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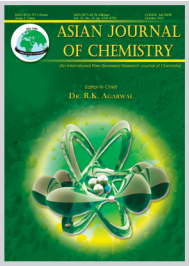

Adsorption of Copper Ions on the Crosslinked Chitosan Resin†

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Chemically modified chitosan using glutaraldehyde as crosslinking agent has been use for the adsorption of cupper ions in aqueous medium. The adsorption capacity of crosslinked chitosan resin increased with increasing temperature indicating the endothermic nature of adsorption process. The adsorption process is found to follow the pseudo-first-order kinetic model. IR analysis showed that Schiff base reaction was occurred between the carbonyl group of glutaraldehyde and amine group of chitosan.

Key Words: Glutaraldehyde, Crosslinked chitosan, Copper ions, Adsorption.

INTRODUCTION

Chitosan has been described as suitable natural biopolymer for collection of metal ions, since the amino group and hydroxyl group on the chitosan chain can act as chelation sites for metal ions. However, chitosan is soluble in dilute organic acids, such as formic acid, acetic acid and the like. Therefore, various physical and chemical modifications have been developed to improve the chemical stability of chitosan in acid media and in its resistance to biochemical and microbiological degradation[1,2]. Although the crosslinking process may reduce the adsorption capacity of chitosan, it can enhance the resistance of chitosan against acidic solutions.

In the present work, the crosslinked chitosan was synthesized glutaraldehyde as crosslinking agent. The adsorption kinetic of crosslinked chitosan at different temperatures was investigated.

EXPERIMENTAL

Chitosan was purchased from Huantai Jinhu Carapace Product Co. Ltd. (Zibo, China), with deacetylation percentage of *ca.* 95 %. Glutaraldehyde obtained from Shanghai Chemical Reagents Co. (Shanghai, China) was analytical reagent grade. All other chemicals were of anlytical reagent grade.

Glutaraldehyde cross linked chitosan: The solution of chitosan was prepared with 3 g of chitosan dissolved into 250 mL of acetic acid (5 %, v/v) and diluted with distilled water. Glutaraldehyde solution was added into the mixture was stirred for 8 h at room temperature. Then 50 mL of 2 M sodium hydroxide solution was added into the mixture to form the precipitate. The precipitate was filtered and washed intensively with distilled water to remove any unreacted glutaraldehyde. Subsequently, it was dried on the vacuum oven for 8 h.

Adsorption isotherms: The different concentrations ratio of $CuSO_4$ diluted solutionand absorbances were detected by UV spectrophotometer at 794 nm wavelength, the liquid water as the reference test, obtaining the standard absorbance concentration curve. Adsorption isotherms were studied at 0.014 mol/L concentration of Cu^{2+} and the experiments were conducted at different temperature in range 20-40 ºC.

RESULTS AND DISCUSSION

Infrared spectra of chitosan, cross linked chitosan, crosslinked chitosan with Cu^{2+} are shown in Fig. 1. The new sharp peak at 1610 cm^{-1} represents stretching vibrations of C=N in Schiff's base formed by the reaction of glutaraldehyde and chitosan. The absorbance of cross linked chitosan with Cu^{2+} at the 3422 cm^{-1} (NH stretching peak) is significantly lower than the crosslinked chitosan, indicatinga cross-linking substances complex be formed after adsorption.

Adsorption equilibria of Cu^{2+} at different temperature: The adsorption capacityof crosslinked chitosan is influenced by the pH value of solution. The adsorption of copper is better at pH value of 6, this result is consistent with previous studies[3,4]. The following experiments are controlled by the pH value of 6.

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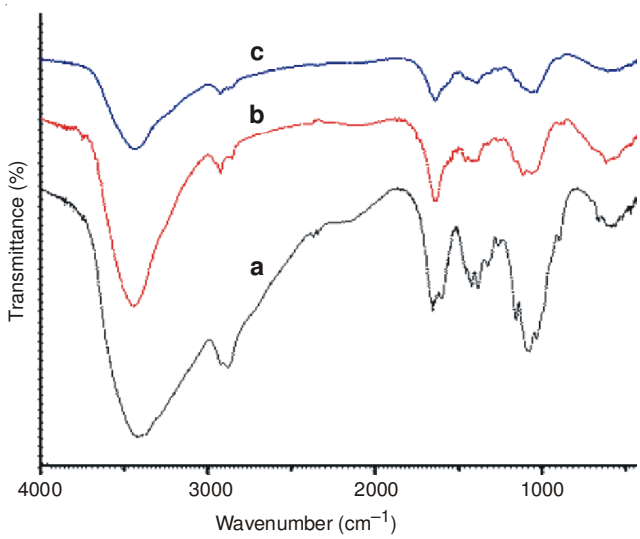

Fig. 1. IR spectra of: chitosan (a), crosslinked chitosan (b), cross linked chitosan-Cu^{2+} (c)

The effect of temperature on adsorption capacity of crosslinked chitosan resin was studied at pH 6 and results are shown in Fig. 2. It is observed that the adsorption capacity of resin for Cu^{2+} increase from to mg/g with the increasing in temperature from 20-40 ºC. The increase of adsorption for Cu^{2+} with increase temperature indicated the endothermic nature of the adsorption process.

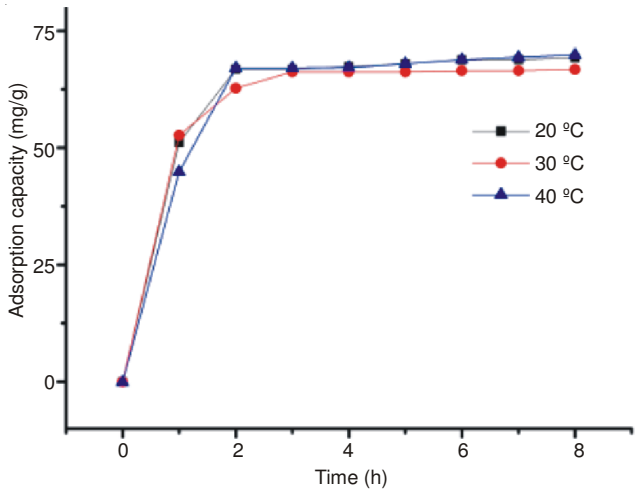

Fig. 2. Adsorption time curve at different temperatures

Adsorption kinetic data of chitosan are analyzed using the pseudo-first-order rate equation:

$$\ln \frac{C_e - C_t}{C_e} = kt \quad (1)$$

where C_e and C_t (mg/g) refer to the amount of chitsan adsorbed at quilibrium and time t (h), respectively and k is the rate constant. The rate constant could be calculated from the Fig. 2.

Fig. 3 showed that at different temperatures fitted slope can be obtained and the apparent adsorption rate constant k. A good linear relationship and the coefficient of determination, shows the cross-linked chitosan resin for Cu^{2+} adsorption process can be fitted with an adsorption kinetic equation is appropriate.

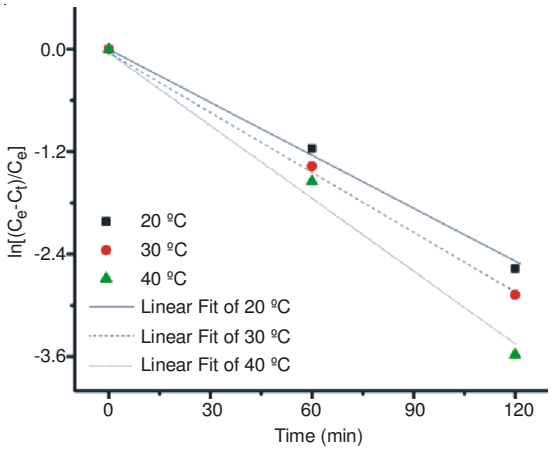

Fig. 3. Pseudo-first-order mode graph

Glutaraldehydeas the cross linking agent to synthesize a cross linked chitosan resin can adsorb copper ions in aqueous medium. The result shows that the adsorption process is the endothermic nature and the adsorption process is found to follow the pseudo-first-order kinetic model.

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