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Short Communication

Adsorption mechanisms and the effect of oxytetracycline on activated sludge

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HIGHLIGHTS

- The adsorption process was highly pH-dependant.
- Zwitterions are the most sorbed oxytetracycline species on activated sludge.
- Different metal ions have different effects on the adsorption process.
- Surface complexation are the main adsorption mechanism of OTC to activated sludge.

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ABSTRACT

The adsorption mechanisms and the effect of Oxytetracycline (OTC) onto activated sludge were studied. The results show that the adsorption of Oxytetracycline (OTC) onto activated sludge was coincident with the Langmuir, Freundlich and Temkin isotherm models. The Freundlich model had the best fit which suggested that chemical adsorption mechanism was dominant. The influences including pH and metal ions on the OTC were examined. It was demonstrated that the adsorption process was highly pH-dependant, which indicate that cationic exchange mechanisms may play an important role in the adsorption process. Na^{+}, K^{+}, Ca^{2+}, Mg^{2+} and Cd^{2+} ions more or less inhibited the adsorption of OTC on activated sludge while Cu^{2+} enhanced the adsorption ability. The phenomenon may reflect the result that a surface complexation mechanism could involved in the adsorption.

1. Introduction

Tetracycline (TC), has been widely used as a feed additive to inactivate diseases and then improve the growth rate of livestock. However, TC is poorly adsorbed in the digestive tract. As a result, 50–80% of the initial TCs dose was discharged in livestock waste (Sarmah et al., 2006). TCs residues have been found everywhere in the environment, including soils, sediments (Xu and Li, 2010), surface water (Lindsey et al., 2001), and wastewater (Miao et al., 2004). Although the concentrations of TC and their byproducts were very low in the environment, it may cause public health issues and other problems (Boxall et al., 2003).

The activated sludge process is one of the most important secondary treatment processes which commonly used in China. TC from livestock is discharged into the sewer (with or without pretreatment) and then flow into the wastewater treatment plants. Previous studies show that the adsorption effect was the principal removal mechanism of TC on activated sludge (Li and Zhang, 2010). However, knowledge gaps still exist on the interaction between TCs and activated sludge. Some previous studies on pure clays, soils, and sediments had proven that the adsorption capacity of sorbent to TCs was influenced by pH due to different mechanisms (Figueroa et al., 2004; Zhang et al., 2011). In addition, some previous studies have pointed out that metal ions influence the adsorption of Oxytetracline (OTC) on soil, organic matter (Pils and Laird, 2007) and chitosan (Kang et al., 2010), but little research has been focused on the effect of the adsorption of OTC on activated sludge.

In this study, in order to assess the adsorption behavior and mechanisms better, comprehensive researches were performed on the influence of pH and metal ions. Furthermore, the activated sludge, before and after adsorption of OTC, was compared with both FTIR and XPS to elucidate the corresponding sorption mechanisms.

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2. Methods

2.1. Sorbents

The activated sludge used in this study was obtained from the wastewater treatment plant for the Technical and Economic Development Area, Tianjin, China. In biosorption tests, mature activated sludge was used. The sludge was washed three times with deionized water to remove the surface soluble ions. The treated sludge was diluted to the required experimental concentrations in subsequent adsorption experiments (Liu et al., 2012) (Appendices).

2.2. Chemicals

Hydrochloride salt of OTC (98% purity), acetonitrile (HPLC grade), and oxalic acid (99% purity) were purchased from sangon biotech (Shanghai, China). All other chemicals, including Cadmium, Sodium, Potassium, Copper, Calcium, and Magnesium salts, were A.R. grade which were bought from Sinopharm Chemical Reagent Co. (Shanghai, China). The analysis methods of OTC were consisted in Appendices.

2.3. Batch adsorption

The batch experiments were carried out in conical flask with stopper. The solution flasks (250 ml) were agitated at a speed of 150 rpm on a temperature-controlled (20 ± 0.5 °C) shaking table in the dark. 120 mg of activated sludge was weighed and put into conical flasks, and MLSS was 800 mg L^{-1}. An aliquot of freshly prepared OTC stock solution was spiked to each conical flask to set the initial TC concentration at 20 mg L^{-1}. The pH in the solutions was adjusted to 2.0, 3.5, 5.5, 8.0 and 10, respectively. The entire amount of OTC adsorbed was calculated as the difference between the initial concentration and the amount still in solution at the various sample times. 5 ml samples were taken and measured after 48 h.

The effect of metal ions on OTC adsorbed on activated sludge were examined in the pH range commonly found in the environment (pH 3.5, 5.5 and 8.0) by a batch experiment in 0.01 M NaCl, KCl, $CaCl_2$, $Cd(NO_3)_2$, $MgCl_2$ and1.0 mM $CuSO_4$ solution. Activated sludge and OTC solution were prepared as described before.

2.4. Quality control and data analysis

To estimate the recovery of OTC in the experiments, blank samples without activated sludge were prepared and analyzed with the same procedure presented in Section 2.3. The average recovery of OTC in blank samples was 97.1 ± 2.1%.

Langmuir, Freundlich, and Temkin models were used to describe the adsorption equilibrium. Mathematical equations of the Langmuir, Freundlich, and Temkin models are represented as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \qquad \text{Langmuir}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \text{Freundlich}$$

$$q_e = K_T \ln C_e + K_T \ln f \qquad \text{Temkin}$$

where q_e (mg kg^{-1}) is the sorption amount of OTC to activated sluge, C (mg L^{-1}) is the equilibrium concentration of the solution phase, K and n are model constants that are related to the sorption capacity and intensity, respectively.

FTIR spectrum of the activated sludge was recorded with a NEXUS 870 spectrophotometer (Thermo Nicolet, USA), scanning from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1}. XPS measurements were undertaken with a KRATOS XSAM 800 equipped with an energy analyser. All the data including the spectra of C1s, N1s and O1s were managed by casaxps software (Appendices).

3. Results and discussion

3.1. Adsorption isotherms of OTC on activated sludge and the effect of pH on OTC adsorption

As seen in Table 1, within a certain pH range, the Langmuir, Freundlich and Temkin models all fit the data well. As Langmuir model, the q_m ranged from 46.7 to 90.9 mg g^{-1} in the range of pH values is tested. The results were consistent with the results from previous work (72 mg g^{-1}) (Prado et al., 2009). When the pH was 5.5, the predominant form of the OTC molecule should be the zwitterion species which could combine with activated sludge through cationic exchange and electrostatic attraction mechanisms. Therefore, activated sludge should be able to provide more adsorption sites for zwitterion species (Xu and Li, 2010). The theoretical adsorption capacity of OTC can reach a maximum of 90.9 mg g^{-1}.

The Temkin model fitted the results very well at all tested pH levels, which indicate that there was electrostatic interaction during the adsorption processes. OTC adsorption onto activated sludge was also well described by the Freundlich model with high regression coefficients (Table 1). The Freundlich K_f values varied from 1.32 to 4.09 under different pH conditions which indicates that the adsorption capacity was highly pH-dependant. The values of n at all pH values were less than unity, indicating L-shape isotherms. This suggests that the higher OTC concentration has disadvantage for adsorption of additional molecules on the activated sludge.

3.2. The effect of metal ions on adsorption of OTC on activated sludge

In Fig. 1, for all five cation electrolytes, adsorption processes of OTC on activated sludge were similar. More than 70% of the OTC was adsorbed on the activated sludge in the first 10 min. All adsorption process reached adsorption equilibrium at 48 h. Compared to the control group; it was observed that the presence of Na^+ and K^+ slightly inhibited adsorption of OTC on the activated sludge. However, Ca^{2+}, Mg^{2+} and Cd^{2+} had a much greater inhibiting effect on adsorption rate which was different from the phenomenon found for goethite (Zhao et al., 2011). This might be due to the different interaction mechanisms between cations and sorbent. Cations inhibit the adsorption of OTC by competing for surface sites. Generally, the replacing power of a cation increases with its charge (Figueroa et al., 2004), which may explain why Ca^{2+}, Mg^{2+} and Cd^{2+} inhibited adsorption more than Na^+ and K^+. As shown in Fig. 2, the maximum sorption of OTC in the presence of metal ions also occurred at pH 5.5, which is consistent with the results from the sorption isotherms. Compared to the control group, Cu^{2+} enhanced the adsorption of OTC to activated sludge at all pH values. Previous studies showed that Cu^{2+} could form strong inner-sphere complexes (binding with amide I group) with

Table 1
Parameters from the fitting of three classic adsorption models for OTC sorption on activated sludge.

pH	Freundlich			Langmuir			Temkin	
	K_F	n	R^2	K_L/L mg^{-1}	q_m/mg g^{-1}	R^2	K_T	R^2
3.5	1.32	0.85	0.966	1.68	82.3	0.937	2.12	0.953
5.5	4.09	0.57	0.998	1.79	90.9	0.927	2.39	0.967
7.0	3.14	0.32	0.931	1.34	80.7	0.913	2.45	0.987
8.0	2.07	0.49	0.990	0.78	60.6	0.884	3.05	0.927
10.0	1.86	0.33	0.943	0.69	46.7	0.850	4.13	0.916