Solid State Science and Technology, Vol. 26, No 2 (2018) 97-105
ISSN 0128-7389 | *http://myjms.mohe.gov.my/index.php/masshp*

ADSORPTION OF Cu (II) ION IN AQUEOUS SOLUTION USING CROSSLINKED CHITOSAN BENTONITE COMPOSITE BEADS AND FILM

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ABSTRACT

Direct casting technique was used in the fabrication of crosslinked chitosan coated bentonite (ChB-ECH) film. The composite of the polymer film was analyzed through Fourier transform infrared (FTIR) spectroscopy and the ability of pure chitosan, crosslinked chitosan coated bentonite ChB-ECH beads and film in the adsorption of Cu (II) ion from aqueous solution were compared. Batch adsorption experiments were carried out and the effect of different contact time, pH, and initial concentration on the removal percentage of Cu (II) were studied. Results show that as initial concentration of Cu (II) increase, the adsorption is increasing and the optimum pH for the adsorption of Cu (II) ion on ChB-ECH film is at pH 4 with more than 50% adsorption.

Keywords: crosslinked chitosan; bentonite; film; Cu (II); removal.

INTRODUCTION

Cu (II) contamination in water is one of the serious worldwide environmental problems. This is mainly due to the inappropriate discharge of wastewater from industries such as manufacturing of batteries, mining activities, and metal fabrication which can be toxic to human, plants, and animals [1]. Ingesting large dosage of Cu (II) can be carcinogen even though it is an essential trace element for human beings. It has been stated by World Health Organization that the criterion of Cu (II) in drinking water is only 2.0 mg/L [2]. Thus, some existing conventional technologies had been implied to remove any excess amount of copper present in wastewater and adsorption is said to be the most effective and economic method [3-8].

Various types of adsorbents for heavy metal removal from aqueous solution have been used based on previous studies and chitosan is found to be an effective biosorbent since it is abundant, biodegradable, inexpensive, and locally available [9]. It contains a large number of hydroxyl (-OH) and amino ($-NH_2$) groups on its backbone, which can act as active adsorption sites of metals ion [10]. Nevertheless, natural chitosan has weak mechanical and chemical properties as it dissolves 0in dilute organic acids and agglomerates to form a gel in aqueous solution that can hinder most of its chelating sites [11, 12]. Therefore, physical and chemical modifications need to be carried out to overcome these limitations [13].

The crystalline state of chitosan can be reduced by the physical modification, results an expansion of the polymer networks which allows metal ions to be chelated more and it also can decrease the usage amount of chitosan in synthesizing the composite material [14]. Bentonite is widely used in the physical modification since it has high cation exchange capacity and large specific surface area [15].

In order to enhance the mechanical strength of the chitosan, chemical modification need to be carried out as its chemical stability can be increased either in acidic or alkaline media [16]. Besides, its resistance to microbiological and biochemical degradation also can be increased [17]. Chemical modification can be achieved by using crosslinking agents such as ethylene glycol diglycidyl ether (EDGE) [18], glutaraldehyde (GLA) [10], and epicholorohydrin (ECH) [19] that will increase the performance of chitosan in removing different types of metal ions. Figure 1 (a) and (b) shows the structure of chitosan and crosslinked chitosan respectively [13].

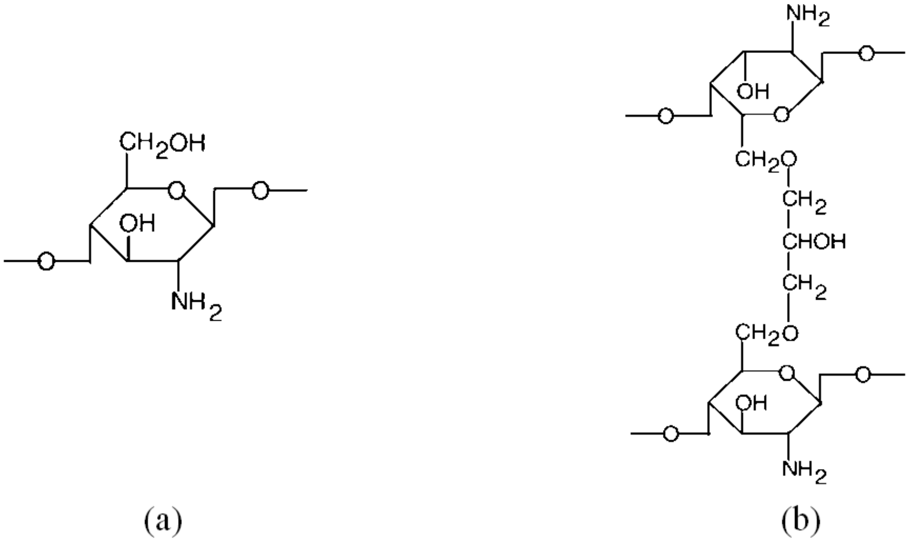

Figure 1: Schematic representation of (a) chitosan (b) chitosan-epichlorohydrin (Ch-ECH)

Since the study of Cu (II) ions adsorption on crosslinked chitosan bentonite film is still scarce, the aim of this study is to test the removal efficiency of this film since it is more practical and less time consuming compared to the beads adsorbent.

EXPERIMENTAL

Material and Reagents

Medium molecular weight chitosan with deacetylation degree of 75-85%, bentonite, epichlorohydrin (ECH) with 99% purity and glycerol were purchased from Sigma Aldrich (Cambridge, MA, USA). Atomic absorption spectroscopy standard solution of

Cu (II) ion was purchased from Fischer Scientific and acetic acid was purchased from RM Chemicals. All chemicals were used without further purification.

Preparation of Crosslinked Chitosan-coated Bentonite Beads

Chitosan powder (5 g) was dissolved in 600 mL of 5% (v/v) HCl solution under vigorous stirring for 2 h and 50 g of bentonite was added slowly and stirred for 3 h. About 1.162 mL of the crosslinker, epichlorohydrin (ECH) was added into the solution to obtain a ratio of 1:1 with chitosan and the solution was heated to 45 ^{0}C for 2 h and stirred continuously. The crosslinked chitosan-clay solution was neutralized by 1 M NaOH that was added drop wise until the chitosan has precipitated. The beads were then filtered, rinsed using DI water to remove excess NaOH and ground before sieved.

Preparation of ChB-ECH Films by Direct Casting Technique

ChB-ECH films were prepared by direct casting technique. 2 g of chitosan was dissolved in 100 mL of 1% (v/v) acetic acid at 55 ^{0}C while 1 g bentonite was dissolved in 100 mL DI water and both solution were stirred overnight. 3 wt% of glycerol was added into chitosan before mixing with bentonite and the solution was stirred vigorously for overnight. ECH was added with equimolar ratio to chitosan and stirred for another 2 h. The final solution was then being directly casted and allowed to dry at 60 ^{0}C for 24 h. The films were then peeled off to be used for further study. It was dipped in 0.1 M NaOH before used to neutralize the films, rinsed with DI water and dried before being used.

Characterization of ChB-ECH beads and Films

Fourier transform infrared (FTIR) spectra of the samples have been recorded using Perkin-Elmer spectrophotometer (CA, USA) in the range between 400 and 4000 cm^{-1} in order to identify the functional groups present in the films besides obtaining information on the nature of possible interactions between functional groups in ChB-ECH film and Cu (II) ion molecules [15].

Adsorption study

Metal adsorption was performed by soaking 0.1 g of the adsorbent beads and film in 100 mL of Cu (II) solution in 125 mL Erlenmeyer flask respectively. The solution was agitated at 50 rpm for 4 h at 25 ^{0}C and the beads adsorbent was then filtered and the filtrate was analyzed using flame atomic absorption spectroscopy (FAAS). The effects of pH (pH 1-4) and initial concentration (50 to 200 mg/L) on the removal efficiency and adsorption capacity were determined. The removal percentage of Cu (II) ion is calculated using Eq. 1:

$$\% R = \frac{(C_0 - C)100}{C_0} \qquad (1)$$

where C_0 and C are the initial and final Cu (II) concentration (mg/L), respectively.

Adsorption capacity of the polymer adsorbent was calculated using Eq. 2:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q_e is the adsorption capacity (mg/g), V is the volume of the Cu (II) solution (mL), m is the mass of the adsorbent, and C_0 and C_e are the initial and final concentration (mg/L) of Cu (II) ions, respectively.

RESULTS AND DISCUSSION

Figure 2 shows the changes of ChB-ECH film before being immersed in the Cu (II) ion solution and after adsorption for about 4 hours. The film turned its color from light yellow into light blue after the adsorption process. This color change was attributed to the loading of Cu (II) ion on the ChB-ECH film surface.

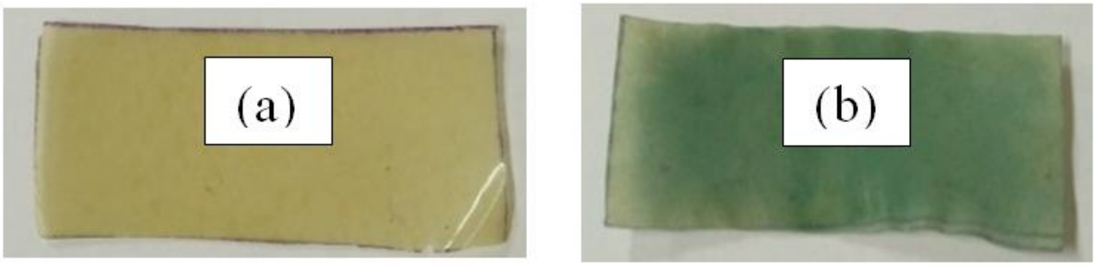

Figure 2: Digital images of ChB-ECH film (a) before and (b) after adsorption of copper ion.

FTIR Analysis

The FTIR spectra of pure chitosan, ChB-ECH beads before adsorption, and ChB-ECH film before and after Cu (II) ion adsorption are shown in Figure 3 (a), (b), (c) and (d), respectively. The spectrum of pure chitosan shows a broad peak at 3345.1 cm^{-1} (stretching vibration of N-H and O-H groups), at 2866 cm^{-1} (C-H symmetric stretch), at 1377.5 cm^{-1} (C-H bending vibration), at 1653.9 cm^{-1} (amide II band and C=O stretching vibration), at 1424.6 cm^{-1} (N-H stretching vibration), at 1155.6 cm^{-1} (C-O-C bending vibration), and at 1060.8 cm^{-1} (C-OH stretching vibration) [9].

Figure 3 (b) and (c) show the peak shifted from 3345.1 cm^{-1} to 3311.3 cm^{-1} as there is addition of –OH group from glycerol onto raw chitosan chain. Besides, the peak at 1007 cm^{-1} belongs to Si-O-Si linkage and peaks at ~3440 cm^{-1} also attributed to stretching vibration of Al-OH and Si-OH [21]. The medium stretch peaks at 850 cm^{-1} indicates that C-Cl (alkyl halide) bond appeared after chitosan is being crosslinked with ECH.

As for the IR spectrum of ChB-ECH film after adsorption Figure 3 (d), the wide band at 3311.3 cm^{-1} changed very much in the intensity. This is due to the vibration of N-H bond that is modified while forming a bond between the nitrogen (by its free lone pair of electrons) and the metal ion [22]. Plus, it also suggests a possible hydrogen bonding between Cu (II) ion and –OH group of chitosan. The peak was shifted from 1647.3 cm^{-1} to 1640.7 cm^{-1} after Cu (II) ion adsorption, also suggesting the involvement of amine groups in the binding of Cu (II) ion molecules.

There are no changes or reduction in their intensity of few bands in the IR spectrum indicating that the metal ion does not associated with the functional groups that generate those bands.

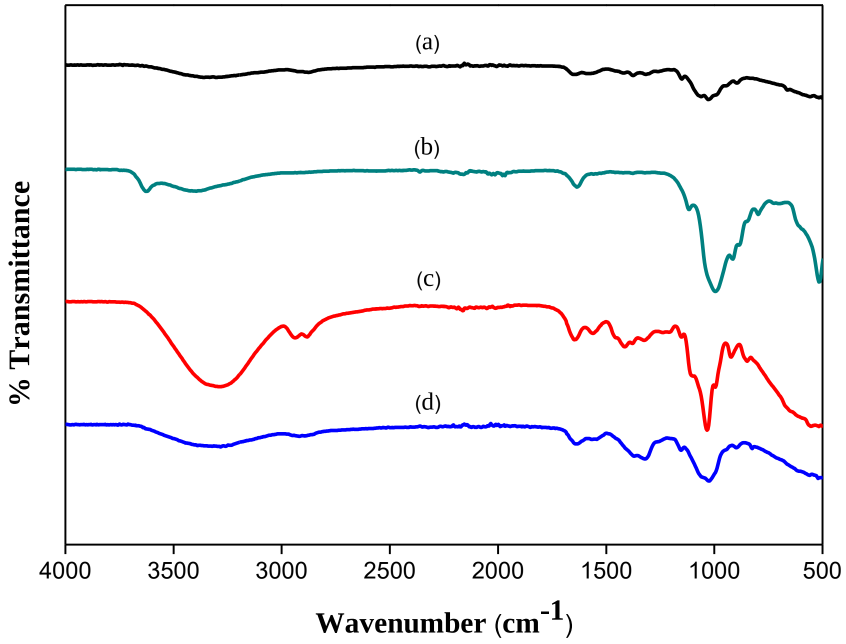

Figure 3: FTIR spectra of (a) pure chitosan, (b) ChB-ECH beads before adsorption, (c) ChB-ECH film before adsorption, and (d) ChB-ECH film after adsorption

Adsorption Study

Effect of Initial Cu (II) Concentration

As shown in Figure 4, the percentage of removal of Cu (II) ion by ChB-ECH beads is much greater compared to pure chitosan. This is because of the addition of bentonite and crosslinker to the chitosan which increase the stability and the binding sites of the chitosan. So, this proved that ChB-ECH beads can be fabricated into a film that is capable to adsorb Cu (II) ion in aqueous solution in a more practical way [23]. However, the adsorption percentage of Cu (II) ion by the film is not as much as the beads as the surface area of the beads are greater compared to film.

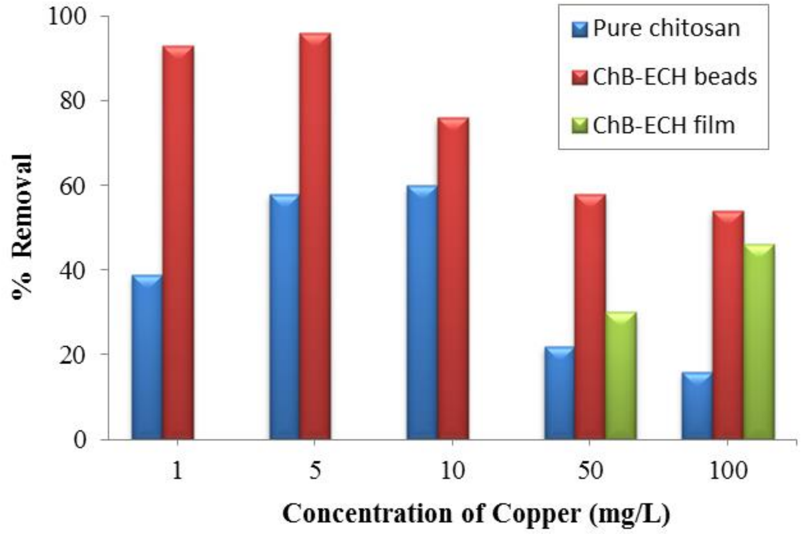

Figure 4: Comparison between the percentage removal of Cu (II) ion by pure chitosan, ChB-ECH beads and ChB-ECH film

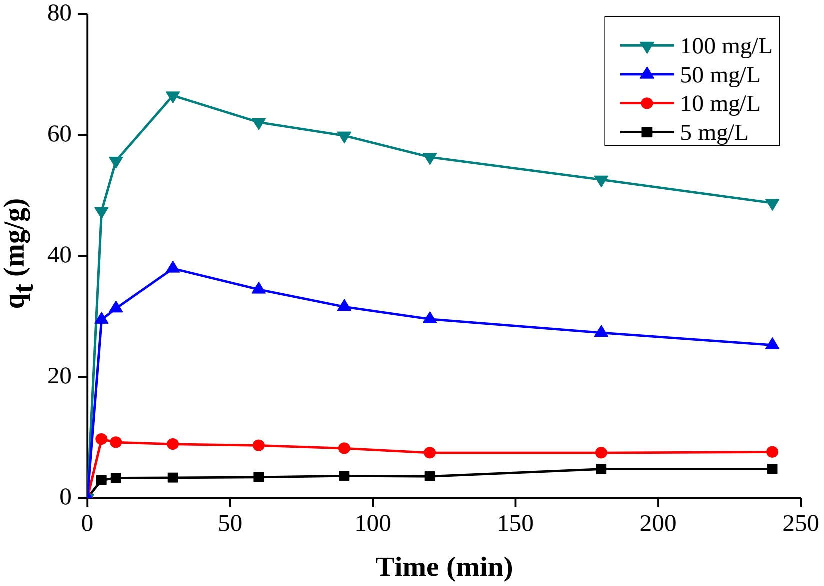

Figure 5: Effect of initial concentration and contact time on adsorption of Cu (II) ion onto ChB-ECH beads

Based on the experiments, the adsorption percentage decreased as the initial concentration increased due to the binding sites which were not sufficient to accommodate all Cu (II) ions. Figure 5 shows the adsorbent reaches equilibrium gradually as the initial concentration increases from 5 mg/L to 100 mg/L. The formation of driving force by the mass gradient between the solutions and the adsorbent that lead a large number of Cu (II) ion molecules to be attracted to the film cause the higher adsorption capacity at higher Cu (II) concentration [24].

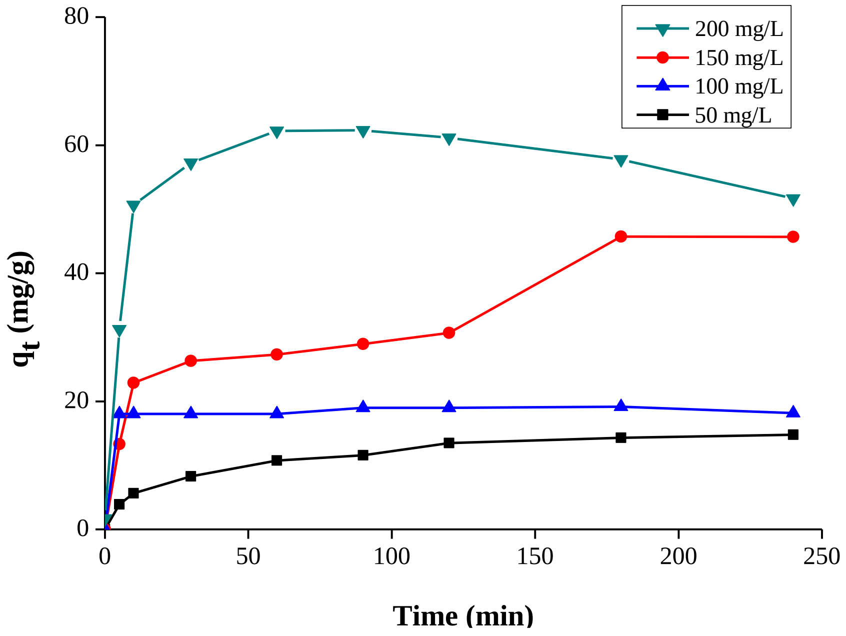

Figure 6: Effect of initial concentration and contact time on adsorption of Cu (II) ion onto ChB-ECH film

The effect of initial Cu (II) concentration (50 to 200 mg/L) on the adsorption capacity of the adsorbent film was also examined as shown in Figure 6. In this study, the films were tested for concentration of Cu (II) ion 50 mg/L because the film started showing adsorption percentage at higher concentration. Moreover, at concentration lower than 50 mg/L, inadequate adsorption was observed which is less than 0.1% due to the surface area of film which is not as greater as the beads.

Effect of Solution pH

In this study, the adsorption capacity of the beads and films in copper solution with pH ranging from 1 to 4 was studied. From Figure 7, the adsorption capacity of ChB-ECH beads and film increase as the solution becomes less acidic from pH 1 to 4. This is because of the higher H^+ ion concentration at lower pH that competes with the Cu (II) ion for the binding sites of the ChB-ECH film [25]. On the other hand, beyond this pH value, precipitation of Cu (II) ions as $Cu(OH)_2$ occurs simultaneously and could lead to inaccurate interpretation of adsorption.

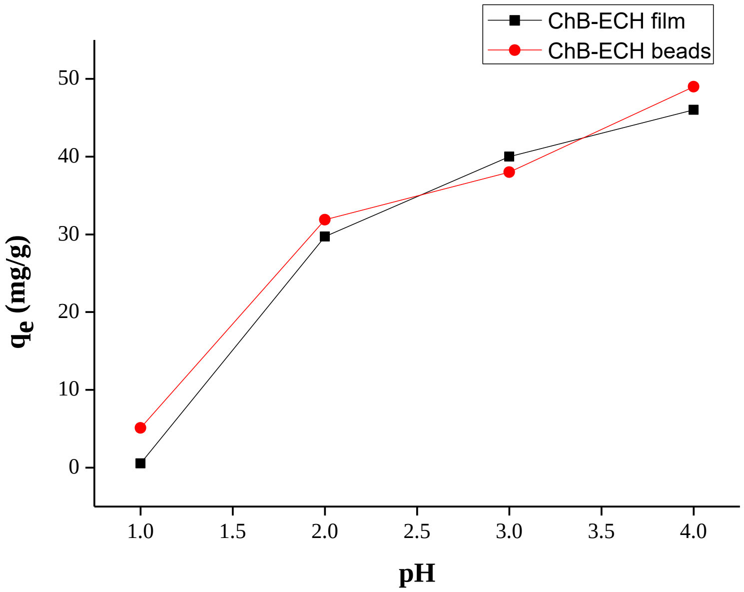

Figure 7: Effect of pH on Cu (II) adsorption by ChB-ECH beads and film

CONCLUSION

A simple and inexpensive procedure was developed for the fabrication of crosslinked chitosan bentonite films and tested on the adsorption of Cu (II) ion from aqueous solution. FTIR result shows that there are changes in the functional group between pure chitosan and the bead and film before the adsorption of Cu (II) indicating the additional functional group of –OH, Cl, Si and Al to the chitosan backbone that assist in the adsorption process of Cu (II) ion. Future research should be performed by optimizing the film modification to be used at lower concentration of heavy metal ions.

ACKNOWLEDGEMENT

The authors would like to thank the Malaysian Government for the fund support through FRGS (No. 5524815) research grants. The laboratory facilities provided by the Department of Physics and Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, are also acknowledged.

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