Removal of tetracycline from water by Fe-Mn binary oxide

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Abstract

Significant concerns have been raised over the presence of antibiotics including tetracyclines in aquatic environments. A series of Fe-Mn binary oxide with different Fe:Mn molar ratios was synthesized by a simultaneous oxidation and coprecipitation process for TC removal. Results showed that Fe-Mn binary oxide had higher removal efficiency than that of hydrous iron oxide and hydrous manganese oxide, and that the oxide with a Fe:Mn molar ratio of 5:1 was the best in removal than other molar ratios. The tetracycline removal was highly pH dependent. The removal of tetracycline decreased with the increase of initial concentration, but the absolute removal quantity was more at high concentration. The presence of cations and anions such as Ca^{2+}, Mg^{2+}, CO_3^{2-} and SO_4^{2-} had no significant effect on the tetracycline removal in our experimental conditions, while SiO_3^{2-} and PO_4^{3-} had hindered the adsorption of tetracycline. The mechanism investigation found that tetracycline removal was mainly achieved by the replacement of surface hydroxyl groups by the tetracycline species and formation of surface complexes at the water/oxide interface. This primary study suggests that Fe-Mn binary oxide with a proper Fe:Mn molar ratio will be a very promising material for the removal of tetracycline from aqueous solutions.

Key words: Fe-Mn binary oxide; tetracycline; abatement and removal; water treatment

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Introduction

Antibiotics are widely used therapeutically for humans and animals, and as growth promoters in livestock and aquaculture operations. A statewide survey of wastewater treatment plants in Wisconsin, USA revealed that the compound tetracycline (TC) was the most frequently detected antibiotic, being present in 80% of the wastewater influent and effluent samples (Gu and Karthikeyan, 2005). TC is poorly absorbed by human and animals after intake, about 50%–80% is eventually excreted as unmetabolized parent compound into domestic sewage (Sarmah et al., 2006). In recent years, TC has been reportedly found in surface water, and even groundwater (Batt and Aga, 2005; Lindsey et al., 2001). The present of TC and other antibiotics in natural environments can cause bacteria to acquire and transmit antibiotic-resistant genes, which potentially threatens ecosystem functions and human health (Gilliver et al., 1999; Halling-Sørensen et al., 1998; Sarmah et al., 2006). Therefore, it is of great importance to develop efficient and cost-effective treatment technologies for removal of TC from contaminated waters to minimize its ecological risks.

Various techniques such as ozonation (Khan et al.,

2010), photo-Fenton process (Bautitz and Nogueira, 2007), photoelectrocatalytic degradation (Bai et al., 2010; Liu et al., 2009) and adsorption (Chang et al., 2009; Figueroa et al., 2004; Ji et al., 2009; Kulshrestha et al., 2004; Wang et al., 2008; Xu et al., 2009) have been employed for the removal of tetracycline from water. Among these available methods, adsorption is a widely used effective technology for treatment of low concentration antibiotics. Recently, adsorption of tetracycline on sorbents based on metal or metal oxides such as montmorillonite (Figueroa et al., 2004; Kulshrestha et al., 2004), magnesium-aluminum hydrotalcites (Xu et al., 2009), hydrous oxides of aluminum and iron (Gu and Karthikeyan, 2005), iron oxides and iron oxide-rich soils (Figueroa and Mackay, 2005) were reported.

Hydrous oxides of aluminum and iron are important mineral components of environmental particles. These minerals are considered as major "sinks" for many inorganic and organic contaminants because of their high surface area and reactivity (Gu and Karthikeyan, 2005). Researches indicated that tetracycline sorption to hydrous oxides of aluminum and iron involved the formation of water-soluble complexes between tetracycline and the surface of hydrous oxides (Figueroa et al., 2004; Gu and Karthikeyan, 2005). However, sorption of tetracycline on

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hydrous iron oxide was quite rapid and the soluble metal-tetracycline complexes formation efficiency was small than that of aluminum oxide (Gu and Karthikeyan, 2005). Manganese oxides are among the strongest natural oxidants found in soils and sediments. Studies have revealed that oxytetracycline could be rapidly degraded by MnO_2 (Rubert and Pedersen, 2006). Hydrous iron oxide and manganese oxide are both low cost and environmentally friendly. It can be anticipated that a Fe-Mn binary oxide originating from the combination of iron oxide and manganese dioxide will have the potential for the oxidation and sorption of tetracycline simultaneously. To our best knowledge, no information on the Fe-Mn binary oxides for removal has been reported.

In this study, a series of Fe-Mn binary oxides with different Fe:Mn molar ratios (from 1:1 to 7:1) were synthesized and were tested for removal. The removal efficiency was investigated by a series of experiments under different experimental conditions such as reaction time, solution pH, initial tetracycline concentration and coexisting anions. High performance liquid chromatography (HPLC) was used to analyze the TC concentration in water before and after the adsorption. Moreover, total organic carbon (TOC) was used to evaluate the removal of tetracycline, because some soluble metal-tetracycline could be formed after the adsorption (Gu and Karthikeyan, 2005) and the oxidation intermediate products might be released into water (Chen and Huang, 2011). In addition, a tetracycline removal mechanism was elucidated.

1 Materials and methods

1.1 Materials

Tetracycline hydrochloride was purchased from Beijing JingKeHongDa Biotechnology Co., Ltd. China and used without further purification. The main physicochemical properties of tetracycline are: MW: 444.43; aqueous solubility of 0.52–117 mmol/L; $\log K_{ow}$ of –1.97 to –0.47; and pK_a, values of 3.3, 7.7 and 9.7. Molecular structure of tetracycline and its speciation as a function of pH are presented in Fig. 1 (Kang et al., 2010). All other chemicals were analytical grade and were obtained from Beijing Chemical Co. (China). The aqueous solutions for experiments were prepared using de-ionized water.

1.2 Preparation of Fe-Mn binary oxides

The Fe-Mn binary oxide with a Fe:Mn molar ratio of 3:1 was prepared by a simultaneous oxidation and coprecipitation process. Potassium permanganate ($KMnO_4$, 0.015 mol) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 0.045 mol) were dissolved in 200 mL of deionized water, respectively. Under vigorous magnetic-stirring, the $FeSO_4$ solution was slowly added into the $KMnO_4$ solution, and 5 mol/L NaOH solution was simultaneously added to keep the solution pH in the range of 7 and 8.

The formed suspension was continuously stirred for 1 hr, aged at room temperature for 12 hr and then washed
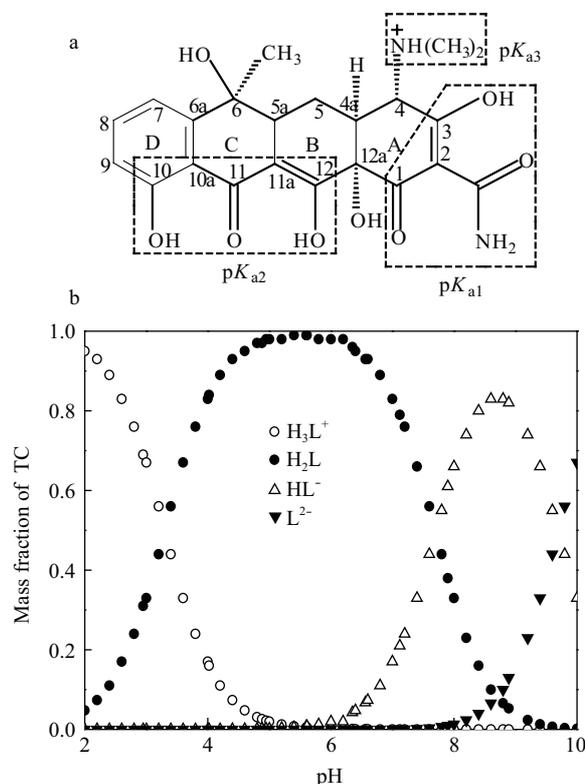

Fig. 1 Molecular structure of tetracycline (TC) (pK_{a1} = 3.3, pK_{a2} = 7.7, pK_{a3} = 9.7) (a), and its speciation as a function of pH (b)

repeatedly with deionized water. The suspension was then filtrated and dried at 105°C for 4 hr. The dry material was crushed and stored in a desiccator for use. The Fe-Mn binary oxide with other Fe:Mn molar ratio was prepared in the similar way. The pure amorphous FeOOH was synthesized by mixing 0.5 mol/L $FeCl_3$ and 1 mol/L NaOH first, and then aging the formed suspension for 4 hr and drying at 105°C for 24 hr. The prepared Fe-Mn binary oxide has been well characterized elsewhere (Zhang et al., 2007).

1.3 Batch experiments

All the experiments were carried out at (20 ± 1)°C. All the reaction vessels were wrapped with aluminum foil to prevent them from light. For the kinetics experiments, 1.5 g of Fe-Mn binary oxides with different Fe:Mn molar ratios were respectively added into 1500 mL of 88.8 mg/L tetracycline solution at pH 7.0 ± 0.1. The suspension was stirred at 150 r/min. The pH was maintained throughout the experiment by addition of 0.1 mol/L HCl and/or 0.1 mol/L NaOH. The samples were taken at different time intervals, filtered through a 0.45 μm membrane filter and analyzed for TOC or TC.

In the pH effect experiments, 40 mL of 88.8 mg/L tetracycline solution at various pH values (3–9) were prepared in vessels. Fe-Mn binary oxides of 0.04 g with Fe:Mn molar ratio of 5:1 was added into the solution. The flasks were shaken at 150 r/min for 24 hr. The solution pH was measured and adjusted accordingly during the experiments by 0.1 mol/L HCl or 0.1 mol/L NaOH. After the reaction, the residual TOC was measureded.

The effect of initial tetracycline concentration on the

removal efficiency were investigated in the similar way as the pH effect experiments. The initial tetracycline concentration was from 44.4 to 222.2 mg/L and the pH was kept at 6.5 ± 0.1.

1.4 Zeta potential analysis

A zeta potential analyzer (Zetasizer 2000, Malvern, UK) was used to analyze the zeta potential of Fe-Mn binary oxide particles. The content of the Fe-Mn binary oxide with Fe:Mn molar ratio of 5:1 in the solution was 1 g/L. NaCl with concentration of 0.5 mol/L was used as background electrolyte to maintain an appropriate constant ionic strength. After mixing for 24 hr, 10 mL of suspension was transferred to a sample tube. Zeta potential of the suspensions was then measured by electrokinetic analysis.

1.5 Fourier transform infrared spectroscopy (FT-IR)

Crystalline tetracycline, virgin Fe-Mn binary oxide, and the binary oxide reacted with 88.8 or 444.4 mg/L tetracycline were analyzed by FT-IR spectroscopy (Nicolet 5700, Thermo, USA). Each sample was mixed with pure potassium bromide which acts as background at an approximate mass ratio of 1:100 (sample:KBr) and then ground in an agate mortar. The resulting mixture was pressed at 10 tons for 5 min to form a pellet which was characterized using FT-IR spectrometer. Thirty-two scans and 2 cm^{-1} resolution were applied in recording the spectra. The background obtained from scan of pure KBr was automatically subtracted from the sample spectra. All the spectra were recorded and plotted in the same scale on the absorbance axis.

1.6 Chemical analysis

The TOC concentration was measured by a TOC analyzer (TOC-V$_{CPH}$, Shimadzu, Japan). The concentration of tetracycline was measured by HPLC (L-2130, Hitachi Co., Japan) using a C-18 (250 mm long, 4.6 mm i.d., 5 μm particle size) column. The detection was performed by UV absorption at a wavelength of 360 nm. The mobile phase used as eluent was 0.01 mol/L oxalic acid:methanol:acetonitrile (67:11:22). The injection volume was 20.0 μL and the flow rate was 1 mL/min.

2 Results and discussion

2.1 Tetracycline removal by Fe-Mn binary oxide with different Fe:Mn molar ratios

Results from control experiments (no sorbents) showed that there were no significant losses of tetracycline because of photodegradation or sorption to glassware. Figure 2 shows the tetracycline removal (on the basis of HPLC and TOC) by Mn oxide, FeOOH and Fe-Mn binary oxides with different Fe:Mn molar ratios. It can be seen that the tetracycline removal efficiency based on HPLC and TOC were different. For the Mn oxide, on the basis of HPLC detection, nearly 99% of tetracycline was removed from the solution after 5 hr of reaction. However, on the basis of TOC, only about 8% of removal was observed after 24 hr. For the FeOOH, the tetracycline and TOC removal efficiency was about 56% and 45%, respectively. The HPLC is compound-specific and only detects the free form of tetracycline, while TOC provides a substitute of the total organic concentration, including the parent compound and its products from other reactions in the solution. Therefore, the difference of the measurements in this study could be caused by oxidation, or by the metal-tetracycline complexes in solution (Gu and Karthikeyan, 2005). For the water treatment, it is better to enhance the TOC removal efficiency, so we used TOC to analyze the removal efficiency.

As shown in Fig. 2, the TOC removal efficiency was elevated when Fe-Mn binary oxides were used to oxidate/sorb tetracycline from water. The Fe-Mn binary oxides with Fe:Mn molar ratio of 7:1 failed to get equilibrium within 24 hr and the tetracycline kept on decreasing slowly. This trend might be due to the low oxidation rate resulting from the less content of Mn. Compared to Mn oxide, the component of FeOOH promoted the absorption of tetracycline to it. However, the long equilibrium time
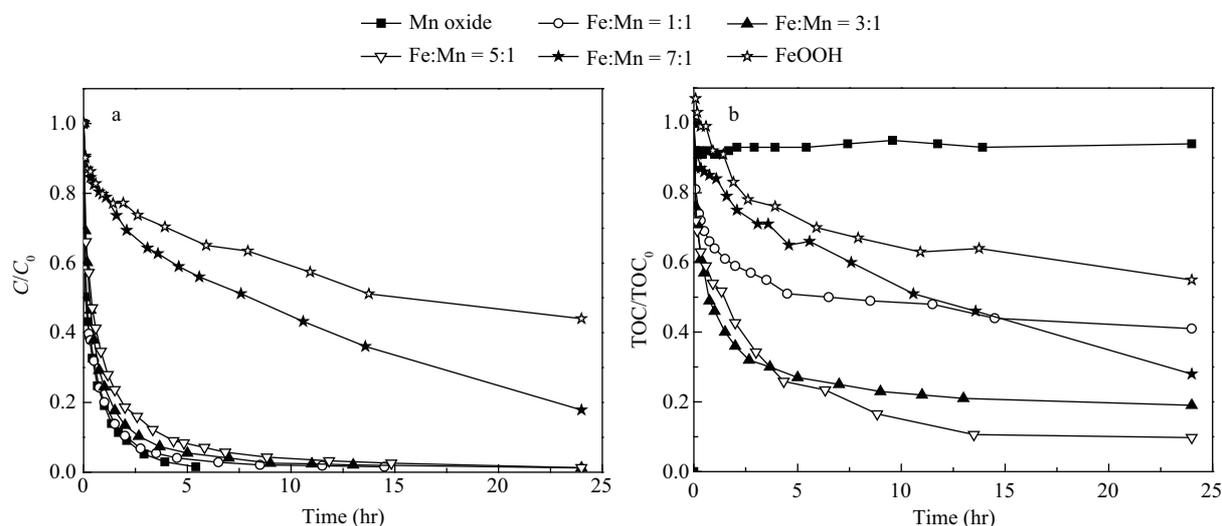

Fig. 2 Tetracycline (TC) (a) and TOC (b) removal efficiency by FeOOH, Mn oxide, and Fe-Mn binary oxide with different Fe:Mn molar ratios. Fe-Mn binary oxide content 1 g/L; initial tetracycline concentration (C_0) 88.8 mg/L; TOC$_0$ 52.8 mg/L.

restrict the use in water treatment. While, the Fe-Mn binary oxides with Fe:Mn molar ratio of 5:1 has high efficiency, and 91% TOC removal efficiency is found after 24 hr of reaction. It is obvious that the removal process could be divided into two steps. In the first step, the removal rate was fast and appropriate 85% of the equilibrium TOC removal capacity is achieved within the initial 6 hr. In the second step, the removal rate slowed down. The maximum removal took place after 14 hr reaction, and over 91% of the total TOC is removed. Fourteen hours was chosen as the reaction time in the subsequent experiments as it was an adequate time for the maximum TOC removal occur.

2.2 Effect of pH

The result in Fig. 3 demonstrates the effect of pH on the removal of tetracycline (on the basis of TOC) by the Fe-Mn binary oxide with a Fe:Mn molar ratio of 5:1. As can be seen, the tetracycline removal is evidently dependent on pH. The TOC removal increases when pH is increased from 3.0 to 5.3. It may reach the maximum removal in the pH range of 5.3–6.2 and decreases greatly as the pH is further increased. The observed sorption behavior can be attributed to the combination of pH-dependent speciation of tetracycline (Fig. 1b) and surface charge characteristics of the Fe-Mn binary oxide.
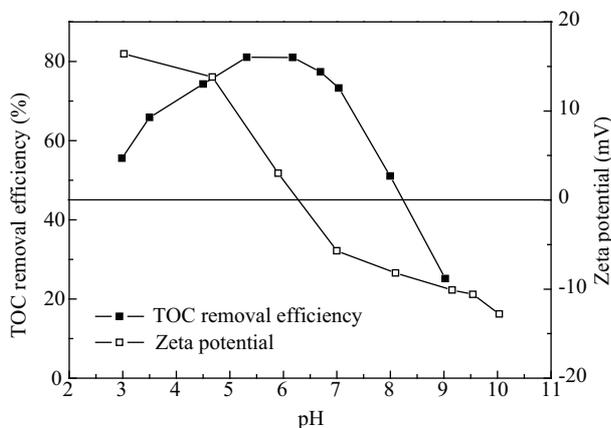
The zeta potential of the Fe-Mn binary oxide suspension (Fe:Mn = 5:1) is also presented in Fig. 3. It decreases with the increasing solution pH. The Fe-Mn binary oxide is found to have an isoelectric point of about 6.3. That is to say, the surface of the binary oxide is positively charged at pH < 6.3 while it is negatively charged at pH > 6.3. Tetracycline (symbolized as H_2L) is an amphoteric molecule with multiple ionizable functional groups and may exist as cation (H_3L^+), zwitterions (H_2L^0), or negatively charged ions (HL^-, L^{2-}) at different pH values. At $3.0 < pH < 5.3$, the predominating tetracycline species are H_3L^+ and H_2L as shown in Fig. 1b. Both the binary oxide surface and tetracycline species carried less positive charge with the increasing pH, thereby decreasing electrostatic repulsion between tetracycline and the oxide surface and causing an increase in the tetracycline removal. At $5.3 < pH < 6.3$, negatively charged tetracycline species appears (Fig. 1b), and tetracycline could be removed by the binary oxide through electrostatic attraction. At pH > 6.3, both tetracycline species and the binary oxide carried more negative charge (Figs. 1b and 3), leading to an enhancement in electrostatic repulsion between tetracycline and the oxide surface. This may account for the decrease of the tetracycline removal.

2.3 Effect of coexisting ions

Coexisting ions such as magnesium, calcium, carbonate, sulfate, silicate, and phosphate are generally present in the wastewater. If electrostatic interaction is the dominating mechanism for tetracycline removal, these ions may interfere in the removal of tetracycline by the Fe-Mn binary oxide through competitive for the charged sites on the oxide surface. The effects of these coexisting ions at two concentration levels (1.0 and 10 mmol/L) on tetracycline removal were assessed and the results are shown in Fig. 4. For magnesium, calcium, carbonate, sulfate, only slight change in TOC removal and tetracycline removal is observed when the concentration of coexisting ions is increased from 1.0 to 10 mmol/L. This leads to a hypothesis that tetracycline may be removed through the interaction with some specific sites in the binary oxide surface. However, TOC removal and tetracycline removal
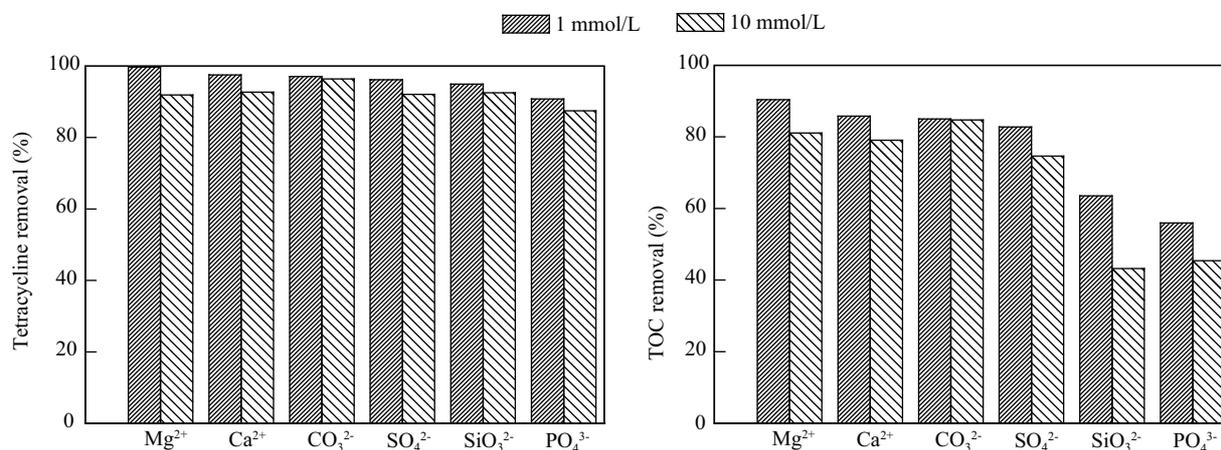

Fig. 3 Removal of tetracycline by Fe-Mn binary oxide at different pH. Initial tetracycline concentration 88.8 mg/L, zeta potential of Fe-Mn binary oxide at different pH. Fe-Mn content 1 g/L, and Fe:Mn 5:1.

Fig. 4 Effect of coexisting ions on tetracycline (a) and TOC (b) removal by Fe-Mn binary oxide. Fe-Mn content 1 g/L; Fe:Mn 5:1; initial tetracycline concentration 88.8 mg/L; pH 6.5 ± 0.1.
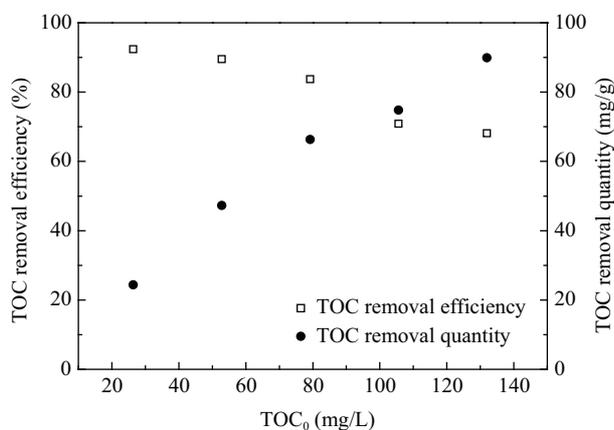
Fig. 5 TOC removal efficiency and capacity by Fe-Mn binary oxide at different initial tetracycline concentrations. Fe-Mn content 1 g/L, Fe:Mn 5:1, pH 6.5 ± 0.1.

Fig. 6 FT-IR spectra. (a) virgin Fe-Mn binary oxide; (b) Fe-Mn binary oxide after the reaction with 88.8 mg/L tetracycline; (c) Fe-Mn binary oxide after the reaction with 444.4 mg/L tetracycline; (d) crystalline tetracycline.

have a distinct decreasing at the present of phosphate and silicate with a concentration range from 1.0 to 10 mmol/L. As silicate (Roberts et al., 2004) and phosphate (Chitrakar et al., 2006; Zhang et al., 2009) can be removed via electrostatic attraction and ligand exchange and form inner-sphere complex, they would occupy the site which contribute to the adsorption on Fe oxide. Then this influence can reduce the removal efficiency of tetracycline to Fe-Mn binary oxide. Therefore, the tetracycline may have some ligand exchange reactions with Fe-Mn binary oxide.

2.4 Effect of initial concentration

The TOC content of the drainage after biochemical treatment remain over 200 mg/L. In order to test the practical application of the material, the tetracycline removal by Fe-Mn binary oxide (Fe:Mn = 5:1) at different initial concentrations were investigated. As shown in Fig. 5, the removal efficiency of tetracycline decreases with the increase in initial concentration, but the absolute removal quantity is more at high concentration. When the initial tetracycline concentration is 222.2 mg/L, the TOC removal efficiency is about 70%, indicating that the Fe-Mn binary oxide is a potential material for tetracycline removal.

2.5 FT-IR analysis

Figure 6 shows the FT-IR spectrums of virgin Fe-Mn binary oxide, the binary oxide reacted with different concentrations of tetracycline and crystalline tetracycline. For the Fe-Mn binary oxide sample, the band at 1626 cm^{-1} can be assigned to the deformation of water molecules and indicates the presence of physisorbed water on the oxides; three peaks at 1115, 1091, and 1045 cm^{-1} could be primarily attributed to the bending vibration of hydroxyl groups of iron hydroxides (Fe-OH) vibration (Zhang et al., 2009).

After the reaction with tetracycline, the Fe-OH bending band at 1045 cm^{-1} becomes less obviously when initial tetracycline concentration increases from 0 to 88.8 mg/L and nearly disappears at high tetracycline concentration (444.4 mg/L). These changes may be attributed to the replacement of the hydroxyl groups on the oxide surface by tetracycline species. It can be observed that some new
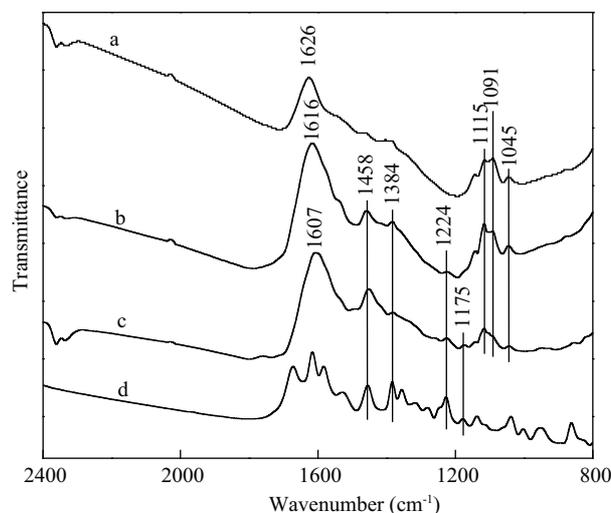
peaks appear at 1460–1170 cm^{-1} (1458, 1384, 1224, 1175 cm^{-1}) in the FT-IR spectra of the Fe-Mn binary oxide after the reaction with tetracycline (curve b, c in Fig. 6). Some characteristic vibration bands of the tetracycline occur in this range as indicated by the FT-IR spectra of crystalline tetracycline (curve d). The appearance of the new peaks at 1458 and 1384 cm^{-1}, which correspond to the groups in the tetracycline molecular, suggests that tetracycline has been transferred from the aqueous to the oxide surface. Therefore, it could be concluded that tetracycline can be removed by the Fe-Mn binary oxide through the replacement of hydroxyl groups in the oxide surface and the formation of surface complexes at the water/oxide interface (Gu and Karthikeyan, 2005).

3 Conclusions

A series of Fe-Mn binary oxide with different Fe:Mn molar ratios were prepared by a simultaneous oxidation and coprecipitation method, and that with molar ratio of 5:1 was found to be effective for the removal of tetracycline from water. The TOC removal efficiency increased as the pH increased and got the maximal value at pH 6–7, and then decreased after that. The TOC removal efficiency for tetracycline could be reached at least 90%. The coexisting ions such as Ca^{2+}, Mg^{2+}, CO_3^{2-} and SO_4^{2-} did not greatly interfere in the removal of tetracycline, while SiO_3^{2-} and PO_4^{3-} had hindered the adsorption of tetracycline in our experimental conditions. The FT-IR data indicated that the tetracycline was removed by the Fe-Mn binary oxide through the replacement of hydroxyl groups and the formation of surface complexes at the oxide surface. This oxide should be a promising material for the removal of tetracycline from water.

of Education.

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