

## Adsorption of Copper from Aqueous Solution by Chitosan using Molecular Imprinting Technology

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### Abstract

In nature chitosan is a plentiful polymer with high heavy metal ion uptake capacity due to chitosan's functional groups that chelate with the positive surfaces of heavy metal ions. In this study, epichlorohydrin was used as a crosslink to prepare the copper-imprinted chitosan as a pattern to enable the selectivity property and increase adsorption capacity. The effects of the cross-linker, pH, initial concentration and time were examined in this study to identify the optimum amount of each to remove copper metal ions from waste water by imprinted chitosan. This composite was characterized by Fourier-transform infrared spectroscopy (FTIR) test to determine the existence of copper ions in chitosan crosslinked with epichlorohydrin. Scanning electron microscopy (SEM) tests were also done to compare the surfaces of crosslinked chitosan and the removal of copper by imprinted chitosan. pH adsorption was tested from 3 to 7 and the initial concentration and time investigated were between 10 and 100 mg/l and 0 and 120 minutes respectively. The maximum capacity to adsorb was found to be at pH 7, initial concentration of 100mg/l at 90 minutes with 0.1 gr chitosan. Ultimately, the maximum adsorbent amount achieved for effective Cu(II) removal was 74.37 mg/g.

### Keywords

Adsorption, cooper, chitosan, imprinting

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## 1. INTRODUCTION

The contamination of aquatic systems with heavy metal ions and toxic organic pollutants is on the increase (Wang et al., 2016a). Heavy metal ion pollution has become one of the most dangerous and serious environmental problems due to the ions' properties, such as non-biodegradable nature, high toxicity, recalcitrance, the tendency to accumulate in living organisms, carcinogenic potential and persistence in the environment (Fu and Wang, 2011; Ahmed and Ahmaruzzaman, 2016). The earth's crust consists of heavy metal ions. Consequently, plenty of experiments have been conducted and attempts made to distinguish heavy metal ions (e.g. Copper, Cadmium, Lead, Mercury, Arsenic, etc.) in the environment and to remove them to prevent their negative impacts (Zhou et al., 2016). Chitin is one of the most abundant materials on earth and is extracted from crustacean shells, such as prawns, crabs, shrimp, fungi and other crustaceans. Chitosan is a derivative of chitin that is prepared through the chitin deacetylation process. It has exceptional features, like non-toxicity, biocompatibility and degradability (Kumari et al., 2015; Hamed et al., 2016). Chitin and chitosan are from the polysaccharides family that

includes a large number of  $\beta(1\rightarrow4)$  linked remains of N-acetyl-2 amino-2-deoxy-D-glucose and 2 amino-2-deoxy-D-glucose. According to Figure 1, to increase the amount of 2 amino-2-deoxy-D-glucose units in chitin, it should be deacetylated and turned into chitosan for dissolving in aqueous acid (Aranaz et al., 2009; Sayari et al., 2016).

As mentioned previously, chitosan is a natural material with high heavy metal ion adsorption capacity owing to the chelating of chitosan functional groups with negatively charged, heavy metal ions. Nonetheless, chitosan has some drawbacks, such as unsuitable surface area and chemical features that require modification. There are several methods of modifying chitosan properties, like imprinting (Nishad et al., 2012), crosslinking (Ngah et al., 2002), magnetic combination with other materials (Reddy and Lee, 2013) and creating composites like chitosan-zeolite composite (Ngah et al., 2002), chitosan-PVA (Jin and Bai, 2002), chitosan-graphene (Wang et al., 2016b), etc. There are various substances for crosslinking chitosan to modify its physical and chemical features (Chen et al., 2011), such as glutaraldehyde (Park et al., 2013), epichlorohydrin and ethylene glycol diglycidyl (Li and Bai, 2005). The crosslink reaction rate

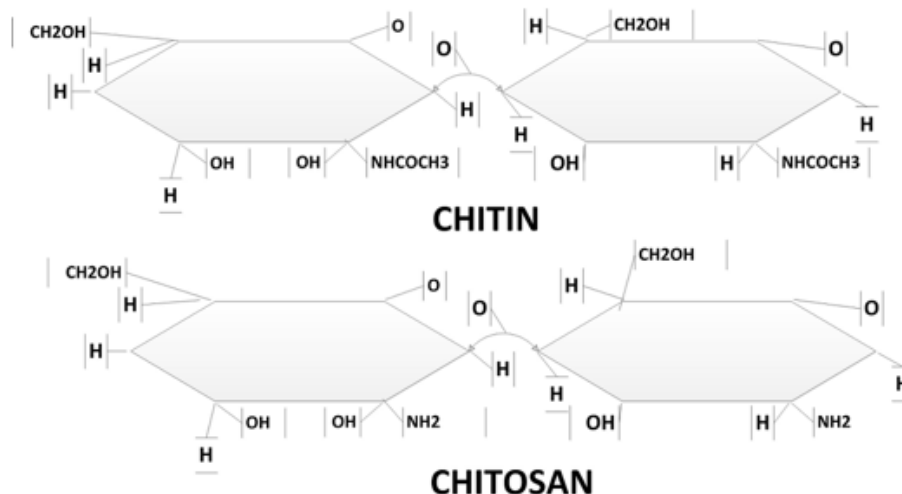


Figure 1. Chitin and chitosan structures

as well as type and amount of crosslinking is responsible for the polymer system strength and the binding of specific sites to the template. Since a very high degree of crosslinking is required to obtain polymer identifier properties, only a limited number of crosslinks are used in the molecular deposition process (Sun et al., 2006).

## 2. EXPERIMENTAL SECTION

### 2.1 Chemicals

Chitosan was obtained from Sigma-Aldrich with approximately 85% deacetylation degree and 120,000 gr/mol average molecular weight. Epichlorohydrin (C<sub>3</sub>H<sub>5</sub>ClO) with average molecular weight of 92.5 gr/mol was applied as a crosslink. Copper(II) nitrate trihydrate with molecular weight of 241.599 gr/mol was provided by Merck.

### 2.2 Imprinted chitosan preparation

First, 100 mg chitosan and 10 mg/l copper nitrate trihydrate were placed in a test tube along with 4 ml distilled water. Then 1ml of 1 μ NaOH was added to the solution, which was placed in a 60° paraffin bath on a heater stirrer. The solution was stirred for 4hr, after which 0.3 ml epichlorohydrin was added and stirring continued for 24hr to obtain a fully crosslinked gel. In the first stage, this gel was dried and turned into powder. In the second stage, heavy metal copper nitrate trihydrate ions were removed to create cavities in the synthesized chitosan and improve copper adsorption. According to the FTIR test results, synthesis occurred successfully. On the other hand, the SEM test illustrated cavities and discrepancies between chitosan synthesis and epichlorohydrin and imprinted chitosan.

### 2.3 Characterization

#### 2.3.1 Characterization of crosslinked chitosan

Scanning electron microscopy (SEM) micrographs of raw chitosan and crosslinked chitosan were analyzed to identify the

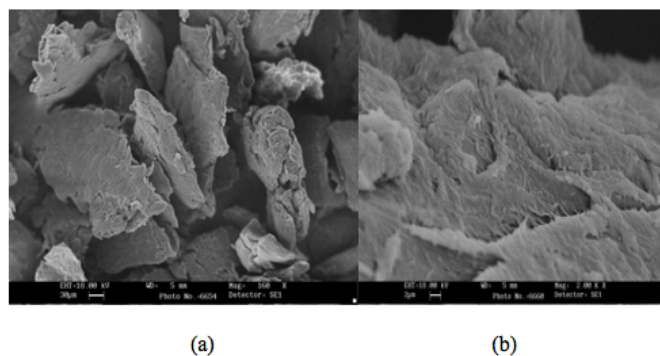
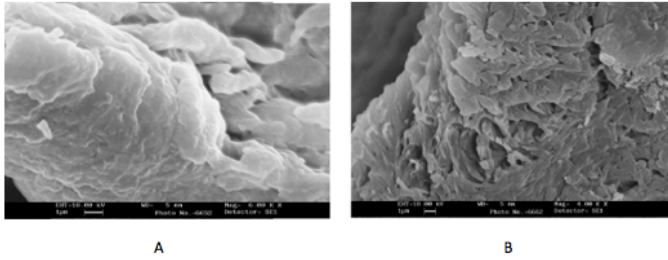


Figure 2. a) raw chitosan, b) crosslinked chitosan

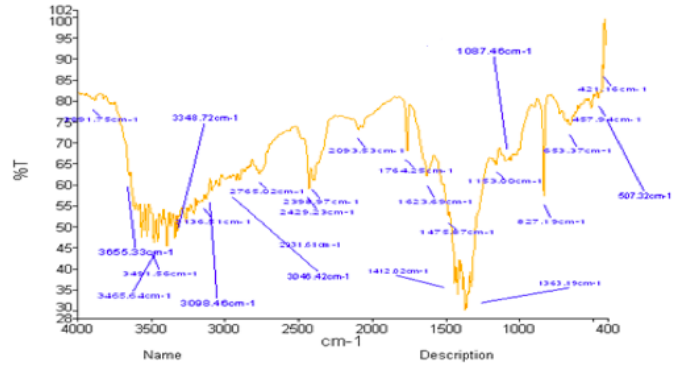
crosslinking function and adsorbing properties, as shown in Figures 2 (a, b). Figure 2(b) demonstrates that the epichlorohydrin chains in chitosan powder caused an increase in chitosan strength and adsorption properties.

#### 2.3.2 Imprinted chitosan characterization

Crosslinked copper-imprinted chitosan microparticles were prepared by ion imprinting method. Chitosan was first chelated with Cu(II) ions through ion-dipole and ion-ion interactions, followed by chemical crosslinking with epichlorohydrin. Images of the adsorbent before and after imprinting were captured by SEM (scanning electron microscope) as shown in Figure 3. The imprinted chitosan surface morphology and structure were analyzed, and it can be seen there are some holes on the chitosan crosslink surfaces with epichlorohydrin. These holes are left after Cu(II) is removed in preparation for the imprinted chitosan. In the FTIR test, KBr powder was utilized as background spectrum to identify the structures of Fig4 raw chitosan, Fig5 imprinted chitosan crosslinks and Fig6 copper adsorption by imprinted chitosan. When comparing the peaks



**Figure 3.** A) Chitosan and epichlorohydrin without molecular imprinting, B) chitosan imprinted with Cu(II) particles



**Figure 6.** FTIR test of Cu(II) adsorption by imprinted chitosan

concentrations and times. In this research, the sorption capacity and removal percentage of copper(II) nitrate trihydrate ions was calculated with Eq. (1) and (2):

$$R\% = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

$$Q = \frac{C_i - C_f}{W} V \tag{2}$$

Where  $C_i$  is the initial concentration of metal ions (mg/mL),  $C_f$  is the concentration of metal ions (mg/mL),  $V$  (mL) is the amount of metal ion solution, and  $W$  (gr) is the weight of particles.

**2.4.1 Effect of pH**

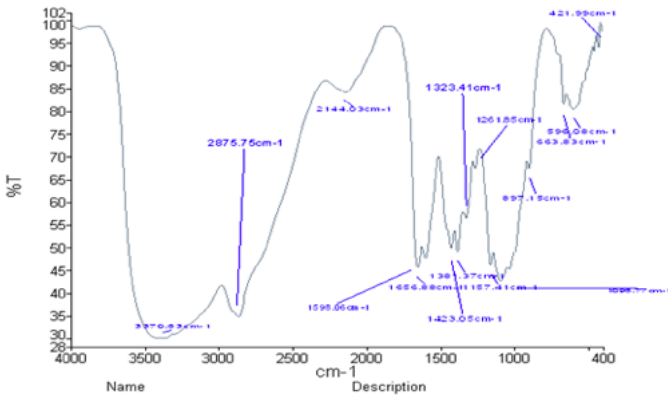
To investigate the effect of pH on the adsorption process, 0.1 gr of imprinted chitosan was poured in 5 polyethylene dishes with lids, to which 20 mL of 100 ppm copper(II) nitrate trihydrate solution was added. The pH was set in the range of 3 to 7 by adding NaOH. After filtering, the solutions' adsorption was identified with atomic adsorption spectrometry

**2.4.2 Effect of initial copper concentration in solution**

Copper(II) nitrate trihydrate was prepared in concentrations ranging between 10 and 100 ppm. A control solution was made in order to determine the amount of adsorption removal. Then 20 ml of each concentration was crossed with 0.1 gr imprinted chitosan.

**2.4.3 Effect of time equilibrium**

Time equilibrium is another parameter with an important role in adsorption. To survey this factor, 12 polyethylene dishes with lids were prepared. In each dish, 0.1 gr imprinted chitosan was added along with 20 ml of 100 ppm copper solution. The PH was set at 7. The dishes were put in the shaker for 2 to 120 min.

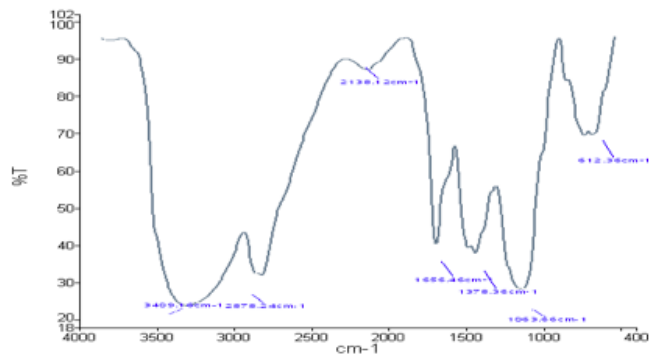


**Figure 4.** FTIR test for raw chitosan

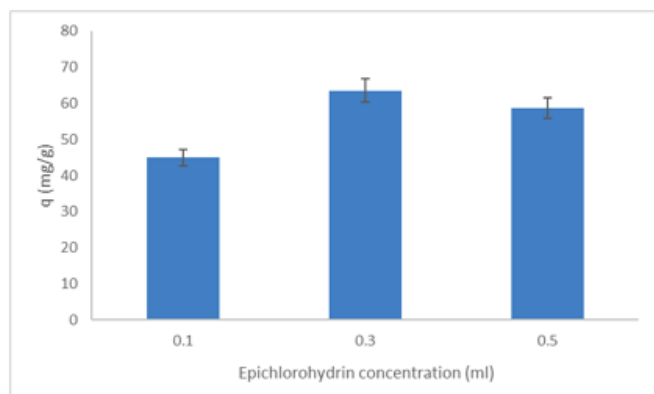
in Fig4 and 5, it is evident that some peaks in the 1000-1500 range have changed.

**2.4 Sorption study**

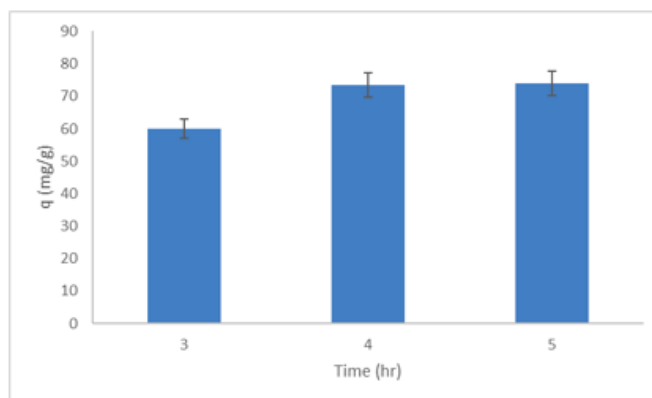
To create optimum chitosan with Cu(II) ions on the surface, the preparations involved 0.1 gr chitosan with 0.1, 0.3 and 0.5 ml epichlorohydrin as a crosslinker at different addition times (3, 4 and 5hr) and with various metal ion amounts (5, 10 and 15 mg/l) at 60 °C and 24hr stirring. Then the copper ions were removed with HCL 2μ and NaOH 1.2μ after filtering. The maximum adsorption was found for different PH, initial



**Figure 5.** FTIR test of imprinted crosslinked chitosan



**Figure 7.** Cu(II) adsorption with different amounts of crosslinking



**Figure 8.** Cu(II) adsorption after adding crosslinks for different times

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of epichlorohydrin amount

The crosslinking agent amounts used were 0.1, 0.3 and 0.5 ml per 100 mg chitosan. It was observed that the copper uptake of metal ions by chitosan was greater when 0.3 ml crosslinking agent was used than 0.1 ml. This was due to the polymer's increased crosslinking density and strength. According Fig. 7, when 0.5 ml crosslinking agent was used the polymer adsorption capacity dropped and adsorption was dependent on the emigrating concentration.

#### 3.2 Effect of epichlorohydrin addition time

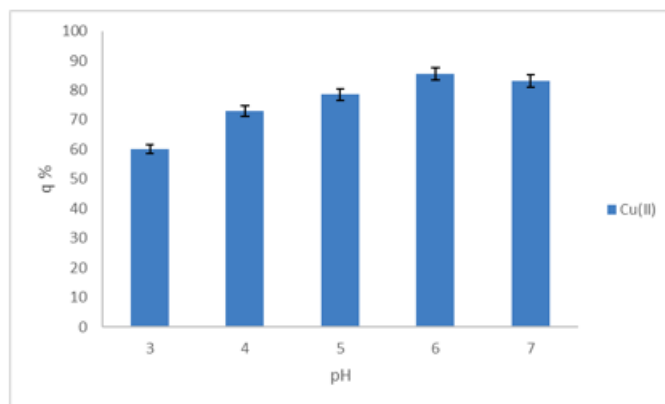
Figure 8 indicates that with increasing the time of adding the crosslinking agent, chitosan adsorption capacity increased. The reason is that the time required for metal complexes to form on chitosan along with the number of these complexes increased. After crosslinking agent addition time reached about 4 hours, extra time had no significant effect on adsorption capacity. Thus, the time required for complex formation was approximately 4 hours. It is understood that optimum adsorption happened with 3 ml of crosslinking agent at 4 hours, which led to the adsorption of 70.9mg/g Cu(II) ions.

#### 3.3 Effect of pH

The effect of pH on Cu(II) adsorption was tested in the 3.0-7.0 range. Figure 9 indicates that increasing the pH enhanced the adsorption amount. The maximum removal of Cu(II) ions (85.6%) occurred at pH 6. By reducing the pH, the amine groups in synthesized chitosan were protonated to different degrees, which caused the electrostatic removal of metal cations. At lower pH, the H<sup>+</sup> ions competed with the metal ions. H<sup>+</sup> ions were adsorbed on the adsorbent surface and the functional groups available and adsorbent holes were limited to the adsorbed Cu(II) ions, which caused reduced adsorption.

#### 3.4 Effect of initial adsorbing copper concentration

Another factor that affected the adsorption of metal ions was the initial concentration of ions in the test solution. In this



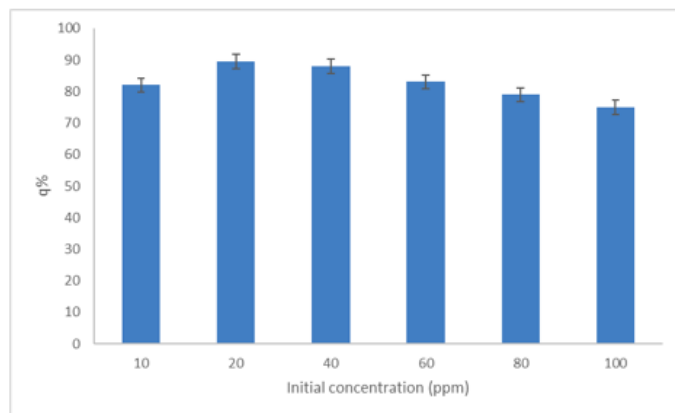
**Figure 9.** Percentage of Cu(II) removal with imprinted chitosan based on pH efficiency

study, the percentage of metal ion removal was investigated by chitosan imprinting under the effect of initial metal ion concentrations from 10 to 100 ppm, pH 6 and 1 gr of adsorbent. According to Fig 10, increasing the initial concentration of metal ions diminished the removal rate, and the highest Cu(II) removal percentage was 89.5% by imprinted chitosan at a concentration of 10 mg/l, 1 gr of adsorbent and pH 6.

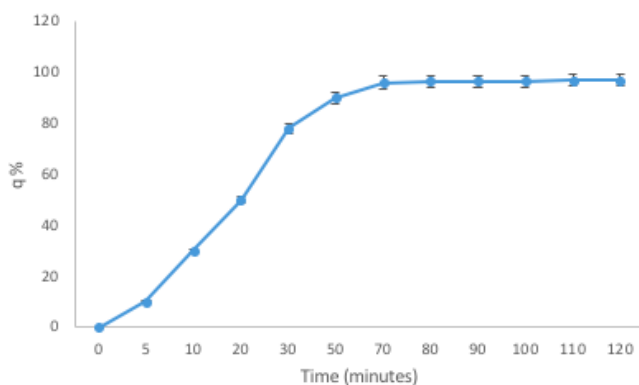
At lower metal ion concentrations there were fewer metal ions than the number of available adsorption places and thus greater adsorption efficiency was obtained. Higher metal ion concentrations meant fewer available adsorption sites, and the saturation of active sites led to reduced adsorption efficiency.

#### 3.5 Effect of time

The adsorption percentage increased rapidly in the first 30 minutes of the process and then moderately up to 70 min. Hence, the time factor is a key parameter in practical adsorbent applications. From Figure 11 it is understood that adsorption was rapid and sudden in the first 30 min owing to various functional groups available and adsorbent holes. Therefore, a majority of Cu(II) ions were adsorbed in the initial minutes,



**Figure 10.** Cu(II) removal percentage by imprinted chitosan based on copper ion concentration



**Figure 11.** Cu(II) removal with imprinted chitosan based on contact time

but beyond 70 min adsorption continued approximately at the same level and remained stable.

#### 4. CONCLUSIONS

This study indicates that a variety of methods of separating heavy metals are available, a suitable method being to use chitosan. Chitosan is a good adsorbent for the removal of anionic and cationic dyes as well as heavy metals due to the presence of functional groups such as amine and hydroxyl groups that chelate with heavy metal ions. In this study, chitosan was imprinted with Cu(II) metal ions, and the results illustrate that imprinted chitosan has superior uptake capacity to crosslinked chitosan. Crosslinked materials chelate with active chitosan functional groups. Although chelating boosts the chemical and physical properties of chitosan, it may decrease the adsorption capacity. In this study, imprinting chitosan with Cu(II) produced a selectivity feature for Cu(II) adsorption and increased the adsorption percentage for removing Cu(II) up to 96% via the imprinting method.

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