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Effect of Solution pH on Adsorption of Cefradine by Wheat Straw and Thermodynamic Analysis

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ABSTRACT

As to many pollutants in aqueous solution, wheat straw is considered to be an environment friendly and low-cost adsorbent. Cefradine is a kind of broad-spectrum semisynthetic antibiotics widely used in clinical practices, which causes pollution in natural water bodies. As such, natural wheat straw was tentatively used for adsorptive removal of cefradine. Effect of solution pH on the adsorption of cefradine by wheat straw was investigated. It was found that the optimal solution pH for cefradine adsorption was pH 5.0. The typical functional groups present on raw and exhausted wheat straw after cefradine adsorption were confirmed through fourier-transform infrared spectroscopy. The isotherm data were analysed by Langmuir, Freundlich and Temkin isotherm models. It demonstrated that Freundlich model described the adsorption isotherm better. By Langmuir model, the maximal adsorption capacity for cefradine was 39.5 mg/g at 298 K. The thermodynamic analysis indicates that the cefradine adsorption process on the wheat straw was endothermic in nature and the increase of reaction temperature was beneficial to the uptake of cefradine. This demonstrates that wheat straw could be an ideal and cost-effective bio-sorbent used for effective removal of antibiotics such as cefradine from water.

INTRODUCTION

Cephalosporin is a broad-spectrum of semisynthetic antibiotics, commonly used in humans, animals and aquaculture, accounting for 60% of the total consumption of antibiotics (Kümmerer 2009). They have strong antibacterial activity, resistance to penicillinase, high clinical efficacy, less allergic reactions than penicillin, widely used in clinical practice. According to statistics, about 100000~200000 tons of antibiotics are used in medical, aquatic and livestock farming every year. The annual consumption of our country is about 25000 tons (Wise 2002). The continuous use and discharge of antibiotics has caused water pollution. However, these antibiotics do not undergo measurable biodegradation in natural water environments (Jiang et al. 2010). Up to 80 kinds of antibiotics have been detected in rivers, seawater, underground water and sewage treatment plants in Europe, the United States, Canada, Japan and China. Long-standing antibiotics may induce drug resistant bacteria, inhibit the growth of microbes, and have potential ecological risks, such as the emergence of “super resistant bacteria” (Han et al. 2010, Zuccato et al. 2010).

The treatment technologies for antibiotics wastewater include chemical treatment, physical treatment and biological treatment (Tam et al. 2002, Stackelberg et al. 2007). Nevertheless, there are many problems such as high operating cost, energy demand, low efficiency and so on (Homem & Santos 2011, Yang et al. 2011). Comparatively speaking, adsorption technology is an important cost-effective technology for water treatment. Adsorption process is regarded as one of the most powerful, efficient and cost-effective water treatment technologies due to ease of operation, universal nature and high efficiency (Qu 2008). Therefore, it is very important to study the cheap, efficient and practical adsorption materials.

China is a large agricultural country with rich straw resources, producing about 8 million tons of crop straw per year. Wheat straw is one of the main agricultural wastes especially in north China. Improper disposal of crops such as incineration straw has a serious negative impact on the atmospheric environment (Owamah 2014). The chemical components of wheat straw are as follows: 5.71% water, 6.41% ash, 1.04% crude fat, 2.38% crude protein and 32.95% crude fibre (Yi 2003). As a comparison, these natural components are deduced to be more environment friendly. Peng et al. (2017) studied the excellent adsorption performance

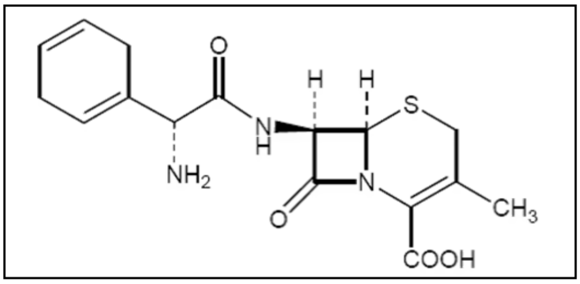


Fig. 1: The molecular structure of cefradine.

of sulfonamide antibiotics on rice straw biochar. Hu et al. (2012) have studied the thermodynamics and kinetics of the adsorption of cefradine on peanut shells. Accordingly, raw wheat straw can be selected as an efficient, inexpensive and natural adsorbent for antibiotics removal.

In this study, cefradine was selected as a target pollutant subjected for the adsorptive removal by wheat straw. Effect of solution pH was emphatically investigated as the solution pH is one of the key parameters for the uptake of various pollutants. Nonlinear simulation for adsorption isotherm and thermodynamic analysis were conducted to better understand adsorption mechanism and adsorption capability of wheat straw. This could provide a reference for practical application of raw agricultural waste.

MATERIALS AND METHODS

Chemicals: Cefradine was purchased from the Tianjin Kermal Chemical Reagent Co., Ltd. and used without further purification. The molecular structure of cefradine is shown in Fig. 1.

Preparation of wheat straw: Wheat straw was collected from farmland in Zhengzhou, Henan Province. The collected biomass was washed, dried, crushed, and sieved through a 40 mesh sieve.

Characterization before and after cefradine adsorption: The wheat straw before and after cefradine adsorption were characterized by Fourier-transform infrared spectroscopy (FTIR). FTIR spectra were collected on a transmission model. Samples for FTIR determination were prepared by grinding 1 mg of sorbents with 80 mg of spectral grade KBr in an agate mortar. All the IR measurements were carried out at room temperature.

Batch adsorption studies: Adsorptive removal of cefradine was conducted by batch experiments in a series of conical flasks. A dose of 50 mg wheat straw was added into conical flasks containing 50 mL of cefradine solution (10~200 mg/L). These mixtures were shaken at 125 rpm for 24 h to achieve equilibrium. The temperature was kept at 288, 298 and 308 K, respectively. Finally, samples were collected and filtered through a 0.45 μm pore-size membrane before analysis.

Analysis of cefradine: The concentration of cefradine was analysed using an UVmini-1240 spectrophotometer (Shimadzu) by monitoring at the wavelength of maximum absorption (266 nm) (Hu et al. 2012). The adsorption capacity (q_e) of cefradine is calculated as equation (1).

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

Where, q_e (mg/g) is the adsorption capacity at equilibrium; C_0 is the initial concentration of cefradine in solution, and C_e (mg/L) is the concentrations of cefradine at equilibrium; V (L) is the volume of solution, and m (g) is the mass of the wheat straw.

RESULTS AND DISCUSSION

FTIR spectra of the raw and exhausted wheat straw: The FTIR spectra of the raw and exhausted wheat straw after cefradine adsorption are shown in Fig. 2. The characteristic absorbance band at 2916 cm^{-1} is ascribed to the stretching of $-CH_3$ groups. The weak absorption peaks at 1736 and 1620 cm^{-1} are ascribed to the vibrations of -OH and –C=O, respectively. However, no characteristic absorption band of cefradine was observed on the exhausted wheat straw. This is because the limited amount of cefradine on the exhausted

Table 1: Parameters of Langmuir, Freundlich and Temkin models for the adsorption of cefradine on wheat straw.

	Nonlinear method		
	288 K	298 K	308 K
Langmuir			
q_{max} (mg/g)	36.2	39.5	46.3
k_L (L/mg)	0.0264	0.0275	0.0289
R^2	0.988	0.963	0.935
Freundlich			
k_F (mg/g)	3.457	4.189	5.152
n	0.4315	0.4131	0.4076
R^2	0.958	0.991	0.985
Temkin			
A	-7.134	-2.545	-1.446
B	7.1176	6.6031	7.4876
R^2	0.975	0.940	0.937

Table 2: Thermodynamic parameters at different reaction temperatures.

T/K	$\ln K_0$	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 ($J \cdot mol^{-1} \cdot K^{-1}$)
288 K	7.277	-17.43	24.31	145.0
298 K	7.727	-18.50	24.31	145.0
308 K	8.488	-20.32	24.31	145.0

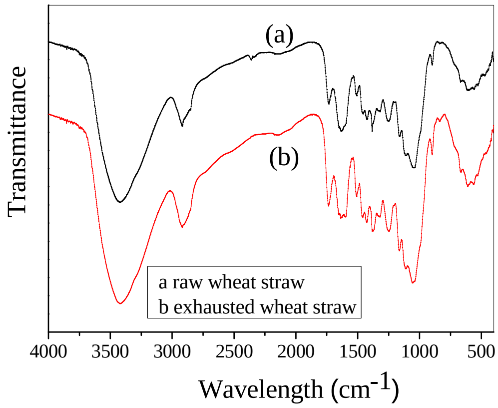


Fig. 2: FTIR spectra of the raw wheat straw and exhausted wheat straw after adsorption.

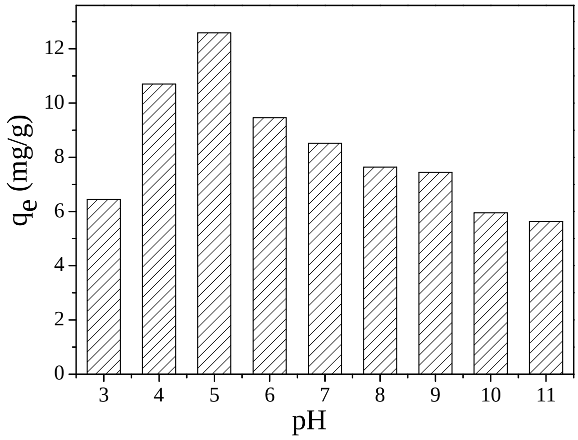


Fig. 3: Effect of solution pH on cefradine adsorption.

wheat straw and the influence of the strong absorption of the wheat straw.

Effect of solution pH on cefradine adsorption: Both, the surface charge properties of wheat straw and cefradine, are deduced to be significantly influenced by solution pH as the functional groups of the wheat straw and cefradine vary with changing solution pH. As such, the effect of solution pH for cefradine adsorption on wheat straw was investigated from pH 3.0 to 11.0, as presented in Fig. 3. At pH 4.0, 5.0, 6.0 and 7.0, the uptake of cefradine was of 10.70, 12.59, 9.46 and 8.52 mg/g, respectively. Apparently, the highest uptake of cefradine was achieved at pH 5.0. It can be deduced that weak acidic solution pH is especially favourable for the cefradine removal.

Adsorption isotherms: Adsorption isotherm is the basis for analysis of adsorption capacity and design of adsorption tests. The adsorption model was well established to analyse the adsorption isotherm. Three classical isotherm models including Langmuir, Freundlich and Temkin equations were used to fit the experimental data. The three equations can be expressed as follows (Langmuir 1916, Freundlich 1906, Fu et al. 1994):

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

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

Temkin $$q_e = A + B \ln C_e \qquad ...(4)$$

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, and A and B are Temkin constants.

The fitting curves by Langmuir, Freundlich and Temkin models at 298 K are illustrated in Fig. 4. Meanwhile, the typical adsorption parameters obtained from the simulated isotherm models are listed in Table 1.

From Fig. 3, the three isotherm models well fitted the experimental data as the experimental data are much closer to the simulated curves. Even though, from Table 1, the correlation coefficients (R^2) of Freundlich model are slightly higher than those of Langmuir and Temkin model. This indicates that the surface of wheat straw is more heterogeneous in nature.

By Langmuir model, the calculated maximum adsorption capacities at 288, 298 and 308 K were 36.2 mg/g, 39.5 mg/g and 46.3 mg/g, respectively. It indicates that the adsorption capacity of cefradine on the wheat straw increases with rising reaction temperature. As a result, the adsorption process is deduced to be an endothermic process in nature. This is because the thermal motion of cefradine molecules in solution was accelerated with the increasing temperature, and adsorption activation energy decreased, promoting the adsorption reaction and increasing the adsorption amount.

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

$$\Delta G^0 = RT\ln K_0 \qquad ...(5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad ...(6)$$

$$\ln k_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad ...(7)$$

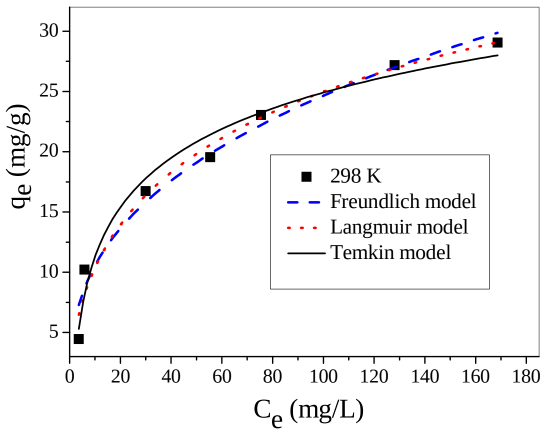
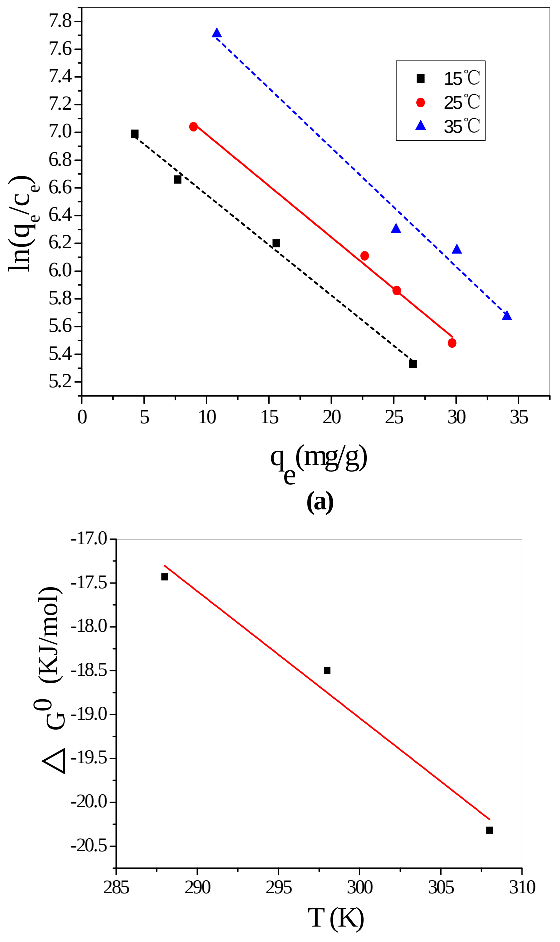


Fig. 4: Adsorption isotherms for the uptake of cefradine on wheat straw.

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}). The intersection with the vertical axis gives the value of lnk_0 at the three different temperatures. 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, Li et al. 2015). The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a plot lnk_0 versus the reciprocal of absolute temperature (1/T) (Fig. 5).

It can be seen from Table 2 that the enthalpy and entropy of the adsorption process are 24.31 KJ mol^{-1} and 145.0 J mol^{-1} k^{-1}, respectively. The negative value of ΔG^0 and positive value of ΔH^0 indicate that the adsorption process is spontaneous and endothermic, which is consistent with the aforementioned results.



(b)

Fig. 5: Plots of $\ln q_e/C_e$ versus q_e for cefradine adsorption on wheat straw (a); changes of free energy (thermodynamic calculations) (b).

CONCLUSIONS

In summary, the wheat straw is a low-cost and abundantly available biomass adsorbent, which can be used for effective removal of antibiotics cefradine from water. The optimal pH adsorption of cefradine is found to be pH 5.0, and weak acidic pH conditions are especially favourable for cefradine removal. The isotherm data were analysed by Langmuir, Freundlich and Temkin isotherm models. It demonstrated that Freundlich model described the adsorption isotherm better. By Langmuir model, the maximal adsorption capacity for cefradine was 39.5 mg/g at 298 K. The thermodynamic analysis indicates that the cefradine adsorption process on the wheat straw was endothermic in nature and the increase of reaction temperature was beneficial to the uptake of cefradine.

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