Kinetics of Carboxylated Bagasse Hemicellulose Adsorption to Cd^{2+}

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Abstract. In this paper, Cd^{2+} was absorbed by the carboxylated bagasse hemicellulose, and the kinetics has been studied. The results show that absorption of the carboxylated bagasse hemicelluloses to ions Cd^{2+} can be well described by the pseudo second-order kinetics model. The theoretical value of the maximum absorption capacity $q_{e,cal}$ to ions Cd^{2+} was 29.41 mg/g. In addition, at temperature of 293 K, the pseudo second-order kinetics equation for ions Cd^{2+} adsorption was $dq_t/dt= 0.0433(29.41-q_{t)}^2$.

Introduction

Sugarcane bagasse, a major by-product of sugar industry, is the fibrous residue of sugarcane after the stem was crushed for juice extraction, which was considered an agricultural solid waste but a renewable resource now. Sugarcane bagasse is principally composed of cellulose, hemicellulose (about 28-35 %), and lignin. Hemicellulose has unique chemical structure and is a heterogeneous polymer composed of several different types of monosaccharide.Carboxyl modification of hemicellulose is a modified reaction by introducing carboxyl to the skeleton of hemicellulose. Research has shown that carboxyl introduced on the skeleton of hemicellulose via chemical modification is an active site, which is capable of metal chelating[1-3].

Heavy metal pollution has become a global topic, and cadmium is a significant biological toxicity of heavy metals, which enters the body through the biological enrichment and livestock, causes bone pain, bone defect , natural fractures ,systemic nerve pain and other symptoms. Drinking the water polluted by cadmium for a long time, the human will be kidney damaged, osteomalacia, aches.What′s more,chronic cadmium poisoning can affect the fertility of human.

In this study, Cd2+ absorbed by the carboxylated bagasse hemicellulose was investigated, and the kinetics was detected for providing a scientific basis for the technological extension of the modified bagasse hemicellulose adsorption to heavy metal.

Experiment

Raw Materials and Reagents

Bagasse hemicelluloses were obtained from Nanning Sugar Corperation. The hemicellulose-rich material was ground to pass a 0.7 mm size screen and finally dried in a cabinet oven for 16 h at 50 ℃. Benzene, succinic anhydride, anhydrous alcohol, and N-bromination succinic imide (analysis pure) were purchased from Chengdu Kelong Chemical Factory. The sodium chlorate (80% purity), anhydrous acetic acid (analysis pure), and sodium hydroxide (analysis pure) were supplied by Tianjin Beichen Founder Reagent Plant. N, N-DMF (analysis pure) was purchased from Nanjing Aoduofu Biological Technology Co. Ltd. Cadmium chloride($CdCl_2$) (analysis pure) were supplied by Tianjin Tanggu Chemical Reagent Factory.

Extraction Process

(1) 25 ml of water was added to 1.0 g sugar bagasse. This mixture was heated in a microwave at 1200 W for 20 min. In order to obtain a good solid-liquid separation, 2.0 g sodium hydroxide was added to the mixture following the heating. (2) This solution was allowed to cool down and acetic acid was added to the liquid phase to adjust the pH to 5.1.Once the solution turned turbid, 4 times the volume of 95% ethanol was added to produce large amount of precipitate. (3) Finally, to extract hemicellulose, the precipitate was dried at 50 ℃ for 24 hours[4-6].

Carboxyl Modification

1.0 g dried sugarcane bagasse hemicelluloses and succinic anhydride and N-bromination succinic imide were added into a three-neck flask and mixed using a magnetic stirrer. The flask was then connected to a condensation backflow tube which was attached to link with a drying tube filled with calcium chloride. Finally, sugarcane bagasse hemicelluloses were modified with DMF flowing back. The modified product was filtered and washed for a period time, then dried in the oven at 50 ℃ for 16 h [1].

Preparation of Cd^{2+}Solution

The corresponding masses of $CdCl_2$ was added to 50 mL solution of hexamethylenetetramine at pH 6.0.In order to prepare the analog solution of Cd^{2+},0.1 M NaCl was used to regulate the ionic strength and hexamethylenetetramine was used to maintain proton balance.

Adsorption of Cd^{2+}

Adsorption experiments were conducted to evaluate adsorption capacities of the carboxylated bagasse hemicellulose. The adsorption experiments were conducted in a 25 mL beaker which was equipped with a stirrer. The reaction volume (20 mL) contained 20 mg of the adsorbent. After a certain time, the pH of the solution was adjusted. The equilibrated supernatant was filtered from the polymer. The remaining concentration of metal ions was measured .In the appropriate pH, blank experiment was added to eliminate the precipitation effect of adsorbent.

Calculation of Adsorption Capacity

The adsorption capacity qe (mg/g) was calculated as described by the following Eq.1.

$$q = \frac{(C_i - C_f)V}{m} \qquad (1)$$

where, C_i (mg/L) is the initial metal ion concentration, C_f (mg/L) is the final metal ion concentration, V (L) is the volume of the metal ion solution and m (g) is the mass of adsorbent.

Pseudo Second-Order Kinetics

This research adopted pseudo-second order kinetics to analyze the experimental data, the model can be expressed as Eq.2, and the linear can be expressed as Eq.3[7-10].

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (2)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (3)$$

where, t is the adsorption time (min), q_t and q_e (mg/g) is the amount of metal adsorbed at equilibrium, respectively, and k_2 is the rate constant of pseudo-second order kinetics (g/mg min). The kinetic parameters (q_e and k_2) were calculated from the slope and intercept of the plot t/ q_t by linear regression analysis.

Results and Discussion

Effect of Reaction Time on Carboxylated Bagasse Hemicellulose Adsorption to Cd^{2+}

The adsorption experiments were conducted in a 25 mL beaker. The 20 mL Cd^{2+} simulation solution with a concentration of 350 mg/L was contained as well as 20 mg of the the carboxylated bagasse hemicellulose and the pH of Cd^{2+} simulation was kept at 5.5. The mixture was stirred for 5 h at 293 K. At a certain interval, samples were measured to determine the remaining concentration of metal ions. Blank experiment was added to eliminate the precipitation effect of adsorbent. The effect of reaction time on carboxylated bagasse hemicellulose adsorption to Cd^{2+} was studied and the results were shown in Fig.1.

As shown in Fig.1, adsorption capacity of the carboxylated bagasse hemicellulose for Cd^{2+} was increased with an increase in reaction time. However, the trend flattened out when the adsorption time exceeded 30 min, and was hardly growing when the reaction time was more than 180 min.This is because the adsorption came into the slow adsorption stage after 30 min. The adsorption capacity reached a maximum when the reaction time was 180 min.

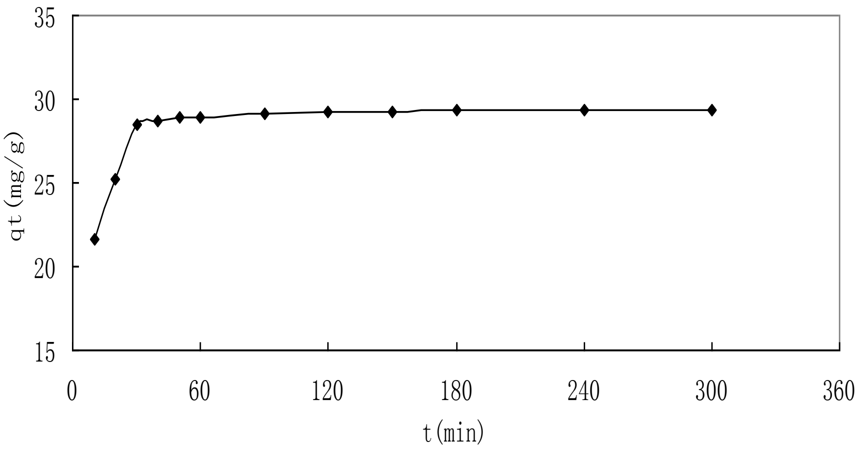

Fig.1 Effect of reaction time on carboxylated bagasse hemicellulose adsorption to Cd^{2+}

Pseudo Second-Order Kinetics Model

At the temperature of 293 K, the obtained experimental data were analyzed by the Pseudo second-order kinetics model. The fitting figure was shown in Fig.2, and the dynamic model was shown in Table 1.

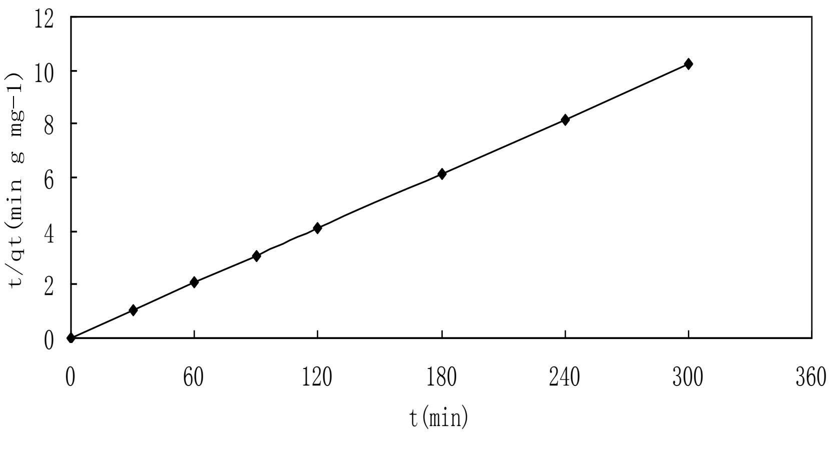

Fig.2 Pseudo second-order kinetics model fitting diagram of carboxylated bagasse hemicellulose adsorption to Cd^{2+}

Tab. 1 Pseudo-second kinetic parameters of carboxylated bagasse hemicellulose adsorption to Cd^{2+}

Metal ion	Fitting curve	R^2	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_2 \times 10^2$ (g/mg min)	RD (%)
Cd^{2+}	y=0.034x+0.0267	1	29.39	29.41	4.33	0.0680

Kinetic studies show that absorption of the carboxylated bagasse hemicelluloses to ions Cd^{2+} can be well described by the Pseudo second-order kinetics model (R^2=1). Based on the fact that the qe,cal (the saturated adsorption capacity of the theoretical value) which was 29.41 mg/g, was very close to qe,exp (the saturated adsorption capacity of the actual measured value, which was 29.39 mg/g), and the small value of RD (relative deviation of qe,expand qe,cal) which was 0.0680%, it is indicated that Pseudo second-kinetic can be used to describe the absorption of the carboxylated bagasse hemicelluloses to ions Cd^{2+}. By taking the parameters of Table 1 into equation (2), we can obtain the Pseudo second-order kinetics model for ions Cd^{2+} : $dq_t/dt = 0.0433(29.41-q_t)^2$ at 293K.

Conclusion

In this paper, Cd^{2+} was absorbed by the carboxylated bagasse hemicellulose, and the kinetics has been studied. The kinetic study shows that absorption of the carboxylated bagasse hemicelluloses to ions Cd^{2+} can be well described by the Pseudo second-order kinetics model. The theoretical value of the maximum absorption capacity $q_{e,cal}$ for ionCd^{2+} was 29.41 mg/g. In addition, at temperature of 293 K, the Pseudo second-order kinetics model for Cd^{2+} is $dq_t/dt = 0.0433(29.41—q_t)^2$.

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References

[1] Lijun WANG, Xinliang LIU, Mengling WENG,Fusheng WU, ZhouJun LI, and Shuangfei WANG. Amphoteric modification of sugarcane bagasse hemicelluloses and characterization of the novel derivatives. Asian Journal of Chemistry. Vol. 25, No.14, (2013) pp. 7660-7664.

[2] Lijun WANG, Xinliang LIU, Mengling WENG,Fusheng WU, ZhouJun LI, and Shuangfei WANG. Carboxyl modification of sugarcane bagasse hemicelluloses with succinic anhydride in aqueous solution. Journal of Testing and Evaluation ,Vol. 41,No.3, 2013,pp 517-524.

[3] Lijun WANG, Liu Xinliang, Zhu Hongxiang, Weng Mengling, Li Zhoujun, Lu Yiguan, Wu Fusheng, Wang Shuangfei.Study on the Effect of Carboxyl Bagasse Hemicellulose on Heavy Metal Adsorption. Advanced Materials Research Vols. 415-417 (2012) pp 1630-1636.

[4] Lijun WANG, Xinliang LIU, Mengling WENG, ZhouJun LI, Fusheng WU, and Shuangfei WANG. Process Optimization of Hemicellulose Lye Extraction from Sugarcane Bagasse. Advanced Materials Research Vols. 581-582 (2012) pp 1206-1212.

[5] Lijun WANG, Xinliang LIU, Mengling WENG,Fusheng WU, ZhouJun LI, and Shuangfei WANG. Extraction of Hemicellulose from sugarcane bagasse under Microwave Radiation. Advanced Materials Research Vols. 634-638 (2013) pp 975-980.

[6] Mathialagan T,Viraraghavan T. Adsorption of cadmium from aqueous solutions by perlite [J].Journal of Hazarddous Materials,2002,94(3):291-303.

[7] Uzun I,Guzel F.Kinetics and thermodynamics of the adsorption of some dyestuffs and p-nitrophenol by chitosan and MCM-chitosan from aqueous solution[J].Journal of Colloid and Interface Science.2004,274(2):398-412.

[8] Sugihara q Shigematsu D S et al.Thermodynamic study on the langmuir adsorption of various bile salts including taurine and glycine conjugates onto graphite in water [J]. 2000,16(4):1825-1833.

[9] Leandro Vinícius Alves Gurgel, L.F.G., "Adsorption of Cu(II), Cd(II) and Pb(II) from aqueous single metal solutions by succinylated twice-mercerized sugarcane bagasse functionalized with triethylenetetramine". Water Res., Vol. 43, 2009, pp. 4479-4488.

[10] HoY.S., Mckay G.Kinetic Models for the Sorption of Dye from Aqueous Solution by Wood[J].Process Safety and Environmental Protection, 1998, 76(2): 183-191.