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Preparation of Polyamine Wheat Straw Cellulose for Adsorption of Cd(II)

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Wheat straw cellulose modified by diethylenetriamine was investigated as an adsorbent for removal of Cd(II) from aqueous solution. The preparing parameters on preparation of polyamine wheat straw cellulose were optimized. The effects of pH, adsorbent dose, contact time and initial concentration on the Cd(II) removal process were studied by using batch methods. The maximum adsorption capacity of adsorption of Cd(II) onto polyamine wheat straw cellulose was found to be 21.37 mg/g and the removal percentage was more than 90 %. The adsorption isotherms were analyzed using the Langmuir and Freundlich isotherms. The results showed that the adsorption process was well described by Langmuir isotherm model with correlation coefficients (R) of 0.9981 for adsorption of Cd(II).

Keywords: Wheat straw cellulose, Polyamine, Adsorption, Cd(II).

INTRODUCTION

Cadmium(II) is a highly toxic element. Removal of Cd(II) in waste water has become urgent issue in environmental protection[1]. A number of methods are available for the removal of Cd(II) such as chemical precipitation, ion exchange resin, electrochemical reduction method and activated carbon adsorption[2,3]. But there are some disadvantages such as high cost and complex operation by using these methods, so application is limited. In recent years, making use of low-cost agricultural wastes as adsorbent for removing of heavy metal ions in waste water has attracted researcher's attention[4,6]. The agricultural wastes such as wheat straw, peanut shell, cotton, corn cob etc. have a natural capacity for adsorption of heavy metal ions because they have some natural group and micro-pore structure for ion-exchange adsorption.

In this paper, the wheat straw cellulose (WSC) was modified by diethylenetriamine to prepare polyamine wheat straw cellulose (PWSC), The absorption of Cd(II) in water by polyamine wheat straw cellulose was tested. The effects of pH, adsorbent dose, initial concentrations of Cd(II) and adsorption time on adsorption of Cd(II) were studied providing theoretical basis for removal of Cd(II) by chemically modified cellulose based agricultural wastes materials. The adsorption properties of polyamine wheat straw cellulose were studied. Isotherm models (Freundlich and Langmuir) were employed to describe the experimental data.

EXPERIMENTAL

Wheat straw, diethylenetriamine (AR), $K_2Cr_2O_7$ (AR), sodium hydroxide (AR) sodium carbonate (AR) and epoxy chloropropane (AR) were used.

Preparation of polyamine wheat straw cellulose: The synthesis route used to obtain polyamine wheat straw cellulose is shown in Fig. 1. The wheat straw (WS) was washed clean, dried and grinded to powder before preparation. Take a certain amount of wheat straw and sodium hydroxide into a flask and mix with some distilled water. After reaction for 2 h at room temperature, drain the filtrate, add 10 % sodium hydroxide solution and a certain amount of epoxy chloropropane into the reaction flask, then heat for 8 h, filter, wash for 1-2 times with acetone, dry at 75 °C after filtering, get epoxidation of wheat straw cellulose (EWSC). After that add epoxidised wheat straw cellulose and diethyl-enetriamine (1:1 by mass) in the reaction flask and add 200 mL water, 2 g sodium carbonate at a certain temperature reaction for 3 h, wash to neutral, dry to constant weight at 75 °C, get polyamine wheat straw cellulose (PWSC).

Preparation of Cd(II) solution: The stock solution containing 1000 mg/L Cd(II) was prepared by dissolving $Cd(NO_3)_2$ in distilled water. Cadmium(II) solutions of different concentrations were prepared for test as required.

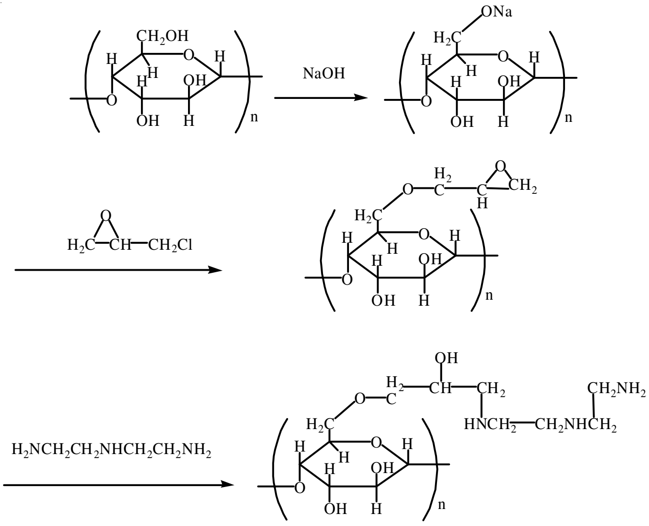

Fig. 1. Synthesis route of polyamine wheat straw cellulose

Static sorption experiments: At room temperature, a different series concentrations of Cd(II) aqueous solution were placed in flasks, The batch experiments were performed with pH varied between 2 to 8, contact time from 20 to 140 min, adsorbent dose from 1 to 14 g and initial concentration from 10 to 100 mg/L. The adsorption isotherm experiments were performed at 180 rpm on a shaker with 1 g of adsorbent in flasks containing Cd(II) solution at various concentrations. The Cd(II) concentrations in the filtrate were determined by FAAS.

The mass percent gain (mpg) of polyamine wheat straw cellulose after preparation process was calculated according to eqn. 1:

$$\text{mpg}\ (\%) = \frac{(m_1\text{-}m_0)}{m_0} \times 100 \quad (1)$$

where m_1 and m_0 are masses of materials after and before the modification, respectively.

The amount of adsorbate adsorbed at time *t* (q_t, mg/g) and the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (q_e, mg/g) were calculated from eqns. 2 and 3.

$$q_t\,(\text{mg/g}) = \frac{(C_0\text{-}C_t)}{m} \times V \quad (2)$$

$$q_e\,(\text{mg/g}) = \frac{(C_0\text{-}C_e)}{m} \times V \quad (3)$$

The removal percentage (R, %) was calculated according to the eqn. 4:

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (4)$$

where C_0 and C_e (mg/L) are the initial and the equilibrium concentrations of Cd(II) in flasks. C_t is the concentrations of Cd(II) in flask at time *t*. V is the volume of the solution (L) and m is the mass of adsorbent used (g).

Equilibrium adsorption isotherms: The Freundlich isotherm model and Langmuir isotherm model were employed to describe the adsorption process. The linearized forms of Freundlich isotherm model and Langmuir isotherm model[7] are given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F and n are Freundlich constants representing the adsorption capacity and intensity of adsorption. The adsorption capacity (K_F) and the adsorption intensity (1/n) are directly obtained from the slope and the intercept of the linear plot of log q_e *versus* log C_e.

Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (6)$$

where q_{max} is the maximum adsorption capacity and b is the equilibrium Langmuir constant related to adsorption energy. A dimensionless constant called separation factor (R_L) describing the essential characteristics of the Langmuir isotherm is calculated using the formula[7]:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where C_0 is the initial concentration of Cd(II). The R_L value indicates the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

RESULTS AND DISCUSSION

Optimization of preparation: The effects of the sodium hydroxide (20-50 g/L), epoxy chloropropane (1-10 mL) and reaction time (1-5 h) on the preparation of polyamine wheat straw cellulose adsorbent were investigated. The results suggested that the mass percent gain was maximum when the sodium hydroxide was 30 g/L, the epoxy chloropropane was 6 mL and the reaction time was 8 h.

Effect of solution pH: The removal of Cd(II) from wastewaters by adsorption is highly dependent on the pH of solution. The solution pH can affect the surface charge of the adsorbent, the degree of ionization and the speciation of Cd(II) ions. When Cd(II) aqueous solution concentration was at 100 mg L^{-1} and volume was 200 mL, contact time was 2 h, The effect of pH on adsorption capacities was investigated in the range 2-8. The results suggested that when pH of aqueous solution was at 4.5, the removal efficiency was maximum. The pH of the solution affects the adsorptive process through protonation and deprotonation of functional groups of the active sites of the adsorbent surface. H^+ competes with metal cations for the available adsorption site. The optimum pH value was found to be 4.5.

Effect of dose: The amount of polyamine wheat straw cellulose adsorbent for Cd(II) removal was studied by changing the dose of adsorbent from 1 to 14 g/L while the concentration of Cd(II) was 100 mg/L and the volume was 200 mL without change (Fig. 2). The results show that the removal percentage of polyamine wheat straw cellulose increases with increasing of the amount of adsorbent at first. When the dose of adsorbent was 6 g/L, the removal percentage was maximum, it was 92.58 %. This is an optimum dosage beyond which the value of efficiency does not significantly change. Because the concentration of initial Cd(II) was fixed and the adsorbent was excessive when the amount of adsorbent over ran the optimum dosage. so when the amount of adsorbent was more than 6 g/L, the equilibrium adsorption capacity did not increase.

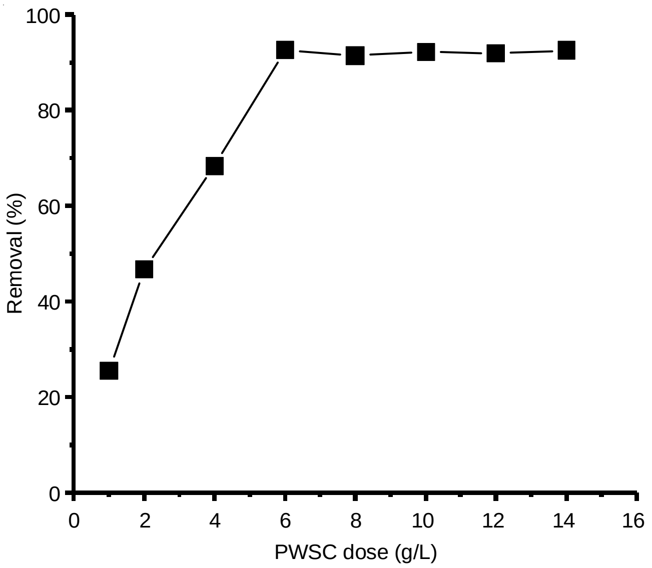

Fig. 2. Effect dose

Effect of time: The effect of contact time on the adsorption of Cd(II) by polyamine wheat straw cellulose is shown in Fig. 3. The adsorption time experiments were carried out for different contact times (20-140 min) with a fixed adsorbent quantity (6 g/L) with 200 mL of 100 mg/L Cd(II) solution at a pH of 4.5.

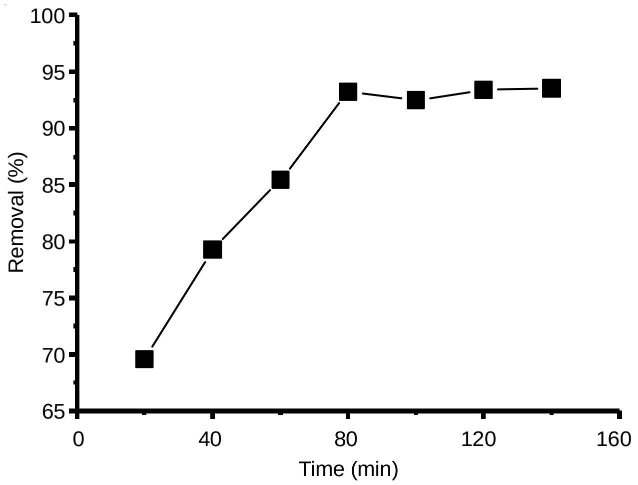

Fig. 3. Effect of time

During short contact times, adsorption was very fast .The removal percentage of Cd(II) increased with contact time. The equilibrium time was achieved after 80 min for Cd(II). While the removal percentage of Cd(II) was 92.25 % and then remained roughly constant to about a adsorption balance. So the absorption time selected was 80 min.

Effect of initial concentration: The removal percentage of Cd(II) by polyamine wheat straw cellulose powder was tested at different initial concentrations (10-100 mg/L) of Cd(II) at a fixed condition adopted above. The results suggested that the Cd(II) adsorption is significantly influenced by the initial concentration of Cd(II) in aqueous solution. The removal percentage was reduced with initial concentration of Cd(II) increasing. It may be due to when the polyamine wheat straw cellulose was added at a certain dose, the active adsorption sites of the absorbent were in certain quantities. When the absorption process reached a balance saturation point, Cd(II) ions in aqueous solutions increased with the initial concentration, so the removal percentage decreased with the increasing of the initial concentration.

Adsorption isotherms: Freundlich isotherm and Langmuir isotherm for Cd(II) adsorption process are shown in Figs. 4 and 5. The related parameters of the isotherms are given in Table-1.

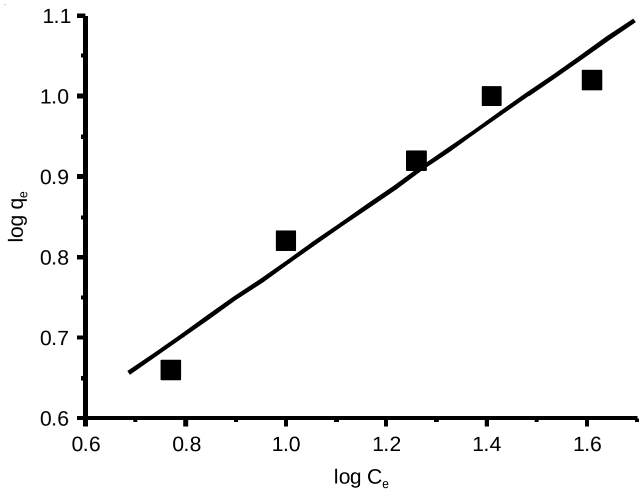

Fig. 4. Fitting of adsorption data with Freundlich isotherm

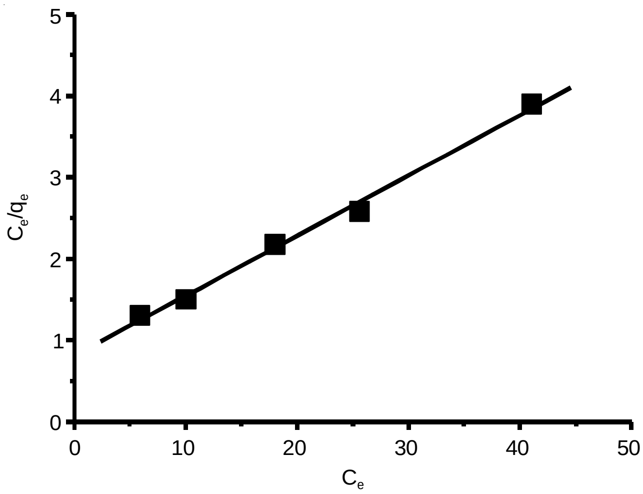

Fig. 5. Fitting of adsorption data with Langmuir isotherm

Investigation of the isothermal characteristics shows that Cd(II) removal by polyamine wheat straw cellulose is in high accordance with Langmuir isotherm by comparing the correlation coefficients (R), Langmuir isotherm provides a good model for the adsorption system which describes a monolayer adsorption onto the surface of the adsorbent with finite number of identical sorption sites. The maximum adsorption capacity of Cd(II) found was 21.37 mg/g, the value of the dimensionless parameter R_L (0.21) indicates that the adsorption is favorable ($0 < R_L < 1$).

Conclusion

In summary, the results described above indicate that the polyamine wheat straw cellulose adsorbent has a good adsorption

TABLE 1
PARAMETERS OF ADSORPTION ISOTHERM MODELS

Freundlich isotherm			Langmuir isotherm			
n	K_F	R	q_{max}(mg/g)	R_L	b	R
2.23	2.15	0.9653	21.37	0.23	0.091	0.9981

capacity for Cd(II) from aqueous solutions. The removal percentage of Cd(II) was more than 90 % and the maximum equilibrium adsorption capacity was 21.37 mg/g, compared with the similar adsorbent[7], the adsorption capacity was improved obviously. The obtained results showed that the Langmuir isotherm model is the best fitting model with the experimental data with high R value. So it can be used for removal of Cd(II) from wastewaters and industrial effluents to overcome water pollution as a highly effective, non-hazardous and low cost adsorbent. Continuing research may lead to the development of green technologies for utilizing cellulose in water pollution treatment area.

ACKNOWLEDGEMENTS

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