



ADSORPTION STUDIES OF Fe(III) ION ON GLUTARALDEHYDE CROSS-LINKED CHITOSAN AND ITS APPLICATION IN PURIFYING VETIVER OIL

**PURWANTININGSIH SUGITA^{*}, HENNY PURWANINGSIH and
MUHAMMAD FATHURRAHMAN**

Department of Chemistry, FMIPA, Institut Pertanian Bogor, Dramaga,
BOGOR 16880, INDONESIA

ABSTRACT

Adsorption of Fe(III) ion by glutaraldehyde cross-linked chitosan (chitosan-GA) has been studied by using batch method. The objectives of this research are to determine the optimum adsorption condition of Fe(III) ion by chitosan-GA, to study the isothermal, kinetics, and effects of Cu(II) ion for adsorption of Fe(III) ion and its application in purifying vetiver oil. The optimum condition is found through response surface Box Behnken method. The adsorption isotherm follows Langmuir and Freundlich models. Percent adsorption value of Fe(III) ion by Chitosan-GA (DD = 78%) is 92% in optimum conditions, i.e. 0.75 g adsorbent weight, 25°C, and 360 min contact time. The adsorption process of Fe(III) ion by chitosan-GA fits into Freundlich and pseudo second-order models. The existence of Cu(II) ions is able to decrease the percent adsorption value of Fe(III) ion by chitosan-GA. Percent adsorption of Fe(III) ion by chitosan-GA is higher than that of Cu(II) ion at all conditions. Percent adsorption of Fe(III) and Cu(II) ion by chitosan-GA in vetiver oil is lower than other conditions (solution of Fe³⁺ and Cu²⁺ ion with its concentration ratio of 1:1).

Key words: Adsorption, Chitosan-glutaraldehyde, Fe(III) ion, Vetiver oil.

INTRODUCTION

One of the non-oil export commodities of Indonesia is vetiver oil, which in the world of international trade is often called java vetiver oil. This oil is produced by distilling vetiver (*Vetiveriazizanioides*) leaves. High grade of vetiver oil is widely used as fixative in perfumery, while the low-quality is commonly used as deodorant soap. Vetiver oil produced in Garut plantation can reach 50-75 tons/year. The production is of course depends on the

^{*} Author for correspondence; E-mail: atiek_ps@yahoo.com

availability of raw materials, climate, and demand. The volume of Indonesian vetiver oil products can compete with other countries, but the price is still low. For comparison, in 2011 the lowest price of Indonesian vetiver oil is \$111.11/Kg while that of Haitian products at least \$150.10/Kg. This is due to the differences in quality.

The result of observations indicate that vetiver oil distillates in Garut still look darker in color. According to Hernani¹, the dark color is due to contamination by Fe(III) and Cu(II) metal ions. In short, the oil contains two metal ions that affect the physical and chemical properties of the oil. Purification is one process that is used to improve the oil quality to get higher resale value. Vetiver oil refining process can be done by chemical or physical ways. Physical refining process can be done by redistilling the crude oil, producing clearer and higher main chemical components. However, this method requires specific support equipment and also operational costs that are relatively expensive. Chemical purification can be done in several ways; one of them is adsorption method. Adsorption is an appropriate and easy method to adsorb metal ions. Adsorption can be performed using simple equipment, just mixing the oil with the adsorbent in certain condition².

Studies to improve the quality of vetiver oil by using adsorbents has been done. Bentonite 2% (w/v) that were applied to vetiver oil increases vetiverol levels of 48.67% to 49.18%, and iron ion decreases from 2.76 ppm to 2.53 ppm. In addition, copper ion decrease from 2.13 ppm to 1.96 ppm¹. Other study by Firdaus² reported that the use of zeolite 2% (w/v) on vetiver oil can increase vetiverol levels of 51.90% to 78.68%, but the acid content still exceeds the standard limit. In addition, the use of activated charcoal on vetiver oil has been reported to adsorb the dye as much as 90% of the original dye contained in the oil, but the activated charcoal has pores that adsorbed the oil. Oil in the the pores of the activated charcoal is very difficult to separate³.

One of the emerging adsorbent developed is chitosan. Chitosan is abundant polymers in nature that are produced from chitin deacetylation process. Research on chitosan as an adsorbent with or without modification has been widely reported. The ability of chitosan to attract metal ions is through chelating or ion exchange mechanisms (depending on the type of metal ions and pH of the solution) by the amino and hydroxide groups on the chemical structure of chitosan.

The use of chitosan directly as an adsorbent is less effective because it is mechanically fragile and easily degraded biologically, and easily soluble in dilute acid. This weakness can be overcome by modifying cross-linked chitosan. One of the cross-linker

materials that are often used is glutaraldehyde (GA). GA have been selected as a cross linker because it can improve the mechanical properties of chitosan so that increases the stability of the chitosan structure either thermally or under acidic condition⁴.

Related research on the application of chitosan-GA was done by Rahmi and Julinawati⁵, who reported that the use of 5 g of chitosan-GA on diesel oil for the adsorption of Cu(II) metal ions at 70°C for 75 min resulted in adsorption by 73%. Another study conducted by Muharram et al.⁴ reported that 0,875 g of chitosan-GA adsorb [Au(CN)₄] ion at pH 2 for 120 min and resulted in percent adsorption of 97,874%. Study on the use of chitosan-GA as adsorbents of metal ions on vetiver oil has yet to be done. The objectives of this experiment are to determine optimum adsorption condition of Fe(III) ion by chitosan-GA, and observe the isothermal, kinetics, and effects of Cu(II) ion for adsorption of Fe(III) ion and its application to vetiver oil purification.

EXPERIMENTAL

Materials and methods

The main materials used in this study were chitosan and vetiver oil. Chitosan was purchased from Brataco with 78% degree of deacetylation and vetiver oil samples obtained from one distillery in Garut district. Instrument used was atomic absorption spectrophotometer (AAS) Shimadzu Model AA 7000 and Fourier transform infrared (FTIR) Model Bruker Tensor 37.

The stages are carried out in this study are: (i) Analysis of the levels Fe(III) metal ions and Cu(II) metal ions in vetiver oil, (ii) Preparation of chitosan-GA flakes and its characterization, (iii) Optimization of adsorption Fe(III) ions by chitosan-GA, (iv) Determination of isothermal and kinetics of adsorption, and (v) Effect of Cu(II) metal ions to the adsorption of Fe (III) metal ions.

Analysis of the levels Fe(III) metal ions and Cu(II) metal ions in vetiver oil

Vetiver oil sample was weighed ± 5 g in crucible porcelain. Furthermore, vetiver oil samples along with the crucible porcelain were heated at 600°C for 5 hrs. Ash from the furnace was then diluted with 5 mL of HCl p.a. and then carefully heated until the volume is reduced to half of the initial volume. The mixture was filtered, and the filtrate was put in a 25 mL volumetric flask. Levels of metal ions Fe(III) and Cu(II) in vetiver oil were analyzed using AAS at a wavelength of 248.3 and 324.7 nm.

Preparation of chitosan-GA flakes and its characterization

Chitosan flakes weighed ± 5 g and then soaked in 75 mL of 2.5% GA while agitated at 220 rpm and at room temperature for 24 hrs. Furthermore, chitosan-GA flakes washed and dried at room temperature. Chitosan and chitosan-GA, which has been formed subsequently analyzed using FTIR functional group.

Optimization of adsorption Fe(III) ions by chitosan-GA

The optimization process is carried out on three parameters: Contact time, temperature and weight of the adsorbent. Procedure: Flakes of chitosan-GA were added to 50 mL of Fe(III) 10 ppm, which was adjusted to pH = 5. Determination of pH conditions is based on the research results of Dai et al.⁶, who have reported that the adsorption of metal ions Fe(II) and Fe(III) by thiourea cross-linked chitosan achieve optimum conditions at pH = 5. After the mixture was stirred at the appropriate experimental conditions Box Behnken experimental design. The mixture is then filtered and Fe(III) ions content in the filtrate was analyzed using AAS at a wavelength of 248.3 nm.

Determination of isothermal and kinetics of adsorption

Optimal parameters (time, temperature, and weight of adsorbent) are used as experimental conditions in the study of isothermal and kinetics adsorption. Experiments conducted in the determination of isothermal adsorption is as follows: Chitosan-GA was added to 50 mL of solution with a concentration Fe(III) 10, 20, 30, 40, 50 mg/L, and then stirred at optimum conditions. Furthermore, chitosan-GA was filtered and Fe content in the filtrate was analyzed by AAS at a wavelength of 248.3 nm. Experiments: The effect of the initial concentration of a solution of Fe(III) on the adsorption kinetics was performed as follows: Chitosan-GA respectively added to 50 mL of Fe(III) with concentrations of 10 and 30 mg/L was then stirred at optimum conditions. At an interval of 150 min, every 30 min 10 mL aliquots was taken. Furthermore, the levels of Fe(III) ions in the aliquot was analyzed by AAS at a wavelength of 248.3 nm.

Effect of Cu(II) metal ions to the adsorption of Fe (III) metal ions

Experiments influence of metal ions Cu(II) on the adsorption of metal ions Fe(III) is carried out under two conditions. These conditions are artificial and natural conditions. An artificial condition is a sample solution containing metal ions Fe(III) and metal ions Cu(II) with a concentration ratio of 1:1, while natural condition is vetiver oil. The effect of foreign ions was carried out by stirring a number of chitosan-GA in the 50 mL sample of artificial and natural conditions at room temperature for 6 hrs. Furthermore, chitosan-GA filtered and

concentration of metal ions Fe(III) and Cu(II) in the filtrate was analyzed by AAS in the same manner as the initial metal ion concentration measurements.

RESULTS AND DISCUSSION

Initial concentration of Fe(III) and Cu(II) ions in vetiver oil

Analysis of the levels of Fe(III) and Cu(II) ions in a sample of vetiver oil has been done. The results showed that the vetiver oil samples contained ions Fe(III) and Cu(II) of 2.1724 and 0.3937 ppm, respectively. Contamination Fe(III) and Cu(II) ion is thought to originate from the minerals in the soil, refinery equipment, and vetiver oil storage drums. Supriyanto and Zainul⁷ have reported that the content of iron and copper in soil may reach 360.59 and 0.355 ppm, respectively. The iron and copper elements are essential micro-nutrients needed by plants. Plants can absorb metal elements in the form of ions or complex compounds. This element plays an important role in metabolic processes in plants. Refinery equipment and storage of vetiver oil is commonly made of metal that contains iron and copper elements. This does not rule out the possibility that during the process of refining and storage, these ions react and form complexes with the organic compounds in the vetiver oil.

Characteristics of chitosan-GA flakes

Flakes of chitosan-GA of each synthesis step were homogenized prior to characterization. This is done so that the data obtained can represent the entire chitosan-GA generated from each step. Analysis of functional groups of chitosan and chitosan-GA was performed to determine the success of the synthesis. Absorption peaks, which can be marked for chitosan and chitosan-GA based FTIR analysis results, are presented in Table 1.

Table 1: Analysis of functional groups of chitosan and chitosan-GA based on infrared spectrum

No.	Wavenumber (cm ⁻¹)		Analysis of functional groups ⁸
	Chitosan	Chitosan-GA	
1	3427,97	3431,01	-OH and -NH _{stretch}
2	2924,59	2926,65	C-H _{stretch}
3	-	1654,10	C=N _{stretch}
4	1045,94	1079,25	C-O _{stretch}

There are some differences between the IR spectra of chitosan and those of the chitosan-GA. Wave numbers for the O-H stretching vibration, C-H, and C-O are shifted to higher wave numbers. Wave number shift is due to the cross-link formed between the chitosan plimer chains. The cross-link limits the movement of molecules and requires greater energy to perform vibration. The amount of energy (E) and wave number (ν) is directly proportional, according to the Plank equation: $E = h.c.v$. It means that the larger is wave numbers, the greater is the energy. Cross-links that occur between chitosan and glutaraldehyde that led to the formation of a new bond is C=N bond. This can be proved by the appearance of absorption peaks at wave numbers 1654.10 cm^{-1} , which is the stretching vibration of C = N⁹.

Optimization of adsorption Fe(III) metal ions by chitosan-GA

Adsorption of Fe(III) ion by chitosan-GA has been optimized using three independent variables, namely the weight of adsorbent, temperature, and contact time, while the response is used as the ion concentration of Fe(III) at equilibrium in adsorbent. The magnitude of the effect of the interaction of two independent variables on the responses is presented in the form of contours in Fig. 1.

Figs. 1a and 1c show that in general the response will increase, if the contact time increases. This indicates that the contact time is very influential on the amount of Fe(III) ions bound to the chitosan-GA. The longer is the contact time, the higher is the Fe(III) ions adsorbed until equilibrium is reached. Another independent variable is temperature. Figs. 1a and 1b show that in general the optimum response area produced at temperature 30-35°C. High temperature may increase the rate of adsorption, but it can cause damage that leads to reducing functional groups active sites so that less adsorption of metal ions that can be sequestered. If the adsorption process is applied on the vetiver oil, the recommended temperature to be used is 25°C. The reason is that if the temperature is raised, the important components of the oil will evaporate. Fig. 1a shows that at 25°C, the optimum response can be achieved at the contact time of 280-360 mins. While Fig. 1b shows that at 25°C, the optimum response can be achieved on the adsorbent weight of 0.9 to 1.0 g. Based on the Figs. 1b and 1c, the general response is achieved at the optimum adsorbent weight of 0.7 to 0.8 g. The greater weight of the chitosan-GA means more amine and hydroxyl groups of chitosan-GA as an active center so that more adsorption of metal ions Fe(III) that can be sequestered. Although the response to the ion adsorption Fe (III) can still be achieved by the use of adsorbent weight 1.0 g (Fig. 1b.), but the response was decreased if the use of adsorbent weight is greater than 0.8 g. This is because the effect of temperature that has been described previously.

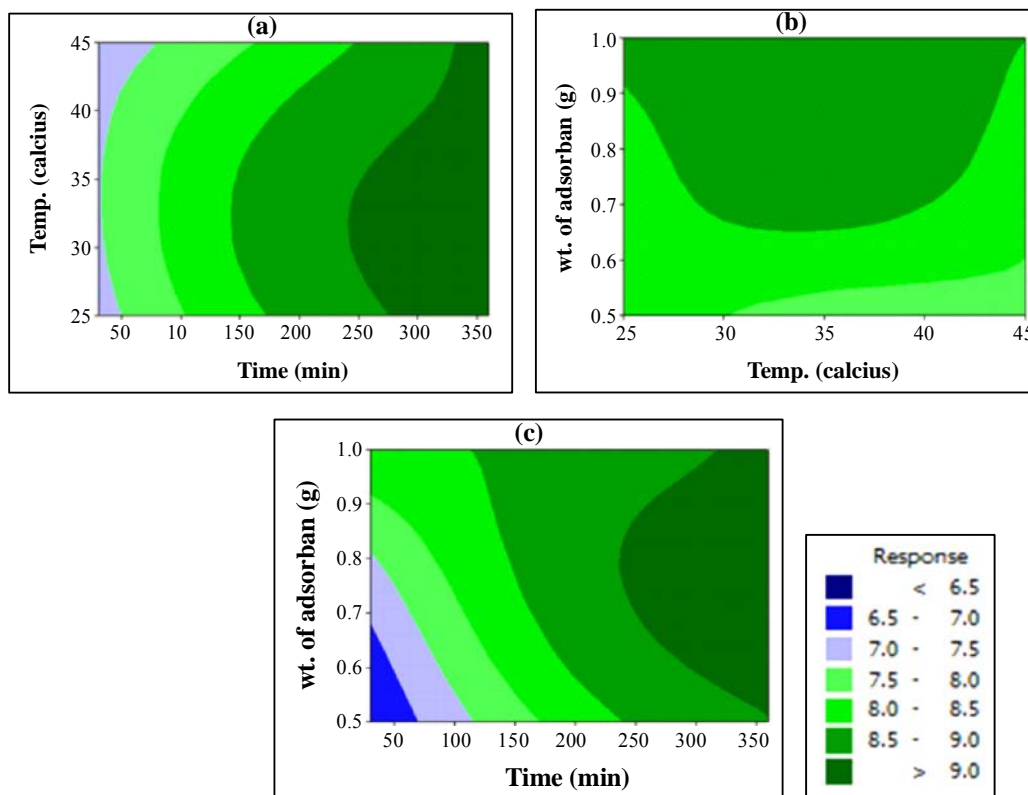


Fig. 1: Surface contour response of Fe(III) ion adsorption by chitosan-GA

Based on the experimental results of Box Behnken response surface, the best condition is: 0.75 g adsorbent weight, 25°C, and 360 min contact time. This conclusion is drawn due to the adsorption of metal ions Fe(III) by chitosan-GA in this condition, which resulted in the greatest percent of adsorption i. e. 91.9521%.

Isothermal adsorption process of Fe(III) ion by chitosan-GA

Isothermal adsorption was studied to determine the effect of the initial concentration of metal ions to the adsorption capacity at optimum conditions as well as the interaction between the adsorbent with the adsorbate. Fig. 2 shows the relationship between the adsorption capacity with the initial concentration of Fe(III). It is seen that at first, the curve appears to rise significantly and then remained constant. It shows that the adsorption capacity of Fe(III) increased with increasing the initial concentration of Fe(III). This can be understood by the concept that if the concentration of the adsorbate increases, the number of Fe(III) ions, which interacts growing at an early stage and will tend to a constant as the surface of chitosan-GA already saturated.

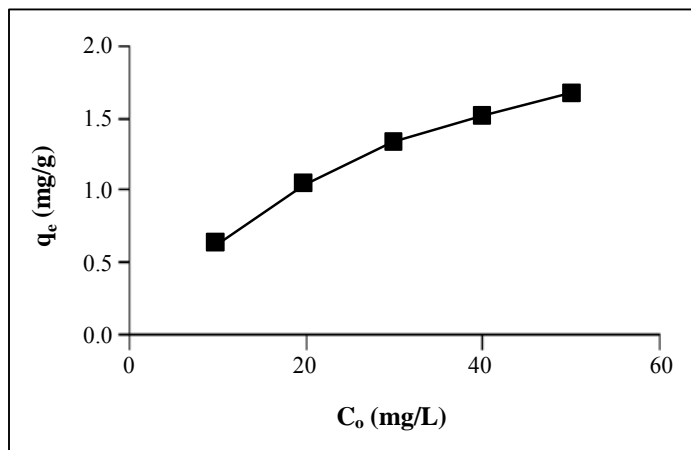


Fig. 2: Relationship between adsorption capacity (q_e) with the initial concentration of Fe(III) ion

Analysis of isothermal adsorption of Fe(III) ions by chitosan-GA was performed using two models, that is Langmuir and Freundlich models. Langmuir isotherm and Freundlich equations are written in Equation 1 and 2, respectively. q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g), C_e is the adsorbate concentration at equilibrium (mg/L), q_m is a Langmuir adsorption capacity constant (mg/g) and b is the Langmuir adsorption energy constants (L/mg), K_f is the Freundlich adsorption capacity constant, n is the Freundlich adsorption intensity constant. Another important parameter of the process of adsorption is R_{SF} , which is called the equilibrium parameter to determine whether the favorable adsorption process or not. The equation for calculating the R_{SF} is written in Equation 3. C_o is the initial concentration of the adsorbate (mg/g).

$$\frac{C_e}{q_e} = \frac{1}{qm^b} + \frac{1}{qm} C_e \quad \dots(1)$$

$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n} \log C_e \quad \dots(2)$$

$$R_{SF} = \frac{1}{1 + b C_o} \quad \dots(3)$$

Isothermal model analysis was carried out by making a linear equation between C_e against C_e/q_e for the Langmuir isothermal models and $\log q_e$ against $\log C_e$ for the Freundlich isothermal models. Isothermal parameter values (qm , b , R_{SF} , K_f and n) can be

determined based on the slope and intercept of a linear equation isothermal of Langmuir and Freundlich. Table 2 shows the parameter values of Langmuir and Freundlich isothermal adsorption.

Table 2: Parameters of Langmuir and Freundlich isothermal adsorption of metal ions Fe(III) by Chitosan-GA

Langmuir			Freundlich			R_{SF}
q_m	B	R^2	K_f	n	R^2	
1,767	0,440	0,988	0,741	3,977	0,999	0,043

The R^2 value for the model of Freundlich is larger than that of the Langmuir model. Freundlich adsorption isotherm equation is based on the assumption, (i) Formation of the adsorption of multiple layers (multilayer) of the adsorbate molecules on the adsorbent, (ii) Part of the active site on the surface of the adsorbent is heterogeneous, and (iii) Involve only the van der Waals force that the adsorbate can move from one part of the surface to the other surface of the adsorbent. The result of this study is similar to that conducted by Muharam et al.⁴, who reported that chitosan-GA flakes for adsorption of Au (CN)⁴⁻ also followed the Freundlich isothermal models. Similar results were also obtained by Kartikeyan et al.¹⁰ for the adsorption of Fe(III) with chitin and Zaid and Mohammed¹¹ for the adsorption of Fe(III) by olive cake.

Other parameter related to the adsorption process is R_{SF} . R_{SF} is a separation factor which states that if the value of the $R_{SF} > 1$, then the adsorption process is not beneficial, and if the value of the $R_{SF} = 1$, then the adsorption process is linear. Furthermore, if the value is $0 < R_{SF} < 1$, then the adsorption process is favorable, and if $R_{SF} = 0$ then the adsorption process is irreversible. Table 2 shows that the value of the R_{SF} for the adsorption of Fe(III) by chitosan-GA is in the range of values $0 < R_{SF} < 1$. This indicates adsorption process is favorable because it can be done the desorption process¹². Desorption process can occur because of interactions between Fe(III) metal ions and chitosan-GA is a physical interaction by using the Van der Waals force. Van der Waals force is the intermolecular interaction forces and are relatively weak, so it is easily broken.

Kinetics of adsorption Fe(III) metal ions by chitosan-GA

The kinetics of adsorption describes the rate of retrieval of solutes by adsorbent during adsorption takes place. Adsorption kinetics study is important to determine the efficiency of the adsorption process. The adsorption kinetics can be studied through a

pseudo-first order kinetics equation and pseudo-second order. Adsorption kinetics of pseudo-first and second order was calculated using equations (4) and (5), respectively. q_e is the amount of metal ions adsorbed at equilibrium, q_t is the amount of metal ions adsorbed at t time and k_1 and k_2 are the rate constants of pseudo-first and second order, respectively¹². The kinetic parameters were determined from the slope and intercept based on equations (4) and (5) (Table 3).

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \dots(4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots(5)$$

Based on Table 3, the correlation coefficient of the pseudo-second order is larger than that of the pseudo-first order. Additionally, q_e value for the pseudo-second order is theoretically closer to the experimental q_e value. Hence, the mechanism of adsorption of Fe(III) metal ions by chitosan-GA is controlled by a pseudo-second order kinetic model. Pseudo-second order kinetic model is based on the assumption that the amount of metal ion adsorption does not exceed the number of places at the adsorbent surface. Therefore, the addition of the initial concentration of metal ions affect the kinetics constant of the adsorption process¹³. Dai et al.⁶ obtained kinetics model similar to adsorbent of chitosan cross-linked thiourea to adsorb Fe(II) and Fe(III) ions.

Table 3: Parameters of kinetics the pseudo-first and second order

Kinetics model	Parameters of kinetics	[Fe] ₀ (ppm)	
		10	30
Pseudo-first order	k_1 (min ⁻¹)	0,0170	0,0267
	q_e theoretical (mg/g)	0,1835	0,7520
	R^2	0,8559	0,8885
Pseudo-second order	k_2 (g mg ⁻¹ min ⁻¹)	0,1430	0,0398
	q_e theoretical (mg/g)	0,5354	0,9536
	R^2	0,9943	0,9949
	q_e experiment (mg/g)	0,5016	0,8157

Note: [Fe]₀ = Initial concentration of Fe(III) ions

The effect of ion Cu(II) ion on adsorption Fe(III) ions

The effect of Cu(II) ions adsorption on Fe(III) ions has been studied in artificial and natural conditions. Artificial conditions is a solution consisting of Fe(III) and Cu(II) metal ions with a concentration ratio of 1:1. whereas the natural conditions in this study is the existence of ion Fe (III) and Cu (II) a real in vetiver oil. The results of this study are presented in Table 4. Adsorption of Fe(III) ion, which is initially 92% decrease to 80% because the existence of Cu(II) ion. The decrease in percent adsorption indicates that there is competition between adsorption of Fe(III) ions and Cu(II) ions. Adsorbents are also used the most active site to adsorb Cu(II) ions with the percent adsorption of 30%. Percent adsorption for adsorption of Fe(III) ions is greater than that of the Cu(II) ions. This can be explained by the HSAB theory (hard soft acid base). Fe(III) ion belongs to the hard acids because it has a small ionic size, large ionic charge, and small electronegativity (0.7 to 1.6) while the Cu(II) ion belongs to the borderline (intermediate region between hard acids and soft acids). Active groups of chitosan-GA are amine group (RNH₂) and hydroxyl (ROH), which belong to the hard base because it has a high electronegativity¹⁴. Hard acid-base interactions will generate the attractive force that is stronger than the interaction between soft or borderline acids with the hard bases.

Table 4: Percent of simultaneous adsorption of Fe(III) and Cu(II) ions by chitosan-GA

Sample	Metal ions	Concentration		% Adsorption
		Initial	Final	
Artificial	Fe(III)	10,264	2,081	80
	Cu(II)	10,277	7,222	30
Vetiver Oil	Fe(III)	2,172	0,883	59
	Cu(II)	0,394	0,308	22

Table 4 also presents data on percent adsorption of Fe(III) and Cu(II) ions on vetiver oil by chitosan-GA. The result shows that the percent adsorption decrease both; adsorption of Fe(III) and Cu(II) metal ions. This is because the mobility of metal ions in vetiver oil is lower as compared to the artificial conditions, so that the rate of adsorption decreases. In addition, Fe(III) and Cu(II) metal ions in vetiver oil can form strong complexes with the constituent components of oil as vetiverol. This ligand is more bulky than the water molecule, so that the adsorption of metal ions in vetiver oil becomes more difficult.

CONCLUSION

Percent adsorption value of Fe(III) ion by chitosan-GA (DD = 78%) is 92% in optimum conditions: weight adsorbent 0,75 g, temperature 25°C, and 360 min contact time. Adsorption process of Fe(III) ion by chitosan-GA fitted to Freundlich and pseudo-second order models. The existence of Cu(II) ions decreases percent adsorption of Fe(III) ion by chitosan-GA. Percent adsorption of Fe(III) ion by chitosan-GA is higher than the adsorption of Cu(II) ion at all conditions. Percent adsorption of Fe(III) and Cu(II) ion by chitosan-GA in vetiver oil is lower than that in other conditions (solution of Fe³⁺ and Cu²⁺ ion with its concentration ratio 1:1).

REFERENCES

1. T. M. Hernani, Peningkatan Mutu Minyak Atsiri Melalui Proses Pemurnian, Di dalam: Konferensi Nasional Minyak Atsiri 2006, Solo, 18-20 Sept. 2006. Bogor: Balai Besar Litbang Pascapanen Pertanian (2006).
2. Firdaus, Aplikasi Bentonit-Zeolit dalam Meningkatkan Mutu Minyak Akar Wangi Hasil Penyulingan Daerah Kabupaten Garut [Skripsi], Bogor: Departemen Kimia, Fakultas MIPA, Institut Pertanian Bogor (2009).
3. Sani, Minyak Dari Tumbuhan Akar Wangi. Surabaya: Unesa University Press (2011).
4. S. Muharam, P. Sugita and A. Wulanawati, Adsorption of Au(III) onto Chitosan Glutaraldehyde Cross-linked in Cyanide Solution. Prosiding Seminar Nasional Sains III IPB. 13 November 2010. Bogor (2010).
5. Rahmi dan Julinawati, Application of Modified Chitosan for Adsorben Ionic Cu²⁺ Metal in Diesel Oil, *J. Nat.*, **9(2)**, 32-38 (2009).
6. J. Dai, F. Ren and C. Tao, Adsorption Behavior of Fe(II) and Fe(III) Ions on Thiourea Cross-linked Chitosan with Fe(III) as Template. *Molecules*, **17**, 4388-4399 (2012).
7. Z. K. Supriyanto, Penentuan Kadar Cu, Fe, Zn dalam Tanah, Tanaman Teh, Daun Teh dan Minuman Teh. *Ganendra*, **IX(1)**, 25-28 (2006).
8. Pavia, Lampman, Kriz, Introduction to Spectroscopy, Thomson Learning, USA (2001).
9. B. Li, C. L. Shan, Q. Zhou et al., Synthesis, Characterization and Antibacterial Activity of Cross-Linked Chitosan-Glutaraldehyde, *J. Marine Drug*, **11**, 1534-1552 (2013).

10. G. Kartikeyan, A. Muthulakshmi and K. Anbalagan, Adsorption Studies of Iron (III) on Chitin, *J. Chem. Sci.*, **117**, 663-672 (2005).
11. A. Zaid and A. Mohammed, Thermodynamics and Kinetic Studies of Iron(III) Adsorption by Olive Cake in a Batch System, *J. Mex. Chem. Soc.*, **52(2)**, 108-115 (2008).
12. Y. S. Ho, Removal of Copper Ions from Aqueous Solution by Tree Fern, *Water Res.*, **34**, 2323-2330 (2003).
13. A. H. Chen, S. C. Liu, C.-Y. Chen and C.-Y. Chen, Comparative Adsorption of Cu(II), Zn(II), and Pb(II) Ions in Aqueous Solution on the Crosslink Chitosan with Epichlorohydrin, *J. Hazard. Mater.*, **154**, 184-191 (2008).
14. K. H. Sugiyarto, *Kimia Anorganik I*. Yogyakarta: Jurusan Pendidikan Kimia, FMIPA, UNY (2000).

Revised : 23.10.2015

Accepted : 24.10.2015