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Research Article

Adsorption of Norfloxacin from Aqueous Solution onto Modified Coal Fly Ash

Batch adsorption experiments were carried out for the removal of norfloxacin from aqueous solution using modified coal fly ash as adsorbent. The effects of various parameters such as contact time, initial solution concentration and temperature on the adsorption system were investigated. The optimum contact time was found to be 100 min. The equilibrium experimental data can be well fitted by the Freundlich model. Thermodynamic parameters such as ΔG , ΔH and ΔS were also calculated. The negative Gibbs free energy change and enthalpy change indicated the spontaneous and exothermic nature of the adsorption, and the negative entropy change indicated that the adsorption process was aided by decreased randomness.

Keywords: Adsorption, Isotherm, Modified coal fly ash, Norfloxacin

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1 Introduction

Norfloxacin, one of the quinolones, which are among the most important classes of synthetic antibacterial agents used in human and veterinary medicines, is active against many pathogenic bacterial species as gyrase inhibitor, which selectively inhibits bacterial DNA synthesis. Quantities of these drugs are potentially excreted as the parent compound or its metabolites and may enter the environment due to the spreading of manure and its slurry on agricultural land, or through direct deposition by grazing livestock [1]. Its properties make it difficult to biodegrade norfloxacin or remove norfloxacin from aqueous solution. Among the techniques for the removal of norfloxacin from wastewater, adsorption has been proved to be an effective and attractive process because of its inexpensive nature and ease of operation [2–6]. However, only limited information on the adsorption behavior of norfloxacin has been reported [7]. In this study, the effects of different parameters, including contact time, initial solution concentration, and temperature, were studied. The isotherms and thermodynamics were also investigated in detail.

2 Experimental

2.1 Materials

Norfloxacin, obtained from Daming Biotech. Co. Ltd., was further purified by recrystallization from aqueous solutions. After filtration and drying, its purity was determined by UV spectrometry (UV-2401PC; Shimadzu) to be 0.996 in mass fraction. The structure of norfloxacin is displayed in Fig. 1. H_2SO_4 and NaOH used in the experiments were analytical-grade reagents. The coal fly ash was sampled from the Dengfeng Electric Power Plant in China, mixed with 6 mol/L NaOH in a stainless-steel beaker and maintained at 363 K for 1 h with stirring. The latter mixture was left for 4 h to let the complexes settle down, which were then dialyzed against distilled water, powdered, ground and stored in a desiccator until required. The modified product, i.e. modified coal fly ash (MCFA), contained SiO_2 (43.5%), Al_2O_3 (17.8%), CaO (20.7%), MgO (1.6%), Fe_2O_3 (10.8%), and SO_3 (0.8%), and the loss on ignition (LOI) was 5.8%. The BET surface area of MCFA was

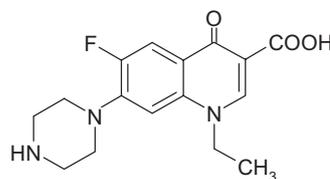


Figure 1. Molecular structure of norfloxacin.

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found to be $17.5 \text{ m}^2/\text{g}$ (the BET surface area of raw coal fly ash is $5.4 \text{ m}^2/\text{g}$) by the N_2 adsorption isotherm at 77 K, using a QUADRASORB SI automated surface area analyzer (Quantachrome Corporation, USA).

2.2 Methods

The MCFA adsorbent (4.0 g) was added to 100 mL norfloxacin solution. The initial concentrations of the norfloxacin solutions used were 40, 60, 80, 100, 120 and 140 mg/L. The initial pH values of the norfloxacin solutions were not adjusted. The adsorption experiments were conducted under constant stirring at controlled temperatures for a certain period. The concentrations of norfloxacin in the residual solutions were analyzed by means of a UV spectrometer (UV-2401PC; Shimadzu) [8]. The wavelength used to analyze the norfloxacin concentrations was 274 nm. The adsorption capacities were calculated according to the mass balance of norfloxacin in the solutions and were represented in units of milligrams of norfloxacin per gram of adsorbent. The adsorption capacities at equilibrium were computed according to Eq. (1):

$$Q_e = (c_0 - c_e)V/m \quad (1)$$

where Q_e and c_e are the amount adsorbed (mg/g) and the residual concentration (mg/L) at equilibrium, respectively; c_0 is the initial concentration of norfloxacin (mg/L); V and m are the volume of the norfloxacin solution (L) and the mass of adsorbent used (g), respectively.

3 Results and Discussion

3.1 Effect of Contact Time

Fig. 2 shows the effect of contact time on the adsorption of norfloxacin by MCFA for different initial norfloxacin concentrations. The adsorption was rapid in the initial 100 min; thereafter, the rate of adsorption decreased gradually. At some point in time, when the amount of norfloxacin being adsorbed onto the adsorbent was equal to the amount of norfloxacin being desorbed from the adsorbent, the adsorption process reached a dynamic equilibrium and the adsorption amount remained nearly constant. From contact time curves, it was observed that the equilibrium time was 100 min for all norfloxacin concentrations. This is the reason why the optimum contact time was 100 min in the above batch equilibrium experiments.

3.2 Effect of Initial Norfloxacin Concentration and Temperature

The effects of the initial norfloxacin concentration and the temperature on the adsorptive removal of norfloxacin by MCFA are shown in Fig. 3. It can be observed that the unit

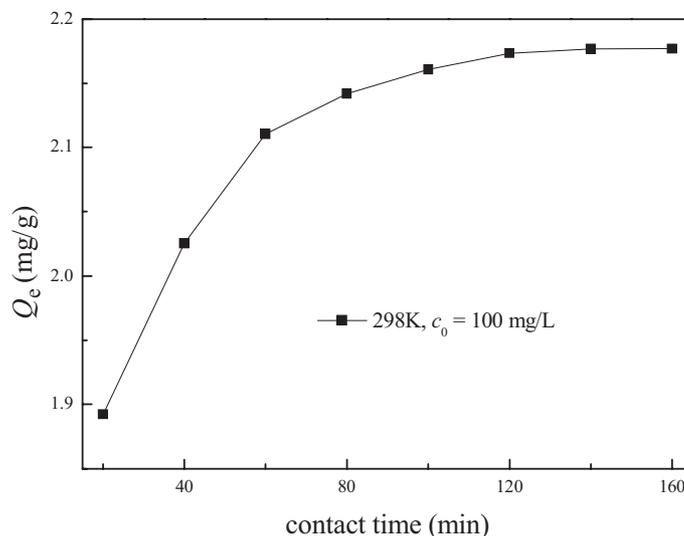


Figure 2. Effect of contact time on the adsorption of norfloxacin by MCFA.

adsorption increased while the percentage adsorption decreased with increasing initial norfloxacin concentration. The number of norfloxacin ions around the adsorbent sites of MCFA increased with increasing initial norfloxacin concentration. Hence, the adsorption process was carried out more efficiently, resulting in the increase of the unit adsorption. It can be found that the maximum adsorption capacity of norfloxacin occurred at 298 K, with the adsorption capacities decreasing in the order $298 \text{ K} > 308 \text{ K} > 318 \text{ K}$. The decrease in the adsorption capacity upon increasing the temperature indicates that the adsorption was an exothermic process.

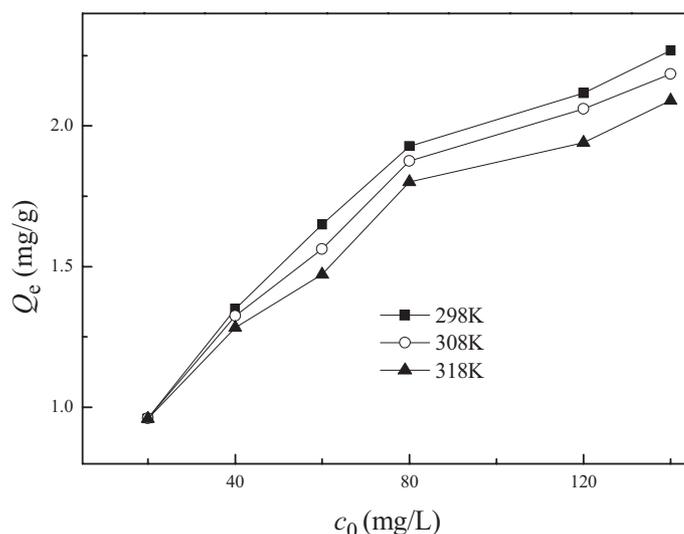


Figure 3. Effect of initial norfloxacin concentration and temperature on the adsorption process.

3.3 Adsorption Equilibrium of Norfloxacin on MCFA

Adsorption isotherms were measured for norfloxacin on MCFA at 298, 308 and 318 K, and the results are shown in Fig. 4. It was found that the adsorption capacity of MCFA increased as the concentration of norfloxacin in water increased, and the adsorption capacity tended to decrease with increasing temperature. The adsorption isotherms were simulated by the Freundlich model [9] (Eq. 2):

$$\log Q_e = \log K_f + \frac{1}{n} \log c_e \quad (2)$$

where K_f and n are parameters indicating the capacity and intensity of adsorption, respectively. The corresponding parameters of MCFA are summarized in Tab. 1. Tab. 1 shows that the experimental data fit well to the Freundlich model. The value of K_f decreases with increasing temperature, and it is obvious that low temperature is helpful for adsorption and that the adsorption mechanism is physical adsorption.

In order to further understand the adsorption mechanism of norfloxacin on MCFA, thermodynamic analysis was performed. The isosteric enthalpies of adsorption were calculated with a derivative of the Van't Hoff equation [10] (Eq. 3):

$$\Delta H = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \left(\frac{c_{e1}}{c_{e2}} \right) \quad (3)$$

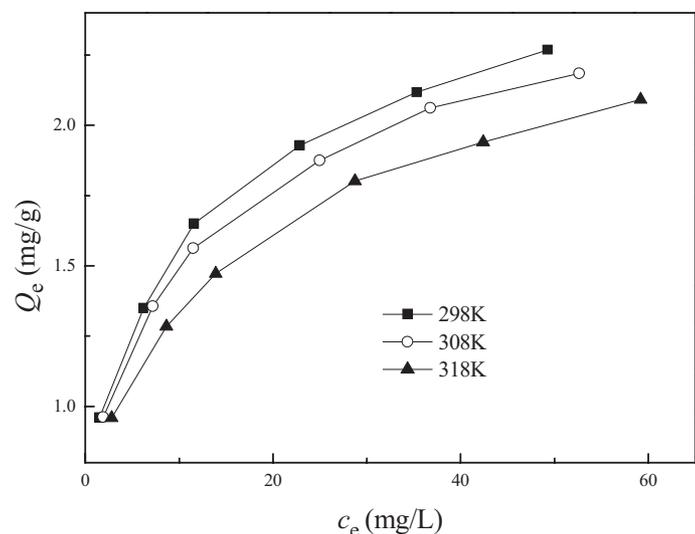


Figure 4. Adsorption isotherms of norfloxacin on MCFA at 298, 308 and 318 K.

Table 1. Freundlich parameters for norfloxacin on MCFA at various temperatures.

Temperature [K]	Isotherm equation	K_f	n	r^2
298	$\log Q_e = 0.2507 \log c_e - 0.0612$	0.8686	3.989	0.9972
308	$\log Q_e = 0.2515 \log c_e - 0.0827$	0.8266	3.976	0.9971
318	$\log Q_e = 0.2583 \log c_e - 0.1308$	0.7399	3.871	0.9980

where c_{e1} and c_{e2} are the equilibrium concentrations of solutions (mg/L) at the same Q_e , at the absolute temperatures T_1 (K) and T_2 (K), respectively. ΔH is the enthalpy change in adsorption (J/mol) and R is the gas constant (8.314 J/K mol).

If the adsorption can be simulated by the Freundlich model, the Gibbs free energy change for the adsorption process is obtained with a derivative equation [11] (Eq. 4):

$$\Delta G = -nRT \quad (4)$$

where ΔG is the Gibbs free energy change in adsorption (J/mol) and n is the corresponding parameter of the Freundlich equation.

The adsorption entropies were calculated according to the Gibbs-Helmholtz equation [12] (Eq. 5):

$$\Delta S = (\Delta H - \Delta G)/T \quad (5)$$

where ΔS is the entropy change in adsorption (J/mol K). The calculated isosteric enthalpy changes (ΔH), Gibbs free energy changes (ΔG) and entropy changes (ΔS) of MCFA are presented in Tab. 2.

Based on the analysis of the results in Tab. 2, the negative values of the Gibbs free energy changes at all temperatures indicate that the adsorption process is favorable and spontaneous. The negative values of all the enthalpy changes imply that the adsorption process of norfloxacin on MCFA is exothermic. Compared with the movement of norfloxacin in solution, the movement of norfloxacin absorbed on MCFA was greatly restricted, which is suggested by the negative values of all the entropy changes.

4 Conclusions

Batch adsorption experiments were carried out for the removal of norfloxacin from aqueous solution using MCFA as adsorbent. The effects of various parameters such as contact time, initial solution concentration and temperature on the adsorption system were investigated. The optimum contact time was found to be 100 min. The equilibrium experimental data at 298, 308 and 318 K can be well fitted by the Freundlich model. Thermodynamic parameters such as ΔG , ΔH and ΔS were also calculated. The negative Gibbs free energy change and enthalpy change indicated the spontaneous and exothermic nature of the adsorption, and the negative entropy change indicated that the adsorption process was aided by decreased randomness.

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The authors have declared no conflict of interest.

Table 2. Thermodynamic parameters for norfloxacin on MCFA.

Q_e [mg/g]	ΔH [kJ/mol]	ΔG [kJ/mol]			ΔS [J/mol K]		
		298 K	308 K	318 K	298 K	308 K	318 K
0.9	-24.28	-9.883	-10.18	-10.23	-48.31	-45.78	-44.18
1.2	-22.95				-43.85	-41.46	-40.00
1.5	-21.92				-40.39	-38.12	-36.76
1.8	-21.08				-37.57	-35.39	-34.12
2.0	-20.59				-35.93	-33.80	-32.58

Symbols used

c_0	[mg/L]	initial concentration of norfloxacin
c_e	[mg/L]	residual concentration at equilibrium
ΔG	[J/mol]	Gibbs free energy change in adsorption
ΔH	[J/mol]	enthalpy change in adsorption
K_f	[-]	parameter indicating the capacity of adsorption
m	[g]	mass of adsorbent used
n	[-]	parameter indicating the intensity of adsorption
Q_e	[mg/g]	residual amount adsorbed at equilibrium
r	[-]	correlative coefficient for the Freundlich model
R	[J/K mol]	gas constant
ΔS	[J/mol K]	entropy change in adsorption
T	[K]	absolute temperature
V	[L]	volume of norfloxacin solution

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