Efficient and economical degradation of minocycline by natural bornite-activated hydrogen peroxide and persulfate: kinetics and mechanisms

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Abstract

Natural bornite (NBo), a sulfide mineral of copper and iron, is one of the main mineral raw materials for copper extraction. In this study, NBo-activated hydrogen peroxide (H_2O_2) and persulfate processes (PS) for the degradation of minocycline (MNC) in aqueous solution were systemically investigated and compared. The MNC removal rates with the NBo/PS and NBo/ H_2O_2 processes were 86.40% and 87.50%, respectively. The mineralization rate of NBo/PS (33.96%) was higher than that of NBo/ H_2O_2 (29.94%) after reaction for 180 min. The effects of oxidant and activator dosage, pH, common inorganic anions (i.e., Cl^- , NO_3^- , and HCO_3^-), and water composition on MNC degradation were systematically evaluated. In addition, the degradation of MNC in natural water matrix and toxicity evaluation were also studied to better evaluate the feasibility of practical application of those two processes. The results of free radical quenching experiments and electron paramagnetic resonance spectroscopy (EPR) showed that $\text{HO}\cdot$ was the main activated species in the NBo/ H_2O_2 system, while $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$ were the main activated species in the NBo/PS system. The degradation of MNC in the NBo/PS system was achieved through electron transfer, while the degradation of MNC in the NBo/ H_2O_2 system was mainly achieved through free radical addition. The degradation pathway mainly included deamidation reactions, C-C bond breakage and hydroxylation. Reusability of NBo showed that NBo was considerably stable in activating PS and H_2O_2 for degradation of MNC, which was cost-effective activator. This work provides a new perspective on the degradation mechanism of pollutants by Fe-Cu bimetallic sulfide activation of PS and H_2O_2 .

1 Introduction

Due to the rapid development of the pharmaceutical field, the discharge of antibiotic-contaminated medical wastewater has increased significantly (Qu et al. 2020; Kang et al. 2016). As an emerging pollutant, the impact of this discharge on ecosystems has received extensive attention. Minocycline (MNC) is a broad-spectrum antibacterial tetracycline antibiotic which has been frequently detected in water bodies with increasing concentrations in recent year. Since MNC has a variety of potential toxicities to organisms (such as liver and kidney damage, bacterial flora, and allergic reactions, etc.), its health risks to the environment have received considerable attention (Nowak et al. 2012; Maavia et al. 2019).

The emerging pollutants are difficult to be removed in the conventional sewage treatment plants (Rodriguez et al. 2011, 2017; Mantzavinos et al. 2017). Therefore, it is of great significance to develop low-cost and environmental-friendly method to effectively remove it from wastewater. Recently, advanced oxidation processes (AOPs) based on activate PS and H_2O_2 has proven to be a promising method to remove refractory pollutants in the aquatic environment (Fan et al. 2021; Huang et al. 2020). Sulfate radicals ($\text{SO}_4^{\cdot-}$) and hydroxyl radicals ($\text{HO}\cdot$) have high standard reduction potentials, namely $\text{SO}_4^{\cdot-}$ ($E^0 = 2.5\text{--}3.1\text{ V}$) and $\text{HO}\cdot$ ($E^0 = 1.9\text{--}2.7\text{ V}$), so it has strong oxidation ability (Cashman et al. 2019). PS and H_2O_2 can be activated in many ways to generate $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$, such as UV (Yang et al. 2010), heat (Lv et al.

2020), alkali (Giannakis et al. 2021), transition metals (Saïen et al. 2011) and nano carbon materials (Xing et al. 2020), etc.

Among these activation methods, transition metal activation, especially Fe^{2+} activation, has been relatively extensively studied because of its relative non-toxic, high efficiency and low-cost advantages, as described in Eqs. ((1), (2)) (Niu et al. 2012; Song et al. 2019). However, shortcomings of Fe^{2+}/PS and the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ processes such as fast consumption of Fe^{2+} and generation of iron sludge greatly limits the degradation effects on pollutants (Cai et al. 2014). To solve these problems, the methods such as adding complexing agents (e.g., citric acid, EDTA) to the Fe^{2+}/PS and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ processes (Dulova et al. 2017), heterogeneous catalysts like zero-valent iron (Mossmann et al. 2019) synthetic transition metal oxides (e.g., CuFe_2O_4 , $\text{Fe}_2\text{O}_3@\text{CuO}_2$ and $\text{Fe}_4@\text{SWNT}$) were developed (Karimipourfard et al. 2019). Although these artificially synthesized catalysts have good activation performance for PS or H_2O_2 , it has the disadvantages such as complicated processes, high costs and being difficult to recycle. At the same time, the dosage ratio of the complexing agent should be strictly controlled, which limits the practical application (Dulova et al. 2017).

So far, exploring the potential application of AOPs for the treatment of MNC is still in the early stage (Lv and Li 2018). Previous studies showed that free radicals (e.g., $\text{SO}_4^{\cdot-}$, $\text{HO}\cdot$) were consumed by non-target water substrates, such as natural organic matters and inorganic anions, which greatly limited their application in practice (Lei et al. 2015; Jose et al. 2021). The degradation of antibiotics by AOPs was mainly achieved through the breaking of C-O bonds and the cleavage of functional groups by the addition of free radicals (Liu et al. 2019). However, there are few studies on the degradation process (mechanisms and pathways) of tetracycline antibiotic MNC. To the best of our knowledge, this is the first study on MNC degradation by AOPs based on $\text{SO}_4^{\cdot-}$; at the same time, natural bornite (NBo, Cu_5FeS_4) has not been reported as activator of H_2O_2 . Therefore, the degradation of MNC induced by NBo/PS and NBo/ H_2O_2 processes is worthy of further study.

Natural bornite (NBo) is one of the main products of copper refining, and its proven reserves rank second in the world (Zhang et al. 2020). Previous studies showed that the formation of free radicals in heterogeneous processes based partly on PS and H_2O_2 depends on the dissolution of metal ions on the surface of the activator (Teel et al. 2011; Sabri et al. 2020). The reducible sulfur in minerals contributed to the conversion of $\text{Fe}^{3+}(\text{Cu}^{2+})$ to $\text{Fe}^{2+}(\text{Cu}^+)$, which improved the degradation of pollutants. Coincidentally, the bimetallic effect between Fe and Cu was extensively studied in terms of the activation of PS and H_2O_2 (Torres-Blancas et al. 2017; Yao et al. 2017; Wang et al. 2018). Hence, in this study, NBo is used as activator to activate PS and H_2O_2 to eliminate MNC.

This study conduct an in-depth and systematic study on the degradation of MNC in the NBo/PS and NBo/H₂O₂ processes, respectively. The objectives of this study are (i) to explore the influence of various experimental parameters, such as the PS and H₂O₂ concentrations, NBo dosage, common inorganic anions (e.g., Cl⁻, NO₃⁻, and HCO₃⁻) and pH value; (ii) to determine the dominant activated ingredients involved in MNC processes; (iii) to evaluate the pathways and mechanisms of MNC degradation in both the NBo/PS and NBo/H₂O₂ processes; (iv) to identify the technical feasibility of both the NBo/PS and NBo/H₂O₂ processes for MNC degradation in different natural waters; and (v) to evaluate the toxicity of MNC samples by acute toxicity tests. Finally, the reusability of the NBo activator was studied.

2 Materials And Methods

2.1 Chemicals and materials

Minocycline hydrochloride (MNC, 98%) was purchased from Yuanye Biological Technology Co., Ltd. Sodium persulfate (Na₂S₂O₈, 99%) and hydrogen peroxide (H₂O₂, 30%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO, ≥ 98%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile (C₂H₃N, HPLC), methanol (CH₃OH, HPLC), ethanol (EtOH, 95%) and tertiary butanol (TBA, 98%) were purchased from Tianjin Komio Chemical Reagent Co., Ltd. High-purity bornite ore (NBo) was purchased from Hunan Geological Museum, Changsha, Hunan Province, China. After NBo was fully ground and sieved (< 180 μm), the resulting black powder was used as the activator for this experiment. Use Milli-Q water (18.2 mΩ·cm, Millipore system) to prepare the solution.

2.2 Experimental procedures

All experiments were performed on a magnetic stirrer with constant temperature at 25 ± 0.5 °C. During the experiment, the initial concentration of MNC was 10 mg/L, which was significantly higher than its concentration in actual water. A certain dose of NBo was firstly introduced to the 100ml vial containing 10 mg/L aqueous solution of MNC, after half an hour of adsorption-desorption equilibrium, added a certain volume of PS/H₂O₂ to start the reaction. Before the reaction started, 0.01 M H₂SO₄ or NaOH were used to adjust the pH of the solution, and the pH was no longer adjusted during the degradation process. At a specific time, taked 2 mL water sample and immediately quenched it with 1 mL EtOH (17.2M), and filtered by a 0.22 μm membrane filter (Jinteng, Tianjin, China) to quantitatively analyze the remaining contaminants. All experiments were repeated at least three times to ensure repeatability.

The influence of PS/H₂O₂ concentration (0-1000μM) and NBo dosage (0-0.2g/L) on the degradation of MNC were investigated at pH = 4.5 (unadjusted), respectively. At the same time, the effect of typical inorganic anions (i.e., Cl⁻, NO₃⁻, and HCO₃⁻) on MNC degradation in the water body was explored at pH = 4.5 as well. Under the condition of pH 2.5–9.5, the influence of pH on NBo/PS and NBo/H₂O₂ oxidation processes were studied. It was worth mentioning that the pH adjustment must be carried out before addition of NBo to avoid the influence of oxidation of NBo and trace metal ions in the solution. To

evaluate the reusability of NBo, the used NBo was suction filtered after 180 min reaction, the retained NBo powder was collected and washed with ultrapure water, and dried overnight in a vacuum drying oven at 60°C for the next use. This process repeated several times.

2.3 Identification of MNC concentrations and MNC transformation products

The concentration of MNC was analyzed by LC-2000 (JASCO, Japan). The separation column was a C-18 reverse chromatographic column, and the mobile phase was 0.2% phosphoric acid: acetonitrile = 12:88 (v: v). The flow rate was 1 ml/min, and the column temperature was 25°C. The injection volume was 50 µL, and the UV detection wavelength was 252 nm.

As described above in Sect. 2.2, the samples were collected at specific time intervals and filtrated with 0.22 µm filter for further analysis. The conversion products during the degradation of MNC were determined by I-Class-VION-IMS-Qtof (Waters, USA). The separation column was a Thermo Scientific HPLC Betasil C18 column (2.1 mm i.d. × 150 mm, 3.5 mm particles). The mobile phases were 0.1% formic acid and acetonitrile. The two mobile phases were proportioned by gradient elution within 6 minutes, the gradient table as showed in Table S2. The flow rate was 0.4mL/min, the temperature of the column was 35°C, and the injection volume was 5µL. The sample temperature of the sample bin was kept at 10°C. Mass spectrometry with an ESI source worked in the positive mode. The mass-to-charge ratio (m/z) acquisition range was 50 to 2000. For more detailed operating parameters of MS mode were shown in Table S3.

2.4 Identification of dominant active species

Free radical scavengers were added to the aqueous solution before the reaction started to capture the main free radicals in the NBo/PS and NBo/H₂O₂ processes. EtOH and TBA were used as target scavengers at a concentration of 50 mM to capture SO₄^{•-} and HO•, respectively. The remaining conditions were the same as the reaction conditions under the optimal activator and oxidant dosage.

5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) could capture SO₄^{•-} and HO•. At a specific time, quickly added 0.1 mL (100 mM) DMPO solution to 1 mL reaction solution, and shook for approximately 2 minutes. Then an electron paramagnetic resonance spectrometer (EPR, Bruker, Germany) was used to record the spectra of the radical adducts. Terephthalic acid (TA, 10 mg/L) could react with hydroxyl radicals to form a stable fluorescent substance 2-hydroxyterephthalic acid (2-HTA). This substance could be used to quantitatively measure hydroxyl radicals under a fluorescence spectrophotometer (F-7000, Hitachi, Japan). The detection conditions were excitation wavelength of 315 nm and emission wavelengths of 250 nm and 425 nm. The concentration of persulfate was determined by spectrophotometry.

2.5 Characterization of the NBo powder

X-ray fluorescence spectroscopy (XRF, ARLAdvant'XIntellipower3600) and X-ray electron spectroscopy (XPS, Thermo, Scientific K-Alpha) were used to analyze the element distribution on the surface of the NBo

powder. The crystal phase of the NBo powder was analyzed using an X-ray diffractometer (XRD, Ultima IV, Japan). The mineralization rate of the solution was measured with a total organic carbon analyzer (TOC, Shimadzu, Japan).

2.6 Acute toxicity tests

The toxicity changes during MNC degradation were determined by *V. fischeri* with bioluminescence instrument. The bacteria were resuscitated before toxicity test. 100 μ L of the resuscitated bacterial solution was mixed with 1 mL of aqueous solution evenly, and use CentroPRO LB962 bioluminescence detector (Berthold Technologies, Germany) to record the initial luminosity of each sample and the luminosity after 15 min. It is worth nothing that the NaCl solution (2%) was used as a negative control, and recorded its initial luminous intensity (Liu et al. 2019).

The toxicity of samples is expressed by luminescence inhibition rate, as described in Eq.

$$I(\%) = (S_0 * C_f - S_t) / (S_0 * C_f) * 100\% \quad (3)$$

Where S_0 is the initial luminous intensity of the sample and S_t is the luminous intensity of the sample mixed for 15min. C_f is the ratio of the luminous intensity after the negative control for 15 minutes to the initial luminous intensity ($0.6 \leq C_f \leq 1.8$). The change of toxicity is expressed by the percentage of luminescence inhibition rate of samples.

3 Results And Discussion

3.1 Degradation kinetics of MNC

3.1.1 Effect of initial oxidant concentration

As shown in Fig. 1a and b, the effect of different initial oxidant doses (i.e., PS and H_2O_2) on the degradation rates of MNC was investigated. Only 1.44% of MNC was degraded by addition of 0.15g/L NBo alone, indicated that the adsorption and degradation of MNC by NBo could be negligible. However, in the NBo/PS and NBo/ H_2O_2 processes, the degradation rates of MNC increased to 86.40% and 87.50% after 180 min (when $[H_2O_2]_0 = [PS]_0 = 500\mu M$), indicated that PS and H_2O_2 were effectively oxidated by NBo, respectively. Obviously, when the concentration of oxidants (i.e., PS and H_2O_2) increased from 25 μM to 500 μM , the degradation rates of MNC gradually increased, indicating that a higher concentration of oxidant is needed to achieve a better degradation rates in the target time. When the concentration of H_2O_2 increased from 500 μM to 1000 μM , the degradation rates of MNC only increased by 3.63% after 180 min, and there was no obvious change in the degradation rates of MNC, because the ion (e.g., Fe^{2+} , Cu^+) leaching from solution was insufficient, this will be limited the degradation rate of MNC (Eqs. (1)) (Song et al. 2019; Bi et al. 2020). It was worth noting that when the PS concentration increased from 500 μM to 1000 μM , the degradation rates of MNC decreased slightly after 180 min of reaction. This phenomenon

was attributed to the excessive PS reacted with $\text{SO}_4^{\cdot-}$ to produce $\text{S}_2\text{O}_8^{\cdot-}$ with low activation activity, and an insufficient concentration of metal ions limited the production speed of $\text{SO}_4^{\cdot-}$, while the S_n^{2-} in the solution was partially consumed by $\text{S}_2\text{O}_8^{2-}$, which hindered the continuous chain reaction (Eqs. (3)-(5)) (Wang et al. 2019). Although H_2O_2 could react with the $\text{HO}\cdot$ formed in the solution to produce $\text{HO}_2\cdot$ with weaker activation activity (Eq. (6)), it does not affect the chain reaction in this process (Basiri et al. 2018). In short, in these two advanced oxidation processes (AOPs), considering the appropriate removal effect and cost-effectiveness, the optimal oxidant dosage was taken as $[\text{H}_2\text{O}_2]_0 = [\text{PS}]_0 = 500 \mu\text{M}$.

3.1.2 Effect of initial NBo dose

As shown in Fig. 1c and d, the degradation rates of MNC was 14.67% and 11.07%, respectively, after the addition of 500 μM PS or H_2O_2 alone, which implied that the MNC with stable structure could not be effectively degraded by PS or H_2O_2 separately. Evidently, the amount of activator directly affects the removal efficiency of target pollutants. Previous studies showed that with the increase of the transition metal ions (e.g., Fe^{2+} , and Cu^+) concentration, more $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$ were produced in the NBo/PS and NBo/ H_2O_2 processes, which resulted in the degradation rate of target pollutants increased (Zhang et al. 2020). With the concentration of initial oxidants (PS and H_2O_2) fixed at 500 μM , with the dosage of NBo increased from 0.00g/L to 0.15g/L the degradation rate of MNC was increased.

Interestingly, when the dosage of NBo was 0.05 g/L, the degradation rates of MNC by the two oxidation processes was quite different. The reason was that the concentration of oxidants (PS and H_2O_2) far exceeded that of the activator at this time, and the second-order reaction rate constants (k) of the self-quenching reaction caused by oxidants are quite different, with $k_{\text{PS}} = 6.5 \times 10^5 \text{ L}/(\text{mol} \cdot \text{s})$ and $k_{\text{H}_2\text{O}_2} = 3.3 \times 10^7 \text{ L}/(\text{mols})$ (Feng et al. 2018). When the dosage of NBo was 0.1 g/L, there was almost no slow reaction stage in the NBo/ H_2O_2 process because Cu^{2+} could rapidly react with the $\text{HO}_2\cdot$ generated in the reaction ($k_{\text{HO}_2\cdot} = 1.6 \times 10^8 \text{ L}/(\text{mol} \cdot \text{s})$), and the reduced Fe^{3+} continues to participate in the chain reaction (Eqs. (1), (7), (9)). Nevertheless, when the dosage of NBo increased to 0.2 g/L, the degradation rate of MNC in both the NBo/PS and NBo/ H_2O_2 processes decreased. Because excessive NBo increased the turbidity of the solution, promoted NBo agglomeration and reduced the activated sites on NBo

surface. In addition, excessive metal ions (e.g., Fe^{2+} and Cu^+) consumed free radicals (i.e., $\text{SO}_4^{\cdot-}$ and $\text{HO}^\cdot$), which inhibited the degradation of MNC (Eqs. (10), (11)) (Wang et al. 2014).

3.1.3 Effect of inorganic anions

Many studies showed that degradation rates of pollutants in AOPs was affected by inorganic anions in water (Avetta et al. 2015; Sharma et al. 2018; Yang et al. 2019). In this study, typical inorganic anions (i.e., Cl^- , NO_3^- , and HCO_3^-) were selected to investigate the effect of different anion concentrations (i.e., 10mM, 20mM, and 50mM) on the degradation of MNC in the NBo/PS and NBo/ H_2O_2 processes. As shown in Fig. 2a and b, three inorganic anions with a concentration of 10–50 mM inhibited the two processes to varying degrees. In the presence of 10–50 mM Cl^- , the degradation rate of MNC in the NBo/PS process decreased to 79.78%, 79.59%, and 67.89%, while that in the NBo/ H_2O_2 process decreased to 81.87%, 58.01%, and 36.63%. Similarly, degradation of MNC was significantly inhibited in the presence of higher concentration of NO_3^- . Equally, HCO_3^- was also considered a quencher of free radicals, which had a certain negative impact on AOPs (Wang and Wang 2018). The degradation rates of MNC reduced to 38.38% and 36.49% with 10 mM HCO_3^- in the NBo/PS and NBo/ H_2O_2 processes. However, when the HCO_3^- concentration increased to 50 mM, the degradation rates of MNC increased to 79.91% and 70.30%, respectively.

Cl^- could react with $\text{SO}_4^{\cdot-}$ ($k_{\text{Cl}^-} = 1.3 - 6.6 \times 10^8 / (\text{M}^{-1} \text{s}^{-1})$) and $\text{HO}^\cdot$ ($k_{\text{Cl}^-} = 3.0 - 4.3 \times 10^9 / (\text{M}^{-1} \text{s}^{-1})$) to generate relatively weak chlorine radicals (e.g., $\text{Cl}^\cdot$, $\text{Cl}_2^{\cdot-}$, $\text{ClOH}^\cdot$) and free chlorine (Cl_2). Similarly, NO_3^- could also react with $\text{SO}_4^{\cdot-}$ to generate $\text{NO}_2^{\cdot-}$, $\text{NO}_3^{\cdot-}$, N_2 , etc. Since the relative activity of the generated free radicals was weaker than that of $\text{SO}_4^{\cdot-}$ and $\text{HO}^\cdot$, the degradation rates of MNC reduced in the presence of Cl^- and NO_3^- in the NBo/PS and NBo/ H_2O_2 processes. It was not difficult to see that Cl^- and NO_3^- had major inhibitory effects on the NBo/ H_2O_2 process. This was similar to the results of Neta et al. (1977), wherein $\text{SO}_4^{\cdot-}$ -based AOPs were more stable than $\text{HO}^\cdot$ -based AOPs.

Although HCO_3^- could also react with $\text{SO}_4^{\cdot-}$ ($k_{\text{HCO}_3^-} = 2.1 - 9.6 \times 10^6 / (\text{M}^{-1} \text{s}^{-1})$) and $\text{HO}^\cdot$ ($k_{\text{HCO}_3^-} = n \times 10^7 / (\text{M}^{-1} \text{s}^{-1})$) to form relatively weak free radicals (e.g., $\text{HCO}_3^\cdot$ and $\text{CO}_3^{\cdot-}$), the mechanism of HCO_3^- inhibition of the reaction was different from that of Cl^- and NO_3^- . As mentioned earlier, the degradation rates of MNC increased with increase of HCO_3^- concentrations. On the one hand, carbonate radicals could react well with electron-rich pollutant such as MNC. On the other hand, the pH of the

solution increased by the addition of buffer salt HCO_3^- , which resulted in the leaching of copper ions reduced. At that time, HCO_3^- had good complexing ability with Fe^{2+} and Cu^{2+} , which was the main reason for the increase of MNC degradation rates. Previous studies also found that the degradation of phenol and the TOC were improved in the presence of HCO_3^- in the $\text{CuO-Fe}_3\text{O}_4$ process (Lei et al. 2015). In addition, the high concentration of HCO_3^- contributed to produce $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$ from PS and H_2O_2 , to enhance the MNC degradation.

3.1.4 Effect of pH

pH plays an important role in heterogeneous AOPs based on free radicals (Li et al. 2020). The typical pH of most natural water bodies is between 3 and 9, so it is necessary to investigate the influence of the initial pH of the solution on AOPs, and the degradation kinetics are presented in Fig. S1a and b (Feng et al. 2017). Figure 2c summarized the MNC degradation rates with different initial pH of the solution in the NBo/PS and NBo/ H_2O_2 processes after 180 min. Obviously, these two processes had a better MNC degradation rates under acidic pH because acidic condition was conducive to the dissolution of metal ions to activate PS or H_2O_2 to produce more free radicals. When the pH was 6.5, the degradation rates in the NBo/PS and NBo/ H_2O_2 processes were sharply decreased to 67.37% and 54.52%, respectively. With increase of pH, the degradation rates increased until pH = 7.5. After that, the degradation rates decreased as the pH increased to 9.5, because Fe^{2+} precipitated easily under alkaline pH conditions. Interestingly, when the pH increased from 6.5 to 9.5, the degradation rates of MNC in the NBo/PS process always higher than that of in the NBo/ H_2O_2 process because $\text{SO}_4^{\cdot-}$ could react with OH^- to form $\text{HO}\cdot$ with strong catalytic activity under alkaline conditions. In the NBo/ H_2O_2 process, H_2O_2 was decomposed under alkaline conditions to reduce the amount of $\text{HO}\cdot$ and oxidation ability of hydroxyl radicals according to Nernst equation (Eqs. (13)).

$$E^0 = E^0_{\text{HO}\cdot/\text{H}_2\text{O}} - 0.059\text{pH} \quad (13)$$

Compared with the higher pH, the loss of activated ability at pH 6.5 may be due to the formation of a barrier layer on the surface of the material caused by the precipitation of iron ions, which limited the activated ability of the material (Liu et al. 2019). With continuously increase of pH, although the problem of ion precipitation still existed, the high pH was beneficial to the formation of hydroxyl groups on the activator surface, which served as the center of electron transfer activity to improve the activated performance of the activator. It was worth noting that after 180 min of reaction, the pH (2.5–9.5) of all solutions decreased due to the hydrolysis of ferrous ions and the formation of acidic intermediate products. Moreover, acidic conditions resulted in a high degradation rate of MNC in the two processes, indicated that AOPs based on the NBo/PS and NBo/ H_2O_2 processes had high application value in degradation of pollutants such as MNC in a wide pH range.

3.2 Identification of dominant reactive radicals

In this study, EtOH and TBA were selected as quenchers to participate in the reaction. As suggested, EtOH contains an α -hydrogen that reacts with $\text{SO}_4^{\cdot-}$ at a rate of $1.6\text{--}7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $\text{HO}\cdot$ at a rate of $1.2\text{--}2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The reaction rate of TBA without α -hydrogen with $\text{HO}\cdot$ ($3.8\text{--}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is much higher than that of $\text{SO}_4^{\cdot-}$ ($4\text{--}9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) (Lei et al. 2015; Wu et al. 2019). As shown in Fig. 3, in the NBo/PS system, the degradation rate of MNC was 86.48% after 180 min in the absence of a quencher, but after the addition of 50 mM EtOH and TBA, the degradation rate was reduced to 41.82% and 77.20%, respectively. The results showed that $\text{SO}_4^{\cdot-}$ was the main activated species in the NBo/PS process. In the NBo/ H_2O_2 system, the degradation rate of MNC was 87.47% after 180 min without a quencher and decreased to 50.62% and 56.80% after the addition of 50 mM EtOH and TBA, respectively. EtOH and TBA had a greater inhibitory effect on the degradation of MNC in the H_2O_2 process than in the other process, indicated that $\text{HO}\cdot$ was the main factor in the NBo/ H_2O_2 system. It was not difficult to see that higher concentrations of EtOH and TBA could not completely inhibit the degradation of MNC in the two systems. Studies pointed out that EtOH and TBA with high hydrophilicity could not accumulate on the surface of the activator or effectively capture free radicals bound on the surface of the activator to completely terminate the reaction in a heterogeneous process. Concurrently, the formation of superoxide radicals ($\text{O}_2^{\cdot-}$) in the heterogeneous process was promoted by the dissolved oxygen in the solution during the degradation process, and the free radicals converted by chain reactions (such as $\text{S}_2\text{O}_8^{\cdot-}$, and $\text{HO}_2\cdot$) contributed to the degradation of MNC in the presence of quenchers. In addition, Fig. S3 provides a quantitative analysis of $\text{HO}\cdot$ in the NBo/PS and NBo/ H_2O_2 processes.

The generated activated species were further detected by EPR. As shown in Fig. 3c and d, in the NBo/PS process, the spectra of DMPO- $\text{HO}\cdot$ and DMPO- $\text{SO}_4^{\cdot-}$ adduct were clearly observed. In the NBo/ H_2O_2 process, EPR signals of $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$ were also observed because the formation of small amount of $\text{SO}_4^{\cdot-}$ through a series of chain reactions even though leaching of S^{2-} caused by NBo. The above results indicated that the free radicals in the solution were the main reason for MNC degradation.

3.3 Characterization of NBo

To discuss the composition and electronic properties of NBo surface elements, the XPS spectra of NBo were studied. As shown in Fig. 4a, the XPS spectra showed that NBo was mainly composed of Cu, Fe, O, S, Si and Al, which was consistent with the XRD and XRF results (Fig. S4 and Table S5). C and O might be originated from the adsorption of air by NBo powder samples (e.g., Si and Al) during the XPS test (Nie et al. 2019). According to the high-resolution spectra of Cu 2p, the fresh and used NBo had strong Cu 2p₃ and Cu 2p₁ peaks near 932.2 eV and 951.1 eV, respectively, and obvious satellite peaks were observed in Cu 2p. Because the binding energies of CuS and Cu₂S were too close to 932.2 eV and 932.5 eV, respectively, it was impossible to accurately distinguish the valence state of Cu near 932.2 eV. However, according to the analysis of Cu 2p₃, the Cu on the surface of fresh and used NBo was mostly in the +2 oxidation state. It can be seen from the changes in the Cu-S and Cu (II) contents that there was not much difference in the valence content of Cu before and after the use of NBo, which indicated that the activator

could continuously release stable Cu in the valence state to be used repeatedly. Figure 4c shows the high-resolution Fe 2p spectra of the fresh and used NBo. Fe 2p₃ and Fe 2p₁ characteristic peaks appeared at 708 eV, 709.8 eV, 711.58 eV, 720.8 eV, 722.6 eV, and 724.98 eV, respectively. Fe 2p satellite peaks appeared at 713.52 eV, 717.38 eV, 727.83 eV and 731.04 eV, all of which indicated that the surface of NBo had the characteristics of Fe (II) and Fe (III). After being used, the ratio of Fe (II) on the NBo surface decreased from 52.15–45.51%, which indicated that active performance of NBo repeated use would slightly decrease the. In addition, the peak positions of Fe₀, Fe (II) and Fe (III) in the used sample present an obviously negative shifting compared to the fresh sample, this results indicated electron transfer phenomenon during activation. Figure 4d shows the high-resolution S 2p spectrogram before and after use. At 162.30 eV, 163.81 eV, 164.76 eV and 168.74 eV, the characteristic peaks corresponded to S²⁻, S_n²⁻, S₀ and SO₄²⁻, respectively. Clearly, the contents of S_n²⁻ and SO₄²⁻ in NBo increased from 19.10% and 2.66–25.53% and 11.03%, respectively, and the content of S₀ hardly changed, while the content of S²⁻ decreased from 68.10–53.91%. Results showed that during the reaction, S²⁻ was converted into S_n²⁻, S₀ and SO₄²⁻ in sequence; the content of S₀ decreased slightly, possibly because it was partially consumed as a reducing agent in the reaction with Fe (III) and Cu (II).

3.4 Degradation products and pathways

The degradation products of MNC were determined by I-Class-VION-IMS-Qtof. Fig. S5a and b showed the total ion chromatogram (TIC) of the oxidative degradation of MNC in the NBo/PS and NBo/H₂O₂ processes, respectively. The appearance of new peaks and different intensities in the ion chromatogram indicated the formation of new substances (Taha et al. 2016; Dulova et al. 2017; Zhang et al. 2020). The possible degradation pathway of MNC was showed in Fig. 5. Fourteen potential degradation intermediates were observed in the NBo/PS process at elution times of 2.14 min, 3.11 min, 3.64 min and 3.84 min, while ten potential degradation intermediates of the NBo/H₂O₂ process were observed at elution times of 0.36 min, 2.14 min, 3.13 min, 3.45 min, 3.64 min and 3.83 min. The mineralization rates were 33.96% and 29.94% in NBo/PS and NBo/H₂O₂ process, respectively. In the NBo/PS process, MNC was firstly attacked by active specoes in aqueous solution and converted into P1 (m/z = 370) by ring opening, and then P2 (m/z = 337), P3 (m/z = 316) and P5 (m/z = 237) were further generated by deamidation of P1. Xu et al. (2017) showed that the cleavage of C-O bonds and the hydroxylation of target substances were the main mechanisms for the degradation of pollutants by free radical systems. In the same way, the organic compounds P4 (m/z = 281), P6 (m/z = 269), P7 (m/z = 260), P8 (m/z = 255), P10 (m/z = 204) and p14 (m/z = 135), with smaller relative molecular weights, were further obtained by the ring-opening reaction of P2 and P3. It has been reported that HO· can react with pollutants by direct addition or electron transfer and then form different reaction products (Zhang et al. 2016). Figure 5b shows the possible degradation pathway of MNC by the NBo/H₂O₂ process. First, the hydroxyl group replaced the H in the C-H bond and adducted with pollutants to form TP1 (m/z = 473). TP1 was decomposed to P2 (m/z = 445) via deamidation reaction. Then, P2 was further degraded into the smaller mass organic substances P3 (m/z = 337) and P4 (m/z = 309) by ring-opening reaction under the action of

HO $\cdot$. The cyclic pollutants were oxidized to hydroxylated derivatives and further decomposed into degradable pollutants (TP5-TP10) under the action of HO $\cdot$. In addition, substances with relatively low mass responses were generated in those two systems, which might be secondary intermediates generated in the degradation process.

The possible mechanisms and degradation pathways based on the oxidative degradation of MNC in NBo/PS and NBo/H₂O₂ processes were as follows: a large number of free radicals (mainly SO₄ $\cdot^-$ and HO $\cdot$) were generated under the action of activators and oxidants in the system, which were dispersed to the NBo surface and MNC solution. On the one hand, the C-C bond of MNC was destroyed by electron transfer, and a deamidation reaction occurs to generate pollutants with ring structures (P1, P12), and the C-C bond and C = O bond of the pollutants were further destroyed to generate small molecules. On the other hand, one active site of the pollutants was replaced by free radicals to form adducts (TP1). The C-C bonds and C = O bonds of TP1 were further oxidized to form the hydroxylated derivative. Finally, these intermediates were further oxidized to carbon dioxide and H₂O to achieve inorganic treatment of pollutants.

3.5 Degradation of MNC in natural water

To evaluate the feasibility of NBo activating PS and H₂O₂, MNC removal by the two processes in natural water matrix (Table S4) was studied. The pH of the collected water samples (i.e., tap water and river water) was between 7 and 8. The experiment was carried out under optimal conditions. As shown in Fig. 6, the degradation rates of MNC in natural water was lower than that in ultrapure water. Clearly, the degradation rate achieved with the NBo/PS and NBo/H₂O₂ processes in the untreated river water matrix was lower than that in tap water. Because the existence of a large number of anions in river water with alkaline condition, the formation of metal ions was aggravated. As mentioned above, pH had an important influence on the two systems in this study. The degradation of MNC was significantly improved in both system by adjust the pH of river water and tap water to 4.5 with 0.1M H₂SO₄ and NaOH. The results indicated that degradation of pollutants with different water matrices in the NBo/PS and NBo/H₂O₂ systems were inhibited because of high pH. Consistent with the results of Sect. 3.1.4, SO₄ $\cdot^-$ -based AOPs were more stable than HO $\cdot$ -based AOPs in different water materials. In short, MNC could be effectively degraded in natural waters by adjusting the pH appropriately. Results obtained in this study showed that the degradation of MNC based on the NBo/PS and NBo/H₂O₂ systems had high industrial application potential.

3.6 Reusability of NBo activator

To evaluate the stability of the activator, the reaction solution was suction filtered after 180 min of reaction, and the retained NBo was washed repeatedly with 2 L of ultrapure water and finally dried under vacuum at 60°C. The stability of NBo in the two processes (NBo/PS and NBo/H₂O₂ processes) was evaluated on the basis of its reusability. Figure 7a showed that NBo still had high activated performance for PS after repeatedly use three times in the NBo/PS process. Compared with the unused NBo, the

degradation rate of MNC decreased by 4.59% after second run for 180 min, which indicated that NBo had excellent reusability in the NBo/PS process. Figure 7b showed that in the NBo/H₂O₂ process, after second and third reactions, the degradation rate of MNC decreased by 8.28% and 9.00%, respectively. The slight decrease of the MNC removal rate might be due to the precipitation of metal ions during reaction, resulted in slight changes of the surface element distribution. In brief, NBo had considerable stability in activating PS and H₂O₂ to degrade MNC.

3.7 Toxicity evaluation

The ultimate goal of degrading pollutants through AOPs is to eliminate the harm of pollutants to aquatic organisms and humans. However, in the process of pollutant degradation, the transformation of macromolecular substances into small molecular substances will cause change in the properties of the substances (Long et al. 2014; Yao et al. 2019). Therefore, it is important to evaluate the change of toxicity during the degradation of MNC solutions.

The luminescence inhibition rate of the MNC aqueous solution was showed in Figs. 8 and S2. In general, the biological toxicity of MNC tended to decrease after degradation. The results of toxicity assessment were closely related to the properties of MNC degradation products. In the NBo/H₂O₂ system, the inhibition rate decreased to 49.92% after 30 min of reaction because the products (TP3, TP4) with lower biological toxicity produced by the ring-opening reaction at this time. It was obvious that the toxicity after 90 min and 180 min was greater than that after 30 min, which due to the formation of more hydroxylated derivatives (TP5-TP9) during the degradation of MNC, and the hydroxylated derivatives were not further degraded within 180 min. In the NBo/PS system, toxic degradation products such as hydroxylated derivatives (P2, P3, P12) and carbonylation derivatives (P9, P11) were also produced. However, these organic substances could be decomposed into degradable organic substances (P11, P13, P14). Therefore, the toxicity of degraded MNC was lower than that of the parent compound. The results of the toxicity test showed that the NBo/PS and NBo/H₂O₂ systems were effective ways to degrade MNC.

4 Conclusions

In this study, the degradation of MNC under different experimental parameters in NBo/PS and NBo/H₂O₂ systems was investigated. The main conclusions are as follows.

NBo can effectively activate PS and H₂O₂ to degrade MNC. After reaction for 180 min, the efficiencies of MNC degradation in the two processes were 86.40% and 87.50%, and the mineralization rates were 33.96% and 29.94%, respectively. The metal ions and reductive S released from NBo play an important role in enhancing the degradation rates. The NBo and oxidant dosages have an important influence on the degradation of MNC, and a high pH can inhibit the MNC degradation. The identification of intermediate products shows that degradation of MNC in the two processes was achieved by free radical addition and electron transfer, respectively, and the degradation pathways mainly include ring-opening reactions and deamidation reactions. The natural water components Cl⁻ and NO₃⁻ have inhibitory effects

on NBo/PS and NBo/H₂O₂ processes, and the inhibitory effect is proportional to the concentration of Cl⁻ and NO₃⁻, while the inhibitory effect of HCO₃⁻ on the reaction is inversely proportional to its concentration. NBo/PS and NBo/H₂O₂ processes have strong industrial application potential of degradation of pollutants because the degradation rate of MNC was similar to that in ultrapure water through adjust the pH of different water source. To the best of our knowledge, this is the first study on the degradation of organic pollutants by activating PS and H₂O₂ with Fe-Cu bimetallic sulfide; moreover, there has been no previous report on the degradation mechanism and reaction pathway of MNC pollutants. This work will provide a new perspective for the mechanism of Fe-Cu bimetallic sulfide activation of PS and H₂O₂ degradation of pollutants.

Abbreviations

Natural bornite (NBo); minocycline (MNC); persulfate (PS); hydrogen peroxide (H₂O₂); advanced oxidation processes (AOPs)

Declarations

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

The data used to support the findings of this study are available from the corresponding author upon request.

Competing interests

The authors declare that they have known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors' contributions

Taikang Yuan: Design experiment, conduct experiment, write papers

Xudong Wang: Provide funds, guide experiment, modify this paper

Xiaochen Zhao: Assist experiment, Verify experiment

Tingting Liu: modify this paper

Hongmin Zhang: Assist experiment

Yongtao Lv: Guide experiment

Lei Wang: Guide experiment

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Figures

Figure 1

Effect of oxidant concentration (a, b) and NBo dosage on MNC degradation by NBo/PS and NBo/H₂O₂ processes. Experiment conditions: [MNC]₀=10mg/L, pH=4.5±0.3. [NBo]₀=0.15g/L, [H₂O₂]₀=[PS]₀=0-1000uM in (a, b); [H₂O₂]₀=[PS]₀=500uM, [NBo]₀=0-0.2g/L in (c, d)

Figure 2

Effect of common inorganic anions (a, b) and pH (c) on the degradation of MNC in the NBo/PS and NBo/H₂O₂ processes. Experiment conditions: [MNC]₀=10mg/L, [H₂O₂]₀=[PS]₀=500μM, [NBo]₀=0.15g/L. pH=4.5±0.3 in (a, b) and pH= 2.5-9.5 in (c)

Figure 3

The effect of the presence of free radical quenchers EtOH and TBA on MNC degradation in the NBo/PS (a) and NBo/H₂O₂ (b) processes. EPR spectra of hydroxyl and sulfate radicals captured by DMPO in the (c) NBo/PS and (d) NBo/H₂O₂ processes. Experiment conditions: [MNC]₀=10mg/L, pH=4.5±0.3, [H₂O₂]₀=[PS]₀=500μM, [NBo]₀=0.15g/L

Figure 4

XPS spectra of fresh and used NBo: (a) survey spectra; (b) high-resolution Cu 2p; (c) high-resolution Fe 2p; (d) high-resolution S 2p

Figure 5

Products and pseudotransformation pathway of MNC degradation by the NBo/PS and NBo/H₂O₂ processes

Figure 6

Degradation of MNC in different aqueous media by NBo/PS (a) and NBo/H₂O₂ (b) processes. Experiment conditions: [MNC]₀=10mg/L, pH=4.5±0.3, [H₂O₂]₀=[PS]₀=500uM, [NBo]₀=0.15g/L

Figure 7

Activated performance of NBo reused in NBo/PS (a) and NBo/H₂O₂ (b) processes. Experiment conditions: [MNC]₀=10mg/L, pH=4.5±0.3, [PS]₀=500uM, [NBo]₀=0.15g/L

Figure 8

Luminescence inhibition rate of MNCs in the NBo/PS and NBo/H₂O₂ processes. Experiment conditions: [MNC]₀=10mg/L, pH=4.5±0.3, [H₂O₂]₀=[PS]₀=500μM, [NBo]₀=0.15g/L

Supplementary Files

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