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Combination of rice husk and coconut shell activated adsorbent to adsorb Pb(II) ionic metal and it's analysis using solid-phase spectrophotometry (sps)

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Abstract. The purpose of this research was to know the effect and determine the mass comparation which most effective combination between rice husk and coconut shell activated adsorbent to adsorb Pb (II) ion using SPS method. This research used experimental method. Technique to collecting this datas of this research is carried out by several stages, which are: (1) carbonization of rice husk and coconut shell adsorbent using *muffle furnace* at a temperature of 350˚C for an hour; (2) activation of the rice husk and coconut shell adsorbent using NaOH 1N and $ZnCl_2$ 15% activator; (3) contacting the adsorbent of rice husk and coconut shell activated adsorbent with liquid waste simulation of Pb(II) using variation comparison of rice husk and coconut shell, 1:0; 0:1; 1:1; 2:1; 1:2; (4) analysis of Pb(II) using *Solid-Phase Spectrophotometry* (SPS); (5) characterization of combination rice husk and coconut shell activated adsorbent using FTIR. The result of this research show that the combined effect of combination rice husk and coconut shell activated adsorbent can increase the ability of the adsorbent to absorb Pb(II) ion then the optimum adsorbent mass ratio required for absorbing 20 mL of Pb(II) ion with a concentration of 49.99 µg/L is a ratio of 2:1 with the absorption level of 97,06%Solid-Phase Spectrophotometry (SPS) is an effective method in the level of µg/L, be marked with the Limit of Detection (LOD) of 0.03 µg/L.

1. Introduction

The disposal of industrial waste effluent into riverine system has given rise to heavily localized pollution and threatens seriously to the environment. The pollution level of the river is increasing sharply and can cause serious problem in near future. For the polluted situation of the river maternal and child health of nearby riverbank slam are in a danger position [1]. The pollution of water is caused of any heavy metals. Most of these metals such as cadmium, lead, arsenic, mercury, copper, chromium, cobalt and nickel are very toxic. They are carcinogenic and at very high concentrations, may lead to brain damage [2]. Industrial potential as a source of pollution of lead (Pb) are all industries that use lead (Pb) as a raw material as well as material support, such as casting industry, the manufacture of batteries, cable, chemical industry and in the manufacture of paint. Whereas the toxicity Pb dangerous for the environment or human being [3]. Environment containing Pb with high concentrations, can affect human health disorders, as well as an increase in the levels of Pb in blood which resulted in disruption of the central nervous system, and can reduce intelligence (IQ) for children.

The impact of the pollution of Pb in the aquatic environment can be dealt with adsorben. Adsorbent of the Pb can be made from agricultural waste in Indonesia, such as rice husk and coconut shell. Rice husk can be used as adsorbent because cellulose and hemicellulose has a considerable potential for absorbing that has tied OH cluster so that it can interact with the component adsorbat. One of the heavy metals that can be absorbed by the rice husk adsorbent is lead (Pb)[5]. On the other hand coconut shell that has been activated shows high ability to adsorb Pb, the active carbon of coconut shell efficient to absorb the metal ion Pb2 + on liquid waste [6]. Adsorbent from coconut shell is cheap and easily adsorbent and obtainable where using them efficiently to absorb metals from water that has been contaminated [7]. The analysis that used to find out the capabilities of active adsorbent from coconut shell is SPS (Solid Phase Spectrophotometry). This method is more sensitive compared to conventional methods that use expensive instrumental, moreover, it can determine the levels up to the level of μ g/L[8]. SPS showed that teak sawdust and zeolite can be used as adsorbents to adsorb Cr(VI) metal ions with the adsorption capacity 1.19 μg/g analyse by solid-phase spectrophotometry (SPS) [9]. And then by using SPS activated rice husk charcoal can adsorbed Cd(II) metal with percentage of adsorbed amount 77.87%[10]. Solid Phase Spectrophotometry are extremely sensitive and highly accurate because it can detect up to the size of the ppb. Higher sensitivity can be obtained by using 20 cm^3 volume of the sample [11]. Solid Phase Spectrophotometry is a method of analysis using the spektofotometer UV rays-looks. This method is based on measuring the sample directly through the absorption phase ion exchanger resin that absorbs the sample in the form of complex [12].

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 rice husk, coconut shell $Pb(NO_3)_2$, HCl 1 M, HCl 5M, 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 and coconut shellcleaned 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 hours. Results obtained are mashed and then sieved with a 100 mesh size.

2.2.2. Adsorbent activation. Rice husk in a solution of NaOH 2N and coconut shell in a solution $ZnCl_2$ 15% 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 110°C for 24 hours.

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, 4μg/L, and 8μg/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 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 Cd(II) species in simulated liquid waste. Simulated liquid waste solution of 50 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 483 nm and 558 nm. ΔA obtained will be substituted in equation Cd(II) calibration curve (ΔA vs concentration), so that the Pb(II) ions in the effluent can be known.

2.2.6. Determination of the most effective adsorbents comparison. Incorporating active carbon of rice husk and coconut shell with a comparison of 1:0; 0:1; 1:1; 2:1; 1:2 into the beaker of solution already contains sewage Pb (II) simulation of as many as 25 mL. Stir that solution for 30 minutes. The solution obtained then filtered with a filter paper and diluted from 5 mL filtrate into a 50 mL. Take 20 mL and then adding 0.06 mL resin, 2 mL and 1 mL of H_2SO_4 dithizon. Stir it for 20 minutes. The filtrate obtained tested with s with 483 nm wavelength and 558 nm. Test comparison with most effective adsorbents using FTIR. Determination of detectionlimit.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 483 nm and 558 nm. ΔA obtained will be substituted in the equation of the calibration curve.

3. Result and Discussions

3.1 Production of activated carbon from rice husk and coconut shell

The process consists of 3 stages, namely the stage of dehydration, and the carbonation stage stage of activation. At the stage of dehydration rice husk and coconut shell with an oven at a temperature of 105 ° C for 1 hour to eliminate the water levels.The carbonation stage done by inserting it into the furnace at a temperature of 350 ˚ C for 1 hour because higher temperatures can increase the rate of reduction of impurity and the volatile compounds that fills pore adsorbents, thus optimizing the establishment of active pore [13].

3.2 Fourier transform infra red spectra analysis

Based on FTIR Spectra analysis of combination adsorbent between rice husk and coconut shell before activation, after activation and after contacted with Pb ion is just little difference. There is O-H stretching vibrations increasing after activation and after contacting with Pb ion then C = C bonds of aromatics is also getting stronger. In addition the existence of activation and contact with metal Pb lead to the emergence decrease force of C = O and Si. All of that can be represented in that picture below.

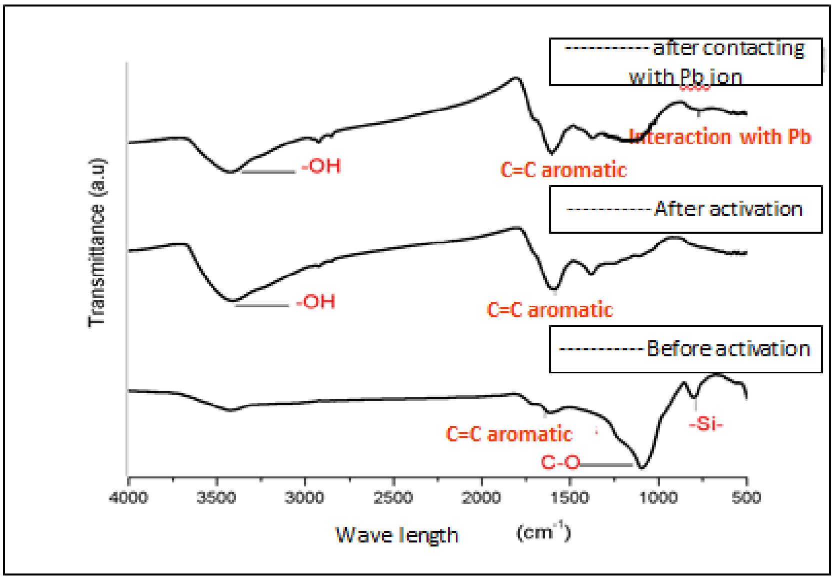

Figure 1. FTIR Spectra

3.3 Determination of Cd(II) calibration curve

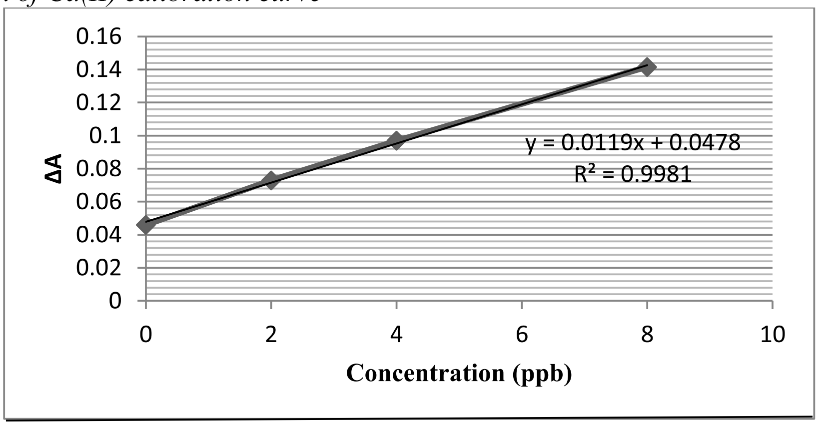

Figure 2. Calibration curve of Pb(II) solution.

From Figure 4. The equation y = 0.011 x + 0.047, where y is and x is ΔA concentration. The equation which will be used to determine the concentration of Pb (II) contained in the waste water simulation.The results of Pb(II) levels in simulated waste water.

Table 1. The results of Pb(II) levels in simulated waste water

Sample	[Pb(II)] (ppb)	ΔA	[Pb(II)] real (ppb)
Sample Pb(II)	4.99	0.101	49.96

3.4 The comparison of most effective adsorbents

Table 2. Optimum adsorbent mass comparison between rice husk and coconut shell

Mass Comparison	Initial [Pb(II)] (μg/L)	Final [Pb(II)] (μg/L)	Adsorbed [Pb(II)] (μg/L)	Adsorbed [Pb(II)] (%)
0:1	49.96	8.85	41.11	82.27
1:0	49.96	10.08	39.89	79.90
1:1	49.96	3.789	46.17	92.41
1:2	49.96	4.695	45.27	90.60
21	49.96	1.495	48.50	97.06

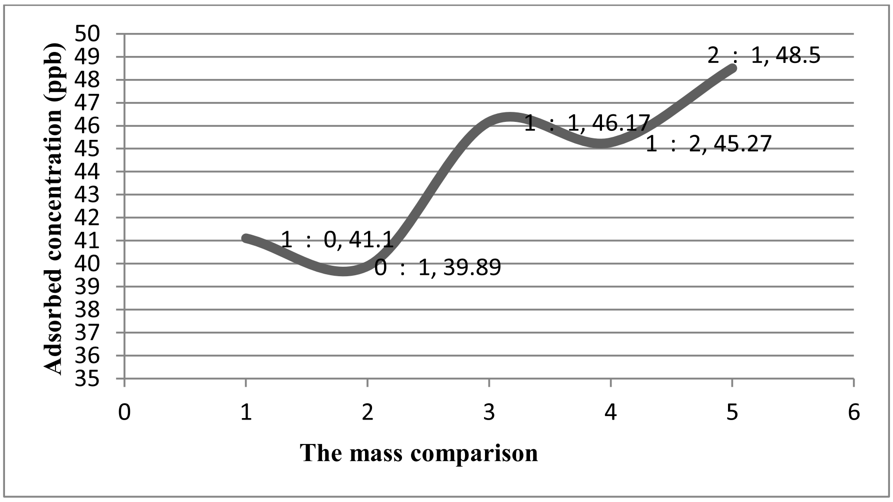

Figure 3. Optimum adsorbent mass comparison

The most effective adsorbent is the combination of active carbon rice husk: coconut shell 2:1 can adsorb the highest Pb ion amount . 48.50 μ g/L or 97.06 % adsorbed.

Table 3. Determination limit of detection

Blank	ΔA	Concentration	Deviation standar	LoD
A	0.1213	6.75		
B	0.1213	6.75		
C	0.1212	6.75		
D	0.1210	6.73		
E	0.1212	6.74		
Average			0.01	0.03

In the experiments that have been conducted obtained rating LOD 0.03 μ g/L.

4. Conclusion

The combination of active adsorbent rice husk and coconut shell can improve the ability of adsorbents to absorb heavy metals Pb (II), the most effective mass comparison of active adsorbent rice husk and coconut shell to adsorb Pb ion is 2:1 with the absorption of heavy metals Pb (II) of 97,06% and Solid-Phase

Spectrophotometry (SPS) is an effective method to determining the levels of heavy metals ions, Pb (II) results of active adsorbent the most effective in the level μ g/L with LoD amount 0,03 μ g/L

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References

[1] Halder J N, Islam M N 2015 *J. Environ. Human Health* **2**(1)
[2] Yoo H Y, Lee H Y, Jeong W J 2002 *J. Korean Environ. Sci.* **11** 993
[3] Sudarmaji, Mukono J, & Corie I P 2006 *Jurnal Kesehatan Lingkungan* **2**(2) 129
[4] Suksmerri 2008 *Jurnal Kesehatan Masyarakat* **11**(2)
[5] Nurhasni, Hendrawati, & Nubzah S 2014 *Jurnal Valensi* **4** (1) 36
[6] Chengwen S, Shuaiha W, Murong C, Ping T, Mihua S, Guangrul G 2014 *Suistanability* 85
[7] Bernand E, Jimoh A, and Odigure J O 2013 *Res. J. Chem Sci.* **3**(8) 231
[8] Matsuoka S, Nakatsu Y, Takehara K, Saputro S, & Yoshimura K. 2006 *Anal. Sci.* **22**1519
[9] Saputro S, Masykuri M, Mahardiani L, Mulyani B, Qorina I, Yoshimura K, Takehara K, Matsuoka S 2017 *IOP Conf. Ser.: Mater. Sci. Eng* **176** 012019
[10] S Saputro, M Masykuri, L Mahardiani, S Arini and A H Ramelan 2017 *IOP Conf. Ser.: Mater. Sci. Eng* **193** 012046
[11] Saputro S, Yoshimura K, Matsuoka S, Takehara K, & Narsito 2009 *Anal. Sci.* **25** 1445
[12] Yoshimura K, Waki H, & Ohasi S 1975 *Anal. Sci.* **23** 449
[13] Siburian A M, Pardede A S D, & Pandia S 2014 *Jurnal Teknik Kimia USU* **3 (4)**