Utilization of Rice Husk as Pb Adsorbent in Blood Cockles

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Abstract. Water pollution by lead affects blood cockles, a potential source of food. The aim of this research is to compare rice husk (RH) and rice husk carbon (RHC) in reducing the concentration of lead in blood cockles. RH and RHC were activated with NaOH 1 M, and then the optimal conditions and maximum capacity were determined. This research showed that RH and RHC had maximum adsorbancy capacities of 28.7326 mg/g and 51.5464 mg/g at optimal condition. The optimal adsorption condition for RH in 100 ml Pb solution is 0.32 gram, pH 5, for 4 hours. The optimal adsorption condition for RHC in 100 ml Pb solution is 0.20 gram, pH 5, for 2 hours. Lead content in blood cockles from the north waters of Jakarta (1.9658 mg/kg) is beyond the threshold limit. Lead adsorption by RH and RHC could reduce lead content in blood cockles by about 40% and 31%, respectively.

1. Introduction

The advancement of technology and industries play a role in environmental pollution, especially water pollution. The contaminants in the water may include heavy metals like arsenic (As), lead (Pb), mercury (Hg), and cadmium (Cd). Pb is widely used in metal production, such as in batteries, dyes, and ammunition industries [1], which may greatly contribute to the water pollution. Water pollution by lead affects potential foodstuff that live in water, such as blood cockles. Many studies demonstrate that the level of Pb in blood cockles is higher than the threshold limit allowed by WHO. The level of Pb reaches 1.750 mg/Kg, 2.33 mg/kg, 1.956 mg/kg, 1.37 mg/kg [2-5]. Therefore, efforts are needed to reduce the level of Pb in blood cockles.

Adsorption is a well-known method to remove heavy metals from aqueous solution. This method is simple and relatively cost-effective, thus it is widely used. Rice husk and rice husk carbon are potential adsorbent sources from agricultural waste. Rice husk is a waste (about 20%) from rice production process which availability is quite abundance. In 2013, Statistics Indonesia (BPS) reported that rice production in Indonesia was about 71 million ton. Rice husk capability to adsorb metallic ions is on the active groups of CO–, OH–, Si – H, Si– O– Si, Si–OH [6]. Efficient adsorption of rice husk toward Pb has been reported, among others, by Surchi (2011), in which a decrease of 85% in Pb concentration in the test solution was achieved [7]. Hengpeng, et al. (2010) reported that rice husk’s adsorption capacity of 70.8 mg/g was obtained after soaking in phosphoric acid [6]. Elham, et al. (2010) was also reported that rice husk was able to reduce Pb level in dairy industries wastewater up to 98% [8]. Rice husk has also been reported as an alternative source of raw material for the preparation of activated carbon widely used as adsorbent.

The aim of this research is to compare rice husk and rice husk carbon in reducing lead concentration in blood cockles. The rice husk and rice husk carbon were activated by NaOH 1 M, then their adsorption capacities toward lead solution and lead in blood cockles were determined.
2. EXPERIMENT

Adsorbent preparation:
Rice husk-based adsorbent was prepared with two treatments in order to obtained rice husk powder and rice husk carbon, and then both were activated by using NaOH. The rice husk was prepared with the first treatment: rice husk was washed and dried at 60°C for 24-48 hours. The dried rice husk was grounded to a size of 100 mesh. The rice husk carbon was prepared with the second treatment: rice husk that had already been washed was burned in a special-designed furnace. The rice husk was placed around a cylinder with a hole with fire in it. The rice husk near the cylinder will burned first and then the flame will spread to the farthest rice husk. The rice husk and the rice husk carbon were then activated by soaking in NaOH 1 M with the proportion of the adsorbent to NaOH 3:10. Soaking was continued for 24 hours. Subsequently, the adsorbent was washed with aquadest until NaOH-free adsorbent was obtained, and then dried at 100°C.

Adsorbent Characterization
Activated rice husk and rice husk carbon adsorbents were characterized by determining the moisture content and ash content, and analyzing the SEM and FTIR spectra. Furthermore, the adsorbent properties toward Pb$^{2+}$ ion were tested.

The moisture content and ash content were determined according to gravimetric method [9]. The surface structure of rice husk carbon adsorbent before and after activation was analyzed using SEM. Functional groups observation was conducted by using IR spectrophotometer to find out the functional groups in the rice husk and rice husk carbon with Pb adsorption capacity.

The adsorbent’s adsorption properties toward Pb$^{2+}$ ion were determined by measuring the adsorption capacity of adsorbent using batch method. First, it was determined the optimum conditions for adsorption by measuring the capacity in various pH, adsorbent weight, and contact time. Subsequently, the maximum adsorption capacity and the isotherm pattern of adsorption were determined by measuring the capacity in various adsorbate concentrations under optimum conditions. Pb$^{2+}$ ion level before and after the adsorption were measured by AAS.

Determination of adsorption optimum condition
Rice husk and rice husk carbon 0.20, 0.35, and 0.50 gram were placed into a 100 ml Pb solution 100 ppm that was previously added with HNO$_3$ to obtained solutions with pH of 2.0, 3.5, and 5.0. The solutions were stirred for 2, 3, and 4 hours and then filtered. The adsorption capacity of each solution was determined according to the following formula:

\[ q = \frac{v(C_0-C)}{m} \]

wherein:
- \( q \) = adsorption capacity
- \( v \) = solution volume
- \( C_0 \) = initial adsorbate concentration
- \( C \) = final adsorbate concentration
- \( m \) = adsorbent mass

Optimum condition was determined through optimization by using 3 factors box-Behnken experimental design.
Table 1. Pb adsorption capacity optimization variables

| Variable          | Level (code) |
|-------------------|--------------|
|                   | 1  | 0 | -1 |
| Adsorbent weight  | A  | 0.2 | 0.35 | 0.5 |
| pH                | B  | 2  | 3.5  | 5  |
| Contact time      | C  | 2  | 3    | 4  |

**Determination of Maximum Adsorption Capacity**

Maximum adsorption capacity was determined according to the following: 100 ml of Pb(NO$_3$)$_2$ solution in concentration of 12.75, 35.50, 75.00, 150.00 and 300.00 ppm were each placed into polyethylene bottles. To these solutions, adsorbent (rice husk or rice husk carbon) was added under optimum conditions that had been determined in previous step. Subsequently, the solutions were filtered to separate the adsorbent. Pb level in the solution was analyzed with AAS and the adsorption capacity was calculated. Maximum adsorption capacity, $q_{\text{max}}$, was obtained using adsorption isotherm.

**Determination of adsorbent’s adsorption capacity toward Pb in blood cockles**

Blood cockles sample was obtained from a traditional market, originated from Jakarta Bay. The blood cockles were then cooked (boiled) for 30 minutes and the meat was separated from the shell. To 30 gram of meat, it was added 1.5 gram adsorbent (rice husk or rice husk carbon) and 50 ml water. Adsorption was performed for 30 minutes. Subsequently, the adsorbent was separated. Pb level in the blood cockles was determined before and after cooking, and after the adsorption. Pb in the blood cockles’s meat was determined after destruction in a mixture of 30 ml HNO$_3$ and 5 ml of concentrated H$_2$SO$_4$.

3. RESULTS AND DISCUSSION

**Adsorbent Characterization**

**Fourier Transformation Infra Red Spectra**

FTIR spectra was used to find out the functional groups in the samples. Results of analysis (Figure 1) showed that rice husk contained alcohol groups that are seen in a wide stretch in wave number of 3406 cm$^{-1}$, which is the absorption peak of $-$OH bond, intensified with the absorption peak in 1080 cm$^{-1}$, which is the adsorption peak of $-$C–O bond [10]. Absorption peak in 1648 cm$^{-1}$ showed conjugatable $-$C=O groups. According to Hengpeng, *et al.* (2010), $-$C=O and $-$OH groups are effective in adsorbing Pb heavy metal. There is a decrease in absorption intensity around the wave number of 2940 cm$^{-1}$ in activated rice husk carbon, which is a bonding group of $-$OH and a methyl radical [6]. This decrease may happen as a result of decomposition of cellulose, hemisellulose, and lignin due to heating to 500°C in the process of carbonization [11].
Surface morphology of rice husk carbon

Rice husk and rice husk carbon were activated by soaking in NaOH 1M to remove silica. Silica is a mineral found in a large amount in rice husk, which level reaches 20% [12]. Treatment with NaOH will dissolved the silica covering the surface of the pores. The structure and morphology of rice husk carbon before and after NaOH activation are shown in Fig 2. It can be seen that after activation, the pore is clear. The pores formed in various sizes, the pore size shown in the picture is 12.06 x 10.72 μm.

Moisture content and ash content

The ash content indicates the amount of minerals contained in the sample. The ash content of the husk in this study is 22%. This result is slightly higher than that reported [6, 11, 13]. The difference may be due to the place of origin of the husk and the condition to grow the rice, such as soil condition, irrigation, and fertilizers used.
The ash content in the rice husk pre-treated with NaOH reduced as much as 20%. This reduction is due to SiO₂, which is the most mineral found in rice husk ash, reacts with NaOH to form natrium silicate (Na₂SiO₃) that could be washed away with water [12]. This result is in line with that of Taha, et al. (2011) who reported that there was about 20% reduction of silica weight in the husk.

Moisture content correlates to the adsorptivity of an adsorbent toward adsorbate. The higher the water content in an adsorbent, the smaller the adsorptivity of the adsorbent because of the covering of water molecules on the pores. Moisture content analysis showed that the rice husk contained 8% water.

**Optimum condition for adsorption**

Optimization of adsorption was performed with Pb²⁺ solution using box-Behnken experimental design by using weight of adsorbent (A), pH (B), and contact time (C) as the variables. Based on the analysis of variance, the model and the three variables significantly affect the adsorption capacity. The model is expressed according to the following equation

\[
Q_{\text{activated rice husk}}(\text{mg/g}) = 18.41 - 0.52A + 0.40B + 1.74C - 2.58A^2 + 1.17B^2 + 1.69C^2
\]

\[
Q_{\text{activated rice husk charcoal}}(\text{mg/g}) = 25.04 - 8.44A + 6.04B + 0.20C - 7.23AB + 2.80A^2 - 2.94B^2
\]

Based on the equation, it can be determined the optimum condition for adsorption, the condition resulting in a maximum adsorption capacity value (Q). The optimum condition for rice husk is 0.32 gram, pH 5, and contact time of 4 hours providing an adsorption capacity prediction of 23.4713 mg/g. This value is higher than that reported by Zulkali et al. (2011), which was only 8.6 mg/g. This difference is presumed as the result of increase in the surface area due to silica dissolution in the activation process [14]. Kumar and Bandyopadhyay (2006) reported that rice husk pre-treatment by soaking in NaOH would increase the adsorption capacity from 8 mg/g, initially, to 20 mg/g [15].

The optimum condition for Pb ion adsorption of rice husk carbon is 0.20 gram, pH 5, and contact time of 2 hours. The adsorption capacity under the condition is predicted to be 46.5004 mg/g. Based on the result, Pb adsorption capacity of rice husk carbon is higher than the rice husk.

**Adsorption isotherm**

The most common way to see the effect of adsorbate concentration to the amount adsorbed is through adsorption isotherm, which is a curve correlating the amount adsorbed to the adsorbate concentration in equilibrium at a specific temperature. The process of adsorption is explained by two types of isotherm, Langmuir and Freundlich.

Langmuir isotherm assumes that every site of adsorption is equivalent and the capacity to adsorb particles is not depending on the availability of particles in adjacent places. Langmuir isotherm assumes that adsorption on the adsorbent surface will form a monolayer. Langmuir isotherm is expressed according to the following formula:

\[
\frac{C_e}{q_e} = \frac{1}{Kq_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

Ce is adsorbate concentration in a solution in equilibrium (weight/volume), qe is adsorption capacity expressed in adsorbate weight unit per adsorbent weight, K is Langmuir adsorption constant, qmax is monolayer adsorption capacity.
Freundlich isotherm proposes heterogeneous energetic distribution of active sites, combined with interaction among the adsorbent molecules. The Freundlich isotherm is expressed by the following equation:

\[ \log q_e = \log K + \frac{1}{n} \log C_e \]

Wherein, \( K \) is a constant related to the adsorption capacity.

The result of this research showed that Langmuir isotherm is more suitable with the adsorption isotherm patterns of both rice husk and rice husk carbon for the \( R^2 \) value in the Langmuir isotherm is higher than the Freundlich isotherm, 0.9586 and 0.9450, respectively. The slope represents the value of \( 1/\text{max. capacity} \) and the intercept represents the value of \( 1/K \). \( K \) is the value of sorption energy constant (Table 2).

![Figure 3. Freundlich Isotherm (a) and Langmuir Isotherm (b) of activated rice husk and rice husk carbon](image)

Table 2. Langmuir isotherm for rice husk and rice husk carbon

| Sample | \( Q_{\text{max}} \) | \( K \)  | \( R^2 \) |
|--------|----------------|--------|--------|
| RH     | 28.7356        | 0.0741 | 0.9633 |
| RHC    | 51.5464        | 0.2849 | 0.9991 |

### Adsorption of Pb\(^{2+}\) in Blood Cockles

Blood cockles were obtained from a fish-seller in Bekasi, originated from Cilincing, Jakarta, with size of between 1.5-3.5 cm. Amriani et al. (2011) reported that the size of blood cockles effecting the Pb accumulated in them [2]. The size of the blood cockles relates to the age of the cockles. The longer the blood cockles live in a Pb polluted water, the more Pb accumulated in them.

The result of this research demonstrated that the uncooked meat of the blood cockles (TR) had been polluted with lead. The lead level was 1.9628 mg/kg, while the threshold limit for Pb in shellfish according to the Head of National Agency of Food and Drug Control Regulation No. HK.00.06.1.52.401, is 1.5 mg/kg.

The lead level in the blood cockles’s meat was slightly decrease after cooking (DR), 1.79 mg/kg (Figure 4). However, cooking did not decrease Pb level adequately to be safely consumed [16].
Rice husk and rice husk carbon adsorptions are able to reduce Pb level by 40.15% and 31.50%, respectively, that the final level are under the lower limit of safe consumption. Based on the data, adsorption of Pb in blood cockles by rice husk (DRS) is higher than rice husk carbon (DRA). This may be due to more hydroxyl and carbonyl groups are found in rice husk than in rice husk carbon. Those groups are able to function as ligands and form complexes with Pb. Process of adsorption can also occur in 3 steps: Pb is adsorbed in the surface of the adsorbent, Pb is then moved to the carbon pore, and finally adsorbed in the inner wall of the pore [4].

Figure 4. Effect of various treatments to lead level in blood cockles’s meat

4. Conclusion:

Both rice husk (RH) and rice husk carbon (RHC) have the capability to adsorp lead ions from a solution. Maximum adsorption capacities of RH and RHC are 28.7326 mg/g and 51.5464 mg/g respectively at optimal condition. The optimal adsorption condition for RH in 100 ml Pb solution is 0.32 gram, pH 5, for 4 hours. The optimal adsorption condition for RHC in 100 ml Pb solution is 0.20 gram, pH 5, for 2 hours. Lead content in blood cockles from the north waters of Jakarta (1.9658 mg/kg) is beyond the threshold limit. Lead adsorption by RH and RHC could reduce lead content in blood cockles by about 40% and 31%, respectively.

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