Adsorptive removal of trace oxytetracycline from water by acid-modified zeolite: influencing factors

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ABSTRACT

Because of the wide use of antibiotics in the livestock industry, trace tetracycline antibiotics are frequently detected in swine wastewater and water bodies near pig farms. Based on natural zeolite, modified zeolite was synthesized by treatment with nitric acid. As one kind of typical tetracyclines, oxytetracycline (OTC) was chosen as the target adsorbate. Removal of trace OTC by modified zeolite and the effects of several main matrices on OTC adsorption were studied in detail. OTC removal efficiency by acid-modified zeolite was about 90%, compared to less than 20% by natural zeolite. In general, in acidic conditions the removal efficiency of OTC by modified zeolite was about 90%, which was much higher than 20–35% in alkaline conditions. An increase in ionic strength from 0.01 to 1.0 M led to a decrease in adsorption efficiency from 90 to 27%. The presence of 10.0 mg L\(^{-1}\) dissolved humic acid accelerated sorption of OTC on modified zeolite, while 100.0 mg L\(^{-1}\) humic acid resulted in the opposite effect. An increase in temperature contributed to enhancing the adsorption efficiency.

Key words | adsorption, modified zeolite, oxytetracycline, water matrices

INTRODUCTION

As the most widely used antibiotics in the world, tetracyclines (TCs) are often used in the livestock industry. Most of the TCs used enter the aquatic environment via the urine and feces from livestock. Recently the occurrence of antibiotics in water bodies has been recognized as an emerging issue (Halling-Sorensen et al. 1998; Jiang et al. 2013). There is more and more evidence that TCs at trace levels, from ng L\(^{-1}\) to \(\mu\)g L\(^{-1}\), are frequently detected in surface water, groundwater sampled near wastewater lagoons and hog lagoons. For example, TCs were detected in the effluent from a wastewater treatment plant located in Seoul for livestock wastewater (Kim et al. 2013), and the maximum concentration of TCs was 4.0 \(\mu\)g L\(^{-1}\). A high frequency of detection with a concentration range of 25–1,000 \(\mu\)g L\(^{-1}\) for TCs was reported from swine-waste storage lagoon samples in the USA, and TCs in the range of 1.0–2.0 \(\mu\)g L\(^{-1}\) were also detected in surface and groundwater samples collected close to the swine and poultry farms (Campagnolo et al. 2002). Multiple classes of antimicrobial compounds were detected in the swine wastewater collected from three concentrated swine feeding plants located in Beijing (China) area, and the TCs which were detected in each water sample showed a largest concentration range of 1.14–32.67 \(\mu\)g L\(^{-1}\) (Ben et al. 2008).

Hence there is an increasing interest in the study of the removal of tetracycline antibiotics from aquatic environment. In recent years, more and more researchers have focused on the sorption of TCs and the removal of TCs from water by adsorption. For the adsorption of antibiotics a variety of materials have been used as adsorbents, including natural clay minerals (Aristilde et al. 2013), synthetic metal oxides (Zhao et al. 2011), activated carbon (Huang et al. 2011), soils (Carraquillo et al. 2008; Zhang et al. 2011). Adsorption of TCs on aluminum oxide and montmorillonite has also been investigated (Pils & Laird 2007; Gu & Karthikeyan 2008; Chen & Huang 2010; Aristilde et al. 2013). These studies demonstrated that clay minerals have strong adsorption ability for TCs, but the results showed that dissolved humic acids in water significantly reduced adsorption efficiency of TCs. In these studies antibiotics of relatively high concentration (10–1,000 mg L\(^{-1}\) were

doi: 10.2166/wst.2013.505
selected as the target adsorbate, but there were rarely further studies on the adsorption of trace antibiotics (10–1,000 μg L⁻¹). Generally, the composition of swine wastewater is very complex, and it contains a large amount of dissolved organic matter (DOM). Even the chemical oxygen demand (COD) value of the effluent after biological pretreatment is as high as 100–1,000 mg L⁻¹. However, the concentration of antibiotics in swine wastewater is mainly low (mostly in the ng L⁻¹–μg L⁻¹ range), and so the DOM could significantly inhibit adsorption removal of trace antibiotics. Therefore the problem of the removal of trace antibiotics in swine wastewater has not been well resolved up to now.

In order to successfully adsorb trace antibiotics in complex wastewater, the most important aspect is the selection or preparation of a highly selective absorbent. Zeolite, with its abundantly porous structure, has a huge surface area, and it has a strong cation-exchange ability. Zeolite may show a strong adsorption of low concentration polar organics. A zeolite (Zadaka et al. 2007) yielded 99.9% removal for the antibiotic trimethoprim from its dispersion, and a zeolite/sand filter gave 91% removal.

H-type zeolite is prepared by acid-modification of natural zeolite. It was anticipated that H-type zeolite would be a better sorbent for TC removal, although no studies were available on the adsorption of TCs onto this sorbent. In this study, H-type zeolite was used as a sorbent for the removal of aqueous oxytetracycline (OTC). A series of batch adsorption experiments were conducted to investigate the adsorption of OTC onto the H-type zeolite. The aim of the research was to evaluate the effects of pH, DOM, ionic strength and temperature on OTC adsorption.

**MATERIALS AND METHODS**

**Sorbents**

Acid-modified zeolite was synthesized based on natural zeolite treated with nitric acid. Natural zeolite was added into a solution of 50% nitric acid and the solid : liquid ratio was 1.0 g : 20 ml. The mixture was continuously stirred on a magnetic stirrer at 200 rpm at 303 K for 12 hours. Then the supernatant solutions were discarded, the solid precipitate was filtered and rinsed five times with deionized water to remove dissolved impurities. Finally the solid obtained was dried in a forced air oven at 393 K overnight until it reached a constant weight.

**Chemicals**

Hydrochloride salt of OTC (98.5% purity) and acetonitrile (HPLC grade) were purchased from Augsburg Co. and Merck Co. (Germany) respectively. The structural formula of OTC and its pKa values are in Table 1. Humic acid (HA, Fluka No. 53680) was purchased from Sigma-Aldrich and used without further purification. Natural zeolite was obtained from Zhejiang Magical Stone Mineral Co. (China). All other chemicals, including nitric acid, hydrochloric acid, oxalic acid, sodium hydroxide, and other salts were A.R. grade from Sinopharm Chemical Reagent Co. (Shanghai, China).

**Methods of analyses**

OTC was quantified by high-performance liquid chromatography (HPLC) using a Dionex P680 pump and 170U UV detector at 270 nm, while an Agilent TC-C18 column (4.6 × 250 mm, 5 μm) was used for species separation. The mobile phase consisted of 0.01 M oxalic acid/acetonitrile (80:20) with a final pH of 2.5. At a flow rate of 1.0 mL min⁻¹ and injecting 80 μL, the retention time of OTC was 5.4 min. The standards were adjusted to the same pH as the samples in the experiments. Calibration was made with six standards between 0.05 and 2.00 mg L⁻¹ with an r² of no less than 0.99, and the detection limit was 0.03 mg L⁻¹.

**EXPERIMENTS**

For all batch experiments, the amount of sorbent used was 0.1 g, the volume of solution added was 100 mL and the initial OTC concentration was 0.002 mM (1.0 mg L⁻¹). They were combined in 150 mL glass vials and mixed on
a reciprocal shaker at 200 rpm. The vials were wrapped with aluminum foil to prevent light-induced decomposition. The samples were collected at different time intervals. After being collected, samples were centrifuged at 5,000 rpm for 10 min and the equilibrium OTC concentration in the supernatant was measured by HPLC. For the ionic strength experiment, the solution was adjusted with 0.01, 0.1, and 1.0 M of NaCl. The influence of HA on OTC sorption was investigated at three HA levels (0, 10, and 100 mg L$^{-1}$). The pH effect was studied at five different values (4.06, 5.10, 6.54, 7.38 and 9.94), from acidic to alkaline, adjusted with 0.1 M NaOH and 0.1 M HCl. For the temperature experiment, the temperature was maintained at 286, 293, and 303 K. All adsorption experiments were performed in duplicate.

**RESULTS AND DISCUSSION**

**OTC adsorption on natural and modified zeolite**

The experimental results of OTC adsorption on natural and modified zeolite are shown in Figure 1. It was found that 70% of the uptake of OTC by the modified zeolite quickly occurred in 1 hour, followed by a relatively slow process, and OTC adsorptive removal efficiency was nearly 90% when the adsorption reached equilibrium. Based on this observation, 8 hours was chosen as the equilibration time to ensure adequate time was given to reach adsorption equilibrium. However, only 15% of OTC adsorption by the natural zeolite was observed in 8 hours. Therefore, adsorption capacity of zeolite after modification with regard to OTC was greatly improved compared with that of natural zeolite.

**Effect of pH**

The pH is one of the most important factors influencing adsorption of TCs in aqueous solution, as it changes the speciation of TCs and the surface charge characteristics of adsorbent material (Wang et al. 2010). The adsorption of OTC on modified zeolite at different pH values is shown in Figure 2.

The adsorption efficiency increased a little when the pH was increased from 4.06 to 5.10, and then clearly decreased as the pH was further increased to 9.94. The adsorption behavior may be associated with the pH-dependent speciation of OTC and the surface charge characteristics of modified zeolite. OTC (symbol H$_2$L) is an amphoteric molecule with multiple ionizable functional groups, and may exist as cation (H$_3$L$^+$), zwitterions (H$_2$L$^0$), or anions (HL$^-$ and L$^2$) at different pH values (Sarmah et al. 2006). The species distribution of OTC at different pH values demonstrates that the predominant species is H$_3$L$^+$ at pH < 3.6, H$_2$L$^0$ at 3.6 < pH < 7.5, HL$^-$ at 7.5 < pH < 9.9, and L$_2^-$ at pH > 9.9, respectively. At a lower pH, OTC mainly exists as positively charged species. Increasing the solution pH increased the negative charge density of the zeolite, thus enhancing the electrostatic attraction between H$_3$L$^+$ or H$_2$L$^0$ and the positive or weakly negative zeolite surface, which would increase the adsorption of OTC onto the zeolite. As the pH is further increased, the hydrogen ion concentration decreases noticeably; while both the OTC species and the sorbents (the modified zeolite) become progressively more negatively charged, which enhances the electrostatic repulsion between the OTC species and the zeolite surface. As a result, less adsorption occurs. These findings indicated that OTC cation and zwitterion species exhibited a stronger interaction with the zeolite than OTC anionic species.
Effect of ionic strength

Ionic strength effects were investigated by conducting sorption experiments at different salt concentrations. It should be pointed out that data at 0 M NaCl was nearly the same as data at 0.01 M NaCl, so conditions at 0 M NaCl are not shown in Figure 3. As shown in Figure 3, increasing of monovalent cation concentrations (from 0.01 to 1.0 M of NaCl) caused a great decrease of OTC amounts sorbed on to modified zeolite. At an ionic strength of 0.01 M NaCl, 88% of the initial OTC was removed from the water, and at an ionic strength of 0.1 M NaCl, 78% of the initial OTC was adsorbed. Only 30% was sorbed on to modified zeolite at an ionic strength of 1.0 M NaCl. These results indicate a competition for attractive surface sites between OTC species and Na\(^+\) cations. At higher electrolyte concentrations, the Na\(^+\) cation is highly charged enough to compete with OTC species and occupy surface sites, which decreases the amount of OTC adsorbed. By contrast, when NaCl concentration decreases, Na\(^+\) cations are no longer important competitors, hence the relatively higher adsorption of OTC. The observed low sorption of OTC at high ionic strength may result from a competition between the cationic/zwitterionic tetracycline species and deprotonated functional groups in HA. Similarly, in the zeolite–HA–OTC ternary system, OTC could either complex with the surface sites of zeolite or interact with dissolved HA in solution or HA sorbed onto zeolite surfaces. Under such conditions, it is reasonable to speculate that HA might act as a bridge to complex with both zeolite surfaces and OTC molecules. Hence the sorption of OTC was enhanced at a relatively low concentration of HA. But at the higher concentration of HA, almost no sorption was observed. This phenomenon may be explained by hydrophobic partitioning of OTC between zeolite-associated HA and ‘free’ HA in the solution phase. The sorption capacity of zeolite for HA may be exceeded, resulting in ‘free’ HA at high DOM content. As the ‘free’ HA increased in solution, more OTC was desorbed from the zeolite-associated HA; therefore a decrease of sorption on zeolite was observed.

Effect of humic acid

The adsorption of TCs may be decreased by the presence of DOM as has been demonstrated in many previous studies (Kulshrestha et al. 2004; Pils & Laird 2007; Gu & Karthikeyan 2008). The effect of DOM on the adsorption of OTC was investigated with the addition of HA. As shown in Figure 4, adsorption of OTC was accelerated to 30 min in the presence of 10 mg L\(^{-1}\) HA but the adsorption was entirely inhibited in the presence of 100 mg L\(^{-1}\) HA.

It has been reported that there is strong surface interaction between HA and oxide minerals through ligand-exchange mechanism (Yoon et al. 2004, 2005; Gu & Karthikeyan 2008). On the other hand, tetracycline was sorbed by HA and the sorption was strongly pH-dependent, with a maximum around pH 4.5 (Gu et al. 2007), which was consistent with complexation between the cationic/zwitterionic tetracycline species and deprotonated functional groups in HA. Similarly, in the zeolite–HA–OTC ternary system, OTC could either complex with the surface sites of zeolite or interact with dissolved HA in solution or HA sorbed onto zeolite surfaces. Under such conditions, it is reasonable to speculate that HA might act as a bridge to complex with both zeolite surfaces and OTC molecules. Hence the sorption of OTC was enhanced at a relatively low concentration of HA. But at the higher concentration of HA, almost no sorption was observed. This phenomenon may be explained by hydrophobic partitioning of OTC between zeolite-associated HA and ‘free’ HA in the solution phase. The sorption capacity of zeolite for HA may be exceeded, resulting in ‘free’ HA at high DOM content. As the ‘free’ HA increased in solution, more OTC was desorbed from the zeolite-associated HA; therefore a decrease of sorption on zeolite was observed.

Effect of temperature

Adsorption processes are often endothermic or exothermic (Li et al. 2010), so the reaction temperature must be
a factor with an effect on OTC adsorption. From Figure 5 it can clearly be observed that OTC removal efficiency in 2 hours at 286, 293 and 303 K was 70, 80 and 90% respectively, that is to say, the increase of temperature from 286 to 303 K resulted in the increase of OTC adsorption on modified zeolite. Since chemical binding or electrostatic attraction may be promoted by rising temperatures, sorption of OTC increased with increasing temperature.

**CONCLUSIONS**

To summarize, OTC adsorptive removal efficiency by modified zeolite was about six times that of natural zeolite. OTC uptake was found to be significantly influenced by the pH of the solutions, the maximum adsorption efficiency in acid environment being 95%, and the minimum efficiency in alkaline environment being 18%. Ionic strength was also found to affect the adsorption, and a higher adsorption capacity was observed in a lower ionic strength solution. The effect of DOM on adsorption of OTC depended on the concentration of DOM, and the presence of DOM (10 mg L⁻¹) had a little positive influence on adsorption of OTC, which was entirely inhibited in the presence of 100 mg L⁻¹ HA. Sorption of OTC is an endothermic reaction, and thus increasing the temperature from 286 to 303 K enhanced the uptake of OTC from 70 to 90%. Based on our experimental results, we propose that H-type zeolite could be used to selectively adsorb trace TCs in swine wastewater. The mechanism for OTC sorption on modified zeolite may involve electrostatic attraction and cation exchange.

**ACKNOWLEDGEMENTS**

This work was supported by the National Natural Science Foundation of China (Grant No. 20907045), by the Zhejiang Provincial Applied Research Project of Public Technology (Grant No. 2011C23053), and by the Zhejiang Provincial Natural Science Foundation of China (Grant No. Y5110338).

**REFERENCES**


First received 20 March 2013; accepted in revised form 12 August 2013. Available online 22 October 2013.