HVS Wastepaper as Low-Cost Adsorbent for Pb(II) Treatment

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Abstract

One of the methods to solve the problem of lead metal in water is adsorption. One of the adsorbents that can be used is cellulose because it has an active group that can bind Pb(II). In this study, cellulose from the HVS wastepaper was used as the adsorbent to adsorb the Pb metal. HVS wastepaper was extracted with 10% w/v NaHCO₃ and refluxed with 5% w/v Na₂HPO₄. Cellulose was characterized using Fourier Transforms Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). Pb(II) adsorption was carried out by the batch method, and it was evaluated using Atomic Absorption Spectrophotometry (AAS) with varying adsorbent mass, concentration, contact time, and pH. FTIR characterization showed that the presence of O–H, C–H, C=O, and C–O groups played a role in the adsorption process. The surface morphology of cellulose from SEM analysis showed form like a fiber shape with agglomerated fine particles. The optimum conditions for adsorption were 0.100 g of adsorbent mass, Pb(II) concentration of 105 ppm, contact time of 10 minutes, and pH of solution 5. An adsorption isotherm model that is preferable for this adsorption process is the Freundlich isotherm model. From the results of this study, HVS paper waste can be used as an adsorbent to handle Pb(II) metal ions to be an alternative as a low-cost adsorbent.

Keywords: Adsorbent, Adsorption, HVS paper, Optimum, Pb(II).

Introduction

Water is one of the sources of life in nature and is needed by living things besides air and the sun. In monitoring the quality of the aquatic environment, one of many important parameters of pollution is heavy metals. Environmental pollution of water originates from nature (volcanic dust, rock erosion) and human activities such as domestic waste and industrial waste. These activities produce waste that can have a dangerous effect on living things. Polluted water cannot be consumed and used for other needs because of the heavy metal content in water pollution. Heavy metals from industrial waste are usually directly disposed of without controlled processing. The contents of heavy metals in water will cause severe problems because heavy metal exposure can lead to cancer in humans if continuously consumed [1].

There are several types of wastewater treatment processes to resolve these problems, including adsorption [2], precipitation [3], coagulation [4], filtration with membranes [5], and others. Among all the processing, adsorption has advantages compared to other methods. It is because the process is simple, effective, and highly
efficient without the side effects of toxic substances. Adsorption is the process of collecting substances on the surface between two phases [6].

The adsorption process is influenced by several factors, such as stirring, contact time, pH, adsorbate concentration, amount of adsorbent, and others [7-8]. These factors determine the capacity of adsorbents in adsorbing heavy metals. One of the heavy metals that will be analyzed in this research is Pb(II). The Pb is considered a heavy metal because of its chronic and cumulative nature. Pb(II) poisoning can cause anemia, kidney disorders, mental decline in children, intestinal colic, liver disease, nervous system disorders, and disrupt blood circulation [9]. Pb will eventually gather in the teeth and bones.

Recently, many alternative adsorbents have been developed to adsorb heavy metals, especially low-cost adsorbent with an equivalent capacity of activated carbon [10]. One of them is developing bio-adsorbents derived from cellulose [1]. HVS paper has cellulose content that can bind heavy metals. Therefore, it can be used for the adsorption process. Paper pulp complex cellulose material consists of thermo-mechanical pulp that can absorb metal [11]. The use of paper as an adsorbent is also an alternative to wastepaper processing in addition to being used as food packaging that endangers health if the ink on the paper sticks to food, or only a landfill or incineration process is carried out. Besides, the paper is easy to obtain, inexpensive, easy to handle (non-toxicity), environmentally friendly, and can be degraded [12]. HVS paper is suitable as a low-cost adsorbent because of the many uses of paper and wastepaper that are no longer in use.

Based on the explanation above, HVS paper has the potential to be used as a low-cost adsorbent that can absorb metal Pb(II). The adsorbent characteristics were analyzed using a Scanning Electron Microscope (SEM) to determine surface morphology and Fourier Transform Infrared (FTIR) to determine functional groups, especially those that assist the adsorption process. The adsorption capacity of the adsorbent for Pb(II) metal was determined using an Atomic Absorption Spectrophotometry (AAS) instrument. The results of this study are expected to be one alternative in the handling of Pb(II) metal ions in waters by using cheap and obtainable materials. The appropriate adsorption isotherm model (Lamguir isotherm and Freundlich isotherm) was also determined in the adsorption process.

Materials and Methods

Reagents and Instruments

The materials used in this study were HVS paper, demineralized aqua, NaHCO₃ (technical), Na₂HPO₄ (technical), NH₃ (Merck) 25% w/v, HNO₃ (Merck) 65% w/v, Pb(NO₃)₂ (Merck), and Whatman filter paper No. 40.

The instruments used in this study were Scanning Electron Microscope (JEOL, JCM-6000), Fourier Transform Infrared (Shimadzu, IRPrestige21), and Atomic Absorption Spectrophotometry (Agilent Technologies, 240FS).

Adsorbent Preparation

Used a small piece of HVS paper that has been soaked in a 10% w/v NaHCO₃ solution for 2 h. Then refluxed with Na₂HPO₄ 5% w/v for 3 h. After that, filtered with Whatman filter paper while rinsed with demineralized water. Then dried in the oven at 105°C for 5 h [1].
Adsorbent Characterization

An analysis was conducted using Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM) to learn the functional groups and morphological shapes of HVS paper adsorbents.

Optimization of Adsorption by The Batch Method

Optimization was done by using adsorbent mass of 0.060; 0.080; 0.100; 0.120; 0.140 g, initial concentrations of Pb(II) 75; 90; 105; 120; 135 ppm, contact times of 5; 10; 15; 20; 25 min, and solution pH of 2; 3; 4; 5; 6. With these variations, the samples were analyzed using AAS. After that the adsorption capacity and efficiency are calculated using the following equation:

\[
Q_e = \frac{C_i - C_e}{m} \times 100\%
\]

\[
\text{Removal} = \frac{C_i - C_e}{C_i} \times 100\%
\]

\[
\frac{1}{Q_e} = \left( \frac{1}{Q_m \times b} \right) + \frac{1}{C_e}
\]

\[
Q_e = \frac{1}{\frac{1}{Q_m \times b} + \frac{1}{C_e}}
\]

\[
\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log c
\]

\[1 \leq \frac{1}{Q_m \times b} \leq Q_e \leq Q_m\]

Whereas the Freundlich isotherm equation can be written as follows:

\[k \text{ and } n \text{ are Freundlich's provisions, } k: \text{will absorption, } n: \text{adsorption intensity.}\]

Results and Discussion

Adsorbent Preparation

Adsorption capacity (Qe) is the amount of Pb(II) adsorbed by HVS paper waste (mg·g⁻¹), Ci is the initial concentration of Pb(II) (mg·L⁻¹), Ce is the final concentration of Pb(II) (mg·L⁻¹), V is the total volume of the solution (L), and m is the paper mass of HVS [13].

Adsorption Isotherms

Adsorption isotherm is a method to describe the equilibrium state between the concentration of solute adsorbed on the surface of a solid and the amount of absorption at a constant temperature. The isotherm models used in this study are Langmuir adsorption isotherms and Freundlich adsorption isotherms. The Langmuir adsorption isotherm is written as follows.

\[
\frac{1}{Q_e} = \left( \frac{1}{Q_m \times b} \right) + \frac{1}{C_e}
\]

\[
Q_e = \frac{1}{\frac{1}{Q_m \times b} + \frac{1}{C_e}}
\]

\[
\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log c
\]

\[1 \leq \frac{1}{Q_m \times b} \leq Q_e \leq Q_m\]

\[k \text{ and } n \text{ are Freundlich's provisions, } k: \text{will absorption, } n: \text{adsorption intensity.}\]
adsorbents in this study by looking at the functional groups contained therein and then compared with commercial cellulose. From the data shown in Fig. 1(a), there is a peak of 3376.36 cm\(^{-1}\), which shows stretching \(\text{–OH}\) group bonds. At the peak of 2900.93 cm\(^{-1}\), there was a C–H vibration from the alkyl group on cellulose [16-17]. While the peak that occurred around 1639.49 cm\(^{-1}\) indicates water absorption, one of these peaks comes from the stretching of hydrogen bonds and the bending of the hydroxyl group (\(\text{–OH}\)) to the cellulose structure. Hydrogen bonds are formed between hydrogen atoms from one hydroxyl group of a glucose monomer and an oxygen atom from another hydroxyl group from a glucose monomer in a cellulose parallel polymer chain [18]. It obeys the chemical nature of cellulose which is insoluble in water. C–O strain of C–O–H and or C–O–C is characterized by the appearance of the absorption area at wave number 1163.08 cm\(^{-1}\) [19].

This FTIR analysis shows that there were active groups in adsorbents such as \(\text{–OH}\), C=O, and C-O, which were polar. FTIR spectra of cellulose showed O-H strong stretch vibration in the 3,200-3,600 cm\(^{-1}\) [20]. Therefore, they can absorb metal Pb(II) as well because in the -OH group, C=O and C-O were free electrons that could absorb metal Pb(II). Furthermore, the HVS paper adsorbent can absorb metal Pb(II) to the maximum. At the peak of the area, there was no shift in wavenumber uptake between adsorbents before and after adsorption. Therefore, the adsorption that occurs is physical adsorption.

**Morphological Examination Using Scanning Electron Microscope (SEM)**

Figure 1(b) shows the morphological shape of the HVS paper analyzed by an SEM. It consists of fibers with agglomerated fine particles that fill the space between fibers. SEM photo results adhere to the references obtained in Okada Kiyoshi's research pore analysis of activated carbon from newspaper waste (2003) [21-22].

![Figure 1. (a) FTIR spectrum of HVS paper, (b) Results of HVS paper adsorbent SEM](image-url)
Determination of Optimum Adsorbent dose, Concentration, Contact Time, and pH on Capacity and Efficiency of Adsorption

Figure 2(a) shows the decrease in adsorption capacity due to the mass of adsorbent used more and more while the number and concentration of Pb(II) used are the same. So the equilibrium concentration of metal Pb(II) is lower if the mass of the adsorbent is high. These results adhere to the research conducted by Dehghani (2016) about the adsorption of Cr(VI) using newspapers [23]. However, the results of adsorption efficiency show the opposite of the adsorption capacity due to the greater mass of the adsorbent used that will increase the surface area of the adsorbent and the availability of the side to adsorb Pb(II) [4]. The amount and concentration of Pb(II) solutions used are the same. Thus, the amount of Pb(II) solution absorbed will increase as the mass of adsorbent is used. However, the mass of 0.120 g decreased adsorption efficiency. This is because there has been a desorption process, which results in a saturated adsorbent surface. In the saturated state, the adsorption rate is reduced. Therefore, the mass addition of the adsorbent does not affect anything.

![Figure 2. Effect on adsorption capacity and efficiency: (a) The adsorbent mass, (b) Initial concentration, (c) Contact time, (d) pH](image)
Figure 2(b) shows that the greater the concentration of adsorbate used, the greater the adsorbate absorbed. However, at a concentration of 120 ppm, it decreased again. The high analyte concentration caused a decrease in adsorption efficiency. So the number of metal ions in the solution is not proportional to the number of available adsorbent particles. This causes the surface of the adsorbent to become saturated. In addition, because the adsorption capacity of the adsorbent is optimal, it is no longer able to adsorb Pb(II) and causes desorption. This can be seen from the decrease in the value of adsorption efficiency.

Figure 2(c) shows that the adsorption capacity produced is insignificant. This means that the adsorbent has reached its optimum even though contact time has been added. This is because when there has been an equilibrium, there is no change in the adsorbate in the sample or the time when the adsorption rate is equal to the desorption rate.

It is due to the adsorbent being saturated for more than 10 min and reaching the maximum limit value for absorbing metal Pb(II) ions. Therefore, the desorption process occurs, and it is also because the adsorbent functional groups have reached a constant state to interact with metal Pb(II). Even though the contact time is getting longer, it will not increase the capacity and efficiency of adsorption. This adheres to the research by Mardiah (2016) about the adsorption of metal Cu(II) and Fe(II) by using a newspaper [1].

The capacity and efficiency of adsorption increase with increasing pH until it reaches the optimum pH and then decreases. The decrease is due to the desorption process. Even if the pH is increased, it will not increase the capacity and efficiency of the adsorption. The adsorbent surface contains a large number of active sites -OH, which are bound by intramolecular hydrogen bonds. At pH 2, 3, and 4, the adsorption efficiency and the adsorption capacity produced are small because there is the competition between the H⁺ ions from acids with metal Pb(II) ions to bind to the negatively charged adsorbent. At low pH, the surface of the adsorbent is surrounded by H⁺ ions that make the functional groups contained in the adsorbent protonated.

It causes repulsion between the surface of the adsorbent with metal Pb(II) ions and results in low capacity and adsorption efficiency [24].

In acidic conditions, the surface of the adsorbent is also positively charged, which will cause repulsion between the surface of the adsorbent and the metal ion, which leads to low adsorption. At neutral pH, metal ions can undergo hydrolysis reactions in solution. Therefore, it is not stable in the form of the original metal ions and causes the ability of adsorbents to absorb it to decrease. Whereas at alkaline pH, metal ions can form hydroxide deposits. These deposits can inhibit the adsorption process, so the efficiency of adsorption is difficult to determine [25].

**Determination of Adsorption Isotherm Model**

The Langmuir adsorption isotherm is an adsorption process occurring in a one-layer chemisorption process. Chemisorption is adsorption that occurs due to strong chemical bonds between the active site of the surface and the adsorbate molecule. It is influenced by electron density. Because chemical bonds are usually specific in nature, the surface of the adsorbent can bind Pb(II) with chemical bonds between the two so that absorption occurs in one layer.
Figure 3 shows the value of $R^2 = 0.9564$. Therefore, the graph above is suitable for the Langmuir adsorption isotherm graph that forms a single layer. From Fig. 3, we can learn the essential characteristics of the Langmuir adsorption isotherm, which can be formulated with a constant called the equilibrium parameter ($R_L$) as follows.

$$R_L = \frac{1}{1 + (K \times C_0)}$$  \hspace{1cm} (5)

$K$ is the Langmuir constant, and $C_0$ is the optimum initial concentration of the Pb(II) solution. $R_L$ values explain that the adsorption of Pb(II) metal ions on HVS paper adsorbents occurs in several ways. For example, irreversible ($R_L = 0$), spontaneous ($0 < R_L < 1$), linear ($R_L = 1$), or cannot occur spontaneously ($R_L > 1$). The $R_L$ value obtained for the adsorption process of the Pb(II) solution on the HVS paper adsorbent is 0.009. In conclusion, the adsorption process in Pb(II) metal ions with HVS paper adsorbents occurs irreversibly [23].

In the Freundlich isotherm, adsorbents have heterogeneous surfaces. Each molecule has different absorption abilities. The Freundlich isotherm considers that an adsorption process will occur under the given conditions on all sides of the surface of the adsorbent. The Freundlich isotherm is unable to estimate the presence of surfaces on the surface that can prevent adsorption when equilibrium is reached, and only a few active sides are capable of adsorbing dissolved molecules.

Figure 4 shows the value of $R^2 = 0.9999$. This result is greater than the Langmuir adsorption isotherm. Therefore, the mechanism of Pb(II) metal ion adsorption adheres to the Freundlich adsorption isotherm. Interactions that occurred between adsorbates and adsorbents are physical interactions with weak bonds and involve Van Der Waals interactions. It is supported by Gibbs’ free energy value $\leq -40$ kJ/mol, indicating that the adsorption process occurs physically. Besides, the results of FTIR characterization that did not experience a shift and the absence of new groups formed in the adsorbent after the adsorption process showed that the adsorption process occurred between the adsorbent with Pb(II) metal ions was physical adsorption. It means that metal ions are only trapped on the surface or pores of the adsorbent and do not form new bonds [26].
Conclusion

HVS paper is used as an adsorbent by utilizing the cellulose content inside. The existence of functional groups such as -OH, C-H, C=O, and C-O, which possess many free electrons in the oxygen atom, can help the adsorption process by binding to metal Pb(II) ions. The capacity and efficiency of HVS paper adsorbent adsorption are 51.890 mg.g⁻¹ and 92.69%. The isotherm model suitable for this adsorption is the Freundlich adsorption isotherm. From the results of this study, HVS paper waste can be used as an adsorbent to handle Pb(II) metal ions that can be an alternative as a low-cost adsorbent.

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Conflict of Interest

All authors declare that we have no conflicts of interest.

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