



Short communication

Adsorption removal of pefloxacin from water by halloysite nanotubes



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ABSTRACT

Batch adsorption experiments were carried out for the removal of pefloxacin from water using halloysite nanotubes 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 isotherm adsorption data fit well with Freundlich model, and the kinetic data fit well with the pseudo-second order and the intra-particle diffusion model. Intra-particle diffusion analysis demonstrates that pefloxacin diffuses quickly among the particles at the beginning of the adsorption process, and then the diffusion slows down and stabilizes. Thermodynamic parameters such as ΔG , ΔH and ΔS were also calculated. The negative Gibbs free energy change and the positive enthalpy change indicated the spontaneous and endothermic nature of the adsorption, and the positive entropy change indicated that the adsorption process was aided by increased randomness.

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Introduction

Pefloxacin, 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 inhibitors, which selectively inhibit bacterial DNA synthesis. The potential exists for quantities of these drugs to be excreted as the parent compound or metabolites and enter the environment due to the spreading of manure and its slurry on agricultural land, or direct deposition by grazing livestock [1]. The properties make it difficult to biodegrade pefloxacin or remove pefloxacin from aqueous solution. Among the techniques for removal of pefloxacin 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 a limited amount of the adsorption behaviors of quinolones have been reported [7]. Halloysite nanotube (HNT) is a two-layered aluminosilicate clay mineral, consisting of one alumina octahedron sheet and one silica tetrahedron sheet in 1:1 stoichiometric ratio, which is available in abundance in China as well as other locations around the world [8]. It is chemically similar to kaolin, differing mainly in the morphology of crystals. HNTs possess hollow nanotubular structure in the submicrometer range and large specific surface area [9]. Their novel physical and chemical properties derived from the structural versatility provide opportunities for advanced applications in the fields such as electronics,

catalysis, biological systems and functional materials [10]. 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.

Experimental

Materials

Pefloxacin, obtained from Daming Biotech. Co. Ltd., were further purified by recrystallization from aqueous solutions. After filtration and drying, its purity was determined by UV spectrometry (UV-2401PC, Shimadzu Co. Ltd), to be 0.996 in mass fraction. The structure of pefloxacin is displayed in Fig. 1. H_2SO_4 and NaOH used in experiments were all analytical reagents. The halloysite sample was obtained from Henan province, China. After milled, sieved by 75 μm sieve, dispersed in water for a period of time and sprayed to dry at 473 K, the powder of halloysite nanotubes (HNTs) was refined. The HNTs have an average length of 0.5–2.0 μm , a diameter in the range of 30–80 nm. The inner diameter is more or less 30 nm, while the thickness of the wall is about 8 nm. The BET surface area of HNTs was found to be 83.2 m^2/g by N_2 adsorption isotherm at 77 K using QUADRASORB SI automated surface area analyzer (Quantachrome Corporation, USA).

Methods

The HNTs adsorbent (0.1 g) was placed into 100 mL of pefloxacin solution. The initial concentrations of pefloxacin

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Nomenclature

c_0	initial concentration of pefloxacin (mg/L)
c_e	residual concentration at equilibrium (mg/L)
ΔG	Gibbs free energy change in adsorption (J/mol)
ΔH	enthalpy change in adsorption (J/mol)
k_1	the pseudo-first order rate constant (min^{-1})
k_2	the pseudo-second order rate constant (g/mg/min)
K_f	Freundlich parameters indicating the capacity (L/g)
K_1	Langmuir adsorption constant (L/mg)
k_p	the intra-particle diffusion rate constant (mg/g/ $\text{min}^{1/2}$)
m	mass of adsorbent used (g)
n	Freundlich intensity of adsorption
q_e	amount adsorbed at equilibrium (mg/g)
q_m	monolayer adsorption capacity of the adsorbent (mg/g)
q_t	amounts of pefloxacin (mg/g) adsorbed at time, t
R	gas constant (8.314 J/mol/K)
ΔS	entropy change in adsorption (J/mol/K)
T	temperatures (K)
t	time (min)
V	volume of pefloxacin solution (L)

solutions used were 20, 40, 60, 80, 100 and 120 mg/L. The initial pH values of the pefloxacin solutions were not adjusted. The adsorption experiments were conducted under constant stirring at controlled temperatures for a certain period. The concentrations of pefloxacin in the residual solutions were analyzed by means of the UV spectrometer (UV-2401PC, Shimadzu Co. Ltd) [11]. The wavelength used to analyze the concentrations of the pefloxacin was 281 nm. The adsorption capacities were calculated according to a mass balance of pefloxacin in the solutions and were represented in units of milligrams of pefloxacin 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 pefloxacin (mg/L); V and m are the volume of pefloxacin solution (L) and the mass of adsorbent used (g), respectively.

To quantitatively compare the applicability of each model, a data analysis was carried out using correlation analysis employing least-square method, and the average relative standard error (ARSE, %) is calculated by Eq. (2):

$$\text{ARSE} = 100 \times \sqrt{\frac{\sum_{i=1}^n [(q_{e,\text{exp}} - q_{e,\text{cal}})/q_{e,\text{exp}}]^2}{(n-1)}} \quad (2)$$

where n is the number of data points.

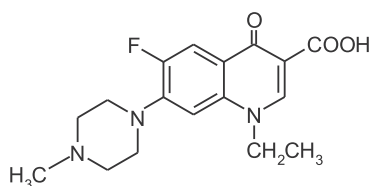


Fig. 1. Molecular structure of pefloxacin.

Results and discussion

Effect of contact time

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

Effect of initial pefloxacin concentration and temperature.

The effects of initial concentration and temperature on the adsorptive removal of pefloxacin by HNTs are shown in Fig. 3. It can be observed that unit adsorption increased while the percentage adsorption decreased with an increase in initial pefloxacin concentration. The pefloxacin ions around adsorbent sites of HNTs became much more with the increase of initial pefloxacin concentration. Hence, the adsorption process was carried out more sufficient resulting in the increase of unit adsorption. It can be found that the maximum adsorption capacity of pefloxacin occurred at 308 K, with the adsorption capacities decreasing in the order 308 K > 303 K > 298 K.

Adsorption equilibrium of pefloxacin on HNTs.

Adsorption isotherms were measured for pefloxacin on HNTs at 298, 303 and 308 K and the results are shown in Fig. 4. It was found that the adsorption capacity of HNTs increased as the concentration of pefloxacin in the water increased and the adsorption capacity tended to increase with increasing temperature. The adsorption isotherms were simulated by Freundlich model [12] and Langmuir model [13], Eqs. (3) and (4):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_1} \left(\frac{1}{c_e} \right) \quad (4)$$

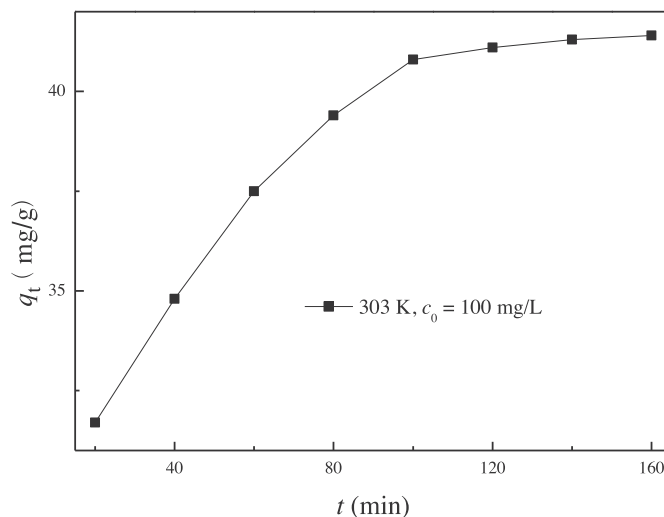


Fig. 2. Effect of contact time on the adsorption of pefloxacin by HNTs.

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