Alkali modified jackfruit wood sawdust as bio adsorbent for removal of Pb(II) ions from wastewaters

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Abstract. This work was conducted to study the adsorption behaviour of bio adsorbent of alkali modified jackfruit wood sawdust and to investigate its possibility as adsorbent to remove heavy metals from wastewaters. The effects of sodium hydroxide concentration on the bio adsorbent adsorption capacity were investigated. The bio adsorbent prepared through chemical modification with solution of 2% sodium hydroxide showed the highest adsorption capacity with the value 3.32 mg/g at initial Pb(II) concentration 18.69 mg/L and percent removal Pb(II) ions was 88.86%. This study proved that adsorption process of Pb(II) ions onto bio adsorbent was perfectly illustrated by second order kinetic equation and adsorption isotherm of bio adsorbent was well represent by Freundlich isotherm model.

1. Introduction

The world is facing major problem related to human health called water scarcity. Almost 1.1 billion people worldwide have problem to access water. Even though water is covering up 70% of the earth, ironically fresh water is very scarce. Only 3% of world’s water is fresh and 2/3 of it is in frozen glaciers form and cannot be used. With the growth of technology and industry, environmental health and hygiene are also increasingly threatened, especially the clean water. Hazardous contaminants in wastewaters include chemicals, heavy metal ions, dyestuffs, pathogenic bacteria, agricultural waste and household waste.

Industrial processes such as mining, painting, smelting, batteries manufacture, and others, release various types of side product streams containing high amount of residual metal ions dispose to wastewaters [1]. Several processes have been applied and developed to remove heavy metals from wastewaters, for example adsorption, chemical precipitation, ion exchange, electrochemical, biological operation, membrane processes [2] and many others. However, some of these methods are not very effective, expensive and require large energy input. Adsorption becomes popular in the last decades because of its advantages, such as low operation cost, simple in design and easy to operate [3]. Usually wastewaters contain low concentration of heavy metals. Adsorption has been proven as a proper method to eliminate heavy metals in wastewaters, since it is able to treat wastewaters containing heavy metals as low to 1 ppm [4].

Many kinds of bio-based adsorbent have been studied as low cost adsorbent to treat wastewaters. The advantages of using bio adsorbents are low cost, biodegradability and no disposal problems [5]. For example, white pine sawdust [6], Beech wood sawdust [7], salviniandans biomass [1], coffee grounds [5], and many more. In the previous work, it was proven that untreated jackfruit wood sawdust has higher adsorption capacity compared to the ones which treated by acetic acid, citric acid and tartaric acid [8]. According to Sciban et al. [9] alkali modification of softwood sawdust resulted higher
adsorption capacities compared to unmodified ones. Sodium carbonate solution can be used to modify, but this alkaline solution is less efficient than sodium hydroxide solution. This experiment also established that the ion exchange is not only adsorption mechanism, but also precipitation of metal-hydroxide in the liquid.

In this work, jackfruit wood sawdust was modified by alkali solution sodium hydroxide to investigate the effect of chemical modification on jackfruit wood sawdust adsorption capacity. Adsorption experiments performed to determine the adsorption capacity of alkali treated jackfruit sawdust, adsorption kinetics and adsorption isotherm.

2. Materials and methods

2.1. Materials
Jackfruit wood sawdust used in this study obtained from local sawmill industries around Yogyakarta, Indonesia. The sawdust was sieved to 80 mesh size and rinsed several times with distilled water. After clean sawdust was obtained, then the sawdust oven dried at 50 °C for 48 h. All chemicals used throughout this study were analytical grade and distilled water used to prepare all solutions.

2.2. Methods
Bio Adsorbent Preparation: clean jackfruit wood sawdust was soaked in sodium hydroxide (NaOH) solution with concentration 1%, 2% and 3%. The ratio between sawdust and alkali solution was 1 gram to 10 ml. The mixture sawdust in alkali solutions constantly mixed for 6 hours at room temperature. Afterwards, the sawdust was separated from solution by filtration using filter paper and washed with distilled water for several times until the pH of washing water was constant. After that, the sawdust put in the oven at 50 °C until it dry.

Adsorption Experiments: batch Adsorption was performed to determine the adsorption capacity of bio adsorbent prepared with various concentration of alkali solution. 0.5 gram bio adsorbent was equilibrated with 100 ml of Pb(II) solution with known concentration. The mixture was stirred at 150 rpm for a day. A 10 ml sample was taken and analysed using Atomic Absorption Spectroscopy (AAS) to determine the final concentration of solution after adsorption process.

The amount of Pb(II) ions adsorbed in every gram of bio adsorbent was calculated by the following equation:

\[ q_e = \frac{(c_o - c_e)V}{W} \]  

(1)

The percentage removal of Pb(II) ions was calculated by the following equation:

\[ R\% = \left( \frac{c_o - c_e}{c_o} \right) \times 100\% \]  

(2)

Where \( q_e \) (mg/g) is the mass of Pb(II) ions adsorbed in every gram of bio adsorbent at equilibrium, \( c_o \) (mg/l) and \( c_e \) (mg/l) are concentration of Pb(II) ions at initial condition and at equilibrium, respectively. \( V \) (liter) is the volume of Pb(II) solution and \( W \) (gram) is the mass of bio adsorbent.

To investigate the kinetics adsorption behaviour of Pb(II) ions onto bio adsorbent, time varied adsorption experiment was conducted. 2.5 gram bio adsorbent soaked and mixed in 500 ml Pb(II) solution with known concentration. Sample taken every certain time and the concentration analysed using AAS. The kinetics of adsorption Pb(II) ions onto bio adsorbent was tested using Lagergren first order and second order equation.

The Lagergren first order equation is in the following form:

\[ \frac{dq_i}{dt} = k_1 (q_e - q_i) \]  

(3)

With the boundary condition \( q_i = 0 \) at \( t = 0 \) and \( q_e = q_i \) at \( t = t \), equation 3 becomes the following:
\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  

Where \( q_t \) (mg/g) is the amount of Pb(II) ion adsorbed in a gram of bio adsorbent at \( t \) time (minute) and \( k_1 \) is the rate constant of Lagergren first order (1/min). Rate constant \( k_1 \) can be obtained by plotting \( \ln(q_e - q_t) \) versus \( t \) [1011].

The second order equation is in the following form:

\[ \frac{dq_t}{dt} = k_2 \left( q_e - q_t \right)^2 \]  

With the boundary condition \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_e \) at \( t = t \), equation 5 becomes the following:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]  

Where \( k_2 \) is the rate constant of second order equation (g/mg/min), can be obtained by plotting the value of \( t/q_t \) versus \( t \) [12, 13, 14].

Adsorption isotherm of bio adsorbent was tested by Langmuir and Freundlich isotherm equation. Langmuir isotherm equation is used to ensure whether the adsorption is caused by chemical forces metal ions to the surface of adsorbent and Freundlich isotherm equation is applied to non-specific adsorption on heterogeneous solid surfaces [15]. The Langmuir isotherm equation [16] and Freundlich isotherm equation [17] are in the following form:

\[ q_e = \frac{q_o K_o c_e}{1 + K_o c_e} \]  

\[ q_e = K_F c_e^{1/n} \]  

Where \( q_o \) and \( K_L \) are Langmuir equilibrium coefficients, \( K_F \) and 1/n are Freundlich equilibrium coefficients.

### 3. Results and discussion

This experiments were conducted to study the adsorption behaviour of jackfruit wood sawdust which chemically modified by alkali to remove Pb(II) ions from aqueous solutions. The effects of alkali concentration on the adsorption capacity of bio adsorbent, the adsorption kinetics and the adsorption isotherm were investigated.

#### 3.1. Effect of alkali concentration on adsorption capacity

This experiment was performed to investigate the effect of alkali concentration on the adsorption capacity of bio adsorbent. Sodium hydroxide was used to modify jackfruit wood sawdust to enhance the adsorption capacity of sawdust and to prevent plant materials release soluble organic compounds during water treatment. The effect of alkali concentration on adsorption profile of bio adsorbent is shown in Figure 1. At low concentration of NaOH, the increase of alkali concentration follows by the increase of adsorption capacity of sawdust. At Pb(II) initial concentration 18.69 mg/L, maximum adsorption capacity has been achieved by bio adsorbent which modified by 2% NaOH solution with adsorption capacity at equilibrium was 3.32 mg/g and percent removal Pb(II) ions was 88.86%. This probably happened because of wood modification with a mild alkaline solution causes the liberation of new adsorption sites on the sawdust surface [9].

In this study, the adsorption capacity decrease at bio adsorbent modified by 3% NaOH solution. It needs further detail study to investigate the optimum NaOH concentration within 1% to 3%, to treat jackfruit wood sawdust into low cost bio adsorbent.
Figure 1. The adsorption capacity of modified jackfruit wood sawdust at various NaOH concentration. Mass of sawdust was 0.5 gram, Pb(II) initial concentration was 18.69 mg/L and volume of solution was 100 ml.

3.2. The adsorption kinetics
The kinetics of adsorption Pb(II) ions onto bio adsorbent was analysed using Lagergren first order and second order equation. The amount of Pb(II) ions adsorbed in every gram of bio adsorbent at equilibrium $q_e$, the rate constants of first order and second order equation $k_1$, $k_2$, and Sum of Squared of Errors (SSE) are shown in Table 1.

Table 1. Lagergren first order and second order rate parameters for Pb(II) ions adsorption on bio adsorbent

| Kinetics equation | $q_e$ (mg/g) | $k$       | SSE     |
|-------------------|--------------|-----------|---------|
| First order       | 0.5890       | 0.0027 min$^{-1}$ | 0.6566  |
| Second order      | 0.5890       | 0.0885 g/mg/min | 0.0680  |

Both first order and second order equation have relative small SSE, but the SSE value for second order is smaller, so the second order equation is more suitable for Pb(II) ions adsorption on bio adsorbent from jackfruit wood sawdust modified by NaOH. Adsorption kinetics equation of Pb(II) ions onto bio adsorbent is in the following form:

$$\frac{dq}{dt} = 0.0885 (0.5890 - q_e)^2$$

The visual comparison of both kinetics models and experiment data is expressed in Figure 2.
Figure 2. The mathematics equation of adsorption kinetic of bio Adsorbent. Mass of sawdust was 2.5 gram, Pb(II) initial concentration was 3.5 mg/L, and volume of solution was 500 ml.

3.3. The adsorption isotherm

This experiment was performed to determine data for adsorption isotherm of bio adsorbent at 30 ºC. The experiment data were tested with Langmuir and Freundlich isotherm model. The Langmuir equilibrium coefficients $q_e$, $K_L$, Freundlich equilibrium coefficients $K_F$, $1/n$, SSE value for both models are shown in Table 2 and Figure 3 shows the adsorption isotherm of Pb(II) ions on bio adsorbent.

Table 2. Langmuir and Freundlich adsorption isotherm parameters of bio adsorbent at 30 ºC

| Isotherm            | $q_e$ (mg/g) | $K_L$    | SSE    |
|---------------------|--------------|----------|--------|
| Langmuir Isotherm   | -26.9542     | -0.0058  | 0.0147 |
| Freundlich Isotherm | 1.0895       | 0.1365   | 0.0053 |

Figure 3. The adsorption isotherm of Pb(II) ions on bio Adsorbent at 30 ºC. Mass of sawdust was 2.5 gram and volume of solution was 500 ml.
The relative small value of SSE and good linearity of the graph mean that the plot is well represent experiment data to both Langmuir and Freundlich isotherm model. Based on Figure 3 and value of SSE can be concluded that the adsorption of Pb(II) ions on bio adsorbent follows the Freundlich isotherm. This model is suitable to non-specific adsorption on heterogeneous solid surfaces [15]. Adsorption isotherm equation of bio adsorbent is in the following form:

\[
q_e = 0.1365c_e^{1.0895}
\] (10)

Table 3 summarizes adsorption capacity of this work to previous works. Based on Table 3, there is a significant progress in adsorption capacity of jackfruit wood sawdust treated by NaOH compared to untreated sawdust and other chemical treatment.

| Jackfruit wood sawdust | Heavy metal | Initial concentration (mg/L) | Adsorption capacity (mg/g) | References |
|------------------------|-------------|-------------------------------|---------------------------|------------|
| Untreated              | Fe(II)      | 24                            | 1.05                      | [8]        |
| Treated by acetic acid (CH₃COOH) | Fe(II) | 24                            | 0.81                      | [8]        |
| Treated by phosphoric acid (H₃PO₄) | Pb(II) | 25                            | 1.40                      | [18]       |
| Treated by sodium hydroxide (NaOH) | Pb(II) | 24                            | 4.43                      | This work |

4. Conclusion

Bio adsorbent from jackfruit wood sawdust modified by alkali NaOH was succeed to remove Pb(II) ions from aqueous solutions. The optimum concentration of NaOH to treat jackfruit wood sawdust was 2%, with the value of adsorption capacity 3.32 mg/g at initial Pb(II) concentration 18.69 mg/L and the removal percentage of Pb(II) ions was 88.86%. The kinetics of adsorption Pb(II) ions onto bio adsorbent was analyzed using Lagernren first order and second order equation. The second order equation resulted lower SSE compared to first order equation, this indicates that kinetics adsorption of Pb(II) ions onto bio adsorbent correlated well with second order kinetic equation. The data for adsorption isotherm of bio adsorbent were tested with Langmuir and Freundlich isotherm. Freundlich isotherm model is well represent the experiment data with smaller SSE value compared to Langmuir isotherm model.

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6. References

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