The effectiveness of the activated carbon from coconut shell and corn cob to adsorb Pb(II) ion and it’s analysis using solid-phase spectrophotometry

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Abstract. This research aimed to know the mass ratio of adsorbent combination of activated carbon from coconut shell and corn cob to adsorb Pb(II) ion and it’s analysis using the solid-phase spectrophotometry (SPS). The technique of data collection is carried out by several stages, which are: (1) the production of carbonated coconut shell and corn cob using muffle furnace at a temperature of 350 °C for 60 minutes; (2) the activation of the coconut shell carbon using ZnCl₂ 15% activator and the corn cob carbon using HCl 1M, (3) contacting this adsorbent combination between activated carbon from coconut shell and corn cob for 20 mL of liquid simulations waste Pb(II) ion on variations ratio of 1:0; 0:1; 1:1; 2:1; 1:2; (4) the analysis levels of Pb(II) using SPS; (5) the characterization of adsorbents in the most optimum combination between activated carbon of coconut shell and corn cob using FTIR. The results showed that the adsorbent can increase the capabilities and the effectiveness of the absorption to Pb(II) ion and the optimum ratio from the comparison between coconut shell and corn cob is 1:2 with the absorption ability to adsorb Pb(II) ion in the simulations waste is 86.78%. SPS is an effective method with high sensitivity in the level of μg/L and the limit of detection (LoD) of 0.06 μg/L.

1. Introduction

We know that Indonesia is located in the tropical region and is traversed by the equator, besides Indonesia is also known as one of the agricultural countries, where the agricultural sector is very abundant. The tropical region is known to have unlimited potential for natural resources for the future of life. Based on statistical data, coconut plantation results in Indonesia reach 176,575.82 tons/year, while corn reaches 3,212,391 tons/year [1], agricultural products in the form of coconut and corn have byproducts in the form of coconut shells and corn cobs which are relatively more than the main product. These byproducts need to be processed so it does not become useless waste. Today, many resolutions have been found for the processing of solid waste, ranging from making souvenirs, biobriquettes, fertilizers, and even making environmentally friendly alternative energy.

On the other hand, the development of an increasingly advanced era has caused industry in Indonesia to also develop rapidly, as a result new problems arise in the form of environmental pollution, such as water pollution. Water pollution according to the Decree of the Minister of Population and Environment No: KEP-02/MENKLH/1988 concerning the Determination of

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Environmental Quality Standards are: the entry or inclusion of living things, energy substances, and/or other components into the water or changes in the water order by human activities or by natural processes, so that the quality of water falls to a certain level which causes water to become deficient or no longer functioning according to its designation [2]. Water pollution is mostly caused by industrial and household waste that is dumped carelessly without being processed first. The main sources of water pollutions come from industry sector. Some type of industry that contributes greatly are the mining and construction, manufacturing, power-generating, and food processing industries. One of the impacts from the mining industry is heavy metal contamination in the water [3]. Heavy metals contained in water can cause various problems. Starting from the problem of damage to the environment and ecosystems, to the health and safety problems of living things. Water pollution could be minimized among others; by recycling, by reusing, waste minimization, by mitigating, by preventing, and by compost [4]. Lead (Pb) is one of the heavy metals that can cause these problems.

Lead is a metal with a bluish gray color with high density (11.48 g ml-1 at room temperature) [5]. Acute lead toxicity in natural waters causes severe damage to the kidneys, reproductive system, liver, and brain, and the central nervous system, and can cause death [2]. Most Lead wastes are produced by Industrial activities and other produced by natural processes. The high content of Pb in the waters could be due to weathering and leaching of lead from waste rocks dumps [6]. Therefore, absorbents that can reduce lead content in polluted water are now being developed. Absorbent made activated carbon from coconut shell combined corn cobs is possible to be more effective in adsorbing Pb$^{2+}$ ion in water, besides economical, both materials are also easy to obtain, and can be a useful waste treatment.

Solid-phase spectrophotometry is one method that can be used to determine the adsorption capacity of an adsorbent with better sensitivity (the ability to read concentration to the level of ppb or µg/L than other methods. In this research, the effectiveness of activated carbon from coconut shell and activated carbon corn cobs is tested to be used for Pb$^{2+}$ ion adsorption using solid-phase spectrophotometry.

2. Experimental
The research method applied was laboratory experiment method. The basis of this research was a decrease in Pb$^{2+}$ ion levels by using adsorbents from a combination of activated carbon from coconut shell with corncobs and analysis conducted using solid-phase spectrophotometry. Then the analysis of sample characteristics using Fourier Transform Infrared Spectroscopy (FTIR).

2.1. Materials, Tools and Instrument.
Materials used are coconut shell, corn cobs, Pb(NO$_3$)$_2$, ZnCl$_2$ 15%, HCl 1M, H$_2$SO$_4$ 0.5M, resin AG Muromac 50W-X2 H$_2$O form (100-200 mesh), distilled water, chloroform, and dithizone (diphenylthiocarbazone) 0.005%. The used tools were a muffle furnace, pan, oven, analytical balance, volumetric flask, volume pipette, drop pipette, beaker glass, measuring cup flask, whatman filter paper, blue litmus, erlenmeyer, watch glass, stirrer glass, aliquoting devices which are assembled using a syringe, blender, mortar and pestle, a 100 mesh sieve, porcelain bowls, stirrer bar, and a magnetic stirrer. The used Instruments were a UV-visible spectrophotometer from K-MAC and FTIR spectrophotometer from Shimadzu [7].

2.2. Research procedure
2.2.1. Production of adsorbent. Coconut shells and corn cobs are removed first and then washed clean to remove impurities with destilled water. Then dried in an oven for 60 minutes then put into muffle furnace at 350 °C for 60 minutes to become carbon. Mash coconut shell carbon and corn cobs separately then sieve with a size of 100 mesh [8].

2.2.2. Adsorbent activation. Coconut shells carbon soaked in a solution of ZnCl$_2$ 15% and corn cobs carbon soaked in a solution of HCl 1M at room temperature for 24 hours. Filter and rinse the residue
to make the filtrate become neutral with distilled water, and then dried in an oven at 110°C for 24 hours. Adsorbent was tested by FTIR spectrophotometer before and after activation [7].

2.2.3. Resin preparation. In this research used Muromac resin AG Muromac 50W-X2 H+ solid form (100-200 mesh size) before that is used, the resin dissolved in distilled water and silence a few moments to get more fluffy resin.

2.2.4. Determination of Pb(II) calibration curve. Pb (II) solution was 0 µg/L, 2 µg/ L, 4 µg/L, and 8 µg/L each taken 20 mL. Then added 2 mL of dithizon solution, 1 mL of H₂SO₄ 0.5M solution, and 0.06 mL of fluffy resin. Then it was stirred for 20 minutes and analyzed using solid-phase spectrophotometry (SPS) with a wavelength of 483 nm and 558 nm. Then the absorbance difference from the two wavelengths is taken, namely ΔA = A₄₈₃nm – A₅₅₈nm. Where the ΔA obtained will be made a standard curve Pb(II) (ΔA vs. concentration).

2.2.5. Determination of Pb(II) species in simulation liquid waste. Simulation liquid waste solution was taken 20 mL, then added 1 mL of H₂SO₄ 0.5M solution, 2 mL of dithizon solution, and 0.06 mL of resin. Then it was stirred for 20 minutes and analyzed using a UV-visible spectrophotometer with a wavelength of 483 nm and 558 nm. Then the absorbance difference is calculated from both wavelengths, namely ΔA = A₄₈₃nm – A₅₅₈nm. Where the ΔA obtained will be substituted in the equation of the calibration curve Pb(II) (ΔA vs. concentration), so that the Pb (II) species in the simulation waste are known.

2.2.6. Determination of the most effective comparison of adsorbents from coconut shells and corn cobs. Combine activated coconut shell carbon and activated corncob carbon in a row with a ratio of 1:0; 0:1; 1:1; 2:1; and 1:2 into a beaker glass containing 25 mL of Pb(II) simulated solution then input in the stirrer (stirred for 30 minutes). The solution obtained was filtered with Whatman filter paper. The resulted filtrate was taken as much as 5 mL and then diluted it until 50 mL with distilled water in the volumetric flask. Furthermore, taken 20 mL from the resulting filtrate diluted and added with 1 mL of H₂SO₄ 0.5M, 2 mL of dithizone, and 0.06 mL resin then stir it for 20 minutes. The mixture than 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). Based on, the concentration of Pb(II) in a simulated liquid waste after the Pb(II) adsorption is known. Lastly the most effective adsorbent comparisons using Fourier Transform Infra Red (FTIR).

2.2.7. Determination limit of detection (LoD). The blank solution is 20 mL. Then added 1 mL of 0.5M H₂SO₄ solution, 2 mL of dithizon solution, 0.06 mL of resin and then stirred for 20 minutes and then analyzed using solid-phase spectrophotometry with a wavelength of 483 nm - 558 nm. The absorbance difference of the two wavelengths is calculated, namely ΔA = A₄₈₃nm – A₅₅₈nm. Where the ΔA obtained will be substituted in the equation of the calibration curve Pb (II) (ΔA vs. concentration), so that the blank content is obtained. The determination of Relative Standard Deviation (RSD) was carried out to determine the limit of detection which was formulated as LoD = 3RSD. In this experiment data retrieval was repeated five times to obtain accurate results.

3. Results and Discussion

3.1. Production of activated carbon from coconut shell and corn cobs. The earliest process is dehydration, both coconut shell and corn cobs, both of which have to go through this dehydration process, this process begins with the cleaning of impurities that are still in the coconut shell and corn cobs, such impurities, sand, coconut fiber and epidermis on coconut shells, corn hair, etc. After all the ingredients are free from impurities, the next stage is washing with distilled water. Furthermore, the dehydration stage is done by heating all the ingredients in the oven to a
temperature of 100°C for 60 minutes, the purpose of the dehydration process is to remove the water content contained in the sample. After the dehydration process, the sample then enters the carbonization process. This carbonization process uses a muffle furnace, which is a device that functions to fabricate a sample with a certain temperature. Both coconut shell and corn cobs were put into the furnace at 350°C for 60 minutes. The temperature selection is based on several experiments carried out, and obtained the perfect results of drying at 350°C, because if the temperature is too high the sample coconut shell and corn cobs will run out and become ash, and vice versa when the temperature is too low, carbon will produce not perfect. After the carbonation process using this muffle furnace, the carbon obtained is ready to be activated. In this experiment activators used in both carbon were different. This is based on research journals that use different activators on different ingredients. In this research coconut shell carbon activator is ZnCl₂ 15%, and corn cobs used HCl 1M. The activation process is carried out by soaking each carbons into each activator for 24 hours.

Chemical activation in making activated carbon that is often used are KOH, ZnCl₂, and H₃PO₄. Some of these activators produce activated carbon that has a fairly large surface area with large pores. Activators that can be used in the manufacture of activated carbons, among others, strong acids, strong bases and salts of strong acids [9]. Activated carbon from coconut shell is activated using ZnCl₂. ZnCl₂ activator is a salt from strong acid namely HCl. Before activation of coconut shell carbon contains a lot of water, this is due to the hydroscopic nature and also was caused from water molecules trapped inside the hexagonal structure of carbon. Good quality activated carbons is which has lowest moisture content. The presence of water content in activated carbon can affect decrease of absorption ability. ZnCl₂ activator is a substance that is hydroscopic, so the use of ZnCl₂ as an activator will produce better activated carbon. ZnCl₂ 15% is used because ZnCl₂ in levels 15% was able to produce the highest yield with activated carbon, more effective than KOH and H₃PO₄ [10]. The process of activating corn cobs carbon is by using HCl 1M solution. Hydrochloric acid (HCl) as a chemical activator that has hydroscopic characters, so it can reduce water content in activated carbon. compared with other strong acid activators such as H₂SO₄ dan HNO₃, carbon was activated with HCl has better iodine absorption because HCl is better to reduce impurities so that more pores are formed and the absorption process becomes more maximal [11]. The activation stage in an materials that will be made as an adsorbent is very important to clean impurities in the pores and increase the surface area [12].

3.2. Determination of Pb(II) calibration curve and Pb(II) levels in simulated liquid waste

![Figure 1. Calibration curve of Pb(II) solution](image)
Based on the experimental results obtained a standard calibration curve with the equation \( y = 0.021x + 0.017 \). From this equation \( y \) is \( \Delta A \) and \( x \) is concentration. The equation is used to find the concentration of simulated liquid waste.

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

| Sample | [Pb(II)] calculation (ppb) | \( \Delta A \) | [Pb(II)] actually (ppb) |
|--------|-----------------------------|----------------|-------------------------|
| Sample Pb(II) | 50 | 0.127 | 48.87 |

From the table, we know that actually concentration of simulated waste is 48.87 part per billion. Its mean there is 48.87 μg of ions Pb\(^{2+}\) in the 1 Liter simulated waste. In the natural water, mean Lead metals maximum permissible concentration in water samples by NAFDAC, SON (2007), and WHO (2006) standards is 0.01 mg/L [13]

3.3. Determination the optimum combination of adsorbent for coconut shell and corn cob in a decrease levels of Pb(II) ions.

In the Table 2, shows the results of the contact obtained from the experiment and has been analyzed using solid-phase spectrophotometry (SPS). SPS is one type of UV-Vis instrument spectrophotometry which has the ability to analyze up to μg/L levels. The basic principle of using UV-Vis spectrophotometry is to measure the spectrum of light absorbed by a solution. Therefore, the solution to be analyzed must be sensitive to light. In simulated liquid waste samples containing heavy metal ion Pb\(^{2+}\), the color of the solution is less sensitive. Therefore, to increase the sensitivity of the solution complexing is used. The complex that is formed can later increase the sensitivity of the solution and usually form a certain color, each compound or ion has a certain complex that matches. In this experiment, diphenylthiocarbazon (dithizon) complexing was used.

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

| Composition of the mass | Final [Pb(II)] (μg/L) | Adsorbed [Pb(II)] (μg/L) | Adsorbed [Pb(II)] (%) |
|-------------------------|-----------------------|--------------------------|----------------------|
| 0 CS : 1 CC (1)         | 6.86                  | 42.00                    | 85.94                |
| 1 CS : 0 CC (2)         | 8.14                  | 40.72                    | 83.32                |
| 1 CS : 1 CC (3)         | 8.13                  | 40.73                    | 83.34                |
| 1 CS : 2 CC (4)         | 6.45                  | 42.41                    | 86.78                |
| 2 CS : 1 CC (5)         | 7.06                  | 41.80                    | 85.53                |
Based on the data research in Table 2 and the graph in Figure 2, the optimum combination mass of adsorbent to adsorb Pb(II) metal ions in the simulated liquid waste was 1:2 with adsorbed concentration was 42.41 μg/L, and the percentage of adsorbed as 86.78 %. Beside on the data shown in the ratio of comparasion 0:1 and 1:0, we known the activated carbon from corn cobs is better than activated carbon from coconut shell. But after being combined it can increase adsorption ability.

3.4. Fourier transform infrared spectra analysis.
Analysis of structure and functional groups of activated carbon can be one of the reinforcement results of the research. In this research, the functional group analysis of the adsorbent on the most optimum combination of activated carbon are before activation, after activation, and after going through the contacting process with simulation waste containing Pb²⁺ ions. The analysis was performed using Fourier Transform Infra Red (FTIR) instrument. Fourier transform infra red (FTIR) is an infrared spectrophotometer which is an instrument used to measure infrared radiation absorption at various wavelengths [14]. The working principle of FTIR is to recognize the functional group of a compound from the infrared absorbance carried out on the compound.

| wavelength (cm⁻¹) | Interpretation                           | Before Activation | After Activation | After Contacting |
|------------------|------------------------------------------|-------------------|------------------|------------------|
| 1600.02          | There is C=C aromatic                    | 1603.88           | 1604.84          |
| 1701.29          | The existence of C=O carbonyl group       | 1698.40           | 1694.54          |
| 1357.94          | The existence of C-O group               | -                 | -                |
| 2835.48          | There are C-H aldehyde                   | 2837.41           | 2836.45          |
| 2876.95          |                                           | 2900.10           | 2890.45          |
| -                | Stretching vibration O-H                | 3326.39           | 3328.31          |
| -                |                                           | 3456.59           | 3432.80          |

In the interpretation of IR spectra, it is known that the adsorbent before activation has several differences with the adsorbent after activation, especially the presence of the -OH group formed after activation. Meanwhile, the results of the adsorbent activated after and before contacting have spectra
readings that are not too much difference. In general, the three results of analysis using FTIR showed similarities in groups C=O carbonyl, C=C aromatic, and C-H aldehyde.

Based on the interpretation guide of IR spectra results, if there is a sharp absorption between 1820-1600 cm⁻¹, it can be ascertained that the sample contains a C=O carbonyl group. In the adsorbent sample before activation, this uptake appeared in spectra 1701.29, while the adsorbent after absorption activation appeared in spectra 1698.40, then on the adsorbent after absorption absorption appeared at 1694.54. Between the spectra after activation with the spectra after contacting, there is an absorption that occurs at almost the same number. This shows that there is no significant change in the C = O carbonyl group after contacting simulations.

3.5. Determination of detecting limit
An analytical instrument has a detection limit value, otherwise known as a limit of detection (LoD), which means the smallest number of analytes in a sample that can still be detected and still provide a more significant response than blank. In this research. The limit of detection (LoD) for each element was achieved as follows

$$\text{LoD} = \frac{3 \times S}{m}$$

Where S is the standard deviation of the blank readings and m represents the gradient of the calibration [6]. Limit of Detection (LoD) from the instrument (solid-phase spectrophotometry) was 0.06 µg/L, so it can be said that the sample at a concentration of 0.06 µg/L can be read. In the another instrument for examples. at atomic absorption spectroscopy (AAS) instruments had LoD of 0.290 µg/L and UV-Vis (HACH DR 5000 UV-Vis Spectrophotometer) is 3-300 µg/L [15][16].

So that the solid-phase spectrophotometry is a sensitive and effective method to use in the analysis the decreased levels of Pb(II) adsorption results of activated carbon from coconut shell and corn cob in levels µg/L. Moreover on the previous research. solid-phase spectrophotometry had a limit of detection (LoD) until 0.014 µg/L [17].

4. Conclusion
The results showed that the adsorbent combination between activated carbon from coconut shell and corn cob can increase the capabilities and effectiveness of the absorption to adsorb Pb(II) ion in the simulations waste and the most optimum ratio from the comparison between coconut shell and corn cob is a ratio of 1:2 with the absorption ability to adsorb Pb(II) ion in the simulations waste is 86.78%. Solid-phase spectrophotometry is an effective method with high sensitivity in the level of detection up to µg/L. be marked from the limit of detection (LoD) of this research until 0.06 µg/L.

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