seawater compared with the control group that did not contain AOM. The SMX removal rate increased as the AOM concentration increased from 5.40 to 10.81 mg/L and slightly decreased as the AOM concentration increased from 10.81 to 21.61 mg/L in seawater. This result was most likely related to the oxidation of SMX by the reactive species formed during the reaction of PMS with AOM.

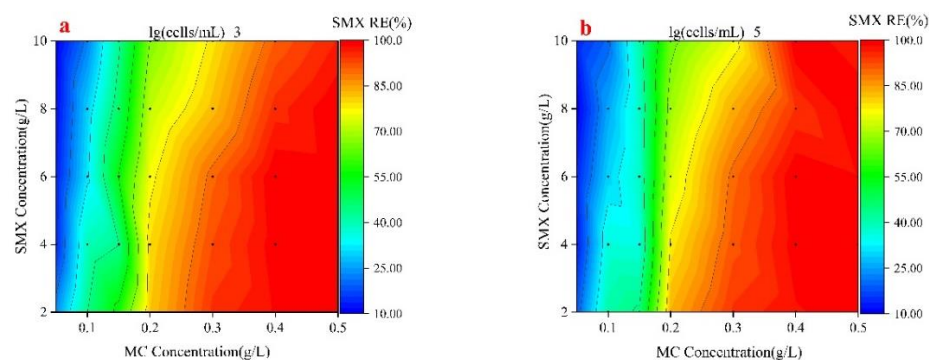


Figure 3. Effect of the *Heterosigma akashiwo* with algal densities of 10^3 cells/mL (a) and 10^5 cells/mL (b) on the SMX removal efficiency by the Fe-PMS-MC.

3.3. Mechanism of SMX Removal by the Fe-PMS-MC

PMS has a strong oxidative capacity, and it has been found that the PMS system can effectively oxidize and degrade SMX [44]. As a reducing agent, Fe^{2+} has been found to be an efficient activator that promotes the PMS oxidative capacity [45]. To further clarify the mechanism of SMX removal, the concentrations of PMS and Fe(II) were measured according to the methods in Sections 2.3.2 and 2.3.3 along with the SMX removal by Fe-PMS-MC, and then the variation and effects of PMS and Fe(II) were analyzed. The consumption rate of PMS was found to be much higher in the Fe-PMS-MC system compared to the control PMS-MC and MC systems during the removal of SMX. As illustrated in Figure 4a, the results showed that the changes in PMS also followed a two-phase kinetic model with the first 5 min as the rapid-reaction stage and the range from 5 to 360 min as the slow stage.

A total of 81.9% of the PMS was rapidly consumed in the first 5 min, and only 5.3% of the PMS was reduced in the 5–360 min phase. The variation in PMS concentration was similar to the trend in the SMX removal rate, so the result of our preliminary analysis was that the PMS in Fe-PMS-MC played a major role in SMX removal. Moreover, the Fe(II) variation process had characteristics similar to those of PMS. As shown in Figure 4b, the Fe(II) in Fe-PMS-MC was rapidly and completely consumed in the first 5 min, but the Fe(II) in the Fe-MC control system was essentially not consumed. This also verified that the Fe(II) activation action was highly effective and rapid with PMS. Fe^{2+} could be oxidized to Fe^{3+} , and both were converted to precipitates and separated out of the solution during the reaction. Fe^{2+} promoted the production of reactive radicals and the oxidative degradation of organic pollutants by PMS [46]. Fe(II) promoted the generation of radicals by PMS, improving the oxidative degradation of SMX by Fe-PMS-MC. This result suggested that the efficient SMX removal by the Fe-PMS-MC was caused by the oxidation of PMS (HSO_5^-) and the activation of Fe(II) (Equation (1)).

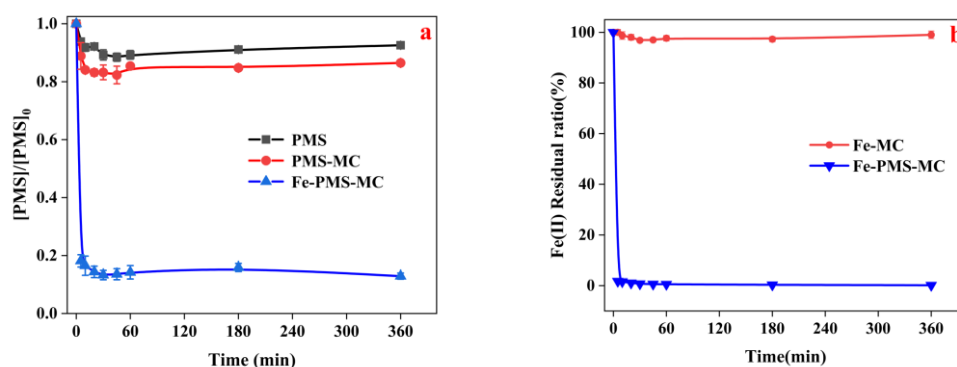
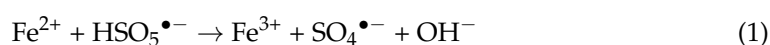


Figure 4. Kinetic variation curves of PMS (a) and Fe(II) (b) concentrations in the Fe-PMS-MC ($[\text{SMX}]_0 = 10 \text{ mg/L}$; $\text{Fe(II):PMS:MC} = 0.135:0.15:1.0 \text{ wt/v\%}$; 25°C).

Some studies have found that the process of removing SMX is mostly comprised of radical oxidation and non-radical oxidation by PMS [47]. Non-radical oxidation comprises singlet oxygen ($^1\text{O}_2$) and direct electron transfer, and radical oxidation occurs mostly to produce $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ [39]. MeOH contains $\alpha\text{-H}$ and has a high quenching rate for both $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ ($k_{\text{MeOH-SO}_4^{\bullet-}} = 3.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$; $k_{\text{MeOH-}\bullet\text{OH}} = 9.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). However, TBA does not contain $\alpha\text{-H}$ and has a higher affinity for $\bullet\text{OH}$ ($k_{\text{TBA-}\bullet\text{OH}} = 3.8\text{--}7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) compared to $\text{SO}_4^{\bullet-}$ ($k_{\text{TBA-SO}_4^{\bullet-}} = 4.0\text{--}9.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$), and L-His is a typical $^1\text{O}_2$ quencher ($k_{\text{L-His-}^1\text{O}_2} = 5.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) [34,48,49]. As a result, the impact variations of these three quenching agents on the different radical species were investigated for the reactive species of the Fe-PMS-MC.

As shown in Figure 5, MeOH, TBA, and L-His all showed strong quenching effects on the Fe-PMS-MC and decreased the SMX removal rate by the Fe-PMS-MC from 90.3% to 26.6%, 42.8%, and 15.0%, respectively. On the one hand, MeOH and TBA inhibited the SMX removal by a wide margin, and the inhibition effect of MeOH was more significant than that of TBA ($K_2 < K_1$). This showed that the PMS in Fe-PMS-MC was activated to generate a large amount of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ to remove SMX via radical oxidation. On the other hand, L-His also had a significant inhibitory effect on SMX removal, which suggested $^1\text{O}_2$ -based non-radical oxidation was also a key process for the Fe-PMS-MC. Therefore, the process for SMX removal by the Fe-PMS-MC included both radical oxidation and non-radical oxidation.



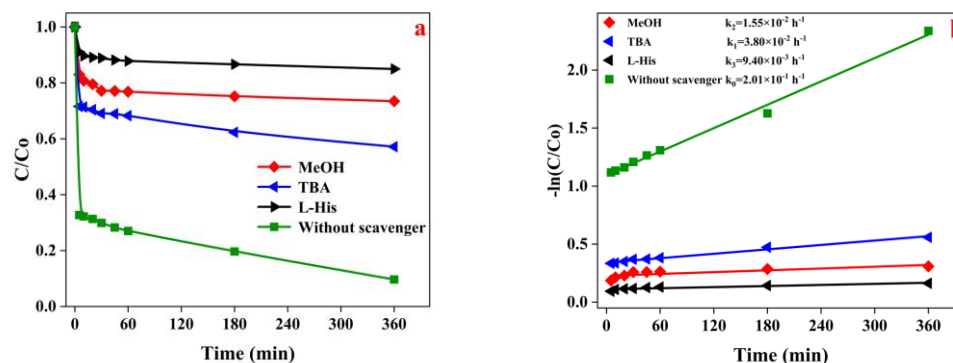
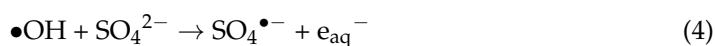


Figure 5. Effects of the three quenching agents on the SMX removal (a) and pseudo-first-order kinetic curve (b) ($[\text{SMX}]_0 = 10 \text{ mg/L}$; $\text{Fe(II)}:\text{PMS}:\text{MC} = 0.135:0.15:1.0 \text{ wt/v\%}$; 25°C).

Based on the mechanism of Fe-PMS-MC removal of SMX, the varied impacts of diverse marine environmental factors on SMX removal via Fe-PMS-MC were analyzed. An increase in temperature produced more $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ (Equation (2)) by promoting the breaking of the asymmetric peroxide bonds in PMS to increase the SMX removal rate [17,20,50]. However, at $\text{pH} = 11.0$, the production of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ was inhibited. The system could convert SO_4^{2-} to SO_5^{2-} , which lowered the oxidation rate at $\text{pH} > 9.4$ [49]. Moreover, the alkaline solution inhibited the conversion of O_2 to $^1\text{O}_2$, which reduced the production of $^1\text{O}_2$ in the system [51]. The free Fe(II) and Fe(III) were prone to hydroxide precipitation in the alkaline environment; thus, Fe(II) was partially consumed, limiting the PMS activation.

Cl^- was used as a nucleophilic reagent to directly attack PMS to generate HOCl , which has a high oxidative capacity for non-radical oxidation [19,37], and HOCl could rapidly oxidize and remove SMX (Equation (3)). In addition, HCO_3^- was able to promote the production of $^1\text{O}_2$ from PMS to increase SMX removal through non-radical oxidation [38]. SO_4^{2-} contributed to SMX removal by inducing the formation of $\text{SO}_4^{\bullet-}$ from $\bullet\text{OH}$ (Equation (4)) [40]. This result showed that high salinity and inorganic anion content could facilitate SMX removal by the Fe-PMS-MC in seawater. Some studies have also shown that microalgae could remove antibiotics to a certain extent, which was mainly attributed to the production of reactive radicals (such as $\bullet\text{OH}$ and $^1\text{O}_2$) by AOM that promote the degradation of antibiotics [43]. Additionally, it was reported that quinone and phenolic groups from AOM could activate PMS to form $^1\text{O}_2$ to remove antibiotics [15].

The various marine environmental factors primarily influenced SMX removal by affecting the non-radical oxidation and radical oxidation of the Fe-PMS-MC. Non-radical oxidation typically has higher selectivity [16,51] to enhance the applicability and stability of the Fe-PMS-MC to complex environmental matrices with high salinity, abundant complex ions, microalgae, and AOM and is an essential reason for the steady and effective SMX removal by the Fe-PMS-MC in complicated marine systems. The results showed that Fe-PMS-MC is promising for large-scale and field applications to treat antibiotic pollution in seawater.

4. Conclusions

This study is aimed at antibiotic pollution control in aquaculture seawater. It is necessary to estimate the ecological safety and test the efficacy of the modified clay method in actual aquaculture seawater before field applications. In this study, it was found for the first time that modified clay complexes could effectively reduce SMX concentrations in seawater, and the Fe-PMS-MC method was developed accordingly. Fe-PMS-MC had a higher SMX removal rate in seawater than in freshwater. SMX removal by the Fe-PMS-MC process included a rapid reaction in the first 5 min and a slow reaction in the time range from 5 to 360 min. Both an increase in temperature and the presence of Cl^- , HCO_3^- , and SO_4^{2-} in seawater increased the SMX removal efficiency by the Fe-PMS-MC; in contrast, the high

pH (≥ 11.0) inhibited the removal of SMX. There were different pathways that influenced SMX removal by Fe-PMS-MC treatment. Heat could promote the breakage of the peroxy bonds of PMS and activate the generation of more radicals. High salinity and inorganic anions increased the efficiency of SMX removal. Similarly, both radical oxidation and non-radical oxidation rates increased when PMS was attacked by Cl^- , HCO_3^- , and SO_4^{2-} in seawater. Overall, the combined effect of all factors caused an evident enhancement of the SMX removal efficiency in seawater. Therefore, the Fe-PMS-MC could be a promising material for both antibiotic pollution treatment and microalgae control in mariculture.

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