

Combination of sawdust from teak wood and rice husk activated carbon as adsorbent of Pb(II) ion and its analysis using solid-phase spectrophotometry (sps)

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Abstract. This research aimed to know the usage of sawdust of teak wood and rice husk waste as Pb (II) ion adsorbents in simulated liquid waste, the combined optimum mass required adsorbent to adsorb Pb(II) ion, the sensitivity of the solid-phase spectrophotometry (sps) method in determining the decrease of Pb (II) metal ion levels in the $\mu\text{g/L}$ level. This research was conducted by experimental method in laboratory. Adsorbents used in this study were charcoal of sawdust sawdust activated using 15% ZnCl_2 solution and activated rice husk using 2 N NaOH solution. The adsorption processes of sawdust and rice husk with Pb(II) solution was done by variation of mass combination with a ratio of 1: 0; 0: 1; 1: 1; 1: 2; and 2: 1. Analysis of Pb(II) ion concentration using SPS and characterization of sawdust and rice husk adsorbent ads using FTIR. The results showed that activated charcoal from sawdust of teak wood and rice husks can be used as Pb (II) metal ion adsorbents with adsorption capacity of 0.86 $\mu\text{g/L}$, charcoal from sawdust of teak wood and rice husk adsorbent with a combination of optimum mass contact of sawdust and rice husk is 2:1 as much as 3 grams can adsorb 42.80 $\mu\text{g/L}$. Solid-phase spectrophotometry is a sensitive method for analysis of concentration decreasing levels of Pb(II) ion, after it was absorbed by sawdust of teak wood and rice husk with high sensitivity and has the limit of detection (LOD) of 0.06 $\mu\text{g/L}$.

1. Introduction

Indonesia is a country that is promoting development in all sectors, one of them in the industrial sector. Development in the industrial sector has mixed impacts. These impacts can be generated by the presence of industrial waste and increasing levels of human activity. Industrial waste is generally contained heavy metals therein and the waste is immediately discharged into the environment without any prior processing. The waste will have a negative impact on the environment. The waste comes from a production process using materials or compounds containing such heavy metals. One of the harmful metal ions present in the waste is the Pb metal ion. Pb metal is widely used as packaging material, plumbing such as pipes, household appliances and decoration. In the form of lead oxide is used as pigment/dye in the cosmetic and glaze industries and ceramic industries, some of which are used in home appliances [1].

To reduce the heavy metal content of waste is usually used conventional methods such as chemical precipitation, ion exchange (ion exchange), and adsorption. A widely used method is adsorption for many reasons, which are more economical and do not cause harmful effects. Adsorption



is defined as the removal of molecules on the outer surface or surface in an adsorbent solid or by the surface of the solution. Adsorption occurs because the molecules on the surface of solids or liquids that have tensile forces in an unbalanced state tend to be attracted inward (the adsorbent cohesion force is greater than the adhesion force). Such tensile gravity imbalances result in solids or liquids used as adsorbents tending to attract other substances that come into contact with their surfaces.

Indonesia's total sawn timber production reaches 2.6 million m³ per year. Assuming that the amount of waste formed 54.24% of the total production, the resulting sawmill waste is 1.4 million m³ per year. This figure is quite large because it reaches about half of the production of sawn timber[2]. Sawdust waste generated from the sawmill industry can still be utilized for various purposes, such as planting medium, raw materials of furniture and raw material of charcoal briquettes. One effort to increase the added value of this sawdust is to make activated charcoal as an adsorbent making material.

Indonesia is an agrarian country whose majority population is a farmer. Farmers usually have problems with waste that is a by-product of agricultural products. This is due to the considerable availability of rice husk waste in all places around the rice mill and the limited utilization of the waste. In Indonesia, especially in Klaten district, rice husks are still not getting attention and are limited to a few simple uses such as ash, as a medium for crops and as fuel. In fact, rice husk ash is a very potential material as a heavy metal absorber in water, so it can be an alternative solution to environmental pollution problems. Rice husk has low nutrient value, abrasive, and contains high carbon [3]. Activated rice husk charcoal can be used as adsorbent to adsorb Cd(II) metal ions in the simulated liquid waste[4].

Lately, many adsorbents have been developed to absorb heavy metals. However, many studies are done using a single sorbent as a process. Preparation of adsorbent by combining two materials is still rare, for that in this research will be done merging between sawdust teak and rice husk as absorber of heavy metal ion Pb (II). The combination of coal fly ash, sawdust and coconut shell can increase the adsorption of chromium and cadmium metal ions [5]. Teak sawdust and zeolite can be used as adsorbents to adsorb Cr(VI) metal ions in the simulated liquid waste with the percentage of adsorption was 62.72% in the amount of 0.5 g [6]. Combination of activated charcoal rice husk and zeolite can be used as adsorbent in adsorption Cr (VI) metal ion with the adsorption capacity 0,28 µg/g analyse by solid-phase spectrophotometry[7]. This study combining sawdust from teak wood and rice husk is expected to increase the adsorption of Pb (II) metal ions.

Determination of concentration of Pb (II) in water is very important even if the concentration is very small, therefore to know Pb (II) contamination must use instrument that has high sensitivity. Other instruments that have been available can only detect up to ppm, whereas maximum levels of Pb in drinking water according to SNI are 0.005 mg/L. Solid-Phase Spectrophotometry (SPS) is a method of determining the level of a substance in which the absorption of light by the target chemical component is concentrated in the solid phase. This method is more sensitive than conventional methods, and can determine levels up to µg/L level[8]. This is evidenced by previous research on the determination of Cr(VI) in natural water by analysis of SPS obtained the limit of detection (LOD) of 0.014 g/dm³ [9]. Thus, researchers interested in conducting research of the application of activated carbon from sawdust and rice husk waste as adsorbent of Pb(II) with an analysis using SPS.

2. Experimental

2.1. Tools and materials

The used tools were a UV-visible spectrophotometer from K-MAC, FTIR spectrophotometer from Shimadzu, muffle furnace, oven, pan, analytical balance, volumetric flask, volume pipette, beaker glass, measuring cup, flask, erlenmeyer, watch glass, stirrer glass, drop pipette, aliquoting devices which are assembled using a syringe, blender, mortar and pestle, a 100 mesh sieve, porcelain bowls, stirrer bar, and a magnetic stirrer. Materials used are sawdust from teak wood, rice husk, Pb(NO₃)₂, ZnCl₂ 10%, NaOH 2N, H₂SO₄ 0,5 M, resin AG Muromac 50W-X2H⁺ form(100-200 mesh), distilled water, chloroform, Whatman filter paper, blue litmus, and dithizone.

2.2. Research procedure

2.2.1. *Production of adsorbent.* Sawdust from teak wood and rice husk is cleaned and washed with distilled water, then it is dried at 105°C then charred in a muffle furnace at a temperature of 300°C for 1 hours for sawdust and 250°C for 1 hours for rice husk. Results obtained are mashed and then sieved with a 100 mesh size.

2.2.2. *Adsorbent activation.* Charcoal sawdust soaked in a solution of ZnCl₂ 10% and rice husk charcoal soaked in a solution of NaOH 2 N for 24 hours at room temperature. Filter and rinse the residue with distilled water until the filtrate become neutral, and then dried in an oven at 105°C for 24 hours. Adsorbent was tested by FTIR before and after activation.

2.2.3. *Resin preparation.* Muromac resin AG Muromac 50W-X2 H⁺ form(100-200 mesh) dissolved in distilled water and silence a few moments until the resin becomes more fluffy.

2.2.4. *Determination of Pb(II) calibration curve.* A 20-mL of standard solution of Pb(II) 0 µg/L, 2 µg/L, 4 µg/L, and 8µg/L respectively were added with 1 mL of H₂SO₄ 0,5 M, 2 mL of 0.005% dithizone, and 0.06 mL resin. Stir it for 20 minutes and analyzed using UV-vis spectrophotometer at a wavelength of 483 nm and 558 nm and then absorbance difference of the two wavelengths determined, $\Delta A = A_{483nm} - A_{558nm}$, which ΔA will be made standard curve (ΔA vs concentration).

2.2.5. *Determination of Pb(II) species in simulated liquid waste.* Simulated liquid waste solution of 50 µg/L was taken 20 mL then added 1 mL of H₂SO₄ 0,5 M, 2 mL of 0.005% dithizone, and 0.06 mL resin. Then, stir it for 20 minutes and analyzed using UV-Vis spectrophotometer at a wavelength of 483 nm and 558 nm. ΔA obtained will be substituted in equation Pb(II) calibration curve (ΔA vs concentration), so that the Pb(II) ions in the effluent can be known.

2.2.6. *Determination the optimum combination of adsorbent for sawdust and rice husk.* Inserting a 20-mL of simulated liquid waste solution 50µg/L in the 5erlenmeyer. Insert each adsorbent sawdust and rice husk with a ratio of 1:0; 1:1; 1:2; 2:1 dan 0:1 and stir it for 30 minutes. Each adsorbent was filtered with Whatman filter paper. The resulted filtrate was taken as much as 5 mL and then diluted with distilled water until 50 mL in volume. Furthermore, the filtrate diluted taken as much as 20 mL added with 1 mL of H₂SO₄ 0,5 M, 2 mL of 0.005% dithizone, and 0.06 mL resin then stir it for 20 minutes and analysed using a UV-vis spectrophotometer with a wavelength of 483 nm and 558 nm. ΔA obtained will be substituted in equation of Pb(II) calibration curve (ΔA vs concentration) so species of Pb(II) in a simulated liquid waste after the Pb(II) adsorption is known.

2.2.7. *Determination of detection nlimit.* Taking five blank solution 20 ml, then each added 1 mL of H₂SO₄ 0,5 M, 2 mL of 0.005% dithizone, and as much as 0.06 ml resin, then stir it for 20 minutes. Furthermore, it analyzed by UV-vis spectrophotometer at a wavelength of 483 nm and 558 nm. ΔA obtained will be substituted in the equation of the calibration curve.

3. Result and Discussion

3.1. Production of activated charcoal from sawdust and rice husk

Production of activated charcoal from sawdust consists of three stages: the stage of preparation, is the removal of impurities in sawdust, stage of carbonization, breakdown of organic matter into carbon by heating it at 300°C for 1 hours for sawdust and 250°C for 1 hours for rice husk, and the activation stage, soaking with an activator solution which is ZnCl₂ 15% for sawdust and NaOH 2 N for rice husk for 24 hours. ZnCl₂ 15% is used because ZnCl₂ was able to produce the highest yield with activated

carbon compared with KOH and H₃PO₄ [10]. The use of NaOH activator on rice husk can dissolve more and result in a silica surface area became greater than using aquades and HCl Activator.

3.2. Fourier transform infrared spectra analysis

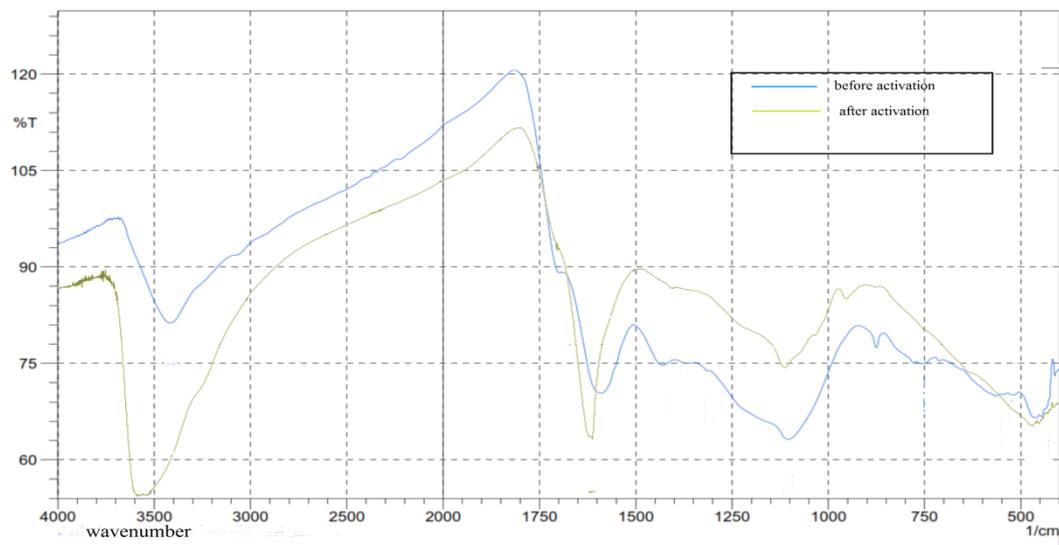


Figure 1. FTIR spectra of sawdust charcoal before and after activation

Based on Figure 1. adsorbent sawdust from teak wood before activation and after activation using the activator ZnCl₂ not many changes are happening. From the spectra can be inferred that the sawdust charcoal adsorbent before and after activated contains cluster -CH, C-O, -CH₃, C = C C = O, aromatic, and - OH.



Figure 2. FTIR spectra of rice husk charcoal before and after activation

Based on Figure 2. adsorbent rice husk before and after activation using the activator NaOH not many changes are happening. Based on spectra can be inferred that the rice husk charcoal adsorbent before and after activated cluster containing C=C aromatics, -OH and, Si-O of the Si-O-Si.

3.3. Determination of Pb(II) calibration curve

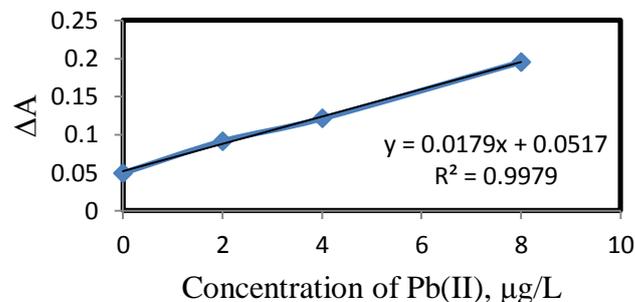


Figure 3. Calibration curve of Pb(II) solution

Based on the graph in Figure 3, $y = 0,017x + 0.051$ where y is ΔA and x is the concentration. The equation is used to determine the concentration of Pb(II) in simulated liquid waste.

3.4. Determination results of Pb(II) levels in simulated liquid waste

Table 1. Determination results of Pb(II) levels in simulated liquid waste

Sample	[Pb(II)] calculation (ppb)	ΔA	[Pb(II)] actually (ppb)
Sample Pb(II)	50	0.135	49.18

3.5. Determination the optimum combination of adsorbent for sawdust and rice husk in a decrease levels of Pb(II)

Table 2. The influence of the composition of the mass to Ion adsorption of Pb (II)

Composition of the mass	Final [Pb(II)] ($\mu\text{g/L}$)	Adsorbed [Pb(II)] ($\mu\text{g/L}$)	Adsorbed [Pb(II)] (%)
1 SG : 0 SP (A)	9.17	40.02	81.36
0 SG : 1 SP (B)	9.63	39.55	80.41
1 SG : 1 SP (C)	8.66	40.52	82.39
1 SG : 2 SP (D)	7.87	41.31	83.99
2 SG : 1 SP (E)	6.39	42.80	87.01

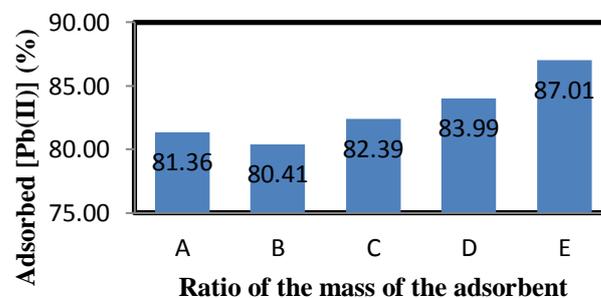


Figure 4. Determination the optimum combination mass of adsorbent

Based on data research in Table 2 and the graph in Figure 4, the optimum combination mass of adsorbent to adsorb Pb(II) metal ions in the simulated liquid waste was 2:1 with adsorbed concentration was 42.80 $\mu\text{g/L}$, percentage of adsorbed as 87.01% and adsorption capacity was 0.86 $\mu\text{g/g}$.

3.6. Determination of detecting limit

In this research, limit of detection (LOD) was 0.06 $\mu\text{g/L}$, so it can be said that the sample at a concentration of 0.06 $\mu\text{g/L}$ can be read, so that the solid-phase spectrophotometry (SPS) is a sensitive and effective method to use in analysis the decreased levels of Pb(II) adsorption results of activated charcoal from rice husk in levels $\mu\text{g/L}$.

4. Conclusion

Activated charcoal from sawdust of teak wood and rice husks can be used as Pb (II) metal ion adsorbents with adsorption capacity of 0.86 $\mu\text{g/L}$. Charcoal from sawdust of teak wood and rice husk adsorbent with a combination of optimum mass contact of sawdust and rice husk is 2:1 as much as 3 grams can adsorb 42.80 $\mu\text{g/L}$. *Solid-Phase Spectrophotometry* (SPS) method is a sensitive analysis method for analysis of concentration decreasing levels of Pb(II) ion, after it was absorbed by sawdust of teak wood and rice husk with highly sensitivity and has the *Limit of Detection* (LOD) of 0.06 $\mu\text{g/L}$.

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