Experimental study of Pb (II) solution sorption behavior onto Coffee Husk Bioactivated Carbon

Z Fona and U Habibah

Department of Chemical Engineering, State Polytechnic of Lhokseumawe, Jl. B. Aceh-Medan, km.280.5 Buketrata, Lhokseumawe, Aceh, Indonesia

E-mail: zahrafona@yahoo.com

Abstract. Coffee husk which is abundantly produced in the coffee plantations is potential to be a challenging adsorbent. The fate of Pb (II) solution in the sorption mechanism onto the adsorbent has been investigated. This paper aimed to study the efficiency of Pb (II) aqueous solution removal using activated carbon from coffee husk (CAC). The sorption characteristics were using two isotherm models, Langmuir and Freundlich, were also reported. The coffee husk from local plantations in Middle Aceh was carbonized and sieved to 120/140 mesh. The charcoal was activated using hydrochloric acid before contacted with the different initial concentrations of Pb (II) solution. The remaining concentrations of the metal in the specified contact times were determined using Atomic Adsorption Spectrophotometer at 283.3 wavelength. The result showed that the equilibrium concentrations were obtained in about 30 minutes which depended on the initial concentration. The sorption mechanism followed Freundlich isotherm model where the adsorption constant and capacity were accordingly 1.353 and 1.195 mgg^{-1}. The iodine sorption was up to 1,053 mgg^{-1}. Based on the ash and moisture content, as well as iodine sorption, the activated carbon met the national standard.

1. Introduction

The natural water resources quality nowadays is worrying. Therefore, using natural water directly is not recommended anymore due to the lack of quality, high possibility of contaminant from industrial process, including pharmaceutical and cosmetic, agricultural activity, and household wastewater, where go to and contaminate water body. Additionally, natural water resources might contain contaminants come from natural organic matters which also have some negative impact to human health. However, the artificial contaminants such as toxic organic compounds: heavy metals, dyes, pesticides, and pharmaceuticals and even the wastes of water treatment [1]. These, might cause to enhance the toxic compounds on the natural occurring pollutants in the water body [2].

Heavy metals can occur as solution in water, such as lead, and they are non-degradable. Therefore, it is very important to find out the effective, efficient and inexpensive materials to eliminate the compounds. Many research has been conducted to eliminate the heavy metal solution in the water. Among the other methods, adsorption using activated carbon found to be the most effective and low-cost process. Hence, it is widely used in water purification process, and industrial systems as well as home applications [3-4].

Activated carbon, also named activated charcoal is carbon which tremendously high surface area, where the adsorption is taking place. The surface area can be from 500 to 1500 m^2. It can adsorb a wide diversity of organic and inorganic pollutants in aqueous solution [5-7]. However, the adsorption efficiency might depend on the ion type in the solution as well as the origin of carbon itself. Every

biomass carbon source has a specific characteristic in the carbon active form, beside the chemical used for activation or the activated method performed.

The activated carbon can be produced from natural resources such as biomass waste. Huge amount of biomass waste disposed improperly all over the world [8]. Using them as carbon active is one of the competitive way offered. Some organic waste from agricultural process or crop residues such as tea seed shells [9], rice husk [5], coconut shell [6], doom palm shell [10], and many other sources. In current research, coffee husk collecting from community plantation in Middle Aceh converted to be activated carbon (CAC). Biomass activated carbon, nevertheless, become the most promising adsorbent due to it enormously high adsorption capacity, very cheap, easy to be produced and used.

In advanced method of production of activated carbon, nitrogen is used as a treating gas to produce highly porous carbon. However, this process is costly and complicated to perform. In this research, the carbon produced from coffee husk (coffee husk activated carbon/CAC) using a simple method, carbonization and activation using dilute hydrochloric acid solution. The fate of heavy metal pollutant, Pb (II) were investigate, the equilibrium concentrations and isotherm characteristics using Langmuir and Freundlich models.

2.   Materials and method
Coffee husk biomass waste was collected from the coffee plantation in Middle Aceh. Hydrocloric acid and $Pb(NO_3)_2$ from Merck, Germany.

2.1 Preparation of CAC
Coffee husk was washed and dried under sunshine. The carbonization was performed using traditional process in closed vessel for 2 hours. The charcoal was sieved to 40, 60, 80, 100, and 120 mesh and activated using 0,1 N hydrochloric acid for 48 hours. Finally, the activated carbon (CAC) was filtered, neutralized using aquadest, and dried in oven of 105 °Ctemperature for 3 hours.

2.2 Batch experiment of sorption process
Activated carbon was weighed 1 g, put into 5 different Erlenmeyer flasks, each poured with lead solution of 10, 20, 30, 40, and 50 ppm. Therefore, they were stirred using the electric shaker of 200 rpm, and taken after 10, 20, 30, 40, and 50 minutes to analyze the concentration using Atomic Absorption Spectrophotometer at 283.3 mm wavelength.

2.3 Characteristics of CAC determination
Water content of the activated carbon were analyzed using Moisture Analyzer Mx 50 by heating sample to 105°C until reach constant weight, while the ash content determined according to SNI 1995, by heating sample to 650 C for 3 hours. Iodine sorption capacity of the CAC was determined using national standard (SNI 1995) by titration method. Iodine solution of 0.1 N was poured into the flask containing 0.25 g CAC and stirred for 15 minutes, the adsorbed iodine measured as iodine adsorption capacity.

3.   Results and discussion

3.1 Equilibrium concentration
The lead solution concentrations after different contact time adsorption onto CAC through different initial concentrations have been measured. Therefore, the equilibrium concentrations obtained by plotted the concentration each time per initial concentration (C/Co) to time, as shown in Figure 1. The equilibrium stage was one of the specific characteristic depends on natural of the adsorbate and adsorbent used.
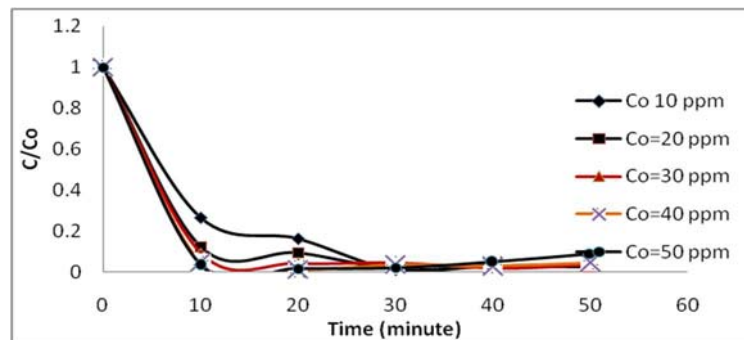
Figure 1. Equilibrium stage of lead solution adsorption under different initial concentration.

The equilibrium obtained approximately in 30 minutes varies along with the initial adsorbate concentrations. Higher concentration yielded shorter time to meet the balance between the ion in the solution and the ion adsorb onto sorbent, and vice versa.

3.2 Removal of lead solution
The removal percentage of lead solution onto CAC depended on contact time and initial lead concentrations. Figure 2 shows the removal percentage in each initial concentration and contact time, where 73.31-98.77% of lead removed.

At high initial concentration, the lead ions existing for the sorption onto the CAC surface are very high. According to El-Ashtoukhy [11], at low concentration the adsoption occurred in specific site, while in higher concentrations the sites are saturated and load the exchange place. Moreover, M. Karnib, et al., 2014 found that the removal percentage of activated carbon decreased by increasing the metal ion concentrations.
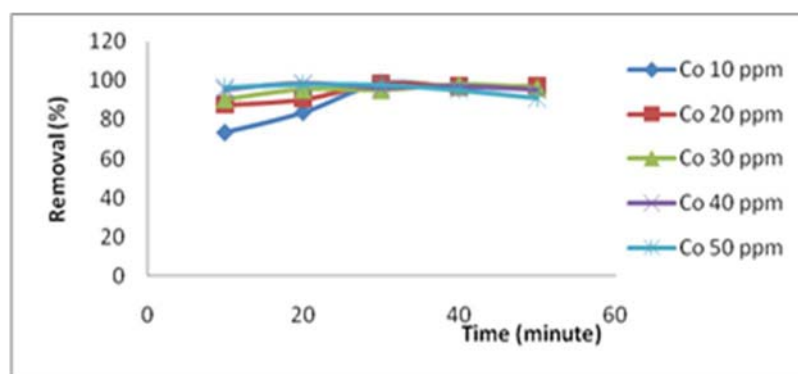

Figure 2. Lead solution removal under different initial concentration.

3.3 Adsorption isotherm
Adsorption isotherm shows the natural characteristics of the sorbent in accordance to solute-sorbent interface interaction. The sorbate concentration and deposit onto sorbent at constant temperature was also indicated in the isotherm. The equilibrium data from the experiments were fitted to the Langmuir and Freundlich isotherm models.

Langmuir isotherm sorption model suppose the adsorption of the sorbate onto the sorbent occurs only in monolayer. It has the uniform energies over the surface. There is no sorbate migration in the surface plane [12-13]. Langmuir model was explained by Equation 1.

$$\frac{Ce}{Qe} = 1 / q_0 b + C_e / q_0 \qquad\qquad\qquad (1)$$

where *Ce* is the equilibrium concentration (mgL^{-1}), *qe* is the amount of adsorbed concentration at equilibrium (mgg^{-1}) and q_0 and bare Langmuir parameters related to maximum adsorption capacity (mgg^{-1}) and bonding energy of adsorption (Lmg^{-1}) respectively. Plot of Ce/Qe to Ce is represented in Figure 3. According to Langmuir model, the linear equation y = 0.143x + 0.583. The maximum adsorption capacity (q_0) and bonding energy adsorption (b) are 6.993 mgg^{-1} and 0.245 Lmg^{-1} respectively (See Table 1). Unfortunately, the linearization parameter R^2 for the isotherm was very low, 0.332. It pointed out that the adsorption of lead solution onto CAC did not fit to the model.
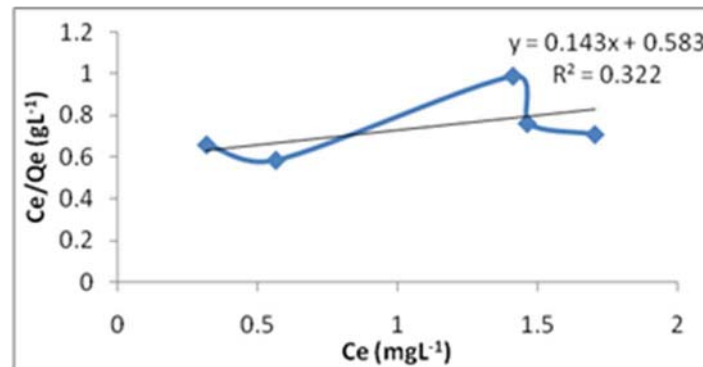

Figure 3. Langmuir isotherm model

The Langmuir model has a dimensionless constant separation factor called equilibrium parameter, R_L. It indicates the characteristics of isotherm: R_L = 1 means linear, R_L>1 unfavorable, R_L = 0 irreversible, and 0< R_L<1 favorable. The parameter is determined [14] by Equation 2.

$$R_L = 1/(1+b.Co) \tag{2}$$

Figure 4 shows the correlation between R_L to initial concentration of adsorbate. The R_L values ranged from 0.050 to 0.300, which specify that the adsorption was favorable. Furthermore, lower R_L value (closer to 0) more favorable the adsorption process would be. Increasing initial adsorbate concentration produced lower RL value. This result was according to Gao, et al [10], beside it was found that the R_L value more favorable at lower temperature. Freundlich isotherm model is suitable to the sorption of relatively low sorbate concentration and heterogeneous surface of adsorbent [12]. The model was expressed as:
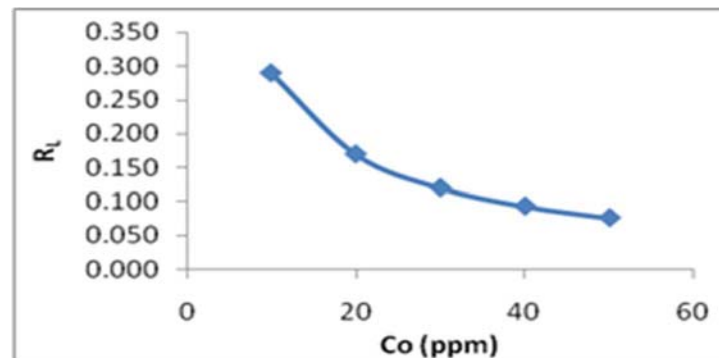
$$Qe = Kf. Ce^{1/n} \tag{3}$$

Figure 4. R_L values under different initial lead solution concentration.

where Qe is the amount of sorbate adsorb per unit adsorbent (mgg^{-1}), Ce is the equilibrium concentration, 1/n and Kf are Freundlich constants related to the favorability of adsorption process and capacity of sorbate respectively. The value of 1/n < 1 means the adsorption is favorable. Figure 5 represented the plot of log Qe to log Ce of Freundlich isotherm model.

The n parameter shows the adsorption intensity, which is the energies of metal ions and adsorbent. Additionally, the Kf value is the constant of multilayer adsorption, which shows the bond strength. The calculated values of each parameter are shown in Table 2.

In Table 2, the constant of 1/n from the adsorption of lead solution onto CAC was 0.837. It indicated that the process was favorable. The n value describes the adsorption intensity of the adsorbent, where 1.195 for CAC. Furthermore, the bond strength (Kf) was 1.353 mgg^{-1}.

The values of correlation coefficient (R^2) were important to find out the best-fitted linear equation. From the result, R^2 of Freundlich model was 0.937, while the Langmuir correlation coefficient was 0.332. According to the values, the adsorption of lead solution onto CAC was the best fitted to Freundlich model, which imply that the process appeared in heterogeneous surface. This result was in accordance to Karnib, et al., [7] where the adsorption of lead solution onto activated carbon was in shape to Freundlich isotherm model.
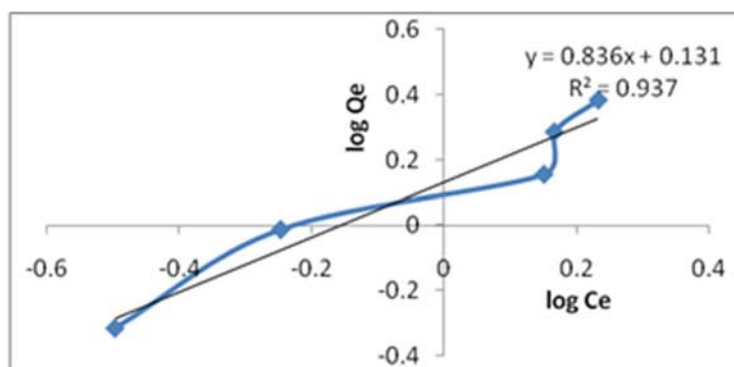

Figure 5. Freundlich isotherm model.

Table 1. Isotherm model parameters and correlation coefficients for adsorption of lead solution onto CAC

Langmuir isotherm model			Freundlich isotherm model			
Q$_0$ (mgg^{-1})	b (Lmg^{-1})	R^2	Kf (mgg^{-1})	1/n	n	R^2
6.993	0.245	0.322	1.353	0.837	1.195	0.939

3.4 Characteristics of CAC

The characteristics including moisture and ash content, as well as iodine adsoption capacity have been investigated. The characteristics obtained were compared to national standard. Tabel 2 reported the current results compared to Indonesian National Standard (SNI).

Table 2. CAC characteristics

Parameter	National Standard SNI 06-3730-1995	Current work
Water content	Max 15%	5.36 %
Ash content	Max 10%	3.00 %
Iodine adsorption capacity	Min750 mgg^{-1}	723.3-1053.3 mgg^{-1}

Moisture in AC affects significantly the adsorptive quality. High water content of AC decreases the ability of adsorbent to adsorb ions, the surface area occupied mostly by the water molecules. Water content in CAC was 5.36%, less than the standard where max 15%. Ash content indicates the metal oxide and other impurities contained in the activated carbon. The residue obtained after heating the sample to 650 ℃ for 3 hours was weighed as ash. The ash content in the CAC activated by 0.1 N HCl was 3%. This value was under the ash content of national standard for activated carbon. In another research, Huda, et al., [15] reported that the ash content of activated carbon originated from coffee waste was 9.2%.

4. Conclusion

The removal of lead ions up to 98.77% at 10 ppm initial concentration for 30 minutes adsorption. Lead ions adsorption onto CAC best fitted to Freundlich isotherm model with the adsorption intensity and relative capacity were accordingly 1.195 and 1.353 mgg^{-1}. Activated carbon from coffee husk was favorable for elimination of lead solution. In accordance to ash, water content and iodine adsorption capacity, CAC produced met the national Indonesian standard.

Acknowledgement

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