Adsorption of Pb(II) ion from aqueous solution onto Chitosan/silica/polyethylene glycol (Ch/Si/P) composites membrane

F W Mahatmanti¹, W D P Rengga², E Kusumastuti¹, Nuryono³
¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Indonesia 50229
² Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Indonesia 50229
³ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta, Indonesia 55281

email: widhimahatmanti@rocketmail.com, fwidhi_kimia@mail.unnes.ac.id

Abstract. In this research, chitosan/silica/polyethylene glycol (Ch/Si/P) composites membrane was studied for selective adsorbent of Pb(II) from aqueous solution. This study started by preparation of Ch/Si/P composites membrane. The structure and surface morphology of Ch/Si/P composites membrane was characterized by X-ray diffraction (XRD), Fourier Transform Infra Red (FTIR) spectroscopy, and Scanning Electron Microscopy (SEM). Batch adsorption experiments were conducted with various contact time and Pb(II) concentrations to evaluate the adsorption kinetics and thermodynamics. Results show that adsorption fitted to Langmuir model and followed a kinetic model of pseudo-second-order. The adsorption capacity of Pb(II) onto the Ch/Si/P composites membrane is 0.16 mmol/g. The relative selective factor (α̂) value of Pb(II)/Rhodamine B is 2.38. This means that Pb(II) can be determined even in the presence of Rhodamine B interference.

1. Introduction
The textile industry is one of the industrial activities that are developing in Indonesia. One note on the textile industry is their products waste, which can pollute the environment in particular, the pollution of water. The textile industry waste will flow directly into sewers or rivers, so the wastewater can reduce potential natural cleaning power of water, can change the color of the river water, may even result in the death of aquatic organisms that are important for human life. The type of metal ions produce by the textile industry wastes mainly metal ions As, Cd, Cr, Pb, Cu, and Zn.

The intensity of the dye and the metal ion content in a textile industrial waste can be reduced by physics, chemistry or biology. In the chemical method, researchers used several methods to reduce pollution in the textile industry waste such as: coagulation-flocculation, electrochemical oxidation, adsorption and membrane filtration [1]. Membrane technology is considered an effective way to reduce chemical pollutants dye and metal ions in the waste. Membrane technology has several
advantages compared with other processes, among others: (a) there are small, (b) low pressure, and (c) high separation selectivity [2].

The manufacture of Chitosan-silica-polyethylene glycol (Ch/Si/P) membrane was mixed with silica isolated from rice husk ash (ASP) and polyethylene glycol (PEG) as plasticizer. The addition of silica in the manufacture of chitosan-silica membranes increases the tensile strength and Young's modulus, the pore size of the membrane, and the stability of the temperature rise [3]. In this paper studied the Ch/Si/P membrane to absorb Pb(II) ion in aqueous solution. Influencing factors that was studied were the effect of pH, contact time and initial concentration of the solution. The influence of the presence of Rhodamine B in aqueous solution was also studied.

2. Experimental

2.1. Material
Chitosan with the deacetylation degree of 83% was supplied from CV Ocean Fresh Bandung, Polyethylene-glycol (MW 400), sodium silicate solution from rice hull ash silica (25% SiO$_2$), sodium hydroxide pellet, HCl 37%, acetic acid (2% v/v), fumed HNO$_3$, Pb(NO$_3$)$_2$. All in analytical grade were purchased from Merck.

2.2. Adsorption experiment
The adsorption experiment was performed using a batch method at various pH (4.0 - 9.0). The solution pH was adjusted using HCl and NaOH solutions. An aqueous solution of Pb(II) ion 100 mg/L was shacked with 0.12 g membrane for 24 h at various pHs. The optimum pH was used to evaluate the kinetics parameter by varying the contact time (1, 2, 4, 8, 16, 24, and 26 hours) and thermodynamics parameter by varying the concentration (50 to 250 mg/L). Selectivity of adsorption was evaluated by competitive Pb(II) and Rhodamine B. The concentration of unabsorbed Pb(II) ion was detected by atomic absorption spectrophotometry. The concentration of unabsorbed Rhodamine B was detected by visible spectrophotometer.

3. Results dan Discusions

3.1. pH Effect
The pH effect on the adsorption of Pb(II) ion onto Ch/Si/P composites membrane is shown in Figure 1. The results showed the highest adsorption of Pb(II) ion at pH 5. Increasing of pH lowers the level of -NH$_2$ protonation on the membrane surface, followed by decreasing in partial positive charge, consequently increasing of pH tends to increase adsorption of metal ions. At a higher pH, the metal ions that was adsorbed decreased. This was because of a decreasing in the adsorption of the adsorbate interaction is thought to occur due to the electrostatic repulsion between the active site NH$_3^+$ and metal ions have the same positive charge [4,5].
3.2. Kinetics Adsorption

In this study, the kinetic parameters obtained with the metal ion encounters at optimum pH and temperature variations in space and time of 1-26 hours. The observation of the effect of time to metal ions on the membrane is presented in Figure 2. In Figure 2, it appears that the adsorption of Pb(II) in the membranes Ch/Si/P has a high increasing at 4 hours among the contact time between 1-16 hours in the numbers of adsorbed metal ions, while the 16-26 hour of contact time has no increasing significantly. This indicates that there has been a balance between the amount of metal ions adsorbed by the number of metal ions remaining in the solution.

Based on these phenomena, it can be predicted that the amount of adsorbate that is adsorbed is proportional to the number of active sites on the membrane that has not bonded with the adsorbate. The more the number of active sites on the membrane that is not binding adsorbate, adsorption occurs more easily and vice versa. At the beginning of the interaction, there are many empty active sites so there are many adsorbent are quickly bound to the membrane. At the time of the interaction time lasts longer then vacant positions provided the less so as the number of adsorbate bound decreases. Referring to Figure 2, the adsorption data at a different time of interaction can be processed using a pseudo-order kinetic model one proposed by Lagergren and pseudo-order kinetic model of two proposed by Ho. Some researchers have previously used equation kinetics pseudo first order Lagergren and equality kinetics pseudo-order 2 (Ho) to evaluate the tendency kinetic model that applies to the process of adsorption of metal ions by the adsorbent made of chitosan [6].
The kinetics of Pb(II) ion adsorption have been described on the basis of the pseudo-first-order and pseudo-second-order models. A simple kinetic model given by Lagergren is the pseudo-first order relation:

\[
\frac{dQ}{dt} = k_1 (q_e - q)
\]

(1)

And the pseudo-second-order model is given by the following equation:

\[
\frac{dQ}{dt} = k_2 (q_e - q)^2
\]

(2)

Where \( q \) and \( q_e \) are the adsorbed Pb(II) ion onto the membrane at time \( t \) and equilibrium, respectively. The \( k_1 \) and \( k_2 \) are the kinetic rate constants of pseudo-first-order and pseudo-second-order models, respectively. We can obtain a linear equation for the pseudo-first-order and pseudo-second-order modes by integrating Eqs. (1) and (2), respectively:

\[
\ln (q_e - q) = \ln q_e - k_1 t
\]

(3)

\[
\frac{t}{q} = \frac{1}{k_2 h} + \frac{t}{q_e}
\]

(4)

A fitting result for the kinetic models is given in Table 1.

**Table 1.** Fitting results of the pseudo-first-order and pseudo-second-order kinetic models for adsorption of Pb(II) ion onto membrane

| Adsorbate | pseudo-first-order Lagergren model | pseudo-second-order kinetic model (Ho) |
|-----------|-----------------------------------|----------------------------------------|
|           | \((h^{-1})\) | \((\text{mmol/g})\) | \(R^2\) | \((\text{gmmol}^{-1}h^{-1})\) | \((\text{mmol/g})\) | \(R^2\) |
| Pb(II)    | 0.071     | 0.0089       | 0.951      | 0.0123   | 0.203       | 0.996 |

Table 1 obtained from research data were correlated according to an equation on kinetic models Lagergren pseudo-first order and pseudo-order kinetics equation 2 (Ho), for ions Pb (II). Data correlation factor \( R^2 \) values that is contained in Table 1, provides some significant data between the results obtained by pseudo first order kinetics model and the Lagergren pseudo second-order kinetic model. In general there is a tendency of correlation factor \( R^2 \) values higher pseudo second-order kinetic model [4,5]. In the pseudo second order kinetic model, the value \( q_e \) (adsorption equilibrium) more in line with the value \( q_e \) experimental results.

### 3.3. Adsorption isotherm models

The adsorption isotherm was studied by varying the initial concentration of Pb(II) ion (10 to 150 mg/L) at pH optimum. The effect of concentration Pb(II) ion on the adsorption is shown in the Figure 3. The observation of the ion adsorption Pb(II) in the membranes showed an increased number of metal ion adsorbed along with the increasing concentration of metal ion. At higher concentrations, the increase in the concentration of metal ion is not accompanied by an increase adsorption of metal ion significantly. Evaluation of adsorption data using the model of Langmuir isotherm and Freundlich isotherm models done by transforming the adsorption data to variables that correspond to the linear equation model of Langmuir and Freundlich isotherm. Data Langmuir and Freundlich isotherm parameters are presented in Table 2.
The $R^2$ obtained can be used to track the suitability of the process of adsorption by Langmuir and Freundlich isotherm models. In Table 2 shows that the Langmuir isotherm models provide conformity to the majority of the interaction between the metal ions with the membrane.

Table 2. Isotherm constant for adsorption of Pb(II) ion onto membrane

| Adsorbat | Langmuir Isotherm | Freundlich Isotherm |
|----------|-------------------|--------------------|
|          | $q_e$ (mmol/g)    | $\Delta G$ (KJ/mol) | $R^2$ | $R^2$ |
| Pb(II)   | 0.16              | -25.97             | 0.995 | 2.040 | 1.573 | 0.984 |

The phenomenon that occurs in the ion Pb(II) with active sites on the membrane following the Langmuir isotherm models. Langmuir isotherm concept states that the increase in concentration followed by increasing the number of adsorbed substances so as to achieve equilibrium quantity. Langmuir adsorption theory suggests that at the adsorbent surface there are a certain number of active sites proportional to the surface area of the adsorbent. In a state of active sites has not been saturated by adsorbate, there will be an increase in adsorption. Increasing the concentration of adsorbate that interaction does not increase the amount of adsorbate that is adsorbed adsorbent when active sites have been saturated by the adsorbate. If this trend occurs, then the interactions of metal ions involved in the surface of each adsorbent is monolayer / one layer. And vice versa, if the trend does not happen then the possibility of interaction between the metal ions and multilayer membrane occurs following the pattern Freundlich isotherm. Metal ion adsorption on an adsorbent is influenced by several factors, among others, the ability of the adsorbent, the size of the metal ion, and the environment in the process of adsorption. The ability of the adsorbent can be viewed through two different sides, namely active group and the pore size of the adsorbent.

The selectivity of the membrane against a mixture of dye Rhodamine B and Pb(II) ion. Adsorption of Rhodamine B dye mixture and ion Pb(II) is done by creating a mixture of Rhodamine B/Pb(II). The results of adsorption on a mixture of dye Rhodamine Band Pb(II) ion are presented in Table 3. That means that Pb(II) can’t be determined even in the presence of Rhodamine B.

Table 3. Selective adsorption ion Pb(II)/Rhodamin B

| Initial Concentration | D (L/g) | $\alpha$ |
|------------------------|---------|----------|
| Rhodamine B            | Pb(II)  | Rhodamine B | Pb(II) | Pb(II)/Rhodamine B |
| 0.5                    | 0.5     | 28.73     | 68.40   | 2.38                |
| 0.5                    | 1       | 25.71     | 15.81   | 0.62                |
4. Conclusions
In the adsorption by a batch system for membrane obtained optimum at pH 5 for Pb(II). Adsorption of Pb(II) onto Ch/Si/P membrane follow the Langmuir isotherm model. Values ion adsorption capacity for Pb(II) was 0.16 mmol/g. In general the adsorption kinetics of data, there is a tendency of linearity coefficient $R^2$ values higher pseudo- second order kinetic model. The Pb(II) ion can’t be determined even in the presence of Rhodamine B.

References
[1] Min M She L Hong G Zhu M Zhang Y and Wang X 2012 Micro-nano structure poly(ether sulfones)/poly(ethyleneimine) nanofibous affinity membranes for adsorption of anionic dyes and heavy metal ions in aqueous solution Chem. Eng. J. 197 88-100
[2] Barakat M A 2011 New trends in removing heavy metals from industrial wastewater Arab. J.Chem 4 361-377
[3] Mahatmanti F W Nuryono Narsito 2014 Physical Characteristics of Chitosan based Film Modified with Silica and polyethylene glycol Indones. J. Chem. 14(2) 131-137
[4] Salehi E and Madaeni S S 2014 Influence of poly(ethylene glycol) as pore-generator on morphology and performance of chitosan/poly(vinyl alcohol) membrane adsorbents Appl. Surf. Sci. 288 537-541
[5] Madaeni E S S Rajabi V Vatanpour A A Derakhsan S Zinadini Sh Ghorabi and H A Monfared 2012 Novel chitosan/poly(vinyl) alcohol thin adsorptive membranes modified with amino functionalized multi-walled carbon nanotubes for Cu(II) removal from water: Preparation, characterization, adsorption kinetics and thermodynamics Sep. Purif. Technol. 89 309-319
[6] Mahatmanti F W Nuryono Narsito 2016 Adsorption of Ca(II), Mg(II), Zn(II), and Cd(II) on Chitosan Membrane With Rice Hull Ash Silica and Polyethelyne Glycol Indones. J. Chem. 16(1) 45-52

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