A New Adsorbent Chitosan-based That Modified using Epichlorohydrin and Diethylene Triamine for Treating Heavy Metal (Cu^{2+}, Zn^{2+} and Fe^{2+})

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Abstract: In the current study, chitosan was modified using epichlorohydrin and diethylene triamine. Grafting diethylene triamine chitosan is synthesized through alkylation of chitosan with epichlorohydrin and followed by amination with diethylene triamine. The formation of chitosan grafted diethylene triamine was confirmed using FT-IR spectrum which has a band at 1581 cm^{-1} that assigned as C-N-C (secondary amine). The morphological analysis using SEM showed the surface became smoother after grafting process. As adsorbent, the chitosan grafted diethylene triamine had the adsorption capacity 72, 67, and 63 ppm for Cu^{2+}, Zn^{2+}, and Fe^{2+}, respectively.

1 INTRODUCTION

As a developing country, the government set the industrial sector to be the first priority. The growth of new industries gives many negative impacts to the environment, in the form of solid and liquid waste that quite dangerous for human (Cahayaningrum et al., 2011). In the study that conducted by Laksono et al. (2008), in the solid or liquid waste it will be common to obtain the presence of heavy metal waste, as the example in the painting industry, in the liquid waste will be found the ion of Cu, Fe, Cr, Ni, and Zn.

The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment (Faisal & Hasnain, 2004). The rate at which effluents are discharged into the environment especially water bodies have been on the increase as a result of urbanization. Most of these effluents contain toxic substances especially heavy metals. The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment (Horsfall & Spiff, 2005; Igwe & Abia, 2003).

Several treatments have been developed to solve this kind of issue, i.e. precipitation, ion exchange resin, filtration, and adsorption (Tangio, 2013). Adsorption technique is the quite effective method because of the low operational cost, high efficiency and easy method for regenerating (Juir et al., 2017). This method can be done by utilizing natural polymers (biopolymers) as an adsorbent with one of them, namely chitosan (Schumul et al., 2001).

Chitosan is the result of deacetylation of chitin that commonly found in crabs, shrimp and squid (Bhatnaga & Sillanpaa, 2009). Chitosan consist of glucosamine unit and N-acetyl glucosamine unit (Ngah & Fatinathan, 2010). Chitosan as an adsorbent has highest adsorption capacity when compared activated carbon, peat, biomass, agricultural solid waste, industrial by products, silica, zeolite and clay (Crini & Badot, 2008). Abudantly the availability and ease of modification process make chitosan become one of the ingredients adsorbents are widely use in process adsorption (Ngah & Fatinathan, 2010).

Adsorption is the ability of the adsorbate to adhere or attach to the adsorbent. It is a well established separation technique to remove dilute pollutants as well as to recover valuable products from aqueous streams. In the conventional adsorption process, the particle size of the adsorbent is restricted because of hydrodynamic phenomena such as pressure drop.

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Solid surfaces that come into contact with a solution tend to collect layers of solute molecules on their surface due to an imbalance of forces on the surface. Chemical adsorption results in the formation of a monomolecular layer of adsorbate on the surface through the forces of the residual valence of the molecules on the surface. Physical adsorption results from molecular condensation in the capillaries of the solids. In general, elements with greater molecular weight will be more easily adsorbed. There is a rapid formation of an equilibrium interface concentration, followed by slow diffusion into carbon particles. The overall adsorption rate is controlled by the diffusion rate of solute molecules in the capillary pores of carbon particles (Malkoc et al., 2006).

The use of the neat chitosan as adsorbent is not effective due to its high solubility in the acid medium, especially in acetic acid solution, HNO_3, HCl, etc. To resolve the issue, a modification technique is needed to improve the performance of chitosan, this modification can give several advantages, i.e. could be use for several cycles and enhance the stability of chitosan. If an amine compound added to the chitosan's structure, at the end the number of amine group in chitosan will increase. As the impact, it will improve the adsorption capacity due to the new bond, also the selectivity and stability of adsorption.

This study is involved with the introduction of diethylene triamine into chitosan backbone through the reaction of an intermediate of epoxy activated chitosan and diethylene triamine. On the other hand, several studies have indicated that amino groups in chitosan are the main sites for the adsorption. Yi et al. (2006) synthesized chitosan diethylene triamin (DETA) epoxy and compared the capacity of crosslinked chitosan and diethylene triamin chitosan epoxy in adsorbing Pd^{2+}, Ag^{+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Co^{2+}. Yan et al. (2013) carried out the preparation and adsorption properties of chitosan granules modified with diethylene triamine for acid dye adsorption. Juir et al. (2017) crosslinked epichlorohydrin with chitosan to test the mechanical properties and absorption as an adsorbent.

Based on the description above, in this study synthesis of chitosan compound which has been grafting with diethylene triamin (DETA) which occurs through alkylation with epichlorohydrin and amination with diethylene triamin (DETA) and adsorption testing of Cu^{2+}, Fe^{2+} and Zn^{2+} metal ions.

2 MATERIAL AND METHODS

2.1 Material

Chitosan was purchased from Merck (DDA 80%). Acetic acid glacial, sodium hydroxide, methanol, ethanol, acetone, ether, nitric acid, copper sulfate pentahydrate, iron sulfate heptahydrate, and zinc sulfate heptahydrate were obtained from Merck. Epichlorohydrin and diethylene triamine were purchased from TCI.

2.2 Characterization

The functional group of material was determined using FT-IR (Shimadzu). The morphological surface material was analyzed using SEM (JSM-35 C Sumandju). The presence on heavy metal in the material after adsorption process was determine using atomic absorption spectrometer (GF Perkin Elmer).

2.3 Synthesis of Epoxy Chitosan

About 3 g of chitosan was suspended in 250 mL of sodium hydroxide 0.4 M and 30 mL of epichlorohydrin, the mixture was stirred for 5 h at temperature of 50°C. The obtained residue was washed using distillate water, acetone, and ether, respectively. The residue was dried until the constant weight was obtained

2.4 Chitosan Grafted Diethylene Triamine

About 0.5 g of epoxy chitosan was suspended in 30 mL of sodium hydroxide 0.1 M and 0.5 g of diethylene triamine, this mixture was stirred for 4 h at temperature of 60°C. the obtained residue was washed using distillate water, alcohol, and acetone, respectively. The residue was dried until the constant weight was obtained. The above procedure was repeated for the other variation of diethylene triamine (1 and 1.5 g).

2.5 Adsorption of Heavy Metal Solution

The adsorption of heavy metal ion was performed using the sulfate salt solution of each heavy metal, i.e.$CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$. About 0.01 g chitosan grafted diethylene triamine was weighed and suspended in 50 mL of the heavy metal solution (200 ppm). The mixture was stirred for 20 min at room temperature and then filtered. The obtained filtrated was added with concentrated nitric acid and the pH was adjusted into 3. The final solution then was measured using AAS.

The capacity adsorption of modified chitosan can be determined using the following equation:

$$q = \frac{(Co - C)}{Co} \times 100\%$$

where, q was the percentage of capacity adsorption. Co and C was the heavy metal ion concentration before and after treatment (ppm). In Fig. 1 below showed the proposed mechanism of the formation of chitosan grafted diethylene triamine.

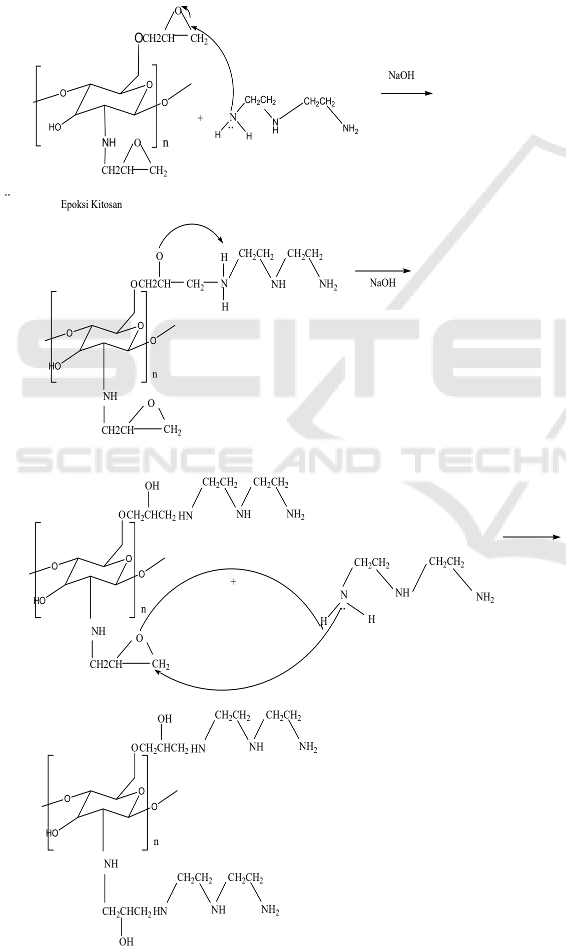


Figure 1: Proposed mechanism of the formation of chitosan grafted diethylene triamine.

3 RESULT AND DISCUSSION

3.1 FT-IR

Chitosan grafted diethylene triamine was synthesized using chitosan, epichlorohydrin, and diethylene triamine. This synthesis was performed in two steps, i.e. the formation of epoxy chitosan and the grafting of diethylene triamine.

In the first step, alkylation reacts with chitosan with epichlorohydrin. Where the OH group changes in chitosan to C-O-C epoxy. The FT-IR spectrum (Figure 2) shows that the wave number 3448.72 cm^{-1} shows the -OH and $-NH_2$ groups (Sastrohadmijojo, 2018). At wave number 2924.09 cm^{-1} shows stretching –CH (sp^3) bonds (Hartomo & Purba, 1986). The amine C-N group appears at wave number 1381.03 cm^{-1}. For C-O-C epoxy groups appear at wave number 1319 cm^{-1}. At wave number 1072.42 cm^{-1} is a C_1-C_5 bond and is a β-1,4-glycosidic bond (Pavia, 2001).

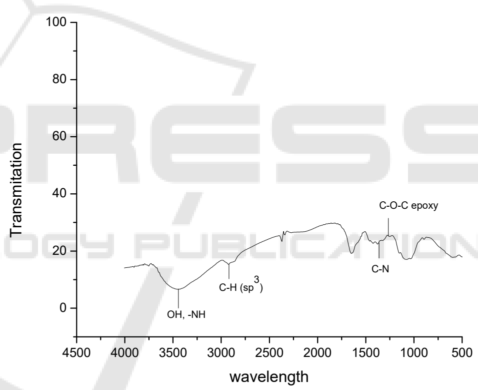


Figure 2: FT-IR Result of Epoxy Chitosan.

In the second step, the formation of diethylene triamin chitosan grafting through the epoxy chitosan amination with diethylene triamin. The FT-IR spectrum (Figure 3) shows the -OH and $-NH_2$ groups that appear at the wave number 3425.58 cm^{-1} (Sastrohadmijojo, 2018). At wave number 2924.09 cm^{-1} indicates the presence of –CH (sp^3) bonds (Hartomo & Purba, 1986). The formation of C-N-C groups in diethylene triamin chitosan grafting compounds appears at wave number 1458.18 cm^{-1}. The amine C-N group appears at wave number 1381.03 cm^{-1}. At wave number 1080.14 cm^{-1} is a C_1-C_5 bond and is a β-1,4-glycosidic bond (Pavia, 2001).

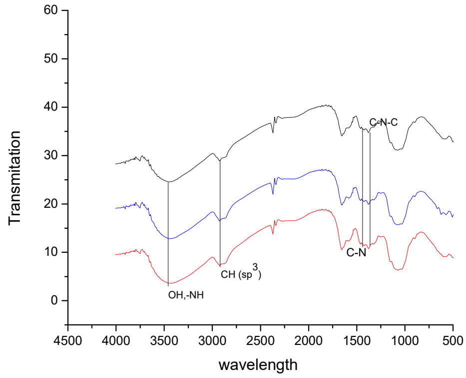


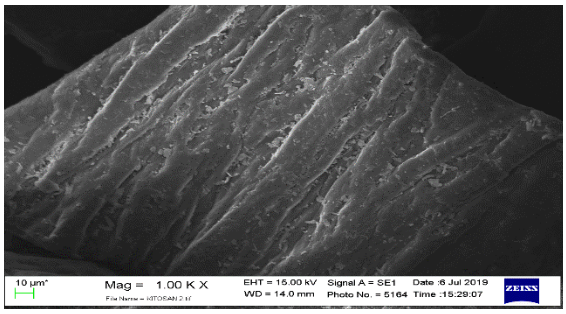
Figure 3: FT-IR spectrum of modified chitosan (chitosan grafted DETA (with varian DETA).

3.2 Scanning Electron Microscopy (SEM)

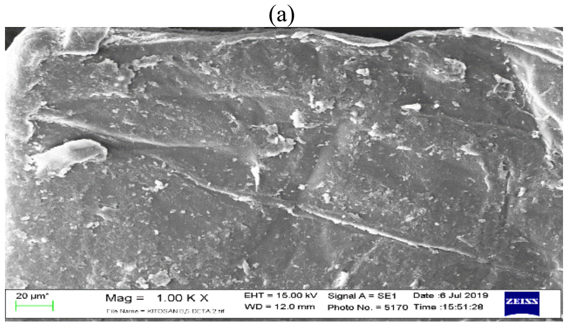
Fig. 4 showed the morphological surface of chitosan and modified chitosan which has a significant difference. The number of chitosan fibril on the surface was decrease after the addition of epichlorohydrin and diethylene triamine. The increase of diethylene triamine caused the film's surface became smoother. The presence of tiny particle and crust layer on the film's surface can be indicated as the successful of grafting process. The change of surface morphology as the result of chemical interaction between the hydroxyl and aine of chitosan. With this change in the film's morphology could improve the adsorption performance.

3.3 Adsorption of Heavy Metal

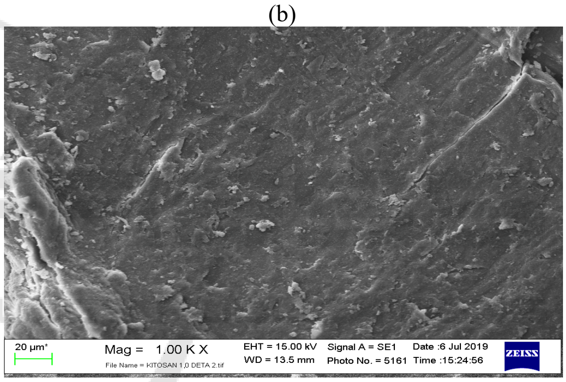
Adsorption performance of modified chitosan to Cu^{2+}, Zn^{2+} dan Fe^{2+}can be seen in Table 1 and Table 2. Chitosan grafted with 1.5 g diethylene triamine showed the highest performance to adsorb Cu^{2+}, with adsorption capacity 72.0 ppm. It adsorbed 36% of Cu^{2+} that presence in the solution of Cu^{2+} 200 ppm. The obtained of this result as the impact of the modification of chitosan structure. This modification improves the reactivity of chitosan due to the presence of new amine group from diethylene triamine in the modified chitosan. The increase of amine group improves the ability of modified chitosan to form a chelate with the heavy metal ion, it means the adsorption capacity will enhance. The lone pairs electron in nitrogen can be used to form a complex with transition metal through coordination bonding (Lerivrey et al., 1986).



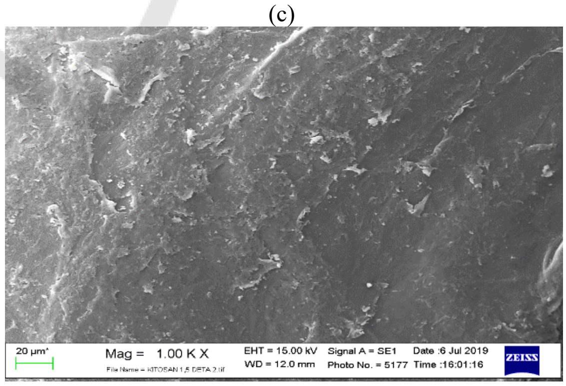
(a)



(b)



(c)



(d)

Figure 4: SEM images of a) chitosan b) chitosan grafted 0.5 g diethylene triamine, c) chitosan grafted 1.0 g diethylene triamine, d) chitosan grafted 1.5 g diethylene triamine.

Table 1: The adsorption capacity of modified chitosan.

Adsorbent	Adsorption capacity (mg/L)		
	Cu^{2+}	Zn^{2+}	Fe^{2+}
Chitosan	25.7	27.0	37.2
Chitosan grafted 0.5 g diethylene triamine	51.8	48.8	58.9
Chitosan grafted 1.0 g diethylene triamine	64.3	52.1	62.4
Chitosan grafted 1.5 g diethylene triamine	72.0	67.0	63.9

Table 2: Adsorp of modified chitosan.

Adsorbent	% Adsorb		
	Cu^{2+}	Zn^{2+}	Fe^{2+}
Chitosan	12.8	13.5	18.6
Chitosan grafted 0.5 g diethylene triamine	25.9	24.4	29.5
Chitosan grafted 1.0 g diethylene triamine	32.2	26.1	31.2
Chitosan grafted 1.5 g diethylene triamine	36.0	33.5	32.0

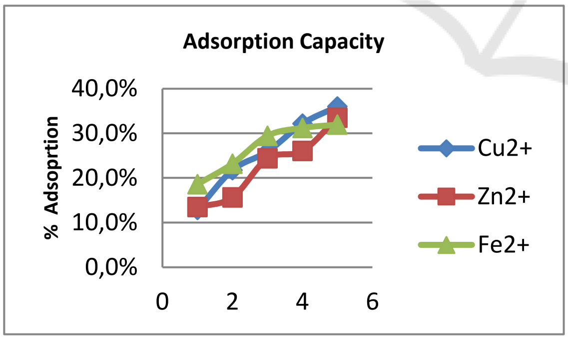


Figure 5: Adsorption capacity curve of modified chitosan.

According to Fig. 5, the highest performance from three kinds of modified chitosan is shown in chitosan grafted with 1.5 g diethylene triamine, especially for adsorbing Cu^{2+}. This is caused by the highest acidity level of Cu^{2+} compared to Zn^{2+} and Fe^{2+}, it caused Cu^{2+} is easier to form complex with chitosan. The ability of adsorbent to adsorb the specific component is influenced by pH, related to protonation or deprotonation of adsorbent's active site. The system's pH will influence the charge on the adsorbent surface, degree of ionization, and the species that able to absorb in the process.

4 CONCLUSIONS

Chitosan grafted diethylene triamine was synthesized through alkylation and amination using epichlorohydrin and diethylene triamine, respectively. The formation this modified chitosan was confirmed from FT-IR spectrum with the presence of C-N-C vibration at 1581 cm^{-1}. The morphological analysis showed the surface became smoother after grafting process. The modified chitosan has specific adsorption capacity for each heavy metal ion, i.e. Cu^{2+} = 72,0 ppm; Zn^{2+} = 67.0 ppm dan Fe^{2+} = 63.9 ppm.

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