Study on the kinetic and thermodynamic behaviors of adsorption ciprofloxacin on porous carbon

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Abstract. The porous carbon materials were prepared by the following processes of evaporation induction self-assembly (EISA), thermal polymerization process and calcination step at high temperature with the nano-zinc oxide as a hard template and phenol resin as carbon source. The adsorption performance was investigated via removed ciprofloxacin antibiotic. The adsorption temperature showed important for absorption rate of ciprofloxacin with the as-prepared porous carbon. When the adsorption temperature exceeded 40 ℃, the adsorption rate could reach balance in 10 min, The adsorption kinetics and thermodynamics were also discussed.

Introduction

Ciprofloxacin, as one kind of the second generation product of fluoroquinolones, is a broad spectrum macrolide antibiotic, which is widely used for treating people and livestock in bacterial infections [1-2]. Although the medicine was partly metabolized in the body, oral doses as high as 90% was directly excreted. In some ways, antibiotics, which always caused the resistance to drugs, brought the environmental pollution because of discharging in industrial production process [3]. Even if concentrations of ciprofloxacin is low in the sewage or surface water, it could lead to serious drug resistance. These residual antibiotics are hardly removed by the traditional wastewater treatment methods [4-5]. Therefore, the technique and mechanism of removing the antibiotics wastewater is the one of present hot research [6-10]. In this work, we report that the removal of ciprofloxacin using the porous carbon and the thermodynamics and kinetics of adsorption processes through adsorption of ciprofloxacin with as-obtained porous carbon.

Experimental

Porous carbon synthesis: Phenolic resin and F127 of mole ratio 1:1 was fully dissolved in absolute ethyl alcohol and kept stirring for 3 h to dissolve fully under the water bath condition of at 50℃. A certain amount of nano-sized ZnO was uniformly distributed in the above solution, and remained magnetic stirring for 30 min under the water bath condition of at 50℃. Then, the mixed solution was put in the Petri dish and fully evaporated at room temperature. The samples were solidified at 100℃ for 24 h in drying oven, and it was still sequentially solidified for 12 h at 150 ℃. The rough samples were obtained and pulverized uniformly, and the samples were calcined in tube furnace without oxygen at 900℃. At last, the above samples were put into 1mol/L hydrochloric acid solution and stirred 12 h, filtration and drying in the oven at 80℃. The porous carbon was obtained.

Determination of porous carbon adsorption. A certain amount of adsorbent material was put into 100 mL 15mg/L ciprofloxacin solution at room temperature. The sampling analysis was conducted in 10 min interval. The adsorption rate (AR) was calculated by the following formula (1):

$$AR=（1 - A_i/A_0）\times 100\%. \quad (1)$$

Where A_0 is the initial absorbency of ciprofloxacin antibiotics solution and A_i is the absorbance of reaction solution.The factors of experimental parameters initial concentration and temperature on the removal of ciprofloxacin were studied. In study of adsorption kinetics, and the residual amount of ciprofloxacin in the aqueous phase was measured using UV-vis spectrophotometer. The amount of adsorbed (mg/g) at time t was calculated by a mass balance relationship:

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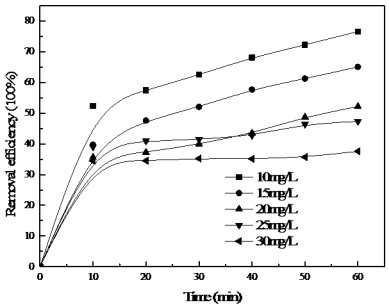
$$Q = \frac{(C_0 - C)V}{W} \quad (2)$$

Where, C_0 is the initial ciprofloxacin concentration (mg/L), C represents the residual concentration in solution at time t (mg/L), V stands the solution volume (L), W is the adsorbent mass of porous carbon (g), and Q is the absorbed amount (mg/g)

Results and discussions

Concentration influence. Figure1 showed the influence of different ciprofloxacin concentrations on adsorption rates, the lower concentration of ciprofloxacin solution, the better adsorption rates under the same conditions. And the adsorption rate for ciprofloxacin gradually reduced with increasing the concentration of ciprofloxacin. The reason can be owe to the higher concentration of ciprofloxacin needs more adsorption sites of surface porous carbon and correspondingly the adsorption rate decreased.



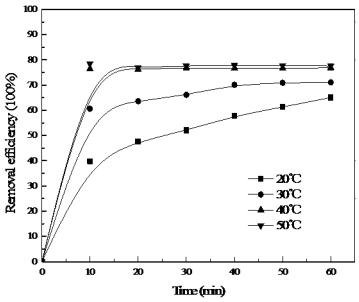


Figure 1 The influence of different concentration Figure 2 The influence of different temperature

Temperature influence. Figure 2 showed the influence of different reaction temperatures. The results indicated that the temperature was important for adsorption performance of ciprofloxacin with as-prepared porous carbon, especially the adsorption equilibrium of ciprofloxacin was fast reached at 40℃ and 50℃ in 10 min. It maybe owe to the molecular thermal motion intensified along with increasing the temperature. As a result, the adsorption rate of ciprofloxacin antibiotics increased. In addition, the adsorption curves of 40℃ and 50℃ showed almost the same adsorption rate in adsorption processes, which proved that temperature did not change porous carbon adsorption efficiency. But it could change adsorption speed rate and make it quickly reach adsorption equilibrium.

Adsorption kinetics. In order to understand the adsorption mechanism of ciprofloxacin onto as-prepared porous carbon, the adsorption process of the ciprofloxacin onto as-prepared porous carbon s was studied as a function of contact time, the result follows the Figure 3-a, obviously, the contact time is the important parameter for the adsorption process [11]. In order to investigate the mechanism of adsorption including mass transport and chemical reaction, the kinetic parameters of the adsorption process were evaluated by using the pseudo-first-order and pseudo-second-order equation. The pseudo-first-order equation is described as Eqs. (3).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where q_e and q_t are the amount of ciprofloxacin onto as-prepared porous carbon at the equilibrium and at contract time t (min), respectively. And k_1 is the pseudo-first-order rate constant. The values of k_1 and q_e are calculated from the plot of ln (q_e - q_t) versus t [12]. The result follows Figure 3-b. The value of correlation coefficient (R^2) obtained is relatively poor (0.43087), indicating that the pseudo-first-order equation is not suitable for expressed the adsorption process.

The kinetic behavior of the adsorption process was further evaluated by the pseudo-second-order equation. The pseudo-second-order equation is described as Eqs. (4).

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

Where k_2 is the pseudo-second-order adsorption rate constant. The values of k_2 and qe were calculated from the slope and intercept of plots of t/q_t versus t [13], the result follows the Figure 9-c. The correlation coefficient, calculated by the pseudo-second-order equation, is 0.97314, implying that the adsorption process is well suitable the pseudo-second-order kinetic equation.

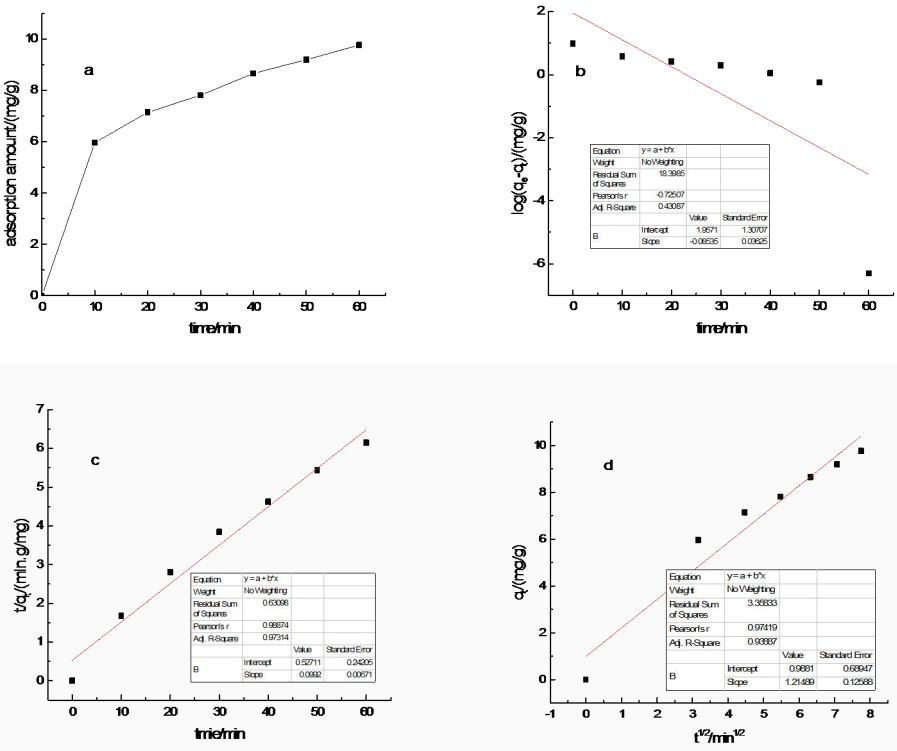


Figure 3 (a) Effect of contact time on the adsorption of ciprofloxacin at room temperature; (b) Plot of log (q_e–q_t) vs t for adsorption of ciprofloxacin onto as-prepared porous carbon by using the pseudo-first-order kinetic equation; (c) Plot of t/q_t vs t for adsorption of ciprofloxacin onto as-prepared porous carbon by using the pseudo-second-order kinetic equation; (d) Plot of q_t vs $t^{1/2}$ for adsorption of ciprofloxacin onto as-prepared porous carbon.

To further understand the adsorption process, the intra-particle diffusion equation was used to express the transport of as-prepared porous carbon from the exterior surface to the pores of the porous carbon [12]. The intra-particle diffusion equation is followed Eqs.(5), the result follows Figure 3-d.

$$q_t = k_3 t^{1/2} + C \qquad (5)$$

From the Figure 3-d, although the linear fitting of intra particle diffusion is well exhibited, which found the R2=0.93887, it does not pass through the origin, indicating that intra particle diffusion is not the rate controlling step of the adsorption process and film diffusion and intra particle diffusion occurred simultaneously [11, 14].

Adsorption isotherms. The Langmuir isotherm model supposes uniform adsorption on the surface, which is used to depict monolayer adsorption on a surface containing a finite number of identical sites [15]. The Langmuir equation is given in the following equation (6):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \qquad (6)$$

Where C_e is the equilibrium concentration of adsorbate in solution (mg/L), Q_e is the equilibrium adsorption capacity (mg/g), Q_m is the Langmuir monolayer adsorption amount, K_L represents the Langmuir constant related to the energy of adsorption. The langmyir isotherm equation is normally used to descript monolayer sorption process, and the results follow the Figure 4.

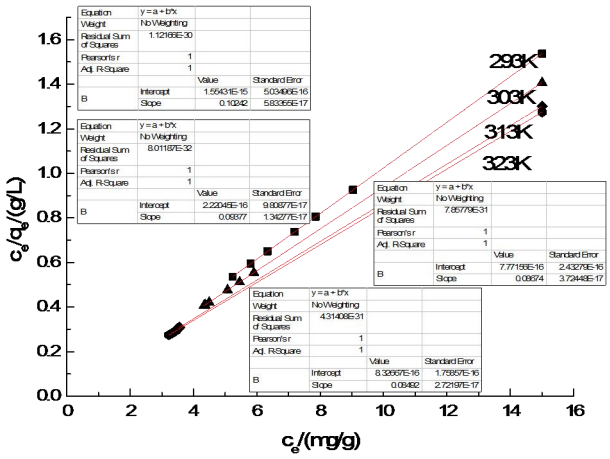


Figure 4 Langmuir isotherms for the adsorption of ciprofloxacin onto as-prepared porous carbon at four different temperatures.

The Freundich isotherm model is given as follows (7) [16]:

$$\log Q_e = \log K_F + n \log C_e \qquad (7)$$

Where K_F is an indicative constant for adsorption capacity of the sorbent (mg/g) and the constant n indicates the intensity of the adsorption, and the results follow the Figure5. Compared the adsorption isotherms of Langmuir and Freundlich equations, it is clearly seen that the isotherm data of ciprofloxacin on the as-prepared porous carbon are well-fitted to Langmuir isothermal equation with high R^2 which reached 1, and it is better than the R^2 of Freundlich equation. Indicting that the Langmuir adsorption equation is better suitable to the adsorption process, it is also descript that the adsorption of ciprofloxacin on the as-prepared porous carbon belong the monolayer adsorption. From the Langmuir and Freundlich equation, it can be clearly found that the adsorption isotherm is well fitted by the Langmuir equation under the low and high temperature. And it is poor fitted by the Freundlich equation under low temperature, but it is suitable the Freundlich equation under the high temperature.

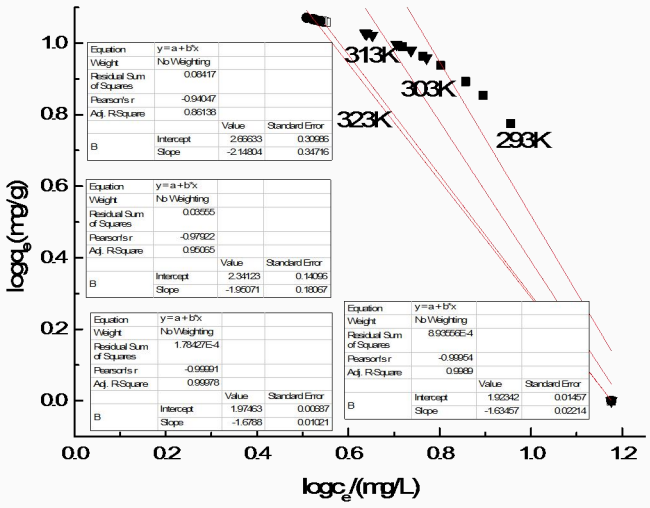


Figure 5 Freundlich isotherms for the adsorption of ciprofloxacin onto as-prepared porous carbon at four different temperatures.

Conclusions

This work mainly showed the adsorption mechanism of ciprofloxacin on porous carbon. The adsorption rate of ciprofloxacin was decreased with increasing the concentration of ciprofloxacin.

Temperature seldom influenced on adsorption rate of ciprofloxacin, but it could affect on adsorption speed. According to analysis of the adsorption data, the adsorption kinetics and thermodynamics of adsorption processes are well fitted the pseudo-second-order kinetic equation and Langmuir equation, respectively.

Acknowledgements

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