Adsorption of chromium ions by candlenut shell based carbon activated with H₃PO₄

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Abstract. Candlenut shell based carbon which was chemically activated using a solution of phosphoric acid and modified with nitric acid has been used to adsorb chromium ions (Cr(VI)). This study aims to examine the effect of phosphoric acid activation on the surface area of the candlenut shell carbon and the effect of nitric acid on the adsorption capacity of metal ions Cr(VI). The study was carried out by activating the candlenut carbon with 10% phosphoric acid for 24 hours then modified with 6 N nitric acid for 24 hours. The activated carbon that has been modified is then optimized with several parameters, namely time, pH and the number of adsorbents to maximize the performance of activated carbon. The surface area of candlenut based activated carbon was determined by methylene blue method and the adsorption capacity was measured using Atomic Absorption Spectrophotometer (AAS). The results showed that the carbon surface area before and after activation increased from 1557.3 m²/g to 1669.5 m²/g, respectively, and the surface area increased dramatically after HNO₃ modification to 2090.8 m²/g. The adsorption capacity to the metal ions (Cr(VI)) tends to follow the Langmuir isotherm model which is equal to 20.4 mg/g.

1. Introduction
Activated carbon can be made from all carbon-containing materials, provided that the material has a porous structure. The adsorption capacity of activated carbon is due to the presence of very large numbers of micropores, which results in adsorption performance. Activated carbon is composed by C atoms that are covalently bound in a flat hexagonal lattice with one C atom at each angle whose surface area ranges from 300-3500 m²/g and this is related to the pore structure so that it has the properties as an adsorbent [1].

Activated carbon preparation is carried out in several stages. The first stage is the formation of carbon and the second stage is the activation process to remove hydrocarbons that line the surface of the carbon so that the porosity of charcoal increases. Chemical activation in the production of activated carbon using KOH, ZnCl₂, and H₃PO₄ has been used very often to produce activated carbon which has a large surface to absorb and large pores [2].

Generally, activated carbon is widely used as an adsorbent for impurities contained in water and used commercially in the industrial world [3]. Heavy metal ions: Cr(VI) is a toxic metal with very difficult handling compared to other toxic metals, one of them is by removing hazardous metals before being discharged into the environment so that pollution by toxic metals can be minimized. Chrome separation method can be done by reduction, ion exchange, adsorption using activated carbon, electrolysis, reverse osmosis, and filtration membrane. One efficient and inexpensive effort to reduce metal content in the waters is by the adsorption system [1].
Improvement of surface properties of biomass waste carbons might be a realistic and favorable way to enhance their chemical functionalities toward many utilizations of these materials. A modified biomass carbon containing various functional groups could be used for many applications such as heavy metals adsorption from aqueous and non-aqueous solutions, catalyst, toxic and radiolytic effluents treatment from industrial processes, and energy storage [4, 5].

Candlenut shell are indeed an organic waste that can be decomposed but with a fairly hard texture, it takes time to decompose them naturally so that various efforts are made to utilize candlenut shell waste. The use of candlenut shell waste is intended to reduce waste accumulation, it is also expected to produce products that are safe and environmentally friendly. By paying attention to these environmental factors, the candlenut shell can be used as a raw material for activated carbon preparation [3].

Candlenut (*Aleurites moluccana*) is a plant that belongs to the Euphorbiaceae family which can grow at an altitude of 0-1200 above sea level. Candlenut has many benefits including: for cooking spices, industrial raw materials, household furniture, firewood, matches and raw materials for making pulp (paper-making materials). Meanwhile, the candlenut shell is used by the community as fuel and ashes as fertilizer. Candlenut shell is still a waste and has not been managed as much as a material that is beneficial to the community. To our knowledge, there are only two literatures related to utilization of candlenut shell carbon [6, 7].

Adsorption is a selective process of separation of a component or impurity contained in a fluid by contacting the fluid with adsorbent solids. The adsorption process is influenced by several factors including system pH, the adsorbent mass ratio with adsorbate, adsorption temperature, adsorption time, adsorbate concentration. In order for the high adsorption power to be obtained, the optimum conditions for the adsorption process need to be determined first, for example determining the optimum pH and time of adsorption. In this study, Cr (VI) ions was removed using candlenut shell based carbon which was activated and also modified.

2. Materials and Methods

2.1. Materials

Candlenut shell, aquadest, H₃PO₄ 10%, HNO₃ 6N, NaOH 0.05N, Na₂CO₃ 0.05N, NaHCO₃ 0.05N, 0.05N HCl, 0.05N NaOH, Whatman filter paper 42, aluminum foil, universal pH paper, MM indicator, PP indicator and tissue roll.

2.2. Methods

The samples of the candlenut shell were washed thoroughly and split into small pieces. Furthermore, it was dried under the sun.

Candlenut shell samples were cleaned and dried, and then put in a porcelain dish and heated in a furnace at 600°C for 1 hour. This process will produce a carbon of candlenut shell. After carbonization, the resulting carbon is then cooled, smoothed, then sieved with a size of 100 mesh.

Candlenut shell carbons were soaked with activator solution of H₃PO₄ 10% by volume ratio H₃PO₄/carbon mass of 6:1 for a 24 hour soaking time. Then the candlenut shell carbon is filtered using a Buchner funnel and washed with distilled water until a neutral pH. Samples were dried in an oven at 110 °C for 6 hour. Activated carbon of candlenut is cooled in desiccators [12].

Activated carbons are mixed with a chemical agent HNO₃ 6 N, with a mass ratio of 5:1 (volume: active carbon mass), then shaken at a constant rate (130 oscillations per minute) for 24 hours. Afterwards washing with aquadest until the pH is neutral, the samples were then dried in the oven for 6 hours at 110 °C.

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A total of 0.25 g of activated carbon was put into four 25-mL volumetric flask, 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 [8]. The amount of adsorbed methylene blue is proportional to the surface area of adsorbent as shown in the following formula:

\[
S = \frac{2aN Xm}{M}
\]

where \( S \) is surface area (m\(^2\)/g), \( N \) is Avogadro’s number (6.02 x 10\(^{23}\) mol\(^{-1}\)), \( Xm \) is fractional coverage (g/g), \( a \) is coverage by 1 molecule MB (197 x 10\(^{-20}\) m\(^2\)), and \( M \) is molecular weight of MB (320.5 g/mole).

2.3. Determination of Optimum Adsorption Condition
Activated carbon which has been modified with nitric acid is taken as much as 0.1 gram into Erlenmeyer containing 50 mL of Cr (VI) 50 mg. L\(^{-1}\). Adsorption procedure can be found elsewhere [9]. The mixture is stirred with a magnetic stirrer for 10 minutes then filtered. The absorbance of the filtrate was measured using SSA. The experiment was repeated with variations in stirring time 5, 10, 15, 20, 40, 80, 100, 180, 240 and 300 minutes, respectively.

Activated carbon which has been modified with nitric acid is taken as much as 0.1 gram into Erlenmeyer containing 50 mL of Cr (VI) 50 mg. L\(^{-1}\). Then the acidity of the solution is adjusted to pH 5. Then the mixture is stirred with a magnetic stirrer during the optimum time. The mixture was filtered using a vacuum filter with Whatman 42 filter paper. The absorbance of the filtrate was measured using SSA. Experiments were repeated with variations in pH 6, 7, 8 and 9.

Activated carbon which has been modified with nitric acid is taken as much as 0.1 gram into Erlenmeyer containing 50 mL of Cr (VI) 20 mg.L\(^{-1}\). Then the acidity of the solution is adjusted to optimum pH. Then the mixture is stirred with a magnetic stirrer during the optimum time. The mixture was filtered using a vacuum filter with Whatman 42 filter paper. The absorbance of the filtrate was measured using SSA. The experiment was repeated with variations in the number of adsorbents 0.2; 0.3; 0.4; 0.5; 0.6 and 0.7 gram.

Activated carbon which has been modified with nitric acid is added as much as 0.1 gram into Erlenmeyer containing 50 mL of Cr (VI) solution with concentrations of 50, 100, 150, 200 and 250 mg.L\(^{-1}\). Then the acidity of the solution is adjusted to optimum pH. Then the mixture is stirred with a magnetic stirrer during the optimum time. Then the mixture was filtered using a vacuum filter with Whatman 42 filter paper. The absorbance of the filtrate was measured using SSA.

3. Results and Discussions
3.1. Modification of the Activated Carbon Surface of Candlenut Shell
Modification of the surface of activated carbon with HNO3 is done to increase the group containing oxygen. The presence of this group on the carbon surface can increase the hydrophilicity of the carbon which supports the absorption of electrolyte ions into the pores of the carbon and can give the effect of pseudocapacitance.

The presence of oxygen-containing functional groups is determined by FTIR analysis as shown in Table 1 and chemical characterization by the Boehm titration method shown in Figure 1.
Table 1. Wave number of FTIR spectrum of (a) candlenut shell carbon, (b) candlenut shell activated carbon, (c) HNO₃ modified activated carbon and (d) Modified activated carbon after adsorption of metal ions Cr (VI)

| Functional groups | Wave frequency | a     | b     | c     | D     |
|-------------------|----------------|-------|-------|-------|-------|
| OH (Carboxylic)   | 3200-3500      | 3417.86 | 3414  | 3415.93 | 3417.86 |
| C=O (Lactone)     | 1665-1760      | -     | -     | -     | -     |
| C=O (Quinone)     | 1590-1640      | 1591.27 | 1595.13 | 1614.42 | 1614.42 |
| Aromatic          | 1425-1600      | 1427.32 | 1436.97 | 1525.69 | 1519.91 |
| C-O (Lactone)     | 1370-1160      | -     | -     | -     | -     |
| C-O (Phenol)      | 1000-1400      | 1026.13 | 1026.13 | 1118.71 | 1338.6  |

Boehm titration explains that NaHCO₃ can neutralize the carboxyl group, Na₂CO₃ can neutralize the carboxyl and lactone groups, NaOH can neutralize the carboxyl group, lactone and phenol, and HCl can neutralize the total base group. In this study, there was an increase in acidic functional groups in KATK (Candlenut Shell Activated Carbon) and KATKM (Modified Candlenut Shell Activated Carbon) because of the presence of H₃PO₄ activators which can oxidize the carbon surface.

Whereas for the determination of base groups, on the surface of the candlenut shell carbon, is obtained around 1.4456 meq/gram. After activation with H₃PO₄, the base group level becomes 0. This is because the activator used can reduce or eliminate basic functional groups found on the carbon surface [10].

Figure 1. Functional group analysis diagram with the Boehm titration method

Figure 2. Graph of surface area by methylene blue method
The surface area of the candlenut carbon has increased after activation with a 10% H₃PO₄ solution of 1557.3 m²/g to 1669.5 m²/g, as shown in Figure 2. This shows that the activation process can increase the functional group of the candlenut shell carbon to remove impurities attached to the carbon surface. The surface area of activated carbon also increased after the modification process was carried out using HNO₃ 6 N, which was 2090.8 m²/g. This shows that modification using HNO₃ can increase the surface area of the candlenut shell carbon [10].

3.2. Optimization of Adsorption Conditions of Cr (VI) Ions

Figure 3a shows that the contact time is 5 to 20 minutes, the adsorption capacity of modified activated carbon is still increasing. The optimum contact time for modified activated carbon adsorbing Cr (VI) metal ions was 40 minutes with the number of metal ions adsorbed at 3.7216 mg/g. When contacting 80 to 300 minutes the number of adsorbed metal ions decreases. This is because the balance of adsorption has been achieved or the adsorbent is damaged with long contact time.

The number of adsorbed Cr (VI) ions increases from pH 5 to pH 6, which reaches a maximum value of 4.8997 mg/g as shown in Figure 3b. At pH 5 the concentration of H⁺ is high so that the active group on carbon is positively charged so that it refuses to resist with Cr (VI) ions so that the number of ions adsorbed is low. The optimum pH of the modified activated carbon adsorbs Cr (VI) metal ions is pH 6 because at pH 6 Cr (VI) will be stable. However, if the pH of the solution increases, namely pH 7 to pH 9, the adsorption power will slowly decrease due to the formation of Cr(OH)₃ deposits on the carbon surface which cover the pore so that the interaction between carbon and metal ions Cr(VI) is not optimal [11].

![Figure 3a](image1.png) ![Figure 3b](image2.png) ![Figure 3c](image3.png)

**Figure 3.** Effect of (a) contact time, (b) pH and (c) Cr (VI) concentration on the number of Cr (VI) metal ions adsorbed by the modified activated carbon of the candlenut shell.

Figure 3c shows the effect of the concentration of Cr (VI) ions on the number of adsorbed ions. The greater the concentration of Cr (VI) ions, the greater the Cr (VI) 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.
Candlenut shell activated carbon (KATKM) which has been adsorbed is then determined its adsorption capacity. In this study, we are using the isothermal adsorption method, namely the Langmuir isothermal model and Freundlich isothermal. The graph of the Langmuir isothermal model is made by linking the linear $C_e$ curve to $C_e/q_e$, while the graph of the Freundlich isothermal model is made by connecting the linear log $C_e$ curve to log $q_e$. The results of chart mapping can be seen in Figures 4(a) and 4(b).

![Figure 4. (a) Langmuir isothermal linear curve; (b) Freundlich isothermal linear curve](image)

The results of the Langmuir and Freundlich isothermal equations can be seen in the linearity line where the value of $R^2$ in Langmuir isothermal is 0.966 and the price of $R^2$ in Freundlich isotherm is 0.958. The coefficient value of the current adsorption study tends to follow the isothermal Langmuir adsorption model with $R^2 = 0.966$ and the adsorption capacity value is 20.4081 mg/g.

4. Conclusions
The conclusion of the current study is the candlenut shell carbon surface area is 1557.3 m$^2$/g, the candlenut shell carbon after activation with 10% $\text{H}_3\text{PO}_4$ is 1669.5 m$^2$/g and the $\text{HNO}_3$ modified candlenut shell activated carbon is 2090.8 m$^2$/g. The optimum adsorption condition of Cr (VI) ion by $\text{HNO}_3$ modified candlenut shell activated carbon occurred at 40 minutes and pH 6. The adsorption capacity of Cr (VI) ions by $\text{HNO}_3$ modified candlenut shell activated carbon was more likely to follow the Langmuir isotherm model with $R^2$ value of 0.966 and adsorption capacity value is 20.4081 mg/g.

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