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The removal performance and mechanisms of tetracycline over Mn-rich limonite

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Abstract

Naturally occurring Mn-rich limonite mainly composed of goethite and manganese oxides was used to remove tetracycline (TC) from the aqueous solution. The physicochemical properties of limonite were illustrated by various characterization techniques such as XRD, FE-TEM, XPS and FT-IR. The effects of dosage, initial solution pH, temperature and coexisting anions on TC removal were investigated. The results showed that TC could be efficiently adsorbed by limonite with high specific surface area and mesoporous structure through electrostatic interaction and

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21 complexation. The co-existence of PO_4^{3-} inhibited the adsorption of TC by
22 limonite due to the competition with TC for active sites. In addition,
23 manganese oxides exhibited oxidative properties to TC, and the singlet
24 oxygen ($^1\text{O}_2$) generated during the redox reaction was responsible for TC
25 degradation. Furthermore, the regenerated limonite displayed an efficient
26 recycling performance after four cycles. This study revealed that the Mn-
27 rich limonite was a promising adsorbent for TC removal from aqueous
28 solutions and promoted the application of natural mineral material in the
29 environmental field.

30 **Keywords:** Mn-rich limonite; Tetracycline; Adsorption; Electron transfer;
31 Singlet oxygen; Degradation

32

1 Introduction

Tetracyclines (TCs) are broad-spectrum antibiotics and are extensively used in the pharmaceutical industry and veterinary medicine (Sarmah et al., 2006; Wammer et al., 2011). However, a variety of TCs is directly excreted into the environment in parent compounds or metabolites due to their incomplete absorption and metabolism in bodies (Cheng et al., 2016; Zhou et al., 2017). The residual antibiotics in natural water and soil will promote the generation of antibiotics resistance genes (ARGs) and antibiotics resistance bacterias (ARBs) (Daghrir and Drogui, 2013; Rodriguez-Mozaz et al., 2015; Liu et al., 2018), which has aroused increasing concerns about their potentially severe risks to public health. To date, various methods of treating TC-containing wastewater have been applied, such as adsorption (Ji et al., 2011), photocatalytic degradation (Xie et al., 2018), biodegradation (Yang et al., 2016) and advanced oxidation process (Tian et al., 2018). Adsorption has been widely applied in the treatment of wastewater containing antibiotics because of its advantages of low cost, simple operation and no secondary pollution.

Metal oxide minerals in soils, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), goethite ($\alpha\text{-FeOOH}$), and manganese oxides (MnO_2), play essential roles in inducing the transformation of antibiotics (Hafner and Parikh, 2020; Huang and Zhang, 2020). Goethite with high specific surface area and large surface hydroxyl contents is considered as an effective

adsorbent for antibiotics. Wu et al. (Wu et al., 2019b) reported that TC molecules were adsorbed by goethite through complexation and electrostatic interaction. Carrasquillo et al. (Carrasquillo et al., 2008) found that oxytetracycline was more likely to be immobilized on the surface of goethite than norfloxacin, because two adjacent hydroxyl groups on the oxytetracycline molecule facilitated surface complexation. In addition, manganese oxides have been proved to exhibit excellent oxidation capacities to antibiotics. Analysis of TC transformation products indicated that MnO_2 facilitated C-ring isomerization and further oxidized phenol diketones and tricarbonyl groups, leading to the interposition of oxygen on the two labile sites (Chen and Huang, 2011). Chen et al. (Chen et al., 2011) found that $\delta\text{-MnO}_2$ could oxidize chlortetracycline to form less toxic intermediate products. Encouraged by the above research, the application of ferric and manganese binary oxide (FMBO) for the efficient removal of pollutants has aroused widespread concerns. Joshi et al. (Joshi et al., 2017) and Qin et al. (Qiu et al., 2020) synthesized FMBO to remove organic pollutants and As(III) efficiently coupled the adsorption properties of FeOOH and the oxidation properties of MnO_2 . The development of FMBO provided new insights into the treatment of wastewater containing TC.

Previous studies discovered a naturally occurring Mn-rich limonite ore mainly composed of goethite and manganese oxides (Chen et al., 2018). The Mn-rich limonite is a natural nano-mineral with nano-acicular

morphology and rich porous structure, which has great potential application prospects in environmental remediation (Chen et al., 2017). In this work, the naturally occurring Mn-rich limonite was used for TC removal from aqueous solutions. The main objectives are: (1) to explore the removal performance of TC by limonite; (2) to test the effects of dosage, pH, temperature and coexisting anions on TC removal; (3) to investigate the removal mechanisms of TC by limonite.

2 Materials and methods

2.1 Materials and reagents

The tetracycline hydrochloride (Aladdin Co., Ltd, Shanghai, China), acetonitrile, methanol (Tedia Company Inc., USA), tert-butyl alcohol (TBA), furfuryl alcohol (FFA) and oxalic (Sinopharm Group Chemical Reagent Co., Ltd., China) were used in this work. All other analytical grades inorganic chemicals including HCl, NaOH, KOH, NaCl, NaNO₃, Na₂SO₄, NaH₂PO₄, Fe(NO₃)₃·9H₂O, Oxone (KHSO₅·0.5KHSO₄·0.5K₂SO₄) and MnO₂ were used. The Mn-rich limonite was collected from the Yeshan, Tongling city, Anhui Province, China. Table. S1 shows the chemical compositions of the limonite were Fe₂O₃ = 65.5 wt.%, MnO = 20.1 wt.%, SiO₂ = 6.8 wt.%, Al₂O₃ = 4.3 wt.% and ZnO = 1.5 wt.%. The minerals were crushed, ground and sieved for further experiments.

2.2 Batch experiments

Batch experiments were initiated by mixing 40.0 mg limonite with 50.0 mL 30.0 mg/L TC solutions in a 100.0 mL tube. The initial pH of TC solutions was adjusted to 5.0 using HCl and NaOH. Then the tube containing suspension was placed onto a shaker at a constant temperature until sampling. After reaction, 1.0 mL sample was extracted and filtered at pre-set interval for measurement.

The TC adsorption amount (q_e), kinetic model and the apparent activation energy (E_a) are given in Eqs. (1)-(3), respectively (Weng et al., 2018):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\frac{1}{C_t} - \frac{1}{C_0} = k_{obs}t \quad (2)$$

$$\ln k_{obs} = \ln A_0 - \frac{E_a}{RT} \quad (3)$$

where C_0 and C_e (mg L^{-1}) are the TC concentrations before and after reaction, respectively. V (L) and m (g) represent the volume of TC solution and the mass of limonite adsorbent, respectively. C_t (mg L^{-1}) is the TC concentration at time t (min). k_{obs} ($\text{mg}^{-1} \text{ L min}^{-1}$) represents the rate constants of the reaction kinetic model. A_0 represents the pre-exponential factor ($\text{mg}^{-1} \text{ L min}^{-1}$). E_a is the activation energy (kJ mol^{-1}). R is the ideal

gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). T represents the reaction temperature (K).

2.3 Analytical methods

TC concentration was analyzed by ultrahigh performance liquid chromatography (UHPLC, U3000, Thermo, America) equipped with a C18 column ($4.6 \times 250 \text{ mm}$) at a UV wavelength of 357 nm. The mobile phase was 45/35/20 (v/v/v) of oxalate/acetonitrile/methanol at a flow rate of 1.0 mL min^{-1} at 30°C . A total organic carbon analyzer (TOC, Jena, Germany) and atomic absorption spectrometer (AAS, WYS2200, WAYEE Technology Co., Ltd) were used to measure the concentration of residual organic carbon and dissolved metal ions, respectively. HPLC-MS (ACQUITY UPLC LCT Premier XE, Water, USA) detected the intermediates produced during TC degradation. Electrochemical experiments were carried out on CHI-660E electrochemical workstation (CHI-660E, China).

2.4 Characterization methods

X-ray fluorescence spectrometry (XRF, XRF-1800, Shimadzu), X-ray diffraction (XRD, DX-2700, Dandong), transmission electron microscopy (TEM, JEM-2100F, JEOL), Fourier transform infrared spectrometer (FT-IR, VERTEX 70, Bruker), X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo) analyzed the chemical

composition, crystalline structure, morphology, functional groups and element state of limonite, respectively. Specific surface area analyzer (NOVA 3000e) measured the specific surface area, pore volume and pore size distribution of limonite. The zero-point charge of limonite was analyzed by Potentiometric titrator (Titration 888, Metrohm).

3 Results and discussion

3.1 Characterization of limonite

[Fig. 1a](#) shows the XRD patterns of limonite before and after reaction. Four dispersed reflections at 21.2° , 33.2° , 36.7° and 53.2° were indexed to the (110), (130), (111) and (221) planes of goethite (JCPDS 3-251) due to the low crystallinity. Besides, a reflection at 26.7° was accordant with quartz (JCPDS 85-794). The absence of manganese oxides in the XRD spectra could be ascribed to the high dispersion degree of manganese oxides. Compared with the raw, the intensity and position of the goethite reflections in used limonite remained almost unchanged. The TEM images ([Fig. 2a](#)) shows that limonite particles were arranged in short rod-shaped aggregates, which was the typical morphology of goethite with the (021), (101) plane ([Fig. 2b](#)) ([Paul et al., 2014](#)). Besides, the (210) plane was identified as ramsdellite. The appearance of Mn in the mapping image ([Fig. 2e](#)) further indicating the presence of manganese oxides. XPS results of limonite ([Fig. 1c](#)) indicated that three Mn $2p_{3/2}$ peaks correspond to Mn^{2+} ,

Mn³⁺ and Mn⁴⁺, which evidenced the co-existence of Mn²⁺, Mn³⁺ and Mn⁴⁺ on the surface of limonite with a percentage content of 5.23%, 26.21% and 68.56%, respectively. The fitting of the Fe 2p_{3/2} peaks (Fig. 1d) reveals that both Fe²⁺ and Fe³⁺ existed on the surface of limonite with a percentage content of 58.13% and 41.87%, respectively. On the basis of the above results, it could be concluded that the Mn-rich limonite mainly comprised of goethite, manganese oxides and a small amount of quartz.

According to Fig. 1b, the N₂ adsorption/desorption isotherms of limonite could be classified as a type IV isotherm, indicating the mesoporous structures of limonite (Hayati et al., 2020). The specific surface area (145.0 m²/g), total pore volume (0.3 cm³/g) and average pore size (0.3 cm³/g) suggesting that limonite exhibited high porosity and specific surface area, thereby facilitated the adsorption (Rahimi et al., 2015).

Fig. 1 XRD patterns (a), N₂ adsorption/desorption isotherm and pore size distribution (b), XPS spectra for Mn 2p_{3/2} (a) and Fe 2p_{3/2} (b) of limonite.

Fig. 2 TEM images and elemental mapping images of limonite.

3.2 Removal performance of TC

3.2.1 Effects of dosage and solution pH

The influence of dosage on TC removal was systematically investigated (Fig. 3a). In the first stage (60 min), sufficient active sites on the surface of limonite enhanced the adsorption of TC. Subsequently, an evident decrease in the adsorption rate of TC was observed. The inhibitory adsorption of TC could be ascribed to the decline of available surface binding sites of limonite as the adsorption proceeded. On the other hand, the decreased amount of TC molecules in solution reduced the collision chance with limonite, decreasing the removal efficiency. The TC removal significantly improved from 58% to 96% after 540 min with the dosage increased from 0.2 g/L to 0.8 g/L. Correspondingly, the k_{obs} values increased from 0.8×10^{-4} to $13.0 \times 10^{-4} \text{ mg}^{-1} \text{ L min}^{-1}$ (Fig. S1 and Table. S2). The higher dosage of limonite led to more active sites resulting in the improvement of TC removal. When the dosage further increased from 0.8 to 2.0 g/L, the k_{obs} values increased from 13.0×10^{-4} to $43.0 \times 10^{-4} \text{ mg}^{-1} \text{ L min}^{-1}$, while the total TC removal rate was almost unchanged, which could be on account of the mass transfer resistance (Li et al., 2021). Based on the consideration of economic and environmental reasons, 0.8 g/L was selected as an optimum dosage for subsequent experiments.

Solution pH is a key factor controlling the TC molecule removal process due to its effects on the surface electric charge of limonite as well

as the existing state of TC. According to Fig. 3b and Table. S2, the TC removal efficiency peaked at pH = 5.0 with the highest k_{obs} value ($13.0 \times 10^{-4} \text{ mg}^{-1} \text{ L min}^{-1}$). This pH was closed to the zero potential point (4.5) of limonite (Fig. 3c). When the pH below 4.5, both surface zeta potential of TC and limonite were positive and increased with the decreasing solution pH (Wang et al., 2020b), resulting in the declining trend of TC removal. Evidently, when the pH value was greater than 4.5, the electrostatic repulsion was enhanced between the negatively charged surface of limonite and anion TC species, especially when the pH value = 11.0. Therefore, it could be concluded that the adsorption was greatly affected by electrostatic effect. In addition, the increase of pH suppressed the reduction of MnO_2 to Mn^{2+} as shown in Eqs. (4) (Lin et al., 2009). The improvement of solution pH decreased the overall reduction potential of the aqueous limonite system (Chen et al., 2010), which weaken the oxidizability of MnO_2 . Thus, more TC molecules were adsorbed by limonite rather than degraded, leading to the decrease of active sites of limonite and inhibited the adsorption. This was another vital factor responsible for the lower TC transformation at higher pH.

Fig. 3 Effects of limonite dosage (a), initial solution pH (b) on TC removal, the potentiometric titration of limonite under various pH (c) and effect of temperature (d) on TC removal (conditions: TC = 30.0 mg/L, dosage = 0.8 g/L, pH = 5.0).

3.2.2 Effect of temperature

As shown in Fig. 3d, it could be observed that TC removal improved with increasing temperature. From Table. S2, the k_{obs} values increased from 2.4×10^{-4} to $18.0 \times 10^{-4} \text{ mg}^{-1} \text{ L min}^{-1}$ with an increase in temperature from 283 to 303 K, indicating that the removal of TC was an endothermic reaction (Gu et al., 2021). As the temperature increased, the

driving force between the adsorbent and solution became more extensive, which promoted the adsorption of TC (Wang et al., 2020a). The activation energy (E_a) could be quantified from the slope of the Arrhenius plot (Fig. S2) and the value was found to be 71.6 kJ/mol. Previous study reported that the reaction could be regarded as a chemically controlled process when the E_a value higher than 21.0 kJ/mol (Liu et al., 2013).

3.2.3 Effects of coexisting anions

Natural water existed various inorganic anions which may affect TC removal, including nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) and chloride (Cl^-). The interfering of inorganic anions with concentrations ranging from 1.0 to 10.0 mM on TC removal was investigated. Fig. 4 depicts that the TC removal was slightly affected in the presence of Cl^- , NO_3^- and SO_4^{2-} under various concentrations. The slight influences by anions strength indicated that the adsorption of TC by limonite might mainly interact through the inner-sphere surface complexation (Zhao et al., 2014). However, the TC removal decreased with the addition of PO_4^{3-} . In detail, when the PO_4^{3-} concentration was 1.0 mM, the TC removal decreased from 92% to 87% after 540 min, and the k_{obs} values decreased from 6.7×10^{-4} to $3.9 \times 10^{-4} \text{ mg}^{-1} \text{ L min}^{-1}$ correspondingly (Table. S2). It was reported that PO_4^{3-} could be adsorbed by goethite through electrostatic attraction and inner-sphere surface complexation, leading to the reduction

of binding sites on the surface of limonite, which inhibited TC adsorption (Liu et al., 2012b; Ajmal et al., 2018). However, the increased PO_4^{3-} concentration has a negligible effect on TC removal, perhaps due to the formation of PO_4^{3-} bridging between TC and limonite.

Fig. 4 Effects of coexisting anions: Cl^- (a), NO_3^- (b), SO_4^{2-} (c), and PO_4^{3-} (d) in the concentration of 1.0 mM, 5.0 mM and 10.0 mM on TC removal (conditions: TC = 30.0 mg/L, dosage = 0.8 g/L, pH = 5.0).

3.3 Removal mechanisms

3.3.1 Adsorption

As mentioned above, TC was efficiently removed by limonite under various conditions. The electrostatic interaction and inner-sphere surface complexation have been proved to participate in the adsorption of TC. To further shed light on the adsorption mechanism between limonite and TC, the FT-IR spectra of the limonite before and after TC adsorption were analyzed and depicted in Fig. 5. For limonite, the peak at 1625 cm^{-1} could be assigned to the bending vibration of H_2O that existed on the oxides (Zhang et al., 2009). The typical peaks of limonite at 793 and 890 cm^{-1} were assigned to O-H bending vibration of Fe-OH in and out of the plane, respectively (Oliveira et al., 2008). The main characteristic peaks of TC were concentrated at the range of $1200\text{-}1700\text{ cm}^{-1}$, and the bands at 1523 , 1616 , 1582 , 1456 cm^{-1} could be assigned to the vibration NH_2 amide and ketone $\text{C}=\text{O}$ stretching of ring A, ketone $\text{C}=\text{O}$ stretching of ring C and C-C stretching, respectively (Zhang et al., 2015; Wu et al., 2019a). After adsorption, the appearance of the above characteristic peaks of TC in the spectra of TC-adsorbed limonite indicated that TC molecules were adsorbed on limonite successfully. Specifically, the intensity of O-H bending band of limonite decreased, which might be attributed to the substitution of surface hydroxyl groups by TC molecules (Liu et al., 2012b). The TC-adsorbed limonite showed the characteristic peak at 1456 cm^{-1}

corresponding to the C-C stretching of TC. The NH₂ amide of ring A and C=O of rings A and C enhanced and shifted to lower frequencies after adsorption, suggesting they were involved in complexation (Wu et al., 2019b).

Fig. 5 FT-IR spectra of limonite before and after reaction.

The pseudo-first-order and pseudo-second-order models were applied to explore the adsorption behavior between the limonite and TC. As presented in Fig. S3a-b and Table. S3, the pseudo-second-order model was more consistent with the TC adsorption behavior based on the higher R² value (R² = 0.999) and calculated equilibrium adsorption capacity closer to the experimental data (q_{ecal} = 37.9 mg/g, q_{exp} = 36.2 mg/g), demonstrating the adsorption process was much affected by chemisorption (Ghobadi et

al., 2018). The adsorption process between TC and the limonite was also investigated by the Langmuir and Freundlich adsorption isotherms models. The results and fitted data are shown in Fig. S3c-d and Table. S4, respectively. It was evident that the Freundlich isotherm model was a better model to fit the adsorption of TC with the higher R^2 value of 0.995, implying the adsorption process of TC occurred on the heterogeneous surface of the limonite, and the adsorption was multi-layered (Ma et al., 2019). The maximum adsorption capacity of limonite obtained from the Freundlich isotherm model was 102.5 mg/g. Table 1 lists the comparative maximum adsorption ability between the Mn-rich limonite and other previously reported adsorbents. Although the experimental conditions were different, one should be noted that the q_m of limonite was relatively encouraging compared to other adsorbents such as MgAl layered double oxide (Zhang et al., 2020). This finding demonstrated that the Mn-rich limonite was a promising adsorbent for TC removal from aqueous solution.

Table 1 Comparison of maximum adsorption capacity of Mn-rich limonite with various adsorbents for TC

Adsorbents	q_m (mg g ⁻¹)	Temperature (K)	pH	C_0 (mg L ⁻¹)	References
Chitosan	23.9	298	6.7	0-471.0	(Kang et al., 2010)
Cow manure BC	22.6	298	6.0	10.0-80.0	(Zhang et al., 2019)
TiO ₂ (B) nanosheets@hydrochar composites	49.3	298	7.0	5.0-100.0	(Zhu et al., 2020)
Kaolinite	8.8	298	5.5	1.0-35.0	(Song et al., 2019)
Clay-biochar composites	78.0	-	7.0-8.0	0.3-250.0	(Premarathna et al., 2019)
Graphene oxide	313.5	298	3.6	8.3-333.3	(Gao et al., 2012)
MgAl layered double oxide	44.8	298	10.0	0-125.0	(Zhang et al., 2020)
Mn-rich limonite	102.5	298	5.0	10.0-100.0	This work

3.3.2 Degradation

[Fig. 6a](#) displays TOC and TC removal efficiencies by limonite with reaction time. After reaction 540 min, 74% of the TOC was removed, which was less than the removal efficiency of TC (92%), indicating the presence of other forms of organic carbon in the solution. This phenomenon indicated that degradation was presented in the removal of TC ([Dong et al., 2018](#)). [Fig. 6b](#) shows the HPLC spectra of TC under various reaction times. A well-defined TC peak appeared at retention time (t_R) = 0.53 min, and the peak intensity gradually weakened. Besides, new

peaks were emerged in the HPLC spectra during the degradation process, which could be regarded as generated by-products. Transformation products of TC degradation by analyzing the mass spectra, as shown in Fig. S5. For TC, observed a protonated form of m/z 445 molecular, and one representative intermediate with m/z value of 415 was identified. The result further evidenced that degradation was included in the removal of TC. In addition, the Mn components gradually dissolved during the whole reaction (Fig. 6c), indicating that the reduction of MnO_2 occurred due to electron transfer (Zhang et al., 2021b). However, almost no dissolution of Fe ions was observed during the reaction, demonstrating that goethite didn't participate in the redox reaction, which was consistent with previous analysis that the goethite only played an adsorption role in TC removal (Wu et al., 2019b). It should be noted that there was no dissolution of Mn ions in deionized water with the same pH during the whole reaction process (Fig. 6d). Therefore, it was speculated that TC participated in the process of electron transfer and mediated the degradation of TC.

Fig. 6 Changes in TC and TOC concentration (a), HPLC spectra (b), dissolved Mn and Fe ions in TC solution (c) and deionized water (d) during the reaction (conditions: TC = 30.0 mg/L, dosage = 0.8 g/L, pH = 5.0).

Oxygen has been evidenced to interact with MnO_2 to influence the degradation process (Chien et al., 2009; Mahamallik et al., 2015). As shown in Fig. 7a, experiments of anoxic, aerobic and control groups on TC removal were conducted, and the corresponding dissolved oxygen content were 0.1, 7.9 and 7.0 mg/L, respectively. The nitrogen and air were continuously purged into the solution to create an anoxic and aerobic environment, respectively. In the aerobic system, the TC removal

efficiency increased to 85% at 60 min of reaction compared with the control group (74%). Conversely, under anoxic conditions, the TC removal efficiency decreased to 67 %, which was slightly lower than the control group. Therefore, oxygen played a vital role in the oxidation process. Previous researches reported that manganese oxides could react with oxygen to generate singlet oxygen ($^1\text{O}_2$) and H_2O_2 , and hydroxyl radical ($\cdot\text{OH}$) could also be formed by a series of electron transfers between manganese oxides and H_2O_2 (Zhang et al., 2011; Pham et al., 2020). To confirm the contributions of $^1\text{O}_2$ and $\cdot\text{OH}$ in the degradation of TC, quenching experiments were performed. It has been reported that TBA and FFA can quench $\cdot\text{OH}$ and $^1\text{O}_2$, respectively (Fan et al., 2019). In Fig. 7b, the addition of TBA showed a negligible impact on TC removal, while FFA has a more obvious inhibitory effect, decreasing TC removal efficiency from 92% to 87% after 540 min. Therefore, $^1\text{O}_2$ was formed during the reaction and was responsible for TC degradation.

Fig. 7 Comparison of TC removal under various oxygen environments (a); effects of various quenchers on the TC removal by limonite (b); LSV curves obtained by limonite in Na_2SO_4 solution (c); regeneration of limonite on TC adsorption with four cycles (conditions: TC = 30.0 mg/L, dosage = 0.8 g/L, pH = 5.0, TBA/FFA= 100.0 mM, Na_2SO_4 = 100.0 mM, PMS = 1.0 mM).

Electron transfer from adsorbed pollutants to MnO_2 has been widely accepted for the oxidation mechanism of pollutants (Joshi et al., 2017; Kamagate et al., 2020; Zhang et al., 2021b). Additionally, no Mn ions leaching was observed in the absence of TC, confirming the role of TC as an electron donor. To further verify the existence of electron transfer, linear

sweep voltammetry (LSV) and cyclic voltammetry (CV) were tested. As shown in Fig. 7c, the limonite in TC solution has a stronger current response than in deionized water with the same pH and electrolyte concentration, illustrating that higher surface charge transfer occurred in limonite-TC system (Huang et al., 2020). Fig. S4 shows that the current of limonite in TC solutions was higher than that in deionized water, proving that the electron transfer was promoted in limonite-TC system (Xia et al., 2019). Besides, a recent study confirmed that Mn^{3+} can contribute electrons to adsorbed O_2 to produce superoxide radicals ($\cdot\text{O}_2^-$) (Zhang et al., 2021a). Therefore, it could be speculated that both TC and Mn^{3+} played the role of electron donor mediated the production of $^1\text{O}_2$ to degrade TC. A continuous interaction was occurred between $\text{Mn}^{3+}/\text{Mn}^{4+}$ and O_2 , leading to the production of $^1\text{O}_2$ to degrade TC molecules. In addition, the Mn leaching was very low during the whole experiment, revealing good stability of the limonite, which was beneficial for future application.

On the basis of the above studies and discussion, it's rational to propose the removal mechanism of TC by limonite. Firstly, TC molecules were adsorbed by limonite through electrostatic interaction and surface complexation. Subsequently, $\text{Mn}^{3+}/\text{Mn}^{4+}$ was reduced to $\text{Mn}^{2+}/\text{Mn}^{3+}$ by accepting electrons derived from TC. Finally, $\text{Mn}^{2+}/\text{Mn}^{3+}$ produced by the above reduction and the $\text{Mn}^{2+}/\text{Mn}^{3+}$ derived from limonite contributed electrons to O_2 to generate $^1\text{O}_2$, degrading adsorbed TC molecules to other

intermediate products:

3.4 Synergistic effects of goethite and manganese oxides

The synergistic effects of goethite and manganese oxides in the removal of TC by Mn-rich limonite were evaluated by comparing the removal of TC by Mn-free limonite, goethite and MnO₂. The Mn-free limonite was collected from the Xinqiao of Tongling, Anhui Province, China. Goethite was synthesized according to previous research (Liu et al., 2012a). Fig. S6a shows that the crystal structure of Mn-free limonite was almost identical to goethite, while the former was a natural mineral and the latter was synthetic. The reflections of MnO₂ were consistent with that of pyrolusite (JCPDS 81-2261). Fig. S6b reveals that over 90% TC removals were achieved in the presence of the Mn-rich limonite, which was more reactive than other materials (Mn-free limonite, goethite and MnO₂) with lower TC removal rates. Based on the comparison results, it could be derived that the synergistic effects between goethite and manganese oxides favored TC removal.

3.5 Regeneration of limonite

The recyclability of limonite is another essential indicator for its application. Fig. 7d shows that limonite displayed a gradual decrease in the removal of TC in recycling experiments. The low reused capacity of limonite might be ascribed to the decline of available surface active sites with the occupation of TC molecules. On the other hand, the leaching of Mn ions could be another reason (Fig. 6c). To regenerate the used limonite, the limonite after each reaction was added to peroxymonosulfate (PMS) solution to oxidize adsorbed TC. The treated limonite was washed with deionized water and dried for the next recycling experiment. Obviously, a good recycling performance of treated limonite could be observed with a negligible decrease of TC removal after four runs. Therefore, the Mn-rich limonite exhibited excellent regenerated recyclability and low-cost advantages, which was useful for the enrichment and centralized treatment of antibiotics in wastewater.

4 Conclusion

In this study, the removal performance and mechanisms of TC by Mn-rich limonite were investigated. The TC adsorption behavior of limonite was fitted well by the pseudo-second-order model and Freundlich isotherm model. Results revealed that both electrostatic interaction and complexation participated in the adsorption of TC. In addition, the analysis

of TOC, metal ions dissolution, HPLC-MS, quenching experiment and XPS indicated that TC was degraded by manganese oxides to intermediates during the removal process. The $^1\text{O}_2$ was formed under the redox reaction of TC, manganese oxides and O_2 , which led to TC degradation. Based on the above discussions, it could be concluded that TC was removed by electrostatic interaction and surface complexation with goethite and oxidation by manganese oxides. These discussions were helpful for the exploration of the Mn-rich limonite as a promising material to treat antibiotics-contaminated wastewater.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

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