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The usage of activated carbon from teak sawdust *(tectona grandis* l.f.*)* and zeolite for the adsorption of Cr(VI) and its analysis using solid-phase spectrophotometry (sps)

S Saputro[1], M Masykuri[1], L Mahardiani[1], B Mulyani[1], I Qorina[1], K Yoshimura[2], K Takehara[3], S Matsuoka[4]

[1]Chemistry Education, Faculty of Teacher Training and Education, Sebelas Maret University, Jl. Ir. Sutami 36A Surakarta, Central Java-57126, Indonesia

[2]Kyushu Environmental Evaluation Association, Matsukadai, Higashi-ku, Fukuoka 813-0004, Japan

[3]Department of Chemistry, Faculty of Sciences, Kyushu University, 744, Motooka, Nishi-ku, Fukuoka 819–0395, Japan

[4]Department of Environmental Science, Faculty of Science, Niigata University, Ikarashi, Niigata 950–2181, Japan

E-mail: sulistyo68@yahoo.com

Abstract. This study aims to evaluate the usage of teak sawdust and zeolite as an adsorbent of Cr(VI) ion; optimal composition ratio of the composite adsorbent; and the sensitivity of solid-phase spectrophotometry (SPS) as a method to determine the levels of Cr(VI) ion as an adsorption results of adsorbents. The adsorbent used were teak sawdust activated carbon and zeolite as a single and composite adsorbents. The teak sawdust carbonization using *muffle furnace* and then activated with H_3PO_4 10% while the zeolite with H_2SO_4 10%. The contacting process of the adsorbents with Cr(VI) was done by varying the compositions. Analysis of Cr(VI) level was done using SPS method. Characterization of adsorbent before and after being activated is done using a FTIR. The results showed that teak sawdust and zeolite can be used as adsorbents to adsorb Cr(VI) in the simulated liquid waste with the adsorption capacity 1.19 µg/g; the optimum composition ratio of teak sawdust activated carbon and zeolite was 75%:25% with the percentage of adsorption was 62.72%. Solid-phase spectrophotometry is a sensitive method to analyze the decreased levels of Cr(VI) as an adsorption results in µg/L level with the limit of detection (LOD) was 0.03 µg/L.

1. Introduction

Industrial development in Indonesia which is fast enough can boost the economy, but the impact is waste production. One of the waste is heavy metal which caused serious pollution to the environment if it exceeds the limit and have a very dangerous toxic and will cause serious disease to humans when it accumulates in the body [1]. Indicator used to detect water pollution is the contamination of heavy metals in it. It called harmful heavy metals because it generally has a high mass density (5 gr/mL) and a small concentration can be toxic and dangerous, and one of them is Cr(VI). Water quality that contains Cr(VI) particles that exceed standard quality (0,05 mg/L), could endanger human health [2].

Determining the concentration of Cr(VI) in water is very important even in a very small concentration, because it will be absorbed by human body if the water that contains Cr(VI) is consumed. Chromium (VI) can cause liver and kidney damage, bleeding, repiratory tract damage, and lung cancer. Long-term exposure to the respiratory tract and the skin can cause inflammation of the nasal cavity, nasal and skin ulcer bleeding [3]. Thus, to determine Cr(VI) in water with a very low concentrations, *solid-phase spectrophotometry* (SPS) is used because it has a high sensitivity.

Solid-phase spectrophotometry (SPS) is a method of determining the concentration of a substance in which the light absorption by the target chemical components concentrated in a solid phase. This method is more sensitive than conventional methods that use expensive instrumentation. Additionally, it can determine up to μg/L levels [4]. If the use of existing methods are still limited to the level of mg/L, then the method solid-phase spectrophotometry (SPS), which is more sensitive to the μg/L levels, can be used in waters with lower levels of contamination.

Various methods were developed to reduce the levels of heavy metals in waters, one of the methods is the adsorption. The adsorption has proven a useful tool to control the degree of contamination of chromium in the water, low cost materials which have an adsorption capacity [5]. The adsorbent that often used is porous solids, such as charcoal, zeolite, allophane, sand, and silica gel. Most research on adsorption was performed using a single adsorbent, whereas in this study conducted adsorption with single and combination adsorbent, which are activated carbon from teak sawdust and zeolite.

The amount of waste sawdust from the sawmill industry is 15-20% of the total production [6]. This number is huge and its use is not maximized. Thus, in this study teak sawdust utilized as activated carbon using an activator H_3PO_4 10%. The largest contents of teak wood is cellulose 47.5% and 29.9% lignin. The presence of cellulose showed that teak can be used as an adsorbent.

Zeolite is a mineral group consisting of a double oxide Al_2O_3, SiO_2, Fe_2O_3, CaO and MgO. Boron can be found in the sedimentary rocks, mainly crystal of aluminum and silicate groups. Zeolites are natural materials that are widely available in Indonesia, so that knowledge and research on natural zeolite and ways of processing is very important [7]. Zeolites have a high adsorption capacity, because it can separate molecules by size and configuration of the molecule. Adsorption mechanism that may occur is the physical adsorption (involving Van der Waals force), chemical adsorption (involving electrostatic forces), hydrogen bonds, and the formation of coordination complexes [8]. The abundance of teak sawdust and zeolite needs to be maximized. Thus, in this study, both of the material used as an adsorbent for lowering the concentration of Cr(VI).

2. Experimental

2.1. Tools and materials

The tools used was a UV-Visible spectrophotometer from K-MAC, FTIR spectrophotometer Shimadzu, muffle furnace, oven, pan, analytical balance, volumetric flask, volume pipette, glass beaker, measuring cup, flask, erlenmeyer, watch glass, stirrer glass, drop pipette, aliquoting devices are assembled using a syringe, blender, mortar and pestle, a 100-mesh sieve, porcelain bowls, stirrer, and a magnetic stirrer. Materials used are teak sawdust, zeolite, $K_2Cr_2O_7$, H_3PO_4 10%, H_2SO_4 10%, resin AG 50W-X2 Muromac H^+ form 100-200 mesh, distilled water, acetone, Whatman filter paper, blue litmus, and 1,5-diphenylcarbazide (DPC).

2.2. Research procedure

2.2.1. Preparation of adsorbent

Teak sawdust is cleaned and washed with distilled water to clean, dried at 110°C then charred in a muffle furnace at a temperature of 900°C for 30 minutes. Results obtained mashed and then sieved with a 100 mesh size. Natural zeolites are cleaned with distilled water and then dried at a temperature of 105°C. Results obtained mashed and then sieved with a 100-mesh sieve.

2.2.2. Adsorbent activation

Charcoal soak in a solution of 10% H_3PO_4 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 110°C for 24 hours. Adsorbent was tested by FTIR before and after activation. Zeolite soak in a solution of 10% H_2SO_4 for 24 hours. 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 tested by FTIR before and after activation.

2.2.3. Resin preparation

Muromac resin AG 50W-X2 H^+ form 100-200 mesh is dissolved in distilled water and silence a few moments until the resin becomes more fluffy.

2.2.4. Determination of Cr(VI) calibration curve

Standard solution of Cr(VI) 0 μg/L, 2 μg/L, 4 μg/L, dan 8 μg/L respectively 20 mL plus 1 mL of H_2SO_4 0.5 M, 1 mL of 1,5-diphenylcarbazide (DPC), and 0.06 mL resin. Stir it for 20 minutes and analyzed using UV-Vis spectrophotometer at a wavelength of 540 nm and 682 nm and then absorbance difference of the two wavelengths determined, $\Delta A = A_{540nm}\text{-}A_{682nm}$, which ΔA will be made standard curve (ΔA vs concentration).

2.2.5. Determination of Cr(VI) species in simulated liquid waste

A 20 mL of simulated liquid waste solution of 50 μg/L was taken then added with 1 mL of H_2SO_4 0.5 M, 1 mL of 1,5-diphenylcarbazide (DPC) 0.25%, and 0.06 mL of resin. Then, stir it for 20 minutes and analyzed using UV-Vis spectrophotometer at a wavelength of 540 nm and 682 nm. ΔA obtained will be substituted in equation Cr(VI) calibration curve (ΔA vs concentration), so that the Cr (VI) ions in the effluent can be known.

2.2.6. Determination of optimum adsorbent composition

Inserting 20 mL of a simulated liquid waste solution of 50 μg/L in each of the 4 erlenmeyer. Insert each adsorbent composition with a ratio of teak sawdust:zeolite at 100%:0%, 0%:100%, 25%:75%, 75%:25% and stir it for 20 minutes. Each adsorbent was filtered with Whatman filter paper. The resulting filtrate was taken as much as 5 mL and then diluted with distilled water until 50 mL. Furthermore, the filtrate diluted taken as many as 20 mL added with 1 mL of H_2SO_4 0.5 M, 1 mL of solution DPC 0.25% and 0.06 mL resin then stir for 20 minutes and analyzed using UV-Vis spectrophotometer with a wavelength of 540 nm and 682 nm. ΔA obtained will be substituted in equation of Cr(VI) calibration curve (ΔA vs concentration) so species of Cr(VI) in a simulated liquid waste after the adsorption known.

2.2.7. Determination of detection limit

Taking five blank solution of 20 ml, then each added 1 mL of H_2SO_4 0.5 M, 1 mL of 0.25% DPC, 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 540 nm and 682 nm. ΔA obtained will be substituted in the equation of the calibration curve.

3. Results and discussion

3.1. Preparation of activated carbon from teak sawdust adsorbent

Preparation of activated carbon from teak sawdust adsorbent consists of three stages, including the stage of dehydration, is the removal of impurities in teak sawdust, stage of carbonization, breakdown of organic matter into carbon by heating at 900°C for 30 minutes, and the activation stage, soaking with an activator solution which is H_3PO_4 10% for 24 hours. H_3PO_4 10% is used because it is a good dehydrating agent and an oxidizing agent, so it can eliminate impurities from the adsorbent.

3.2. Preparation of zeolite adsorbent

Zeolite preparation is done by washing zeolite from impurities by using distilled water and then drying in an oven at 105°C for 24 hours, which are expected pores formed by evaporation of water through heating. At this stage of activation, zeolite soaked with a solution of 10% H_2SO_4 for 24 hours. Activation aims to clean up the surface pores, removing impurities compounds, and increase the surface area. H_2SO_4 activator used as an oxidizing agent, so as to eliminate impurities on zeolite that cause cavities formerly closed by impurities into the open, so the adsorption become more effective and can increase the adsorption capacity.

3.3. Fourier Transform Infra Red Spectra Analysis

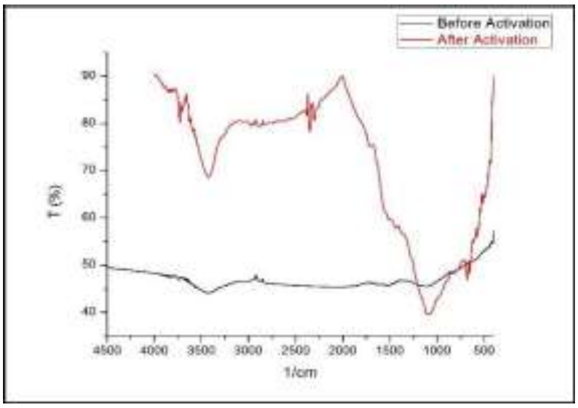

Figure 1. FTIR Spectra of Teak Sawdust Before and After Activation

Based on Figure 1, shows the presence of the -OH group at wavenumber of 3426.69 cm^{-1}, aromatic group at 1568.19 cm^{-1}, C-O at 1114.9 cm^{-1}, and O-Si-O at 679.94 cm^{-1}

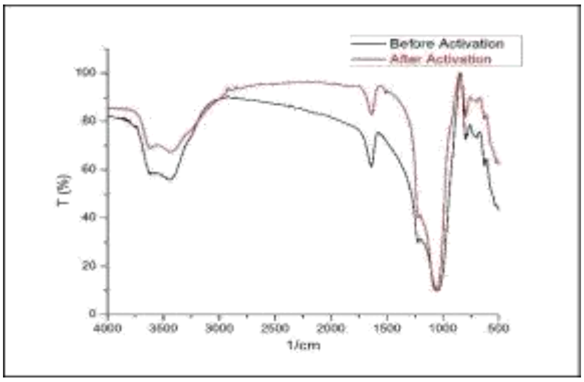

Figure 2. FTIR Spectra of Zeolite Before and After Activation

Based on Figure 2, note that the structure of the zeolite containing Al-O-Si at wavenumber of 1061.86 cm^{-1} and NH_2 groups at 3425.75 cm^{-1} and 3626.33 cm^{-1}.

3.4. Determination of Cr (VI) Calibration Curve

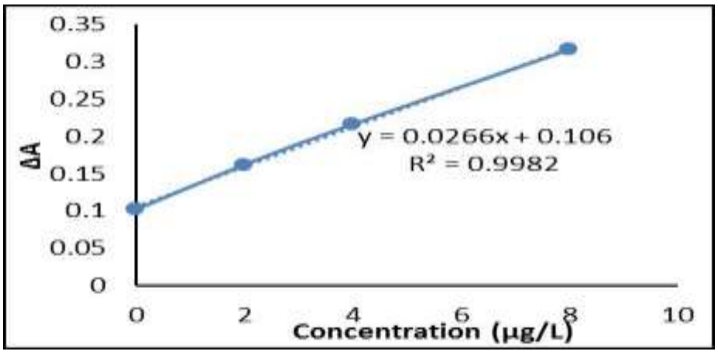

Figure 3. Cr(VI) Calibration Curve

Based on the graph in Figure 3, $y = 0.0266x + 0.106$ where y is ΔA and x is the concentration. The equation is used to determine the concentration of Cr (VI) in simulated liquid waste. By using this equation, the Cr(VI) levels in a simulated wastewater was 47.4 µg/L.

3.5. Determination of optimum adsorbent mass composition activated carbon from teak sawdust (TS) and zeolite (Z) in a decrease levels of Cr(VI)

Table 3. Determination of optimum composition

TS : Z Mass (%)	Final Concentration (µg/L)	Adsorbed Concentration (µg/L)	Adsorbed Percentage (%)
100 : 0	24.81	22.59	47.65
0 : 100	29.32	18.08	38.14
25 : 75	24.06	23.34	49.24
75 : 25	17.67	29.73	62.72
80 : 20	18.05	29.35	61.93
90 : 10	21.05	26.35	55.59

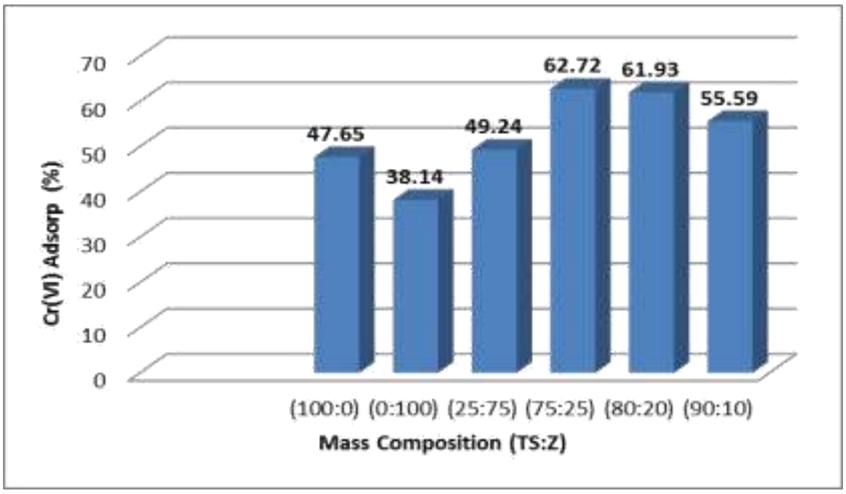

Figure 4. Adsorption percentage chart

Based on data in Table 3 and the chart in Figure 4, the mass ratio that produce the most optimum adsorption percentage is combination of adsorbent with ratio of 75%:25% are 62.72% with the adsorption capacity of 1.19 µg/g, then the ratio of 80% : 20%. Based on the analysis on a single adsorbent, the mass ratio of 100%: 0% resulted in a greater adsorption percentage than the ratio of 0%: 100%. This shows that in this study, single adsorbent activated carbon from teak sawdust is more effective at adsorption of Cr(VI) ions compared to single zeolite adsorbent. These results indicate that a combination adsorbents are more effective in the adsorption of Cr(VI) compared to a single adsorbent [9]. The process of adsorption on activated carbon or zeolites was possible because their pores and the ion exchange.

Adsorption on activated carbon from teak sawdust and zeolite may occur by way of ions of Cr(VI) enter the pores of adsorbent without forming a bond or interact with a weak binding energy (Van der Waals forces). Weak attractive force causes the metal ions of Cr(VI) can move from one surface to the other surface of adsorbent. In addition, the active groups on the adsorbent will interact with the metal ions of Cr(VI).

Greater mass ratio of activated carbon in composite adsorbents showed greater percentage of adsorption, it is possible for the adsorption process in this research is dominated by the pores, so the activated charcoal more influential in decreased levels of Cr(VI). Combination with zeolite enables the ion exchange process more optimal, because zeolites have a large ion exchange capacity [10], so that the metal ions of Cr(VI) are not only adsorbed into the pores, but rather an ion exchange process. In addition, based on the research showed that the addition of activated carbon in the composite adsorbent is directly proportional to the porosity of the adsorbent, where the greater percentage of porosity, the larger the pores, resulting in better adsorption [11].

3.6. Determination of detection limit

In this research, Limit of Detection (LOD) was 0.03 μg/L, so it can be said that the sample at a concentration of 0.03 μg/L can be read, so that the solid-phase spectrophotometry (SPS) is a sensitive and effective method for use in analysis decreased levels of Cr(VI) adsorption results of composite activated carbon from teak sawdust and zeolite in levels μg/L.

4. Conclusions

The results showed that teak sawdust and zeolite can be used as adsorbents to adsorb Cr(VI) metal ions in the simulated liquid waste with the adsorption capacity 1.19 μg/g; the optimum composition ratio of teak sawdust activated carbon and zeolite was 75%:25% with the percentage of adsorption was 62.72% in the amount of 0.5 g; and solid-phase spectrophotometry (SPS) is a sensitive method to analyzed the decreased levels of Cr(VI) as an adsorption results of a single and combination adsorbents of activated carbon from teak sawdust and zeolite in the level of μg/L with the limit of detection (LOD) was 0.03 μg/L.

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