Preliminary study on the adsorption of lead (II) ions from aqueous solution with breadfruid's bark (*Artocarpus altilis*) by un-modified and modified with citric acid

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Abstract. The adsorption of lead(II) ions from aqueous solution with breadfruit's bark by unmodified and modified with citric acid was investigated. The results by using adsorbent dosage 20 g/L indicated the adsorption efficiency was up to 99%, and the best result is obtained about 99,963% when adsorbate is conducted with modified bark for 90 minutes. The adsorption behavior by modified bark followed the Langmuir isotherm model and the Freundlich isotherm model for modified bark. The maximum adsorption capacity of lead(II) ions are 34,98 mg adsorbate/g adsorbent for unmodified bark when contact time is 60 minutes. The influence of contact time showed that adsorption reached the equilibrium rapidly. A batch adsorption model followed the pseudo second order kinetic.

Keywords: Adsorption, breadfruit's bark, lead(II) ions, isotherm models

Introduction

One of water pollutant that is harmful to living things is the dissolved metal content in it. Excessive amount of metals in water, especially heavy metals are very harmful to living things, so to minimize it there are various ways or treatment, one of which is adsorption using adsorbent material. Several types of commercial adsorbents are commonly used in the process is activated carbon, silica gel, activated alumina, zeolite and synthetic polymers or resins.

In this study, the breadfruit's bark was used as an alternative raw material in the manufacture of the adsorbent. Utilization of renewable natural resources, in this case the breadfruit's bark (*Artocarpus altilis*), based on economic considerations, availability (the amount of raw materials are abundant in nature) and the absence of a negative impact on the environment. Breadfruit's bark has the potential to be used to create an adsorbent material for heavy metals. Several studies on the manufacture of adsorbents have been using the skin of tropical trees as raw materials, such as aspen bark, wood fiber palm trees and teak bark. Rowell (2006) mentioned that the bark of woody ability to absorb metal ions is much larger than the wood itself. Oak's bark has a larger absorption capacity of 6.8 mg/g when compared with the wood of 2.3 mg/g. James D. McSweeny et al..(2006) using aspen's bark as an adsorbent to absorb metal ions copper (valence 2), obtained the maximum absorption capacity of 13.8 mg Cu^{2+}/ g adsorbent (with citric acid modification at 1300C after 2 hours) and 4.1 mg Cu^{2+} / g of adsorbent (without modification).
The objectives on this research were:

a. to learn about capacity and efficiency of absorption of the metal ions Pb^{2+} by the bark of the breadfruit tree by varying the sample concentration and contact time.
b. to study the effects of treatment with non-modified adsorbent and modified adsorbent toward the capacity and efficiency of absorption of the metal ions Pb^{2+} in order to obtain the optimum process conditions.
c. knowing and studying the adsorption kinetics

Materials and Methods

This study was conducted in November 2008 to January 2009 in the Laboratory of Bioprocess, chemical Engineering Department-UNSYIAH, Research and Development Center of Biomaterials of LIPI Cibinong, Chemical Research Center of LIPI Serpong ; and Laboratory of Analysis at Center of Research and Industry Standardization, Banda Aceh

Equipment and Materials

The equipments used in this research were: Atomic Absorption Spectrophotometer (AAS) Shimadzu AA 6200, Fourier Transform Infrared (FTIR) IRPrestige-21 Shimadzu, electric oven Memmert, Panasonic blender, sieve 80-60 mesh (2000-250 microns), universal pH indicator Merck, magnetic Stirrer, hot plate Yamato MH 800, scales Sartorius BP 211 D, desiccator, stopwatch, filter paper, measuring cups 100 mL, 50 mL & 500 mL volumetric flasks, 25 mL measuring pipettes, drops pipette, funnels and aluminum foils.

The materials used in the study were: breadfruit's (*Artocarpus altilis*) bark, aquades, HCl p.a., lead acetate trihydrate -Pb $(CH_3COO)_2$.3H2O p.a., and citric acid -$C_6H_8O_7$ p.a.

Variables

Fixed variables in this study were temperature (room temperature) and adsorbent dose (20 g / L), while no fixed variables were contact time (15; 30; 60; 90 and 120 minutes); and concentration of sample: 20; 40; 60; 80; and 100 mg/L

Research Procedures

Breadfruit's barks were cut to a size of 5 mm, then washed with aquades. Then barks were dried in an oven at 105^0C until a constant mass (5 hours). Barks were blended until the size of 80-60 mesh and then stored in a desiccator.

Adsorbent Purification

Adsorbent was washed with 0.01 M HCl p.a. as much as 5 mL / g of adsorbent, and neutralized to pH 7 with aquades. The experiments followed by drying the adsorbent at a temperature of 105^0C for 5 hours. To identify the content of hydroxyl groups in the adsorbent substrate, it is taken 1 mg of adsorbent which has been smoothed for analysis using infrared spectroscopy (FTIR).

Modified Adsorbent with Citric Acid

Adsorbent which has been purified is stirred with 200 g/L $C_6H_8O_7$ as much as 20 mL/g of adsorbent for 90 minutes using magnetic stirrer at room temperature. Then adsorbent was neutralized with aquadest to obtain pH of 7 and dried at a temperature of 105^0C for 2½ hours. To identify the presence of a hydroxyl group substituted by carboxyl groups of citric acid, then taken 1 mg of adsorbent which has been smoothed for analysis using infrared spectroscopy (FTIR).

Preparation of lead standard solution

In the preparation of lead standard solution of 1000 mg/L, weighed as much as 1.8309 grams of Pb $(CH_3COO)_2.3H_2O$ and dissolved with aquadest in a 1 L volumetric flask until mark boundaries. To have the solution concentration of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L by 50 mL, the standard solution was sucked with a pipette as much as 1 mL, 2 mL, 3 mL, 4 mL and 5 mL .

Adsorbent Test

Adsorbent was tested with variables of concentration and contact time specified. Weighed as much as 1 gram of adsorbent and placed in a 50 mL measuring cup (20 g/L). A total of 50 mL samples containing ions lead to a concentration of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L was poured into the measuring cups that already contains the adsorbent. The contact time was varied to test adsorbents of 15 minutes, 30 minutes, 60 minutes, 90 minutes and 120 minutes while stirred at 150 rpm. The filtrate was filtered with filter paper and prepared for analysis using Atomic Absorption Spectrophotometer (AAS).

Results and Discussion

Effect of Contact Time and Concentration on Absorption Capacity

The longer of time of contacting, the amount of metal absorbed was increased. It was occurred when the adsorption has not yet reached the equilibrium. Figure 1 shows that the contact time and adsorbate concentration is directly proportional to the absorption capacity. This is caused by the absorption capacity is a function of time when equilibrium has not yet occurred. The length of contact time between the adsorbate with the adsorbent led to a growing number of filled empty spaces on the adsorbent, so that more adsorbate is trapped in a cellulose matrix. Increasing the amount of adsorbate in the cellulose matrix can also lead to the possibility for the occurrence of the binding of metal ions on the functional group in lignin.

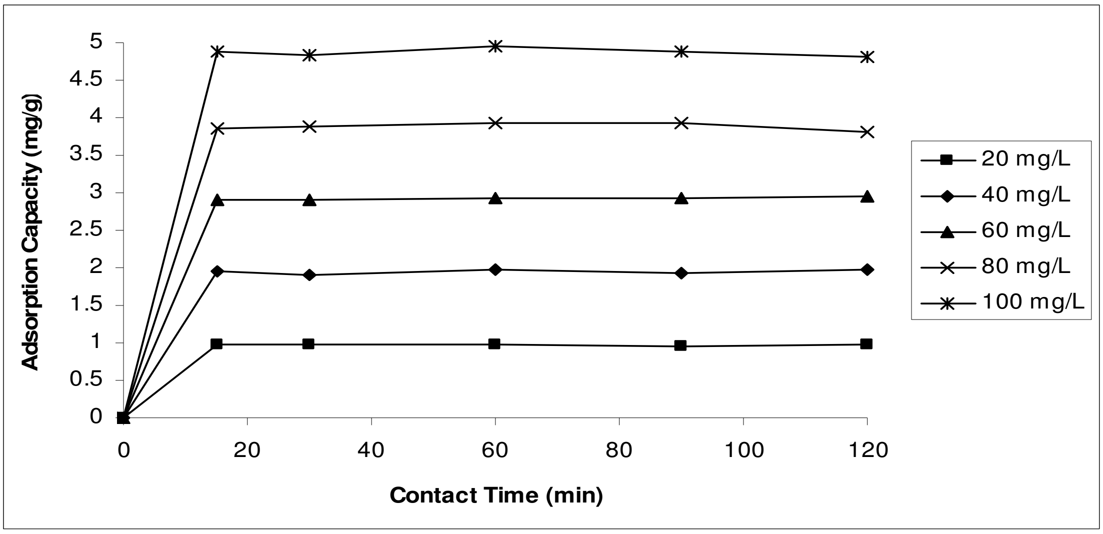

Figure 1. Effect of contact time on the absorption capacity of the breadfruit's bark without modification

As the results shown at Figure 1, at a concentration of 60 mg/L, the absorption capacity obtained at 15, 30, 60, 90 and 120 minutes is 2.9045; 2.9066; 2.9243; 2, 9346 and 2.9528 mg/g, respectively. While at the time of 120 minutes, the absorption capacity has the highest values, at a concentration of 20, 40, 60, 80 and 100 mg/L is 0.9647; 1.9762: 2.9528: 3.8077 and 4.8188 mg/g, respectively.

Figure 2 shows the effect of contact time on the absorption capacity of the breadfruit's bark with modification by citric acid. As the results, the contact time and adsorbate concentration is directly proportional to the absorption capacity. At a concentration of 60 mg/L, the absorption capacity at 15, 30, 60, 90 and 120 minutes is 2.9517; 2.9701: 2.9681: 2.9987 and 2.9673 mg/g, respectively. While at the time of 120 minutes, the absorption capacity at a concentration of 20, 40, 60, 80 and 100 mg/L, respectively is 0.9653; 1.9653: 2.9673: 3.9340 and 4.9965 mg/g

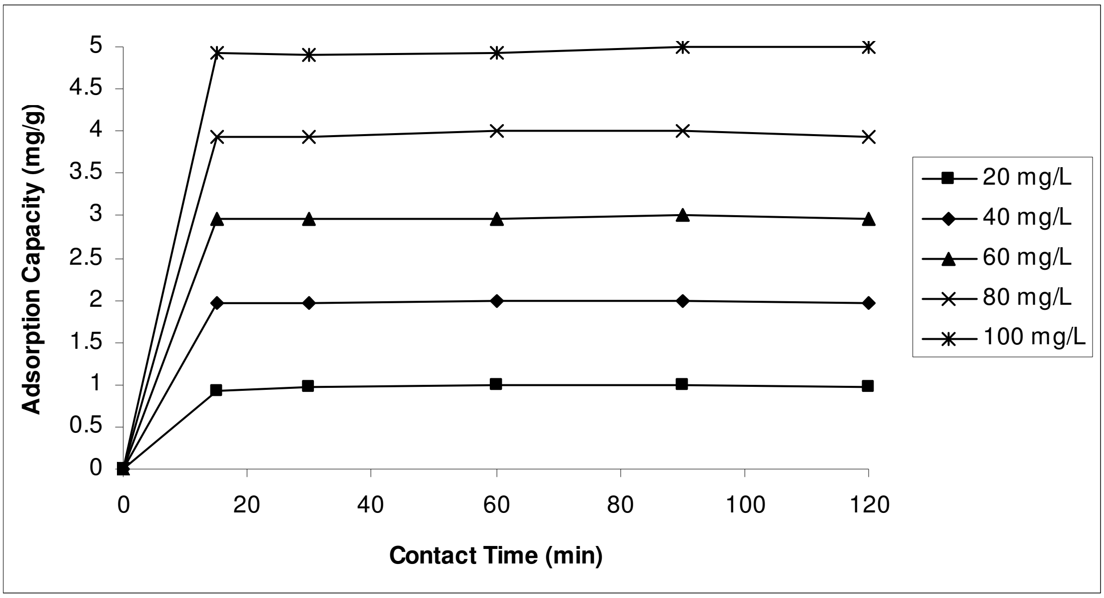

Figure 2. Effect of contact time on the absorption capacity of the breadfruit's bark with modification by citric acid.

Effect of Modification by Citric Acid on the Absorption Capacity

The influence of adsorbent modification on the absorption capacity at concentration of adsorbant of 60 mg/L was shown in Figure 3. The adsorption capacity of the adsorbent with citric acid modification is greater than without modification. At the contact time of 30 minutes, the absorption capacity of the adsorbent obtained without modification was 2.9066 mg/g and 2.9701 mg/g with modification, respectively.

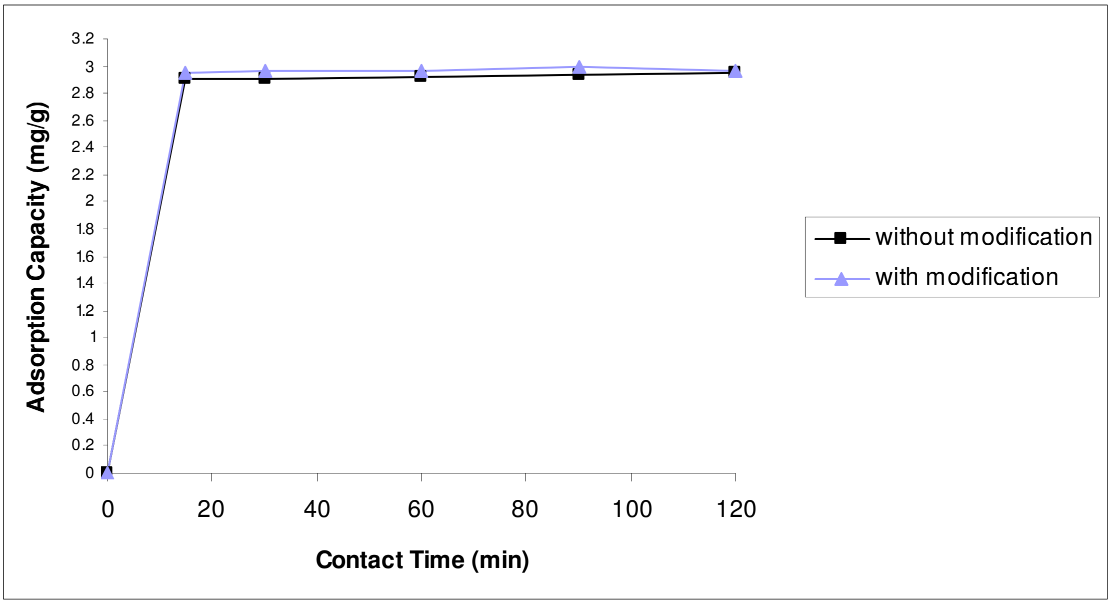

Figure 3. Effect of modification by citric acid on the adsorption capacity at concentration of lead (II) solution of 60 mg / L.

Adsorption Efficiency

Absorption efficiency is a function of contact time. Absorption efficiency increased as the length of contact time. The efficiency of absorption of the adsorbate with adsorbent modifications as shown in Figure 4. At the time contact of 15, 30, 60, 90 and 120 minutes with a concentration of 60 mg/L, the absorption efficiency obtained was 98.39; 99; 98.93; 99.95 and 98.91%, respectively.

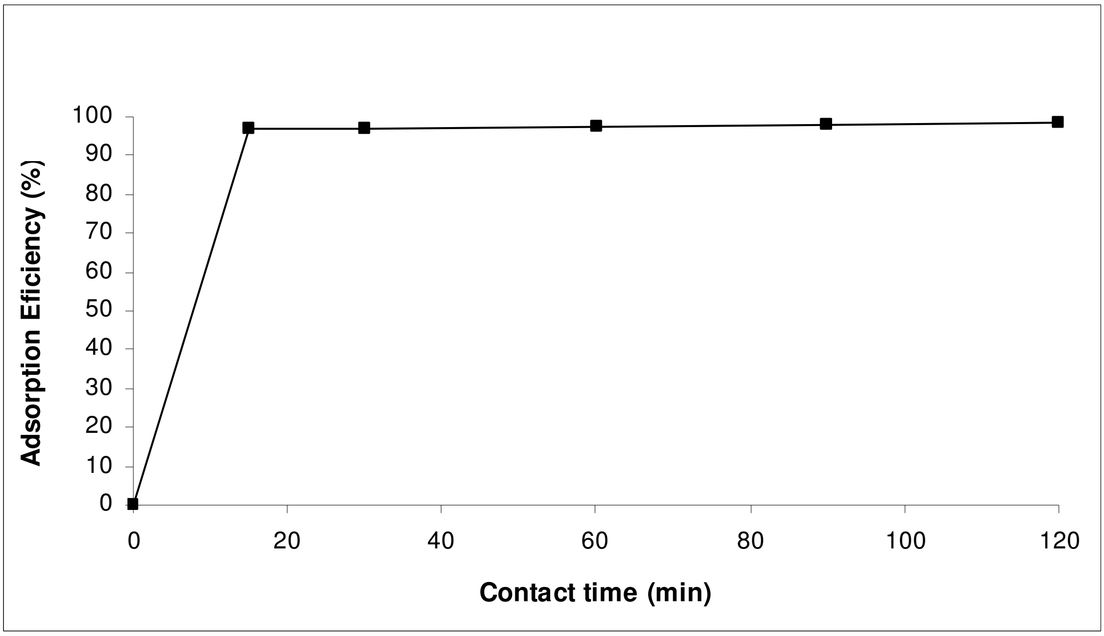

Figure 4. The relation between contact time and the absorption efficiency (at concentration of 60 mg/L) by citric acid modification.

Adsorption Kinetics

Adsorption kinetics of Pb^{2+} by breadfruit's bark was obtained by plotting the curve of contact time (t) versus t/qt. The rate of adsorption kinetics on adsorbents by modification or not was obtained following the second order equation. Rate equation of second order kinetics model is

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{kq_e^{\ 2}} + \frac{1}{q_e}t \tag{2}$$

From Figure 5, the value of k obtained at 0.6946, hence :

$$\frac{t}{q_t} = 0{,}1683 + 0{,}3419t \tag{3}$$

Second order equation is only suitable for describing the mechanism of adsorption after the adsorbent and adsorbate in contact for a long time. This is because at the beginning is still not formed a chemical bond. Unlike the adsorption ability of metal ions Pb 2 + by breadfruit bark, with a maximum contact time for 2 hours, all following a second order equation with the Pearson correlation is quite large (approaching 1). This shows that the adsorbent has been formed chemical bonds with the adsorbate rapidly. The occurrence of chemical bonds can also be evidenced through the results of infra-red spectroscopy analysis after contacting the adsorbent. In Figure 6 k values obtained at 0.5437, hence :

$$\frac{t}{q_t} = 0{,}7736 + 0{,}2019t \quad (4)$$

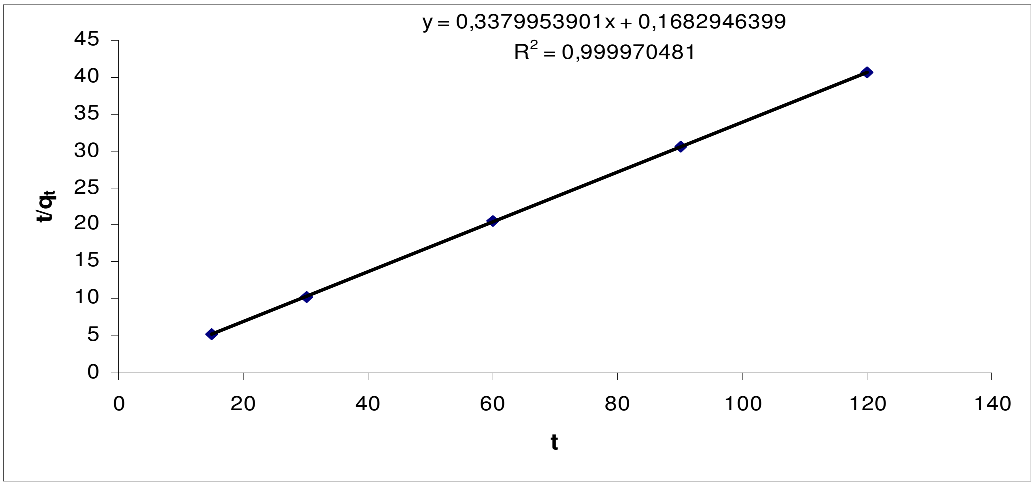

Figure 5. The rate of second order absorption kinetics of metal ions Pb^{2+} without modification (at concentration of 60 mg/L).

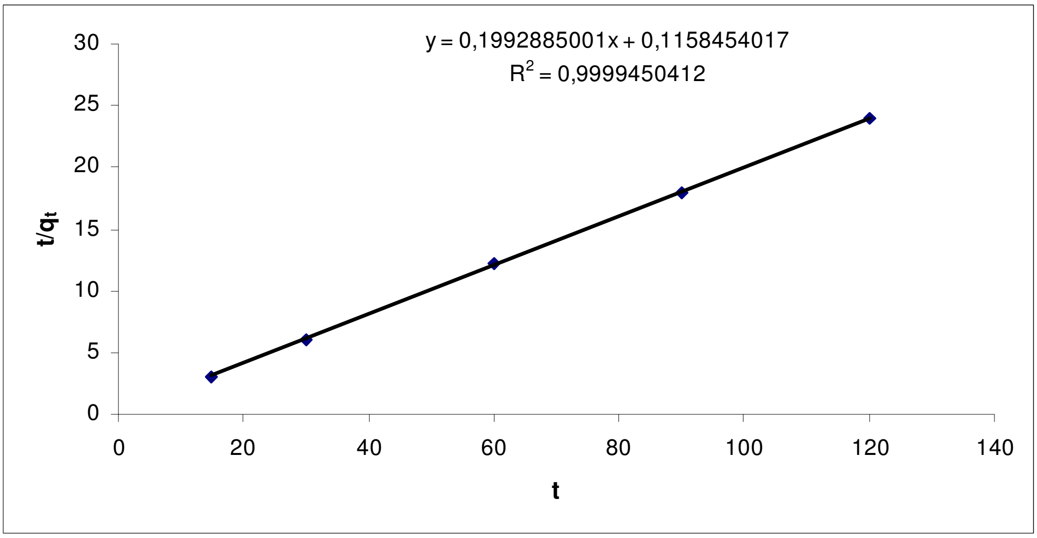

Figure 6. The rate of second order absorption kinetics of metal ions Pb^{2+} with modification (at concentration of 60 mg/L).

Conclusions

The adsorbent with citric acid modification provides greater absorption capacity than the adsorbents without modification. At contact time of 30 minute with the initial concentration of 60 mg/L, the obtained absorption capacity of the adsorbent without modification was 2.9066 mg/g and 2.9701 mg/g with modification.

The contact time is directly proportional to the efficiency of absorption. At contact time of

15, 30, 60, 90 and 120 minutes with the initial concentration of 60 mg/ L before the modification, the absorption efficiency obtained was : 96.81; 96.88; 97.47; 97.82 and 98.42%. The rate on the absorption kinetics of metal ions Pb^{2+} with a concentration of 60 mg/L without modification obtained following the second order equation with a k value of 0.6946.

Acknowledgements
The author would like to thank profusely to the General Directorate of Higher Education (DIKTI) for research funding by COMPETITIVE GRANTS (HIBAH BERSAING) so this research can be done. Author thanks also to UNSYIAH Research Institute (LEMLIT).

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