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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 $Pb(NO_3)_2$, $CuSO_4$ 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).

$$Q = (\rho_0 - \rho_t)V/m \tag{1}$$

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.

$$\frac{\rho_e}{Q_e} = \frac{\rho_e}{Q_0} + \frac{1}{K_L Q_0} \tag{2}$$

$$\ln Q_e = \ln K_f + n \ln \rho_e \tag{3}$$

$$Q_e/Q_0 = K_b \rho_e^n / (1 + K_b \rho_e^n) \tag{4}$$

$$\ln Q_e = \ln Q_0 - BA^2 \tag{5}$$

$$A = RT \ln(1 + 1/\rho_e) \tag{6}$$

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).

$$\Delta G = -RT \ln K_L \tag{7}$$

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

$$\lg K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{9}$$

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:

$$\ln(Q_0 - Q_t) = \ln Q_0 - k_1 t \tag{10}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_0^2} + \frac{t}{Q_0} \tag{11}$$

$$Q_t = A + k_e \ln t \tag{12}$$

$$Q_t = k_i t^{1/2} + C \tag{13}$$

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.