Removal of Heavy Metals (Fe and Pb) in The Mahakam River Water Using Eggshells and Rubbing Ash as Adsorbent

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Abstract. Pollution of heavy metals (Fe and Pb) in the Mahakam River water has become an important problem. The solution for this case is water purification using natural product. There are several purification methods, one of them is the adsorption method to reduce the levels of heavy metals (Fe and Pb). The aim of this study was to reduce the concentration of heavy metals (Fe and Pb) using egg shells and rubbing ash as adsorbents. Characterization of the ability to adsorb heavy metals by adsorbents using Atomic Absorption Spectroscopy (AAS). By varying the mass of the adsorbent, the maximum Fe adsorption ability was obtained at a mass of 10 grams, namely 0.11 mg per liter (eggshells) and 0.3 mg per liter (eggshells+rubbing ash). Meanwhile, the maximum Pb adsorption capacity at 10 grams was 0.24 mg per liter (eggshells) and 0.17 mg per liter (eggshells+rubbing ash). Thus the best adsorbent for Fe is eggshell and the best adsorbent for Pb is a mixture of eggshell and rubbing ash. For modelling Fe sorption by eggshells, the Freudlich isotherm fits better than the Langmuir isotherm. Based on the Freudlich isotherm result, the adsorption process is forable and the maximum adsorption capacity is 0.009601 mg/g. This work gives detailed information about an innovative method to utilize eggshell waste and rubbing ash as an inexpensive adsorbent to remove heavy metals (Fe and Pb) from Mahakam River Waters.

Keywords: Adsorbent · Eggshells. Heavy Metals · Rubbing Ash

1 Introduction

Mahakam River is the largest river in East Kalimantan. It makes the Mahakam River a source of water for the people of Samarinda city. However, the Mahakam River's water cannot be categorized as clean water. Industrial and mining waste make the Mahakam River contain heavy metals such as iron and lead. Heavy metals are dangerous and poisonous materials. It is carcinogenic and can damage skin tissue [1]. It cannot be decomposed by organisms in the environment either. Adsorption can be the right solution for water treatment. Adsorption is one of the methods for removing heavy metals from water [2].This method is widely used for the removal of metal because of its simplicity and effective cost [3].

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An adsorption isotherm can be used to describe the adsorption nature, whether it is favorable or unfavorable, and determine the maximum adsorption capacity. There are many kinds of isotherm models, but the most commonly used models are the Langmuir and Freundlich isotherms [4]. In the adsorption process, the adsorbent election is very important to optimize the process. Eggshells and Rubbing Ash can be used as adsorbents. They are natural substances, so it's bio-degradable and non-toxicity. The aim of this research is to reduce the concentration of heavy metal (Fe and Pb) using eggshells and rubbing ash as adsorbents in the Mahakam River water and determine the best adsorption isotherm for modeling Fe and Pb adsorption by adsorbents.

2 Methods

2.1 Adsorbents Preparation

Eggshell, collected from martabak seller, fried rice sellers, and households, was subjected to a washing treatment with water flowing to remove organic residuals. Then soaked with water at a temperature of 80° for 15 min. Next, sun drying for reducing the water content. After that, it was blended to reduce its size to obtain powder form. Furthermore, it was sifted at 140 mesh to obtain a uniform-size grain. Here in after, the powder was heated at a temperature of 110 °C for 1 h. Finally, the powder was ready to be used as an adsorbent. Figure 1 shows the preparation stages of eggshell powder as an adsorbent.

Further, We prepared the second adsorbent namely rubbing ash. The stages of preparation of the adsorbent for rubbing ash began by drying it using an oven at a temperature of 110 °C for 3 h.

Furthermore, it was blended to reduce its size and continued by sieving 100 mesh to obtain a uniform size. The next step is the activation process using a 0.1 M 1500 ml HCl solution for 1 h. After that, filtering was carried out using a buchner vacuum. Then it was heated at 110 °C for 8 h and the resulting powder was ready to be used as an adsorbent. Fig. 2 shows the preparation stages of rubbing ash as an adsorbent

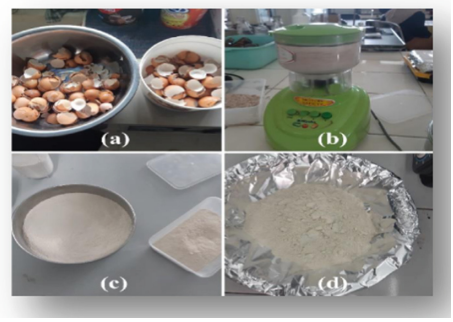

Fig. 1. The Preparation Process of Eggshell Powder as Adsorbent. (a) Eggshell Washing, (b) Reducing the Size of the Eggshell, (c) Sifting of Eggshell Powder, and (d) Eggshell Powder after Heating at 110 °C for 1 h

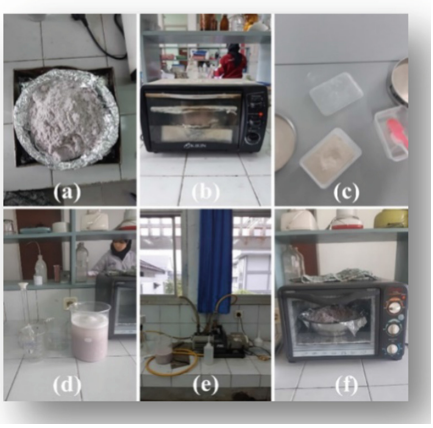

Fig. 2. The preparation process of rubbing ash as adsorbent. (a) Rubbing ash drying, (b) Heating the rubbing ash at 110 °C for 3 h, (c) Sifting of rubbing ash, (d) Activation process of rubbing ash, (e) Filtering of rubbing ash using a Buchner vacuum, and (f) Drying the rubbing ash at 110 °C for 8 h

2.2 Adsorption of Fe and Pb Content

The Mahakam river water sample was tested first to detect the metal content of Fe and Pb before adsorption was carried out. Procedure The adsorption of Fe metal by eggshell powder was started by preparing 20 ml of Mahakam river water and adding 1 g of eggshell powder. Then it was shaken for 10 min. After that it was filtered using filter paper, and the final result can be ready for characterization. The same treatment was carried out on the next 9 samples with a mass variation of 2 g, 3 g to 10 g. The procedure for the adsorption of Pb using rubbing ash as an adsorbent was the same as the treatment using eggshell powder [5].

2.3 Data Analysis Using Isotherm Model

Adsorption isotherm describes the interaction between adsorbate and adsorbent and is also important to optimize adsorbent usage [6]. Isotherms analyzed in this research are Langmuir and Freundlich. The Langmuir isotherm model is an empirical model with the assumption that adsorption can only occur at a certain number of localized sites [7], and the thickness of the adsorbed layer is one molecule or layer adsorption.

The nonlinear expression of the Langmuir isotherm model can be written as equation

$$q_e = Q_m K_L \frac{C_e}{1 + K_L + C_e}$$

where C_e (mg/(L)) is the concentration of the solution at equilibrium; q_e (mg/(g))is the appropriate adsorption capacity; Q_m (mg P/g) and K_L (L/mg) are constants related to adsorption capacity and energy, respectively or net enthalpy of adsorption [8] follows

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}$$

By plotting the data C_e/q_e versus C_e, it can be calculated the constants Q_m and K_L through the intercept and slope obtained [9]. Freundlich's adsorption isotherm model describes a non-ideal and reversible adsorption process. In this case, the Freundlich model is not limited to a monolayer layer, and the heat and adsorption affinity need not be uniformly distributed on the heterogeneous surface. The Freundlich isotherm model can be used to define surface heterogeneity as well as the distribution of active sites and active site energies [10] Isotherm model based on equation.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

By plotting the $\log q_e$ versus C_e, it can be calculated the constants K_F and n through the intercept and slope obtained [9].

3 Results and Discussion

3.1 Characterization

The adsorption ability of the studied eggshell and rubbing ash before and after the adsorption process was analyzed by Atomic Absorption Spectroscopy (AAS). Table 1 shows the results of AAS test on eggshell (ES) and rubbing ash (RA) adsorbents against heavy metals Fe and Pb based on variations in mass or dosage given to Mahakam river water samples.

Adsorbent dosage is one of the most important parameters studied when conducting adsorption study [8]. In this study, Fe and Pb Content removal rates increased as adsorbent

Table 1. Adsorption Test Results in Different Adsorbent Dosage.

Sample		Fe Content	Pb Content
Mahakam River Water		1,5 mg per liter	1,8 per liter
Adsorbent Test Sample Results for ES and RA			
ES (gr)	Fe Content (mg/L)	RA (gr)	Pb Content (mg/L)
1	0,8	1	1,69
2	0,75	2	1,67
3	0,7	3	1,64
4	0,43	4	0,82
5	0,31	5	0,79
6	0,26	6	0,62
7	0,24	7	0,59
8	0,16	8	0,38
9	0,15	9	0,3
10	0,11	10	0,24

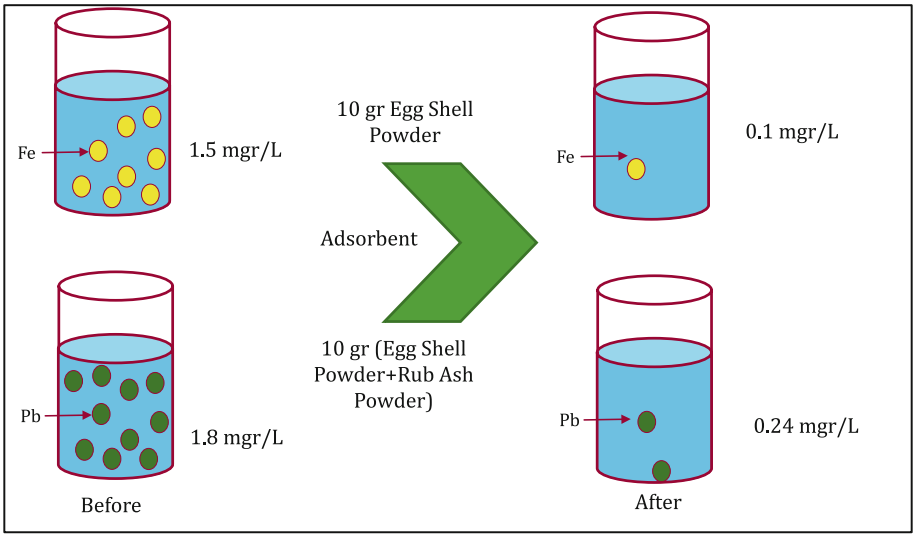

Fig. 3. Ilustration to compare before and after adding adsorbent for Mahakam River Water

dose increased gradually from 1 g to 10 g (Table 1). The removal efficiency was associated with the adsorbent dose due to the availability of more adsorbing sites at higher doses [11] Such a trend is mostly attributed to the increase of the sorptive surface area and the availability of more active adsorption sites.

The Fig. 3 shows illustration to compare before and after adding adsorbent in to the sample for maximum adsorption. The initially Sample contains high concentration adsorbate Fe (1.5 mgr/L), after adding 10 g eggshell powder (ES) adsorbent resulting sample just contains 0.1 mg/L. The initially Sample contains high-concentration adsorbate Pb (1.8 mgr/L), after adding 10 g rubbing ash (RA) adsorbent resulting sample just contains 0.24 mg/L

3.2 Isotherm Modeling

Figure 4 shows Isotherm Model for ES adsorbent to remove Fe content in the Mahakam river water.

Figure 4(a) shows a linear model of the Langmuir Isotherm. By using linear regression, we obtain the linear equation for this model is $y = 71.702x+42.044$, with a coefficient of determinant equal to 0.4743. Meanwhile, Fig. 4(B) shows a linear model of the Freundlich Isotherm. By using linear regression, we obtain the linear equation for this model is $y = 0.6058x-2.0177$, with a coefficient of determinant equal to 0.7931. By using gradient and intercept values from linear equations earlier, we can determine the parameter value for both the Langmuir and Freundlich isotherms. If we compare the coefficient of determinant's value, we find that the Freundlich isotherm model fits better than the Langmuir isotherm model in describing iron metal sorption by eggshells. So, we can use the Freundlich parameter values to determine the nature of adsorption and maximum adsorption capacity. The value of 1/n is between 0 and 1, which means that

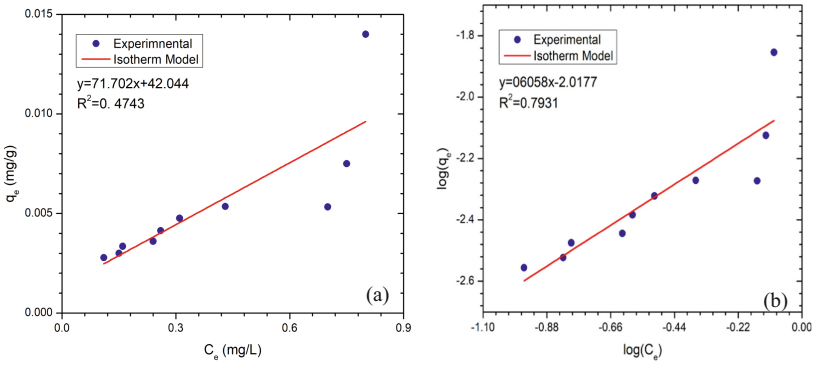

Fig. 4. Isotherm of eggshell (ES) (a) Langmuir model and (b) Freundlich model

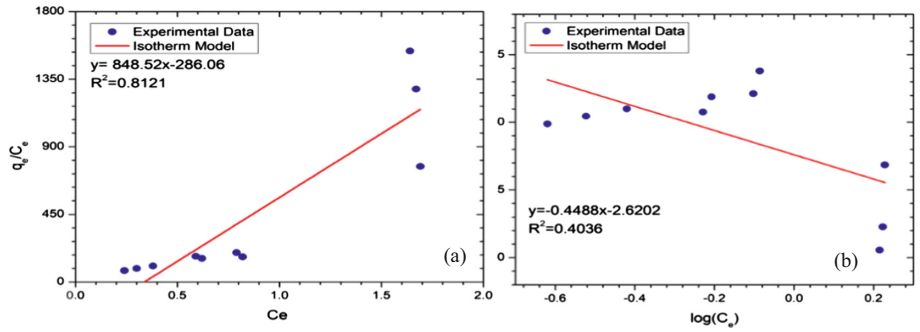

Fig. 5. Isotherm of rubbing ash (RA) (a) Langmuir model and (b)Freundlich

the adsorption is favorable. The maximum capacity is shown by the K_F value, which is 0.009601 mg/g.

Isotherm Model for RA adsorbent to remove Pb content in the Mahakam river water is shown in Fig. 5.

The Langmuir Isotherm for RA adsorbent is shown in Fig. 5(a). By using linear regression, we obtain the linear equation for this model as $y = 848.52-286.06x+42.044$, with a coefficient of a determinant equal to 0.8121. Meanwhile, the Freundlich Isotherm model is shown in Fig. 5(b). By using linear regression, we get the linear equation for this model is $y = -0.4488x-2.6202$, with a coefficient of determinant equal to 0.4036. If we compare the coefficient of determinant's value, we find that the Langmuir isotherm model fits better than the Freundlich isotherm model in describing lead metal sorption by rubbing ash because of the best-fit model according to R^2 value close to 1.

4 Conclusion

It has been successful in reducing the Fe content in Mahakam river water using eggshell and the Pb content in Mahakam river water using rubbing ash. The greater the mass of the eggshell, the greater the decrease in the iron content. For modeling iron sorption by

eggshells, the Freundlich isotherm fits better than the Langmuir isotherm. Meanwhile, The greater the mass of the rubbing ash, the greater the decrease in the lead content. Whereas, for modeling lead sorption by rubbing ash, the Langmuir isotherm fits better than the Freundlich isotherm.

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