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Preparation of Rice Straw Cellulose Xanthate and Study on Its Adsorption Properties of Cadmium(II) from Aqueous Solutions

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Rice straw cellulose xanthate was prepared by modified with carbon disulphide after mercerized by sodium hydroxide solution. The modification parameters (carbon disulphide dose, hydroxide solution concentration, treatment temperature) were studied and optimized in this study. The effects of pH, adsorbent dose and contact time on the removal of Cd(II) ion from aqueous solution was studied. The results suggested that when the initial Cd(II) ion concentration was 20 mg/L, the adsorption capacity of rice straw cellulose xanthate was high effective with the rice straw cellulose xanthate dose was 5.0 g/L and the contact time was 2 h, the equilibrium adsorption capacity of rice straw cellulose xanthate was 3.86 mg/g and the removal rate of Cd(II)ion was 96.41 %. The regeneration capacities of rice straw cellulose xanthate adsorbent was investigated also in this study, the results suggested that the removal rate of Cd(II) ion was more than 76 % after several times of regeneration. All the results suggested that the rice straw cellulose xanthate can be used as a low cost but effective adsorbent for heavy metals removal form aqueous solution.

Keywords: Rice straw cellulose xanthate, Adsorption, Cadmium.

INTRODUCTION

Heavy metal pollution is a big environmental problem in today's world. Among various heavy metals, cadmium is one of the toxic elements. It can be enriched in the human body, mainly stored in the kidney, causing changes of urinary function. Various treatment technologies are using for removal of cadmium in wastewater, including chemical precipitation, adsorption, reverse osmosis, ion exchange, membrane filtration, *etc.*[1,2]. Agricultural waste materials are generally cellulose based fibers. Unmodified cellulose has a certain adsorption capacity. It can be used as an effective, low cost and environmental friendly biosorption material for removal of heavy metal ions in waste water after chemical modification[3,4]. Cellulose has many -OH groups, which can be modified by different reagents to prepare new adsorbent. Through chemical conversion of functional groups which the cellulose fiber itself contains and graft active groups as -NHCO-, -SH, -CS-, $-SO_3H$, -COOH on the carbon chain of cellulose, various of modified cellulose adsorbent can be prepared[5-7]. The advantages of this approach are low prices for raw materials and simple synthesis step, so it is much concern by researchers. There were some reports about synthesis of modified cellulose with natural cellulose. Gong *et al.*[8] have reported that the removal efficiency of rice straw increased to above 93 % after modification. It was effective for removal of heavy metal-ions. This study described a preparation method of rice straw cellulose xanthate (RSCX) modified by carbon disulphide after mercerized by sodium hydroxide. The synthesis conditions were studied and the adsorption properties of RSCX for removal cadmium were investigated in this paper.

EXPERIMENTAL

Synthesis mechanism: The synthesis reaction mechanism is shown as Fig. 1.

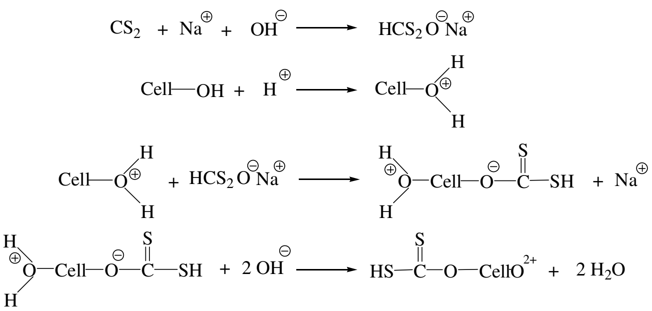

Fig. 1. Synthesis reaction mechanism of rice straw cellulose xanthate (RSCX)

Rice straw, sodium hydroxide, carbon disulfide, hydrochloric acid, cadmium sulfate, methylbenzene, 16-cetyltrimethyl ammonium bromide; boric acid; phenyl fluorine were obtained and used as supplied.

Equipments: UV-Spectrophotometer.

Preparation of mercerized rice straw: The rice straws was soaked for 24 h with water at first, washing clean, drying and grinding it, storage for use. Then using a certain amount of sodium hydroxide solution to soak rice straw powder for 4 h and filter it, washing and drying rice straw powder, got mercerized rice straw cellulose.

Preparation of rice straws xanthate: Take 5 g mercerized rice straw cellulose into a beaker, add a quantitative of carbon disulfide and 100 mL methylbenzene, mixing for awhile, pumping filter, then washing the filter pump with distilled water repeatedly to neutral, drying at 50 ºC to get rice straws cellulose xanthate.

Sorption experiments: Cd(II) standard solution was prepared at a concentration of 1 g/L for testing. Each time take a certain concentration of Cd(II) solution 200 mL in 500 mL beakers. Adding a certain amount of absorbent, adjust the pH, using the thermostatical oscillator, oscillated at a certain temperature and contact time, then filter, take the filtrate. With phenylfluorone (PF) for colour reagent, 16-cetyltrimethyl ammonium bromide (CTMAB) for sensitizer, then determination of Cd(II) content by Spectrophotometric method.

The mass per cent gain (MPG) was calculated according to eqn. 1, the equilibrium adsorption capacity (Q_e, mg/g) and removal percentage (R_p, %) were calculated according to the eqns. 2 and 3.

The mass per cent gain (MPG %)

$$= \frac{(M_1 - M_0)}{M_0} \times 100\ \% \qquad (1)$$

where $M_1$and M_0 are masses of materials after and before the modification, respectively.

$$\text{The adsorption capacity } (Q_e,\ \text{mg/g}) = (C_0 - C_1) \times \frac{V}{m} \qquad (2)$$

$$\text{The removal percentage } (R_p,\ \%) = \frac{(C_0 - C_1)}{C_0} \times 100\ \% \qquad (3)$$

where C_1 and C_0 are concentrations of Cd(II) aqueous solution after and before the absorption, respectively. m is the mass of absorbent.

RESULTS AND DISCUSSION

Effect of CS_2 amount on preparation: The carbon disulfide amount on preparation of RSCX adsorbent was investigated. The result was shown in Fig. 2. As the Fig. 2 show, the mass per cent gain was increased with carbon disulfide amount. When carbon disulfide amount was 20 mL, the mass per cent gain of RSCX adsorbent was maximum. Excessive amount of carbon disulfide would cause subsidiary reaction. It is not benefit to the primary reaction and reduces the productive rate of preparation.

Effect of reaction time and temperature on mass per cent gain: The effect of reaction time was 0.5-2.0 h and temperature was 20-40 ºC on the preparation of RSCX adsorbent was investigated. The result was shown in Fig. 3. As the Fig. 3 shows, the result indicated that the mass per cent gain was maximum when the reaction time was 1.25 h and the temperature was 30 ºC.

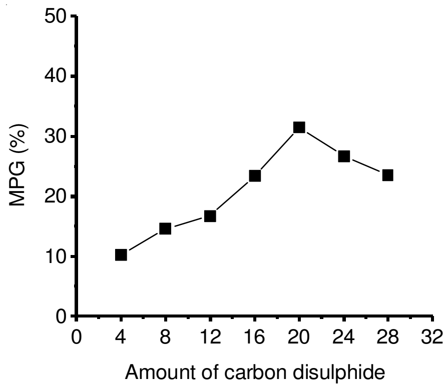

Fig. 2. Effect of CS_2 amount on mass per cent gain

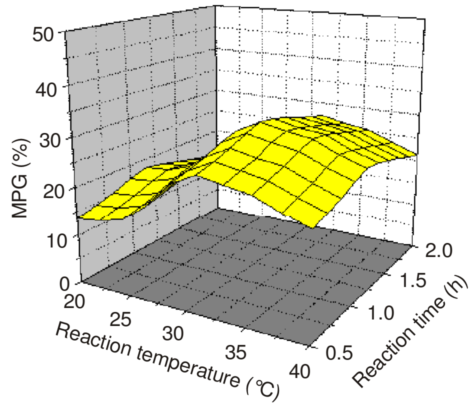

Fig. 3. Effect of reaction time and temperature on mass per cent gain

Effect of pH: The removal percentage of Cd(II) ion from aqueous solution by adsorption is highly dependent on the pH of solution. The variation of pH can affect the surface charge of the adsorbent. The effect of pH on adsorption capacities of Cd^{2+} was investigated by varying the initial pHs of the solutions with different pH intervals which depend on the Cd^{2+}. The pH of the solution affects the adsorptive process through protonation and deprotonation of functional groups of the active sites of the adsorbent surface. When pH values was at 5.6, the removal rate of Cd^{2+} was maximum.

Effect of adsorbent dose: The percentage of Cd^{2+} adsorption capacity (Q_e, mg/g) of RSCX adsorbent was studied by changing the amount of adsorbent from 0.2 to 2.0 g while the concentration of Cd^{2+} was 20 mg/L and the volume of Cd(II)ion aqueous was 200 mL and contact time was 2 h without change. The result is shown in Fig. 4. The adsorption capacity of RSCX increased with the increasing of the adsorbent dose at first. And when the dose of adsorbent was above 1.0 g (5 g/L for Cd^{2+} solution), the percentage of Cd^{2+} removal was 96.41 % and the max equilibrium adsorption capacity was 3.86 mg/g.

Effect of contact time: The adsorption equilibrium time experiments were carried out for different contact times with a fixed adsorbent quantity (1.0 g) with 200 mL of 20 mg/L Cd^{2+} solution at a pH of 5.6, The result was shown in Fig. 5. The result shows that the adsorption equilibrium capacity of Cd^{2+} increased with contact time up. After 2 h the equilibrium time was achieved.

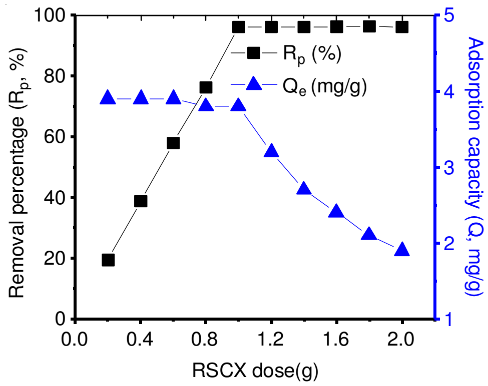

Fig. 4. Effect of RSCX dose on removal percentage and adsorption capacity

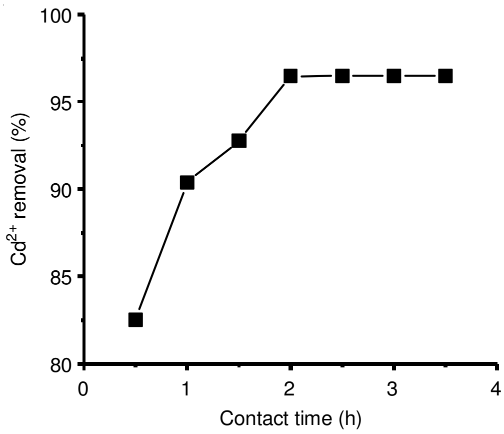

Fig. 5. Effect of contact time on removal rate of Cd^{2+}

Comparison studies: The adsorption capacity of RSCX and rice straw adsorbent for removal of Cd^{2+} from aqueous solutions was investigated in this study with a fixed condition (1.0 g adsorbent for 200 mL of 20 mg/L Cd^{2+} solution at room temperature with pH of 5.6 and contact time of 2 h). The results suggested that the Q_e and R_p of RSCX were 3.86 mg/g and 96.41 %, respectively. And the Q_e and R_p of rice straw were 2.95 mg/g and 73.75 %, respectively. It is obvious that the modified rice straw adsorbent possesses superior performance of heavy metal adsorption over unmodified rice straw adsorbent.

Desorption studies: The regenerated property of RSCX was studied in this paper. The RSCX adsorbent was washing with 10-20 % hydrochloric acid solution and at 20-35 ºC by using water bath after first adsorption. The adsorption capacity was 3.28 mg/g at the second time for Cd^{2+}, it was 85 % of first adsorption. After the RSCX adsorbent was regenerated for several times, the adsorption capacity was more than 76 % of first adsorption. Therefore, the RSCX adsorbent can be regenerated and reused for a potential agriculture waste based adsorbent for removal of heavy ion from aqueous solution.

Conclusion

In summary, the RSCX adsorbent has a good adsorption capacity for Cd^{2+} from aqueous solutions. The removal rate of Cd^{2+} was 96.41 % and the maximum adsorption capacity was 3.86 mg/g with a initial concentration of Cd^{2+} was 20 mg/L and contact time was 2 h. The results shown that the RSCX was a effective adsorbent for removal of Cd^{2+}. It can be used for removal of Cd^{2+} in wastewater as a low cost and effective biosorbent in the future.

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