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Adsorption Isotherm Performance of Zr-Mn Binary Oxide for Efficient Removal of Antibiotics Tetracycline

Gangfu Song, Wei Li, Jingrong Zhai, Shulei Sun, Yalin Li and Guoting Li†

Department of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450011, China

†Corresponding author: Guoting Li

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ABSTRACT

Zr-Mn binary oxide was prepared by a simple co-precipitation method, in which Mn(II) was tentatively used to prepare a precursor solution. Then the prepared Zr-Mn binary oxide was used for the adsorptive removal of tetracycline (TC). Effect of molar ratio of Zr/Mn, adsorbent dose and solution pH was investigated. The Zr-Mn binary oxide with a presumed molar ratio of Zr/Mn at 2:1 had a better adsorption performance. The removal efficiency of TC (15 mg/L) at a dose of 10 mg achieved as much as 97.4%, which demonstrated an excellent adsorption capability of Zr-Mn binary oxide. Acidic and near-neutral solution pH conditions were favourable for the uptake of TC. Freundlich model described the adsorption isotherm better than Langmuir model, indicating a heterogeneous surface of the prepared adsorbent. Using Langmuir model, the calculated maximal adsorption capacities for TC achieved 129.5 mg/g at 298 K. Thermodynamic analysis indicated that the changes of enthalpy and entropy of the adsorption processes were 206.32 KJ mol^{-1} and 752.0 J mol^{-1} k^{-1}, respectively. The negative value of Gibbs free energy change and the positive value of enthalpy also indicated that the adsorption process is spontaneous and endothermic.

INTRODUCTION

Various technologies have been studied and applied for removal of pollutants from water and wastewater so far. Among these technologies, including conventional biotreatment and physico-chemical treatment, adsorption process is regarded as one of the most powerful, efficient and cost-effective water treatment technologies due to ease of operation and high efficiency. Adsorption process can transfer the pollutants from one phase to another efficiently, and no toxic intermediates are generated. A number of adsorbents could be selected for different pollutants such as organic pollutants and heavy metals. At the same time, various studies demonstrated that composite adsorbents exhibited excellent performance as they could combine the properties and advantages of each of their components (Qu 2008, Zhu et al. 2016). Composite adsorbents, especially for the metal oxides, are gaining considerable attention as they inherit the advantages of parent oxides and sometimes show a synergetic effect (Zhang et al. 2007, Dou et al. 2012, Zhang et al. 2014).

Considering widespread occurrence of emerging pollutants in water environment at high levels, treatment of these emerging pollutants, including pharmaceutical and personal care products (PPCPs) seems to be particularly significant. As one of the typical PPCPs, antibiotics such as tetracycline are widely applied over the past decades. Accordingly, antibiotics have been detected in potable water in many countries (Yang et al. 2011). Tetracycline is the second most widely used antimicrobial chemicals in the world, which are widely applied in human therapy and livestock industry (Martinez 2009). Conventional water treatment techniques such as sand filtration and coagulation are not efficient for tetracycline removal as expected because tetracycline molecules are usually neutral or negatively charged in environmental water (Kim et al. 2005).

Differently, adsorption technique has been proved effective for the removal of tetracycline (Liu et al. 2012, Li et al. 2016). In this research, Zr-Mn binary oxide was prepared by a simple co-precipitation method. Zirconium and Mn(II) salt was innovatively used to prepare the precursor solution. Then the prepared Zr-Mn binary oxide was used for the adsorptive removal of tetracycline. Effect of the molar ratio of Zr/Mn, adsorbent dose and solution pH was investigated. The adsorption isotherm was emphatically investigated and thermodynamic parameters were calculated to better understand the adsorption mechanism.

MATERIALS AND METHODS

Chemicals: Tetracycline (TC) was purchased from Hefei Biological Science and Technology Co., Ltd. (Anhui Prov-

ince, China) and used without further purification. The other chemicals used were of analytical grade. Deionized (DI) water was used throughout the study.

Preparation of the Zr-Mn binary hydrous oxide: The Zr-Mn binary oxide with the presumed molar ratios of 2:1, 1:1 and 1:1 were prepared by a simple co-precipitation method. Zirconium and Mn(II) salt with different molar ratios were first dissolved in DI water. Under vigorous magnetic-stirring, 2M NaOH solution was slowly added into the salt solution dropwise till the solution pH at 10, leading to the formation of co-precipitation particles. Then the suspension was continuously stirred for 30 min, aged at room temperature for several hours, and then washed repeatedly with DI water to neutral solution pH. The suspension was filtrated and dried at 80°C for 24 h. The dry adsorbent was crushed and stored in a desiccator for use.

Batch adsorption studies: Stock solutions of TC (500 mg/L) were prepared in DI water. All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. Adsorption of TC onto the Zr-Mn binary hydrous oxide was conducted in a series of conical flasks. A desired amount of adsorbent (20 mg) was added to a conical flask containing 50 mL of TC solution unless otherwise stated. These mixtures were shaken at 120 rpm for 24 h to achieve adsorption equilibrium based on predetermined adsorption kinetics. For kinetic experiments, the adsorbent dosage was 200 mg in 500 mL TC solution with initial TC concentration of 25 mg/L. Constant stirring was maintained by mechanical agitation for 24 h. Finally, samples were collected at desired time intervals and filtered through a 0.45 μm pore-size membrane before measurement. The reaction temperature was controlled at a constant of 298 K unless otherwise stated. All the solution pH were maintained at neutral pH except for the pH effect study. The solution pH adjustment was conducted by addition of diluted HCl or NaOH solution.

Analysis of TC: The concentration of TC was analysed using an UV mini-1240 spectrophotometer (Shimadzu) by monitoring at the wavelength of maximum absorption (360 nm) (Figueroa et al. 2004). The adsorption capacity (q_e) was calculated by the following equation:

$$q_e = \frac{V \times (C_0 - C_t)}{m} \quad ...(1)$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium and t min, respectively; C_0 is the initial concentration of TC in solution, while C_e and C_t (mg/L) are the concentrations of TC at equilibrium and t min, respectively; V (L) is the volume of solution, and W (g) is the mass of the Zr-Mn binary oxide.

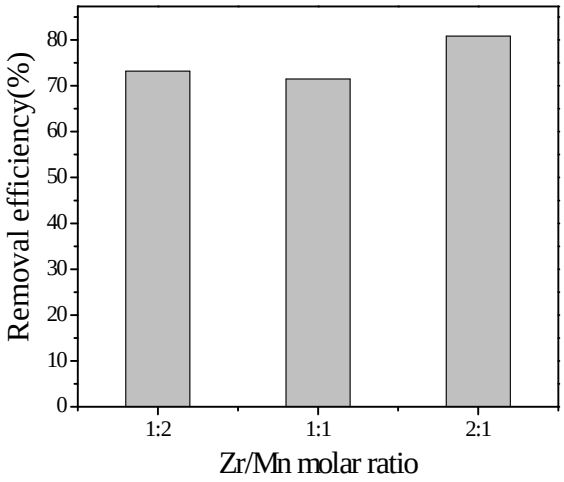

Fig. 1: Effect of the molar ratio of Zr/Mn on TC uptake. TC concentration 25 mg/L, neutral solution pH.

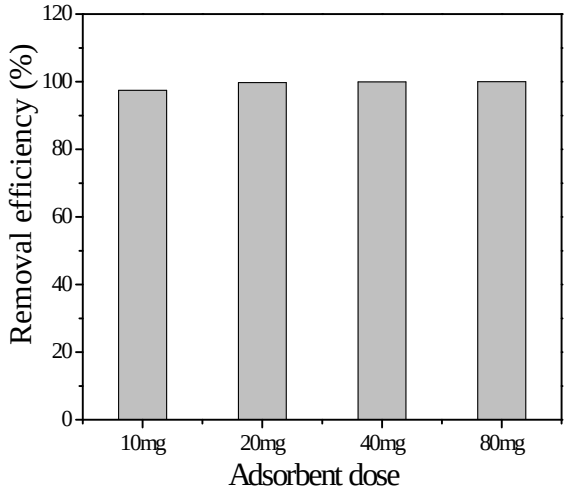

Fig. 2: Effect of the dose Zr-Mn binary oxide on TC uptake. TC concentration 15 mg/L, neutral solution pH.

RESULTS AND DISCUSSION

Effect of the molar ratio of Zr and Mn on TC uptake: Effect of the molar ratio of Zr/Mn on TC (25 mg/L) uptake was initially investigated to optimize the adsorbent composition, as illustrated in Fig. 1. The molar ratios of Zr/Mn at 1:2, 1:1 and 2:1 were involved. The removal efficiency of TC using the adsorbent with the molar ratios of Zr/Mn at 1:2, 1:1 and 2:1 reached 73.2%, 71.4% and 80.8%, respectively. Apparently, the Zr-Mn binary oxide with a molar ratio of Zr/Mn at 2:1 had a better adsorption performance than other two adsorbents. Accordingly, the Zr-Mn binary oxide with a molar ratio of Zr/Mn at 2:1 was selected in the further experiments.

Effect of dose of Zr-Mn binary oxide: Effect of adsorbent

Table 1: Langmuir and Freundlich isotherm parameters for TC adsorption onto Zr-Mn binary oxide.

	Temperature		
	288 K	298 K	308 K
Langmuir model			
q_{max} *(mg/g)*	110.8	129.5	133.5
k_L *(L/mg)*	0.22	0.81	8.26
R^2	0.897	0.801	0.730
Freundlich model			
k_F *(mg/g)*	36.91	62.08	81.08
n	4.16	5.56	7.69
R^2	0.987	0.964	0.975

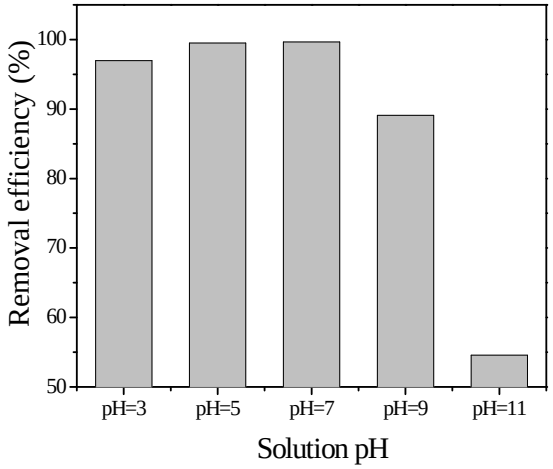

Fig. 3: Effect of solution pH on TC uptake. Adsorbent dose 20 mg, TC concentration 15 mg/L.

dose on TC (15 mg/L) uptake was investigated as well. The dose of Zr-Mn binary oxide with a molar ratio of Zr/Mn at 2:1 was 10, 20, 40 and 80 mg. As presented in Fig. 2, the removal efficiency at the dose of 10 and 20 mg achieved 97.4% and 99.7%, respectively, while TC was removed completely (100%) with increasing adsorbent dose. Obviously, a very limited amount of adsorbent could significantly remove this kind of PPCPs. From this point of view, although Zr-Mn binary oxide is not a carbonaceous adsorbent, it is still capable of removing TC efficiently and effectively.

Effect of solution pH: Solution pH influences both the binding sites on the adsorbent surface and species distribution of TC. It is deduced that solution pH could influence TC adsorption overwhelmingly. The effect of solution pH on TC adsorption was investigated at pH 3.0, 5.0, 7.0, 9.0 and 11.0, as presented in Fig. 3. At an adsorbent dose of 20 mg, the removal efficiency at pH 3.0, 5.0, 7.0, 9.0 and 11.0 reached 97.0%, 99.5%, 99.7%, 89.1% and 54.6%, respectively. Apparently, TC adsorption is highly dependent on solution pH. Acidic and near-neutral solution pH conditions were favourable for the uptake of TC. TC (H_2L) is an amphoteric compound with pK_a values at 3.3, 7.7 and 9.7 (Liu et al. 2012). Its predominant species are deduced to be cation (H_2L^+) at pH<3.3, zwitterions (H_2L^0) at 3.3<pH<7.7, and negatively charged anions (HL^-, L^{2-}) at pH>7.7. As for the Zr-Mn binary oxide, positively charged surface sites will increase with decreasing solution pH, while negatively charged surface sites will increase with increasing solution pH. It can be deduced that both TC and the Zr-Mn binary oxide, are highly positively or negatively charged under highly acidic and basic conditions, respectively. As a result, the repulsion force between TC molecules and the Zr-Mn binary oxide is increased with increasing solution acidity and alkalinity, which could inhibit TC uptake to a large extent. Differently, at weakly acidic and near neutral pH conditions of 3.3<pH<7.7, TC molecules are zwitterions. As such, it is speculated that the attraction force between TC and the Zr-Mn binary oxide achieves the maximum at these pH conditions.

Adsorption isotherm: Adsorption isotherms for TC were investigated at 288, 298 and 308 K, as illustrated in Fig.4. The Zr-Mn binary oxide had an excellent capability for the adsorptive removal of TC at the three reaction temperatures. Both Langmuir and Freundlich models were employed to describe the adsorption isotherms obtained in the figure (Langmuir 1916, Freundlich 1906). The two equations can be expressed as follows:

$$\text{Langmuir model: } q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad ...(2)$$

$$\text{Freundlich model: } q_e = k_F C_e^{\frac{1}{n}} \quad ...(3)$$

Where, q_e and q_m represent the amount of equilibrium adsorption capacity and the maximum adsorption capacity (mg/g), respectively; k_L (L/mg) is the Langmuir coefficient; C_e is the equilibrium concentration (mg/L); k_F is roughly an indicator of the adsorption capacity; n is the heterogeneity factor.

From the fitted curves at different temperatures pre-

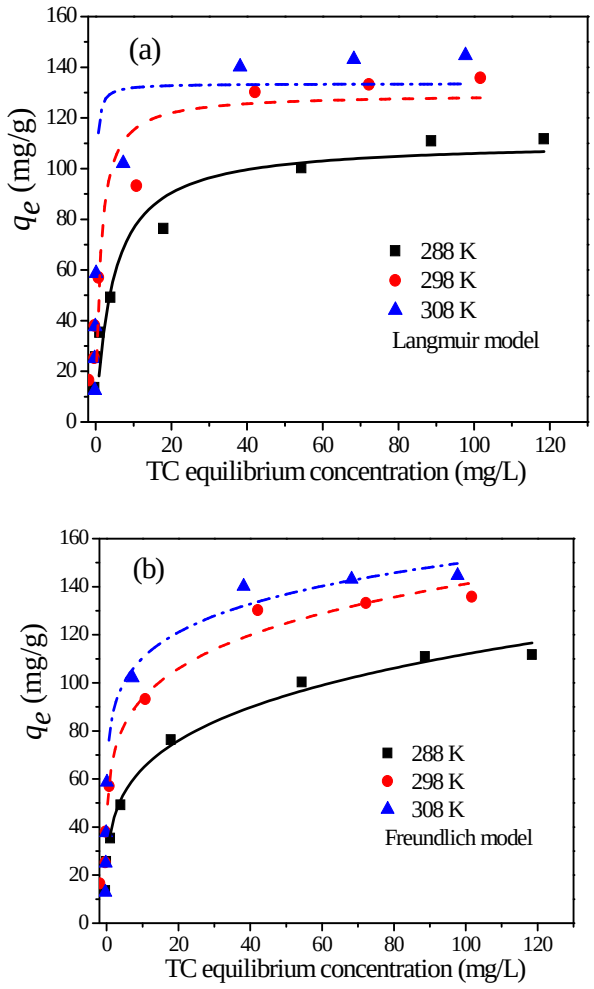

Fig. 4: Isotherms simulated by Langmuir (a) and Freundlich (b) models for TC adsorption onto Zr-Mn binary oxide.

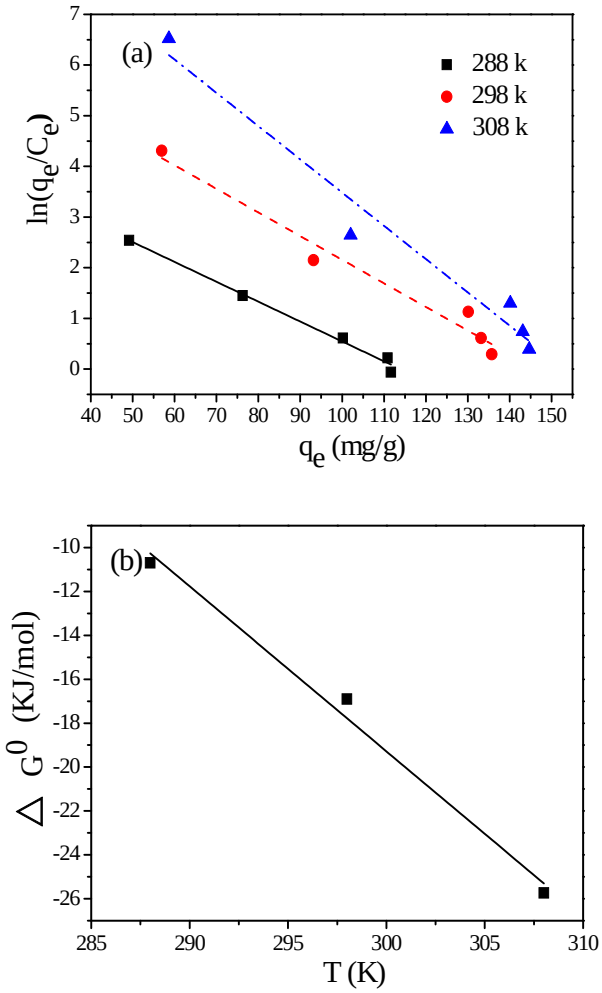

Fig. 5: (a) Plots of $\ln q_e/C_e$ versus q_e for TC adsorption Zr-Mn binary oxide; (b) changes of free energy (thermodynamic calculations).

sented in Fig. 4, it can be observed that Freundlich model described the adsorption isotherms better than Langmuir model as the experimental points are much closer to the curves fitted by Freundlich model. This indicates that the surface of Zr-Mn binary oxide is more heterogeneous. Meanwhile, the adsorption parameters obtained from the simulated isotherm models were listed in Table 1. At the three temperatures, the correlation coefficients (R^2) of Freundlich models are quite higher than those of Langmuir model. By Langmuir model, the calculated maximum adsorption capacities at 288, 298 and 308 K were 110.8, 129.5 and 133.5 mg/g, respectively. It indicates that the adsorption capacity of TC on the Zr-Mn binary oxide increases with the rising temperature. As a result, the adsorption process is deduced to be an endothermic process in nature.

Thermodynamic parameters associated with the adsorption process such as standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated using the following equations:

$$\Delta G^0 = -RT\ln K_0 \quad ...(4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad ...(5)$$

$$\ln k_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad ...(6)$$

In these equations, T is in Kelvin; ΔH^0 is the entropy of adsorption and R is the universal gas constant (8.314 J mol^{-1} k^{-1}). As presented in Fig. 5a, the thermodynamic equilibrium constant K_0 for the adsorption process was determined by plotting $\ln q_e/C_e$ versus q_e and extrapolating to zero q_e using a graphical method (Yuan et al. 2009). The intersection with the vertical axis gives the value of $\ln K_0$ at the

three different temperatures. The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a plot $\ln k_0$ versus the reciprocal of absolute temperature (1/T) (Fig. 5b).

The enthalpy and entropy of the adsorption process are found to be 206.32 KJ mol^{-1} and 752.0 J mol^{-1} k^{-1}, respectively. The positive value of the reaction enthalpy implies that the uptake of TC increases with a rise in the reaction temperature, which is consistent with the aforementioned results. The negative values of ΔG^0 at the three temperatures suggest the spontaneous nature of TC adsorption. The negative value of enthalpy change also indicated that the adsorption process is endothermic, indicating strong forces of attraction.

CONCLUSION

The composite Zr-Mn binary oxide was prepared by a simple co-precipitation method using Mn(II) as Mn source. During the efficient adsorptive removal of tetracycline, it was observed that the Zr-Mn binary oxide with a molar ratio of Zr/Mn at 2:1 had better adsorption performance. The complete of tetracycline could be realized at a very limited dose of the adsorbent. Acidic and near-neutral solution pH conditions were favourable for the uptake of tetracycline. Freundlich model described the adsorption isotherm better than Langmuir model, indicating the heterogeneous surface of the prepared adsorbent. The calculated maximal adsorption capacities for TC achieved 129.5 mg/g at 298 K by Langmuir model. The changes of enthalpy and entropy of the adsorption processes are 206.32 KJ mol^{-1} and 752.0 J mol^{-1} k^{-1}, respectively. The negative value of Gibbs free energy change and the positive value of enthalpy also indicated that the adsorption process is spontaneous and endothermic.

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