

THE ADSORPTION CAPACITY OF CHITOSAN -ALUMINA TO Cr(III) AND Ni(II) IONS

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Abstract

The research is aimed to synthesize of chitosan impregnated on alumina and to characterize its adsorptive capacity towards Cr (III) and Ni(II) ions individual and Cr(III)-Ni(II) mixture. Chitosan was isolated from green crab's shell (*Scylla Serrata*) which then wet impregnated to alumina producing chitosan-alumina. The adsorption experiment was carried out at room temperature for 24 hours at pH system 4,5. A half gram of chitosan-alumina was added into 50 mL solution of Cr(III), Ni(II) and Cr(III)-Ni(II) (1:1) mixture to measure the adsorption capacity. The result shows that metal ions were individually and simultaneously adsorbed by chitosan-alumina. Chitosan-alumina was characterized by FTIR and the adsorption capacity determined by Atomic Absorption Spectrophotometer, and giving the adsorption capacity of Ni(II) ion (47 mg/g) was greater than Cr(III) ion (24 mg/g). Whereas adsorption capacity of each ion in the mixture solution were 28 mg/g for Ni(II) and 21 mg/g for Cr(III) in agree with the result of the adsorption capacity of the individual ions. The greater adsorption capacity of Ni(II) than Cr(III) is due to Cr(III) the clustered faster than adsorbed.

Introduction

The existence of heavy metal in waterways can be endangered to human and its environmental by which it is required a method to reduce the amount of heavy metal in the waterways [1]. One of important method applied is metal adsorption using adsorbent such as bentonite, zeolite and chitosan.

Industrial liquid waste may contain poisonous chemicals i.e Pb(II), Cu(II), Ni(II) and Cr(III) [2], and so need to be processed with a cheap and simple technology. Liquid waste treatment may involve precipitated ion, or adsorption.

Endang W Laksono, Jaslin Ikhsan et al [3] confirms the chitosan can adsorb metal ions such as Cr(III), Fe(II), Pb(II), Zn(II), Ni(II), Cu(II), Cd(II), Co(II), Mn(II) Fe(III) and Al(III) in solution without any complicated initial treatments. Chitosan and metal ions bond in complex mechanism using two functional groups of chitosan i.e -OH and NH₂ and form a multilayer [4].

The highly adsorptive capacity of chitosan to metals can be obtained by studying the adsorption models of metal ions in chitosan. Impregnated can be successfully synthesized by understanding the types

of chitosan-metal interactions. To increase the adsorptive capacity, chitosan are combined with another particular component such as succinate acid [5] or chelated with chelating agent [6] or supported with 3,4 dihydroxybenzoic acid [7].

Chitosan is a deacetylated product of chitin a natural biopolymer found in arthropoda shells such as crab's shell. Darjito [8] arranged the active sites of chitosan by impregnated the chitosan on alumina. Impregnation of Chitosan on the alumina result in distribution active sites randomly over the alumina surfaces. The impregnation of chitosan on the alumina is expected to be able to increase of adsorption ability of chitosan to Cr(III) and Ni(II) ions.

Experimental methods

Chitosan were isolated from green crab's shell. This preparation method is adopted from Hong [9] involving : (i) deproteination (ii) demineralization and (iii) deacetylation. The 40 mesh green crab's shell is refined, pounded and strained and also added with 3,5% NaOH and refluxed at 65^o C for 2 hours. After that the mixture was filtered and the residue was rinsed until neutral. Demineralization is undertaken by mixing residue with dilute chloride acid (1M) and refluxing at the 60^o C. The result of the process is chitin. Deacetylation is undertaken by mixing residue with concentrated sodium hydroxide and refluxing on the 100^oC . At room temperature the strain and residue are washed with water until neutral. The residue is analyzed using Infra Red Spectrophotometer (FTIR).

Chitosan is impregnation onto Alumina to apply wet impregnation method with oxalic acid solvent. Gel of chitosan-oxalic is made by dissolving 5 grams chitosan in 100 mL hot oxalic acid solution 10 % (b/v). Alumina gel is prepared by mixing 1:1 alumina powder with 10 % (b/v) oxalic acid solution at room temperature. In 100 mL of hot aquadest (50 °C) dissolved slowly 43 grams chitosan-oxalic gel and 50 grams alumina-oxalic gel. Mixture then is hushed and decantation. To increase the number of bonds between chitosan and alumina, an extra chitosan-oxalic gel is added to the results and is stirred for 2,5 hours. The precipitate is dissolved with 125 mL NaOH 0,1M and stirred for 30 minutes. The solid

material is dried in the oven at 55°C for 5 hours. The sample is characterized by Infrared spectroscopy.

The adsorption capacity of chitosan- alumina is determined based on the selected cationic concentration that is between 100-500 ppm. The adsorption capacity chitosan- alumina toward Ni(II) and Cr(III) are studied by comparing the concentration each ions before and after adsorption process. The ions concentrations are measured by Atomic Adsorption Spectrophotometer (AAS). The adsorption is carried out at room temperature for 24 hours in optimal pH system using a adsorbent: adsorbent proportion of 100:1.

The pH of the adsorption system is arranged using nitric acid 0,01 M or sodium hydroxide 0,01 M. A half gram of chitosan-alumina was added into 50 mL Cr(III) and Ni(II) solution, and the concentration is 300 ppm. The optimizing of pH experiment was carried out at room temperature for 24 hours. The adsorption capacity of the sorbent is determined by comparing the concentration of the each ions before and after adsorption process.

Result and Discussion

The chitosan is impregnated in the alumina-oxalic gel, and the reaction is described in Figure 1.

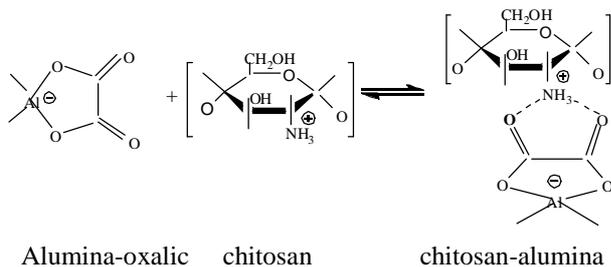


Figure 1. The formation of chitosan- alumina bonds

The carboxyl groups of alumina-oxalic are coordinated with -NH_2 groups of chitosan. The active sites of chitosan-alumina are NH_3^+ groups and carboxyl groups, the carboxyl groups has a negative (-) charge. All of the active sites are possible to bond with cations in adsorption process.

The Infra Red spectra of chitosan-alumina and the interpretation of the spectra are presented in Figure 2c, and Table. 1. The functional groups of chitosan spectra can be seen on the Figure. 2b, and the functional groups of alumina shown in Figure. 2a. Vibration of NH-amine groups of chitosan are indicated by band 1635 cm^{-1} . The amide (NH_2) of chitosan is appeared at $1430,31\text{ cm}^{-1}$ (Fig. 2b)

The absorption band of active sites (NH_2 groups) of chitosan-alumina moved from $1430,31\text{ cm}^{-1}$ to 1419 cm^{-1} , and the other active sites (carboxyl groups) is appeared at $1315,83\text{ cm}^{-1}$. The -NH_2 group of chitosan-alumina is more intens than chitosan (1654

cm^{-1}). The vibration of Al-O groups shifted from $658,9\text{ cm}^{-1}$ (Fig. 2.a) to $780,75\text{ cm}^{-1}$ (Fig.2.c)

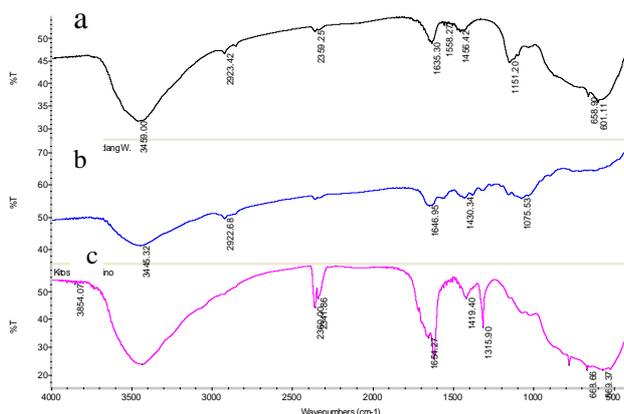


Figure 2. The IR Spectra of Alumina(a), chitosan (b)and chitosan-alumina (c).

Table 1. The interpretation of the IR Spectra

Functional groups	Wave number (cm^{-1})		
	alumina	chitosan	Chitosan-alumina
Vibration of OH Primer amide of NH	3459,00	3445,32	3444,16
Streching NH of amine	--	1635,30	1651,27
Vibration of C=O	--	--	1619,57
NH of amide	--	1430,31	1419,40
Vibration of C-O	--	--	1315, 83
Al-O	658,9	--	780,75

Optimization of pH System

The pH system is optimized for individual of Ni (II) and Cr (II) adsorption. The relation between the adsorption capacity and pH system are presented in the Figure 3 and 4. The pH of the system for optimum individual adsorption Ni(II) and Cr(III) are 4,9 and 4,3 respectively.

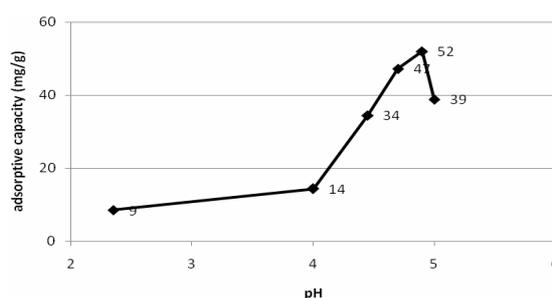


Figure. 3. Curve between pH system and adsorptive capacity chitosan- alumina to Ni(II)

The comparisons of the adsorption capacity of chitosan- alumina to ion Ni(II) and Cr(III) were carried out at the pH at 4,5, i.e the mid value of 4,3 and 4,9.

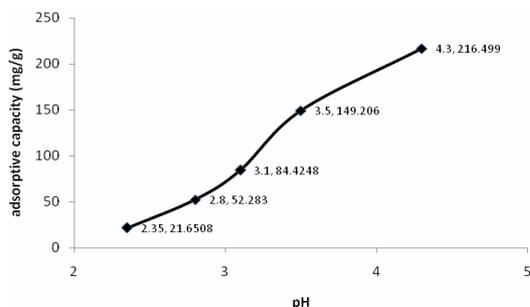


Figure. 4. Curve between pH of system and adsorptive capacity of chitosan- alumina to Cr(III)

Adsorption Capacity of Chitosan- Alumina

Figure 5a shows the adsorption capacity of chitosan- alumina to Ni (II), Cr (III) and Figure 5.b shows the adsorption capacity chitosan-alumina to Ni (II)-Cr (III). The adsorption capacity of chitosan-alumina to Ni (II) is higher than of the Cr (III) for both individual and the mix. The highest adsorption capacity of chitosan- alumina to Cr(III),and Ni(II) is 24 mg/g and 47 mg/g, respectively. And the highest adsorption capacity of chitosan alumina to Ni(II) and to Cr(III) is 21 mg/g and 28 mg/g in Ni(II)-Cr(III) mixture (Figure 5.b). The Figure 5.b also show that at low concentration the chitosan-alumina adsorb, Ni(II) ion similar to the Cr(III) ion. It is possible that the adsorption of chitosan-alumina-Cr(III) ions interaction reached equilibrium first compare to chitosan-alumina -Ni(II)

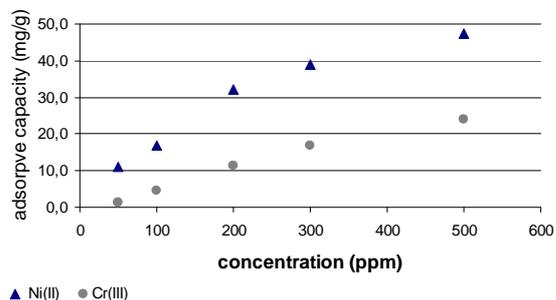


Figure.5a. The adsorption capacity of chitosan-alumina to Ni(II) and Cr(III) individually

If we compare the adsorption capacity of chitosan-alumina to Ni(II) and Cr(III), the adsorption capacity of chitosan-alumina to Ni(II) is higher than Cr(III) individually and their mixture. Although Cr(III) is a hard base, and the carboxyl is a hard acid, and those they are easily combine to form a

cluster on chitosan- alumina. In fact, the chitosan-alumina adsorbs the Ni(II) more than the Cr(III) individually and the mixture Ni(II)-Cr(III).

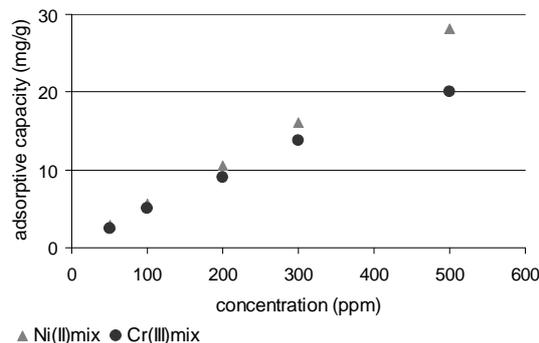
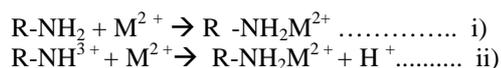


Figure.5b. The adsorption capacity of chitosan-alumina to Ni(II) and Cr(III) in Ni(II)-Cr(III) mixture

Assuming that the condition of their adsorption process is same and the surfaces are homogeneous, it means that the adsorption capacity of chitosan-alumina is really depended on the nature of the cations. The Cr(III) form a cluster in water [10]. It is possible that the Cr(III) cluster formation is faster than that of Cr(III) binding to active sites of the chitosan-alumina. The other reason is that the cluster formed between Cr(III) and water causing slow movement of the Cr(III) cluster binding the active sites of chitosan-alumina sorbent.

There are four forms active site that might be involved in the adsorption process, form of chitosan, chitosan-oxalic, alumina-oxalic and chitosan-alumina. In the experiment of the optimum pH is 4.5, so that cluster amine can changes in ion $R-NH_3^+$ which metal ions still bound up on the surface of chitosan, and there is less possibility of the use NH_2 bonded to the metal ion. The possibility reaction is [11]:



R is a other groups of chitosan , except $-NH_2$

The NH_2 groups as the active sites of chitosan bind with cation M^{2+} directly (reaction i). In reaction (ii), the M^{2+} is exchange with H^+ , so the end of the reaction the pH of the system is decreased. Because in this experiment the pH of the system didn't changed so the reaction (ii) is impossible.

The second possibility is the bonding of cation and active sites of chitosan-oxalic. This reaction are described in the the Figure. 6. Reaction allows cations (M^{2+}) tied to the cluster carboxyl of chitosan-oxalic. Figure.7 describe the binding of cations M^{2+} and the negative sites of alumina-oxalic as another possibility. The alumina-oxalic gel have a negative sites. So the cations can interact with the negative sites of alumina. The fourth possibility is that the cations bind the cluster carboxyl of chitosan-alumina, as described in Figure 8. The interaction of chitosan-alumina and cations is an intramolecular bonding type. The

interaction formed a cluster via the carboxyl groups. Thus the interaction depends on the number of carboxyl groups of chitosan- alumina.

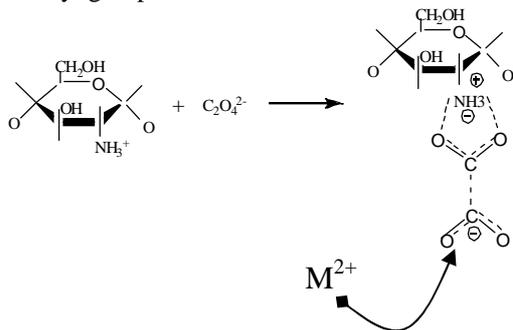


Figure 6. The formation of chitosan-oxalic

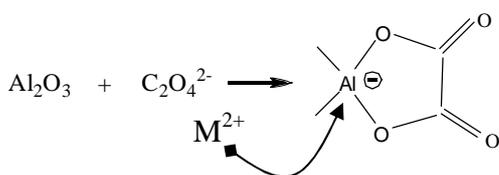


Figure 7. The active sites of alumina-oxalic

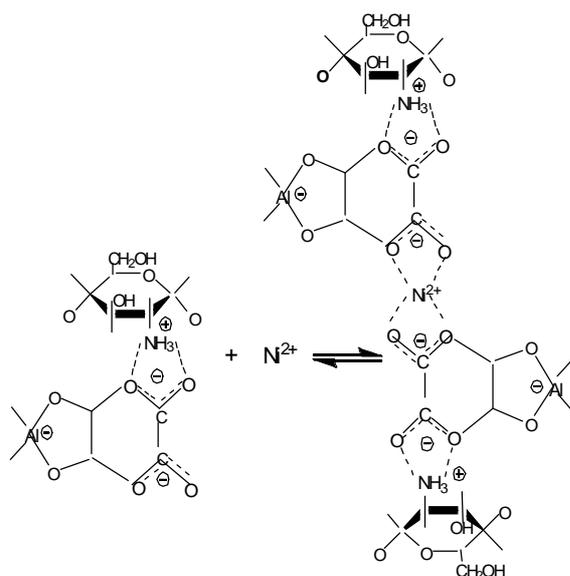


Figure 8. The reaction of cation with chitosan-alumina

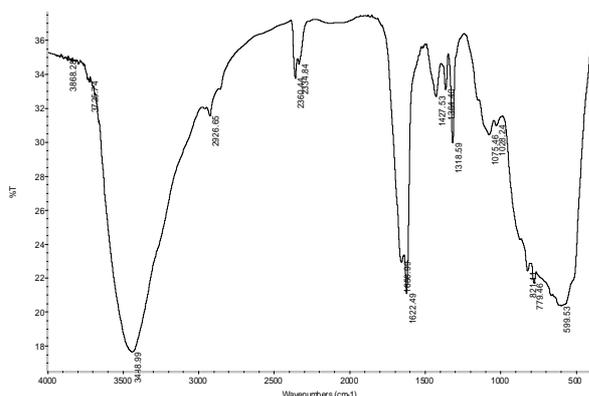


Figure.9. The IR spectra of chitosan-alumina after adsorption

The IR spectra of chitosan-alumina after adsorption is presented in Figure 9. The bands of the functional groups are shifted i.e the carboxyl group from 1619,57 cm^{-1} to 1622,49 cm^{-1} ; the NH amine group from 1419,40 cm^{-1} to 1427,53 cm^{-1} . The movement of the band is indicated that the surface environment is changed. The change is caused by the interaction between surfaces and cations.

In the end of the adsorption process, the pH of the system did not change. It means that the cation is bonded to the cluster carboxyl as active sites directly. There is no ion exchange between hydrogen ions (H^+) and cations.

Conclusion

The results show that the adsorption capacity of chitosan-alumina sorbent towards Cr(III) and Ni(II) is 24 mg/g and 47 mg/g, respectively. The adsorption capacity of the sorbent towards the cations in the competitive sorption system shows significant differences, which are 21 mg/g and 28 mg/g towards Cr(III) and Ni(II) cations, respectively. The Cr(III) cation is less adsorbed than that of Ni(II) because the Cr(III) cation forms a cluster in water, causing low movement of the Cr(III) cluster binding the active sites of chitosan alumina sorbent.

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