

Thermodynamics and kinetics of adsorption for heavy metal ions from aqueous solutions onto surface amino-bacterial cellulose

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Abstract: Amino-bacterial cellulose (amino-BC) was prepared by chemical modification of bacterial cellulose(BC). The adsorption characteristics and mechanism of amino-BC were studied. The results show that adsorption data can be fitted well by Langmuir equation and the pseudo-second order kinetics, indicating that the adsorption of amino-BC would obey monolayer molecule adsorption and the main action was chemisorption. Meanwhile, the adsorption process was studied by the Elovich equation and the intra-particle diffusion model, indicating that the absorption characteristics of metal ions on amino-BC is controlled by both film diffusion and particle diffusion. The increase of reaction temperature will accelerate the adsorbing rate because of endothermic reaction.

Key words: surface amination; bacterial cellulose; adsorption thermodynamics; adsorption kinetics

1 Introduction

Heavy metals found in low concentration wastewater usually exist in nature. An amount of heavy metals go into the atmosphere, water and soil, leading to seriously environmental contamination due to mining, smelting, processing and commercially manufacture. In the meantime, heavy metal pollution will threaten higher life forms including people, because heavy metals have characteristics of enrichment and refractory in the environment. Therefore, people are more and more concerned with pollution of heavy metals. At present, various technologies, such as chemical precipitation, ion exchange, electrochemical process, and adsorption processes, all have been so far proposed and adopted for the removal of heavy metals from wastewater [1–3], while the technology of adsorption for its rapid absorption, low cost, easy operation, no secondary pollution has been widely used in wastewater treatment and recycling of heavy metal ions [4–7]. Bacterial cellulose (BC) has potential to be used as a new adsorbent for effective separation of heavy metal ions [8–10] due to the unique properties including high water

holding capacity, fine fiber network, and high tensile strength, no secondary pollution, high specific surface, porous and many hydroxyl groups in the chains. However, BC is not suitable for heavy metal ions adsorption because of lower adsorption capacity and poorer selectivity. Therefore, the modification by new functional groups that will improve the adsorption activity of BC has become one of hot topics. The focal point of the BC-modified technique study is in two aspects: adding chemicals in the process of fermentation and chemical treatment of gelatinous membrane [11–13].

In this work, a new absorbent, surface amino-BC, was prepared by chemical modification. The product was characterized and analyzed. Adsorption characteristics of thermodynamics and kinetics were studied and adsorption mechanism was further discussed to set up proper mathematics models to provide theory to support the practical application of amino-BC in the water treatment field.

2 Experimental

2.1 Materials and equipments

BC was prepared according to the reported method

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[10,14]. Materials included $\text{Pb}(\text{NO}_3)_2$, CuSO_4 and CdSO_4 (analytical pure). Equipments included AL204 accurate electronic balance, AA7000 atomic absorption spectrometer, TDL80-2B centrifuge, Nicolet5700 infrared spectroscope, X'Pert Pro X-ray diffractometer and JSM-6390LV scanning electron microscope.

2.2 Methods

2.2.1 Preparation of surface amino-BC

According to the method in Ref. [15], epoxy group bacterial cellulose ether was prepared using BC as raw material. 10 g of Na_2CO_3 was placed into reaction vessel and diluted with water to 100 mL. 0.1000 g of sulphamate and 1.0000 g of epoxy group bacterial cellulose ether were added respectively to react for 2 h in thermostatic oscillator at 50 °C. After amination reaction, the product was washed with clean water to be neutral and was dried under the vacuum condition at 60 °C. The product was amino-BC.

2.2.2 Adsorption

The adsorption process was as follows. 1.0 g of adsorbent amino-BC was placed in 20.00 mL of the solution containing heavy metal ions at pH 5.5 for 60 min. The amount of heavy metal ions adsorbed on amino-BC at equilibrium was calculated to evaluate adsorbent quantity by measuring the difference of heavy metal ions before and after adsorption. And the concentration of heavy metal ions was measured by an atomic absorption spectrophotometer. The adsorption quantity was calculated by Eq. (1).

$$Q = (\rho_0 - \rho_t)V/m \quad (1)$$

where Q is the adsorption quantity of heavy metal ions on adsorbent amino-BC; ρ_0 and ρ_t are initial concentration before adsorption and concentration of heavy metal ions at time t in the adsorption process, respectively; m is the mass of adsorbent; V is the volume of heavy metal ions solution.

2.3 Adsorption isotherms

Linear fitting equations of Langmuir, Freundlich, Slips and Dubinin–Raduskevich isotherm models can be expressed by Eqs. (2)–(5), respectively.

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

$$\ln Q_e = \ln K_f + n \ln \rho_e \quad (3)$$

$$Q_e/Q_0 = K_b \rho_e^n / (1 + K_b \rho_e^n) \quad (4)$$

$$\ln Q_e = \ln Q_0 - B A^2 \quad (5)$$

$$A = RT \ln(1 + 1/\rho_e) \quad (6)$$

where ρ_e is the equilibrium concentration of heavy metal ions in aqueous solution; Q_e is the adsorption capacity of

adsorbent at equilibrium; Q_0 is the saturated adsorption capacity of heavy meta ions on amino-BC; K_L is the Langmuir constant, representing adsorption heat in the adsorption process of adsorbent; K_f and n are the constants of Freundlich isotherm model at a given temperature; K_b is the constant of slips isotherm model; B is the constant of Dubinin–Raduskevich isotherm model, representing average free energy in adsorption process; A is the Polanyi adsorption potential energy, defined as the work done by 1 mol molecular adsorbed from infinity to the distance x between adsorbate and adsorbent surface; R is the mole gas constant; T is the thermodynamic temperature.

2.4 Adsorption thermodynamics

The thermodynamics parameters, ΔG , ΔS and ΔH , can be calculated according to the adsorption equilibrium constant K_L as shown in Eqs. (7)–(9).

$$\Delta G = -RT \ln K_L \quad (7)$$

$$\Delta H = R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{K_{L2}}{K_{L1}} \quad (8)$$

$$\lg K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

where K_{L1} and K_{L2} are constants of Langmuir isotherm model at temperature T_1 and T_2 , respectively.

2.5 Adsorption kinetics models

The adsorption mechanism of heavy metal ions on amino-BC are commonly analyzed using Lagergren pseudo-first-order kinetics, pseudo-second-order kinetics, Elovich equation and intra-particle diffusion equation as follows:

$$\ln(Q_0 - Q_t) = \ln Q_0 - k_1 t \quad (10)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_0^2} + \frac{t}{Q_0} \quad (11)$$

$$Q_t = A + k_e \ln t \quad (12)$$

$$Q_t = k_i t^{1/2} + C \quad (13)$$

where Q_t is adsorption capacity at time t ; k_1 and k_2 are the constants of Lagergren pseudo-first-order and pseudo-second-order kinetics, respectively; k_e and A are the constants of Elovich equation; k_i is the constant of intra-particle diffusion equation; C is the constant of intra-particle diffusion equation.

3 Results and discussion

3.1 Characterization and analysis of BC and amino-BC

BC and amino-BC were characterized by FT-IR, XRD and SEM, respectively to compare differences before and after modification.

FT-IR spectrum is a useful tool to identify functional groups of molecule. The FT-IR spectra (400–4000 cm^{-1}) of BC and amino-BC obtained by surface amination are shown in Fig. 1. The major peak located around 3441 cm^{-1} is attributed to —OH stretching vibration. The characteristic bands at 1047 cm^{-1} , corresponding to C—O—C stretching vibration, are also observed in BC and amino-BC. Besides, compared with the spectrum of BC, the increase of broad peak around 1375 cm^{-1} and 3441 cm^{-1} is observed, indicating the existence of —NH— and —NH_2 in amino-BC.

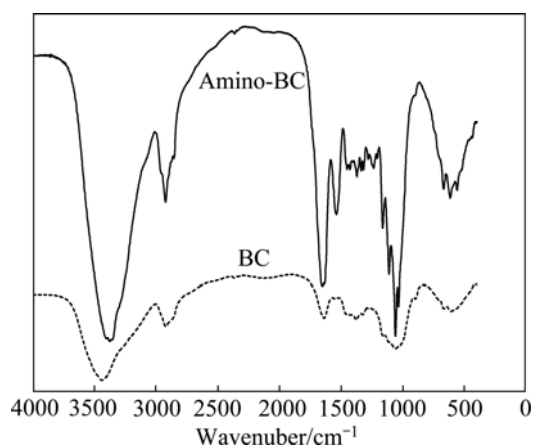


Fig. 1 FI-IR spectra of BC and amino-BC

The degree of crystallinity was smaller than that of BC and crystalline structure was weakened (such as $2\theta=22.5^\circ$) after modification [11] as shown in Fig. 2. This fully shows that if we are trying to improve the accessibility and reactivity of cellulose, it is necessary to alkalinize BC. The larger the accessibility of cellulose is, the lower the degrees of crystallinity and vice-versa are. It is beneficial to decrease the degree of crystallinity of amino-BC by etherification because structure of hydrogen bonding is destroyed. At the same time, adsorption efficiency is improved by the introduction of amidogen into the structure of BC.

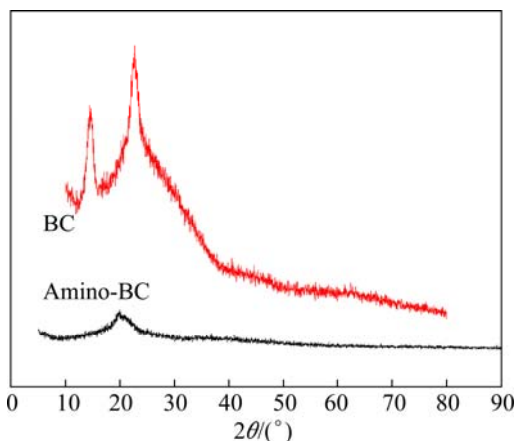


Fig. 2 XRD patterns of BC and amino-BC

The dense network formed with BC is revealed in Fig. 3(a). The width of BC ribbon is 80–100 nm. Compared with BC, amino-BC has a denser network (Fig. 3(b)) and large specific surface area, which would enhance adsorption ability.

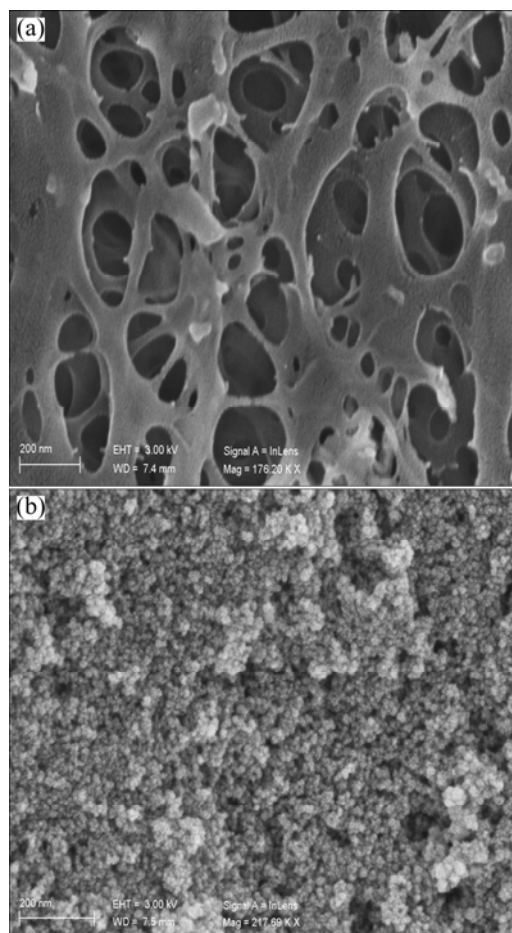


Fig. 3 SEM images of BC (a) and amino-BC (b)

3.2 Research on adsorption thermodynamics

3.2.1 Effect of initial concentration of heavy metal ions

Figure 4 presents that the adsorption capacity of heavy metal ions on amino-BC increases with increasing initial concentration. In the start-up phase the adsorption capacity becomes larger with increasing initial concentration, which is attributed to the fact that the adsorbent and heavy metal ions would meet very often in solution and the possibility of adsorption by amino-BC would be improved. After that the slope of curve decreases obviously and the curve flattens out, which might be explained by the fact that metal ions adsorbed on adsorbent and in solution repel each other. The adsorption capacity tends to be equilibrated until the active sites of amino-BC surface are completely covered by adsorption layer. Therefore, amino-BC could be a potentially effective adsorbent for wastewater containing heavy metal ions.

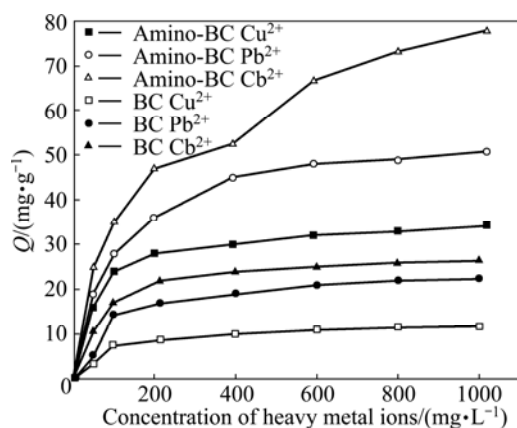


Fig. 4 Effect of initial heavy metal ions concentration on adsorption

3.2.2 Fitting and analysis of adsorption isotherms

It is very important for us to understand adsorption mechanisms by equilibrium adsorption isotherms. Thus, the experimental adsorption data for heavy metal ions on amino-BC were fitted by applying the different equations which are typically used in adsorption of solid-phase adsorbents. And the fitting parameters and correlation coefficients r are shown in Table 1.

Table 1 Fitting parameters of adsorption isotherms models with amino-BC

Model	Parameter	Cu ²⁺	Pb ²⁺	Cd ²⁺
Langmuir	$K_L/(\text{L}\cdot\text{mg}^{-1})$	0.621	1.001	1.106
	$Q_0/(\text{mg}\cdot\text{g}^{-1})$	35.83	55.65	68.57
	r_L	0.9996	0.9998	0.9918
Freundlich	$K_F/(\text{L}\cdot\text{g}^{-1})$	4.131	6.113	6.180
	n	0.2234	0.0914	0.3689
	r_F	0.9619	0.9738	0.9936
Slips	$K_b/(\text{L}\cdot\text{mg}^{-1})$	0.01256	0.01227	0.01521
	$Q_0/(\text{mg}\cdot\text{g}^{-1})$	34.70	56.86	69.85
	n	1.094	1.055	1.578
	r_s	0.9931	0.9989	0.9940
Dubinin-Raduskevich	$Q_0/(\text{mol}\cdot\text{g}^{-1})$	31.34	54.66	60.64
	$B/(\text{mol}^2\cdot\text{J}^{-2})$	3.009^{-4}	3.959^{-4}	4.188^{-4}
	r_D	0.9470	0.9220	0.8598

The Langmuir, Freundlich and Slips adsorption isotherms exhibit an approximately linear relationship for amino-BC. The fitting results of absorption to Cu²⁺ and Pb²⁺ by Langmuir equation are much better than other fitting equations, indicating that adsorption process of amino-BC would obey monolayer molecule adsorption. And fitting results of absorption to Cd²⁺ are much better than those of other fitting equations, indicating that amino-BC has some characteristics of

multiphase and asymmetry because crystallinity decreases during BC etherification modification [12]. The adsorption capacity becomes higher with the increase of the K_F in Freundlich equation; while adsorption process proceeds more easily with decreasing the value of n due to the fact that the adsorption capacity of Cd²⁺ is the maximum and easier to be adsorbed.

3.2.3 Adsorption thermodynamics

As shown in Table 2, K_L increases with the increase in reaction temperature, indicating that adsorption processes are endothermic. ΔH values are positive at different temperatures to account for the endothermic adsorption. According to ΔG values, adsorption to Pb²⁺ and Cd²⁺ is spontaneous in the range of experimental temperature, while adsorption to Cu²⁺ is spontaneous at 308 K.

Table 2 Parameters of adsorption thermodynamics with amino-BC

Ion	T/K	$K_L/(\text{L}\cdot\text{mg}^{-1})$	$\Delta G/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$\Delta H/(\text{kJ}\cdot\text{mol}^{-1})$
Cu ²⁺	293	0.621	1.161		
	298	0.836	0.433	145.4	43.16
	308	1.345	-0.753		
Pb ²⁺	293	1.001	-0.002		
	298	1.489	-0.986	196.7	57.65
	308	1.978	-1.746		
Cd ²⁺	293	1.106	-0.245		
	298	1.813	-1.474	246.5	71.76
	308	2.763	-2.602		

3.3 Research on adsorption kinetics

3.3.1 Effect of absorption time

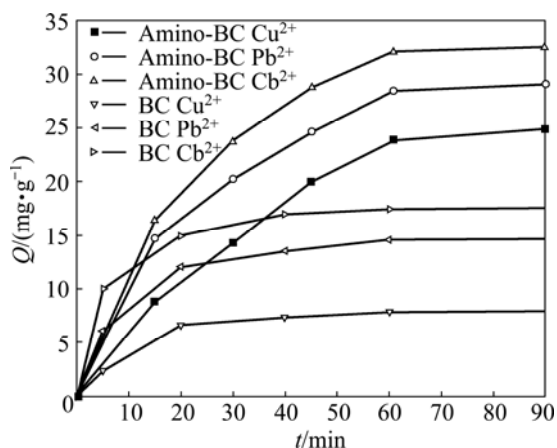
Figure 5 shows the typical results of the time-dependent adsorption performance of BC and amino-BC. The adsorption capacity for heavy metal ions onto BC and amino-BC rapidly increased in the first 30 min and then slowly augmented. The absorption equilibrium has been achieved after more than 60 min, indicating that amino-BC has saturated. Compared with BC, amino-BC has a much higher adsorption capacity, especially for Cd²⁺ adsorption. The results demonstrate that it is beneficial to increase the adsorption quantity by modification of the surface amination on BC. At the same time, the adsorption capacity is greater with the enhancement of the ability to form complex between heavy metal ions and —NH (or —NH₂). It is consistent with the previous research [8].

3.3.2 Fitting of adsorption kinetics

Adsorption kinetics was studied to understand adsorption mechanism of amino-BC. Adsorption rate can actually reflect adsorption capacity of adsorbent in unit time, that is, the slope of the tangent line at the point

Table 3 Fitting parameters of adsorption kinemics with amino-BC

Ion	Lagergren pseudo-first-order			Pseudo-second-order kinetics			Elovich equation			Intra-particle diffusion		
	$Q_0/$ ($\text{mg}\cdot\text{g}^{-1}$)	$k_1/$ min^{-1}	r	$Q_0/$ ($\text{mg}\cdot\text{g}^{-1}$)	$k_2/$ ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	R	A	k_e	r	C	k_i	r
Cu^{2+}	33.12	0.0498	0.9588	41.08	4.66×10^{-4}	0.9757	-17.67	9.733	0.9836	-1.994	3.056	0.9646
Pb^{2+}	36.49	0.0576	0.9583	47.15	1.18×10^{-3}	0.9958	-8.396	8.592	0.9836	5.492	2.691	0.9630
Cd^{2+}	46.22	0.0694	0.9522	52.09	1.17×10^{-3}	0.9952	-9.005	9.645	0.9781	6.850	2.981	0.9443

**Fig. 5** Effect of absorption time on adsorption

represents instantaneous adsorption rate (dQ_t/dt) [13].

Fitting the relationship between adsorption capacities on amino-BC and absorption time by different adsorption kinetic equations is achieved, and the fitting parameters and correlation coefficients r are shown in Table 3.

As illustrated in Table 3, the adsorption capacity of heavy metal ions with different time could be described according to the pseudo-second-order equation, which indicated that both physical and chemical adsorption existed in adsorption process, but chemical adsorption was dominated. The adsorption capacity of Cd^{2+} was the maximum, while that of Cu^{2+} was the minimum. The k_2 values also revealed that adsorption rate was $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$. At the same time, fitting the experimental data also showed that adsorption process kinetics was in good relevance to the particle diffusion equation. The k_i order was $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$, which is the opposite of k_2 . This demonstrated that the faster the adsorption rate on surface of adsorbent is, the slower the diffusion rate of heavy metal ions into inner adsorbent within a long time. At the same time, because C values are not zero, the adsorption process is controlled not only by internal diffusion of particles but by both film diffusion and particle diffusion.

4 Conclusions

1) Adsorption data can be fitted well by Langmuir

equation and the pseudo-second-order kinetics, indicating that the adsorption of amino-BC would obey monolayer molecule adsorption and the main action was a chemisorption.

2) The absorption process of metal ions on amino-BC is controlled by both film diffusion and particle diffusion. And the adsorption process is an endothermic reaction, indicating that the adsorbing rate could be accelerated with the increase of reaction temperature.

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表面氨基化细菌纤维素对水中 重金属离子吸附的热力学与动力学

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摘 要: 以细菌纤维素(BC)为原料, 通过化学改性法制备新型、高效且价廉的吸附材料——表面氨基化细菌纤维素, 并对其进行表征及分析; 同时以 Cu^{2+} 、 Pb^{2+} 和 Cd^{2+} 为研究对象, 对其吸附热力学和动力学特性进行研究, 并探讨吸附机理, 建立数学模型。结果表明: 氨基化细菌纤维素对 Cu^{2+} 、 Pb^{2+} 和 Cd^{2+} 的吸附过程更好地符合 Langmuir 等温方程和准二级反应动力学模型, 说明吸附过程为单分子层吸附, 以化学吸附作用为主。Elovich 方程、粒子内扩散模型也能很好地反映吸附模式, 说明是其吸附液膜扩散和粒子内扩散共同作用的结果。吸附过程是吸热反应, 适当升高反应温度将有利于吸附发生。

关键词: 表面氨基化; 细菌纤维素; 吸附热力学; 吸附动力学

(Edited by Hua YANG)