Thermodynamics and Kinetics of Bacterial Cellulose Adsorbing Persistent Pollutant from Aqueous Solutions

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Abstract The adsorption capability of bacterial cellulose(BC) for anionic dye acid fuchsine was studied. Meanwhile, the processes of the adsorption were investignted and fitted by adsorption isotherm models, adsorption thermodynamics and adsorption kinetics models, respectively. The changes of BC before and after adsorbing acid fuchsine were investigated *via* scanning electron microscopy(SEM) and Fourier transform infrared spectroscopy(FTIR) to further explain the adsorption mechanism. The results show that acid fuchsine could be effectively adsorbed by BC. The adsorption process was fitted well by Langmuir equation and the pseudo-second order kinetics, indicating that the adsorption process was monolayer molecule adsorption with the main action of chemical adsorption. The adsorption process was spontaneous and endothermic. Glucuronic acid groups and hydroxyl groups were responsible for the adsorption of acid fuchsine on BC.
Keywords Adsorption thermodynamics; Adsorption kinetics; Persistent pollutant; Bacterial cellulose

1 Introduction

Dyes and pigments, which are toxic to human and other worldly livings, have been released into wastewater from various industries with the rapid development of China's industries, and therefore their removal from wastewater has been regarded as an important mission in the last few years[1,2]. Several conventional technologies for dyes and pigments removal from wastewater have been applied, such as chemical coagulation, chemical oxidation, electro-chemistry and biochemistry processes. However, these substances are very difficult to be removed by conventional methods. There are many reasons among which two aspects must be mainly mentioned here. On one hand, dyes and pigments usually have a complex chemical structure; and on the other hand, each of conventional methods has certain degree flaws, such as a large amount of sludge formed in the process of chemical coagulation, a high concentration of the oxidant used in the process of chemical oxidation, high cost and energy in the process of electrochemistry, toxicity from organic dyes and pigments to microbes in biochemical process[3—7]. Adsorption processes using different adsorbents have been reported to be more common in dyes and pigments removal due to their many advantages(rapid absorption rate, low cost, easy operation, no secondary pollution). However, the adsorbents used are very expensive and too difficult to be recycled[8—12]. Therefore, development of economic, effective and new adsorbents has been an urgent demand for social and economic development.

Bacterial cellulose(BC) is long, unbranched polysaccharides, composed of *D*-glucose with β-1,4-glycosidic linkage, whose chemical structure is shown in Fig.1[13—15]. BC has been reported to be a new and effective adsorbent for the separation of heavy metal ions due to its unique properties(high holding-quantity to water, a fine fiber network, high tensile strength, no secondary pollution, high specific surface, high porousity and many hydroxyl groups in the chains)[16—18]. However, the studies on the adsorption properties and mechanism of BC for anion dyes and pigments have rarely been reported.

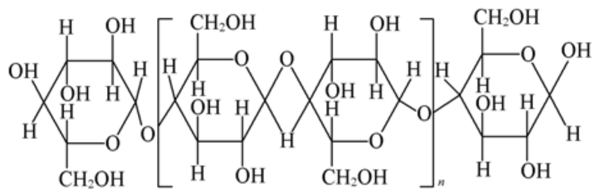

Fig.1 Chemical structure of BC

Acid fuchsine is a typical water-soluble anionic dye and has harmful effects on living organisms. Herein, the factors initial pH and dye concentration and adsorption time, etc. were investigated to analyze the adsorption property of BC for acid fuchsine in the adsorption process. In addition, we fitted the adsorption process by adsorption isotherm, thermodynamics and kinetics to build adsorption models and evaluate adsorption quantity. The changes of BC before and after adsorbing acid

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fuchsine were investigated to further explain the adsorption mechanism using scanning electron microscopy(SEM) and Fourier transform infrared spectroscopy(FTIR).

2 Experimental

2.1 Materials

BC was prepared according to our previous reported methods[19,20]; and acid fuchsine(A. R. grade, $C_{20}H_{17}N_3Na_2O_9S_3$), with chemical structure shown in Fig.2, was bought from Shanghai Dyestuffs Co., Ltd. of China. The experimental solution containing the dye with a certain concentration was obtained by diluting the stock solution with distilled water.

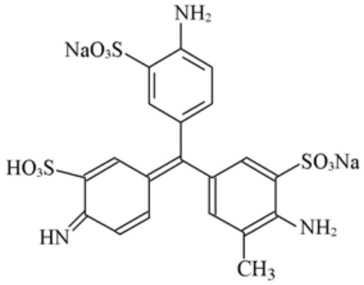

Fig.2 Chemical structure of acid fuchsine

2.2 Adsorption Experimental Methods

The adsorption process was carried out as follows. Briefly, 0.1 g of adsorbent BC was placed in 100 mL of dye aqueous solution with pH adjusted from 1.5 to 5.0, adsorption time ranged from 0 to 180 min and initial concentration of acid fuchsine varied from 0 to 800 mg/L. The concentration of acid fuchsine decreased until the adsorption equilibrium was achieved. The amount of acid fuchsine adsorbed on BC at equilibrium was calculated to evaluate the adsorption quantity(Q, in mg/g) by measuring dye concentration difference before and after adsorption. Dye concentration was measured by a UV-Vis spectrophotometer at the maximum adsorption wavelength of acid fuchsine(*i.e.*, 530 nm). The adsorption quantity was calculated *via* Eq.(1).

$$Q=(c_0-c_t)V/m \quad (1)$$

where c_0(mg/L) and c_t(mg/L) are initial dye concentration before adsorption and dye concentration at time t in the adsorption process, respectively; V(L) is the volume of the solution; and m(g) is the amount of adsorbent.

2.3 Adsorption Isotherm Model

Linear fitting equations of Langmuir, Freundlich and Langmuir-Freundlich(Slips) isotherm models can be expressed as Eqs.(2)—(4), respectively[21].

$$\frac{c_e}{Q_e}=\frac{c_e}{Q_0}+\frac{1}{K_L Q_0} \quad (2)$$

$$\ln Q_e=\ln K_F+n\ln c_e \quad (3)$$

$$\frac{Q_e}{Q_0}=\frac{K_b c_e^n}{1+K_b c_e^n} \quad (4)$$

where c_e(mg/L) is the equilibrium concentration of adsorbate in aqueous solution; Q_e(mg/g) is the equilibrium adsorption quantity of adsorbent; Q_0(mg/g) is the saturated adsorption quantity of dye on adsorbent; K_L(L/g) is the Langmuir constant, which represents adsorption heat in the adsorption process; K_F and n are the constants of Freundlich isotherm model; K_b is the constant of Slips isotherm model.

2.4 Adsorption Thermodynamics

Apparent thermodynamic parameters, ΔG, ΔS and ΔH, can be calculated according Eqs.(5)—(7):

$$\Delta G=-RT\ln K_L \quad (5)$$

$$\Delta H=R\frac{T_1T_2}{T_1-T_2}\ln\frac{K_{L2}}{K_{L1}} \quad (6)$$

$$\lg K_L=\frac{\Delta S}{R}-\frac{\Delta H}{RT} \quad (7)$$

where ΔG(kJ/mol), ΔS(J·mol^{-1}·K^{-1}) and ΔH(kJ/mol) are the changes of Gibbs free energy, entropy, and enthalpy, respectively. K_{L1} and K_{L2} are the constants of Langmuir isotherm model at temperatures T_1(K) and T_2(K), respectively.

2.5 Adsorption Kinetics Model

Lagergren pseudo-first-order and pseudo-second-order equations, Eqs.(8) and (9), are commonly used to further explain the adsorption mechanism of acid fuchsine on BC[21].

$$\ln(Q_e-Q_t)=\ln Q_e-k_1t \quad (8)$$

$$\frac{t}{Q_t}=\frac{1}{k_2Q_e^2}+\frac{t}{Q_e} \quad (9)$$

where Q_t is the adsorption quantity at time t(min); k_1(min^{-1}) and k_2(g·mg^{-1}·min^{-1}) are the constants of pseudo-first-order and pseudo-second-order equations, respectively.

3 Results and Discussion

3.1 Effect of Initial pH on Dye Adsorption

Fig.3 shows that the adsorption quantity of acid fuchsine on BC decreases with the gradual increased pH value due to the fact that the effect of initial pH plays an important role in keeping the active sites of BC and the degree of dye ionization. The change of solution acidity could affect the *zeta* potential of BC surface. As initial pH of dye solution was high, glucuronic acid and hydroxyl groups on BC surface were ionized, resulting

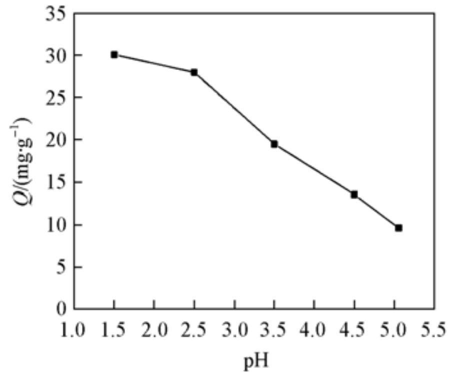

Fig.3 Adsorption curve at different pH values of dye solution

Temperature: 25 °C, t=120 min, c=100 mg/L.

in BC surface to have more negative charges, repelling acid fuchsine and inhibiting adsorption.

$$RCH_2OH \longrightarrow RCH_2O^- + H^+ \quad (10)$$

$$ROH \longrightarrow RO^- + H^+ \quad (11)$$

Both the protonation reactions of glucuronic acid and hydroxyl groups would enhance to endow BC surface with more positive charges that would be favorable for the adsorption with the decreasing of initial pH value(*i.e.*, the increasing of H^+ concentration),

$$RCH_2OH + H^+ \longrightarrow RCH_2OH_2^+ \quad (12)$$

$$ROH + H^+ \longrightarrow ROH_2^+ \quad (13)$$

3.2 Fit and Analysis of Adsorption Isotherm Model

Fig.4 shows the effect of different initial concentration of acid fuchsine in solution on BC adsorbing it, indicating that BC is an efficient adsorbent since an adsorption capacity of over 39 mg/g BC is accomplished after 120 min. It can be seen that the adsorption isotherm curve resembles Langmuir isotherm model. The adsorption quantity increases with the initial dye concentration(from 100 mg/L to 800 mg/L). In the start-up phase, the adsorption quantity is enhanced with the increase of the initial concentration of the dye. After that, the slope of the curve decreases obviously and the curve flattens out, which might be explained by the fact that acid fuchsine adsorbed on the adsorbent and that in aqueous solution tend to repel each other. The adsorption quantity tends to be equilibrated until active sites of BC surface are completely covered by adsorption layer. Therefore, BC could be a promising and effective adsorbent for wastewater treatment. Or, further improved adsorption could be accomplished by modifications, which increase its application.

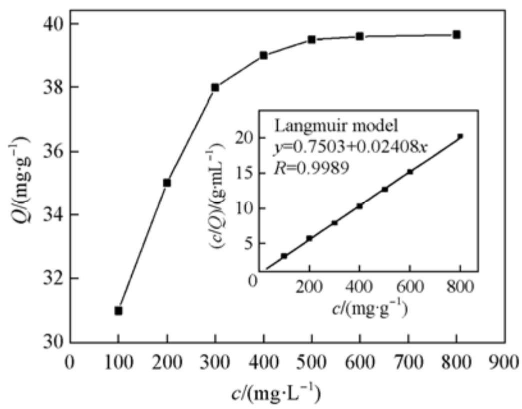

Fig.4 Adsorption curves at different dye initial concentrations

Temperature: 25 °C, t=120 min, pH=1.5. Inset: fitting plot of adsorbing acid fuchsine on BC by Langmuir isotherm model.

It is very important to understand adsorption mechanisms with the aid of equilibrium adsorption isotherms. Thus, the experimental adsorption data for acid fuchsine on BC were fitted by applying the Langmuir, Freundlich and Langmuir-Freundlich isotherm models, which are typically used in adsorption of solid-phase adsorbents(Table 1). The Langmuir, Freundlich and Langmuir-Freundlich adsorption isotherms exhibit an approximately linear relationship for BC adsorbing acid fuchsine. The Langmuir and Slips models show a better relationship between acid fuchsine and BC(R>0.99) than Freundlich model(see Table 1). Therefore, it is realistic to infer that adsorption is limited to monolayer coverage, and intermolecular forces decrease with increasing the distance between the adsorption surface and acid fuchsine.

Table 1 Isotherm constants and values

Langmuir model			Freundlich model			Slips model			
K_L/(L·g^{-1})	Q_0/(mg·g^{-1})	R_L	K_F/(L·g^{-1})	n	R_F	K_b/(L·g^{-1})	Q_0/(mg·g^{-1})	n	R_S
1.03	41.52	0.9989	0.0118	7.29	0.8497	0.75	40.36	1.10	0.9909

Based on the Langmuir isotherm model, absorption strength R_L can be calculated *via* Eq.(14):

$$R_L = 1/(1+K_Lc_0) \quad (14)$$

It is usually thought that when $0<R_L<1$, dyes and pigments are easy to be adsorbed; when $R_L>1$, dyes and pigments are difficult to be adsorbed. K_L(Table 1) is positive to make R_L less than 1, and R_L decreases with increasing the initial concentration of acid fuchsine. It can be illustrated that the adsorption becomes more effective with increasing the initial concentration of acid fuchsine.

3.3 Fit and Analysis of Adsorption Thermodynamics

As illustrated in Table 2, the values of ΔG are negative at different test temperatures, which illustrates the adsorption of acid fuchsine onto BC is spontaneous. Meanwhile that ΔH is positive shows the adsorption process is endothermic. Therefore, increasing temperature could promote the reaction. And that ΔS is positive shows the molecules at solid-liquid interface become more confused than those in solution. It is caused by the fact that molecular volume of acid fuchsine is bigger than that of water molecule. With the adsorption of acid fuchsine on BC solid phase, more water molecules move from solid phase to liquid phase.

Table 2 Thermodynamic parameters

T/K	ΔG/(kJ·mol^{-1})	ΔS/(J·mol^{-1}·K^{-1})	ΔH/(kJ·mol^{-1})
293	–0.05	176.32	53.16
298	–0.78		
308	–4.75		
318	–6.59		

3.4 Fit and Analysis of Adsorption Kinetics Model

Fig.5 shows the typical results of the time-dependent adsorption performance of acid fuchsine on BC. In general, it is shown that adsorption process is divided into three stages (*i.e.*, fast adsorption, slow adsorption and dynamic adsorption equilibrium). In the initial stage, there is a certain amount of adsorption sites on the adsorbent surface to make rapid adsorption. Then adsorption rate is gradually decreased due to the enhanced electrostatic repulsion and decreased concentration difference between the dye on adsorbent and the dye in solution. The adsorption process reaches saturation or equilibrium after 60 min.

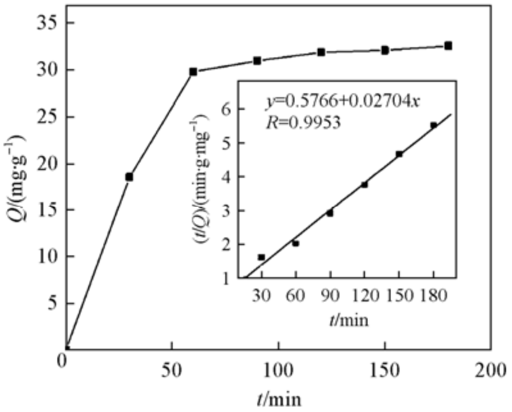

Fig.5 Adsorption curve at different adsorption time
Temperature: 25 °C, c=100 mg/L, pH=1.5. Inset: fitting plot of adsorbing acid fuchsine on BC by pseudo-second-order model.

Adsorption kinetics can be studied to further reveal adsorption mechanism. Adsorption rate can actually reflect the adsorption quantity of adsorbent for adsorbate in unit time, that is, the slope of the tangent line represents instantaneous adsorption rate(dQ_t/dt). According to different adsorption kinetics equations, the fitting parameters and correlation coefficients R values are shown in Table 3. It is very obvious that the correlation coefficient for the pseudo-second-order equation obtained is higher than that for the pseudo-first-order equation. Therefore, physical and chemical adsorptions coexist in the adsorption process, but the chemical adsorption is dominant.

Table 3 Adsorption kinetic constants and values

Pseudo-first-order model			Pseudo-second-order model		
$Q_e/(mg\cdot g^{-1})$	k_1/min^{-1}	R_1	$Q_e/(mg\cdot g^{-1})$	$k_2/(g\cdot mg^{-1}\cdot min^{-1})$	R_2
39.28	–0.029	0.9316	36.98	0.0013	0.9953

3.5 Analysis of SEM Micrographs

Fig.6 presents the SEM micrographs of BC before and after adsorbing acid fuchsine. It is very clear that the structure of BC is composed of an amount of nano-fibers as shown in Fig.6(A). After adsorbing acid fuchsine, the surface of the adsorbent has some grainy or sheet precipitation, illustrating effective adsorption of acid fuchsine onto BC[see Fig.6(B)].

3.6 Analysis of FTIR Spectra

The FTIR spectra(400—4000 cm^{-1}) of BC before and after adsorption are shown in Fig.7. The major peaks of BC before adsorbing acid fuchsine are located at around 3441, 2923 and 1047 cm^{-1}(Fig.7 spectrum *a*), which are attributed to —OH, CH_2—CH and C—O stretching vibrations, respectively. In Fig.7 spectrum *b*, the increased broad peaks at 1375 and 3441 cm^{-1} are obviously observed, indicating the existence of —NH— and —NH_2 on BC after it adsorbing acid fuchsine. Adsorption peaks at 1375 and 1225 cm^{-1} are caused by S═O.

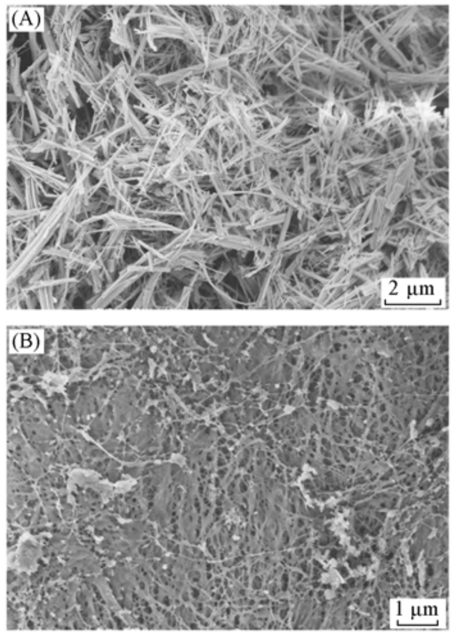

Fig.6 SEM images of BC(A) and BC-acid fuchsine(B)

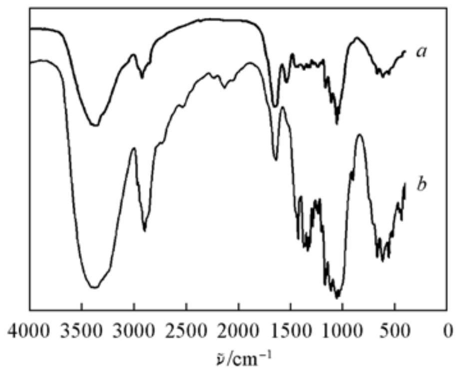

Fig.7 FTIR spectra of BC(*a*) and BC-acid fuchsine(*b*)

4 Conclusions

As a novel and environmentally friendly nano-material, BC could be used to adsorb anionic dye acid fuchsine in future wastewater treatment. pH value is one of the crucial parameters for adsorption efficiency. The adsorption process can be fitted by Langmuir equation and the pseudo-second order kinetics. It is indicated that the adsorption of acid fuchsine onto BC is monolayer molecule adsorption and chemical adsorption. The adsorption process is spontaneous and endothermic. The characteristics of SEM and FTIR also reveal that glucuronic acid groups and hydroxyl groups are responsible for the adsorption of acid fuchsine onto BC.

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