Degradation of chlortetracycline hydrochloride by peroxymonosulfate activation on natural manganese sand through response surface methodology

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Abstract
This work 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), energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM). It can be induced that NMS material may contain C, O, Al, Si, Fe, Mn, and K, and the proportion of each is 6%, 9%, 13%, 34%, 27%, 5%, and 6%. Critical parameters, including initial pH value, catalyst dosage, and PMS amount, were optimized through response surface methodology. One of the essential significances of response surface methodology (RSM) is the establishment and optimization of the mathematical model to reduce the complexity of the experimental process. It can provide the degree of mutual influence between various factors and optimize the response based on the investigated factors. Results indicated that 81.65% of CTC could be degraded under the optimized conditions of PMS amount 2.02 g/L, the NMS dosage 0.29 g/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.

Keywords 
Natural manganese sand · Chlortetracycline hydrochloride · Peroxymonosulfate · Response surface methodology 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. The traditional advanced oxidation process mainly uses \( \bullet \text{OH} \) as the main active species. Under the action of \( \bullet \text{OH} \), organic pollutants can be quickly decomposed into non-toxic or low-toxic small molecular substances until they are completely oxidized to \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and other inorganic salt ions. As a traditional advanced oxidation process, the Fenton reaction is considered a good strategy for the degradation of POPs (Luo et al. 2014). However, the conventional Fenton process may produce iron-rich sludge during the reaction process; in addition, the reaction system has a narrow pH range (2–4) and low \( \text{H}_2\text{O}_2 \) utilization rate, which reduces the degradation efficiency of pollutants (Hug & Leupin 2003). Because \( \text{H}_2\text{O}_2 \) exists in liquid form, it is difficult to store and transport, which greatly increases operating costs and processing complexity. Not only does \( \bullet \text{SO}_4^- \) have a more tremendous redox potential (2.5–3.1 V), which can help break macromolecule structure, but it also has the advantages of a quick reaction, ease of application, longer half-life, broader pH range, and high activity (He et al. 2022). And, \( \bullet \text{SO}_4^- \) is able to selectively and efficiently react with organic compounds containing unsaturated bonds or aromatic π electrons via electron transfer (Ahmed et al. 2012).

Therefore, it obtained widespread attention (Zhang et al. 2018). Besides, sulfate ion radical (\( \bullet \text{SO}_4^- \)) 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. \( \text{Fe}_3\text{O}_4 \) and \( \text{Mn}_3\text{O}_4 \) is one of the essential components of natural manganese sand (NMS), usually used as a catalyst to remove iron and manganese from groundwater. NMS mainly composed of manganese oxides exists widely in soil and sediments. Because of rich geological reserves, NMS is very cheap and easy to obtain (Post 1999). According to related reports, all kinds of manganese oxides contained in NMS can efficiently activate persulfate to degrade pollutants (Zhu et al. 2019).

In addition to this, Mn- and Fe-based catalysts with low in bioxicity and rich in natural stock are identified as relatively non-toxic and cost-effective activators of PMS (Duan et al. 2019; Lin et al. 2009). Using corn stover as the biomass source of biochar, the researchers synthesized natural manganesen ore-corn stover biochar composite material by simple impregnation method and applied PMS to activate and degrade endocrine disruptor bisphenol A (Yang et al. 2021). The researchers propose the degradation of Orange II by PMS activation using NMS containing \( \text{Mn}_3\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \) as catalysts. The NMS/PMS system exhibited extremely high stability and catalytic activity for Orange II elimination (92.2%, 0.0453 min\(^{-1}\)) (Gu et al. 2022).

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 scientific and convenient method. Response surface optimization is a method for optimizing experimental conditions, which is suitable for solving problems related to nonlinear data processing. It includes many experimental and calculation techniques such as experimental design, modeling, testing the suitability of the model, and seeking the best combination conditions. The response value at each factor level. On the basis of the response value of each factor level, the predicted optimal response value and the corresponding experimental conditions can be found. The response surface optimization method takes into account the random error of the test. At the same time, the response surface method fits the complex unknown functional relationship in a small area with a simple linear or quadratic polynomial model, and the calculation is relatively simple. It is an effective means to solve practical problems. The obtained prediction model is continuous. Compared with the orthogonal experiment, its advantages are: in the process of optimizing the experimental conditions, each level of the experiment can be analyzed continuously, while the orthogonal experiment can only analyze the isolated ones. Therefore, the response surface methodology (RSM) has become the scientific 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 PMS by NMS to produce sulfate radicals to degrade CTC, explore the reaction system’s influencing factors, and study the reaction mechanism. To understand better the influence of the determining variables on degradation chlorotetracycline 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. The biggest novelty of this study is that researchers combined inexpensive and easily available natural manganese sand with PMS for the degradation of antibiotics. At the same time, the researchers found that the activation of PMS was mainly due to the electron gain and loss of A, which led to a decrease in the content of A and an increase in the content of B and C before and after the reaction. This work is conducive to clarifying the reaction mechanism of natural manganese sand and PMS, so as to be applied to the treatment of special wastewater more quickly and reduce the treatment cost of special wastewater.

Materials and Methods

Reagents

Natural manganese sand was purchased from Henan Yuan-run water treatment materials Co. Ltd; Potassium monopersulfate triple salt (2KHSO5•KHSO4•K2SO4) was obtained from Aladdin Industrial Co. Ltd; Chlortetracycline hydrochloride (C22H23ClN2O8HCl) was provided by Hefei Bomei Biotechnology Co. Ltd. Potassium bicarbonate (KHCO3), potassium chloride (KCl), potassium nitrate (KNO3), potassium phosphate (K2HPO4), humic acid (HA), potassium sulfate (K2SO4), 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 μm 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:

\[
\text{Removal\%} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}
\]

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

\[
\ln \left( \frac{C_t}{C_0} \right) = -K_{\text{obs}} \times t \tag{2}
\]

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

Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface area, Barrett–Joyner–Halenda (BJH) pore size, and pore volume of the NMS particles were determined using the Tristar 3000 (Micromeritics) analyzer. To analyze the crystallographic characteristics of the prepared NMS, an X-ray diffractometer (Rigaku D/Max 2500 VBZ/PC) was utilized with Cu–K radiation (=0.15418 nm) and operated at 30 kV and 30 m. A 30 kV field scanning electron microscope (SEM, Hitachi, Japan) coupled with an energy dispersive spectrometer was used to examine the catalyst’s surface morphology and fundamental patterns (EDS). At 50 eV, Al K was used as an excitin in X-ray photoelectron spectroscopy (XPS, PHI-5300, ESCA).

Result and Discussion

X-ray diffraction

X-ray diffractometer (Rigaku D/Max 2500 VBZ/PC) was utilized with Cu–K radiation (=0.15418 nm) and operated at 30 kV and 30 m. 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 and 2.455 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.

**N₂ adsorption–desorption analysis**

The Brunauer–Emmett–Teller (BET) surface area, Barrett–Joyner–Halenda (BJH) pore size, and pore volume of the NMS particles were determined using the Tristar 3000 (Micromeritics) analyzer. 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. Figure 1b shows 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 m²/g and the pore volume was 0.09 cm³/g based on the test results.

**Energy dispersive spectroscopy and scanning electron microscopy analyses**

A 30 kV field scanning electron microscope (SEM, Hitachi, Japan) coupled with an energy dispersive spectrometer was used to examine the materials’ surface morphology and fundamental patterns (EDS). From the elemental analysis results, it can be seen that the NMS material contains C, O, Al, Si, Fe, Mn, and K elements. This phenomenon’s formation may be affected by the regular octahedral structure and layered structure of NMS (Yu et al. 2019b). 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%, and 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. 2k and l)(Yu et al. 2019b).

**XPS analysis of NMS**

At 50 eV, Al K was used as an excitation in X-ray photoelectron spectroscopy (XPS, PHI-5300, ESCA). 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 a spin–orbit doublet of Mn 2p¹/₂ and Mn 2p⁻¹/₂. 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% to 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
1. The catalyst before and after the reaction is shown in Fig. 3c. The proportion of Fe$^{2+}$ increased slightly from 28.31% to 31.92%, indicating that part of the Fe$^{3+}$ in the catalyst was reduced to Fe$^{2+}$ 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 g/L-PMS for 120 min, the CTC removal rate was 10.7%, which increased to 70.0% when PMS was increased to 2.0 g/L. The following is an explanation for the above phenomenon: (1) When the PMS concentration is zero, the larger specific surface area of natural manganese sand leads to the adsorption of CTC. (2) When the PMS concentration is low, more SO$_4^{−}$ is produced in the reaction system in a short

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Fig. 2  Morphology characterization of natural manganese sand: (a–h) EDAX mapping, (i-l) HR-SEM images

Fig. 3  a XPS survey spectrum, (b) Mn, (c) Fe XPS spectra of NMS

![Figure 2](image_url)

![Figure 3](image_url)
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 $\text{HSO}_5^-$ will react with $\text{SO}_4^{2-}$ and $\text{OH}^*$ to form $\text{SO}_5^{2-}$, which has a lower redox potential and oxidation power than $\text{OH}^*$ and $\text{SO}_4^{2-}$, as defined by Eqs. 3–7 (Huang et al. 2020; Liu et al. 2015; Zou et al. 2019).

\begin{align}
\cdot \text{OH} + \text{HSO}_5^- & \rightarrow \text{SO}_5^- + \text{H}_2\text{O} & (3) \\
\text{SO}_4^- + \text{HSO}_5^- & \rightarrow \text{SO}_5^- + \text{HSO}_4^- & (4) \\
\text{SO}_4^- + \text{OH} & \rightarrow \text{HSO}_4^- + \text{1/2O}_2 & (5) \\
\text{SO}_4^- + \text{SO}_4^- & \rightarrow \text{S}_2\text{O}_8^{2-} & (6) \\
\text{SO}_4^- + \text{OH} & \rightarrow \text{HSO}_5^- & (7)
\end{align}

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 g/L to 0.35 g/L, the CTC removal rate increased by 28.54%. However, when the catalyst dosage continued to increase to 0.4 g/L, the CTC removal rate dropped to 67.83%. 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. Figure 6a-b indicates the changes in CTC degradation under different solution pH (3–5) when CTC, NMS, and PMS have mass concentrations of 10 mg/L, 0.30 g/L and 2 g/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 point of zero charges of the NMS is 3.35, which is an important property of the surface charge of a solid (Li et al. 2018). The effect of solution pH on the zeta potential of NMS is shown in Fig. 6a. The results showed that when the pH of the solution was lower than 3.35, the surface of NMS was positively charged, and when the pH was higher than 3.35, it was negatively charged.

The main reason for CTC’s low degradation efficiency when the pH is increased from 4 to 2 is that (1) In acidic circumstances, pollutant adsorption increases, forcing CTC molecules on the catalyst’s surface to impede PMS interaction with the active site, preventing CTC breakdown. (2) By consuming PMS, •SO₄⁻, and •OH, certain acidic inorganic compounds are generated, whereby inefficient anions and weaker oxidants would limit the degrading efficiency of CTC. Degradation efficiency is decreased when the pH increases from 4 to 5. The following are the explanations for this phenomenon: (1) SO₄⁻ • reacts with OH⁻ to produce OH• when the pH is greater than 4.0. (2) As pH rises, the amount of surface charge on MnO₂ decreases, resulting in an increase in electrostatic repulsion between the catalyst and PMS, potentially inhibiting catalysis-PMS interaction and slowing CTC degradation (Deng et al. 2017). (3) Increasing the pH of the aqueous solution decreases the oxidability of MnO₂, 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 °C and the reaction time is 180 min, 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 = 2ⁿ + 2N + C₀, where N is the number of experiments to be performed, n is the number of variables, and C₀ is the number of center point runs (Gou et al. 2017). The experimental results are listed in Table 2. The results in Table 2 were analyzed by SAS software, and the quadratic regression equation is:

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

Equation (8) is the regression equation of removal efficiency. The results of the variance analysis are displayed in Table 3. The analysis of variance (ANOVA) for Eq. (8) is shown in Table 3. Because the correlation coefficient (R²) 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.

| Table 1  | Variables and levels of Box-Behnken Design |
|-----------------|--------------------------------------|
| Independent variables | symbol | Actual values of the coded variable levels |
|-----------------------|--------|------------------------------------------|
| [PMS] (mg/L)          | A      | -1.682  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                    |

Fig. 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]
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: 2.02 g/L, nature manganese sand: 0.29 g/L, pH: 3.87, and degradation rate of 81.65%. In the different independent variables such as PMS:2.00 g/L, nature manganese sand: 0.30 g/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 2 Experiment design and results of Box-Behnken

| Run | Coded values A | Coded values B | Coded values C | Actual value % | Predicted value % |
|-----|----------------|----------------|----------------|----------------|------------------|
| 16  | -1             | -1             | 0              | 65.3           | 64.95            |
| 1   | +1             | -1             | 0              | 66.7           | 65.75            |
| 8   | -1             | +1             | 0              | 68.3           | 68.75            |
| 4   | +1             | +1             | 0              | 68.7           | 69.55            |
| 12  | -1             | 0              | -1             | 67.8           | 67.88            |
| 7   | +1             | 0              | -1             | 67.8           | 68.68            |
| 6   | -1             | 0              | +1             | 67.6           | 67.43            |
| 9   | +1             | 0              | +1             | 69.0           | 68.23            |
| 2   | 0              | -1             | -1             | 69.3           | 69.48            |
| 5   | 0              | +1             | -1             | 79.5           | 78.38            |
| 17  | 0              | -1             | +1             | 73.0           | 74.13            |
| 13  | 0              | +1             | +1             | 73.0           | 72.83            |
| 14  | 0              | 0              | 0              | 80.5           | 81.38            |
| 10  | 0              | 0              | 0              | 81.0           | 81.38            |
| 11  | 0              | 0              | 0              | 81.2           | 81.38            |
| 15  | 0              | 0              | 0              | 82.0           | 81.38            |
| 1   | 0              | 0              | 0              | 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.
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, $\text{SO}_4^{2-}$, $\bullet\text{OH}$, and $\text{O}_2^{2-}$ will be produced after activation of PMS. In this study, MeOH ($\text{SO}_4^{2-}$ and $\bullet\text{OH}$ radical scavenger), TBA ($\bullet\text{OH}$ radical scavenger), and PBQ ($\text{O}_2^{2-}$ radical scavenger) were selected as inhibitors (Huang et al. 2020). As shown in Fig. 8a-b, the degradation efficiency decreased by 15.2%, 2.5%, and 8.2%.

Fig. 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).

Fig. 8 Removal efficiency of CTC the absence or presence of reactive species Scavenger. [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]
after adding 5 mM MeOH, 5 mM TBA and 5 mg/L PBQ. Therefore, SO₄²⁻, O₂•• and •OH radical participate in the degradation process of CTC, and SO₄²• plays a leading role in the system.

**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 (SO₄²⁻), nitrate (NO₃⁻), dihydrogen phosphate (H₂PO₄⁻), bicarbonate (HCO₃⁻), and humic acid (HA), the dominant species in natural water environment, were explored. It can be noticed from Fig. 9a that the amount reduced by 4.3% with 5.0 mM Cl⁻ addition. According to the previous studies of AOPs, an amount of Cl⁻ can be able to scavenge SO₄²⁻ and •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)

\[
\text{OH} + \text{Cl}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \\
\text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl}^- \\
\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2 \\
\text{ClO}_2^- + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{OH}^- \\
\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2 \\
\text{Cl}_2 + \text{Cl}^- \rightarrow 2\text{Cl}^- 
\]

In addition, the 5 mM NO₃⁻, H₂PO₄⁻, and HCO₃⁻ all inhibited the degradation efficiency of CTC, which ranged from 80.8% to 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).

\[
\text{NO}_3^- + \text{SO}_4^{2-} \rightarrow \text{NO}_3^- + \text{SO}_4^{2-} \\
\text{NO}_3^- + \text{OH}^- \rightarrow \text{NO}_3^- + \text{OH}^- \\
\text{NO}_3^- + \text{H}_2\text{O} + e^{-} \rightarrow \text{NO}_2 + 2\text{OH}^- \\
\text{H}_2\text{PO}_4^- + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{PO}_4 \\
\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{OH}^- + \text{H}_2\text{PO}_4 \\
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \\
\text{HCO}_3^- + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{SO}_4^{2-} \\
\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}_2 \\
\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{OH}^- 
\]

Figure 9 shows that 5 mM SO₄²⁻ and 5 mg/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). This results indicate the inhibition of anions on the degradation of CTC was arranged in the order of HCO₃⁻ > NO₃⁻ > H₂PO₄⁻ > Cl⁻ > SO₄²⁻ = HA. The 1 mM Cl⁻, SO₄²⁻, NO₃⁻, H₂PO₄⁻, HCO₃⁻, and 1 mg/L HA are added to the system at the same time, which inhibits the degradation efficiency of CTC. The main reason for this phenomenon is the consumption of SO₄²• and •OH by anions and humic acid. In Fig. 8, bicarbonate anion induced the strongest inhibitory effect. The following reasons may cause the phenomenon: (1) Studies have shown that Cl⁻ can capture •SO₄²⁻ to produce Cl•, and Cl• will further react with Cl⁻ to produce Cl₂•. Cl₂• will have an inhibitory effect when the reactivity of organic matter with Cl⁻/Cl₂• is low. On the contrary, Cl⁻ will promote organic matter with a higher reactivity with Cl⁻/Cl₂•. Therefore, the ability of Cl⁻ to degrade the efficiency is relatively weak. (2) There is a large amount of SO₄²⁻ in the NMS/PMS system, so SO₄²⁻ has little effect on the degradation efficiency. (3) NO₃⁻ will react with SO₄²• and •OH to consume free

![Fig. 9 Effects of coexisting ions and humic acid. 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)](image-url)
radicals. But NO$_3^-$ does not affect the pH of the system. (4) HA may affect the consumption of electrons. But the presence of HA promotes the transfer of electrons, thereby increasing the degradation efficiency (Zhang et al. 2022). (5) H$_2$PO$_4^-$ will react with SO$_4^{•−}$ and •OH to consume free radicals. On the other hand, the pH of solution H$_2$PO$_4^-$ is 4.66 close to the zero charges (PZC) of the NMS, so solution H$_2$PO$_4^-$ has little effect on the pH of the system. (6) On the one hand, HCO$_3^-$ will consume free radicals. On the other hand, the pH of solution HCO$_3^-$ is 8.0, so HCO$_3^-$ has a big effect on the pH of system. Therefore, compared with other coexisting ions and humic acid, HCO$_3^-$ has the greatest effect on the degradation efficiency.

**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 Fig. 10a. It can be seen from Fig. 10a that after 5 cycles of experiments, the degradation rate of CTC dropped by 2.39% after 600 min of reaction. Obviously, the degradation effect is still good after five repeated experiments. This is caused by the increased proportion of Mn$^{2+}$ and Fe$^{2+}$ due to the participation of Mn$^{3+}$. In subsequent reactions, both Mn$^{2+}$ and Fe$^{2+}$ lose electrons, resulting in the formation of free radicals. Therefore, the degradation effect of CTC is still very good in the cycling experiments. 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. 11.

In Fig. 11, there are many different kinds of products. CTC is attacked by SO$_4^{•−}$ and •OH to lose the hydroxyl group and hydrogen chloride to form U1 (m/z = 462.89) (Chen et al. 2020). There is a complete degradation pathway in Fig. 11. Firstly, the CTC, which C–Cl is oxidized by SO$_4^{•−}$, 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. 11. 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 obtaining 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**

NMS containing Mn$_3$O$_y$ and Fe$_3$O$_y$ as catalysts (Fig. 1a). Based on the above experimental results and analysis, the possible reaction process of using NMS to activate
| Substance | m/z [M-H]+ | Molecular formula | Proposed structure |
|-----------|------------|-------------------|-------------------|
| CTC       | 515.35     | C_{22}H_{23}ClN_{2}O_{8}·HCl | ![Proposed structure of CTC degradation products in the system](image) |
| U1        | 462.89     | C_{22}H_{20}ClN_{2}O_{7} | ![Proposed structure of CTC degradation products in the system](image) |
| W1        | 443.00     | C_{22}H_{20}ClN_{2}O_{6} | ![Proposed structure of CTC degradation products in the system](image) |
| V1        | 444.15     | C_{22}H_{24}N_{2}O_{7} | ![Proposed structure of CTC degradation products in the system](image) |
| V2        | 362.41     | C_{19}H_{20}O_{7} | ![Proposed structure of CTC degradation products in the system](image) |
| W2*       | 338.78     | C_{17}H_{16}ClO_{5} | ![Proposed structure of CTC degradation products in the system](image) |
| V3        | 318.35     | C_{17}H_{10}O_{6} | ![Proposed structure of CTC degradation products in the system](image) |
| W3*       | 297.75     | C_{17}H_{16}ClO_{4} | ![Proposed structure of CTC degradation products in the system](image) |
| V4        | 274.39     | C_{15}H_{14}O_{5} | ![Proposed structure of CTC degradation products in the system](image) |
| W4        | 244.67     | C_{15}H_{10}ClO_{4} | ![Proposed structure of CTC degradation products in the system](image) |
| W5        | 244.63     | C_{10}H_{6}ClO_{4} | ![Proposed structure of CTC degradation products in the system](image) |
| V5        | 246.31     | C_{15}H_{10}O_{5} | ![Proposed structure of CTC degradation products in the system](image) |
| V6        | 218.33     | C_{12}H_{10}O_{3} | ![Proposed structure of CTC degradation products in the system](image) |
| W6*       | 173.85     | C_{16}H_{10}ClO_{2} | ![Proposed structure of CTC degradation products in the system](image) |
| V7        | 150.65     | C_{6}H_{5}O_{2} | ![Proposed structure of CTC degradation products in the system](image) |
| V8*       | 94.11      | C_{6}H_{5}O | ![Proposed structure of CTC degradation products in the system](image) |
| V9*       | 88.15      | C_{6}H_{2}O | ![Proposed structure of CTC degradation products in the system](image) |
| W7*       | 58.07      | C_{2}H_{5}O | ![Proposed structure of CTC degradation products in the system](image) |
peroxymonosulfate to produce $\text{SO}_4^{2-}$, $\cdot$OH and $\cdot$O$_2^-$ is shown in Fig. 12. First, NMS with a relatively large specific surface area provides enough active sites for sufficient contact with PMS for the reaction (Fig. 1b). Therefore, the iron and manganese ions in the crystal lattice of the catalyst surface react with $\text{HSO}_5^-$ to generate $\text{SO}_4^{2-}$ radicals and $\cdot$OH radicals (Eqs. (25–28)) (Chen et al. 2019). In Fig. 3, the proportions of Mn$^{2+}$ and Mn$^{4+}$ increased by 10.75% and 8.58%, respectively. However, the proportion of Mn$^{3+}$ has dropped to 0%. In addition, $\text{SO}_4^{2-}$ radicals will react with H$_2$O to produce $\cdot$OH radicals. At the same time, $\text{HSO}_5^-$ will react with H$_2$O to produce $\cdot$O$_2^-$ radicals (Guo et al. 2020). In the end, the $\text{SO}_5^{2-}$ radicals, $\cdot$OH radicals and $\cdot$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$_2$O (Chen et al. 2019; Guo et al. 2020; Xiong et al. 2019).
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, the 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 (PMS) = 0.29 g/L, m (manganese sand) = 2.02 g/L, pH = 3.87, and degradation rate of 81.65%. Nature manganese sand is the most powerful catalyst for activation of peroxymonosulfate (PMS) toward degradation of CTC. In the response surface analysis method, the system can not only activate PMS, but also reduce Fe(II) to form Fe(III), and part of Fe(II) can reduce Mn(III) to Mn(II), thereby promoting cycle of Fe(II)/Fe(III) and Mn(III)/Mn(II) (Eqs. (31–32)). The proportions of Fe(III) increased by 3.61%. This strange phenomenon occurs mainly due to the participation of Mn(III).

\[
\text{HSO}_3^- + \text{Mn}^{3+} \rightarrow \text{SO}_4^- + \text{H}^+ + \text{Mn}^{2+} \tag{25}
\]

\[
\text{HSO}_3^- + \text{Mn}^{3+} \rightarrow \text{SO}_4^- + \text{OH}^- + 2\text{Mn}^{4+} \tag{26}
\]

\[
\text{HSO}_3^- + \text{Fe}^{3+} \rightarrow \text{SO}_4^- + \text{H}^+ + \text{Fe}^{2+} \tag{27}
\]

\[
\text{Fe}^{2+} + \text{HSO}_3^- \rightarrow \text{Fe}^{3+} + \text{SO}_4^- + \text{OH}^- \tag{28}
\]

\[
\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{HSO}_4^- \tag{29}
\]

\[
\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^- + \text{O}_2 + 5\text{H}^+ \tag{30}
\]

\[
\text{Mn}^{3+} + \text{Fe}^{3+} \rightarrow \text{Mn}^{4+} + \text{Fe}^{2+} \tag{31}
\]

\[
\text{Mn}^{3+} + \text{Fe}^{2+} \rightarrow \text{Mn}^{4+} + \text{Fe}^{3+} \tag{32}
\]

\[
\text{CTC} + \text{SO}_4^-/\text{OH}/\text{O}_2 \rightarrow \text{By-products} + \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^- \tag{33}
\]

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Data availability All authors approved that the data and material can be accessed from the corresponding author on reasonable request.

Declarations

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.

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