Adsorption of Copper (II) Ion from Aqueous Solution Using Soybean Hulls

Supaporn Douglas1*, Suwassa Pongamphai1, Supanee Lerdrailuck1, Sirarat Ponin1, Sujitra Polchai1, Acharaporn Kaewchana1 and Budsarin Osataworanun2

1 Department of Chemical Engineering, King Mongkut’s University of Technology Thonburi, Bangkok, Thailand
2 The Joint Graduate School of Energy and Environment, King Mongkut’s University of Technology Thonburi, Bangkok, Thailand

Abstract: The aim of this research is to study the efficiency of removing copper ions from copper chloride solution using soybean hulls. The experiment was divided into two parts. In the first part, the time to heat soybean hulls that were soaked in citric acid was determined. In the second part the factors affecting copper ion adsorption by soybean hulls were determined to be initial concentration and pH of the solution, ratio of soybean hulls to copper chloride solution and size of soybean hulls. From the results of the experiment, the optimum conditions were to heat for 90 minutes at an initial pH of 4.8. The ratio of soybean hulls to solution is 10 grams per 1 litre. Size of soybean hulls is 602 micrometers and the initial concentration of copper chloride solution is 50 ppm. The copper ion removal efficiency using soybean hulls is 97.68 % under these conditions and the concentration of copper ion has been reduced below the industrial standard (2.0 mg/l).

Keywords: Adsorption, Citric Acid, Copper Ion, Copper Chloride Solution, Soybean Hulls

1. INTRODUCTION

The pollution in wastewater due to toxic heavy metals is a serious environmental and public health problem. The removal of heavy metals from wastewater and industrial effluents has become important to maintain water quality. Recently, attention has been directed to the development of alternative methodologies such as the use of waste matter from agricultural products as an adsorbent to adsorb heavy metals from wastewater. Large amounts of soybean hulls are produced each year and used in animal feed as a low priced raw material. Soybean hulls could be used as an adsorbent material for the removal of toxic metals from water and wastewater by adsorption. Published studies have demonstrated the utility of soybean hull modification is desirable enhancement of metal ion adsorbing properties [1, 2]. Many researchers have attempted to develop metal ion adsorbents from agricultural by-product, such as cottonseed and rice hulls, rice straw and rice bran, soybean hulls, sugarcane bagasse, almond hulls, cottonseed hulls and macadamia nut hulls [3, 4]. The results have demonstrated that soybean hulls shown the greatest potential as copper ion adsorbents [5, 6].

2. METHODOLOGY

2.1 Effect of modifying soybean hulls with citric acid
Ten grams of soybean hulls with a particle size of 3,175 µm were placed in 200 ml of 0.1N NaOH. The slurry was stirred at 300 rpm for 1 hr and rinsed with distilled water. The moist hulls were added to 200 ml of distilled water and stirred at 300 rpm for 45 min to remove the excess NaOH. This procedure was repeated three times to ensure removal of NaOH [7]. The hulls were then blended with 0.6M of citric acid in a proportion of 1.0 gram of hulls to 7.0 ml acid. The acid/soybean hulls slurry was dried overnight at 50°C. The dried hulls were further heated to 120°C for 0, 15, 20, 60, 90 and 120 minutes. The acid-modified soybean hulls were then cleaned by washing with distilled water and filtered. Finally, the modified hulls were dried overnight at 50°C and sieved to 3,175 µm [8].

2.2 Effect of initial pH of solution
Soybean hulls were extracted with 0.1N NaOH (BE) and modified with 0.6M citric acid (CA). One gram of the so-called BE-CA-modified sample was added to 100 ml of 50 mg/l. The pH of solution was adjusted to 4.8, 5, 7 and 9 using a 0.07M sodium acetate - 0.03M acetic acid solution. The concentration of copper ion in copper chloride solution was measured after 10 hours of adsorption process.

2.3 Effect of soybean hulls to copper chloride solution ratio
The ratio of modified soybean hulls to copper chloride solution was studied at 1:10, 1:25, 1:50, 1:100 and 1:200 g/ml. The initial pH and concentration of copper chloride solution were 4.8 and 50 mg/l respectively. The concentration of the copper ion (Cu²⁺) was determined after 10 hours of adsorption.

2.4 Effect of the size of soybean hulls
Modified soybean hulls with particle sizes of 602, 945 and 3,175 µm were used to adsorb Cu²⁺. One gram of the so-called BE-CA-modified soybean hulls was placed in 100 and 200 ml of 50 mg/l copper chloride solution. The solution was buffered with a 0.07M sodium acetate – 0.03M acetic acid solution to pH 4.8. The adsorption process was run for 10 hours and Cu²⁺ in the liquid phase was periodically measured.

2.5 Effect of the initial concentration of copper chloride solution
One gram of the BE-CA–modified soybean hulls was placed in 100 ml of copper chloride solution; concentrations of 50, 100, 150 and 200 mg/l respectively were used. The initial pH of solution was buffered to 4.8. The particle size of soybean hulls was 602 µm and the adsorption process was run for 10 hours. The copper ion in the liquid phase was measured periodically during the adsorption process.

Corresponding author: supaporn.chu@kmutt.ac.th
3. RESULTS AND DISCUSSION

3.1 Effect of modifying soybean hulls with citric acid

The modified soybean hulls were used to adsorb Cu$^{2+}$ in a copper chloride solution for one and seven hours. The comparison of using modified and non-modified hulls for the adsorption is shown in Fig. 1. It was found that the modified soybean hulls showed the better adsorption of Cu$^{2+}$ than the unmodified hulls. The reason was that acid formed an active anhydride and combined with the cellulosic compound which added more carboxyl group resulting in more adsorption of copper ion when using modified hulls.

![Fig. 1Comparison of Cu$^{2+}$ adsorption using modified and non modified soybean hulls](image1)

The effect of the heating time during the modifying step on adsorption is shown in Fig. 2. The concentration of copper ion in solution slowly decreased with increasing heating time. The difference in the concentration of copper ion left in solution was less than 1 ppm for non-heating and heating for 120 minutes.

![Fig. 2 Effect of heating time at 120°C of modified soybean hulls on Cu$^{2+}$ adsorption](image2)

3.2 Effect of initial pH of copper chloride solution

The effect of initial pH of copper chloride solution on copper ion adsorption using modified soybean hulls was shown in Fig. 3. The concentration of copper ion in copper chloride solution after increased at the initial pH of solution higher and lower than 4.8. The optimum pH for the adsorption was at pH 4.8. At pH 4 more hydronium ion (H$_3$O$^+$) occurred and competed with copper ion (Cu$^{2+}$) on the negative site of cellulose. For pH higher than 4.8 the hydroxyl group interfered the negative site on the absorbent resulting less adsorption of Cu$^{2+}$ on the surface of the hulls.

![Fig. 3 Effect of initial pH on Cu$^{2+}$ adsorption using modified soybean hulls](image3)
3.3 Effect of soybean hulls to copper chloride solution ratio

The adsorption of Cu\(^{2+}\) in copper chloride solution using different ratio of soybean hulls to solution was shown in Fig. 4. The concentration of Cu\(^{2+}\) in solution increased with increasing volume of the solution. The Cu\(^{2+}\) left in the solution was less than 2 ppm when using solid to solution ratios from 1:10 to 1:100 gm/ml which is below the industrial standard.

3.4 Effect of the size of soybean hulls

The concentration of Cu\(^{2+}\) in copper chloride solution increased with an increase in the size of soybean hulls for both solid/solution ratios (Fig. 5). The smaller particle size provided more surface area for the adsorption. The ratio of soybean hulls to solution at 1:100 gm/ml showed better adsorption of Cu\(^{2+}\) and could remove Cu\(^{2+}\) below 2 ppm.
3.5 Effect of the initial concentration of copper chloride solution

The effect of the initial concentration of copper chloride solution on the adsorption of Cu\(^{2+}\) using modified soybean hulls was shown in Fig. 6. The concentration of Cu\(^{2+}\) in the solution decreased with increasing adsorption time. The higher initial concentration of copper chloride solution resulted in less adsorption capacity as shown by a higher Cu\(^{2+}\) concentration remaining in the solution. The reason being, that there was not enough adsorbent to adsorb more Cu\(^{2+}\) in the higher initial concentration of the solution.

![Fig. 6 Cu\(^{2+}\) adsorption using modified soybean hulls at different initial concentration of copper chloride solution.](image)

4. CONCLUSIONS

This purpose of this research was to study the effect of soybean hulls, an agricultural waste product, in removing Cu\(^{2+}\) ions from copper chloride solution. Soybean hulls were modified with citric acid, since it is one of several dicarboxylic acids that could form a reactive anhydride upon heating and then combine with various lignocellulosic and proteinaceous components with soybean hulls to add carboxyl for the by-product substrate. The optimum conditions were found to be: an initial pH of 4.8, 10 grams of 602 µm soybean hulls per litre of 50 ppm copper chloride solution. The copper ion removal efficiency was found to be 97.68 % and the concentration of copper ion has been reduced below the industrial standard.

5. ACKNOWLEDGMENTS

Financial support provided by The Joint Graduate School of Energy and Environment (JGSEE) is gratefully acknowledged.

6. REFERENCES