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Original Research Paper

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Effect of Solution pH and Coexisting Ions on Cefradine Adsorption onto Wheat Straw

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ABSTRACT

Agricultural waste wheat straw was innovatively used for the adsorptive removal of cefradine. The aim of this study is to assess the adsorption behaviour of wheat straw for cefradine removal from the wastewater. Effect of solution pH and coexisting ions was investigated concurrently. Typical kinetic models including pseudo-first-order, pseudo-second-order and Elovich models were used to simulate adsorption kinetics at different pH conditions. Kinetic experiments indicated that both the linear and nonlinear pseudo-second-order kinetic models could describe the adsorption kinetics better. It can be inferred that chemisorption occurred between the cefradine molecules and the wheat straw. It is worthy to mention that most of the uptake occurred within the initial 60 min, indicating a fast removal of cefradine when wheat straw was applied in practical wastewater treatment. Ionic strength experiment demonstrated that cefradine molecules may be specifically adsorbed on the wheat straw via forming outer-sphere surface complexes. A decrease of the uptake of cefradine was observed in the presence of HCO_3^-, HPO_4^{2-}, SO_4^{2-} and SiO_3^{2-}, while the inhibiting effect was in the pecking order Na_2SiO_3> Na_2SO_4>Na_2HPO_4>$NaHCO_3$. The presence of humic acid could decrease the cefradine uptake as well.

INTRODUCTION

Human activities have caused discharge of a number of pollutants into the natural water environment. As such, whether from domestic or industrial wastewater, various pollutants could be detected in the water discharge and the water bodies involved. Drugs in water environment have been globally concerned. Several hundred different antibiotic substances are widely applied in the past years and most of them eventually enter into rivers, lakes and other water bodies. Antibiotics have been considered emerging pollutants due to their continuous input and persistence in the aquatic ecosystem (Yang et al. 2011). Chemicals including antibiotics released into the environment from human activities are responsible for adverse ecological effects if the concentrations are higher than a threshold of environmental self-purification and organism tolerance (Jiang et al. 2010, Homem & Santos 2011, Chen & Guo 2012). Therefore, it will be better if antibiotics can be removed before the antibiotics containing wastewaters are discharged into the environment.

Cefradine is a first generation cephalosporin antibiotic. Some techniques such as hydrolysis, biodegradation, photolysis and adsorption of cephalosporin antibiotics were investigated. Cefradine is easy to degrade in water, but because of the large use in China, the ecological risk caused by its continuous discharge into the water cannot be ignored. The potential toxicity of its degradation products also needs further study (Chen et al. 2012).

Although various water treatment technologies could be applied to the degradation and removal of cefradine, adsorption technology has been identified as one of the most practical and efficient water treatment technology. This is because adsorption has advantages such as ease of operation and high efficiency. Sludge can be used as adsorbent to adsorb cefradine in water, but the amount of adsorption is relatively small. Accordingly, searching out efficient adsorbents emerges to be a fundamental approach to achieve cefradine removal. There are many studies on the adsorption of contaminants on plant materials. Han et al. (2008) used peanut husk as an adsorbent to remove Neutral Red aqueous solutions. The plant materials have a good adsorption performance to remove the pollutants.

One potential adsorbent material can be wheat straw, which can be used for such purposes as it can also bring an unlimited number of economic and environmental benefits to the industrial wastewater treatment. Wheat straw is an agricultural waste, which is extensively cultured in North China. Most of this agricultural waste is arbitrarily discarded or set on fire. These disposals will result in environmental pollution.

Therefore, this study investigated the use of a previously untried biosorbent wheat straw for cefradine removal by adsorption. The adsorption kinetics, effect of ionic strength, effect of coexisting ions in the experiment was investigated. The aim of the study was to develop low-cost adsorbents for an inexpensive cefradine removal technology.

MATERIALS AND METHODS

Chemicals: Cefradine was purchased from Tianjin Kermel Chemical Reagents Co., Ltd (Tianjin, China) and used without further purification. Other chemicals used were of analytic reagent grade. Deionized and doubly distilled water was used throughout this study.

Adsorbent preparation: Wheat straw was collected from farmland in Zhengzhou of Henan Province, China. The collected biomass was washed, dried, crushed and sieved using a 40 mesh sieve. Finally, the wheat straw particles were stored in a desiccator for further use.

Batch adsorption studies: Adsorption of cefradine onto the wheat straw was conducted in a series of cylindrical flasks. The stock solution of cefradine was prepared in DI water. All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. The reaction temperature was controlled at a constant of 25°C. The solution pH adjustment was conducted by the addition of diluted HCl or NaOH solution.

For kinetic experiments, a desired amount of wheat straw (1000 mg) was added to a conical flask containing 1000 mL of cefradine solution with a concentration of 20 mg/L. Constant and vigorous stirring was maintained by mechanical agitation for 24 h. After adsorption, samples of 5 mL were taken from the suspension at predetermined times. To investigate the influence of ionic strength on the cefradine adsorption, experiments were carried out using 150 mL glass vessels containing 50 mL cefradine solution and 50 mg wheat straw. The ionic strength of the solutions varied from 0 to 0.1 mol/L by adding different amount of $NaNO_3$. The effects of coexisting ions in wastewater such as HCO_3^-, HPO_4^{2-}, SO_4^{2-} and NO_3^- on cefradine adsorption were investigated by adding $NaHCO_3$, Na_2HPO_4, Na_2SO_4 and $NaNO_3$ to 20 mg/L of cefradine solution, respectively. The concentration of coexisting anions ranged from 0.01 to 10 mM/L.

Analysis of cefradine: All the samples were collected and filtered through a 0.45 µm pore-size membrane before analysing. The cefradine concentration was determined by measuring the absorbance at a fixed wavelength (266 nm) using a UVmini-1240 spectrophotometer (Shimadzu, Japan) (Hu et al. 2012). The adsorption capacity was calculated using the following equation:

$$q_e=(C_0-C_e)V/W \quad ...(1)$$

$$q_t=(C_0-C_t)V/W \quad ...(2)$$

Where, q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min); C_0 is the initial concentration of cefradine in solution, while C_e and C_t (mg/L) are the concentrations of cefradine at equilibrium and t (min), respectively; V (L) is the volume of solution, and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Adsorption kinetics: In order to assess the adsorption capability for cefradine from wastewater by wheat straw, adsorption kinetics was investigated at pH 4.0, 7.0 and 10.0, respectively. Typical kinetic models, including pseudo-first-order, pseudo-second-order and Elovich models were used to fit the experimental data (Mi et al. 2016).

The nonlinear pseudo-first-order model is expressed as (Lagergren 1898) :

$$q_t = q_e(1-e^{-k_1 t}) \quad ...(3)$$

The nonlinear pseudo-second-order model can be expressed as (Ho & McKay 1999)

$$q_t = \frac{k_2 {q_e}^2 t}{(1+k_2 q_e t)} \quad ...(4)$$

The Elovich model can be expressed as (Kithome et al. 1988)

$$q_t = a + k\ln t \quad ...(5)$$

The mathematical representation of the linear models of pseudo-first-order and pseudo-second-order kinetics are given in the following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad ...(6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad ...(7)$$

Where, q_e and q_t are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at time *t* (min), respectively; k_1(/min) and k_2 (g/[mg min]) are the related adsorption rate constant for pseudo-first-order and pseudo-second-order models, respectively. Where, *a* (g mg/min) and *k* (mg/g) are constants.

From the nonlinear fitting curves presented in Fig. 1, it can be observed that about 99% of cefradine molecules were immediately adsorbed within the initial 60 min, indicating that wheat straw can be directly used for fast removal of cefradine from practical wastewater. The three nonlinear kinetic models could well describe the adsorption kinetics under all the pH conditions, while pseudo-second-order model fitted the experimental data slightly better.

Table 1: Nonlinear kinetic parameters of cefradine adsorption at different pH conditions.

Model	pH=4	pH=7	pH=10
Pseudo-first-order model			
k_1(min^{-1})	0.1563	0.1217	0.102
q_e(mg/g)	12.81	12.04	10. 78
R^2	0.957	0.983	0.989
Pseudo-second-order model			
k_2(g·mg/min)	0.022	0.017	0.015
q_e(mg/g)	13.14	12.42	11.17
R^2	0.904	0.951	0.972
Elovich model			
a	8.617	6.708	5.157
k	0.703	0.902	0.954
R^2	0.794	0.836	0.864

Table 2: Linear kinetics for pseudo-first-order and pseudo-second-order simulation parameters of cefradine adsorption at different pH conditions.

	Linear pseudo-first-order model			Linear pseudo-second-order model		
	q_e(mg/g)	k_1(min-1)	R^2	q_e(mg/g)	k_2(mg/(g·min))	R^2
pH=4	0.964	1.4×10-3	0.133	12.731	0.058	0.999
pH=7	1.763	1.7×10-3	0.278	12.126	0.027	0.999
pH=10	3.034	1.2×10-3	0.611	11.010	0.017	0.999

As shown in Table 1, the correlation coefficients (R^2) of pseudo-first-order models are all above 0.957. Furthermore, only judged from the simulated curves and experimental points, the pseudo-first-order model described the experimental kinetic data are the best under their pH conditions. Accordingly, the rate determining step might be diffusive in nature for the uptake of cefradine in this case.

Meanwhile, as demonstrated in Fig. 2, the experimental data were also comparatively simulated by linear kinetic models, including pseudo-first-order and pseudo-second-order models. The linear kinetic parameters simulated for the two models are listed in Table 2. The correlation coefficient of pseudo-second-order kinetic model is 0.999, which is especially higher than the pseudo-first-order model. The calculated values are much close to the experimental values using pseudo-second-order kinetic model as well. Apparently, pseudo-second-order kinetic model fitted the experimental data better. As such, it can be inferred that chemisorption occurred between the cefradine molecules and the wheat straw.

Effect of ionic strength: The effect of ionic strength on cefradine was investigated by varying the dosage of $NaNO_3$ from 0 to 0.1 mol/L, as illustrated in Fig. 3. A significant decrease of cefradine uptake was observed with increasing ionic strength between pH 3.0 and 11.0. At pH 5.0, the uptake of cefradine reduced from 12.59 mg/g in the absence of $NaNO_3$ to 7.58 mg/g in the presence of 0.1 mol/L $NaNO_3$. It is well known that anions adsorbed by inner-sphere association either show little sensitivity to ionic strength or respond to higher ionic strength with greater adsorption. By contrast, anions adsorbed by outer-sphere association are strongly sensitive to ionic strength. The adsorption process is hindered by competition with strongly adsorbing anions such as NO_3^- since they form outer-sphere complexes through electrostatic forces (McBride 1997). Accordingly, it can be deduced that cefradine molecules may be specifically adsorbed on the wheat straw via forming outer-sphere surface complexes.

Effect of coexisting anions: As we know, adsorption selectivity is an important factor influencing removal effectiveness. Some researchers employed highly selective adsorbents to separate or remove heavy metals from aqueous systems (Lam et al. 2007). Anions such as bicarbonate (HCO_3^-), phosphate (HPO_4^{2-}), sulphate (SO_4^{2-}) and silicate (SiO_3^{2-}) commonly exist in water and wastewater, and might interfere in the adsorption of phosphate cefradine through competing for adsorptive sites on the surface of the adsorbents. The effects of these anions on cefradine adsorption at three concentration levels (0.1, 1.0 and 10 mM) were assessed and the results are shown in Fig. 4.

In general, there was an evident decrease in cefradine adsorption by wheat straw, indicating that these inorganic

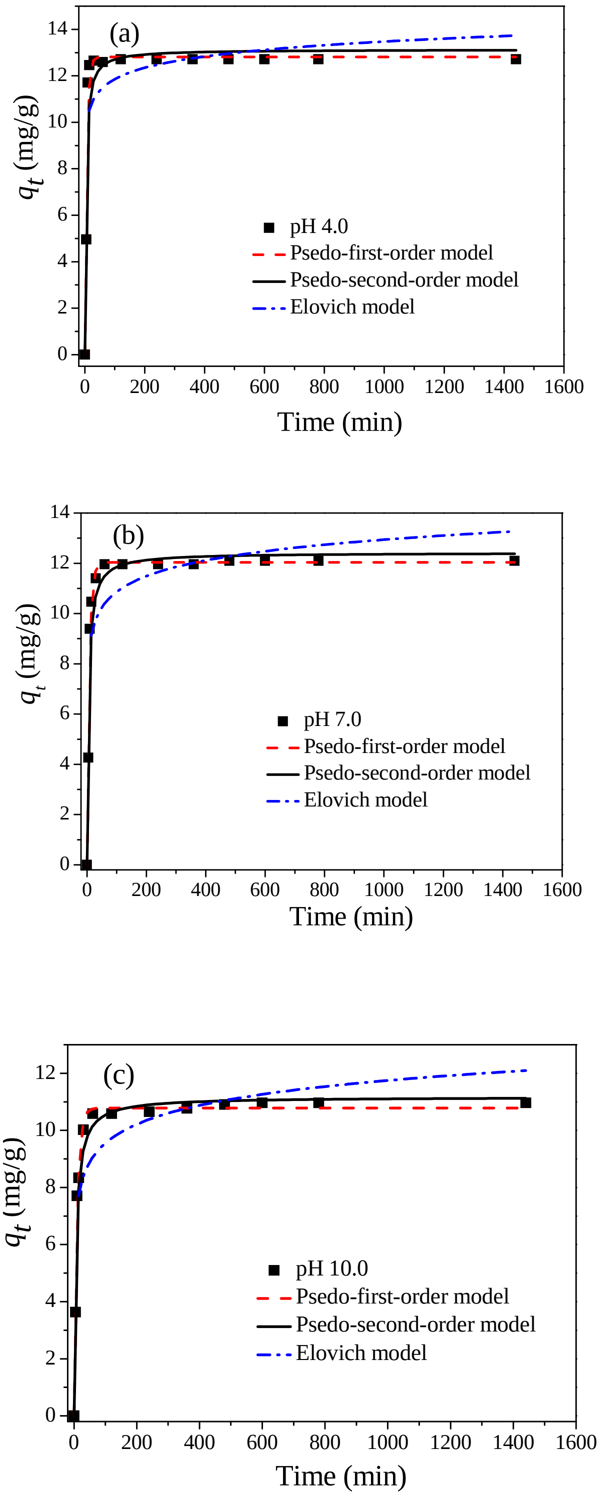

Fig.1: Non-linear kinetic simulation by pseudo-first-order, pseudo-second-order and Elovivch models for cefradine adsorption at pH 4.0 (a), pH 7.0 (b) and pH 11.0 (c).

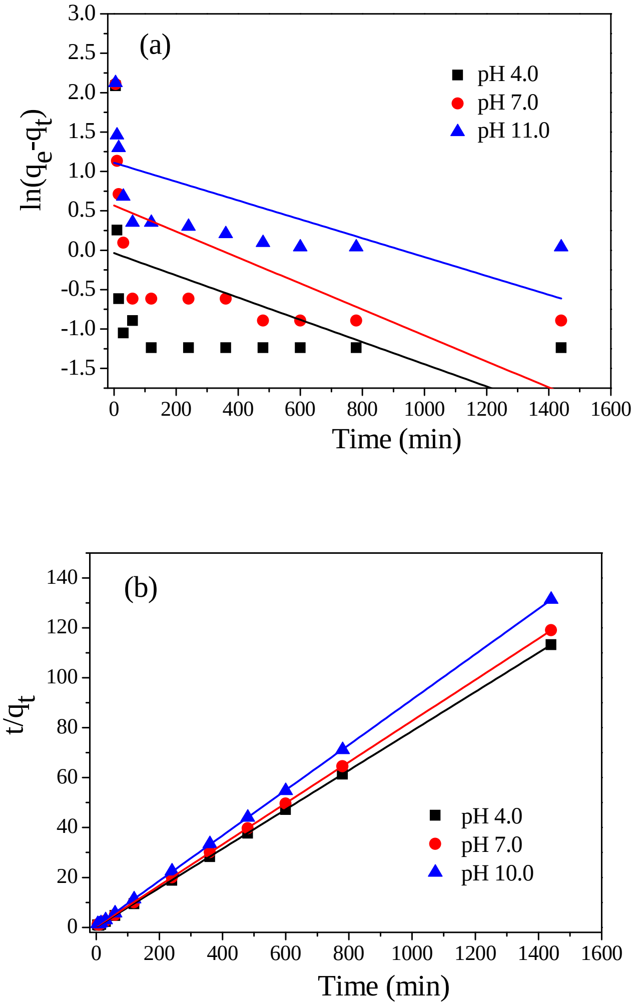

Fig.2: Linear kinetic simulation by pseudo-first-order (a) and pseudo-second-order (b) models for cefradine adsorption at different pH conditions.

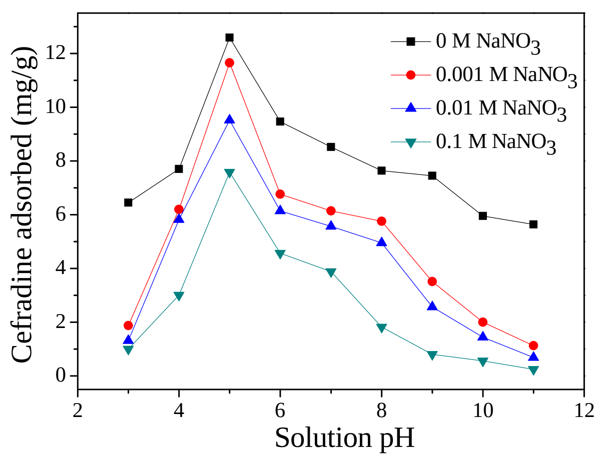

Fig.3 Effect of ionic strength on cefradine adsorption.

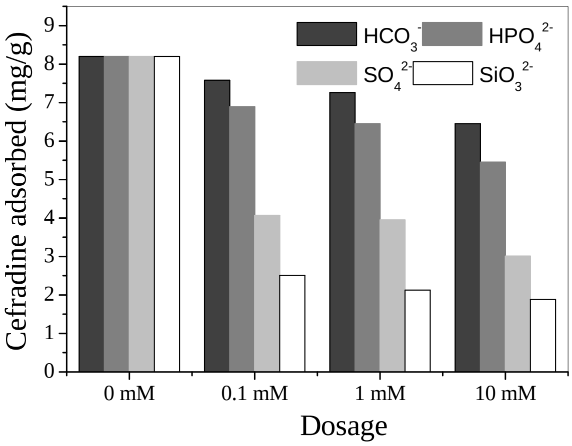

Fig. 4: Effect of coexisting ions on cefradine adsorption.

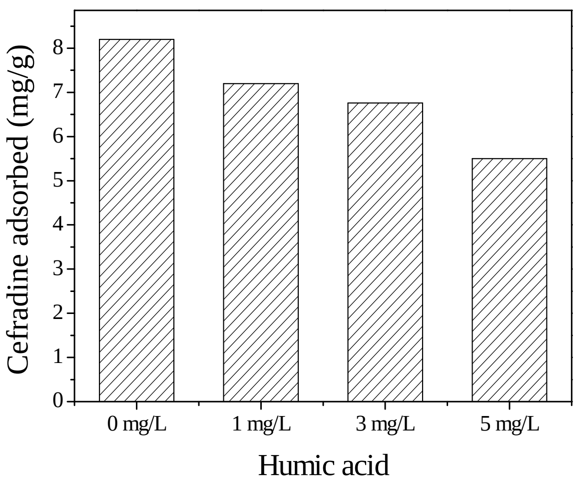

Fig. 5: Effect of humic acid on adsorption of cefradine.

anions might have competed with the cefradine molecules for the same active sites on wheat straw, due to the comparable type of the functional group that exists in the cefradine. An important and progressive decrease of cefradine uptake was observed on wheat straw with increasing dosages of anions HCO_3^-, HPO_4^{2-}, SO_4^{2-} and SiO_3^{2-}. The inhibiting effect was found in the pecking order Na_2SiO_3>Na_2SO_4> Na_2HPO_4>$NaHCO_3$.

Effect of the presence of the humic acid: In nature, natural organic matter such as humic acid is a kind of macromolecule organic compound widely existing in natural water body. Humic acid has the capability of influencing adsorption and removal of pollutants in water and wastewater. The effect of humic acid was investigated and the result is presented in Fig. 5. The uptake of cefradine decreased from 8.2 mg/g without humic acid to 5.5 mg/g in the presence of 5 mg/L humic acid. The increasing dosage of humic acid could inhibit cefradine adsorption profoundly.

CONCLUSION

Wheat straw demonstrated its excellent adsorption capability for cefradine removal. Kinetic experiments indicated that most of the cefradine uptake occurred within the initial 60 min. Weakly acidic pH conditions were proved to be favourable for cefradine removal. Both, the linear and nonlinear pseudo-second-order kinetic model could describe the adsorption kinetics better, indicating that chemisorption occurred between the cefradine molecules and wheat straw. Ionic strength experiment demonstrated that cefradine molecules may be specifically adsorbed on the wheat straw via forming outer-sphere surface complexes. Inhibiting effect by coexisting anions was found to be in the pecking order Na_2SiO_3>Na_2SO_4>Na_2HPO_4>$NaHCO_3$. The presence of humic acid could decrease cefradine uptake significantly as well.

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REFERENCES

Chen, J.Q. and Guo, R.X. 2012. Access the toxic effect of the antibiotic cefradine and its UV light degradation products on two freshwater algae. J. Hazard. Mater. 209-210: 520-523.

Chen, H., Li, X.J. and Zhu, S.C. 2012. Occurrence and distribution of selected pharmaceuticals and personal care products in aquatic environments: a comparative study of regions in China with different urbanization levels. Environ. Sci. Pollut. R., 19(6): 2381-2389.

Han, R.P., Han,P., Cai, Z.H., Zhao, Z.H. and Tang, M.S. 2008. Kinetics and isotherms of Neutral Red adsorption on peanut husk. J. Environ. Sci., 20: 1035-1041.

Ho, Y.S. and McKay, G. 1999. Pseudo-second-order model for sorption process. Process Biochem., 34(5): 451-65.

Homem, V. and Santos, L. 2011. Degradation and removal methods of antibiotics from aqueous matrices a review J. Environ. Manage., 92: 2304-2347.

Hu, Z.J., Wang, N.X., Tan, J., Chen, J.Q. and Zhong, W.Y. 2012. Kinetic and equilibrium of cefradine adsorption onto peanut husk. Desalin. Water Treat., 37(1-3): 160-168.

Jiang, M.X., Wang, L.H. and Ji, R. 2010. Biotic and abiotic degradation of four cephalosporin antibiotics in a lake surface water and sediment. Chemosphere, 80: 1399-1405.

Kithome, M., Paul, J.W., Lavkulich, L.M. and Bomke, A.A. 1988. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. Soil Sci. Soc. Am. J., 62(3): 622-629.

Lam, K.F., Fong, C.M. and Yeung, K.L. 2007. Separation of precious metals using selective mesoporous adsorbents. Gold Bull., 40(3): 192-198.

Lagergren, S. 1898. Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlinga. 24(4): 1-39.
McBride, M.B. 1997. A critique of diffuse double layer models applied to colloid and surface chemistry. Clay & Clay Miner., 45(4): 598-608.
Mi, X., Guo, Y.J., Zhang, C.Y., Wang, L., Zhang, S., Zou, B.B. and Li, G.T. 2016. Effect of solution pH on the kinetic adsorption of methylene blue by sugarcane bagasse biochar under a magnetic field. Nat. Env. & Poll. Tech., 15(4): 81297-81301.
Yang, X., Flowers, R.C., Weinberg, H.S. and Singer, P.C. 2011. Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. Water Res., 45: 5218-5228.