

## Research Article

# Sonocatalytic Degradation of Antibiotics Tetracycline by Mn-Modified Diatomite

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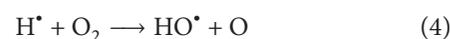
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Mn-modified diatomite was prepared by wet impregnation and subsequent calcinations processes. It was used as catalyst for sonocatalytic degradation of antibiotics tetracycline. Characterizations by scanning electron microscopy and X-ray diffraction pattern showed that the morphology and crystal structure of the modified diatomite were similar to these of raw diatomite. Despite containing very limited amount of Mn oxides, the Mn-modified diatomite showed much higher sonocatalytic activity than the raw diatomite. The increases in both  $\text{MnSO}_4$  concentration of the wet impregnation solution and the catalyst dosage could enhance the degradation of antibiotics tetracycline significantly.  $K_{\text{app}}$  values for ultrasonication, catalyst adsorption, and both processes combined (0.10 mol/L  $\text{MnSO}_4$ -modified diatomite) were  $1.22 \times 10^{-4}$ , 0.00193, and  $0.00453 \text{ min}^{-1}$ , respectively, while the corresponding values of  $R^2$  were 0.956, 0.986, and 0.953, respectively. These results demonstrated the significant synergetic effect by combining ultrasonication and catalyst adsorption processes. The presence of isopropanol, KBr, and  $\text{NaN}_3$  quenched a series of reactive oxygen species sharply, indicating the dominant role of reactive oxygen species in the sonocatalytic process. In contrast, the addition of Fe(II) enhanced the degradation due to the generation of more  $\text{OH}^\bullet$  radicals in the concurrent Fenton reaction. All the results indicated that Mn-modified diatomite had the great potential for water treatment by sonocatalytic oxidation.

## 1. Introduction

As one of the advanced oxidation processes (AOPs), sonochemical process has attracted wide attention because it is capable of degrading a large variety of organic pollutants [1–6]. It is well known that AOPs are characterized by the generation of highly reactive hydroxyl radicals as the main oxidative species for the breakdown and mineralization of organic contaminants [7, 8]. During sonochemical process, acoustic cavitation generates hot spots with localized temperatures and pressures on the order of 5000 K and hundreds of atmospheres, respectively. Thermal dissociation of water vapor into reactive hydroxyl radicals and the formation of other radicals occur as the following equations [4, 9, 10]:



Accordingly, reactive oxygen species (ROSs) such as  $\text{OH}^\bullet$  and  $\text{OOH}^\bullet$  are produced through a series of reactions and contribute to the decomposition of organic contaminants.

However, sonochemical process alone has a very limited efficiency and consumes considerable energy for the decomposition of organic contaminants [5, 11]. In order to enhance the degradation performance, catalysts are needed to assist sonochemical process, which is called sonocatalytic process. A number of catalysts have been tested in sonocatalytic process [2, 5, 11, 12]. It was reported that the efficiency of sonochemical degradation process can be improved by these catalysts dramatically. Recently, natural diatomite was also proven to be capable of catalyzing the sonochemical degradation of methylene blue and a synergetic effect was also observed [13]. As a siliceous and low-cost material abundant in natural environment, diatomite has the potential for practical sonocatalytic process because it possesses advantages such as high

porosity, high permeability, large surface area, and chemical inertness [14]. Meanwhile, Mn oxides were proven to be an excellent catalyst under ultrasonic irradiation as well [15, 16]. The combination of diatomite with Mn oxides might further enhance the sonochemical degradation efficiency due to the possible synergetic effect. In this research, manganese oxides were immobilized onto natural diatomite by wet impregnation and subsequent calcinations processes. The composite of manganese oxides and diatomite was used for the sonochemical degradation of organic pollutants to evaluate sonocatalytic performance.

Tetracyclines are the second most widely used antimicrobial chemicals globally, which are widely applied in human therapy and livestock industry [17]. As tetracycline molecules are usually neutral or negatively charged in environmental water, conventional techniques such as sand filtration, sedimentation, flocculation, and coagulation are not very efficient for tetracycline removal as expected [18]. As a result, tetracycline was selected as a target organic pollutant for the sonocatalytic process in this study. Additionally, the mechanism for the enhanced degradation performance of sonocatalytic process has not yet been reported in detail. Hence, the oxidation mechanism was indirectly evaluated by adding scavengers such as isopropanol,  $\text{NaN}_3$ , and KBr, respectively. The effect of radical promoter Fe(II) was also investigated concurrently.

## 2. Materials and Methods

**2.1. Materials.** Tetracycline (TC) was purchased from Hefei Bomei Biological Science and Technology Co., Ltd. (Anhui province, China), and it was used without further purification. Diatomite was provided by Linjiang Meston Powdery Materials Co., Ltd. (Jilin province, China). Other chemicals used were of analytical grade. Deionized (DI) water was used to prepare all solutions.

**2.2. Preparation of Mn-Modified Diatomite.** A series of  $\text{MnSO}_4$  solutions with a concentration gradient of 0.01, 0.05, 0.10, 0.50, and 1.0 mol/L were used for the wet impregnation of the raw diatomite. The diatomite/solution ratio was 1 g/10 mL. The mixture of diatomite and  $\text{MnSO}_4$  solution was agitated in an orbital shaker at 140 rpm and room temperature for 24 h. The modified diatomite was collected by filtration and dried at 100°C overnight. Finally, the raw diatomite and treated diatomite were calcined at 500°C for 2 h. The prepared 0.10 mol/L  $\text{MnSO}_4$ -modified diatomite is denoted as Mn-modified diatomite.

**2.3. Characterization.** The morphologies of raw diatomite and the Mn-modified diatomite were recorded on a Philips Quanta-2000 scanning microscope coupled with an energy dispersive X-ray (EDX) spectrometer. Their X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-3B X-diffractometer. FTIR spectra (KBr pellets) were recorded on a Nicolet NEXUS 470 FTIR spectrophotometer from 400 to 4000  $\text{cm}^{-1}$ .

**2.4. Sonocatalytic Degradation of TC by Mn-Modified Diatomite.** Degradation of TC was carried out in a beaker for 60 min. The available volume of the beaker was 250 mL and 200 mL of TC solution was added. Sonication was performed in a 40 kHz ultrasonic cleaning bath (AS3120A, Kunshan Ultrasonic Instruments Co., Jiangsu, China). The power of the ultrasonic cleaning bath was 50 W. The water-circulating unit was used to control water bath temperature.

**2.5. Analyses.** Samples were collected and filtered through a 0.45  $\mu\text{m}$  membrane before analyzing. The concentration of TC was determined by measuring the maximum absorbance at a fixed wavelength (360 nm) [19], using an UVmini-1240 spectrophotometer (Shimadzu, Japan).

The removal efficiency of TC was calculated as

$$\text{removal efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%. \quad (5)$$

The pseudo-first-order kinetics for TC degradation was simulated as [20]

$$\ln\left(\frac{C_0}{C_t}\right) = K_{\text{app}}t, \quad (6)$$

where  $C_t$  is the TC concentration at time  $t$ ,  $C_0$  is the initial TC concentration, and  $K_{\text{app}}$  is the apparent first-order rate constant.

## 3. Results and Discussion

**3.1. Characterization of Mn-Modified Diatomite.** The raw diatomite used was comprised of the discoid plates like lotus head and fragments of these plates. Most of the discoid plates were in the range of 5–50  $\mu\text{m}$ . These data had been referred to in our previous study [13]. As illustrated in Figure 1(a), for the Mn-modified diatomite, there was no significant change in the morphologies after the modification. The content of manganese element was found to be about 0.22% (atomic ratio) by EDX analysis, as presented in Figure 1(b). This indicated that only a very limited amount of Mn oxides was immobilized onto the diatomite.

The XRD patterns of the raw diatomite and the used Mn-modified diatomite were examined and presented in Figure 2. The strong and broad peak at  $2\theta = 21.8^\circ$  was related to the diffraction peak of cristobalite (JCPDS number: 39-1425), while the weak peak at  $2\theta = 26.6^\circ$  was attributed to quartz (JCPDS number: 46-1045). Both the two peaks were the major characteristic peaks of diatomite. Apparently, the XRD patterns of the Mn-modified diatomite were almost identical to those of the raw one. This result demonstrated that the structure of diatomite was not significantly changed after the modification.

The FTIR spectra of the raw diatomite, the Mn-modified diatomite, and the used Mn-modified diatomite were recorded in Figure 3, respectively. As the content of silicon element was found to be about 33.34% (atomic ratio) by EDX analysis, the absorption bands at 465 and 800  $\text{cm}^{-1}$  were evidently ascribed to the vibrations of Si–O group.

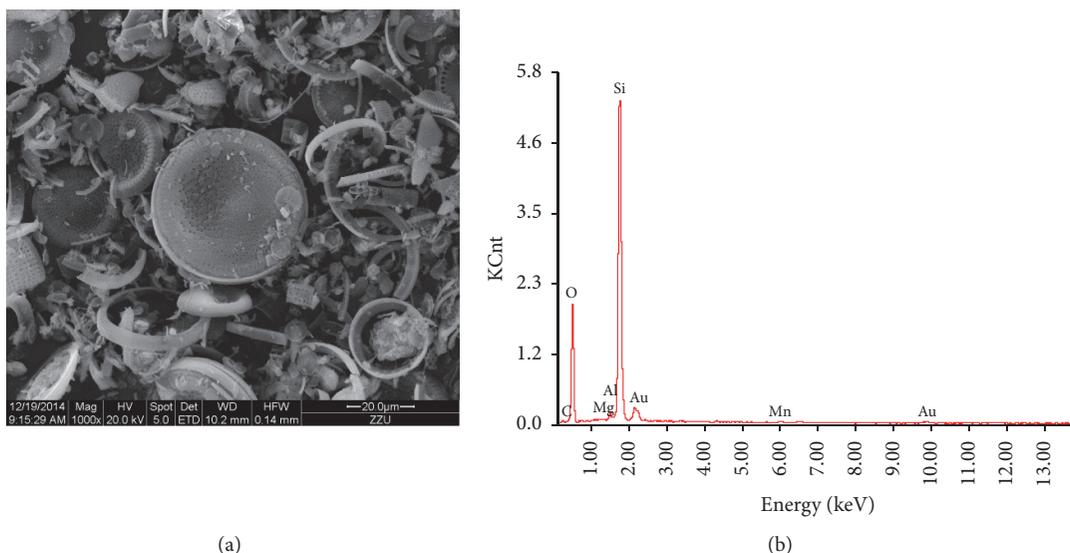


FIGURE 1: SEM image (a) and EDX graph (b) of Mn-modified diatomite.

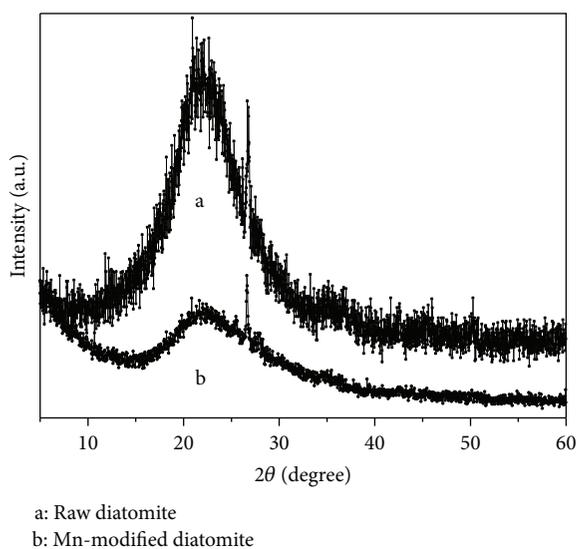


FIGURE 2: XRD patterns of raw diatomite (a) and Mn-modified diatomite (b).

For both the raw Mn-modified diatomite and the used Mn-modified diatomite, after the sonocatalytic degradation, they shared the bands at 556, 616, and 724  $\text{cm}^{-1}$ , which could be attributed to the immobilization of Mn oxides [21]. Here, the presence of Mn oxides on the modified diatomite was evidently confirmed.

**3.2. Effect of  $\text{MnSO}_4$  Concentration on the Sonocatalytic Degradation of TC.** As the concentration of  $\text{MnSO}_4$  used in the wet impregnation solution for the raw diatomite varied from 0.01 to 1.0 mol/L, the content of Mn oxides immobilized on the diatomite was expected to increase accordingly. The effect of  $\text{MnSO}_4$  concentration on catalytic activity of the modified diatomite in the sonocatalytic degradation of TC

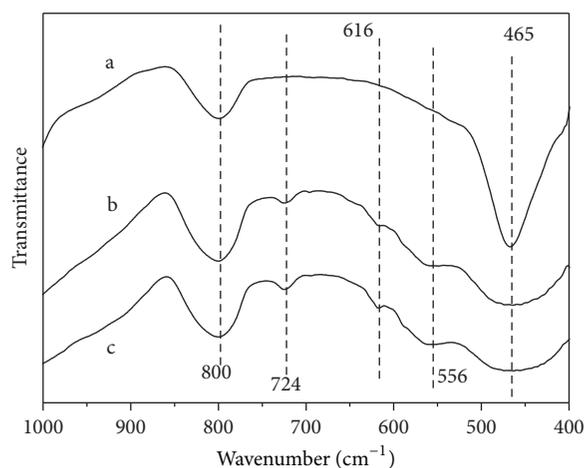


FIGURE 3: FTIR spectra of raw diatomite (a), raw Mn-modified diatomite (b), and used Mn-modified diatomite (c).

was investigated and the results were plotted in Figure 4.  $K_{\text{app}}$  values for the diatomite modified with  $\text{MnSO}_4$  concentration of 0.01, 0.05, 0.10, 0.50, and 1.0 mol/L were 0.00341, 0.00384, 0.00453, 0.00521, and 0.00586  $\text{min}^{-1}$ , respectively, while the corresponding values of  $R^2$  were 0.930, 0.930, 0.953, 0.916, and 0.937, respectively. Evidently, the degradation efficiency of TC increased with the increase in  $\text{MnSO}_4$  concentration because of the increased amounts of Mn oxides immobilized on the modified diatomite. As a comparison,  $K_{\text{app}}$  value for the raw diatomite, that is, when  $\text{MnSO}_4$  concentration was zero in Figure 4, only achieved 0.00163  $\text{min}^{-1}$ , while  $R^2$  value was 0.961, which was only about one-third of  $K_{\text{app}}$  value on the 0.10 mol/L  $\text{MnSO}_4$ -modified diatomite. However, the content of Mn element was found to be only about 0.22% (atomic ratio) on the 0.1 mol/L  $\text{MnSO}_4$ -modified diatomite. It seemed that the very limited amount of Mn oxides

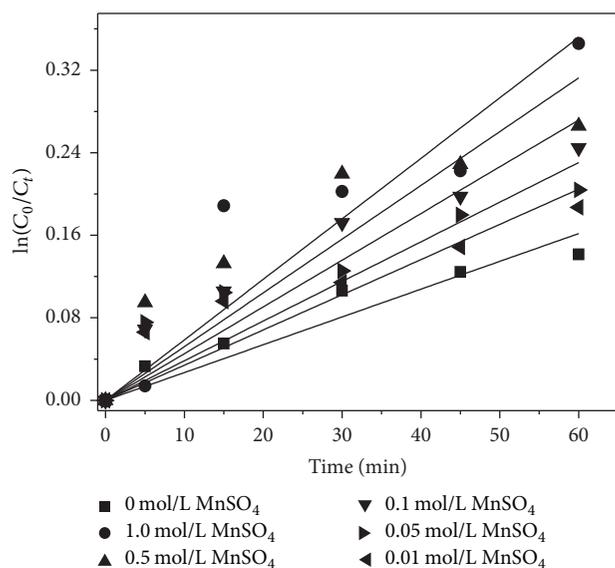


FIGURE 4: Effect of  $\text{MnSO}_4$  concentrations on the sonocatalytic degradation of TC (conditions: catalyst dosage of 160 mg in 200 mL TC solution and TC concentration of 50 mg/L at neutral pH).

could enhance TC degradation significantly. Due to the fact that the enhancement effect of  $\text{MnSO}_4$  concentration only improved slightly when  $\text{MnSO}_4$  was further increased after the concentration value of 0.10 mol/L, the 0.10 mol/L  $\text{MnSO}_4$ -modified diatomite was used in the following study, which was also denoted as Mn-modified diatomite as mentioned previously.

### 3.3. Synergetic Effect for the Sonocatalytic Degradation Process.

As reported in our previous study, the combination of diatomite and ultrasonication could lead to the significant synergetic effect [13]. As presented in Figure 5, the three processes including ultrasonication, catalyst adsorption, and the combined process were compared. However, the TC removal mechanisms concerning ultrasonication and catalyst adsorption were totally different in nature. TC was degraded by a series of oxidizing species generated during ultrasonic process, while its molecules were only transferred from aqueous solution to the surface of Mn-modified diatomite during adsorption process. As to the sonocatalytic degradation involving catalyst and ultrasonic irradiation, the removal was attributed to both degradation and adsorption effects.  $K_{app}$  values for ultrasonication, catalyst adsorption, and the combined process were  $1.22 \times 10^{-4}$ ,  $1.93 \times 10^{-3}$ , and  $4.53 \times 10^{-3} \text{ min}^{-1}$ , respectively, while corresponding  $R^2$  values were 0.956, 0.986, and 0.953, respectively.  $K_{app}$  value for the combined process was 2.21 times the one of the sum of  $K_{app}$  values of the other two processes, which indicated a significant synergetic effect as well. Meanwhile, the degradation efficiency of TC still increased continuously, while the adsorption of TC almost achieved equilibrium within the first several hours. So it could be deduced that the removal of TC in the combined process was mainly attributed to the degradation rather than adsorption.

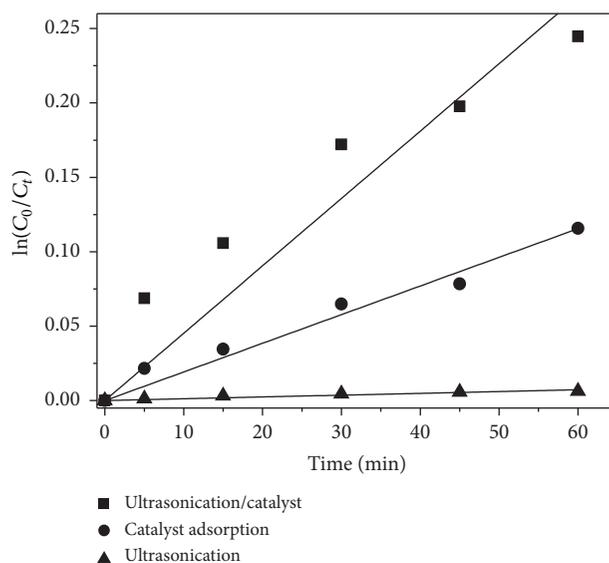


FIGURE 5: Synergetic effect for the sonocatalytic degradation of TC (conditions: catalyst dosage of 160 mg in 200 mL TC solution and TC concentration of 50 mg/L at neutral pH).

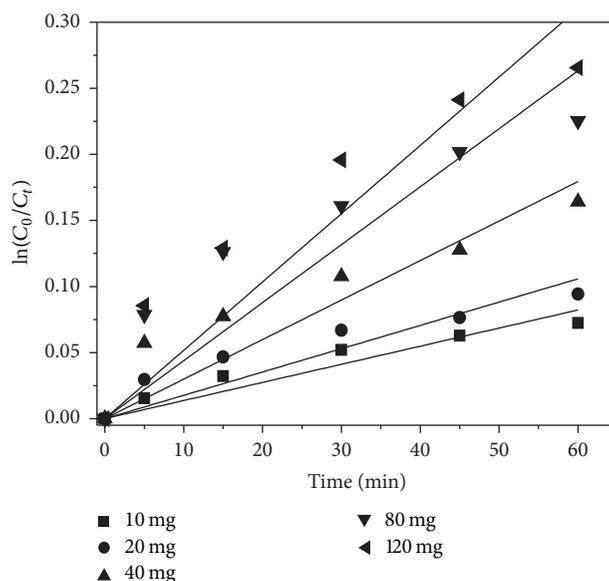


FIGURE 6: Effect of catalyst dosage on the sonocatalytic degradation of TC (conditions: TC concentration of 25 mg/L at neutral pH).

**3.4. Effect of Catalyst Dosage.** The effect of catalyst dosage on the sonocatalytic degradation of TC was also investigated, as illustrated in Figure 6. The dosages of 10, 20, 40, 80, and 120 mg in 200 mL of solution with TC concentration of 25 mg/L were selected. It could be observed that  $K_{app}$  values for the dosages of 10, 20, 40, 80, and 120 mg were 0.00137, 0.00176, 0.00299, 0.00439, and 0.00517  $\text{min}^{-1}$ , respectively, while corresponding  $R^2$  values were 0.962, 0.937, 0.936, 0.921, and 0.938, respectively. It could be confirmed that the

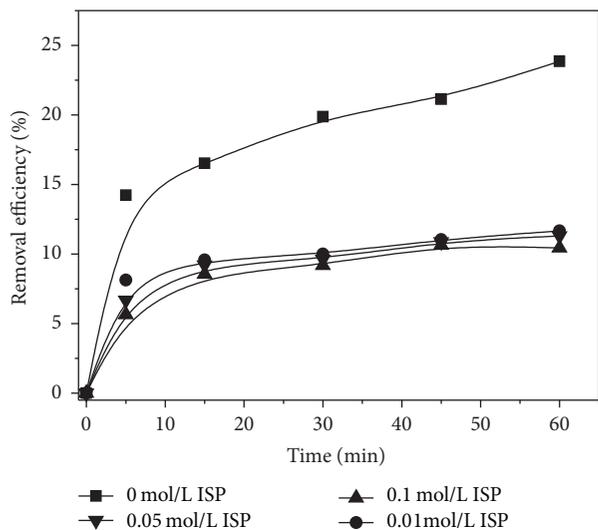


FIGURE 7: Effect of isopropanol (ISP) on the degradation of TC (conditions: catalyst dosage of 60 mg in 200 mL TC solution and TC concentration 15 mg/L at neutral pH and ISP dosages of 0.01, 0.05, and 0.1 mol/L).

increased catalyst dosage enhanced the TC degradation obviously from Figure 6, which was attributed to the increased catalyst sites on the modified diatomite.

### 3.5. Oxidation Mechanism in the Process of TC Degradation

**3.5.1. Effect of Isopropanol on the TC Degradation.** Alcohols such as isopropanol could scavenge hydroxyl radicals and they were often used as the quenchers of hydroxyl radicals ( $\text{OH}^\bullet$ ) to evaluate the production and contribution of the hydroxyl radicals [20, 22, 23]. The inhibitive effect of isopropanol on the oxidation processes could be indicated by the decline in reaction rate constants. As plotted in Figure 7, the effect of isopropanol with different concentrations on the sonocatalytic degradation of TC was investigated. Typically, the degradation of TC was sharply decreased as a consequence of addition of isopropanol.  $K_{\text{app}}$  value in the absence of isopropanol achieved  $0.00548 \text{ min}^{-1}$ , while  $R^2$  value was 0.837. In contrast,  $K_{\text{app}}$  values at isopropanol dosages of 0.01, 0.05, and 0.1 mol/L were 0.00269, 0.00266, and 0.00239, respectively, while corresponding  $R^2$  values were 0.781, 0.822, and 0.819, respectively. The presence of isopropanol with 0.01 and 0.1 mol/L reduced  $K_{\text{app}}$  values by 51.5% and 57.2%, respectively. As a series of ROSs such as  $\text{OH}^\bullet$  and  $\text{H}_2\text{O}_2$  were generated during the sonocatalytic process, it could be deduced that  $\text{OH}^\bullet$  oxidation was absolutely dominant in the degradation process.

**3.5.2. Effect of KBr on the TC Degradation.** As a comparison, the effect of KBr with different concentrations on the sonocatalytic degradation of TC was also investigated, as illustrated in Figure 8. The degradation of TC was even more sharply decreased as a consequence of the addition of KBr. Similarly,  $K_{\text{app}}$  values at KBr dosages of 0.01, 0.05, and 0.1 mol/L were 0.00238, 0.00224, and 0.00197, respectively,

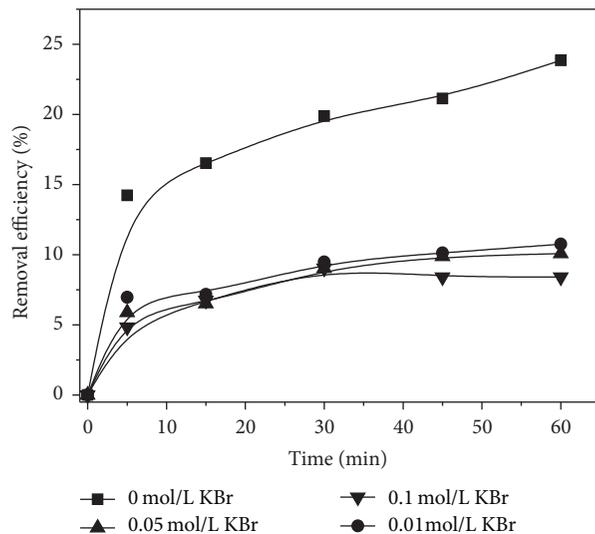


FIGURE 8: Effect of KBr on the degradation of TC (conditions: catalyst dosage of 60 mg in 200 mL TC solution and TC concentration of 15 mg/L at neutral pH and KBr dosages of 0.01, 0.05, and 0.1 mol/L).

while corresponding  $R^2$  values were 0.820, 0.843, and 0.800, respectively. The presence of KBr at the concentration of 0.01 and 0.1 mol/L reduced  $K_{\text{app}}$  values by 56.6% and 64.1%, respectively.

In terms of sonochemical process, alcohol is a known  $\text{OH}^\bullet$  radical scavenger for the gaseous region and/or interfacial region of the collapsing bubble. However, differently, KBr was known as a nonvolatile scavenger which could be readily oxidized by free radicals. These free radicals originated from the bulk liquid region and possibly were from the interfacial region of the cavitation bubble [24, 25]. Accordingly, almost all the free radicals could be quenched by KBr. If the effect of  $\text{OH}^\bullet$  radicals was excluded from the total effect of free radicals, then the difference could be the contribution of other radicals to the TC degradation, which was 6.9% in this case. It demonstrated the very limited effect of other oxidizing radical species in the experiment. The strong oxidizing capacity of  $\text{OH}^\bullet$  radicals was dominant in the sonocatalytic process.

**3.5.3. Effect of  $\text{NaN}_3$  on the TC Degradation.** Similarly, azide ( $\text{NaN}_3$ ) was used as a quencher to scavenge singlet oxygen ( $^1\text{O}_2$ ). The quenching effect has been a diagnostic tool for evaluating the roles of singlet oxygen [20, 26]. As shown in Figure 9, the addition of  $\text{NaN}_3$  actually quenched the degradation considerably. It was well accepted that photosensitized reactions of the first excited state,  $\text{O}_2(^1\Delta_g)$ , played a key role in many natural photochemical and photobiological processes. As ultrasonic irradiation was proven to be capable of generating ultraviolet irradiation with wavelength below 375 nm [27, 28], the Mn-modified diatomite was deduced to be excited by the ultraviolet, which was regarded as photocatalytic process. Accordingly, singlet oxygen was definitely an active oxidizing species in sonocatalytic process.

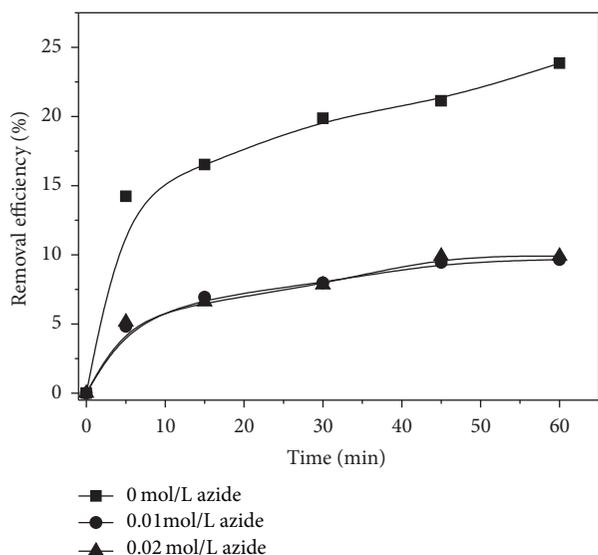


FIGURE 9: Effect of azide on the degradation of TC (conditions: catalyst dosage of 60 mg in 200 mL TC solution and TC concentration 15 mg/L at neutral pH and azide ( $\text{NaN}_3$ ) dosages of 0.01 and 0.02 mol/L).

Meanwhile,  $K_{\text{app}}$  values at azide dosages of 0.01 and 0.02 mol/L were of 0.00212 and 0.00217, respectively, while  $R^2$  values were 0.856 and 0.865, respectively. The presence of azide with concentrations of 0.01 and 0.02 mol/L reduced  $K_{\text{app}}$  values by 61.3% and 60.4%, respectively. Based on the above analysis, it could be concluded that the reduction trends of  $K_{\text{app}}$  were quite close in the presence of 0.1 mol/L of isopropanol, 0.01 mol/L of KBr, and 0.01 mol/L of  $\text{NaN}_3$ . This indicated that ROSs were absolutely dominant for the degradation of TC. The similar quenching effects were reported by other researchers in photocatalytic and sonophotocatalytic degradation processes [29], indicating the probable photocatalytic oxidation process involved in sonocatalytic process as well.

**3.5.4. Effect of Fe(II) on the TC Degradation.** The effect of Fe(II), a radical promoter, was also investigated and demonstrated in Figure 10. Different from quenching effect, addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  could enhance the sonochemical degradation of various organics, which was proven by previous studies [24, 30–33]. The sonocatalytic process was capable of generating particularly higher concentration of  $\text{H}_2\text{O}_2$  compared to ultrasonication alone [5]. Due to the continuous generation of  $\text{H}_2\text{O}_2$  in sonocatalytic process, Fenton reaction is expected to occur as follows:

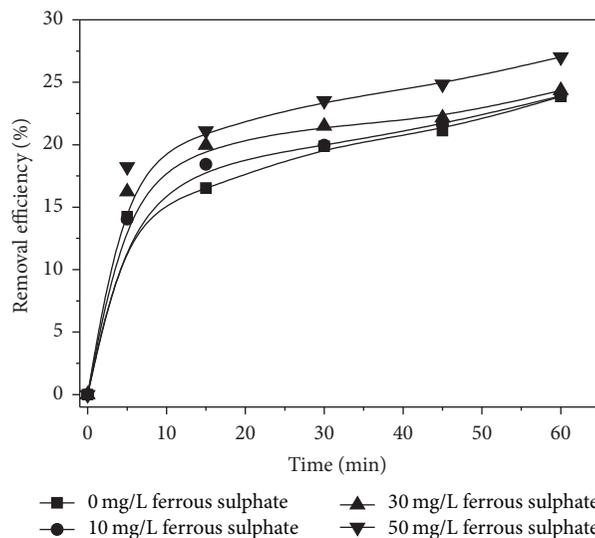
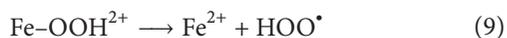
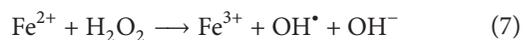


FIGURE 10: Effect of Fe(II) on the degradation of TC (conditions: catalyst dosage of 60 mg in 200 mL TC solution and TC concentration of 15 mg/L at neutral pH and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosages of 10, 30, and 50 mg/L).

A series of strong oxidants such as  $\text{OH}^\bullet$  are transformed concurrently. Similarly,  $K_{\text{app}}$  values at  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosages of 10, 30, and 50 mg/L were 0.00559, 0.00583, and 0.00655, respectively, while corresponding  $R^2$  values were 0.823, 0.786, and 0.800, respectively. The presence of 50 mg/L of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  enhanced  $K_{\text{app}}$  value by 19.5%. As a result, the addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was beneficial for the degradation of TC.

## 4. Conclusion

Mn-modified diatomite was prepared by wet impregnation and subsequent calcination. The morphology and crystal structure of the modified diatomite were not changed apparently compared to the raw diatomite. Only 0.22% (atomic ratio) of manganese was immobilized on 0.1 mol/L  $\text{MnSO}_4$ -modified diatomite, even though the Mn-modified diatomite showed particularly higher sonocatalytic activity than the raw diatomite by comparing their degradation performance for tetracycline. The increase in  $\text{MnSO}_4$  concentration used in the wet impregnation solution and the catalyst dosage enhanced the degradation significantly. The sonocatalytic process which combined ultrasonication and catalyst adsorption demonstrated a significant synergetic effect. The presence of isopropanol, KBr, and  $\text{NaN}_3$  quenched a series of reactive oxygen species sharply, indicating the dominant role of reactive oxygen species in the sonocatalytic process. In contrast, the addition of Fe(II) could enhance the degradation of tetracycline as it facilitated the generation of more  $\text{OH}^\bullet$  radicals.

## Competing Interests

The authors declare that there are no competing interests.

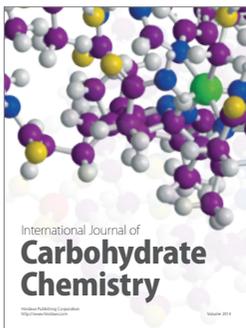
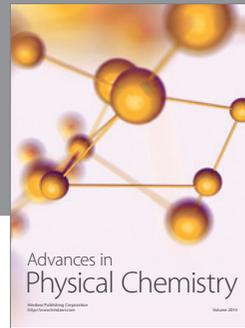
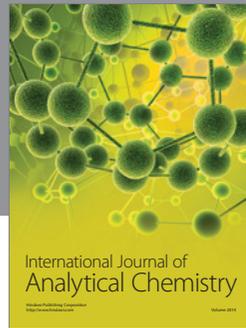
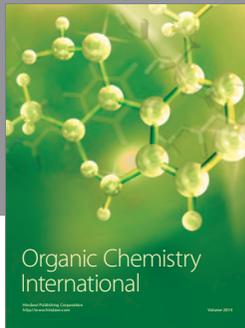
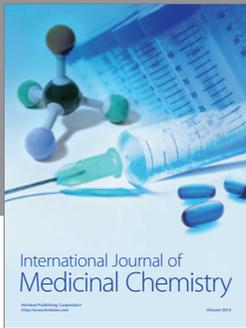
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