Utilization of rice husk waste for Cd(II) adsorbent and its analysis using solid-phase spectrophotometry (sps)

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Abstract. This research aims to know the use of rice husk waste for metal ion adsorbent of Cd(II), the optimum mass which are needed, the sensitivity of SPS as a method to determine the reduction level of Cd(II) metal ions in the level of μg/L. This research was conducted by using an experimental method in the laboratory. The used adsorbent in this research is rice husk charcoal which activated using $ZnCl_2$ 10% solution. Determination of the optimum adsorbent mass was done with reacted 0.5; 1.0; 1.5; 2.0; and 2.5 g of adsorbent and 20 mL Cd(II) which have concentration 75.27 μg/L during 30 minutes. Analysis the levels of Cd(II) used SPS method and characterization of adsorbent used FTIR. The result showed that activated rice husk charcoal can be used as adsorbent for Cd(II) metal ions in the simulated liquid waste with the adsorption capacity of 0.58 μg/g, the optimum mass was 2.0 gram with percentage of the adsorbed Cd(II) of 77.87%, SPS is a sensitive method to determine the reduction levels of Cd(II) metal ions in the level of μg/L with the limit of detection (LOD) was 0.06 μg/L.

1. Introduction

Nowadays, the industry development in Indonesia is relatively rapid. It can be seen from many industries which producing various kinds of human needs such as paper industry, textile, skin tanner, etc. Along with those developments, many unneeded results will be produced which is the waste. One of the wastes is heavy metal which cause serious pollution to the environment if it exceeds the limit and has a very dangerous toxic substance and will cause serious disease to humans when it accumulates in the body [1]. One of the indicators which commonly use to detect water pollution is the contamination of heavy metals in it. It called as harmful heavy metals because it generally has a high mass density (5 g/cm^3) and a small concentration can be toxic and dangerous, and one of them is cadmium(II) [2].

Cadmium (Cd) is a heavy metal which is found as an environmental contaminant, both through natural occurrence and from industrial and agricultural sources. Foodstuff are the main source of cadmium exposure for the non-smoking general population. A number of studies have reviewed cadmium content in a range of different foods. In a collaborative effort under the SCOOP involving 13 EU Member States, cadmium concentrations in many foods ranged from non-detected to a high mean of 1.20 mg/kg for cephalopods. For rice, Japan was reported in having higher values than the general average, 0.061 compared to 0.017 mg/kg, respectively. The average concentration of cadmium in wheat was 0.054 mg/kg, vegetables ranged from 0.012 to 0.040 mg/kg, and in mollusk results varied from 0.20 mg/kg for cephalopods to 1.38 mg/kg for oysters [3].

Cadmium was monitored in 119 retail food categories within the framework of a national total diet study of the United Kingdom general population. Cadmium was presented at low concentrations in eleven of the food groups, and was below the levels of detection in meat, poultry, oils and fats, eggs, fresh fruits, beverages, milk and dairy products. Cadmium concentrations were highest in the offal (0.084 mg/kg) and nuts (0.065 mg/kg) groups. Food that was consumed in larger quantities made the greatest contribution to the dietary exposure; high contributors were potatoes (24%), miscellaneous cereals (21%) and bread (19%) [3].

Cadmium (Cd) is a heavy metal that is very dangerous. The use of Cd and their compounds are found in the battery industry, as a dye, photography, used in the manufacture of tetraethyl-lead, as a stabilizer and others. Additionally, it is widely used in light industries such as the processing of bread, fish processing, beverage processing, textile industry, and others. Thresholds Cd in drinking water both natural mineral water and bottled drinking water is 0.003 mg/L [4].

The determination of the concentration of cadmium in the water is very important even in very small concentrations, because if the cadmium-contaminated water consumed by humans, there will be cadmium ingestion in the body tissues. The impact of chronic cadmium poisoning is generally in the form of damage to the many physiological systems of the body. Body systems which are undermined by this Cd metal poisoning are the urinary system (kidney), respiratory system (respiratory/lung), circulatory system (blood) and heart. Beside that, the chronic poisoning also damage the reproduction glands, the olfactory system, and can lead to brittleness of the bones [5]. Thus, to determine the contamination of Cd (II) in the water at very small concentrations, it is necessary to use instrument with high sensitivity, namely solid-phase spectrophotometry (SPS).

SPS is one of the methods of analysis which is using UV-visible spectrophotometer and is based on spectrophotometric measurements directly from the solid phase that has absorbed the sample components. The advantages of this method of analysis compared to other methods is the simple operation, high sensitivity and accuracy, which reached the level μg/L, so it can detect the metal ions dissolved in very small concentrations [6]. 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/dm^3 [7].

Several chemical and biological methods have been tried to remove heavy metals contained in sewage and surface waters, including adsorption, ion exchange, and separation with membranes. The adsorption process is more widely used in the industry because it has several advantages: more economical, it does not cause toxic side effects, and capable of removing material impurities.

The majority of Indonesia's population are farmers where most residents create rice as a staple food; so that the source of this staple is everywhere and particularly in the rural areas. Indonesia has an estimated number of 60,000 rice milling scattered throughout the area that produce waste such as rice husks 15 million tons per year. In large quantities, some rice milling machines can produce 10-20 tons of waste rice husks per day [8]. Various studies have reported that rice husk generally contain silica which is quite high ranging from 87-97%. Therefore, rice husk can be used as a source of silica in the silica-based material manufacture or adsorbent [9]. However, the use of rice husk is still very little, so that the hull remains as waste material that disturbs the environment. Thus, researchers interested in conducting research of the application of activated carbon from rice husk waste as adsorbent of Cd(II) with an analysis using SPS.

2. Method
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 rice husk, $Cd(NO_3)_2$, $ZnCl_2$ 10%, resin AG Muromac 50W-X2, H^+ form (100-200 mesh), distilled water, chloroform, Whatman filter paper, blue litmus, and dithizone.

2.2. Research procedure
2.2.1. Production of adsorbent
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 350°C for 1.5 hours. Results obtained are mashed and then sieved with a 100 mesh size.

2.2.2. Adsorbent activation
Charcoal soaks in a solution of $ZnCl_2$ 10% 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 Cd(II) calibration curve
A 20-mL of standard solution of Cd(II) 0 μg/L, 40 μg/L, 80 μg/L, and 160 μg/L respectively were added with 1 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 485 nm and 615 nm and then absorbance difference of the two wavelengths determined, $\Delta A = A_{485nm} - A_{615nm}$, which ΔA will be made standard curve (ΔA vs concentration).

2.2.5. Determination of Cd(II) species in simulated liquid waste
Simulated liquid waste solution of 75 μg/L was taken 20 mL then added 1 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 485 nm and 615 nm. ΔA obtained will be substituted in equation Cd(II) calibration curve (ΔA vs concentration), so that the Cd(II) ions in the effluent can be known.

2.2.6. Determination of optimum adsorbent mass
Inserting a 20-mL of simulated liquid waste solution 75 μg/L in the 5 erlenmeyer. Insert each adsorbent with a variation of mass of 0.5; 1.0; 1.5; 2.0; 2.5 gram 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 0.005% dithizone, and 0.06 mL resin then stir it for 20 minutes and analyzed using a UV-vis spectrophotometer with a wavelength of 485 nm and 615 nm. ΔA obtained will be substituted in equation of Cd(II) calibration curve (ΔA vs concentration) so species of Cd(II) in a simulated liquid waste after the Cd(II) adsorption is known.

2.2.7. Determination of detection limit
Taking five blank solution 20 ml, then each added 1 mL of 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 485 nm and 615 nm. ΔA obtained will be substituted in the equation of the calibration curve.

3. Result and discussions
3.1. Production of activated charcoal from rice husk
Production of activated charcoal from rice husk consists of three stages: the stage of preparation, is the removal of impurities in rice husk, stage of carbonization, breakdown of organic matter into carbon by heating it at 350°C for 1.5 hours, and the activation stage, soaking with an activator solution which is $ZnCl_2$ 10% for 24 hours. $ZnCl_2$ 10% is used because it is a good activator for lignocellulose material

like rice husk because lignocellulose material has high content of O_2 that can reacted with acid activating agent [10].

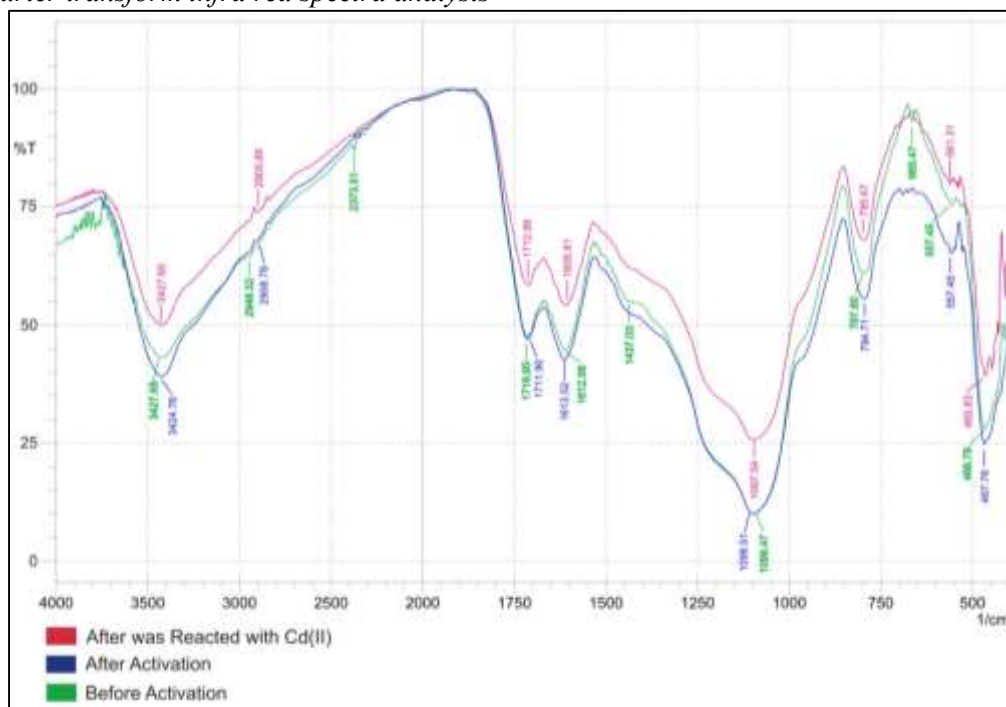*3.2. Fourier transform infra red spectra analysis*

Figure 1. FTIR spectra of rice husk charcoal before activation, after Activation, and after reacted with Cd(II).

Based on figure 1, adsorbent before activation shows the presence of the –OH group from Si-OH (cyanol), Si-O from Si-OH, Si-O from Si-O-Si, -CH, -CH$_3$, C=C aromatic and C=O. In the adsorbent after activation and after contacting not shows any significant difference with the adsorbent before activation, it's just a slight shift in the wavenumber. The shift in the wavenumber of the groups indicates that such groups play a role in the process of adsorption of Cd(II) adsorbent activated charcoal rice husk. Based on changes in the infrared spectra can be seen that all the peaks there will be shorter or in other words the specific surface area decreases. This occurs because the adsorbent has interaction with metal ions which are absorbed so that the pores on the surface of the adsorbent decreases which is covered by Cd(II) adsorbed. It can be seen that there is no a new peak. This indicates that there is no a new group formed in the process of binding metal ions Cd(II) because the binding only disturb the vibration force that binds those ions Cd(II).

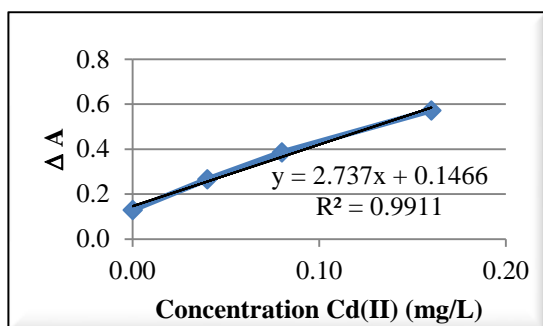### 3.3. Determination of Cd(II) calibration curve
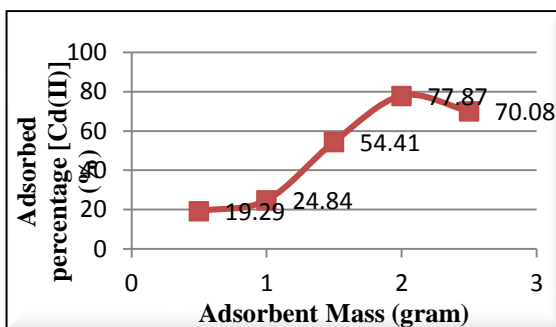

Figure 2. Calibration curve of Cd(II) solution.

Figure 3. Determination of optimum adsorbent mass

Based on the graph in figure 2, y = 2.737x + 0.146 where y is ΔA and x is the concentration. The equation is used to determine the concentration of Cd(II) in simulated liquid waste.

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

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

Sample	[Cd(II)] Calculation (µg/L)	ΔA	[Cd(II)] Actually (µg/L)
Sample Cd(II)	75	0.351	74.947
		0.353	75.595
Average			75.271

3.5. Determination of optimum mass adsorbent in a decrease levels of Cd(II)

Table 2. Determination of the optimum mass of adsorbent

Mass (gram)	Initial [Cd(II)] (µg/L)	ΔA	Final [Cd(II)] (µg/L)	Adsorbed [Cd(II)] (µg/L)	Adsorbed [Cd(II)] (%)
0.5	75.271	0.163	60.604	14.487	19.293
1.0	75.271	0.162	56.442	18.649	24.836
1.5	75.271	0.156	34.236	40.855	54.407
2.0	75.271	0.151	16.620	58.471	77.867
2.5	75.271	0.153	22.465	52.626	70.083

Based on data research in table 2 and the graph in figure 3, the optimum mass of adsorbent to adsorb Cd(II) metal ions in the simulated liquid waste was 2.0 gram with adsorbed concentration was 58.47 µ/L, percentage of adsorbed as 77.87% and adsorption capacity was 0.58 µg/g.

3.6. Determination of detecting limit

In this research, limit of detection (LOD) was 0.06 µg/L, so it can be said that the sample at a concentration of 0.06 µg/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 Cd(II) adsorption results of activated charcoal from rice husk in levels µg/L.

4. Conclusion

The result showed that activated rice husk charcoal can be used as adsorbent to adsorb Cd(II) metal ions in the simulated liquid waste with the adsorption capacity was 0.58 µg/g, the optimum mass of adsorbent to adsorb Cd(II) metal ions in the simulated liquid waste was 2.0 gram with percentage of adsorbed as 77.87%, solid-phase spectrophotometry (SPS) is a sensitive method to determine the reduction levels of

Cd(II) metal ions as an adsorption result of the activated rice husk charcoal in the level of μg/L with the limit of detection (LOD) was 0.059 μg/L.

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