Identification of activated NaOH carbon of synthesis of sea pandanus leaves (P. odorifer) for Fe$^{3+}$ and Cu$^{2+}$ ions adsorption

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Abstract. This research aims to characterize activated NaOH carbon of sea pandanus leaves (P. odorifer) which include water content, ash content, volatile content, carbon content and adsorption capacity of iodine. Further, we investigate adsorption capacity of activated NaOH carbon to Fe$^{3+}$ and Cu$^{2+}$ ions, and its adsorption type. Sea pandanus leaves (P. odorifer) was taken from Trisik Beach in Kulonprogo. The carbonation process is carried out at a temperature of 500 °C, followed by chemical activation using 1% NaOH solution and physical activation with a temperature of 700 °C while carbon dioxide gas flowed for 2 hours. Characterization results show that water content and iodine adsorption capacity of activated NaOH carbon complied with SNI 06-3730-1995, respectively of 5.38% and 2463.63 mg/g. While the volatile content (59.09%), ash content (17.88%), carbon content (17.66%) did not fulfill SNI 06-3730-1995. The adsorption capacity of activated NaOH carbon to heavy metal ions of Fe$^{3+}$ and Cu$^{2+}$ respectively is 0.895 and 0.996 mg/g.

1. Introduction
At present, the industry has grown rapidly. The development of the industry may have a negative impact on the heavy metal content contained in the waste. The content of heavy metals in industrial waste water is very dangerous when disposed directly into the environment. One of the fastest growing industries in Indonesia is the metal coating industry. In metallic coating industry using electroplating method, produces colored waste water and odor [1].

There are various methods that can be used to reduce the pollution of heavy metals in the environment such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, flotation and electrochemical methods [2-4]. A common method for heavy metal adsorption is the adsorption method because it can use a variety of adsorbents at relatively low cost such as active clay [5], activated carbon [6], and zeolite [7].

The adsorbent can also be synthesized from the raw material of sea pandanus leaves [8]. Carbon of sea pandanus leaves can be activated with acid or base solution to increase its adsorption ability. In previous studies, the activator substance to activate carbon of sea pandanus leaves are acid solutions such as HCl and H$_2$SO$_4$ [8], HNO$_3$ [9]. The kind of activator used in the process of carbon activation will greatly affect the ability of the adsorbent [6]. In addition, activator concentration and activation techniques also affect the ability of the adsorbent produced.
Adsorbents are generally synthesized from abundant and under utilized material, such as egg shells [10], and sea pandanus leaves (P. odorifer) [8]. In previous research, synthesis of activated carbon of sea pandanus leaves using acid solution as activator. In this study, we will synthesis activated carbon of sea pandanus leaves using alkaline activator, i.e. sodium hydroxide (NaOH). We want to investigate the ability of alkaline solutions to activate carbon from the ingredients of sea pandan leaves. The resulting activated carbon is then used as an adsorbent for heavy metal ions such as Fe\\(^{3+}\) and Cu\\(^{2+}\).

2. Experimental Section

2.1 Materials
Sea pandanus leaves (P. odorifer) from Trisik Beach in Kulonprogo, 1% (b/v) NaOH, Pb(NO\(_3\))\(_2\), Fe(NO\(_3\))\(_3\), Cr(NO\(_3\))\(_3\), Ni(NO\(_3\))\(_2\), CdSO\(_4\), Cu(NO\(_3\))\(_2\), Zn(NO\(_3\))\(_2\), 0.1 M I\(_2\), 0.1 M Na\(_2\)S\(_2\)O\(_3\), indicator of amylum, distilled water, filter paper, pH paper. All of the materials were purchased from various commercial sources. The grade of them is pure analysis (pa) and used without further purification.

2.2 Instruments
Surface Area Analyzer (SAA), Atomic Absorption Spectrophotometer (AAS), blowing furnace, 80 mesh sieve, analytical scales, oven, magnetic stirrer, pumpkin powder, and laboratory glass ware.

2.3 Synthesis of carbon
The sea pandanus leaves are cleaned and then washed thoroughly. Then, it is cut into small pieces and then dried under the sun to dry. The dried sea pandanus leaf is then carbonated with a furnace at a temperature of 500 °C for 4 hours, then mashed and sieved with an 80 mesh sieve.

2.4 Activation of carbon
200 grams of 80-mesh carbon are added with 600 mL of 1% NaOH solution while stirring for 24 hours. The activated carbon is then filtered and washed with distilled water until the pH is neutral. Then, activated carbon is dried in an oven at 100 °C for 3 hours. Furthermore, the physically activation was done by inserting carbon in the furnace with a temperature of 700 °C while carbon dioxide gas flowed for 2 hours.

2.5 Adsorption of activated carbon to heavy metal ions (Fe\\(^{3+}\) and Cu\\(^{2+}\))
Identification of activated carbon capacity to heavy metals is conducted in batch. Preparing as many as 6 erlenmeyer, each added 1 gram of activated carbon of sea pandanus leaves. Then, each erlenmeyer is added 50 mL of Fe\\(^{3+}\) ion solution with various concentration (3-18 mg/L for Fe\\(^{3+}\) and 4-24 mg/L for Cu\\(^{2+}\)). The mixture is allowed to stand for 24 hours while stirring. Then, the mixture was filtered and the filtrate was taken for AAS testing.

3. Discussion
Activated carbon has been widely known as a good absorbent because it has a high adsorption capacity. The type of activator, activation conditions and time of the activation process affect the physical properties of activated carbon [11]. The activation process has the goal of enlarging pore size by breaking hydrocarbon bonds or oxidizing surface molecules, so that carbon can undergo changes both physically and chemically [9].

Chemical activation was performed using 1% NaOH solution. The filtrate color of its process is brown because NaOH solution is a strong base and corrosive. Thus causing a lot of ash to be released by carbon [12]. Chemical activation is continued with physical activation to optimize the pores of activated carbon. The physical activation is carried out by heating the carbon at a temperature of 700 °C while flowed by carbon dioxide gas.

3.1 Characterization of activated NaOH carbon of sea pandanus leaves
Characterization of activated NaOH carbon of sea pandanus leaves is carried out to determine the quality of the carbon that has been synthesized and compared with the standard quality based on SNI 06-3730-1995.
Characters that are seen at table 1 are water content, ash content, volatile content, carbon content, and absorption capacity of iodine. The result of characterization obtained then compared with SNI 06-3730-1995.

| Characters of carbon from sea pandanus leaves. | Water Content (%) | Ash Content (%) | Volatile Content (%) | Carbon Content (%) | Absorption capacity of iodine (mg/g) |
|-----------------------------------------------|-------------------|----------------|----------------------|-------------------|-------------------------------------|
| SNI Carbon before activation                   |                   |                |                      |                   |                                     |
| Maks 15                                        | 5.42%             | 19.62%         | 70.50%               | 4.46%             | 2157.55                             |
| Maks 10                                        |                   |                |                      |                   |                                     |
| Maks 25                                        |                   |                |                      |                   |                                     |
| Min 65                                         |                   |                |                      |                   |                                     |
| Min 750                                        |                   |                |                      |                   |                                     |
| Carbon after activation                         |                   |                |                      |                   |                                     |
| 5.38%                                         | 17.88%            | 59.09%         | 17.66%               |                   | 2463.64                             |

Generally, characters of carbon from sea pandanus leaves after activation is better than carbon before activation. The value of water content meets the standard which means it has value less than the maximum standard water content that has been established SNI 06-3730-1995. The absorption capacity of iodine also meets the standards which means it has a value of more than a minimum standard of iodine absorption capacity. The percentage of carbon content obtained has not meet the standard. Activated carbon quality that has not met national standards is made possible due to the non-optimal carbonation process. Consequently, many non-carbon elements are still bound in it. During carbonization process, most non-carbon elements such as oxygen, hydrogen, and nitrogen are eliminated as volatile gas species [13].

The activated carbon of sea pandanus leaves is also characterized by using Surface Area Analyzer (SAA). It has surface area of 19.667 m²/g. It is better than surface area of activated carbon of sea pandanus leaves by [9], i.e. 3.575 m²/g.

### 3.2 Identification of capacity adsorption of activated NaOH carbon of sea pandanus leaves

Identification of capacity adsorption in this study was obtained by using Atomic Absorption Spectroscopy (AAS). It is based on concentration before and after activation process. Data of adsorption efficiency and capacity adsorption activated NaOH carbon to Fe³⁺ ions can be observed in the table 2 and figure 1.

| Ion Fe³⁺ | Initial Concentration (mg/L) | Final Concentration (mg/L) | Absorbed Concentration (mg/L) | Adsorption Efficiency (%) | Adsorption Capacity (mg/g) |
|----------|------------------------------|----------------------------|-------------------------------|--------------------------|---------------------------|
| 1        | 18                           | 0.098                      | 17.902                        | 99.453                   | 0.895                     |
| 2        | 15                           | 0.119                      | 14.881                        | 99.205                   | 0.744                     |
| 3        | 12                           | 0.129                      | 11.871                        | 98.920                   | 0.593                     |
| 4        | 9                            | 0.134                      | 8.866                         | 98.503                   | 0.443                     |
| 5        | 6                            | 0.140                      | 5.860                         | 97.668                   | 0.293                     |
| 6        | 3                            | 0.140                      | 2.860                         | 95.336                   | 0.143                     |

The greater the concentration of Fe³⁺ ions, the adsorption capacity of adsorbent increased. At a dilute concentration of the solution, the less number of Fe³⁺ ions causes the chance of analytes interacting with the adsorbent is also smaller. Conversely, at more concentrated concentrations, the greater number of Fe³⁺ ions causes greater opportunities for analytes to interact with the adsorbent. Therefore, the greater the concentration of Fe³⁺ ions solution, the adsorption capacity tends to increase. High adsorption efficiency
values (>99%) show that analytes are almost completely absorbed. But it never reached 100%. It is possible that contact between analytes and adsorbents in batch system cannot be perfect.

![Graph showing curve relation between concentration vs capacity adsorption of Fe\textsuperscript{3+} ion.](image1)

**Figure 1.** Curve relation between concentration vs capacity adsorption of Fe\textsuperscript{3+} ion.

| Ion | Initial Concentration (mg/L) | Final Concentration (mg/L) | Absorbed Concentration (mg/L) | Adsorption Efficiency (%) | Adsorption Capacity (mg/g) |
|-----|-----------------------------|-----------------------------|-------------------------------|---------------------------|---------------------------|
| 1   | 24                          | 0.156                       | 23.844                       | 99.350                    | 0.192                     |
| 2   | 20                          | 0.077                       | 19.923                       | 99.616                    | 0.996                     |
| 3   | 16                          | 0.084                       | 15.916                       | 99.475                    | 0.796                     |
| 4   | 12                          | 0.052                       | 11.948                       | 99.570                    | 0.597                     |
| 5   | 8                           | 0.048                       | 7.952                        | 99.400                    | 0.398                     |
| 6   | 4                           | 0.084                       | 3.916                        | 97.900                    | 0.196                     |

![Graph showing curve relation between capacity adsorption vs concentration of Cu\textsuperscript{2+} ions.](image2)

**Figure 2.** Curve relation between capacity adsorption vs concentration of Cu\textsuperscript{2+} ions.
Adsorption capacity of activated NaOH carbon to Cu$^{2+}$ ions can be observed in the table 3 and figure 2. Based the data, can be stated that the adsorbent adsorption efficiency value of Cu$^{2+}$ ions greater, especially on the concentration of 4, 8, 12, 16 and 20 mg/L Cu$^{2+}$ ions. However, the decrease in adsorption capacity occurs at concentrations of 24 mg/L Cu$^{2+}$ ions. This is possible due to the desorption process after optimal adsorption capacity is achieved.

The adsorption capacity was then determined at the largest adsorption capacity. By this study adsorbent capacity of activated NaOH carbon from sea pandanus leaves to Fe$^{3+}$ and Cu$^{2+}$ ions was 0.895 mg/g and 0.996 mg/g respectively. Adsorption capacity of this adsorbent to Cu$^{2+}$ ions is slightly greater than that of Fe$^{3+}$ ions. This is due to Cu$^{2+}$ ion particle size slightly smaller than Fe$^{3+}$ ion particle size. Actually, adsorption capacity of activated NaOH carbon from sea pandanus leaves is still possible greater than the value considering the efficiency that has not reached 100%. Therefore, in this study the adsorption test with a greater concentration should be carried out.

3.3 Identification of isotherm adsorption type of activated NaOH carbon of sea pandanus leaves
The identification of isotherm adsorption type of activated NaOH carbon of sea pandanus leaves is determined, i.e Langmuir and Freundlich adsorption isotherms [7].

The Langmuir equation used is as follows:

$$\frac{C_e}{X_m} = \frac{1}{ab} + \frac{1}{a}C_e$$

The Freundlich equation used is as follows:

$$log \left( \frac{X_m}{m} \right) = log k + \frac{1}{n} log C_e$$

Information
- $C_e$: concentration of metal ions in solution after adsorption
- $X_m / m$: the mass of metal ions adsorbed per mass of activated carbon
- $b$: Langmuir’s affinity or constant parameters
- $a$ and $k$: maximum capacity of adsorption (mg/gram)

| $C_o$ (ppm) | $C_e$ (ppm) | $X_o / m$ (mg/g) | $C_o / (X_o / m)$ | log $C_e$ | log ($X_o / m$) |
|-------------|-------------|------------------|-------------------|-----------|----------------|
| 3           | 0.1399      | 0.1430           | 0.9783            | -0.8542   | -0.8447        |
| 6           | 0.1399      | 0.2931           | 0.4773            | -0.8542   | -0.5330        |
| 9           | 0.1347      | 0.4432           | 0.3039            | -0.8706   | -0.3534        |
| 12          | 0.1295      | 0.5935           | 0.2182            | -0.8877   | -0.2266        |
| 15          | 0.1192      | 0.7440           | 0.1602            | -0.9237   | -0.1284        |
| 18          | 0.0984      | 0.8951           | 0.1099            | -1.0070   | -0.0481        |

Table 4 and 5 show concentration of Fe$^{3+}$ and Cu$^{2+}$ ions before and after adsorption process. Further, the data is processed into the Langmuir and Freundlich equation. Graph of isotherm type of Fe$^{3+}$ ion can be seen at figure 3 and 4, while graph of isotherm type of Cu$^{2+}$ ion can be seen at figure 5 and 6. Based on the graph is obtained, the $R^2$ Langmuir and Freundlich equation values are different. For Fe$^{3+}$ ion, $R^2$ Langmuir value of 0.4565 and Freundlich of 0.6042. For Cu$^{2+}$ ion, the $R^2$ Langmuir value is 0.0077 and Freundlich is 0.184. However, $R^2$ values of the Langmuir and Freundlich equation for Fe$^{3+}$ and Cu$^{2+}$ ions are ≤ 95% [14]. So, isotherm adsorption of activated carbon does not follow the equation of both, Langmuir and Freundlich.
Figure 3. Graph of Langmuir equation of Fe$^{3+}$ ion, $C_e$ vs $C_e/(X_m/m)$.

Figure 4. Graph of Freundlich equation of Fe$^{3+}$ ion, log $C_e$ vs log $X_m/m$.

Table 5. $X_m/m$, $C_e/(X_m/m)$, log $C_e$, and log $X_m/m$ value of Cu$^{2+}$ ion adsorption.

| $C_o$ | $C_e$ | $X_m/m$ | $C_e/(X_m/m)$ | log $C_e$ | log $X_m/m$ |
|-------|-------|---------|----------------|-----------|-------------|
| 4     | 0.0840 | 0.1958  | 0.4290         | -1.0757   | -0.7082     |
| 8     | 0.0480 | 0.3976  | 0.1207         | -1.3188   | -0.4006     |
| 12    | 0.0516 | 0.5974  | 0.0863         | -1.2874   | -0.2237     |
| 16    | 0.0840 | 0.7958  | 0.1055         | -1.0757   | -0.0992     |
| 20    | 0.0768 | 0.9962  | 0.0771         | -1.1146   | -0.0017     |
| 24    | 0.1560 | 1.1922  | 0.1309         | -0.8069   | 0.0763      |
4. Conclusion
Characters of carbon of sea pandanus leaves after activation 1% NaOH solution are better than carbon before activation. The value of water content and the adsorption capacity of iodine appropriate with the standard SNI 06-3730-1995. However ash content, volatile content, and carbon content are not meet the standard. Capacity adsorption of adsorbent to Fe$^{3+}$ and Cu$^{2+}$ ions were obtained 0.895 and 0.996 mg/g respectively. For the identification of adsorption isotherms, adsorbents do not follow both the Langmuir and Freundlich types.

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