Adsorption pattern on the optimization of interaction time for the reduction of phenol with charcoal activated ZnCl₂

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Abstract. Interaction time significantly influenced the pattern of adsorption. This study aims to determine the characteristic of activated charcoal adsorbent, the decrease in phenol levels and its adsorption capacity, and test the adsorbent applicability to remove phenol from batik wastewater. The concentration of phenol was measured by UV-Vis spectrophotometer. The results showed that the characters of activated charcoal adsorbent in accordance with Indonesian National Standard (INS) 06-3730-1995. Its characters were water content, ash content and iodine adsorption power. Characterization using Surface Area Analyser (SAA) showed that the surface area of activated charcoal was 68.54 m²/g. The percentage decrease in phenol concentration will be greater along with the increase in concentration where 92.90%; 95.60%; and 97.15% of phenol decrease were influenced by the increasing level concentration of 0.6 mg/L; 0.8 mg/L; and 1.0 respectively with 24 hours optimal contact time. The adsorption capacity of activated charcoal was 0.048575 mg/g while the isotherm adsorption pattern of adsorbent fulfilled the pattern of Freundlich isotherm. Therefore, the availability of high surface area makes the activated charcoal of marine pandan leaves has significant impact to the adsorption of phenol where it was contacted optimum at 24 hours interaction with Freundlich adsorption pattern.

1. Introduction
The development of the batik industry in Indonesia has increased along with the increase in demand for clothing products using the batik process. This has caused the waste generated from the batik process to also increase. Wastewater from the batik industry is one of the main sources of water pollution because batik wastewater contains very high organic compounds and also a variety of dangerous chemical compounds, phenol [1]. Phenol is produced from an organic waste originating from the wax dissolving process or coloring and is included in the category of B3 waste [2]. The content of phenol in batik waste will be dangerous and cause an adverse effect on the environment if it is thrown into the environment without prior processing. It will enter the food chain and does not rule out the possibility of reaching the human body, skin and respiratory tract. It can also affect the central nervous system, liver and kidneys, causing coma, gastric damage and respiratory failure. Phenol acts as carcinogenic properties for humans if the concentration is 5-25 mg/L [2]. Phenol content in textile industry waste according to the Living Environment Ministry ordinance No. 5 of 2014 is at a maximum of 0.5 mg/L [3]. Therefore it is necessary to treat phenol in wastewater. One of them is
through the adsorption method using activated charcoal adsorbents. The method of adsorption with activated charcoal is a physical-chemical treatment process that is effective for removing contaminants in wastewater [4]. Activated charcoal preparation is easier, cost effective and has a high adsorption capacity. The use of other methods has the disadvantage of operating conditions that are insensitive, less efficient and for advanced disposal require high costs [5]. The selection of activator types that can be used for activation will greatly affect the quality of activated charcoal obtained, including KOH, H₂SO₄ [6], HNO₃ [7], NaOH [8] and ZnCl₂ [9,10,11]. The use of ZnCl₂ activators can produce activated charcoal which is quite effective for the adsorption process. Efforts to reduce phenol levels in batik waste were carried out with a batch system and the phenol content in the waste was analyzed using UV-Vis spectrophotometry.

The proof was done in research conducted by Kristianingrum and Siswani [12] about making adsorbents from marine pandan leaves which were used for heavy metal adsorption processes such as Cr and Pb. The results showed that the synthesized adsorbent was in accordance with INS and was effectively used as an adsorbent. Activated charcoal that has been activated using ZnCl₂ will adsorb phenol compounds in the waste so that the levels drop and safe if the waste is disposed into the environment. The use of ZnCl₂ activator aims to improve the quality of the adsorbent so that the adsorbent with optimal adsorptivity will be obtained [13]. This study will analyze the characterization of the adsorbent from the activated charcoal of marine pandan leaves (Pandanus tectorius).

Marine pandan leaves are rich in various kinds of chemical compounds, including cellulose which has major content of carbon as sources to synthesize activated charcoal. The optimal adsorbent will be applied to batik industry liquid waste containing phenol. Some studies showed that the most ideal time for the chemical activation process is 24 hours [14]. In this research, activated charcoal was chemically activated (using 5% ZnCl₂ solution) and activation of physics (heating at high temperatures). The treatment of physical activation greatly influenced the formation of micro-pore structures on activated charcoal so as to produce activated charcoal with large surface areas [15]. In addition, the adsorption efficiency of phenol was calculated (percentage reduction in phenol) to the addition of activated adsorbents and their adsorption capacity. The method used in this study is the characterization of the adsorbent including: moisture content, ash content, volatile substance content, absorption rate of I₂ and charcoal content. To find out the surface area of the adsorbent and the pore size distribution, characterization used SAA (Surface Area Analyzer).

2. Experimental Section

2.1. Materials and Instruments
The materials used marine pandan leaves, batik industrial wastewater taken from Godean area, Yogyakarta, 5% ZnCl₂ solution, 0.1M Na₂S₂O₃ solution, starch indicator, 0.1M iodine solution, phenol mother liquor, distilled water, pH paper and filter paper.

The tools used in this study: UV-Vis spectrophotometry (Shimadzu), porosimeter (Quantachrome, NOVAe Series), furnace, magnetic stirrer, drying oven, buchner filter, vacuum device, desiccator, analytic balance, 80 mesh sieve, porcelain exchange rate, and glass-wares.

2.2. Synthesis of activated charcoal
A total of 8.5 kg of marine pandan leaves were dried and then carbonated at 500°C for 6 hours, then the yielded charcoal was smoothed and sifted using an 80 mesh sieve. After that, chemical activation is carried out by taking 200 gr charcoal size 80 mesh with a 5% ZnCl₂ solution for 24 hours at ambient temperature. The next step is washed to neutral pH and continued with physics activation at temperature of 700 °C with NO₂ gas flowed for 2 hours. This activation process is carried out to
expand the surface of activated charcoal in order to increase the adsorption of activated charcoal against the adsorbate. Activated charcoal will experience changes in physical and chemical properties if it has been activated and will increase in adsorption and surface area. When the surface area of activated charcoal is increasing, the adsorption efficiency also increases [16].

2.3. Characterization of Charcoal (INS 06-3730-1995)[16]
The size of porous were identified by porosimeter for both raw and activated charcoals. According to INS 06-3730-1995, the activated charcoal was tested in finding the content of water, ash level, volatile degree, and the capacity adsorption of activated charcoal to I$_2$. The properties of adsorption were investigated by interacting activated charcoal with solutions of artificial waste of phenol (0.2; 0.3; 0.4; 0.6; 0.8 and 1.0 mg/L) in a ratio of 2:100 (g/mL) for 24 hours in medium pace respectively to find the capacity, the efficiency and the isotherm models.

2.4. Adsorption
Adsorption of activated charcoal activated by 5% ZnCl$_2$ in batik simulation waste solution was done by making a hundred millilitre of artificial waste of phenol with 6 variations of concentration (0.2; 0.3; 0.4; 0.6; 0.8 and 1.0 mg / L) contacted with activated charcoal as much as 2 grams during 24 hour time variation, 6 hours and 3 hours with constant stirring. The mixture was filtered and the filtrate was taken to analyze the phenol content using a UV-Vis spectrophotometer.

The phenol levels (INS 06-6989.21-2004)[17] were investigated by testing the sample of 100 mL added by 2.5 mL NH$_4$OH 0.5N reagent and the pH was 7.9 with the addition of a phosphate buffer solution. Added 1 mL 4-aminoanthipyrin solution while stirring, then added 1 mL of potassium ferisianida solution and allowed to stand for 15 minutes. Measurements were carried out by spectrophotometer at a wavelength of 500 nm [18].

Determination of the surface area of activated charcoal used the SAA (Surface Area Analyzer) tool. This is to determine the surface area of the adsorbent, the size of the pore distribution of charcoal before the activation process is carried out and after going through the activation process. All is done by supporting installed program of SAA device.

Decrease in phenol content and adsorption capacity of activated charcoal in marine pandan leaves was calculated by the equation:

$$E_a(\%) = \frac{(C-C_e)}{C} \times 100\%$$
$$q_m (mg / g) = \frac{(C-C_e)}{m \times V}$$

where $E_a$ is a decrease in phenol level (%) while $q_m$ is adsorption capacity (mg/g), $C$ is the initial phenol concentration (mg/L), $C_e$ is the concentration of phenol after adsorption (mg/L), $m$ is the mass of the adsorbent for adsorption (g) and $V$ is the volume of adsorbed (L) wastewater [19].

3. Result and Discussion
3.1. Characterization of Activated Charcoal
The characterization of activated charcoal in accordance with INS 06-3730-1995 includes moisture content, ash content, volatile substances, charcoal content and iodine absorption. Characterization of activated charcoal data before and after activation with ZnCl$_2$ is shown in Table 1.
Table 1. Data on charcoal characterization before and after activation with ZnCl$_2$

| Marine pandan leaves charcoal | Water content (\%) | Ash content (\%) | Volatile content (\%) | Carbon content (\%) | Adsorption to Iodium (mg/g) |
|-------------------------------|--------------------|------------------|-----------------------|---------------------|-----------------------------|
| Before activation process     | 5.42               | 19.62            | 70.50                 | 4.46                | 2157.55                     |
| After activation process      | 4.24               | 8.19             | 45.49                 | 42.15               | 2223.26                     |
| SNI No. 06-3730-1995          | Max 15             | Max 10           | Max. 25               | Min. 65             | Min. 750                    |

From the table 1, it can be seen that the water content, ash content and charcoal adsorption of I$_2$ after activation has been in accordance with INS 06-3730-1995 because of charcoal activation process. From the results, the levels of volatile substances and charcoal content not yet in accordance with INS standards are likely to be caused during the carbonization process. Air leaks still occur even though they have been minimized. Ash is also produced due to oxidized samples from outside air. The incomplete carbonization process results in the majority of non-charcoal elements being eliminated as volatile gas species [20].

The decrease in water content from 5.42\% to 4.24\% in table 1 is likely caused by the surface of the activated charcoal containing fewer polar groups, so that the interaction between water vapor which is polar is also small. In addition, it is assumed that only water is a volatile compound, because it is possible there is still water trapped in the cavity and covering the pores of activated charcoal. The lower water content shows that less water is left behind and covers the active charcoal pore. If the water content is low then many places in the pore of activated charcoal can be occupied by I$_2$ molecules [21].

The results of characterization using a Surface Area Analyzer (SAA) showed that the surface area of activated charcoal in marine pandan leaves activated by 5\% ZnCl$_2$ was 68.543 m$^2$/g. The activation process for activated charcoal causes the breakdown of hydrocarbon bonds on charcoal so that the porous surface area increases [22], whereas the original surface area was only 3.7719 m$^2$/g. Activated charcoal adsorbent of marine pandan leaves that have been activated by ZnCl$_2$ have pore size in the meso-porous category because they have a surface area between 200-100 m$^2$/g [23]. The surface area is related to the crystal structure, number and size of pores present in the adsorbent. A large number of pores and widths will widen the adsorption capacity.

However, when compared to the results of both studies, the charcoal after activation using ZnCl$_2$ has better quality than before the activation process, so that activated charcoal can be applied as an adsorbent to adsorb phenol.

3.2. Decreasing Phenol (Ea) and Adsorption Capacity (qm) in Batik Simulation Waste

The data for decreasing phenol and its adsorption capacity are shown in Table 2.

Table 2. Data on decreasing phenol content and its adsorption capacity of activated charcoal

| The initial phenol content (mg/L) | The decrease of phenol content (\%) | Adsorption capacity of activated charcoal (mg/g) |
|---------------------------------|-----------------------------------|-----------------------------------------------|
|                                 | 3 hours | 6 hours | 24 hours | 3 hours | 6 hours | 24 hours |
| 0.2                             | 41.7    | 49.10   | 90.35    | 0.00417 | 0.00491 | 0.00904  |
| 0.3                             | 50.03   | 72.23   | 91.40    | 0.00751 | 0.01084 | 0.01371  |
It can be clearly observed that the difference between each relationship of the initial concentration of phenol to the decrease in phenol levels as in Figure 1. Both percentage of phenol decrease and the adsorption capacity of activated charcoal significantly increase. The maximum phenol percentage of decrease for 24 hours interaction with the adsorption capacity is 0.04858 mg/g. It shows the more contact time, the interaction of particles more intense. The intensity of time interaction increases the bond strength of phenol and the adsorbent.

![Figure 1](image1.png)

**Figure 1.** The graph of initial phenol content relation toward its decrease

![Figure 2](image2.png)

**Figure 2.** The graph initial phenol concentration toward adsorption capacity
The differences of relation in every initial concentration of phenol to the adsorption capacity value are shown in Figure 2.

3.3. Decreasing Phenol (Ea) and Adsorption Capacity (qm) in Real Batik Waste

Data for decreasing phenol levels and adsorption capacity in real batik industry waste are shown in Table 3.

| Initial phenol level (mg/L) | The decrease of phenol level (%) | Adsorption capacity of activated charcoal (mg/g) |
|-----------------------------|---------------------------------|-----------------------------------------------|
|                             | 3 hours                         | 6 hours                                      | 24 hours                                      |
|                             | 3 hours                         | 6 hours                                      | 24 hours                                      |
|                             | 0.3515                          | 9.87                                         | 19.00                                         | 69.02                                         | 0.00174                              | 0.00334                              | 0.01213                              |

The maximum decrease in phenol content was 69.02% with adsorption capacity of 0.01213 mg/g in batik waste water. The value is slightly different (lower) with results in simulated batik wastewater. This may be due to the condition of the batik industry's real wastewater is viscous so that the adsorption process is less optimal and less maximal due to the presence of disturbing compounds contained in batik waste including the presence of heavy metals, chrome and cobalt [24]. This may be also caused by using difference reagent for analysis phenol by spectrophotometry UV-Vis. In this study, 4-aminoanthipyrin reagents were used as in the INS 06-6989.21-2004 procedure, but in another study the researchers used powder pillow reagents [24] and fenton reagents [26]. The measurement of phenol level by colorimetric method is all phenol in water will react with 4-aminoanthipyrin at pH 7.9 ± 0.1 with the addition of potassium solution hexacyanate forms quinonymin brownish red [27].

3.4. Isotherm Type of Phenolic Adsorption

There are two types of adsorption isotherms used in the adsorption process of activated charcoal in the solution, namely Freundlich and Langmuir adsorption isotherms [28]. By making the relation of log Xm/m and log Ce, it is resulted graph of Freundlich and Langmuir adsorption patterns.

The graph of Freundlich model of 3, 6, and 24 hours of contact time are shown in figure 3. Based on the figure 3 combined with the linearity factors on table 3, it is clearly seen that there were various linearity numbers. From the plotting of linearity formula, the $R^2$ of determination coefficient were 0.7115, 0.9248, and 0.4053 for 24, 6, and 3 hours interaction respectively so that are one formula exceed the $R^2$ as the linearity requirement.
**Figure 3.** Freundlich adsorption isotherm of phenol in 3, 6, and 24 hours interaction time on 5% ZnCl$_2$ activated charcoal.

The linearity value are shown in table 4.

**Table 4.** Data of R$^2$ of phenol adsorption

| Contact time | Isotherm data | Phenol adsorption type of isotherm |  |  |
|--------------|---------------|-----------------------------------|---|---|
| 24 hours     | Linear        | y = $-0.5828x - 1.7285$          | y = $-1.1144x + 0.1722$ | R$^2$ = 0.7115 | R$^2$ = 0.0183 |
| 6 hours      | Linear        | y = $-2.191x - 3.4035$           | y = $28.9x - 1.2385$    | R$^2$ = 0.9248 | R$^2$ = 0.8641 |
| 3 hours      | Linear        | y = $-3.9736x - 4.5517$         | y = $36.843x - 3.1329$  | R$^2$ = 0.4053 | R$^2$ = 0.4043 |
Based on figure 4 and table 4, it can be inferred that all the data for investigating Langmuir pattern cannot support the conclusion of its model. Therefore, it can be concluded that type of activated charcoal adsorption isotherm of marine pandan leaves tends to meet the pattern of Freundlich model because Freundlich and Langmuir equations can be applied if the value of $R^2$ approaches 1 or > 0.9 [24, 28].

Freundlich isotherms can be applied to the adsorption of phenolic organic substance by various adsorbents. This model assumes heterogeneous adsorption on the surface and occurs with more than one layer (multilayer) adsorbent so that each molecule has different adhesion intensity [29, 30].

4. Conclusion
Based on the results and discussions above, it can be concluded that the characters of charcoal that had been activated by ZnCl$_2$ explained in details: for water content, ash content and iodine adsorption power levels have met the required standards, while for levels of volatile substances and charcoal content have not met INS 06-3730-1995 standards. Characterization using SAA showed that the surface area of the adsorbent of activated charcoal was 68.543 m$^2$/g. Moreover, the decrease of phenol concentration was greater along with the increase in concentration. The values were 92.90%; 95.60%; and 97.15% for the level concentration of 0.6 mg/L; 0.8 mg/L; and 1.0 respectively. The highest decrease of phenol reached at 24 hours of contact time. Also, the largest capacity of adsorbent adsorptions was 0.048575 mg/g occurred at 24 hours contact time. And so, type of phenol adsorption isotherm from the activated charcoal adsorbent of marine pandan leaves tends to meet the pattern of Freundlich isotherms.

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