

STUDY OF *EICHORNIA CRASSIPES* POWDER FROM PANTE RIEK FOR Pb^{2+} ION ADSORPTION

Mirna Rahmah Lubis

Department of Chemical Engineering, Engineering Faculty,
Syiah Kuala University, Darussalam, Banda Aceh, 23111, Indonesia
Email: mirna@che.unsyiah.ac.id

Abstract

Adsorption capacity was calculated in *Eichornia crassipes* adsorbent. In several areas of Aceh province such as Meulaboh, Takengon, and Tamiang, people extirpate *Eichornia crassipes* because it is considered disturbing water flow. Therefore, this research tries to investigate the utilization of *Eichornia crassipes* so that it could be used as bioadsorbent in order to reduce heavy metal from waste water. The main objective of this research is to reduce lead content, and to determine the best condition of lead adsorption in solution by using *Eichornia crassipes* powder. The analysis is conducted by using Atomic Adsorption Spectrophotometer. Research result indicates that optimum adsorption occurs at solution with pH of 4.4, lead concentration of 40 mg/L, and contact time of 75 minutes. Lead adsorption by *Eichornia crassipes* biomass follows adsorption isotherm of Langmuir and pseudo-second order with capacity of adsorption (a_m) of 27,78 mg/g, and adsorption constant (K) is 12 L/mg.

Key words: adsorption, *Eichornia crassipes* powder, Pb^{2+} , waste water

Abstrak

Kapasitas adsorpsi telah dihitung dengan menggunakan adsorben *Eichornia crassipes*. Di beberapa daerah di provinsi Aceh seperti Meulaboh, Takengon, dan Tamiang, masyarakat memberantas *Eichornia crassipes* karena dianggap menyumbat aliran air. Oleh karena itu, penelitian ini mencoba menyelidiki penggunaan *Eichornia crassipes* sehingga dapat digunakan sebagai bioadsorben untuk mengurangi logam berat dari air limbah. Tujuan utama penelitian ini adalah untuk mengurangi kandungan timbal, dan untuk menentukan kondisi terbaik penyerapan timbal dalam larutan dengan menggunakan serbuk *Eichornia crassipes*. Analisis dilakukan dengan menggunakan *Atomic Adsorption Spectrophotometer*. Hasil penelitian menunjukkan bahwa adsorpsi maksimum terjadi pada larutan dengan pH 4,4; konsentrasi timbal 40 mg/L, dan waktu kontak 75 menit. Adsorpsi timbal dengan biomassa *Eichornia crassipes* mengikuti isothermal adsorpsi Langmuir dan orde dua semu dengan kapasitas adsorpsi (a_m) 27,78 mg/g, serta konstanta adsorpsi (K) sebesar 12 L/mg.

Kata kunci: adsorpsi, air buangan, Pb^{2+} , serbuk *Eichornia crassipes*

Introduction

Eichornia crassipes often covers watery areas in Aceh, such as in Pante Riek (Banda Aceh) and Krueng Suak Ribee (Meulaboh) (Figure 1). Similarly, in Bendahara Sub-district (Aceh Tamiang) as informed in Suara Tamiang news, *Eichornia crassipes* existence has disturbed so much community particularly people whose jobs are fishermen. Therefore, it is necessary to handle the problem by processing it from the area into an advantage. One of the ways is by using it as bioadsorbent that has been carried out widely, i. e. by changing it into active carbon. It could be used to adsorb various hazardous matters such as toxic metal, organic, agricultural, industrial, and household wastes, that pollute waters [4]. Nevertheless, its utilization as adsorbent in the form of powder is carried out just a little.



Figure 1. *Eichornia crassipes* covers Krueng Suak Ribee, Johan Pahlawan Subdistrict, Meulaboh, Aceh Province

With consideration of abundant material availability, *Eichornia crassipes* from Pante Riek is investigated in order to handle problems

for fishermen and Pb^{2+} metal through bioadsorption by using its powder. The specific purpose of the study is to investigate pH, optimum concentration of waste water toward Pb^{2+} ion adsorption. In this research, it will be investigated the possibility of *Eichornia crassipes* as adsorbent of Pb^{2+} by utilizing $NaHSO_3$ as preservation and HNO_3 as activator. Beside that, optimum contact time and adsorption capacity of *Eichornia crassipes* are also investigated for Pb^{2+} ions.

Theory

Eichornia crassipes' leaves have average size of the pore as much of $4 \times 4 \mu m$ [9]. Unlike *Eichornia azurea* which has buried roots in mud, no inflated stems, and white to bluish-lavender flowers, *Eichornia crassipes* is floating plant which has dark feathery roots, inflated stems, and lavender flowers. Beside that, *Eichornia crassipes* also could be accumulated in the range of time 1 month in the area of $\pm 3 m^2$. The so fast growth characteristic could be meant as cellulose formation potency [4]. It has physical shape as leaves that are arranged in radical shape. This shape enables Pb^{2+} bound on *Eichornia crassipes*. This fact becomes very logic consideration to benefit it with higher additional value such as adsorbent of Pb^{2+} metal waste that is hazardous and toxic material.

Lead is one hazardous, chemical element that has Pb symbol and atomic number 82 in periodic table. It has atomic radius as much of 175 pm [5], which is larger than other heavy metal radius. Lead is heavy metal that is more widely distributed than other toxic metals.

Data from Directorate of Management of Waste and Toxic Material of BAPEDAL indicated that the number of hazardous and toxic waste in Indonesia in 2020 will be 58,248,992 tons. Therefore, it is necessary to control toxic materials such as lead in environment. Estimates of lead emissions to the atmosphere from lead smelters in the EU indicate a projections of 1640 tonnes in 2010 [12]. Its content in environment increases because of mining, smelting, and its various utilization in industry. Based on World Health Organization (WHO) investigation, Pb threshold limit is $10 \mu g/l$, and $5 \mu g/l$ based on USEPA.

In relatively recent times there has been a great deal of concern over the past use of lead-based paints, particularly on surface in living areas children children may be exposed to. This is because lead compounds is very toxic. The pigmen used in lead-based paints is a white basic carbonate, $Pb_3(OH)_2(CO_3)_2$, and its use in

interior paints is now restricted. This metal ion is often used in chemical laboratory such as the one that is available in Chemical Engineering Department of Unsyiah, for example from $Pb(NO_3)_2$, $PbCl_2$, $Pb(OH)_2$, etc. It has low melting point as much of $327^\circ C$ so that it is easy to be used with cheaper operational cost. Not all metal is currently recovered: for example, some cable sheaths are left in the environment after use. During battery recycling, 1 g lead is left per ton of lead produced [12]. Total emissions from recovery of these metals are estimated as 1.35 g of lead to air, and 0.01 g to water [4]. Estimated global emission of lead to water resulting from steam electric is 240 - 1,200 tonnes/year [12].

In order to handle the heavy metal waste, the most simple method is adsorption. It is a separation process of particular components from fluid so that they are transferred to solid surface of adsorbent [8]. Adsorption is diffusion process of molecules from fluid to solid surface of adsorbent [10]. This method is oftenly used because it could be used for various waste types, it is not too costly, economical, and effective to adsorp heavy metal from solution. Some studies have been carried out based on multi-element solutions; however, only a few is based on single metal system.

Research Methods

Procedure

Eichornia crassipes is cleaned from impurities that adhere by using aquadest. Then it is immersed in sodium metabisulphyte 0,3% for 1 hour, and dried by using electrical oven with temperature of $60^\circ C$ until its weight is constant. The *Eichornia crassipes* that has been dry is ground by using blender then it is screened with screen size of 100 mesh to obtain uniform raw material size. After that, it is washed by using HNO_3 0.01 M that functions to activate the adsorbent and to dissolve impurities, then it is washed with aquadest. Finally, it is dried by using electrical oven on temperature of $60^\circ C$ until its weight keeps constant. In order to avoid contact with humidity and air, sample is stored in desicator before used.

Sample solutions of metal are $Pb(NO_3)_2$ solution with concentrations of 20, 25, 30, 35, 40 mg/l at various pH i.e. 2, 3, 4, 5, and 7. The solution is poured as much of 200 ml into beaker glass with size of 500 ml. Adsorbent is added as much of 0.8 grams. Then, it is agitated by using propeller agitator with velocity of 60 rpm (Figure 2). Then filtrate is separated by using centrifuge for 10 minutes, and Pb^{2+} content after agitation is ready to be analyzed by

using atomic absorption spectrophotometer (AAS).

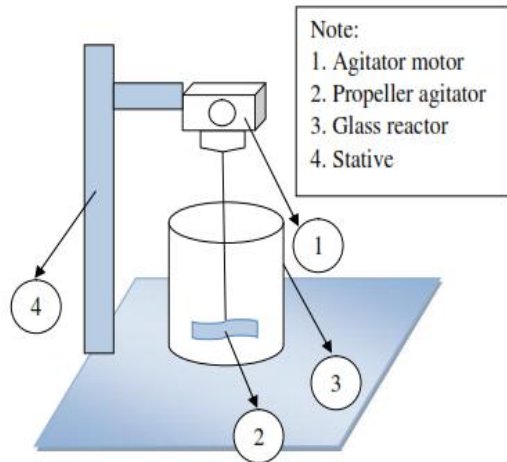


Figure 2. Scheme of equipment set

Adsorbent as much of 0.8 grams is also contacted with sample solution as much of 200 ml with pH and concentration which result in the optimum adsorption percentage. Then it is agitated by using propeller agitator with velocity of 60 rpm [13] in order to be homogeneous. Contact time for this adsorption process is varied i. e. 15 minutes, 30 minutes, 45 minutes, etc. until the adsorption capacity is constant. After that filtrate is separated by using centrifuge and the Pb^{2+} content is ready to be analyzed by using AAS.

Results and Discussion

Optimum efficiency of Pb^{2+} ion adsorption occurs on acid pH. Acidity or media pH is related to species distribution of lead ion in mixture, whereas early lead-ion concentration is attributed to adsorption capacity of lead ion toward particular adsorbent.

Effect of solution pH toward adsorption of lead ion

Research result that indicates solution pH influence toward adsorption of Pb^{2+} on *Eichornia crassipes* is presented in Figure 3. Adsorption of Pb^{2+} in very high amount appeared on acid condition or pH of 5, followed by the reduction on pH above 5. The high adsorption on the low pH indicates that adsorption mechanism of Pb^{2+} is dominated by electrostatic interaction or ion exchange with H^+ ion on active sites of adsorbents. Interaction effectivity between Pb^{2+} ion and amino acid compound depends very much on group species contained in solution.

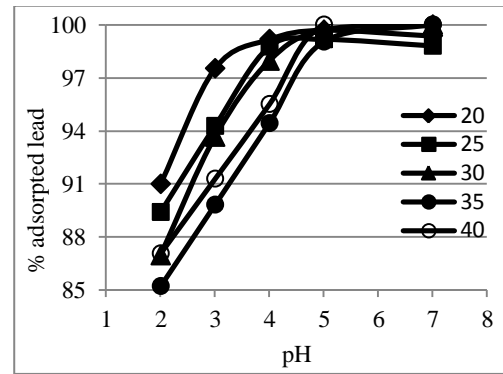


Figure 3. The correlation between solution pH and Pb adsorption percentage on *Eichornia crassipes* adsorbent

The assumption in this research is that active sites available on *Eichornia crassipes* adsorbent is proteins that have amino acid units as constituent. Groups on adsorbent experiences deprotonization as a result of the existing of hydroxyde ion, so that the group will change into very reactive negative charge in order to bind Pb^{2+} (Figure 4).

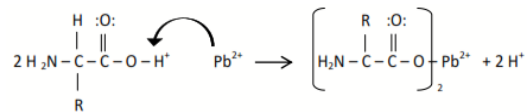


Figure 4. Mechanism of ion exchange

Based on the fact, it can be said that the efficiency of optimum adsorption is on pH between 4 and 5. Below pH of 4, the efficiency is reduced because of competition between Pb^{2+} ion and H^+ ions so that repulsion that blocks metal cation to be close to adsorbent side occurs.

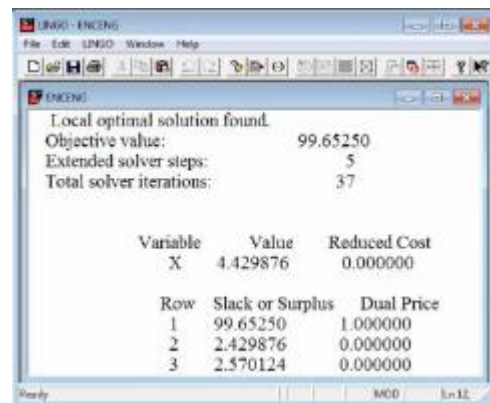


Figure 5. Optimum pH calculation by using Lingo 10 software

This research also try to use Lingo 10 software to determine optimum pH as indicated in Figure 5. The result indicates that on optimum pH of 4,4 and concentration of 40 mg/l,

the efficiency will be 99,6%. Thus, this pH will be used as reference in the next investigation.

Sample pH also influences adsorption capacity of *Eichornia crassipes* adsorbent toward the Pb^{2+} adsorbate (Figure 6). The highest adsorption capacity is indicated on sample pH of 5. However, there is a possibility that the highest adsorption is on pH range of 4 - 5. The assumption of interaction on pH of 5 between biomass and Pb^{2+} is trapping, where Pb^{2+} is just trapped in biomass pores, and no interaction as a result of charge difference. On pH above 5, there is a slight reduction because on the condition Pb^{2+} ions tend to bind hydroxide ions and precipitate to form $Pb(OH)_2$ that causes adsorbent is hard to adsorb the adsorbate.

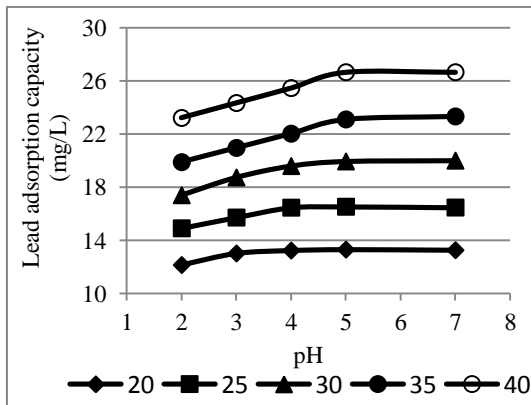


Figure 6. The correlation of pH toward capacity adsorption of Pb^{2+} ion for 60 minutes

Effect of Lead Concentration on Lead sorption

The concentration correlation of Pb ion at the beginning toward adsorption capacity is indicated in Figure 7. Experiments of adsorption are developed at various initial concentration of lead in the range of 20 - 40 mg/l. This appears as common trend that the rise of adsorption capacity equals to the increase of initial concentration ranging from 20 - 40 mg/L. The results are probably caused by the rise of the total ions that compete for existing binding sites even though there is a shortage of active groups on adsorbent surface in larger concentrations. At 40 mg/l concentration, the result still indicates the highest capacity, although more ions of Pb^{2+} were remained un-adsorbed in more concentrated mixture [6].

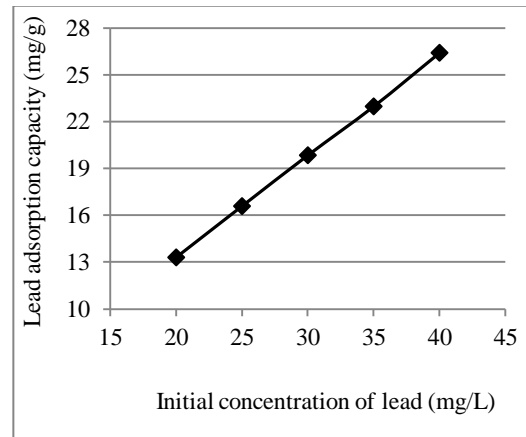


Figure 7. Correlation of initial concentration toward removal of Pb ion for pH of 4.4

Figure 8 indicates contact time correlation for Pb^{2+} removal by *Eichornia crassipes* adsorbent. The result is obtained by connecting contact time in the range 15 to 90 minutes (until the lead concentration is constant) in separate experiment runs. The adsorption capacity or Pb removal percentage slowly increased with the rise of contact time. At the beginning, removal speed of Pb was larger. It is caused by the vacancy of all sites on adsorbent surface. Pb concentration is high; however, decrease of sorption groups influenced speed of adsorbent removal.

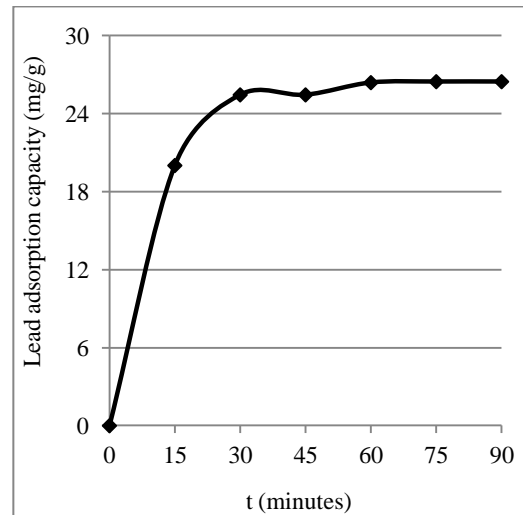


Figure 8. Effect of contact time vs. Pb ion removal at pH 4,4 and concentration 40 mg/l

When the solution sample is agitated, lead is transferred to the adsorbent surface through a intraparticle movement. The intraparticle movement should be the step controlling rate. In initial adsorption, lead adsorption occurs fast up to 30 minutes.

However, after contact time reaches 90 minutes, adsorption capacity tends to be constant. The longer contact time causes the more adsorbent filled so that the more difficult for lead to find available empty space. The small variance of the lines from the trend (on 45 min.) showed that movements of intraparticle limiting rate were not the only step [2]. From the trend it implies that removal of lead ion with *Eichornia crassipes* is probably controlled by chemical adsorption, or by simultaneously physical and chemical adsorption.

Adsorption Isotherm

Adsorption Langmuir isotherm of Pb²⁺ ion is obtained by drawing correlation between equilibrium concentration in liquid phase (C_e) and equilibrium concentration on solid phase (C_e/Q_e). Regression value of Langmuir isotherm was used to obtain maximum value of a_m (capacity of adsorption) as well as K (Langmuir constant) to know the amount of adsorbate per gram adsorbent. Model Langmuir can be presented through the following equation [1]:

$$\frac{C_e}{q_e} = \frac{1}{a_m K} + \frac{1}{a_m} C_e \dots \dots \dots (1)$$

Note:

- C_e = lead ion concentration in equilibrium within mixture (mg/liter)
- q_e = lead ion concentration onto the adsorbent (milligram/adsorbent mass in gram) at equilibrium
- a_m = maximum capacity absorbed (mg/gram)
- K = adsorption constant of Langmuir (liter/mg)

Parameters of a_m as well as K are determined by slope and intercept based on curve obtained by fitting C_e/q_e data versus C_e that is indicated in Figure 9. Adsorption parameters and R² were indicated in Table 1. Equilibrium constant (K) is a constant at the moment equilibrium occurs in the reaction process that indicates reaction activity at the moment of equilibrium. Constant value K at removal of Pb ions by *Eichornia crassipes* was 12. This value is relatively high so that it could be concluded that equilibrium that occurs tends toward reaction result, or could be said that many ions interact with active sites on *Eichornia crassipes*.

Langmuir isotherm can be implemented in conditions where layer of adsorbate molecules was only one formed on adsorbent surface, where it keeps constant even in larger adsorbate concentrations. Isotherm of Langmuir suggests monolayer adsorption on surface containing

definite amount of adsorption groups of uniform pattern without adsorbate transfer in the surface of adsorbent. Adsorption of monolayer has been different because of it indicates that amount adsorbed achieves maximum value at moderate concentration. It is accordance with surface blockage of adsorbent by monolayer of lead molecules.

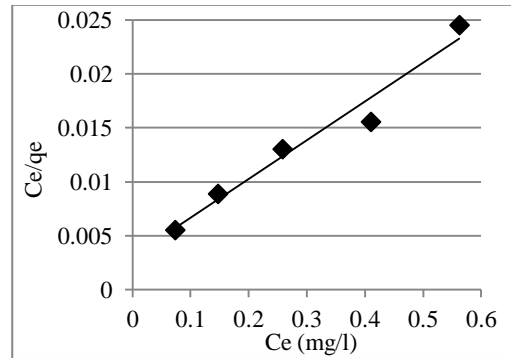


Figure 9. Langmuir model at removal of Pb ion for pH of 4,4

Model of Freundlich isotherm describes that distribution of active groups is energetic and heterogeneous, completed by interaction among adsorbate ions. Linear form of Freundlich is stated by equation as follows.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \dots \dots \dots (2)$$

Where:

- q_e = lead ion concentration at equilibrium onto the adsorbent (milligram/gram)
- K_F = Freundlich parameter
- 1/n = empirical constant connected to adsorption intensity
- C_e = metal ion concentration at equilibrium in the mixture (milligram/liter)

Table 1. Isothermic Data of Langmuir as well as Freundlich

Models	Adsorption Parameters			
	a _m	K	R ²	1/n
Langmuir	27.78	12	0.964	-
Freundlich	-	30.549	0.9	0.314

Regression analysis is carried out in order to determine adsorption equilibrium constant and adsorption capacity. Both parameter, i.e. 1/n as well as K_F could be determined by the slope and intercept from log Pb concentration (q_e) versus log Pb concentration (C_e) as indicated in Figure 10. Parameters of Freundlich together with R² were summarized in Table 1.

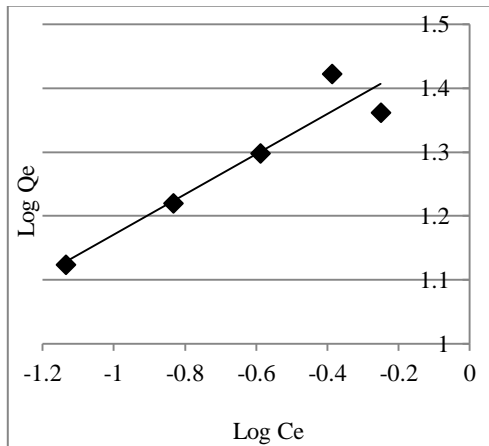


Figure 10. Freundlich isotherm for Pb ion removal at pH 4,4

Figure 10 indicates the value of $1/n$ that is 0.314 (higher than 0) that indicates that the sorption ions of Pb^{2+} into *Eichornia crassipes* was good under the mentioned conditions. The result also indicates the heterogeneity of *Eichornia crassipes* surface, which means the adsorptive site (surface) is consisted of heterogeneous adsorption patches which are the same and small.

Isotherm determination of Langmuir and Freundlich adsorption could be known by visualizing value of R^2 . Adsorption isotherm of Pb^{2+} on *Eichornia crassipes* biomass follows equation that has value of R^2 close to 1. Based on Table 1, it could be seen that Langmuir isotherm equation follows R^2 value close to 1 i.e. 0.964, so that it could be concluded that adsorption of Pb^{2+} ion follows Langmuir isotherm.

Langmuir isotherm assumes that active sites available on adsorbent surface are homogenous where active sites, and type of binding that occurs is the same. Binding interaction between adsorbent and adsorbate occurs on the first layer of adsorbent surface so that binding that occurs is strong binding between active sites and Pb^{2+} ion (monolayer).

Adsorption Kinetics

In addition, model utilized in studying adsorption kinetics is pseudo-first order as well as pseudo-second order. Whereas model to describe bonding of Pb^{2+} ion on *Eichornia crassipes* is obtained by correlation of adsorbed percentage vs. time (Equation 3), and adsorption capacity vs. time (Equation 5). Lagergren (1898) stated that the model of Lagergren's rate (pseudo-first order) is the one that is more commonly used in solute adsorption from liquid

mixture. Linear regression of pseudo-first order equation is stated by:

$$\log (q_e - q_t) = \log q_e - \frac{k}{2.303}t \dots \dots \dots (3)$$

The slope as well as intercept at plot of logarithm $(q_e - q_t)$ versus time in adsorption of Pb on *Eichornia crassipes* had been utilized in determining each value of k as well as q_e . Constant value (k) for Pb ion removal by *Eichornia crassipes* is 0.09. The result was in accordance with those reported in literature [11]. It could be known, eventhough adsorption kinetic model of the pseudo-first order fits to several data, this model could not be accepted by all data obtained from this reserach. Whereas adsorption kinetic model of the pseudo-second order fits to all data of research, and its result is indicated in Table 2.

Table 2. Kinetic parameter at removal of Pb ion by *Eichornia crassipes* adsorbent of 40 g/ml

Kinetic model	q_e (exp) (mg Pb^{2+} /g)	q_e (cal) (mg Pb^{2+} /g)	Δq_e (mg/g)	k (per minute)	R^2
The pseudo-first order	26.467	25.351	1.116	0.09	0.941
The pseudo-second order	26.467	28.571	2.104	0.008	0.998

Experimental data of metal adsorption onto biosorbents can be plotted with equation of pseudo-second order using equation of kinetic rate given by [7]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \dots \dots \dots (4)$$

with limit condition of time from 0 till t, and q_t from 0 until q_e . Integration result of above equation and re-arranging it in the linear form will result in the following equation.

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

The pseudo-second order considers controlling step in the form of chemical binding that shares each other or exchanges electron between adsorbate and adsorbent utilized [3]. Based on pseudo-second order graph, it is obtained the following equation.

$$\frac{t}{q_t} = 0.161 + 0.035t \dots \dots \dots (6)$$

Referring to Equation 6, constant value of adsorption velocity obtained is 0.008. This indicates that adsorbent has formed chemical binding with adsorbate in relatively fast

duration. Equation of pseudo-second order has been favorable to illustrate adsorption mechanism after contacting of adsorbent and adsorbate in a long time. This is caused by the chemical binding has not been formed at first. Regression value (R^2) as well as the slight disparity of between values of experiment and calculation (q_e) (Table 2) showed conformity of the equation of pseudo-second order to describe the result.

Conclusions

pH influences on de-protonization of active groups on *Eichornia crassipes* biomass so that on different pH, active group of biomass forms different species. Below pH 4, active sites on biomass has not been de-protonized, and trapping occurs, in pH range of 4 and 5, no trapping occurs because active site is estimated to be not de-protonized completely. In the pH range of 5 - 6, adsorption increasing occurs because many active sites have been de-protonized, above pH 6, lead adsorption is reduced because lead has deposited to be $Pb(OH)_2$.

Lead adsorption on *Eichornia crassipes* biomass occurs on optimum pH of 4.4 and contact time 75 minutes. Lead adsorption by *Eichornia crassipes* biomass follows pseudo-second order and adsorption isotherm of Langmuir with capacity of adsorption (a_m) of 27,78 mg/g, and adsorption constant (K) is 12 L/mg. Interaction between *Eichornia crassipes* and lead is chemisorption interaction, so that it is potential to be furtherly processed as adsorbent.

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