Application of Ouw natural clay activated acid and base as adsorbent of Rhodamine B dye

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Abstract. A study of the activation of the natural clay of Ouw (LAO) using acids and bases has been done. Activation with a base using KOH 2 M with heating treatment and without heating. Conducted a study of the adsorbent mass. The results showed that activation with KOH 2M along with heating decreased the adsorption ability of LAO to Rhodamin B dye. The optimal adsorbent mass was 5 grams. While activation of LAO with acid using HCl with concentration 2 M, 3M, and 4M. Conducted a study of the adsorbent mass. The results showed that activation using HCl 3 M resulted in optimal adsorption of Rhodamin B. The use of different adsorbent mass of acid activated ouw natural clay adsorbent has no significant effect on the adsorption presentage of Rhodamine B.

1. Introduction
Moluccas is an area of Indonesia with abundant mineral resources, one of which is clay. Ouw Village Saparua Island is one of the locations containing clay. But unfortunately the natural clay mineral Ouw (LAO) has not been optimally utilized. The result of characterization ever done states LAO contains the dominant montmorillonite mineral [1]. Montmorillonite is a pore-structured clay that today is very intensively studied because of its vast application areas, among others as ion exchangers [2], inorganic pollutant adsorbents [3], and biosensor membranes [4]. So far, the clay from Ouw Saparua village is only used as a ceramic material.

Clay activation is a process to increase the clay character to obtain the desired properties in accordance with its use. Chemical activation can be done by addition of acid or base solution. Generally the acid used is sulfuric acid [4] while the base used is sodium hydroxide [5]. Clay surface area and pore volume can be increased through treatment with mineral acids [6]. This treatment is highly dependent on acid strength, time and temperature of the system [7]. Bijang have done activation with 2 M sulfuric acid can increase the surface area of bentonite from 76.4 m²/g to 178.5 m²/g [4]. Putu Apriliana reported that bentonit treatment with NaOH increased the surface area from 12.6602 m²/g to 22.1017 m²/g [5].

The textile industry in terms of woven fabrics also has a brilliant prospect in Maluku Province. However, this activity should be anticipated in terms of waste impacts for the environment due to the use of dyes on textiles. The rhodamine B colorant is widely used by the textile industry. This compound contains the basic amino groups and benzene nuclei, so rhodamine B includes compounds that are difficult to degrade by microorganisms naturally. The entry of rhodamine B dyes in the waters is a
serious environmental problem. Similarly, if the rhodamine B molecule enters the human body it can be carcinogenic \cite{8}. This study aims to determine the ability of activated Hydrochloric acid LAO adsorbent and activated potassium hydroxide LAO adsorbent against organic dye Rhodamine B.

2. Method and Experimental

2.1 Activation of Bases
A total of 25 g of clay was put into a 100 mL cup glass and added 2M KOH. The mixture was stirred continuously with a magnetic stirrer for 8 hours while heated at 80 °C. The same weight clays were treated the same, but not heated, stirred and clay were filtered to obtain supernatant and solid phase. The solid phase was washed with the aquadest several times to free OH\(^-\) (the washwater was tested with the phenolphthalein indicator), then continued by drying the solids in oven at a temperature of 100 °C to dry. Activated clay is crushed with mortar and sieved with 100 mesh sieve.

2.2 Activation of Acid
Into 3 glasses of 250 mL chemicals were inserted each 8 g of clay, then 100 ml of hydrochloric acid added with concentrations of: 2 M, 3 M, and 4 M while stirring with stirrer magnetic stirrer. The activation process is carried out for 24 hours, then filtered and the residue obtained is washed with distilled water to acid-free. This is indicated by a negative test of AgNO\(_3\) solution. Clay is dried in an oven at 110 - 120 °C. Furthermore, the dried clay that has been activated with the acid is stored in the desiccator.

2.3 Application of Activated Base LAO as a Rhodamine B Adsorbent
A total of 0.25 g; 0.5 g; 1g; 2g; 5 g of heated, unheated activated clay and unactivated clay were fed into a 50 mL erlenmeyer then, 50 ml of Rhodamine B 50 ppm was added. Stirrer solution for 24 hours. The obtained filtrate was measured using visible light spectrophotometry at 554 nm wavelength.

2.4 Application of Activated Acid LAO as a Rhodamine B Adsorbent
A total of 0.5 g, 1 g and 2 g of LAO activated HCl (2 M, 3 M, and 4 M) were added to 100 mL erlenmeyer and 50 ml of Rhodamine B 50 ppm solution was added. Stirrer solution for 24 hours. The obtained filtrate was then measured for absorbance using UV-Vis at 554 nm wavelength.

3. Results and Discussion

3.1 Alkaline Activation
The results of the adsorbent performance of activated 2M KOH LAO with unheated treatment and heating treatment were shown in Table 1 and 2 respectively.

| Table 1. The Calculation results of activated 2M KOH LAO without heating |
| --- |
| Mass (W) g | \( C_0 \) (ppm) | \( C_e \) (ppm) | \( C_0 - C_e \) (ppm) | \( \%Q \) (%) |
| 0.25 | 50 | 5.070 | 44.93 | 89.860 |
| 0.5 | 50 | 7.304 | 42.696 | 85.392 |
| 1.0 | 50 | 18.890 | 31.110 | 62.220 |
| 2.0 | 50 | 3.304 | 46.696 | 93.392 |
| 5.0 | 50 | 0.492 | 49.508 | 99.016 |

\(a\): Rhodamine B concentration before adsorption
\(b\): Rhodamine B concentration after adsorption
\(c\): Rhodamine B concentration which adsorbed
\(d\): adsorption percentage
Table 2. The Calculation results of activated 2M KOH LAO with heating

| Mass (W) g | \( C_0 \) (ppm) | \( C_e \) (ppm) | \( C_0 - C_e \) (ppm) | Q (%)  |
|------------|-----------------|-----------------|----------------------|--------|
| 0.25       | 50              | 15.523          | 34.477               | 68.954 |
| 0.5        | 50              | 16.187          | 33.813               | 67.626 |
| 1.0        | 50              | 16.710          | 33.290               | 66.580 |
| 2.0        | 50              | 15.335          | 34.665               | 69.330 |
| 5.0        | 50              | 14.156          | 35.844               | 71.688 |

Based on tables 1 and 2 it is seen that the heating treatment caused a decrease in the adsorption capacity of the activated 2M KOH LAO adsorbent. Maziarz and Matusik stated that alkaline treatment can cause changes in the structure, texture and morphology of clay minerals [9]. This change corresponds to the partial dissolution of the layer structure and subsequently results in the release of \( \text{Si}^4+ \) and \( \text{Al}^3+ \) ions into the solution. The heating treatment causes the release of water molecules from the surface. Further structural changes occur in the clay aluminosilicate framework. Due to the activation and influence of temperature, there is a change of \( \text{SiO}_2 \) content in the activated clay because some of the silica is bonded with \( \text{NaOH} \) during activation process with \( \text{NaOH} \), forming sodium alumina silicate. This resulted in changes in existing elements in the components of clay. The adsorbent mass study states that the use of adsorbents of 5 g shows the maximum adsorption results for both types of samples.

3.2 Acid Activation
The results of the adsorbent performance of activated 2 M, 3 M and 4 M HCl LAO were presented in table 3, table 4 and table 5, respectively.

Table 3. The result of calculation of activated 2M HCl LAO

| Mass (W) g | \( C_0 \) (ppm) | \( C_e \) (ppm) | \( C_0 - C_e \) (ppm) | Q (%)  |
|------------|-----------------|-----------------|----------------------|--------|
| 0.5        | 50              | 1.889           | 48.111               | 96.22  |
| 1          | 50              | 3.311           | 46.689               | 93.38  |
| 2          | 50              | 1.290           | 48.710               | 97.42  |

Table 4. The result of calculation of activated 3M HCl LAO

| Mass (W) g | \( C_0 \) (ppm) | \( C_e \) (ppm) | \( C_0 - C_e \) (ppm) | Q (%)  |
|------------|-----------------|-----------------|----------------------|--------|
| 0.5        | 50              | 0.544           | 49.456               | 98.91  |
| 1          | 50              | 0.529           | 49.471               | 98.94  |
| 2          | 50              | 0.296           | 49.704               | 99.41  |

Table 5. The result of calculation of activated 4M HCl LAO

| Mass (W) g | \( C_0 \) (ppm) | \( C_e \) (ppm) | \( C_0 - C_e \) (ppm) | Q (%)  |
|------------|-----------------|-----------------|----------------------|--------|
| 0.5        | 50              | 1.259           | 48.741               | 97.48  |
| 1          | 50              | 2.332           | 47.668               | 95.33  |
| 2          | 50              | 1.104           | 48.496               | 97.79  |

Activation of clays using acid will produce clays with larger active sites, greater surface acidity and good porosity [10]. Chemical activation using HCl aims to make the clay surface become acidic so that the adsorption capacity of the clay becomes larger to absorb adsorbate. HCl is a suitable and effective...
compound to remove impurities on the clay surface and make the clay surface become acidic, since the conductivity value of the clay will increase with the influence of acidic atmosphere.

The acidity of clay is divided over the active side of Bronsted acid and the active side of Lewis acid. The Bronsted acid side is formed on the Al atom binding to silicon. This bond is called the "hydroxyl bridge" Al-(OH)-Si, where the negative charge is generated in compensation by the proton. The Lewis acid side is formed on Al which has a low coordination number or is formed on Si4+ caused by dehydroxylation [11].

The Rhodamine-B bond and the active site of LAO are shown in figure 1. Based on the data in tables 3, 4 and 5 it is seen that the 3M concentration is the optimal HCl concentration to activate LAO. The use of 4M HCl concentration decreases the percentage of adsorption to Rhodamine B. This may be due to excessive acid use can damage some of the clay lattice so that the ability of the absorption of rhodamine B decreases. The addition of the amount of adsorbent does not give a significant effect on the ability of adsorption. This is due to the addition of the amount of adsorbent resulting in reduced mobility of the clay molecules due to the increasingly viscous mixture.

![Figure 1](image_url)

**Figure 1.** The bond between rhodamine B and H+-surface (bentonite)

The low performance of alkaline activated clays compared to acid activated clays is due to the low acidity side of the alkaline activated clays. This is due to the neutralization of the acid side by a strong base.

**4. Conclusion**

Acid-activated LAO has a higher percentage of adsorption of Rhodamine B than the alkaline nature activated loam. Treatment of acid activation in the LAO using 3M HCl provides the best performance results. The heating treatment of activated KOH 2M LAO decreases the adsorbent's ability. Use of activated KOH 2 M LAO adsorbent of 5 grams gives the best result. The use of different adsorbent mass of acid activated LAO adsorbent has no significant effect on the adsorption percentage of Rhodamine B.

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