The Effect of Activators Against the Ability of Active Charcoal from Nila Fish (*Oreochromis niloticus*) to Adsorb Cd(II) and Pb(II) Ions

M. T. Santi*, I. Banihabib, M. Isnaningrum, and I. B. Miranda
Department of Chemistry Education, Universitas Negeri Yogyakarta

**ABSTRACT**

The purpose of this research is to how to make the active charcoal of Nila fishbone and to know effect of the variety activators against the ability of charcoal from nila fishbone waste in absorbing Cd(II) and Pb(II) ions. This research included in the experimental research. Active charcoal making process through 5 stages, namely: sampling, sample processing, the process of carbonation, the activator, and the process of neutralization. Sampling (Nila fishbone) in the restaurant, sample processing in the form of a fishbone drying in the sunshine, the process of carbonation by injecting bone for the furnace and sifted using a mess. The process of with activator HNO$_3$ and HCl, also neutralization by making active charcoal to a neutral pH. Then, specify a contact time of 30, 60, and 90 minutes. The filtrate is further tested by Atomic Absorption Spectrophotometer (AAS) tool to know the adsorption of lead and cadmium ions. The result shows effect of HCl activator on Cd$^{2+}$ and Pb$^{2+}$ ions is more effective than HNO$_3$ activator.

**Keyword:** active charcoal, bonefish, Nila, Cd(II) ion, Pb(II) ion

1. **INTRODUCTION**

   The growth of industrial production in Indonesia increase and decrease. This is proven by the data of the Central Bureau of statistics of the year 2018 stated that production growth in large and medium manufacturing industry in the first quarter, rising as much as 5.01%. One of the impacts of industrial world grew is heavy metal pollution. Heavy metals are the chemical elements with a heavy type 5 gr/cm$^3$. Some of the heavy metals that can pollute the environment is Fe, Cd, Cu, and Pb (Palar, 2008).

   Cadmium (Cd) is one of the types of dangerous heavy metals because this element of risk to health. Cd includes the non essential metals are very dangerous when found in high concentrations in the environment (soil, water, and air). This is because the metal has damage body tissues of living beings (Darmono, 1995).

   Lead metal (Pb) found in foods, namely mineral water, agricultural water and milk. Based on testing some samples of milk contains 95% lead (Dorabei, Darbandsari, Moghimi, Tehrani, & Nazerdeylami, 2016). Testing samples of lead ions present in water contains 0, 0859mg/L, river water contains 0,0929mg/L, and DI contains 0.0023 mg/L lead (Ehfaed, et al., 2018). Lead can also cause a variety of harmful disease or even death. Other impacts of lead, is poisoning. Lead poisoning causes hypertension and liver disease.
Therefore, heavy metals Cd and Pb which pollute the environment need for efforts to reduce or eliminate. One way with adsorption (Beyki & Shmirani, 2015). Materials that can be attached to heavy metals such as activated carbon, biomass, clay, stone, rock, zeolite and bentonite. In addition, materials that have a hydroxyl group (-OH). A hydroxyl group is in hydroxyapatite (Lokapuspita, Hayati, & Purwanto, 2012). Fishbone is composed of collagen and contains 60-70% inorganic substance in the form of calcium phosphate and hydroxyapatite. Therefore, nila fishbone can be used as adsorption of heavy metals.

Adsorption capacity of charcoal from nila fishbone waste can be enhanced with activation. Activation can be done by using a high-temperature warming or the addition of a chemical solution. Previous research about application of active charcoal test shell aren, activated HCl and active charcoal test durian skin activated HNO₃ can be attached to heavy metals (Lestari, 2014; Lestari & Sunarto, 2015).

Based on explanation above, then researchers would know how the effect of variety activators against the ability of charcoal from nila fish waste (Oreochromis Niloticus) to adsorption Pb(II) and Cd(II) ions.

2. RESEARCH METHOD

This research is a quantitave research that aims to know the effect of variety activators against the ability of charcoal from nila fish waste (Oreochromis niloticus) to adsorption Pb(II) and Cd(II) ions. The subject of the research is active charcoal from nila fish waste. The object of this research is the metal ions of Pb(II) and Cd(II).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Activator</th>
<th>Time contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>HCl</td>
<td>30 60 90</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>30 60 90</td>
</tr>
<tr>
<td>Pb</td>
<td>HCl</td>
<td>30 60 90</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>30 60 90</td>
</tr>
</tbody>
</table>

2.1 Materials

The materials needed in this research was nila fishbone, PbNO₃ solution, CdSO₄, 1 M HNO₃ solution, 1 M HCl solution, aquades, filter paper, and aluminium foil.

2.2 Tools

The tools used in this research is atomic absorption spectrophotometer (AAS), furnace, sieving, Buchner funnel, pH-meter, glass cylinders, erlenmeyer, beaker glass, magnetic stirrer, dropper glass pipette, porcelain evaporating dish, mortal and bowl.

2.3 Procedures

The Sampling and processing of samples

The sampling samples used was nila fishbone waste have been through the process of ripening, are taken from a restaurant in Yogyakarta city and processing of samples is carried out by nila fishbone separated with his flesh, wasted clean, and then dread in the sun.

The process of Carbonation

Carbonation process is carried out by nila fishbone have dried up and put in porcelain evaporating dish, porcelain evaporating dish put in a furnace at temperature of 300 ° C for 2 hours, let stand for 1 hour until charcoal of nila fishbone cool, charcoal crushed and sifted.
The process of Activator
A 10 grams of charcoal put in 20 mL of 1 M HNO₃ solution, let stand for 20 hours, charcoal separated from the filtrate using a Buchner funnel, repeat steps a – c for 1M HCl solution.

The process of Neutralization
The charcoal that has been activated by using HNO₃ solution filtered using a buchner funnel, active charcoal washed with aquades, then the filtrate in the taken to measure pH used pH-meter, measurement of pH of the filtrate done until neutral pH (pH = 7), active charcoal with neutral pH using oven dried at a temperature of 100 °C for 30 minutes, repeat steps a – e for 1M HCl solution, and active charcoal ready to use.

Determination of the Time of contact
An active charcoal which is already activated by activator reagent weighed as much as 0.5 grams, put in 50 mL erlenmeyer and then added PbNO₃ solution at room temperature and pH 7 or neutral, repeat steps a and b for CdSO₄ solution, then stirred using magnetic stirrer with a constant rotation speed variation of the contact time of 30, 60 and 90 minutes, after it is filtered using the filter paper and the filtrate produced accommodated, and the filtrate is analyzed using atomic absorption spectrophotometer (AAS).

2.4 Data analysis techniques
Data analysis was conducted to determine the influence of the variation of active charcoal contact against adsorption of heavy metals Cd and Pb. Data obtained through test on atomic absorption spectrophotometer (AAS). Then analysed with Langmuir equation.

3. RESULTS AND DISCUSSION
Quantitative analysis of data from the adsorption ion Pb(II) and Cd(II) with active charcoal from nila fishbone on a wide variety of contact time obtained, the results that the contact time of the active charcoal with HNO₃ and HCl activator effect on the abundance of Pb(II) ions and Cd(II) the adsorbed. Based on tests using Atomic Absorption Spectrophotometer (AAS), the levels of Pb(II) and Cd (II) ions and using the langmuir adsorption isotherm test calculations obtained the following data.

3.1. Adsorption of Pb²⁺ ions with the HCl Activator
The adsorption data of Pb²⁺ ions by active charcoal from Nila fishbone (Oreochromis niloticus) and HCl activator is presented in Table 2.

<table>
<thead>
<tr>
<th>Contact Time (minute)</th>
<th>Pb²⁺ content early (ppm)</th>
<th>The rate of Pb²⁺ after adsorption process (ppm)</th>
<th>Adsorbed Pb²⁺ content (ppm)</th>
<th>The amount of material adsorbed (mg)</th>
<th>Weight of adsorbent (g)</th>
<th>X/m</th>
<th>C/(X/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>40.886</td>
<td>0.060</td>
<td>40.825</td>
<td>2.041285</td>
<td>0.5</td>
<td>4.082570</td>
<td>0.014770</td>
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<td>0.065</td>
<td>40.820</td>
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<td>4.086300</td>
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The retrieved graph relationships between C/(X/m) Pb²⁺ ion levels against after the adsorption process (chemical equilibrium) as shown in Figure 1.
3.2. Adsorption of Cd$^{2+}$ ions with the HCl Activator

The adsorption data of Cd$^{2+}$ ions by active charcoal from Nila fishbone (Oreochromis niloticus) and HCl activator is presented in Table 3.

<table>
<thead>
<tr>
<th>Contact Time (minute)</th>
<th>Cd$^{2+}$ content early (ppm)</th>
<th>The rate of Cd$^{2+}$ after adsorption process (ppm)</th>
<th>Adsorbed Cd$^{2+}$ content (ppm)</th>
<th>The amount of material adsorbat (mg)</th>
<th>Weight of adsorbent (g)</th>
<th>X/m</th>
<th>C/(X/m)</th>
</tr>
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<tbody>
<tr>
<td>30</td>
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</table>

The retrieved graph relationships between C/(X/m) Cd$^{2+}$ ion levels against after the adsorption process (chemical equilibrium) as shown in Figure 2.
3.3. Adsorption of Pb\textsuperscript{2+} ions with the HNO\textsubscript{3} Activator

The adsorption data Pb\textsuperscript{2+} ions by active charcoal from Nila fishbone (Oreochromis niloticus) and HNO\textsubscript{3} activator is presented in Table 4.

<table>
<thead>
<tr>
<th>Contact Time (minute)</th>
<th>Pb\textsuperscript{2+} content early (ppm)</th>
<th>The rate of Pb\textsuperscript{2+} after adsorption process (ppm)</th>
<th>Adsorbed Pb\textsuperscript{2+} content (ppm)</th>
<th>The amount of material adsorbat (mg)</th>
<th>Weight of adsorbent (g)</th>
<th>X/m</th>
<th>C/(X/m)</th>
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<tbody>
<tr>
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The retrieved graph relationships between C/(X/m) Pb\textsuperscript{2+} ion levels against after the adsorption process (chemical equilibrium) as shown in Figure 3.

![Graph isotherme Langmuir on adsorbent activated carbon from Nila fishbone to Pb\textsuperscript{2+} ion levels against using the HNO\textsubscript{3} activator](image)

3.4. Adsorption of Cd\textsuperscript{2+} ions with the HNO\textsubscript{3} Activator

The adsorption data Cd\textsuperscript{2+} ions by active charcoal from Nila fishbone (Oreochromis niloticus) and HNO\textsubscript{3} activator is presented in Table 5.

<table>
<thead>
<tr>
<th>Contact Time (minute)</th>
<th>Cd\textsuperscript{2+} content early (ppm)</th>
<th>The rate of Cd\textsuperscript{2+} after adsorption process (ppm)</th>
<th>Adsorbed Cd\textsuperscript{2+} content (ppm)</th>
<th>The amount of material adsorbat (mg)</th>
<th>Weight of adsorbent (g)</th>
<th>X/m</th>
<th>C/(X/m)</th>
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<td>10.7090</td>
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<td>21.418</td>
<td>7.69540</td>
</tr>
</tbody>
</table>
The retrieved graph relationships between C/(X/m) Cd\(^{2+}\) ion levels against after the adsorbsi process (chemical equilibrium) as shown in Figure 4.

![Graph isotherme Langmuir on adsorbent activated carbon from Nila fishbone to Cd\(^{2+}\) ion levels against using the HNO\(_3\) Activator](image)

Figure 4. Graph isotherme Langmuir on adsorbent activated carbon from Nila fishbone to Cd\(^{2+}\) ion levels against using the HNO\(_3\) Activator

Langmuir isotherm test results based on each sample can be known that ion adsorption Cd\(^{2+}\) and Pb\(^{2+}\) by active charcoal from waste activated tilapia fishbone HCl and HNO\(_3\) achieve optimum conditions on the contact time of 90 minutes unless adsorption of ions Cd\(^{2+}\) with activation of HNO\(_3\). The longer the contact the more ion levels decrease occurs in solution samples. With other uses, the longer the contact the more chance of active charcoal particles to intersect with the metal ion. This led to more and more of the metal ion Cd (II) tied in the pores of the active charcoal (Turmuzi & Gultom, 2014). So, the longer the time of contact, the metal ion teradsorpsi the more active charcoal adsorption in Events occurring due to Van der Walls i.e. style of attraction between molecules intermolekuler solids with the solute diadsorpsi (in this case metal ion) is greater than the style of attraction fellow solute itself in aqueous samples. This has resulted in solute will be concentrated on the surface of a solid. This type of adsorption is not site specific, where molecules are free teradsorpsi to cover the entire surface of a solid (Rizki, 2015).

The existence of differences in adsorption of ions Cd\(^{2+}\) with activation of organic material due to HNO\(_3\) are still found in the bones of the fish so that it can not expand the surface area and pore size of active charcoal Nila fishbone. Organic material is bonded with a fishbone inhibit biological activity through metal removal so that hinders the process of adsorption on the surface. As well as consuming organic phosphate material as a source of nutrients due to deposits of phosphate adsorption effect on the capacity of heavy metals. (Lokapuspita, biodiversity, Purwanto &

Influence of activators on HCl Ionic Cd\(^{2+}\) and Pb\(^{2+}\) is more effective than HNO\(_3\) activator. The HCl activator can magnify the surface of active charcoal is more effective. While the Activator HNO\(_3\) does not enter between the hexagonal layers of charcoal and cannot open a closed surface, so as not to enlarge the surface of active charcoal Nila fishbone (Aetas Bangkok, Itnalita, & Bali, 2015).

4. CONCLUSION

It can be inferred that effect of HCl activator on Cd\(^{2+}\) and Pb\(^{2+}\) ions is more effective than HNO\(_3\) activator. The HCl activator can magnify the surface of active charcoal is more effective. While the activator HNO\(_3\) does not enter between the hexagonal layers of charcoal and cannot open a closed surface, so as not to enlarge the surface of active charcoal Nila fishbone.
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