Degradation of Chlortetracycline Hydrochloride by Peroxymonosulfate Activation on Natural Manganese Sand Through Response Surface Methodology

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Abstract

This study studies the degradation of chlortetracycline hydrochloride (CTC) by activated peroxymonosulfate (PMS) with natural manganese sand (NMS). Meanwhile, the NMS was characterized and analyzed by isothermal nitrogen adsorption (BET), X-ray energy spectroscopy (EDS) and scanning electron microscope (SEM). It can be induced that NMS material may contain C, O, Al, Si, Fe, Mn, K, and the proportion of each is 6%, 9%, 13%, 34%, 27%, 5%, 6%. Critical parameters, including initial pH value, catalyst dosage and PMS amount, were optimized through response surface methodology. Results indicated that 81.65% of CTC could be degraded under the optimized conditions of PMS amount 2.02g/L, the NMS dosage 0.29g/L and pH 3.87. Also, it shows that NMS is the most powerful of each factor on the degradation efficiency. We proposed the degradation pathways of CTC from the liquid chromatograph-mass spectrometer (LC-MS) results. Therefore, NMS could be applied as an efficient activator of peroxymonosulfate to purify the water and wastewater.

Introduction

Chlortetracycline hydrochloride (CTC), as one kind of antibiotics, is universally used for agricultural planting, animal disease treatment and human medical purpose (Tang et al. 2019). However, as one of the most widely used antibiotics in medicine, CTC is challenging to metabolize by humans and animals' metabolic processes, and has been extensively studied in the ecosystem (Yousefi et al. 2019, Zhou et al. 2020). Modern industrial farming uses widespread antibiotic to meet human demands for animal products. Unfortunately, the accumulation of antibiotics in the human body exceeds human metabolism's capacity (Pulicharla et al. 2018), which was ascribed to the well chemical stability, long-term survival in natural, and resistance of conventional biological and physical processes (Han et al. 2020, Li et al. 2020, Yuan et al. 2020). CTC elimination in wastewater treatment plants is primarily achieved by activated sludge adsorption rather than biodegradation (Zhou et al. 2013a). Its residues and derivatives will accumulate and produce a harmful effect on the ecosystem (Deng et al. 2017).

Advanced oxidation processes (AOPs) have frequently attempted to degrade newly generated organic pollutants in the ecological system (Yu et al. 2019a, Zhang et al. 2019). Advanced Oxidation Process (AOP) has become an advanced organic pollutants degradation technology, which has developed more and more bright application prospects in global environmental governance. The free radical reaction of AOP can quickly degrade organic compounds and even be mineralized (Tang et al. 2020, Yuan et al. 2019). One of the most critical keys to degrading organic compounds using advanced oxidation technologies is a high-efficiency catalyst (AOTs), which bases on peroxymonosulfate (PMS) (Dong et al. 2019, Liu et al. 2019, Yu et al. 2019b). Other advanced oxidations are more expensive than PMS, require more transportation and storage, and are less cost-effective. Its oxidation mechanism is much better at degrading organic contaminants selectively. Therefore, It obtained widespread attention (Zhang et al. 2018). Besides, sulfate ion radical ($\text{SO}_4^{\bullet-}$) has a longer half-life and a broader pH spectrum in the AOP (SR-AOP) (Deng et al. 2013). Therefore, more and more researchers have started to study the PMS catalysts, which include electrolysis, UV, ultrasound, and transition metals. The most widely studied are

transition metals because they do not require external energy input to activate PMS effectively. Fe_3O_4 and Mn_3O_4 is one of the essential components of natural manganese sand(NMS), usually used as a catalyst to remove iron and manganese from groundwater.

The interaction between variables and response is difficult to be resolved by the classical optimization method because it can only deal with the change of one parameter at a time while leaving other factors unchanged(Mukherjee et al. 2020). In statistical design experiments, the response surface methodology(RSM) has become the most humane and convenient method. One of the essential significances of RSM is the establishment and optimization of the mathematical model to reduce the complexity of the experimental process(Khajeh et al. 2013). It can provide the degree of mutual influence between various factors and optimize the response based on the investigated factors. Using the least number of experimental runs to obtain the surface change of the response is one of the main advantages of this statistical analysis method, which provides an excellent way to anticipate the interaction of parameters(Kumari et al. 2021). RSM includes experimental design, modelling, testing the model's suitability, seeking the best combination conditions, and so on. The response value corresponding to each factor can be easily obtained through the regression fitting of the process and the drawing of response surface and contour lines.

This study intends to activate sodium persulfate by NMS to produce sulfate radicals to degrade CTC, explore the reaction system's influencing factors, and study the reaction mechanism.

Materials And Methods

Reagents

Natural manganese sand was purchased from Henan Yuanrun water treatment materials Co. Ltd; Potassium monopersulfate triple salt($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) was obtained from Aladdin Industrial Co. Ltd; Chlortetracycline hydrochloride($\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{O}_8\text{HCl}$) was provided by Hefei Bomei Biotechnology Co. Ltd. Potassium bicarbonate (KHCO_3), potassium chloride (KCl), potassium nitrate (KNO_3), potassium phosphate (K_2HPO_4), humic acid (HA), potassium sulphate (K_2SO_4), tert-Butanol alcohol (TBA), methanol (MeOH) and 1,4-Benzoquinone (PBQ) were acquired from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All the chemicals were analytical grade and used without other purification.

Experimental procedures and analysis

The reactor was a conical flask of 250 ml. NMS and PMS were added at the same time. Finally, the conical flask was placed in a constant temperature shaker at 25°C . Several solutions were collected from the reactor at a given time interval and filtered through a $0.22\ \mu\text{m}$ membrane. Then, the experimenter would use the Evolution-300 UV Vis spectrophotometer to measure the absorbance at the CTC maximum absorption wavelength (366 nm). In this experiment, sodium hydroxide and sulfuric acid were used to change the CTC solution's initial pH. The degradation ratio was determined using the following formula:

$$\text{Removal\%} = \frac{C_0 - C_t}{C_0} \times 100\%$$

1

The degradation rate was calculated by the pseudo-first-order kinetic equation:

$$\ln \left(\frac{C_t}{C_0} \right) = -K_{\text{obs}} \times t$$

2

Where C_t (mg/L) is the CTC concentration at special time, C_0 (mg/L) is the initial CTC concentration, K_{obs} (min^{-1}) is the pseudo-first-order rate constant, t (min) is the reaction time.

High performance liquid chromatography-mass spectrometry (HPLC-MS/MS, Water Acquity Quattro Premier) explored the CTC decomposition intermediates. Stability experiments were carried out on the obtained samples. The recovery experiment was carried out 5 times. The catalyst was collected after each degradation, and the next cycle test was conducted. Moreover, a certain amount of EtOH, TBA and PBQ were applied to the radical scavenging test's solution to quench different active species, respectively.

Result And Discussion

X-ray diffraction and BET surface area analyses

It can be seen from Fig. 1a that because of its good crystallinity, quartz has firm peaks at the interplanar spacing of 1.817, 3.339, and 4.246 Å, which corresponded to the planes of (112), (101), (100) of NMS(Ouvrard et al. 2005). Besides, the three firm peaks of ramsdellite are 2.128, 2.455 and 3.339 Å, and two firm peaks of hematite are 2.526 and 2.708 Å, which corresponded to the planes of (110) and (104) of NMS.

The reactive sites on the surface of the core catalyst that stimulate the reaction were the key to whether the degradation activity was efficient or not in the catalytic reaction system. Therefore, the specific surface area and pore size distribution of natural manganese sand were calculated and analyzed by nitrogen adsorption-desorption isotherm test. According to the IUPAC classification principle, the nitrogen adsorption-desorption isotherm of natural manganese sand conformed to the characteristics of type IV and H3 hysteresis, which indicated that the catalyst material had the properties of mesoporous structure. Fig. 1b showed that the pore size of the catalyst was mainly distributed around 2-20 nm, and its average pore size was 7.4 nm. It can be concluded that the specific surface area of natural manganese sand was 50.6 m^2/g and the pore volume was 0.09 cm^3/g based on the test results.

Energy dispersive spectroscopy and scanning electron microscopy analyses

From the elemental analysis results (Fig. 2i), it can be seen that the NMS material contains C, O, Al, Si, Fe, Mn, K elements. This phenomenon's formation may be affected by the regular octahedral structure and layered structure of NMS(Yu et al. 2019b). It can be seen from Table 1 that the mass percentage of C, O, Al, Si, K, Mn and Fe elements were 18.74%, 57.60%, 5.5%, 9.39%, 0.55%, 4.32%, 3.91%. However, it can be seen from Fig. 2h that the elements in NMS were not uniformly divided. The surface of the NMS was mainly composed of nanosheet, and there were also some holes of different sizes (Fig. 2j and 2k)(Yu et al. 2019b).

XPS analysis of NMS

In order to determine the synergy between the iron and manganese bimetals, X-ray photoelectron spectroscopy was used to analyze the valence changes of the iron and manganese bimetals in the catalyst. For the Mn 2p spectrum (Fig. 3b), the spectrum was composed of spin-orbit doublet of Mn 2p_{1/2} and Mn 2p_{3/2}. The binding energy of Mn 2P in the catalyst before the reaction was located at the three peaks at 639.55, 640.8 and 642.75 eV, which are the binding peaks of Mn(II), Mn(III) and Mn(IV) respectively. The percentages of Mn(II), Mn(III) and Mn(IV) was 51.66%, 22.33% and 26.01% respectively. The content of Mn(II) and Mn(IV) increased slightly from 51.66% and 26.01–62.41% and 34.59%. At the same time, the content of Mn(III) decreased by 22.33% which showed Mn³⁺ participated in the redox reaction on the surface of the catalyst. The energy spectrum of Fe 2p in the catalyst before and after the reaction was shown in Fig. 3c. The proportion of Fe²⁺ increased slightly from 28.31–31.92%, indicating that part of the Fe³⁺ in the catalyst was reduced to Fe²⁺ after the reaction.

Single-factor experiment optimization

It can be seen from Fig. 4a-b that the degradation efficiency and rate of tetracycline were both related to the initial PMS concentration. The CTC degradation was aided by increasing PMS within a certain range. For example, after treating CTC-polluted water with 0.5 g/l-PMS for 120 minutes, the CTC removal rate was 63.08 %, which increased to 70.0 % when PMS was increased to 2.0 g/l. The following is an explanation for the above phenomenon: When the PMS concentration is low, more SO₄^{-•} is produced in the reaction system in a short period time as the PMS concentration increases. Therefore, as PMS concentrations rise, the efficiency and rate of pollution degradation will increase. As the concentration of PMS increases, the efficiency and rate of CTC degradation decrease. When the concentration of PMS continues to increase, the degradation efficiency and degradation rate of CTC decrease. The following are the explanations for this phenomenon: (1) when the concentration of free radicals in a system is higher, they are more likely to contact one another, resulting in a quenching reaction. (2) Excessive HSO₅⁻ will react with SO₄^{-•} and OH• to form SO₅⁻, which has a lower redox potential and oxidation power than OH• and SO₄^{-•}, as defined by Eqs. 3-7 (Huang et al. 2020, Liu et al. 2015, Zou et al. 2019).

In order to rationalize and minimize the budget, it is usually necessary to determine the optimal catalyst dosage in engineering applications. As shown in Fig. 5a-b, when the NMS dosage was changed from 0.1g/l to 0.30g/l, the CTC removal rate and pseudo-first-order rate constant increased by 3.43% and 0.0010min^{-1} respectively. However, when the catalyst dosage continued to increase to 0.4g/l, the CTC removal rate and pseudo-first-order rate constant dropped to 63.72% and 0.0084min^{-1} respectively. Theoretically, the increase in the catalyst's dosage will increase the probability of its contact with the catalyst, thereby increasing the number of free radicals generated in the solution and improving the target pollutants' degradation efficiency. However, a further increase in the catalyst dosage cannot lead to a significant increase in the removal efficiency of pollutants. The experimental results are mainly caused by the quenching effect of free radicals and the autolysis effect of PMS.

During the degradation of CTC, pH mediated the chemical and physical properties of the solution, and emission speciation and the formation of reactive radicals. Fig. 6a-b indicated the changes in CTC degradation under different solution pH (3–5) when CTC, NMS, and PMS have mass concentrations of 10 mg/l, 0.30g/l and 2g/l, respectively. This experiment adjusted the pH with sulfuric acid and sodium hydroxide to prevent the effects of other anions(Yan et al. 2021). CTC's degradation efficiency steadily increased from 3 to 4 as the pH increased in this analysis, reaching 80.79 %. However, the degradation efficiency decreased When the pH was raised to 5.

The main reason for CTC's low degradation efficiency when the pH is increased from 2 to 4 is that the H^+ in the solution traps $\text{SO}_4^{\cdot-}$ and $\text{OH}\cdot$, inhibiting CTC from being extracted. Degradation efficiency is decreased when the pH increases from 4 to 5. The following are the explanations for this phenomenon: (1) $\text{SO}_4^{\cdot-}$ reacts with OH^- to produce $\text{OH}\cdot$ when the pH is greater than 4.0. (2) As pH rises, the amount of surface charge on MnO_2 decreases, resulting in an increase in electrostatic repulsion between the catalyst and PMS, potentially inhibiting catalyst-PMS interaction and slowing CTC degradation(Deng et al. 2017). (3) Increasing the pH of the aqueous solution decreases the oxidability of MnO_2 , which is also a negative consequence(Deng et al. 2017).

Multivariable experimental design

To understand better the influence of the determining variables on degradation chlortetracycline hydrochloride, Box Behnken Design in the response surface analysis method was used to establish a mathematical model CTC removal rate was used to optimize the experimental design(Belgada et al. 2021, Song et al. 2021). When the reaction temperature is 25 degrees and the reaction time is 180 minutes, peroxymonosulfate (A), nature manganese sand (B), and ph (C) are chosen to design a three-factor three-level response surface experiment (Table 1), which included 17 experiments determined by the formula: $N = 2^n + 2n + C_0$, where N is the number of experiments to be performed, n is the number of variables, and C_0 is the number of center point runs(Gou et al. 2017). The experimental results were listed in Table 2. The results in Table 2 were analyzed by SAS software, and the quadratic regression equation is:

$$Y = 81.30 + 0.40A + 1.90B-0.22C-0.25AB+0.35AC-2.55BC-9.85A^2-4.20B^2-3.40C^2$$

8

Eq. (8) is the regression equation of removal efficiency. The results of the variance analysis were displayed in Table 3. The analysis of variance (ANOVA) for Eq. (8) was shown in Table 3. Because the correlation coefficient (R^2) is 0.9889, the experimental and predicted values have a high degree of consistency for degradation efficiency of CTC by manganese sand (Fig. 7d)(Belgada et al. 2021). Meanwhile, this model’s significance level is $P<0.0001$ from Table 3, suggesting that the selected model is highly significant(Belgada et al. 2021). The lack of fit is not significant due to the value of the misfit error $P=0.0848>0.05$. Therefore, the regression equation fits well with the experiment. Comparing the value of F shows that the influence of three factors on the degradation efficiency is in descending order as follows: A(PMS), B(nature manganese sand) and C(pH)(Abdulredha et al. 2020).

The model shows that CTC’s degradation rate has an excellent stable point from Fig. 7a-d (Gou et al. 2017). The regression model prediction indicates that the best theoretical values of the different variables such as PMS: 2.02g/L, nature manganese sand: 0.29g/L, ph: 3.87, and degradation rate of 81.65%. In the different independent variables such as PMS:2.00g/L, nature manganese sand: 0.30g/L, ph:4.00, three parallel verification experiments are performed, and the average degradation rate is 81.02%. The error is 0.77%. The test value and the theoretical prediction value are consistent within the allowable range of the experimental error, indicating that the selected model and factor levels are accurate and appropriate. The quadratic equation obtained by the regression analysis fits well with the actual situation(Das et al. 2020).

Table.1 Variables and levels of Box-Behnken Design

Independent variables	symbol	Actual values of the coded variable levels				
		-1.682	-1	0	1	1.682
[PMS] (mg/L)	A	0.32	1.00	2.00	3.00	3.68
[manganese sand] (mg/L)	B	0	0.1	0.25	0.4	0.50
Initial pH	C	2.32	3	4	5	5.68

Table.2 Experiment design and results of Box-Behnken

Run	Coded values			Independent variables			Actual value /%	Predicted value/%
	A	B	C	A	B	C		
16	-1	-1	0	1.00	0.10	4.00	65.3	64.95
1	+1	-1	0	3.00	0.10	4.00	66.7	65.75
8	-1	+1	0	1.00	0.40	4.00	68.3	68.75
4	+1	+1	0	3.00	0.40	4.00	68.7	69.55
12	-1	0	-1	1.00	0.25	3.00	67.8	67.88
7	+1	0	-1	3.00	0.25	3.00	67.8	68.68
6	-1	0	+1	1.00	0.25	5.00	67.6	67.43
9	+1	0	+1	3.00	0.25	5.00	69.0	68.23
2	0	-1	-1	2.00	0.10	3.00	69.3	69.48
5	0	+1	-1	2.00	0.40	3.00	79.5	78.38
17	0	-1	+1	2.00	0.10	5.00	73.0	74.13
13	0	+1	+1	2.00	0.40	5.00	73.0	72.83
14	0	0	0	2.00	0.25	4.00	80.5	81.38
10	0	0	0	2.00	0.25	4.00	81.0	81.38
11	0	0	0	2.00	0.25	4.00	81.2	81.38
15	0	0	0	2.00	0.25	4.00	82.0	81.38
3	0	0	0	2.00	0.25	4.00	81.8	81.38

Table.3 Analysis of variance for the developed regression

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	Significance
Model	639.85	9	70.43	73.75	<0.0001	Significant
A	1.28	1	1.28	1.34	0.2849	
B	28.88	1	28.88	30.24	0.0009	
C	0.41	1	0.41	0.42	0.5357	
AB	0.25	1	0.25	0.26	0.6246	
AC	0.49	1	0.49	0.51	0.4970	
BC	26.01	1	26.01	27.24	0.0012	
A ²	408.52	1	408.52	427.77	<0.0001	
B ²	74.27	1	74.27	77.77	<0.0001	
C ²	48.67	1	48.67	50.97	0.0002	
Residual	6.68	7	0.95			
Lack of fit	5.20	3	1.73	4.69	0.0848	Not significant
Pure error	1.48	4	0.37			
Cor total	640.54	16				
R-squared 0.9896 Adj R-Squared 0.9761.						

Effects of coexisting ions and humic acid

In order to investigate the application prospect of PMS/NMS system in real water, the effects of chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), dihydrogen phosphate (H_2PO_4^-), bicarbonate (HCO_3^-) and humic acid (HA), the dominant species in natural water environment, were explored. It can be noticed from Fig. 8a-b that the amount and pseudo-first-order rate constant reduced by 4.3% and 0.162 min^{-1} respectively with 5.0 mM Cl^- addition. According to the previous studies of AOPs, a amount of Cl^- can be able to scavenge $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ to form less reactive chlorine species based on the following reactions (Eqs. (9-14))(Anipsitakis et al. 2006, Grebel et al. 2010, Yang et al. 2014)

In addition, the 5 mM NO_3^- , H_2PO_4^- and HCO_3^- all inhibited the degradation efficiency of CTC, which ranged from 80.8–73.2%, 74.3% and 62.2% respectively. The inhibitory effect may be related to the following reactions (Eqs. (9-17))(Cao et al. 2019, Sharma et al. 2015, Zhou et al. 2013b).

Figure 8a-b showed that 5mM SO_4^{2-} and 5mg/L HA had slight influence on the degradation rate of CTC. HA is an important component of natural organic matter which usually competes with reactive species to reduce the degradation rate of the target pollutant. In addition, HA may result in active site masking and inactivation by blocking the active site of the catalyst(Chen et al. 2018). As shown in Fig. 8b, the pseudo-first-order rate constant of Cl^- , SO_4^{2-} , NO_3^- , HPO_4^- , HCO_3^- and HA are 0.0137min^{-1} , 0.0121min^{-1} , 0.0131

min^{-1} , 0.0110 min^{-1} , 0.0113 min^{-1} , 0.0811 min^{-1} and 0.0131 min^{-1} respectively. This results indicate the inhibition of anions on the degradation of CTC was arranged in the order of $\text{HCO}_3^- > \text{NO}_3^- > \text{HPO}_4^- > \text{Cl}^- > \text{SO}_4^{2-} = \text{HA}$.

Scavenging experiments

In order to explore the main roles of CTC in the degradation process, the scavenging experiment was carried out. According to existing literature reports, $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ will be produced after activation of PMS. In this study, MeOH ($\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ radical scavenger), TBA ($\cdot\text{OH}$ radical scavenger) and PBQ ($\text{O}_2^{\cdot-}$ radical scavenger) were selected as inhibitors (Huang et al. 2020). As shown in Fig. 8c-d, the degradation efficiency decreased by 15.2%, 2.5% and 8.2% after adding 5mM MeOH, 5mM TBA and 5mg/l PBQ. Meanwhile, pseudo-first-order rate constant has also gone down from 0.0137 min^{-1} to 0.0089 min^{-1} , 0.0127 min^{-1} and 0.0108 min^{-1} . Therefore, $\text{SO}_4^{\cdot-}$, $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ radical participate in the degradation process of CTC, and $\text{SO}_4^{\cdot-}$ plays a leading role in the system.

Stability studies of NMS

Generally, the stability and reusability of the catalyst are potentially important parameters for wastewater treatment applications. Therefore, we conducted stability experiments on NMS, and the results are shown in the Fig. 9a. It can be seen from Fig. 9a that after 5 cycles of experiments, the degradation rate of CTC dropped by 2.39% after 600 minutes of reaction. The following are the explanations for this phenomenon: (1) Contaminant molecules block the pores of the material. (2) Slight overflow of metal ions on the catalyst (Ma et al. 2019).

NMS/PMS degradation system ion dissolution test

After the entire degradation process is completed, the leaching amount of metal ions introduced into the solution by the degradation system is detected to illustrate the green and low toxicity of the catalyst when it functions in the system.

Possible degradation pathway and products

HPLC-MS identified the degradation of products. According to the related studies and the analysis, the possible degradation products and pathways are displayed in Table 4 and Fig. 10.

In Fig. 10, there are many different kinds of products. The U1 ($m/z = 462.89$) was produced by removing the hydroxyl group and hydrogen chloride from CTC (Chen et al. 2020). There is a complete degradation pathway in Fig. 10. Firstly, the CTC lost one chloride ion and one hydrogen chloride to form V1 ($m/z = 444.45$) (Zhang et al. 2020). Subsequently, V2 was created as due to the loss of two N-methyl, amino and amide group from V1. Then the V2 was transformed into V3 by ring-opening reaction, dehydroxylation, deethylation and addition reaction (Yang et al. 2018). According to the deacetylation on V3, the V3 was changed to V4. Then, the V4 was fragmented into V5 because of the loss of two hydroxyl groups (Yang et al. 2018). Next, the V6 was generated by the ring-opening reaction and other reactions of the V5. The ring-

opening reaction and the other reactions let V6 into V7. The V8 was probably due to the loss of the aldehyde group and methyl on V7. Finally, the V9 was formed via a ring-opening reaction on V9.

There is another one possible degradation pathway in Fig. 10. Firstly, the CTC lost two hydroxyl groups and one hydrogen chloride to form W1. Then W1 was transformed into W2 via the ring-opening reaction. Subsequently, the loss of the carbonyl group and ring-opening reaction on W2 was attributed to the formation of W3. The W3 was transformed into W4 by the obtain of the hydroxyl group and addition reactions. However, the W5 could also become W4 when the W4 became the W5. With the ring-opening reaction and other reactions, the W4 was fragmented into W6. Finally, the W7 was produced via the ring-opening reaction and hydroxyl group oxidation.

Possible mechanism of PMS activation

Based on the above experimental results and analysis, the possible reaction process of using NMS to activate peroxymonosulfate to produce $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ is shown in the Fig. 11. First, the NMS dispersed in the solution provides enough active sites to fully contact with the PMS to react. Therefore, the iron and manganese ions in the crystal lattice of the catalyst surface react with HSO_5^- to generate $\text{SO}_4^{\cdot-}$ radicals and $\cdot\text{OH}$ radicals (Eqs. (25-28))(Chen et al. 2019). In addition, $\text{SO}_4^{\cdot-}$ radicals will react with H_2O to produce $\cdot\text{OH}$ radicals. At the same time, HSO_5^- will react with H_2O to produce $\cdot\text{O}_2^-$ radicals(Guo et al. 2020). In the end, the $\text{SO}_5^{\cdot-}$ radicals, $\cdot\text{OH}$ radicals and $\cdot\text{O}_2^-$ radicals in the system are all involved in the decomposition of CTC, and finally mineralized into small molecular substances such as CO_2 and H_2O (Chen et al. 2019, Guo et al. 2020, Xiong et al. 2015, Zhao et al. 2014, Zou et al. 2019). The redox potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$ were 0.77, 1.51 and 0.15V, respectively. This indicated that Mn^{3+} in the system can not only activate PMS, but also reduce Fe^{3+} to form Fe^{2+} , and part of Fe^{2+} can reduce Mn^{3+} to Mn^{2+} , thereby promoting cycle of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$ (Eqs. (31-32)).

Conclusions

In this study, natural manganese sand was used to activate PMS to degrade CTC. In order to better understand the influence of the determining variables on the removal and degradation of CTC. In the response surface analysis method, Box Behnken Design was used to establish a mathematical model, and the CTC removal rate was used to optimize the experimental design. The optimal theoretical conditions predicted by the regression model are: $m(\text{PMS})=2.02\text{g/l}$, $m(\text{manganese sand})=0.29\text{g/l}$, $\text{pH}=3.87$, and degradation rate of 81.65%. Nature manganese sand is the most powerful of each factor on the degradation efficiency. The result provides a valuable reference for the degradation of medical wastewater containing CTC.

Declarations

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Author contribution Bo He's contribution focused on doing the experiment and writing the manuscript. Ying Yang and Bingrui Liu contributed to guiding and analyzed the data. Zixuan Zhao contributed to revising the manuscript. Xiuwen Cheng and Jiangwei Shang provided financial and technical support.

Availability of data and materials All authors approved that the data and material can be accessed from the corresponding author on reasonable request.

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Ethics approval This manuscript is a manuscript and cannot be transferred to others It has not been published elsewhere. The work is not divided into many parts No falsified, falsified or inappropriate data manipulate. There is no plagiarism in this book.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing of interest The authors declare no competing interests.

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Tables

Due to technical limitations, table 4 is only available as a download in the Supplemental Files section.

Figures

Figure 1

XRD spectra(a), N₂ adsorption/desorption isotherm curve and inset is the pore size distribution(b) of natural manganese sand.

Figure 2

Morphology characterization of natural manganese sand: (a–h) EDAX mapping, (i) EDS spectra, (j-k) HR-SEM images.

Figure 3

(a) XPS survey spectrum, (b) Mn, (c) Fe XPS spectra of NMS.

Figure 4

Influence of PMS on degradation efficiency (a) and pseudo-first-order rate constant (b) by NMS [Reaction conditions: catalyst dosage = 0.3 g·L⁻¹, reaction temperature = 25 °C and initial pH value = 4.5]

Figure 5

Influence of NMS dosage on degradation efficiency (a) and pseudo-first-order rate constant (b) [Reaction conditions: PMS concentration = 2.0 g·L⁻¹, reaction temperature = 25 °C and initial pH value = 4.5]

Figure 6

Influence of initial pH value on degradation efficiency (a) and pseudo-first-order rate constant (b) [Reaction conditions: PMS concentration = 2.0 g·L⁻¹, catalyst dosage = 0.3 g·L⁻¹ and reaction temperature = 25 °C].

Figure 7

Interaction of various factors with 3D surface diagram(a-c), and correction between the predicted and experimental degradation efficiencies of CTC by natural manganese sand(d). [Reaction conditions: CTC concentration = 10 mg·L⁻¹, PMS concentration = 2.0 g·L⁻¹, catalyst dosage = 0.3 g·L⁻¹, reaction temperature = 25 °C and initial pH value = 4.0]

Figure 8

Effects of coexisting ions and humic acid (a-b), removal efficiency of CTC in the absence or presence of reactive species Scavenger(c-d). [Reaction conditions: CTC concentration = 10 mg·L⁻¹, PMS concentration = 2.0 g·L⁻¹, catalyst dosage = 0.3 g·L⁻¹, reaction temperature = 25 °C and initial pH value = 4]

Figure 9

Reusability experiments of NMS (a), metal ions leaching rates during the degradation process(b).
[Reaction conditions: CTC concentration = $10 \text{ mg}\cdot\text{L}^{-1}$, PMS concentration = $2.0 \text{ g}\cdot\text{L}^{-1}$, catalyst dosage = $0.3 \text{ g}\cdot\text{L}^{-1}$, reaction temperature = 25°C and initial pH value = 4.0]

Figure 10

Proposed degradation pathway of CTC degradation products

Figure 11

Proposed mechanism of NMS/PMS system on CTC degradation.

Supplementary Files

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- [Table4ProposedstructureofCTCdegradationproductsinthesystem.docx](#)