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ADSORPTION OF Hg (II) FROM AQUEOUS SOLUTION USING CARBOXYMETHYL GLUCOMANNAN DERIVATIVE

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ABSTRACT

Carboxymethyl glucomannan derivative (CMG) with the degree of substitution of 0.697 was synthesized from the reaction of monochloroacetic acid (MCA) with glucomannan paeoniiifolius (GP) at 60° C, pH10 for 3 h. Its structural characteristics were proven by nuclear magnetic resonance (NMR). The resulting derivative was used to adsorb Hg^{2+} ion from aqueous solutions. The effects of pH, initial concentration of metal ions and contact time on CMG's adsorption behaviors were also investigated. The results have shown that the optimal pH for adsorption was about 6.5; the adsorption capacity rapidly reached equilibrium within 40 minutes; the maximum adsorption capacity of CMG for Hg^{2+} ion was 615 mg/g.

Keywords: glucomannan, carboxymethyl glucomannan, adsorption, mercuric.

1. INTRODUCTION

Environmental pollution caused by toxic heavy metal in industrial effluents is one of the most pressing problems in the world. The presence of heavy metal ions from transition series, viz., Cu, Pb, Fe, Mn, etc. in the environment is of major concern due to their toxicity of many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into any harmless end products. One of the most toxic heavy metals commonly found in the global environment including lithosphere, hydrosphere, atmosphere and biosphere and its toxic nature has been known for centuries is mercury (Hg). The toxicity of mercury depends strongly on its redox state. The most toxic form of mercury is the highly reactive Hg(II), which binds to the amino acid cysteine in proteins. In contrast, the danger of elemental mercury (Hg°) and organo-mercury compounds lies in their transport routes. Symptoms of mercury poisoning are mainly neuronal disorders but also damage to the cardiovascular system, kidney, bones, etc. The three major sources of Hg emissions are natural, anthropogenic and re-emitted sources. Urban discharges, agricultural materials, mining and combustion and industrial discharges are the principal anthropogenic sources of Hg pollution in the environment. In order to minimize the adverse effects of Hg in the environment, it is desirable to find ways to capture it before it becomes a problem. Several techniques are available for this including chemical precipitation, coagulation, ion exchange, chemical reduction, membrane separation, biological treatment, solid phase extraction, and adsorption. Among them adsorption is by far the most versatile and widely used, and activated carbon is the most commonly used sorbent. However, the use of activated carbon is expensive, so there has been increased interest in the use of other adsorbent materials, particularly low-cost adsorbents. The use of adsorbents containing natural polymers has received great attention, in particular polysaccharides such as chitin and chitosan [1, 2]. Although, the investigation of glucomannan that is a high molecular weight non-ionic polysaccharide which constituted from β-(1,4) linked D-glucose and D-mannose units, found in tubers of the amorphophallus species, and its derivatives used to adsorb metal ions have not been reported so far [3, 4]. Therefore, the aim of the present study was concentrated on the synthesis of CMG and the study of using it for Hg (II) ion adsorption from aqueous solution. The influences of experimental conditions such as pH, time and temperature on the adsorption behavior were also studied. This information will be useful for further applications of system design in the treatment of practical wastewater.

2. EXPERIMENTAL

2.1. Materials

Glucomannan was isolated from tubers of Amorphophallus paeoniifolius. Monochloroacetic acid, sodium hydroxide and $HgCl_2$ were purchased from Merck (Germany). All other chemicals and reagents used were of analytical grade.

2.2. Synthesis and characterization of carboxymethyl glucomannan

The CMG was synthesized as follows: glucomannan (1 g) was dispersed in 100 ml of water by vigorously stirring, then monochloroacetic acid (5 g) was added and the mixture was stirred strongly for 30 minutes; then the pH was adjusted to 10 by slowly adding 10 % NaOH solution, while stirring continuously. The reactant system became quite transparent solution due to swelling of glucomannan as the pH was raised, but reverted to a completely transparent solution when the temperature of system was up to 60° C for 3 h. This solution was filtered, cooled to ambient temperature and poured into 90 % ethanol to precipitate the CMG. CMG was separated and washed many times with 90 % ethanol before lyophilizing to obtain CMG. The final product was used for further characterization. ^{1}H-NMR and ^{13}C-NMR spectra of the glucomannan and the CMG were recorded on the 500 MHz Bruker Avance spectrometer, the sample concentration being about 10 g/l for ^{1}H NMR and 70 g/l for ^{13}C NMR spectra in D_2O, at 353 K.

2.3. Adsorption experiments

The solution of salt using for experimental was prepared by dissolving $HgCl_2$ in distilled water. The pH of this solution was adjusted by using NaOH or HCl solutions. Then CMG was added while stirring vigorously. After stirring at a defined time, the mixture was centrifuged and filtered. The metal ion concentration in the filtrate and initial concentration was determined by atomic adsorption spectrophotometer. The adsorption capacity (Q) and removal efficiency (R) were calculated as formula (1) and (2), respectively:

$$Q = \frac{(C_0 - C) \times V}{W} \quad (1) \quad \text{and} \quad R = \frac{(C_o - C)}{C_o} \times 100\% \quad (2)$$

where C_0 and C were the concentration of metal ion before and after adsorption, respectively (mg/l), V was the total volume of the aqueous solution (l) and W was the dry weight of CMG (g). The metal ion concentration was determined with a Perkin Elmer atomic adsorption spectrophotometer (AAS-3300).

3. RESULTS AND DISCUSSION

3.1. NMR analysis

The ^{1}H-NMR and ^{13}C-NMR spectra of GP were shown in [5] and those of CMG were shown in the Fig. 1.

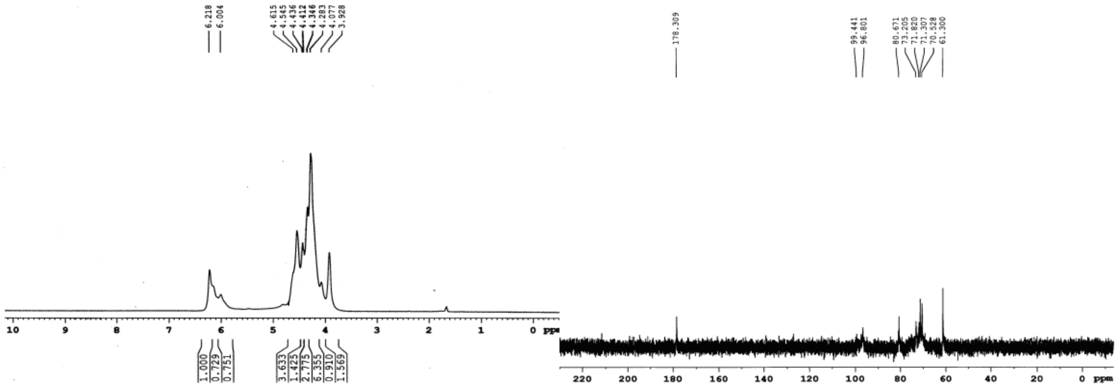

Figure 1. ^{1}H-NMR and ^{13}C-NMR spectra of CMG in D_2O at 353 K.

The ^{1}H-NMR and ^{13}C-NMR spectra of glucomannan were registered directly in state of polymer chain, dissolved transparently in D_2O at 353K (the hydration of glucomannan took place well at this temperature) (no NaOH be used as previously) [5]. The glucose and mannose units were overlapped, so that the spectrum was rather simple. The signals were assigned as follows: In the ^{1}H-NMR, the signal at 5.84 ppm was assigned to H1 proton of both mannose and glucose units (overlapped); the signals of H2 ÷ H6 proton were overlapped in region 3.91 ÷ 4.84 ppm. In the ^{13}C-NMR, the signals were assigned as follow: C1 (δ 101.3 ppm); C2 (72.08); C3 (72.34); C4 (78.14); C5 (74.00) and C6 (61.43).

The NMR chemical shift data of CMG derivative were assigned as follows:

^{1}H-NMR chemical shift data: H1 of substituted units (δ 6.21 ppm); H1 of initial units (6.00 ppm); H2 of both un- and substituted units (4.28 ppm); H3 of both un- and substituted units (4.61 and 4.54 ppm); H4 of un-substituted units (4.07 ppm); H4 of substituted units (3.92 ppm);

H5 of both un- and substituted units (4.43 ppm); H6a (4.43 ppm); H6b (overlapped with the signal of H2) (4.34 ppm) and H signal of OCH_2COONa group (4.61 and 4.54 ppm).

^{13}C-NMR chemical shift data: C1 of initial units (99.44 ppm); C1 of substituted units (96.80 ppm); C2 of both un- and substituted units (71.82 ppm); C3 of both un- and substituted units (73.20 ppm); C4 of un-substituted units (overlapped with other signals); C4 of substituted units (80.67 ppm); C5 of substituted units (75.00 ppm); C5 of un-substituted units (75.00 ppm); C6 of both un- and substituted units (61.30 ppm); C signal of **-C**OONa group (178.30 ppm) and C signal of methylene group (-O**C**H_2COONa) (70.52 and 71.30 ppm).

The success of carboxymethylation process of GP by MCA could be proven by comparing the ^{1}H-NMR and ^{13}C-NMR spectra of glucomannan [5] and that of the CMG derivative. The appearance of the signals at about 70.52 ppm and 71.30 ppm in the ^{13}C-NMR spectrum of CMG, which they could be seen overall were assigned to C atom of methylene group of -CH_2COO- substituted group. The signals assigned to the C atom of –COONa group were observed at 178.30 ppm (Fig.1). These features were taken as evidences that the carboxymethylation was taken place representing to the glucose ring –C(6)H_2-O-CH_2COONa formation of glucomannan derivative. The occurrence of carboxymethyl glucomannan was also denoted by the signal at about 4.615÷4.545 ppm (Fig.1), which were assigned to methylene proton of substitution of the OCH_2COONa groups.

Degree of substitution at O-atom ($\overline{\mathrm{DS}}$) of O-CMG could be evaluated by its ^{1}H NMR integrals using the formula: $\overline{\mathrm{DS}}=(I_{H1'})/(I_{H1+H1'})$. Where $I_{H1'}$ and $I_{H1+H1'}$ were the integrals of the hydrogen atom bonded at C1 of substituted glucomannan unit and C1 of all substituted and unsubstituted glucomannan unit, respectively. The resulting $\overline{\mathrm{DS}}$ value of O-CMG was approximately 0.697.

3.2. Adsorption behavior

***Effect of the initial concentration of metal ions*:** Figure 2 showed the relationship between the initial concentration of Hg (II) ion and the adsorption capacity. It could be seen that the adsorption capacity of CMG to Hg (II) increased with increasing of initial concentration of metal ions before equilibrium was reached. The maximum adsorption capacity in the studied range of the CMG for Hg(II) was about 615 mg/g. Results (Fig. 2) also indicated that removal efficiency increased with an increase in initial concentration of Hg (II) ion from 0.5 to 3.0 mmol/l, meanwhile, as the concentration was higher 3.0 mmol/l, the value of removal efficiency decreased. This might be the Hg (II) adsorption capacity of CMG has reached to its equilibrium state.

***Effect of pH on the adsorption*:** Fig.2 showed the relationship of pH value of the original solution with adsorption capacity and removal efficiency of CMG for Hg (II) ion. As seen in the Fig. 2, it was observed that the Hg(II) adsorption capacity of CMG and Hg (II) removal efficiency increased with increasing the pH value of the solution until a maximum at pH6-7 (pH over 7 was not taken into account to avoid precipitation). This could be due to at acidic pH, a decrease in the adsorption was attributed to the increase in ionic strength of solution and to the protonation of complexation sites (carboxymethyl groups existed in the form of –COOH, and they prevented the adsorption of metal ions onto CMG). Whereas, with increase of pH value, the carboxymethyl groups were free from the protonation, the adsorption mechanism may be occurred via both a chelation and ion exchange mechanism, and so the adsorption capacity increased. The experimental result suggested that the optimum pH for metal ion adsorption of Hg (II) in the solution was around 6.5.

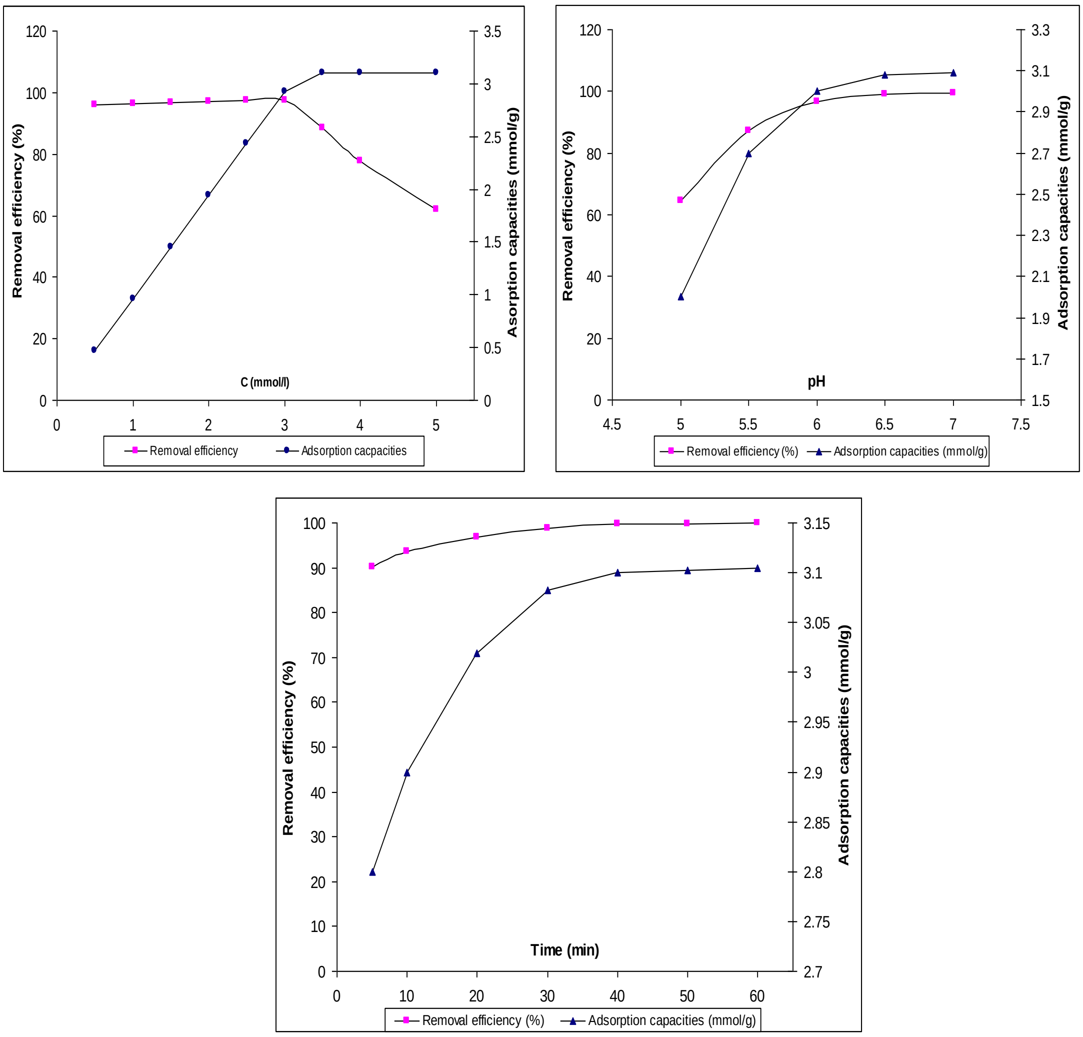

Figure 2. Effects of initial concentration of metal ions, pH and contact time to Hg (II) ion adsorption capacity and removal efficiency of CMG.

***Effect of time*:** The experimental results of metal ions adsorption on CMG versus time were shown in Fig. 2. The adsorption capacity of CMG for the metal ion increased sharply with the increase of adsorption time within 30 minutes and the equilibrium was reached at about 40 minutes. Figure 2 also shown that the Hg (II) ion removal efficiency of CMG was very high even the contact time was 5 minutes. The fast adsorption rate of the CMG derivative may probably be due to the state of it at the beginning of adsorption procedure. These results were important, as equilibrium time was one of the important parameters for an economical wastewater treatment system.

4. CONCLUSION

Carboxymethyl glucomannan derivative was synthesized successfully by the direct alkylation of a glucomannan by monochloroacetic acid at pH10 and temperature of 60 °C for 3 h. Adsorption behavior of Hg (II) ion from aqueous solution using CMG has been investigated. The results showed that the CMG's adsorption capacity rapidly reached equilibrium within 40 minutes; the optimal pH for the adsorption was about 6.5 and the maximum adsorption capacity of CMG for Hg (II) was 615 mg/g.

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TÓM TẮT

HẤP PHỤ Hg (II) TRONG DUNG DỊCH NƯỚC SỬ DỤNG DẪN XUẤT CACBOXYMETYL GLUCOMANNAN

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Dẫn xuất cacboxymetyl glucomannan (CMG) với độ thế bằng 0,697 được tổng hợp từ phản ứng của glucomannan với axit monocloaxetiC (MCA) trong môi trường kiềm (pH = 10), ở 60°C, thời gian 3 giờ. Cấu trúc hóa học của dẫn xuất được chứng minh bằng phương pháp phổ cộng hưởng từ hạt nhân NMR. Khả năng hấp phụ ion Hg (II) trong dung dịch của dẫn xuất CMG và một số yếu tố ảnh hưởng đến quá trình hấp phụ như pH môi trường hấp phụ, nồng độ ion kim loại và thời gian đã được nghiên cứu. Kết quả cho thấy, CMG hấp phụ tốt ion thủy ngân trong môi trường có pH = 6,5; dung lượng hấp phụ tối đa đạt 615 mg/g sau 40 phút.

Từ khóa: glucomannan, carboxymethyl glucomannan, hấp phụ, thủy ngân.