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Removal of Pb^{2+} from Aqueous Solutions by Rice Hull Adsorbent Modified with Citric Acid Anhydride

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Rice hull was chemically modified by reacting with citric acid anhydride after microwave pretreatment to prepare carboxylate functionalized rice hull adsorbent for removal of Pb^{2+} from aqueous solutions. The preparing conditions were optimized in this study. And the effects of carboxylate functionalized rice hull dosage, pH, contact time and initial Pb^{2+} concentration in aqueous solutions on the removal efficiency of Pb^{2+} from aqueous solutions was studied. The results indicated that when the initial Pb^{2+} concentration was 100 mg/L. The adsorption capacity of carboxylate functionalized rice hull was high effective with the carboxylate functionalized rice hull dose was 8 g/L, pH was 4.5 and the contact time was 100 min at room temperature. The equilibrium adsorption capacity of carboxylate functionalized rice hull was 11.45 mg/g and the removal rate of Pb^{2+} was 91.60 %. All the results indicated that the carboxylate functionalized rice hull was a effective adsorbent for removal of Pb^{2+} form aqueous solutions.

Keywords: Rice hull, Carboxyl functionalized, Adsorption, Lead.

INTRODUCTION

In recent times, heavy metal pollution is the most important problems that causing many public health problems. Industrial waste waters contain many heavy metals such as lead, copper, cadmium, mercury, chromium, *etc.*, which discharge into environment directly without treatment would cause serious environmental pollution[1]. There are many traditional methods for removal of heavy metal ion such as chemical precipitation, electrolysis, ion exchange resin and activated carbon adsorption method, *etc.*[2,3]. But these methods have some disadvantages such as low efficiency, high cost and complicated operation. So many researchers are working on development of low cost but efficient method for removal of heavy metal ions from aqueous. At present adsorption onto agro-based waste is considered as one of the most promising techniques for removal of heavy metals from aqueous solutions[4,5]. The agro-base cellulose contains a number of hydroxyls and other chemical groups; which can be modified by various methods to increase its adsorption capacities through grafted chemical functional groups such as carboxyl, amino, xanthate, phenolics and, or phosphate groups[6,7]. Rice hull (RH) is a kind of agriculture waste material with natural lignocellulose; which have some ion adsorption properties and can be improved by chemical modified methodology. Vyas *et al.*[8] have reported that the adsorption capacity of raw rice husk increased from 11.57 to 13.73 mg/g after modification. In this paper, rice hull was modified by etherification reacting with citric acid anhydride after pretreated by microwave to get carboxyl functionalized rice hull (CFRH), which can be use for removal of Pb^{2+} ion from aqueous solutions. The adsorption properties of CFRH were studied. The results suggested that the CFRH was a high efficiency adsorbent for removal of Pb^{2+} from aqueous solutions.

EXPERIMENTAL

Rice hull, citric acid, pyridine, sodium bicarbonate, 95 % ethanol, lead sulphate were obtained and used as suplied.

Preparation of carboxylate functionalized rice hull: The rice hull was washed clean, dried and grinded to powder before preparation, Take 10 g rice hull into a microwave oven for pretreatment with 15 min at 750 w then take the rice hull powder into a round-bottom flask, add a quantitative citric acid anhydride, mixing for awhile, heating for 2 h with pyridine circumfluence. After reaction, cooled down to room temperature and filtering washing with water and ethanol. Then take the product into a blast oven for drying at 60 ºC for 12 h then soaked with saturated sodium bicarbonate solution for 0.5 h filter it after washing with distilled water and ethanol. Drying at 60 ºC for 12 h, the product was carboxylate functionalized rice hull (Fig. 1).

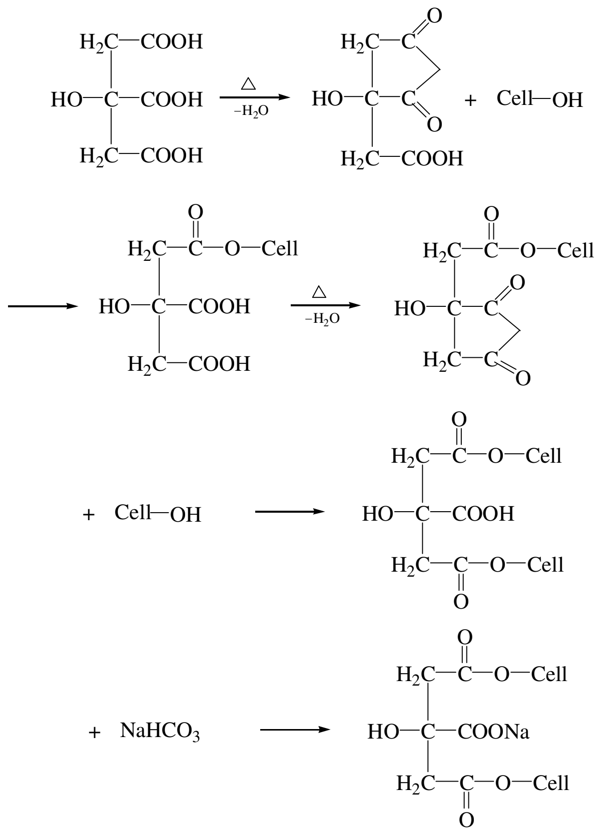

Fig. 1. Synthesis route of carboxylate functionalized rice hull

Preparation of Pb^{2+} aqueous solution: The stock solution containing 1000 mg/L Pb^{2+} was prepared by dissolving a known quantity of lead sulphate ($PbSO_4$) in distilled water. This stock solution was diluted as required to obtain the working solutions containing 50-200 mg/L Pb^{2+}. The solution pH was adjusted by HCl or NaOH solutions.

Batch adsorption studies: Batch adsorption studies were carried out by mixing 2-14 g/L adsorbent with a different series concentration of Pb^{2+} solution in 100 mL conical flasks in a temperature controlled shaker with constant shaking for a certain amount of time. Then the mixtures were filtered out and a Pb^{2+} concentration in the filtrate was determined by flame atomic absorption spectroscopy.

Data evaluation: Mass per cent gain (MPG) after preparation process was calculated according to eqn. 1, the adsorption capacity (Q, mg/g) and removal efficiency (RE, %) were calculated according to the eqns. 2 and 3.

$$\text{The mass per cent gain (MPG \%)} = \frac{(M_1 - M_0)}{M_0} \times 100\ \% \quad (1)$$

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

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

$$\text{The removal efficiency (RE, \%)} = \frac{(C_0 - C_1)}{C_0} \times 100\ \% \quad (3)$$

where C_1 and C_0 are concentrations of Pb^{2+} aqueous after and before the absorption, respectively. m is the mass of absorbent.

RESULTS AND DISCUSSION

Optimization of preparation: The citric acid anhydride concentration (5 to 20 g/L) and microwave power (600-800 w) and reaction time (1 to 3 h) were important factor influencing the modification process. There parameters of the preparation of CFRH adsorbent was investigated through response surface methodology by Design-Expert software. The results are shown in Figs. 2 and 3. The results suggested that the mass per cent gain was maximum when the citric acid anhydride concentration was 12.5 g/L, the microwave power was 700 w and the reaction time was 2 h. At the optimize conditions, the mass per cent gain was 24.03-28.32 %.

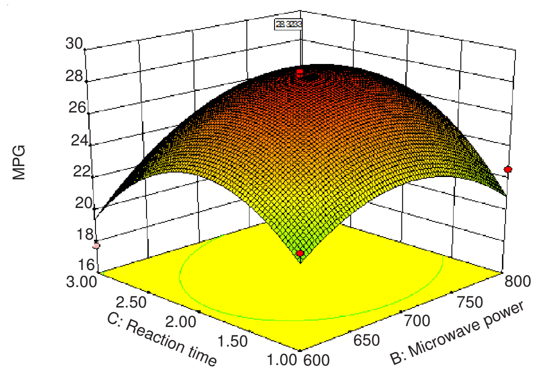

Fig. 2. Effect of reaction time and microwave power on mass per cent gain

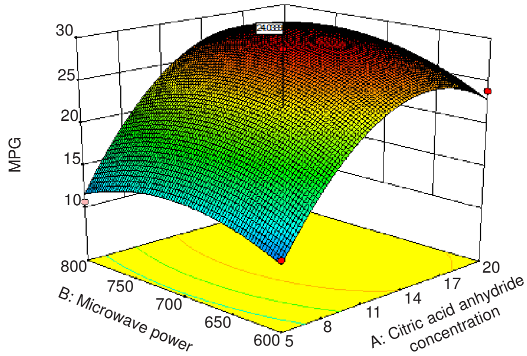

Fig. 3. Effect of microwave power and citric acid anhydride concentration on MPG

Effect of pH: One of the important factors affecting adsorption of metal ions is pH of solution. When aqueous solution of Pb^{2+} concentration was at 100 mg L^{-1} and volume was 100 mL, contact time was 2 h, the effect of pH on adsorption capacities was investigated in the range 2-7. The results suggested that when pH of the 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 whereas activate at higher pH. So the optimum pH value was found to be 4.5.

Effect of dosage of carboxylate functionalized rice hull on adsorption: The removal efficiency (RE, %) and adsorption capacity (Q, mg/g) of CFRH adsorbent for Pb^{2+} was studied by changing the dose of adsorbent from 2-16 g/L while the concentration of Pb^{2+} was 100 mg/L and the volume was 100 mL without change (Fig. 4). The results show that the removal

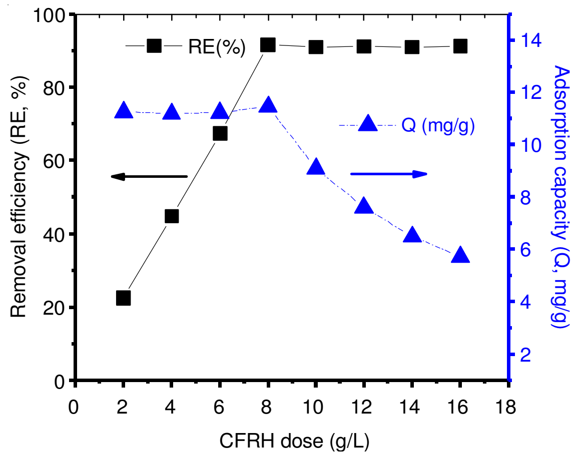

Fig. 4. Effect of CFRH dose on RE and Q

efficiency of CFRH increase with increasing of the amount of adsorbent at first. And when the dose of adsorbent was 8 g/L, the removal efficiency was maximum, it was 91.60 % when the amount of adsorbent was more than 8 g/L and the equilibrium adsorption capacity was 11.45 mg/g.

Effect of contact time: The adsorption equilibrium time experiments were carried out for different contact times with a fixed adsorbent quantity (0.8 g) with 100 mL of 100 mg/L Pb^{2+} solution at a pH of 4.5, The result (Fig. 5) suggested that the removal efficiency of Pb^{2+} increased with contact time up. The equilibrium time was achieved after 100 min for Pb^{2+}. While the time was at 100 min, the removal rate of Pb^{2+} by CFRH was at 91.23 %, it was the highest point in the teat and then remained roughly constant to about a adsorption balance. so the absorption time was selected of 100 min.

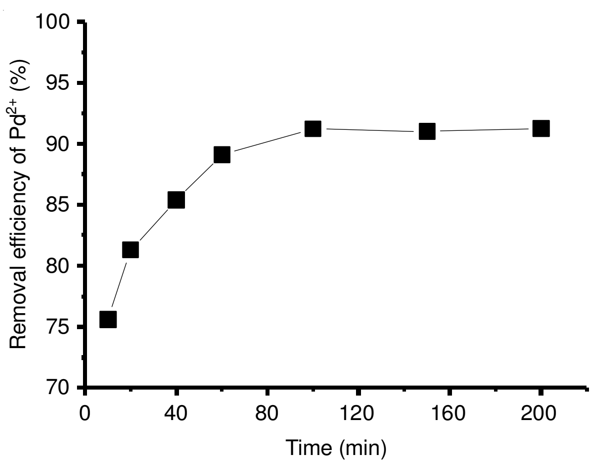

Fig. 5. Effect of time

Effect of initial concentration: The removal efficiency of Pb^{2+} by CFRH powder was tested at different initial concentrations of Pb^{2+} at fixed conditions which adopted above. The results suggested that the removal efficiency was reduced with initial concentration of Pb^{2+} increasing. It may due to when the CFRH added at a certain dose, the active adsorption sites of the absorbent was in a certain quantities for removal of a certain amount of Pb^{2+} ions. When the absorption process reached a balance saturation point, Pb^{2+} in aqueous solutions increased with the initial concentrations continuously increased.

Compared with rice hull: The removal efficiency and adsorption capacity of CFRH and rice hull were tested at a fixed condition (8 g/L adsorbent for 100 mL of 100 mg/L Pb^{2+} solution at room temperature with pH of 4.5 and contact time of 2 h), resulting in the adsorption capacity and removal efficiency of 11.45 mg/g and 91.60 %, respectively. It is more than 30 % improvement compared with unmodified rice hull adsorbent with adsorption capacity and removal efficiency was 8.86 mg/g and 70.88 %, respectively.

Conclusion

The results indicated that the CFRH adsorbent has a good adsorption capacity for Pb^{2+} from aqueous solutions. The removal efficiency of Pb^{2+} was more than 90 % and the equilibrium adsorption capacity was 11.45 mg/g. So the modified rice hull adsorbent can be used for removal of Pb^{2+} from wastewaters and industrial effluents to overcome water pollution as a high effective, non-hazardous and low cost agro-waste adsorbent.

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