Indonesian Journal of Pure and Applied Chemistry
journal homepage: http://jurnal.untan.ac.id/index.php/IJoPAC

ADSORPTION OF Pb(II) BY POLYANILINE/SILICA GEL COMPOSITE: KINETICS AND ISOTHERM STUDIES

Mas Inda Putrinesia[1*], Nurlina[1], Winda Rahmalia

Jurusan Kimia, Fakultas MIPA, Universitas Tanjungpura, Kalimantan Barat, Indonesia

[*]*Corresponding author: indaputrinesia0908@student.untan.ac.id*

ARTICLE INFO

Article history:
Received 25 October 2018
Accepted 17 November 2018
Available online 30 December 2018

Keywords:
Antioksidan,Citrus microcarpa Bunge, Limonin, Triterpenoid

ABSTRACT

Research on the study of kinetics and isotherm adsorption of Pb(II) by polyaniline/silica gel (PANI/SiO_2) composite from glass waste has successfully been done. The polymerization of silica gel was prepared by sol-gel process. Meanwhile, PANI/SiO_2 composite was prepared using sulfuric acid (H_2SO_4) as its dopants and hydrogen peroxide (H_2O_2) for oxidation process. Composition of oxide compound in PANI/SiO_2 composite was analyzed by X-Ray Fluorosence (XRF) and Gas Sorption Analyzer (GSA). Adsorption of Pb(II) was carried out by contacting PANI/SiO_2 with $Pb(NO_3)_2$ solution for 20, 40, 60 and 80 minutes, with concentrations of 150, 200, 250, 300, 350 and 400 mg/L. The optimum contact time was reached at 40 minutes. This adsorption followed pseudo-second order model with R^2= 0.996. The first optimum adsorption capacity was reached in the concentration of 250 mg/L. Isotherm adsorption followed Langmuir models with R^2= 0.954 (monolayer capacity= 51.02 mg/g).

1. Introduction

Heavy metal pollution is one of the most concerned environmental problems nowadays. Lead (Pb) is one of heavy metals that are present in the environment. In water, Pb is present as divalent ion Pb(II). These metal ions are released to water environment by many activities like mining, manufacturing, and farming [1]. Pb(II) is carcinogenic, harmful to liver, kidneys, and could cause abnormalities on pregnant women's babies [2]. There are many ways to reduce concentrations of Pb(II) in water such as precipitation, coagulation, ion exchange and adsorption. However, adsorption is more simple way to do [3;4]. Nowadays, research about adsorbent in combination of organic-inorganic polymeric materials have gained much attention for the removal of heavy metals. Polyaniline (PANI) is one of organic conducting polymer with electrical properties that are tunable by doping [5]. In addition, PANI can be used as an electrode material, electrochromic device, recodable optical disk [6]. As a polymer, PANI can be produced as a film [6] and powder [3;5]. As an adsorbent, PANI has the lone pair of electrons on nitrogen atoms that can make a coordinate bond with positive metal ions [3] In many applications, PANI is recommended to be combined with inorganic materials because of its weaknesses (has low thermal stability and does not have good stability with the change of pH). Meanwhile, among

various inorganic materials, silica gel has gained more attention due to its large surface area, high porosity, has good stability in a wide range of pH, etc [3;4].

Silica gel can be extracted from mineral like quartz. But, taking minerals countinously can damage the enviroment. Extracting silica from renewable natural materials or from waste is one of the wisest ways. Glass waste is material that contains up to 70% silicon dioxide [7]. The utilization of glass waste in the making of silica gel is expected to change the use of minerals that are not renewable. The presence of glass waste in the environment is quite high given the fact that glass is used for buildings, furnitures, beverage bottles and other industries. Glass waste will be processed into sodium silicate. Sodium silicate will be polymerized onto silica gel by adding sulfuric acid in sol-gel process. After that, silica gel will be composited with PANI.

This study will focus on the kinetics and isotherm adsorption of solution contained Pb(II) metal ions. The adsorption process was carried out by contacting the composite in solution of $Pb(NO_3)_2$ with variation of contact time and variation of concentraton.

2. Materials and Methods

2.1 Materials

Glass waste was taken from glass cutting factory in Kubu Raya, West Kalimantan. Aniline ($C_6H_5NH_2$) ACS reagent, ≥ 99,5% was supplied by Sigma-Aldrich (Germany). Analytical grade hydrochloric acid HCl, 37%), sulfuric acid (H_2SO_4, 96%), sodium hydroxide (NaOH) reagent grade, ≥ 98,0% pellets (anhydrous), hydrogen peroxide (H_2O_2), ferrosulfate (pentahydrate) ($FeSO_4.7H_2O$) pellets and lead dinitrate $Pb(NO_3)_2$ pellets were supplied by Sigma-Aldrich, Germany

2.2 Methods

2.2.1 Preparation of silica gel from glass waste

Glass waste was cleaned and dried before destructed. The fine glass then sieved (80 mesh). Then, 100 grams of fine glass powder was added into 300 mL of NaOH. The mixture was stirred and heated until most of the water evaporated. Then, it was heated by furnace at 400°C for 4 hours. After that, sodium silicate in the solid phases was added into 500 ml H_2O and stirred for 3 hours (100 °C). At the end, this process will produce sodium silicate solution.

Hydrochloric acid (3M) then dropped into 100 ml of sodium silicate solution while stirring until the gel was obtained. The hydrogel was then dried in the oven at 80 °C for 18 hours. The form of dry silica (xerogel) then produced. Silica xerogel was crushed and washed with H_2O until it was neutral. Xerogel powder was dried in the oven at 80 °C to make neutral silica xerogel [8].

2.2.2 Polymerization of polyaniline/silica gel composite

Silica gel 2.6 grams were heated for 3 hours (110 °C) to activate its surface. Meanwhile, 0.4 M sulfuric acid 250 ml was prepared, then stirred using magnetic stirer. While it was being stirred, the activated silica was inserted into the beaker slowly. The system then kept stirring for about 2-3 hours until it was homogeneous. Then, 3.2 grams of aniline was added to the system. When it was added, the system should be in cold condition (4-5 °C). The system was constantly stirred until homogeneous. After that, 3 grams of hydrogen peroxide was added into system and let the system strirred for 30 minutes. The last addition was adding about two drops of ferronium sulfate pentahydrate. Then the system was stirred at room temperature for 24 hours. The precipitate was formed, then filtered and washed using sulfuric acid and acetone [9]. Polyaniline/silica gel composite was characterized using XRF.

2.2.3 Determination of kinetica adsorption

A total of 0.1 gram of polyaniline/silica gel composite were added to 25 ml Pb(II) solution at a concentration of 200 mg/L. Both were contacted with contact time variations of 0, 20, 40, 60 and 80 minutes. After that, the system was filtered and the filtrate was taken. Repeated the experiment for 3 times. Analyzed concentration of Pb(II) using AAS. The determination of the adsorption reaction kinetics then was calculated by equation (2.1) - (2.4) [10].

First Order kinetics equation $: \ln C_e = -k_1 t + \ln C_o$ (2.1)

Second Order kinetics equation $: \frac{1}{C_e} = k_2 t + \frac{1}{C_o}$ (2.2)

Pseudo first Order kinetics equation $: \log(q_e - q_t) = \log q_e - \frac{k_3}{2{,}303} t$ (2.3)

Pseudo second Order kinetics equation $: \frac{t}{qt} = \frac{1}{q_e} + \frac{1}{k_4 . q_e^2}$ (2.4)

2.2.4 Determination of isotherm adsorption

Adsorption was carried out by variation of concentration of sample solution 150, 200, 250, 300, 350 and 400 mg/L. A total of 0.1 grams of polyaniline/silica gel adsorbent was added to 20 mL of a solution containing Pb(II) ions. The sample then was contacted with composite using a shaker (153 rpm) for 40 minutes. After that, the solution was filtered. The filtrate was taken and analyzed using AAS. The experiment was done for 3 times of repetitions. Determination of maximum adsorption capacity was calculated using Langmuir isotherm equation (2.5)-(2.8). Freundlich isotherm was calculated using equation (2.9) [11].

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \quad (2.5)$$

$$q_e = Q_o - \frac{q_e}{bC_e} \quad (2.6)$$

$$\frac{q_e}{q_e} = bQ_o - bq_e \quad (2.7)$$

$$\frac{1}{q_e} = \frac{1}{Q_o . bC_e} + \frac{1}{Q_o} \quad (2.8)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (2.9)$$

3. Result and Discussion

The oxide compounds in PANI/SiO_2 was showed in Table 1.

Table 1. Composition of Oxide Compounds in PANI/SiO_2 Composite

Senyawa Oksida	Persentase (%)
Silicon dioxide (SiO_2)	89,11
Titanium dioxide (TiO_2)	0,003
Aluminium dioxide (Al_2O_3)	1,029
Iron (III) oxide (Fe_2O_3)	0,047
Calcium oxide (CaO)	0,190
Magnesium oxide (MgO)	0,198
Potassium oxide (K_2O)	0,055
Diphosphorus pentoxoxide	1,045
(P_2O_5)	0,005
Chromium (III) oxide (Cr_2O_3)	0,014
Chlorine (Cl)	

Composite of PANI/SiO_2 contains up to 89% of silicon dioxide. It means that silica from synthesized glass waste has high purity. Other oxide componds were stand no more that 2 %, such as aluminium dioxide (Al_2O_3) and diphosphorus pentoxoxide (P_2O_5).

Composite was also characterized by GSA to measure its pore size. The volume mikropori is 0.014 cc/g, with 48.570 m^2/g surface area and the pore radius is 19.112 Å. It is can be certain that the composite is able to adsorb Pb(II) ion which the radius size is 1.22.

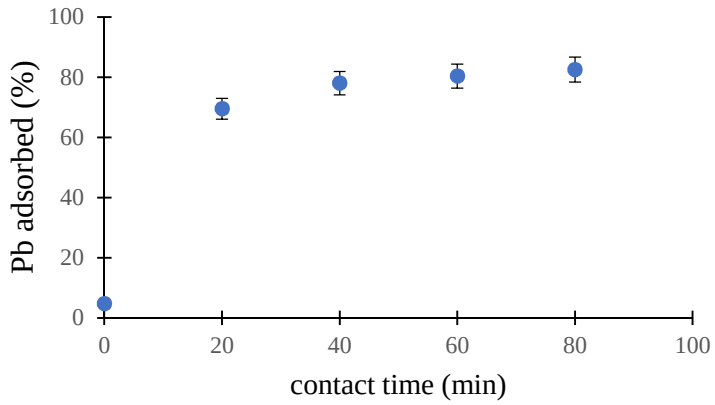


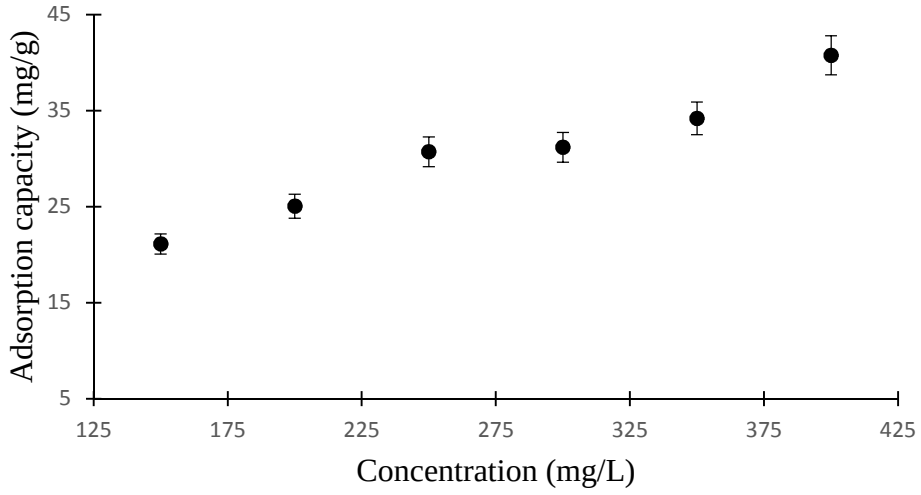
Figure 1. Effect of contact time on adsorption of Pb(II) using PANI/SiO_2 composite

Table 2. Adsorption Kinetic Parameters for the Adsorption of Pb(II) on PANI/SiO_2

Kinetic Models	Parameter	Value
1st Order	k_1 (10^{-2}) (1/min)	-1,92
	R^2	0,772
2nd Order	k_2 (10^{-2}) (g/mg.min)	0,03
	R^2	0,897
Pseudo-first Order	q_e (mg/g)	1,367
	k_1 (10^{-2}) (1/min)	0,074
	R^2	0,125
Pseudo Order	q_e (mg/g)	37,453
	h (mg/g.min)	17,450
	k_2 (10^{-2}) (g/mg.min)	1,244
	R^2	0,996

q_{exp} = 34,202

The effects of contact time on the amount of Pb(II) adsorbed onto PANI/SiO_2 were investigated. In the first minute until 20 minutes, the curve increased sharply. In the periode of 20-40 minutes, the increase of Pb(II) that is adsorbed starts to ramp. This data then calculated by statistical product and service solutions (SPSS) with Duncan Methode. From this calculation, the increasing in 40-60 minutes was not significantly different. When the increase was not significantly different, it can be admitted as equilibrium phase of adsorption. The equilibrium contact time then is used for next adsorption.



Fugure 2. Effect variation of concentration to adsorption capacity

Table 3. Adsorption Isotherm Parameters for the Adsorption of Pb(II) on PANI/SiO_2

Persamaan Isoterm	**Parameter**	**Nilai**
Langmuir	b (l/mg)	0,013
	Q_o (mg/g)	51,02
	R^2	0,954
	E_{ads} (KJ/mol)	10,76
Freundlich	K_f [(mg/g)(l/mg)$^{1/n}$]	0,083
	n	0,470
	R^2	0,943
	E_{ads} (KJ/mol)	6,166

Adsorption process depends on the contact time between adsorbent and adsorbate. The determination of adsorption kinetics models is performed to determine the variables involved in the adsorption process. In addition, the kinetics model is required to predict the rate when adsorbate was adsorbed onto adsorbent [10]. A value of determination coefficient (R^2) showed the most suitable kind of kinetics. Adsorption capacity (qe) which is the most appropriate to the adsorption capacity of the research (qexp) showed the suitable kinetics model too. The value of adsorption parameters showed in Table 2.

Based on Table 2, adsorption process followed pseudo-second order with the highest value of R^2= 0.996. It means that 99.6 % data can be explained by pseudo-second order kinetic model [12]. Furthermore, the calculated of adsorption capacity from equation (qe) in pseudo-second order model has the closest value to the adsorption capacity based on the research. The initial adsorption rate at t →0 (h) was 17.45 mg/g.min. Pseudo Order 2 states that the adsorption rate is equivalent to the quadratic concentration of adsorbate [12]. So, if the concentration of adsorbate increases twice as much, then the adsorption rate will increase.

Initial concentration of Pb(II) effected to quantity of Pb adsorbed at equilibrium (Figure 2). The conection between initial concentration can be investigated by doing adsorption process in many variation of concentrations (from 150 mg/L until 400 mg/L) for 40 minutes. From this process, capacity of adsorption can be determined. At concentration of 0-150 pmm, capacity increased very sharp. It caused by the increasing of mass gradient between solution and

adsorbent. Thus, Pb(II) can easily move from solution to adsorbent surface [13]. Up to 150 mg/L, adsorption capacity was slowly increase. Start from 250 mg/L- 300 mg/L, graphs tend to be stable. It assumpted that at this concentration, the first equilibrium of adsorption was reached. After 300 mg/L, the graph continues to increase. At first equilibrium, can be determined that a chemical adsorption was occured by single layer . But after that there was a physical adsorption involving more than one layer.

The R^2 values produced by the Langmuir and Freundlich isotherms were 0.954 and 0.943, respectively (Table 2). The Q_o parameter describes the maximum adsorption capacity in the monolayer layer. The value of Q_o was 51.02 mg / g. This shows that for every 1 gram of PANI/SiO_2 maximally absorb as much as 51.02 mg Pb(II). When crossing the limit, the monolayer layer will saturate. Kf denotes Freundlich's constant corresponding to the adsorption capacity [11]. When the value of 1 / n ≠ 1, the value of Kf will be influenced by the value of q and concentration (C).

The 1 / n value obtained from the adsorption process of Pb(II) by PANI/SiO_2 was 2,127. This shows the strong intermolecular attraction in the adsorbent layer. Although the adsorption of Pb (II) can occur physically and chemically, when viewed from the value of R^2, the more dominant adsorption occurs chemically by forming bonds of chemical compounds between PANI/SiO_2 and Pb(II) active groups. Karthik and Meenakshi (2014) explained that the PANI/SiO_2 composite will bind the metal to the amine group present in PANI.

4. Conclusion

The optimum contact time of Pb(II) adsorption by PANI/SiO reached at 40 minutes and optimum adsorption capacity reached at concentration of 250 mg/L. Meanwhile, kinetic model followed pseudo second order with rate constant 0.0124 g/mg.min. Isoterm adssorption followed Langmuir model with Langmuir's constant (b) was 0,013 l/mg and monolayer capacity 51.02 mg/g.

Reference

[1] Lim A.P., Aris A.Z., A Review on Economically Adsorbents on Heavy Metals Removal in Water and Wastewater, *rev. Environ biotechno*.2013.

[2] M.Nadeem, R. Nadeem, H.U. Nadeem, S.S. Shah, Accumulation of lead and Cadmium in different Organs of Chicken, Pak. J.Sci. Res. 57 (2005) 71.

[3] Karthik R., Meenakshi S., 2014, Removal of Hexavalent Chromium Ions Using Polyaniline/silica gel Composite, *journal of Water Process Engiineering,* 1(2014)37-45.

[4] Ayad M.M and Nasr A.A., Anionic Dye (Acid Green 25) Adsorption from Water by Using Polyaniline nanotubes salt/silica Composite, *Journal of Nanostructure in Chemistry*, 3(3), 2012.

[5] Niu Z., Yang Z., Lu Y., Han C.C., Polyaniline-Silica Composite Conductive Capsules and Hollow Spheres, *advance function material*, 12(13), 2011.

[6] Ayad M.M and Zaki E.A., Synthesis and Characterization of Polyaniline Films using Fenton Reagent, *Journal of Applied Polymer Science*, 110 (6): 3410-3419, 2008.

[7] Buhani, Suharso, Sembiring Z., Biosorption of Metal Ions Pb(II), Cu(II), And Cd(II) on *Sargassum duplicatum* Immobilized Silica Gel Matrix, 6(3): 245-250, 2006.

[8] Safitri, M.N., Sintesis Silika Gel Fasa Terbalik untuk Kromatografi Kolom dari Limbah Kaca, Universitas Tanjungpura, Fakultas Matematika dan Ilmu Pengetahuan Alam, Pontianak, 2012,(Skripsi).

[9] Khairi S., Fathony Z., Radhiansyah L.Y., Akbar A.Y., Arryanto Y., Sutarno, Sudrajat H., Sintesis Material Komposit *Modified Clay*-Polianilin Tersulfonasi (MC-SPANI) sebagai Elektrolit pada Proton *Exchange Fuel Cell* (PEFC), Universitas Gajah Mada, Yogyakarta, 2009.
[10] Ho, Y. S., dan Mckay, G., Pseudo-second Order Model for Sorption Processes, *Pro. Biochem.*, 34, 451-465, 1999.
[11] Foo K.Y., Hameed B.H., Insights Into the Modeling of Adsorption Isotherm System, *Chemical Engineering*, 156: 2-10, 2010.
[12] Kurniawati P., Wiyantako B., Kurniawan A., Purbaningtias T.E., Kinetic Study of Cr(VI) Adsorption on Hydrotalcite Mg/Al with Molar Ratio 2:1, *EKSAKTA*, 1-2(13): 11-21, 2013.