Adsorption of Pb (II) ions by activated and modified candlenut shell based carbon

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Abstract. A research on the adsorption of Pb2+ ions by candlenut shell carbon that was activated with 10% ZnCl2 and then modified with HNO3 has been done. The candlenut shell was carbonized at 400°C before activation and surface modification. Characterization of the carbon was carried out by surface area test using methylene blue method, identification of functional groups using Fourier Transform Infrared (FTIR) and adsorption experiment at optimum condition. The concentration of Pb (II) ions was determined by Atomic Absorption Spectrophotometer (AAS). Surface area of carbon, activated carbon and modified activated carbon are 503.57 m²/g, 516.63 m²/g and 524.86 m²/g, respectively. Boehm titration and FTIR analysis results showed that functional groups such as -OH (in carboxylic acid and phenol) and C=O (in lactone) increased after modification with HNO3. Based on analysis using AAS, the optimum adsorption time was 30 minutes and the optimum pH was 4. The adsorption capacity of Pb2+ ions by modified activated carbon was higher than un-modified activated carbon.

1. Introduction
Industry in Indonesia is currently growing quite rapidly, this is marked by the increasing number of industries that produce various types of human needs such as textile, paper industry, etc. The increase in the number of industries causes by-products in the form of more wastes. One of the wastes produced is heavy metal waste which will cause pollution to the environment, if the content of heavy metals in it exceeds the threshold and causes serious problems for humans [1].

One of the metals that is harmful to humans that pollute the waters is lead metal. The main source of entry of lead in waters is industrial waste such as battery, cable, paint or dye, ceramic and exhaust gas industries [2]. The accumulation of lead metal in the body can result in chronic poisoning. The maximum level of lead metal in WHO-recommended waters is less than 0.01 ppm [3]. The effects on human health can cause brain damage, convulsions, and death. Therefore, efforts are needed to anticipate the occurrence of lead metal pollution in the waters.

The adsorption process is one of the waste treatment techniques which is expected to be used to reduce excessive metal concentration. One of the adsorbents that are often used in the adsorption process is activated carbon. Activated carbon is chosen because it has a large surface area, large adsorption capabilities, easy to apply and the costs required are relatively cheaper [4].

Several studies have been conducted to look for the possibility of producing inexpensive activated carbon. Activated carbon preparation, especially from natural resources, is attracting attention now. Activated carbon from biomass wastes can be made from various sources that exist in nature such as coconut shells, coffee bean shells, corn cobs, sugarcane milling grounds, rice husks, sawdust,
hardwoods, coal, oil palm shells, candlenut shells, etc. [5]. To the best of our knowledge, there are only few literatures found related to the preparation and application of candlenut shell carbon [6; CO₂ activation] and [7 H₃PO₄ activation].

In this study, fabrication of candlenut shell (Alleurites mollucana) carbon was carried out. The carbon was activated with ZnCl₂ and then modified with nitric acid. The activated carbon was used as an adsorbent for Pb²⁺ ions. The effect of pH, time and concentration on the adsorption of Pb²⁺ metal ions are discussed.

2. Materials and Methods

2.1. Materials
The materials used in this study were candlenut shell, 65% HNO₃, Pb(NO₃)₂, 0.05N NaOH, 0.05N NaHCO₃, 0.05N Na₂CO₃, 0.05N HCl, ZnCl₂ 10%, methylene blue, aquadest, aquabidest, Whatman filter paper number 42, pH meter.

2.2. Methods
Dry and clean candlenut shell is weighed as much as 100 grams and put in a porcelain dish and then carbonized in the furnace for 1 hour at 400°C. This process produces carbon shells. The carbon obtained is cooled in a desiccator, crushed, and sieved with a 100 mesh sieve.

The carbon which is free of silica is then activated using ZnCl₂ 10%. Carbon is added with 10% ZnCl₂ solution with a ratio of 1:5 and then stirred. Container containing the mixture was then tightly closed using aluminum foil and left for 24 hours. The solution was then filtered using a Buchner funnel. The carbon produced is washed with distilled water to a neutral pH and is dried in the oven at 110°C then cooled in a desiccator.

Activated carbon is mixed with a 65% HNO₃ oxidizing solution, each with a ratio of 5:1 (mL of chemical: grams of activated carbon) heated to a temperature of 65°C then stirred at a constant rate (130 rpm) for 24 hours. After that, the carbon is washed with distilled water repeatedly until the pH is neutral. Then the carbon is dried in the oven for 24 hours at 110°C. The functional groups of modified carbon were then analyzed using FTIR.

A total of 0.25 g of activated carbon was put into four 25-mL volumetric flasks, each containing Na₂CO₃ 0.05 N, 0.05 N NaHCO₃, NaOH 0.05 N and 0.05 N HCl and then the mixture allowed to stand for 24 hours. After that, the solution was separated from the carbon by decantation. The separated solution, each taken 5 mL of Na₂CO₃, NaHCO₃ and NaOH solution, then added PP indicator, added excess HCl, then reversed using 0.05 N NaOH solution and for HCl solution was taken as much as 5 mL, added MM indicator and added excess NaOH, then titrated back using 0.05 N HCl.

Determination of carbon surface area was carried out based on the ability of carbon in methylene blue adsorption. The amount of adsorbed methylene blue is proportional to the surface area of adsorbent as shown in the following formula:

\[ S = \frac{X_m N_a}{M} \]  

where S is surface area (m²/g), N is Avogadro’s number (6.02 x 10²³ mol⁻¹), Xm is fractional coverage (g/g), a is coverage by 1 molecule MB (197 x 10⁻²⁰ m²), and M is molecular weight of MB (320.5 g/mole).

2.3. Determination of Optimum Adsorption Condition
The modified activated carbon is added as much as 0.1 gram into Erlenmeyer containing 50 mL of Pb²⁺ 50 mg/L. The mixture is stirred with a magnetic stirrer for 10 minutes then filtered. Absorbance of the filtrate was measured using an atomic absorption spectrophotometer. Experiments were repeated with variations in stirring time, respectively in 30, 60, 90 and 160 minutes.

The modified activated carbon is added as much as 0.1 gram into Erlenmeyer containing 50 mL of Pb²⁺ 50 mg/L. Then the mixture is stirred with a magnetic stirrer during optimum time with a variation
of pH 2, 3, 4, 5, and 6. The mixture is filtered using a vacuum filter with Whatman 42 filter paper. Absorbance of the filtrate is measured using an atomic absorption spectrophotometer.

Activated carbon which has been modified with nitric acid is added as much as 0.1 gram into Erlenmeyer containing 50 mL of Pb²⁺ solution with variations in concentrations of 50, 100, 150, 200 and 250 mg.L⁻¹. Then the mixture is stirred with a magnetic stirrer during the optimum time at optimum pH. Then the mixture was filtered using a vacuum filter with Whatman 42 filter paper. Absorbance of the filtrate was measured using an Atomic Absorption Spectrophotometer.

3. Results and Discussions

3.1. Characterization with FTIR, Boehm Titration and MB method

Table 1 shows the comparison of absorption band wave numbers of KTK (Candlenut Shell Carbon), KATK (Candlenut Shell Activated Carbon) and KATKM (Modified Candlenut Shell Activated Carbon). The activated carbon of the candlenut shell modified by HNO₃ has increased the number of carboxyl group (C = O) which is known to help absorb heavy metal ions. The presence of CO and OH bonds shows that the surface of KATKM tends to be polar.

| Functional groups   | Range of wave number(cm⁻¹) | Wave number (cm⁻¹) |
|---------------------|-----------------------------|--------------------|
|                     | KTK                         | KATK               | KATKM              |
| OH (carboxylic acid) | 3200-3500                   | 3417.86            | 3417.86            | 3417.86            |
| C=O (lactone)       | 1665-1760                   | -                  | -                  | 1722.43            |
| C=O (quinone)       | 1590-1640                   | 1598.99            | 1597.06            | 1616.35            |
| Aromatic            | 1425-1600                   | 1425.40            | 1425.40            | 1533.41            |
| C-O (lactone)       | 1370-1160                   | -                  | -                  | 1344.38            |
| C-O (phenol)        | 1000-1400                   | 1199.7             | 1197.79            | 1238.3             |
| M-CH₃               | 700-900                     | 873.75             | 873.75             | -                  |

Based on the results of Boehm titration shown in Figure 1, the concentration of the acid group namely carboxylic, lactone and phenol increased after modification, while the base group decreased. This condition indicates that the surface of the activated carbon follows the Lewis type and is related to electron-rich bonds in the carbon layer. This is consistent with the fact that an increase in oxygen groups causes a decrease in electron density on the surface of activated carbon thereby reducing the alkaline nature of activated carbon [8, 9].

![Figure 1. Results of functional group analysis with the Boehm titration method](image-url)
The surface area in Figure 2 of the candlenut shell carbon increased after being activated with a 10% ZnCl₂ solution which was from 503.57 m²/g to 516.63 m²/g. This shows that the activation process with ZnCl₂ 10% can remove impurities attached to the carbon surface. The surface area of the modified HNO₃ activated carbon also increased to 524.86 m²/g. This finding is also supported by our previous work on the same candlenut shell, but different activator [7]. This proves that modification with HNO₃ can increase the surface area of carbon. Nitric acid is a strong oxidant and can increase the number of oxygen-containing functional groups on the carbon surface [10] and finally increase the carbon surface area [7, 11-12].

3.2. Determination Optimum Adsorption Conditions of Pb (II) Ions

The contact time of modified activated carbon in Figure 3 with metal ion Pb²⁺ continued to increase until it reached the optimum contact time at 30 minutes with the number of metal ions adsorbed is 24.5 mg/g. The number of adsorbed metal ions then decreases at contact time of 60, 90 and 120 minutes. At the contact time of 10 minutes, not all surfaces and functional groups on carbon work optimally, but the activated carbon becomes saturated at the contact time of 30 minutes. Contact time at 60, 90 and 120 minutes, the number of metal ions adsorbed slowly decreases. This is the opposite by the saturation of the surface that has been achieved, resulting in a decrease in the activated carbon adsorption power.

The number of adsorbed Pb²⁺ ions increases with an increase in pH from 2 to 3, and reaches the maximum value at pH 4 which is 24.69 mg/g as shown in Figure 4. The amount of metal ions adsorbed then decreases at pH 5 and 6. At pH 2 and 3 the concentration of H⁺ is high so that the active group in the positively charged carbon which results in a rejecting resistance with Pb²⁺ ions so that the number of ions adsorbed is small. As the pH increases, the adsorption increases because the concentration of H⁺ decreases. However, if the pH of the solution is high, the adsorption power will slowly decrease due to the formation of Pb(OH)₃ deposits on the carbon surface that cover the pore so that the interaction between carbon and metal ions is not optimal.

![Figure 3. Effect of contact time on the number of Pb (II) metal ions adsorbed by modified candlenut shell carbon.](image)
Figure 4. Effect of pH on the number of metal ions of Pb (II) adsorbed by modified candlenut shell carbon

Figure 5. Effect of metal ion concentration Pb (II) on the number of metal ions of Pb (II) adsorbed by modified activated carbon of candlenut shell

Figure 5 shows the effect of the concentration of Pb (II) ions on the number of adsorbed ions. The greater the concentration of Pb (II) ions, the lower the Pb (II) ion adsorbed by KATKM. This can be explained because of the fact that the greater the concentration of a solution, the more the number of substances that can be absorbed before the adsorption equilibrium is obtained.

The value of the correlation coefficient ($R^2$) of the adsorption of metal ions Pb$^{2+}$ by KATKM tends to follow Freundlich isothermal adsorption and isothermal Langmuir adsorption with the value $R^2 = 0.999$ which means that adsorption occurs physically where adsorption occurs on heterogeneous carbon surfaces. The value of adsorption capacity ($Q_o$) of KATKM from Langmuir isothermal is 2.41 mg/g, while the value of adsorption capacity ($k$) of Freundlich isothermal is 0.009 mg/g. While the value of the correlation coefficient ($R^2$) of the adsorption of metal ions Pb$^{2+}$ by KATKM tends to follow the isothermal Langmuir adsorption with $R^2 = 0.989$ and isothermal Freundlich adsorption which means that adsorption occurs chemically where adsorption occurs on a homogeneous surface and all active groups in KATKM are filled with adsorbates forming monolayers. The adsorption capacity ($Q_o$) of KATKM from Langmuir isothermal is 125.00 mg/g, while the value of adsorption capacity ($k$) of Freundlich isothermal is 48.64 mg/g. The analysis results can be seen in Figures 6(a) and 6(b).
3.3. FTIR Analysis After Adsorption of Pb (II) Ions

From the results of the analysis with FTIR, it can be seen that the shift in absorption band and the change in peak intensity at KATKM (before adsorption) with KATKMA (after adsorption). The absorption band at wave number 1616.35 which is a C = O group from quinone has increased peak intensity and shifts wave number to 1597.06 after adsorption which shows the role of C = O group of quinones in binding Pb²⁺ ions. This is in accordance with the HSAB theory that the Pb²⁺ ion is a borderline acid group which is able to bind to weak bases or strong bases, while the C = O group is a weak base.

4. Conclusions

The surface area of candlenut shell carbon surface after activation with 10% ZnCl₂, and HNO₃ modified shell activated carbon are 503.57; 516.63; and 524.86 m²/g, respectively. The optimum condition of adsorption of Pb²⁺ ions by HNO₃ modified candlenut shell activated carbon occurred at the optimum time of 30 minutes with optimum pH 4. C = O (quinone) groups showed an influence in the adsorption of Pb²⁺ ions. The adsorption capacity of Pb²⁺ ions by HNO₃ modified activated carbon is greater than that of activated carbon before modification.

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