Determination of Pb^{2+} metal ion level in liquid waste from adsorption process by combination adsorbent of rice husk and water hyacinth charcoal using solid-phase spectrophotometry (sps)

S Saputro[1], M. Masykuri, L Mahardiani, and AN Hidayah
Chemistry Education, Faculty of Teacher Training and Education, Sebelas Maret University, Jl. Ir. Sutami 36A Surakarta, Central Java-57126, Indonesia

E-mail: sulistyo_s@staff.uns.ac.id

Abstract. This research are to find out the influence of adsorbent composition between rice husk and water hyacinth in decreasing of Pb^{2+} ion in simulation liquid waste; the optimum composition of combination adsorbent of rice husk and water hyacinth charcoal on Pb^{2+} ion adsorption; and the effectiveness of SPS as a method to determine the decreasing level of Pb^{2+} ion in simulation liquid waste by combination adsorbent of rice husk and water hyacinth charcoal in µg/L level. Rice husk and water hyacinth carbonization using muffle furnace at 350°C for 1 hour. Rice husk charcoal activation in a 2 N NaOH solution and water hyacinth charcoal activated in a 5 M HCl solution. Contacting the combination adsorbent of rice husk and water hyacinth charcoal with a Pb^{2+} solution with variation of mass composition, 1:0 ; 0:1 ; 1:1 ; 1:2 and 2:1. Analysis of the Pb^{2+} ion level using SPS method. Characterization of rice husk and water hyacinth charcoal using the FTIR. The results showed that the combination adsorbent composition of rice husk and water hyacinth charcoal have an impact on decreasing Pb^{2+} ion level. The optimum composition of combination adsorbent of rice husk and water hyacinth charcoal on the adsorption Pb^{2+} ion is 1:2. SPS is an effective method to determine the decreasing Pb^{2+} ion in simulation liquid waste from the adsorption process by combination adsorbent of rice husk and water hyacinth in µg/L, with *Limit of Detection* (LOD) was 0,06 µg/L.

1. Introduction

Indonesia is an agrarian country that has a large agricultural area and as the consequences, it has many agricultural waste like rice husk and water hyacinth. Rice husk is a waste from rice process and water hyacinth is a weed or wild plant that can grow on the water around the agricultural area. Nowadays, management of rice husk and water hyacinth is yet a maximum. Usage of rice husk is just for rub ash and plants media, while the usage of water hyacinth as handicraft material and medicine. In the other hands, rice husk and water hyacinth can be used as a heavy metal ion adsorbent like Pb^{2+} [1-2].

Pb^{2+} is form of the most Pb metal ion in liquid waste. Pb is one of the dangerous environmental contaminant like water that can cause poisoning and even death in living beings. For human, exposure to the Pb impact to reproduction system, nerve system, intelligence system and systemic like decrease the blood pressure. WHO decided Pb limit in the water is 0.1 mg/L [3], and based on Permenkes RI No. 416 Tahun 1990 in Indonesia, Pb limit in the clean water and drink water is 0.05 mg/L [4]. Very small concentration of Pb^{2+} metal ion in the water can give a lot of loss for living beings. Therefore, needed an analysis method to determine Pb^{2+} concentration in the water even in very small concentration.

Solid-phase Spectrophotometry (SPS) is an analysis method that can be used to determine the concentration of a solution in very low concentration, until μg/L level [5]. Determining the concentration of a solution based on the light absorption by the target chemical components concentrated in a solid phase, so this method used UV-Visible spectrophotometer [6]. SPS is better than conventional methods because it has high sensitivity, effective to ion speciation in the water, can minimize the use of reagent and applied green analytical chemistry so this method friendly for environment. SPS is an analysis method that very suitable to analysis the effectivity of an adsorbent in the adsorption process.

SPS can be used to determining the concentration of a solution from adsorption process by rice husk and water hyacinth charcoal in μg/L level. Rice husk and water hyacinth charcoal is chosen to combined become adsorbent because they have good ability in adsorping Pb^{2+} metal ion. Rice husk has low nutrient value, abrasive, and contains high carbon [7], while water hyacinth has smooth and diverge roots system and hollows stem. Both of them also contains high cellulose, rice husk have 32.12% of cellulose [8] and water hyacinth have 72.63% of cellulose after milled [9]. This cellulose make rice husk and water hyacinth have potentially become adsorbent of metal ion in liquid system [9]. In this study, rice husk and water hyacinth used as an adsorbent with various ratio for decreasing the concentration of Pb^{2+} metal ion.

2. Experimental

2.1 Tools and Materials

The tools used were a spectrophotometer UV-Vis brand K-MAC, FTIR spectrophotometer Shimadzu, oven, muffle furnace, 100 mesh sieve, mortar and pestle, magnetic stirrer, desicator, analytical balance, filter paper, universal pH indicator, iron clamp, volumetrick flask, beaker glass, measuring glass, flask, drop pipette, volumetric pipette, spatula glass, funnel glass, saucer glass, porcelain saucer and vial. Materials used were rice husk, water hyacinth, standard Pb^{2+} solution, NaOH crystal, 37% of HCl, 0.5 M H_2SO_4, diphenylthiocarbazone, chloroform, Muromac resin AG 50W X2 100-200 mesh and aquadest.

2.2. Research procedure

2.2.1. Preparation of adsorbent. Rice husk and water hyacinth was cleaned and washed by aquadest and then dried on the oven at 105°C for 1 hour. After that, carbonized them in muffle furnace at 350°C for 1 hour. Mashed the results and then sieved with a 100 mesh sieve.

2.2.2. Adsorbent activation. Rice husk charcoal was soaked in a 2 N NaOH solution for 24 hours at room temperature. Filter and rinse the residue with distilled water until the filtrate became neutral, and then dried in an oven at 105°C for 24 hours. Adsorbent was analyzed by FTIR before and after activation. Water hyacinth charcoal is soaked in 5 M HCl solution for 24 hours at room temperature. Filter and rinse the residue with distilled water until the filtrate became neutral, and then dried in an oven at 105°C for 24 hours. Adsorbent was analyzed by FTIR before and after activation.

2.2.3. Resin preparation. Muromac resin AG 50W-X2 100-200 mesh dissolved in distilled water and left it in a few minutes until the resin became expanded.

2.2.4. Determination of Pb^{2+} calibration curve. Standard solution of Pb^{2+} 0 μg/L, 2 μg/L, 4 μg/L, dan 8 μg/L respectively as much as 20 mL added by 1 mL of 0.5 M H_2SO_4, 2 mL of diphenylthiocarbazone and 0.06 mL resin. The mixture was stirred by magnetic strirrer for 20 minutes and then analyzed it using UV-Vis spectrophotometer at a wavelength of 483,411 nm and 558,111 nm. The difference in absorbance of the two wavelengths was determined, $\Delta A = A_{483,411nm} - A_{558,111nm}$, which was ΔA will be made standard curve (ΔA vs concentration).

2.2.5. Determination of Cr (VI) species in simulated liquid waste. Simulated liquid waste solution of 50 µg/L as much as 20 mL added by 1 mL of H_2SO_4 0.5 M, 2 mL of diphenylthiocarbazone and 0.06 mL of resin. The mixture was stirred by magnetic strirrer for 20 minutes and then analyzed it using UV-Vis spectrophotometer at a wavelength of 483,411 nm and 558,111 nm. ΔA obtained will be substituted in equation of Pb^{2+} calibration curve (ΔA vs concentration) so the Pb^{2+} ions in the simulated liquid waste could be known.

2.2.6. Determination of optimum adsorbent composition. Rice husk charcoal and water hyacinth charcoal was mixed with ratio at 1:0, 0:1, 1:1, 1:2 and 2:1. The mixture was added by 20 ml of simulated liquid waste and then stirred by magnetic stirrer for 30 minutes. Filter the mixture and take 5 ml of filtrate to diluted by distilled water until 50 ml. The 20 ml of it was added by 1 mL of H_2SO_4 0.5 M, 2 mL of diphenylthiocarbazone and 0.06 mL of resin. The mixture was stirred by magnetic strirrer for 20 minutes and then analyzed it using UV-Vis spectrophotometer at a wavelength of 483,411 nm and 558,111 nm. ΔA obtained will be substituted in equation of Pb^{2+} calibration curve (ΔA vs concentration) so the Pb^{2+} ions in the simulated liquid waste after adsorption process could be known.

2.2.7. Determination of detection limit. Distilled water as much as 20 ml was added by 1 mL of H_2SO_4 0.5 M, 2 mL of diphenylthiocarbazone and 0.06 mL of resin. The mixture was stirred by magnetic strirrer for 20 minutes and then analyzed it using UV-Vis spectrophotometer at a wavelength of 483,411 nm and 558,111 nm. ΔA obtained will be substituted in equation of Pb^{2+} calibration curve (ΔA vs concentration). This steps was repeated in five times.

3. Result and Discussion

3.1. Preparation of activated carbon from rice husk

Preparation of activated carbon from rice husk consists of three steps, there were dehydration, carbonization and activation. Dehydration is a process to remove water level in rice husk. Carbonization is a process to breakdown organic cellulose in rice husk into carbon and remove non carbon compounds in form of gas. Activation is a process to remove hydrocarbon deposit that closed the pores on the surface of rice husk charcoal. Activation process of rice husk charcoal was used 2 N NaOH solution to soaked it for 24 hours. NaOH was used because it was a strong base that can clean the residues of organic compound and decrease the silica level on rice husk charcoal. NaOH is suitable activator for rice husk charcoal because rice husk charcoal contains more carbon than oxygen.

3.2. Preparation of activated carbon from water hyacinth

Preparation of activated carbon from water hyacinth consists of three steps, there were dehydration, carbonization and activation. Dehydration is a process to remove water level in water hyacinth. Carbonization is a process to breakdown organic cellulose in water hyacinth into carbon and remove non carbon compounds in form of gas. Activation is a process to remove hydrocarbon deposit that closed the pores on the surface of water hyacinth charcoal. Activation process of rice husk charcoal was used 5 M HCl solution to soaked it for 24 hours. HCl was used because it was a strong acid that can clean the residues of organic compound in water hyacinth charcoal and open the pores with dissolved organic substances and certain metal compound. HCl is suitable activator for water hyacinth charcoal because water hyacinth charcoal contains more oxygen than carbon.

3.3. Fourier transform infrared spectra analysis

Figure 1 shows the presence of the -OH group at wavenumber of 3433.44 cm^{-1} on before activation, 3387.15 cm^{-1} on after activation and 3398.72 cm^{-1} on after contact. C-O group at 1096.58 cm^{-1} on before activation, 1105.26 cm^{-1} on after activation and 1120.69 cm^{-1} on after contact. C=O group at 1580.73 cm^{-1} on after activation and 1601.95 cm^{-1} on after contact.

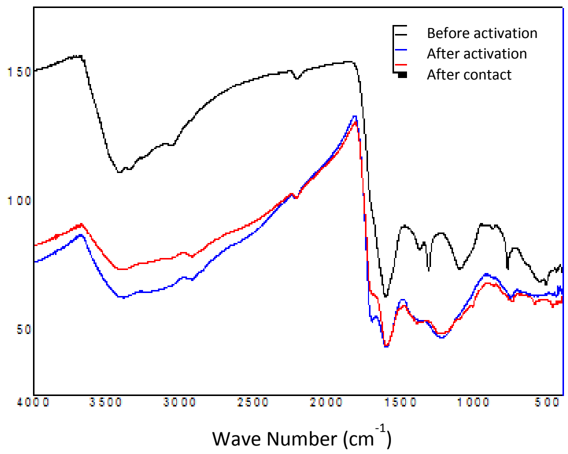

Figure 1. FTIR spectra of rice husk charcoal before activation, after activation and after contact

Figure 2 shows the presence of the -OH group at wavenumber of 3349.53 cm^{-1} on before activation, 3411.26 cm^{-1} on after activation and 3398.72 cm^{-1} on after contact. C-O group at 1109.12 cm^{-1} on before activation, 1225.82 cm^{-1} on after activation and 1227.74 cm^{-1} on after contact. C=O group at 1604.84 cm^{-1} on after activation and 1601.95 cm^{-1} on after contact.

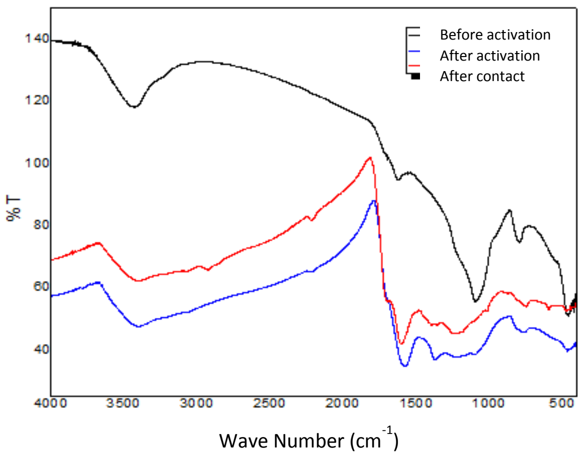

Figure 2. FTIR spectra of water hyacinth charcoal before activation, after activation and after contact

3.4. Determination of Cr (VI) calibration curve

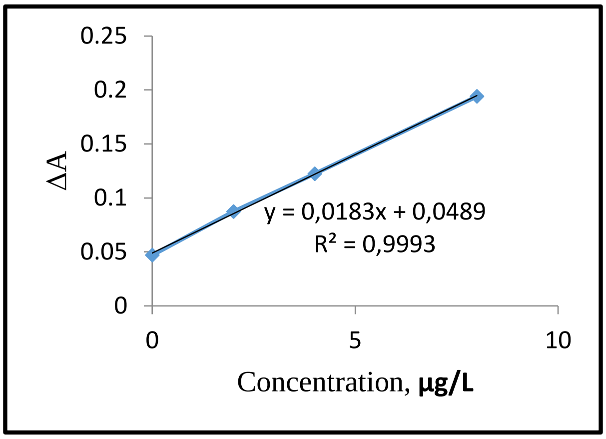

Figure 3. Pb^{2+} calibration curve

Based on the graph in Figure 3, y = 0.0183x + 0.0489 where y is ΔA and x is the concentration. The equation is used to determine the concentration of Pb^{2+} in simulated liquid waste. By using this equation, the Pb^{2+} levels in a simulated waste water was 49,68 μg/L.

3.5. Determination of optimum adsorbent mass composition activated carbon from rice husk and water hyacinth charcoal in a decrease levels of Pb^{2+}

Table 1. Determination of optimum composition

Mass Ratio of Rice Husk and Water Hyacinth Adsorbent	[Pb^{2+} Initial (μg/L)]	[Pb^{2+} Last (μg/L)]	[Pb^{2+} Adsorp (μg/L)]	Percentage of Pb^{2+} Adsorbed (%)
1 : 0 (A)	49.68	9.39	40.29	81.10
0 : 1 (B)	49.68	9.26	40.42	81.36
1 : 1 (C)	49.68	9.51	40.17	80.86
1 : 2 (D)	49.68	8.24	41.44	83.42
2 : 1 (E)	49.68	8.59	41.09	82.71

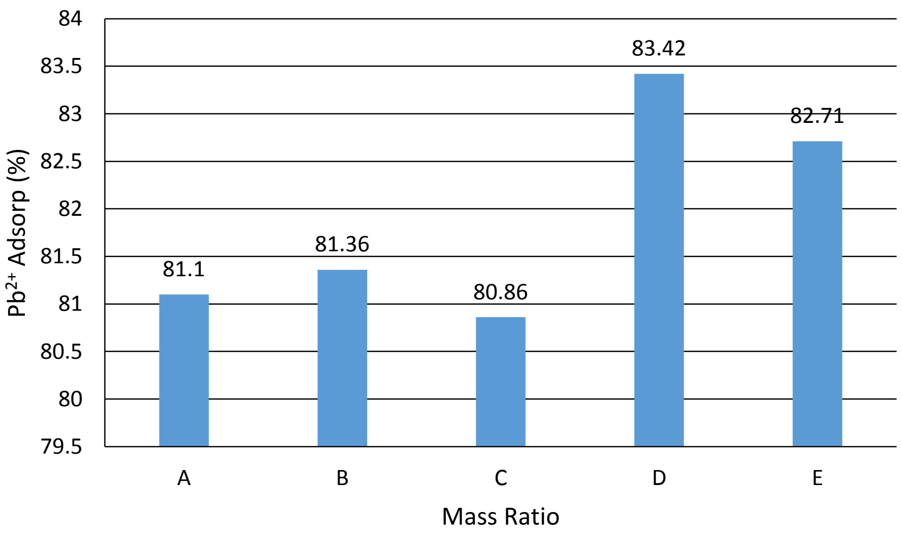

Figure 4. Adsorption percentage chart

Based on the data in Table 3 and Figure 4, the most optimal ratio of combination adsorbent from rice husk and water hyacinth in Pb^{2+} ions adsorption was 1:2. It can decrease Pb^{2+} metal ion concentration until 41,44 μg/L with the adsorption percentage is 83,42%. This ratio showed that the mass of water hyacinth active charcoal was twice from mass of rice husk active charcoal. Its because water hyacinth has a higher cellulose that rice husk. The cellulose showed that the content of carbon in water hyacinth is higher than rice husk.

Cellulose is a polysaccharide that contains D-glucose that connected in uniform by β-glucose bonding. The molecule formula is $(C_6H_{10}O_5)_n$ and it has -OH groups. Based on the result of FTIR spectra, water hyacinth and rice husk charcoal have -OH group. The existence of -OH group allowed the adsorption of Pb^{2+} ions because the ion exchange. H^+ ion in two OH exchange with Pb^{2+} ion, so the metal ion bonded with cellulose. The interaction between cellulose with Pb^{2+} ions happened because the existence of covalent bonding in the interaction [10].

3.6. Determination of detecting limit

Limit of detection (LOD) in this research was 0.06 μg/L, so it can be said that the sample with concentration at 0.06 μg/L can be read. Thus the solid-phase spectrophotometry (SPS) is a sensitive and effective analysis method for use in analysis decreased levels of Pb^{2+} metal ion adsorption by combination adsorbent from rice husk and water hyacinth in μg/L levels.

4. Conclusion

The results showed that rice husk and water hyacinth charcoal can be used as combination adsorbents to adsorb Pb^{2+} metal ions in the simulated liquid waste. Optimum mass ratio of rice husk activated carbon and water hyacinth activated carbon was 1:2 with the percentage of adsorption was 83,42% in the amount of 3 g. Solid-phase spectrophotometry (SPS) is a sensitive method to analyzed the decreased levels of Pb^{2+} metal ions in the level of μg/L with the limit of detection (LOD) was 0.06 μg/L.

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