

Modification of chitosan by swelling and crosslinking using epichlorohydrin as heavy metal Cr (VI) adsorbent in batik industry wastes

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Abstract. Study on chitosan modification by swelling and crosslinking and its application as a selective adsorbent for heavy metals Cr (VI) in batik industry wastes was done. Swelling is intended to improve chitosan porosity, whereas crosslinking is to increase the resistance of chitosan against acid. Natural samples are generally acidic, thus limiting chitosan application as an adsorbent. Modification of chitosan by combining swelling and crosslinking is expected to increase its adsorption capacity in binding heavy metal ions in water. The modified chitosan was later contacted with Cr (VI) to test its adsorption capacity with a variation of pH and contact time. Finally, application of modified chitosan was done in batik industry waste containing Cr (IV). Based on the results, chitosan-ECH 25% (v/v) was the optimum concentration of crosslinker to adsorb Cr (VI) ions. Modified chitosan has a solubility resistance to acids, even though a strong acid. Modification of chitosan also improved its adsorption capacity to Cr (VI) from 74% (pure chitosan) to 89% with contact time 30 min at pH 3. On the application to the batik wastes, the modified chitosan were able to adsorb Cr (IV) up to the level of 5 ppm. Thus, the modified chitosan has a potential to be applied to as an adsorbent of Cr (VI) in batik industry wastes.

1. Introduction

The process of industrialization can not be separated from the negative effects, the presence of residual materials industry either solid or liquid form can affect the surrounding environment. When the remains are released into free waters, there will be changes in the value of the waters both the quality and quantity that can be considered polluted water. The dynamic relationship of the balance of the composition of the nutrient components, organic matter, and biomass are very important for the stability of aquatic ecosystems, but the stability relations will be soon interrupted when occurs input materials which are toxic. The entry of pollutants will be able to reduce the potential of biological resources.

Pollution by industrial materials which contains hazardous materials, such as pesticides, heavy metals, toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), a concerning issue related to threatening human health and ecosystems [1]. Heavy metals, harmful because of the heavy metals tend to accumulate in the body in sensitive organs and tissues. In humans, heavy metal poisoning will cause severe renal dysfunction, disrupt the reproductive system, damaging internal organs such as liver, brain damage, and central nervous system [2].



Type of heavy metal pollution comes from industrial waste that goes into the environment. So that, for treating wastewater that has been generated, requires an environmentally friendly process. Thus, it is necessary to do research to reduce the heavy metal content in the waste industry. As one of the alternative method that is easy and inexpensive in the reduction of heavy metals by using chitosan as an adsorbent [3-4].

Chitosan was selected as the basis of an adsorbent material for its characteristic that can be attributed as a natural polymer, nontoxicity, biodegradability, biocompatibility, bioactivity and attractive physical and mechanical performance[5,6]. In addition, the cost of production is low, does not generate new waste, and effective at low ionic concentration. Chitosan also has a selectivity and high adsorption capacity. Chitosan is an excellent bio-sorbent of the heavy metal ion. It contains a large number of -NH_2 and -OH groups and its able to remove these stuff in near-neutral solutions. The ability of chitosan can be attributed to 1. its high hydrophilicity generated by a large number of hydroxyl groups of glucose unit; 2. the presence of a large number of functional groups; 3. the high chemical reactivity of these groups and 4. the flexible structure of polymer chain [7]. The reactive amino groups selectively bind to virtually all group III transition metal ion but not a group I and II ion [8]. Chitosan shows a cationic behavior in acidic media. The protonation of amine groups leads to adsorption of metal anions by ion exchange [9,10].

Chitosan can absorb heavy metal contaminants in the water due to the presence of amine and hydroxyl groups which are highly reactive and alkaline. Chitosan will exchange protons owned by metal contaminants with electrons owned by nitrogen (N). However, chitosan is easily dissolved in acetic acid and also partially dissolve in dilute acids, such as HNO_3 , HCl , HClO_4 , and others, so that direct use of chitosan as an adsorbent will be less effective. Chitosan adsorption process will be interrupted by the acidic conditions in the solution. In acidic conditions will dissolve chitosan, so that will limit the properties of chitosan as an adsorbent. This is due to acidic will cause a reduction in the amine group which is the active group that is able to bind to metal ions. For that it is necessary to crosslinking chitosan to improve resistance to acid, increasing the stability of chitosan to form intermediate compounds.

Crosslinking chitosan use of aldehydes as a crosslinking agent that makes chitosan not dissolve in acidic media [11-13]. This crosslinking, cross-linking between the polymer chitosan at -NH_2 groups. This can reduce the absorption of chitosan and metal ions. Crosslinking chitosan using epoxy compound classes such as ethylene glycol diglycidyl ether (EDGE) [14-15], Epichlorohydrin (ECH) [16-17].

To increase the speed of chitosan adsorption to adsorb heavy metal ions, as well as to optimize further the adsorption capacity of chitosan, before crosslinking, swelling the chitosan first to improve the chitosan axis value. Thus, modification of chitosan by making it into a composite by combining the two methods of activation of the swelling method chitosan followed by crosslinking chitosan is expected to increase the adsorption capacity of chitosan to bind heavy metal ions in water.

2. Methodology

2.1. Equipment and material

2.1.1. Equipment used. Equipment used includes laboratory glassware, a set of reflux, Buchi evaporator, electronic scales, heater and a magnetic stirrer, Buchner filter, oven, thermometer, magnetic stirrer bar, pH meters, FTIR spectrometer (Shimadzu 8201 PC), AAS (Shimadzu) and SEM (JSM-35C).

2.1.2. Materials used. Materials used in this study include chitosan (local), NaOH (E-Merck), HCl (E-Merk), NaHCO_3 (E-Merck), CH_3COOH (E-Merck), HNO_3 (E-Merck), H_2SO_4 (E-Merck), Epichlorohydrin (ECH) (Aldrich), Dioxane (E-Merck), Benzaldehyde (E-Merck), Ethanol (95%), Aqua bidest (local), Paper filter (Whatman 21), $\text{K}_2\text{Cr}_2\text{O}_7$ (E-Merck), buffer pH and distilled water.

2.2. Research Methods

2.2.1. Preparation of Chitosan Epichlorohydrin adsorbent bead. 2 grams of chitosan was dissolved in 100 ml of 1% acetic acid (v/v) and stirred continuously for 2 hours. Then NaHCO_3 was added to the chitosan solution at room temperature with a composition variation of NaHCO_3 : chitosan = 0,2:2,0 (w/w) and stirred for about 1 hour. After the solution was sprayed with a 5% NaOH solution of 300 mL (w/v) using chitosan gel injection formed, then washed with distilled water until neutral. Then, the formed chitosan beads added ECH crosslinker agent respectively 8%, 10%, 20% and 25% through the following procedure:

2.2.1.1. Protection with benzaldehyde. Two grams of chitosan beads was added 10 ml benzaldehyde and then stirred for 2 hours at room temperature. It was then filtered and washed using ethanol: water= 1:1, and rinsed with distilled water.

2.2.1.2. Crosslink process of chitosan with ECH. Two grams of chitosan suspended in 20 ml of dioxane in the round bottom flask and stirred. 1M NaOH solution of 4 ml was added slowly to a stirred solution and then was added with varying ECH 8%, 10%, 20%, and 25%. The solution was refluxed for 6 hours. The precipitate that has been obtained was then filtered using Whatman 42 filter paper with a Buchner filter and washed with ethanol and excess water. It was dried for 3 hours at a temperature of 1100°C (to dry). Chitosan that has been crosslinked with ECH crosslinker that has been protected with benzaldehyde then analyzed by infrared spectrometry.

2.2.1.3. Deprotection Benzaldehyde on chitosan that has crosslinked with ECH. Chitosan that has crosslinked with treatment as mentioned above, then as much as 2 grams suspended in a solution of 10 ml 0,5M HCl and allowed to stand for 12 hours. The precipitate obtained was filtered with Whatman 42 filter paper using a Buchner filter and washed with ethanol and water. The powder obtained was dried in an oven at a temperature 1100 C for 3 hours. The results were analyzed by infrared spectrometry.

2.2.2. Adsorption of chitosan modified

2.2.2.1. Effect of pH on the adsorption of Cr (VI) using chitosan adsorbent. Adsorption was performed using a batch system at room temperature. A solution of Cr (VI) 5ppm, set the pH (2, 3, 5, and pH 7) and then added 1 ml of pH buffer. The pH was measured using pH meter TOA by adding HCl or NaOH. 20 ml of Cr (VI) 5 ppm that has set its pH is added to 50 ml beaker glass and added 10 mg of adsorbent (chitosan and chitosan-ECH beads) and then stirred with a magnetic stirrer for 30 minutes. The solution was filtered and then measured the concentration using AAS. A standard solution prepared from mother liquor of Cr (VI) of 100 ppm and diluted with distilled water.

2.2.2.2. Effect of contact time adsorption of Cr (VI) using chitosan adsorbent. Adsorption was performed using a batch system at room temperature. A solution of Cr (VI) 5ppm, pH 3 was measured using pH meter TOA by adding HCl or NaOH, then added 1 ml of pH buffer. 20 ml of Cr (VI) 5 ppm that has set its pH was added to 50 ml beaker glass and added 10 mg of adsorbent (chitosan and chitosan-ECH beads) and then stirred with a magnetic stirrer, contact time was set for 15,30,60, and 90 minutes. The solution was filtered and then measured the concentration using AAS. A standard solution prepared from the mother liquor of Cr (VI) of 100 ppm and diluted with distilled water.

2.2.2.3. Effect of Epichlorohydrin crosslinker concentration on adsorption of Cr (VI). Adsorption was performed using a batch system at room temperature. A solution of Cr (VI) 5 ppm, pH 3 was measured using pH meter TOA by adding HCl or NaOH, then added 1 ml of pH buffer. 20 ml of Cr (VI) 5 ppm that has set its pH was added to 50 ml beaker glass and added 10 mg of adsorbent (chitosan and chitosan-ECH bead). Chitosan-ECH bead was made by varying the concentration of epichlorohydrin 8, 10, 20 and 25%. Furthermore, a solution of Cr(VI) was contacted with each chitosan modified with stirring using magnetic stirrer for 30 minutes at pH 3 which measured using

pH meter TOA by adding HCl or NaOH, then add 1 ml of pH buffer. 20 ml of Cr(VI) 5 ppm which has set its pH was inserted into 50 ml beaker glass and added 10 mg of adsorbent (chitosan and chitosan-ECH bead).

3. Results and Discussion

3.1. Preparation of Chitosan-ECH bead adsorbent

The process of making a modified chitosan begins with swelling process by dissolving chitosan in acetic acid until form chitosan gel. After that, the gel formed, sprayed into the NaOH solution until form chitosan bead. The swelling process intended to increase the surface area and to increase the chitosan axis value. After swelling process, then performed chitosan crosslinking process with ECH. The crosslinking process performed by reacting ECH with chitosan that has protected its amine group with benzaldehyde. The purpose of this protection is to prevent the reaction between ECH with the amine group so that the adsorption capacity of chitosan that has crosslinked not decreased since the amine group is dominant binding to metal ions. IR spectra of Chitosan crosslinked by ECH shown in figure 1.

Figure 1 shows that the protection process of the amine group with benzaldehyde successfully performed, indicated by the appearance of imine peak at 1558 cm^{-1} , and reinforced their new peak at 756 cm^{-1} , and 684 cm^{-1} , which is the bending vibration of benzaldehyde. After deprotection process, imine peak decreased significantly, and the peak of 756 cm^{-1} and 684 cm^{-1} disappeared. It can be concluded that almost all benzaldehyde has been separated from the chitosan. The occurrence of chitosan crosslink with ECH is not so apparent when viewed from the infrared spectra, but the physical properties, crosslinked chitosan is insoluble in concentrated acid, indicates there has been a crosslink between chitosan with ECH.

Crosslink reaction occurred between ECH with the hydroxyl group, and after crosslinking, benzaldehyde released from the amine group by soaking in a solution of 0.5 M HCl to decide imine bond. The scheme of crosslinking reaction with Epichlorohydrin is described in figure 2.

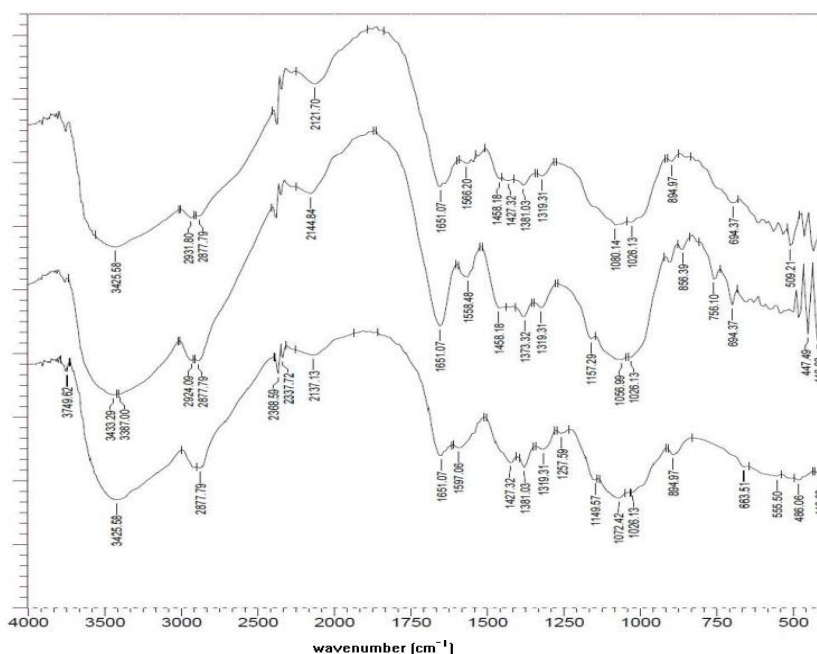


Figure 1. IR Spectra of chitosan-chitosan ECH, benzaldehyde, and chitosan

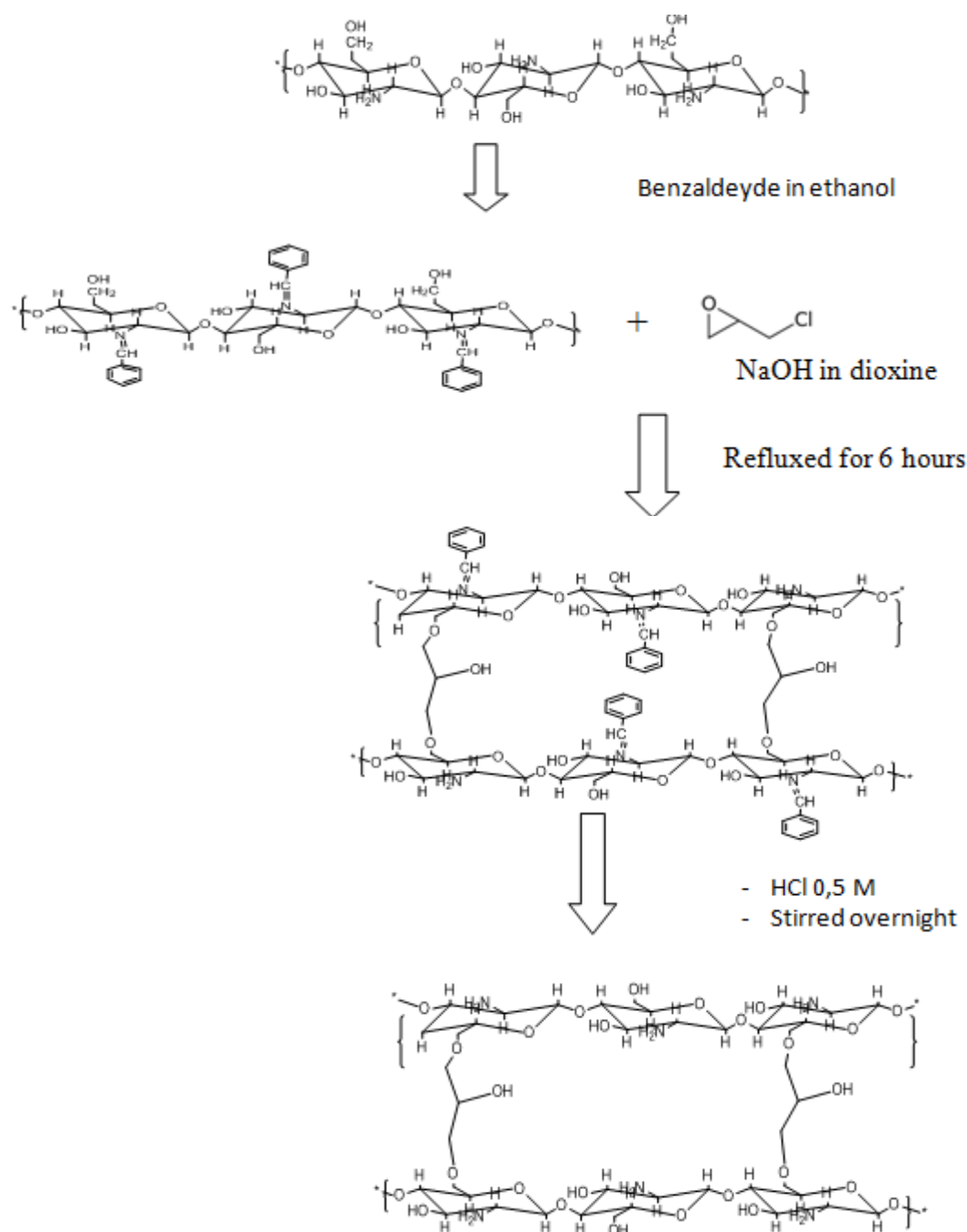


Figure 2. Scheme of crosslink reaction with Epichlorohydrin

3.2. Adsorption process

3.2.1. Determination of optimum pH. Determination of optimum pH was conducted to determine the pH of the interaction in which the adsorbent absorbs to the maximum. Results of research on the effect of pH on an amount of Cr(VI) metal ions adsorbed by the chitosan adsorbent or modified chitosan can be seen in figure 3.

Absorption of the Cr (VI) metal ions by chitosan adsorbent is more stable at various pH compared to modified chitosan, unfortunately, it have lower absorption. It is due to the amine group on the positively charged of chitosan binds the negatively charged of Cr (VI) ions. The greatest absorptive capacity exists at pH 3. At pH 3, the absorption of both chitosan adsorbent has stabilized, thus, pH 3 as a reference for future research. It is in a good agreement with that proposed by Sakkayawong et.al.

(2005), that under acidic condition, the atoms of hydrogen (H^+) in solution can do protonation to an amine group ($-NH_2$) of chitosan, as defined in equation (1).



The protonated amine group that will be used to adsorb Cr(VI) through the mechanism of exchange of bonds. Not only that, but ion exchange also occurs in the H atoms in the OH groups of chitosan, with Cr metal from solution. With this ion exchange, chitosan complexes formed with Cr(VI) metal ions.

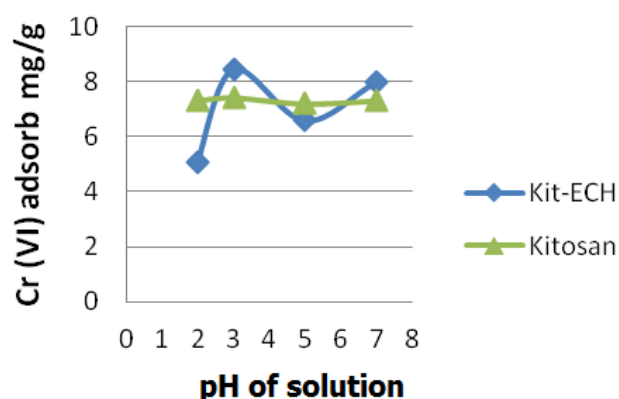


Figure 3. Variations in pH of chitosan adsorption process to Cr(VI)

3.2.2. Determination of contact time. The contact time is the time required adsorbent to adsorb substance of Cr(VI) metal. To determine the optimum contact time, 5 mg of adsorbent in 20 ml of 5 ppm Cr(VI) solution at pH 3 shaken by the variation of contact time of 15, 30, 60, and 90 minutes. Yield curve adsorption of Cr(VI) by chitosan and chitosan modified the contact time variation can be seen in figure 4.

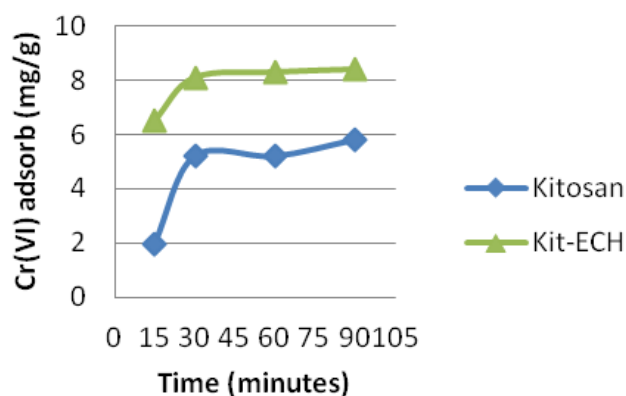


Figure 4. Contact time variation of chitosan adsorbent to Cr(VI)

In figure 4 it can be seen that the adsorption of Cr(VI) show a pattern similar to the adsorption of chitosan and chitosan – ECH adsorbent. On the 15 minutes early the adsorption increase sharply and the addition of the next time experiencing the stability of adsorption. The optimum adsorption of chitosan and chitosan modified adsorb Cr(VI) on the same time at 30 minutes. At 30 minutes, both adsorbents of chitosan were able to absorb optimally, thus, the contact time of 30 minutes serve as a reference for determining the contact time on the adsorption of chitosan and chitosan modified to Cr(VI) in industrial batik waste.

3.2.3. Variation of crosslinker concentration. By varying the crosslinker concentration, epichlorohydrin able to increase chitosan adsorption on the Cr(VI) in solution. figure 5 shows the optimum of crosslinker concentration to adsorb Cr(VI) metal.

Based on figure 5, the ECH concentration of 25% is an optimal concentration to adsorb Cr(VI) metal ion, so it used as a concentration references of crosslinked the chitosan to produce a selective adsorbent that can adsorb heavy metals, especially Cr(VI) with a high capacity.

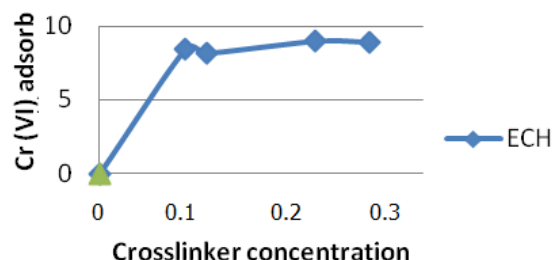


Figure 5. The variation of Epichlorohydrin (ECH) crosslinker concentration to adsorb Cr(VI) metal

3.2.4. Comparison of the adsorption of the Cr(VI) in optimum condition. Adsorption was done at the optimum condition with ECH concentration of 25%, pH 3 and a contact time of 30 minutes. Comparison of adsorption by chitosan and chitosan modified to adsorb 5 ppm Cr(VI) at the optimum condition can be seen in table 1 and figure 6.

Table 1. Comparison of adsorption capacity of chitosan adsorbent

Type of Adsorbent	Concentration of Cr(VI) after adsorption	Adsorption capacity	
	ppm	mg/g	%
Chitosan	1.32	7.4	74
chi-ECH	0.55	8.9	89

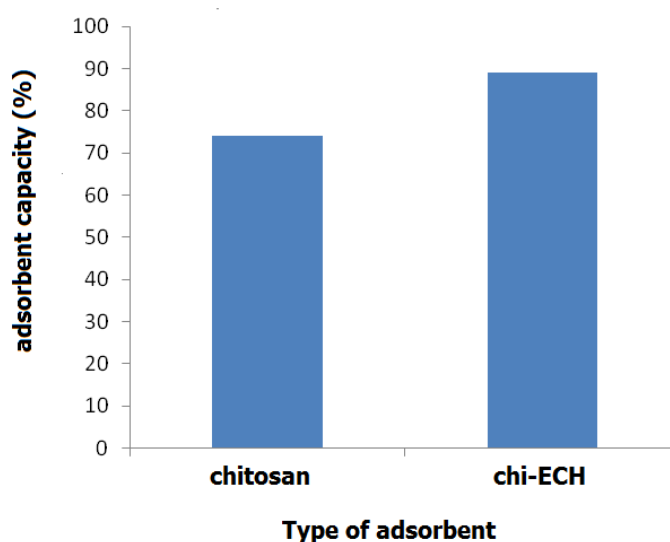


Figure 6. adsorption capacity of chitosan adsorbent

Table 1 and figure 6 show that the modified chitosan and chitosan has a high adsorption capacity due to chitosan has the amine group, there is an element of N that is highly reactive, and alkaline and the hydroxyl groups can bind to the metal through ion exchange mechanism. However, the adsorption capacity of modified chitosan is higher when compared to chitosan, it due to the modified chitosan has through the swelling process and the crosslinking process. The both process seem to further increase the adsorption ability and the resistance to acidic conditions. The presence

of larger cavities on the modified chitosan compared to the chitosan can be seen in figure 7. The scanning electron microscope (SEM) micrograph of the modified chitosan (figure 7b) shows larger cavity on their surface morphology. It proved a great increase in its surface porosity compared to the corresponding non-modified chitosan (figure 7a). It proves that the combination of swelling and crosslink process could increase the adsorption capacity on the Cr(VI) metal. The adsorption capacity of Chit-ECH in adsorbing Cr(VI) ions is 89%; it indicates that the modified chitosan can be used as a good adsorbent for Cr(VI) as well as for Cr(VI) metal in the batik waste.

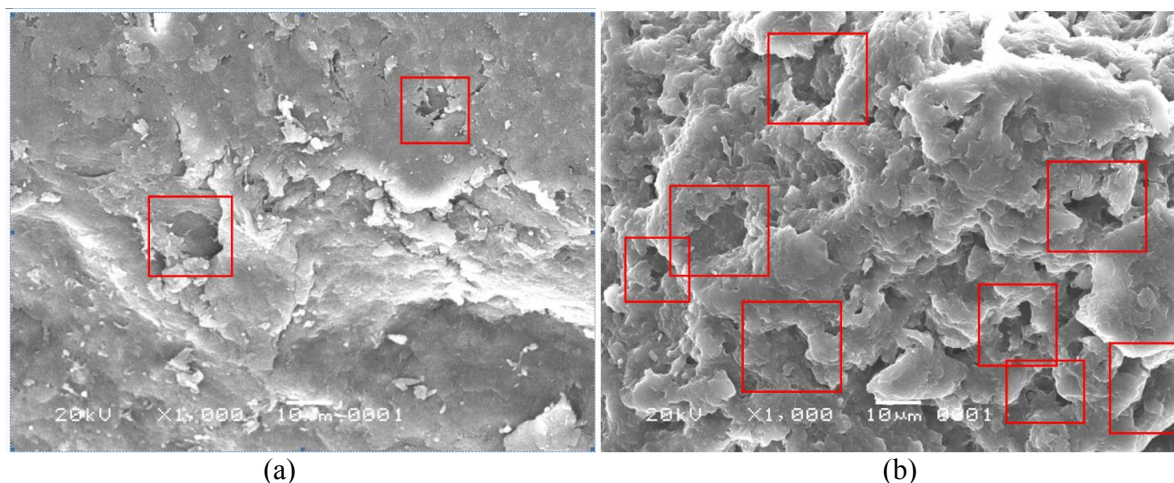


Figure 7. (a) The surface of chitosan and (b) The surface of Chitosan-ECH beads.

3.3. Application of adsorbent on Liquid Batik Waste

Chitosan modified contacted with batik waste is chitosan that is swelled first then crosslinked using epichlorohydrin 25%, with a contact time of 30 minutes at pH 3, subsequently measured the concentration using AAS. AAS test result is shown in table 2.

Table 2. The adsorption of Cr(VI) metal in batik waste by chitosan and chitosan-ECH measured by AAS

Initial concentration of Cr(VI) in batik sample (ppm)	Final concentration after adsorption (ppm)	
	Chitosan	Chitosan-ECH
0.037	0	0

The data in table 2 shows that both of Chitosan and Chitosan-ECH can adsorb Cr(VI) metal in batik waste up to the maximum. Thus, it can be concluded that the Chitosan and Chitosan-ECH are very effective to be used as a super adsorbent to adsorb Cr(VI) heavy metal in the batik waste.

4. Conclusions

The modification of chitosan through swelling process that was combined with crosslinking process produced the modified-chitosan. The modified chitosan then has been used to absorb the Cr (VI) metal. Modification of chitosan with Epichlorohydrin (ECH) 25% crosslinker agent produce an adsorbent that able to adsorb Cr(VI) metal with the adsorption capacity of 89%. Meanwhile, the non-modified chitosan only provide the adsorption capacity of 74%. The modified chitosan also can absorb the Cr(VI) metal in the batik waste. It is proved by the elimination of Cr(VI) content from 0.037 ppm into 0 ppm.

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