Calcined Kaolin as Adsorbent for Organic Compounds in Peat Water

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Abstract. Kaolin is a clay mineral composed of silica tetrahedral and octahedral alumina layers, which have high absorption capacity and are abundant in nature. This study aims at determining the optimum temperature of kaolin calcination and the effect of variations in pH, stirring time, kaolin mass, and stirring speed on the reduction of organic matter in peat water. The decrease in organic matter in peat water was measured using a UV-Vis spectrophotometer. The adsorption process was carried out by the batch method. The organic matter was calculated as the percentage decrease in absorbance at a wavelength of 254 nm. The optimum temperature for kaolin, which gives the best adsorption results, is obtained at a temperature of 400 °C. The process of decreasing the optimum organic matter in peat water with pH = 4, stirring time of 1.5 h, kaolin mass of 500 mg/50 mL of peat water, and stirring speed of 150 rpm with a percentage decrease in organic matter content of 75.53%.

Keywords: Calcination · Kaolin · Organic Compounds · Peat Water

1 Introduction

Water is one of the most important natural resources in living systems, and every living thing needs water for its survival [1, 2]. One surface water source in West Kalimantan is peat water, which is blackish brown because it contains high organic matter [3]. Natural organic matter (NOM) contained in peat water will give the water an aesthetically unfavorable color, taste and smell. In addition, NOM can interfere during the water treatment process, such as forming a by-product as a carcinogenic trihalomethane compound (THM) resulting from the reaction between organic compounds and chlorine disinfectant [4].

Several methods have been developed for removing NOM in water, such as filtration with ion exchange resins, disinfectants, and ozone. Since these methods require advanced technology and are relatively costly, other methods that are cheaper and simpler, such as coagulation-flocculation [5] and adsorption [6, 7] or a combination of coagulation-adsorption [8] have also been developed.

Coagulation-flocculation effectively reduces NOM, which is hydrophobic in nature and has a large molecular weight. Meanwhile, adsorption can reduce NOM with large

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and small molecular weight characteristics [4]. The adsorption method is also considered cheaper, especially when using local raw materials such as clay [7, 9].

West Kalimantan has abundant resources in clay type 1:1, namely kaolin [10, 11], which can be used as an adsorbent to reduce NOM. This is due to the interaction originating from the negative charge of clay and organic matter [3, 9]. To increase its adsorption ability, kaolin can be chemically or physically activated [12]. Balcke et al. [6] used NaClO4 for kaolin activation. The results showed that the adsorption mechanism of humite compounds on the Na-Kaolin adsorbent was dominated by hydrophobic interactions influenced by polarity and surface area.

The calcination of kaolin affects the surface hydrophobicity, which can be seen in the ratio of Si/Al [13]. Therefore, in this study, kaolin will physically be activated by calcination. The process of adsorption of NOM on peat water was carried out by the batch method. Furthermore, the optimum conditions for the absorption of organic matter by kaolin include the effect of pH, stirring time, stirring speed, and mass of kaolin used to decrease the organic matter content of peat water. Peat NOM reduction was based on color measurement using a UV spectrophotometer at a wavelength of 254 nm [5]. The absorbance value of UV254 represents the content of aromatic compounds in peat water [3, 14], which is included in the hydrophobic fraction or humite fraction, with the main constituents being humic acid and fulvic acid [4].

2 Methods

2.1 Equipment and Materials

Equipment used in this research includes a set of glassware, a shaker, a furnace, a digital pH meter, Genesys 10 ultraviolet-visible (UV-Vis) spectrophotometer. The materials used in this research include peat water, sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH). The kaolin was taken from Capkala District, Bengkayang Regency, West Kalimantan.

2.2 Research Procedure

2.2.1 Preparation and Calcination of Kaolin

Kaolin from Capkala Village, Bengkayang Regency, was prepared according to the method developed by Wahyuni et al. [15]. A total of 20 g of kaolin were weighed and calcined for 3 h at temperatures of 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, respectively. Calcined kaolin was then stored in a closed container.

2.2.2 Determination of the Optimum Temperature for Kaolin Calcination

A total of 1 g of uncalcined and calcined kaolin were each mixed into 50 mL of peat water in a glass bottle. After that, the mixture was shaken at 150 rpm for 2 h using a shaker. This step was repeated three times. The absorbance of each bottle was then measured with a UV-Vis spectrophotometer at a wavelength of 254 nm.

2.2.3 Determination of Optimum Conditions for Adsorption of Peat Water Organic Compound

a. *Effect of Water pH*

A total of 1 g of kaolin sample was put into ten glass bottles. 50 mL of peat water (pH = 4) was put into each bottle with a pH variation of 3.5; 4; 4.5; 5; 5.5; 6; 6.5; 7; 7.5; and 8 using a solution of H_2SO_4 and NaOH. After that, the mixtures were shaken using a shaker at 150 rpm for 2 h. This step was repeated three times. The absorbance of each bottle was then measured with a UV-Vis spectrophotometer.

b. *Effect of Stirring Time*

One gram of each activated kaolin sample was put in a glass bottle, and 50 mL of peat water was added. The pH of the peat water is adjusted to the optimum pH measurement. After that, the mixture was shaken at 150 rpm with a stirring time variation of 0.5; 1; 1.5; 2; and 2.5 h.

c. *Effect of Kaolin Mass*

Carefully weighed kaolin sample was put into five glass bottles with a kaolin mass variation of 50, 125, 250, 500, and 1000 mg. Next, 50 mL of peat water was added to each bottle.

d. *Effect of Stirring Speed*

Some kaolin sample activated according to step c was put in a glass bottle, and 50 mL of peat water was added. The pH of peat water was adjusted to the optimum pH as in the result of step a. The stirring speed was varied, namely 90.

2.2.4 Percentage of Decrease in Absorbance

The percentage decrease in absorbance was calculated using Eq. (1).

$$\text{Decrease in absorbance}(\%) = \frac{A_{initial} - A_{final}}{A_{initial}} \text{X}100\% \quad (1)$$

where,

$A_{initial}$ = peat water absorbance at 254 nm before adsorption
A_{final} = peat water absorbance at 254 nm after adsorption

The percentage of the decrease in absorbance was statistically analyzed to obtain the optimum calcination temperature and optimum adsorption conditions using the SPSS 17 application. The value displayed in the discussion section is the average value based on the ANOVA test at a 95% confidence level.

3 Results and Discussion

3.1 Determination of the Optimum Calcination Temperature of Kaolin

The percentages of decrease in absorbance for calcined kaolin for 3 h at temperatures of 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C are −34.54%; −20.65%; 66.07%; 76.33%; 77.31%; and 77.91% respectively (Fig. 1). Using kaolin increases the amount of organic matter in peat water at calcination temperatures of 200 °C and 300 °C. Using calcined kaolin at 300 °C causes the absorbance value of peat water at = 254 nm to

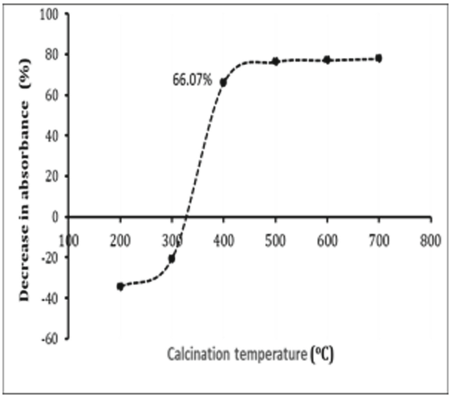

Fig. 1. Graph of the relationship between calcination temperature and the percentage reduction in the absorbance of peat water (Initial peat water absorption, $A_{initial} = 0.815$)

increase to 1.178 A. This indicates that kaolin still contains organic matter that has not been removed during the heating process at 300 °C. Organic matter in natural kaolin may come from nature or be additional during processing [16]. Naturally, organic matter can come from peat water sources [17]. Wahyuni et al. (2008), who studied the characteristics of kaolin originating from the same area as used in the current study reported that organic compounds present in natural kaolin would completely be lost if the calcination is carried out at a temperature above 450 °C [13]. Other researchers have reported that organic matter will be released if kaolin is heated at temperatures starting at 400 °C [16].

The most significant decrease in organic matter content, as indicated by the decrease in absorbance, was between temperatures of 300 °C to 400 °C. At a temperature of 400 °C to 700 °C, the percentage reduction in organic matter was quite high but not significantly different. Thus, the optimum temperature of kaolin calcination is at 400 °C, with a 66.07% decrease in organic matter. The 400 °C calcined kaolin will then be used as an adsorbent of organic matter in peat water.

3.2 Determination of Optimum Conditions for Adsorption of Peat Water Organic Materials

Organic matter will experience deprotonation in alkaline conditions so that functional groups such as carboxyl and hydroxyl become negatively charged. While at an acidic pH, organic matter will experience protonation so that the functional group will become positively charged. The effect of variations in the pH of the solution on the decrease in the absorbance of peat water is shown in Fig. 2.

In general, the result shows the percentage of decrease in absorbance decreases as the pH of the solution increases. The percentage of decrease in absorbance indicates the amount of organic matter absorbed by kaolin. In the pH range of 3.5 to 6, the decrease in absorbance is not significantly different, and then at pH 6.5 to 8, the decrease in absorbance is lower.

Organic compounds with both hydrophobic and hydrophilic sides and acidic functional groups such as carboxyl and hydroxyl will become more hydrophobic because the

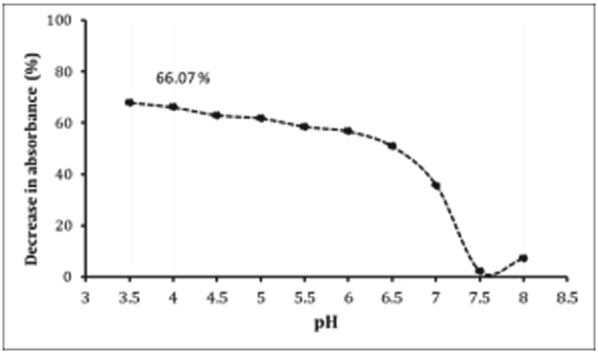

Fig. 2. Percentage of decrease in peat water absorbance at the variation of adsorption pH

acidic functional groups are protonated at low pH. Therefore, hydrophobic interactions can attract organic compounds to the surface of the kaolin. At low pH conditions, ligands are exchanged between the hydroxyl groups on the surface of the protonated and the carboxyl groups in humic acid [9].

At an alkaline pH, the functional groups of organic compounds will experience deprotonation and reduce the ability to form hydrogen bonds. Thus, it will increase the repulsion between organic compounds that can interfere with adsorption. Another mechanism is by decreasing the pH. The electrostatic repulsion force decreases so organic compounds can get closer to the kaolin.

The Limit Standard Deviation (LSD) test showed that at the 95% confidence level, pH 3.5 was not significantly different from pH 4; 4.5; 5; 5.5; and 6, while the water pH 6.5 was significantly different (not identical) with pH 7; 7.5 and 8 on the process of reducing organic matter in peat water. Meanwhile, the data on the percentage of decrease in absorbance shows that peat water with a pH of 3.5 to 6 gives better results than that with a pH of 6.5; 7; 7.5 and 8. This indicates that the pH of peat water which gives a good decrease in absorbance, is 3.5; 4; 4.5; 5; 5.5, and 6. The measurement results show that the adsorption process takes place more effectively in an acidic environment than in an alkaline environment. Because the initial pH of peat water is in the acidic pH range of 4, then pH 4 will be used as a fixed variable to determine the effect of other variables on peat water treatment. The decrease in organic matter obtained at pH 4 is 66.07%.

The stirring time in the adsorption process is related to the time given to the organic matter contained in the peat water to interact with the kaolin surface. The stirring time of 1.5 h gave the highest percent reduction in organic matter (Fig. 3). The optimum adsorption time means that the organic matter adsorption rate by calcined kaolin is the same as the rate of desorption [18].

Longer stirring time results in the release of organic matter previously adsorbed on the kaolin surface, as characterized by a decrease in the percentage of organic matter reduction. Organic matter that is easily released is caused by the adsorption process that occurs is a weak physical adsorption. The percentage of optimum decrease in organic matter of 71.93% was obtained with a stirring time of 1.5 h.

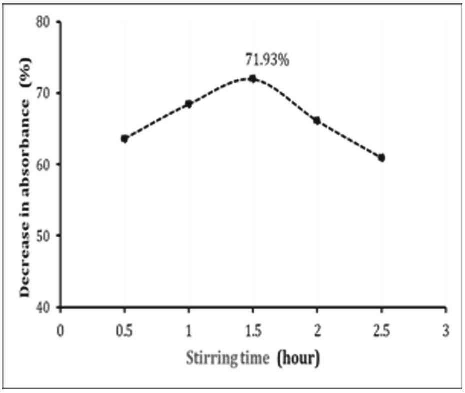

Fig. 3. The Effect of stirring time and the percentage decrease in the absorbance of peat water

Table 1. Comparison of kaolin mass and peat water volume

Kaolin Mass (mg): Peat Water Volume (mL)	% Decrease of Organic Compound
1: 1	32.30
2.5: 1	45.42
5: 1	59.86
10: 1	75.53
20: 1	71.93

The mass of kaolin as an adsorbent affects the adsorption process of organic matter. The percentage of decrease in absorbance tends to increase as the amount of calcined kaolin added increases. This is related to the number of kaolin active sites interacting with NOM. The increase in adsorbent mass will increase the availability of the active site and the surface area of the adsorbent that interacts with the adsorbate to increase adsorption [18]. If the amount of adsorbate increases, there will be aggregation between the adsorbent particles, which can reduce the adsorption rate [1, 19]. The comparison of the mass of kaolin with the volume of peat water can be seen in Table 1.

The stirring speed affects the adsorption process because the stirring speed is related to the activation energy required for organic matter to be adsorbed on the kaolin surface. The stirring speed of 150 rpm gave the optimum percent reduction of organic matter compared to the stirring speed of 90 and 120 rpm. Increasing the stirring speed above 150 rpm tends to decrease adsorption (Fig. 4). Increasing the stirring rate will increase turbulence which can cause the release of adsorbate bound to adsorbent particles [20]. The percentage decrease in optimum peat water absorbance at 150 rpm is 75.53%.

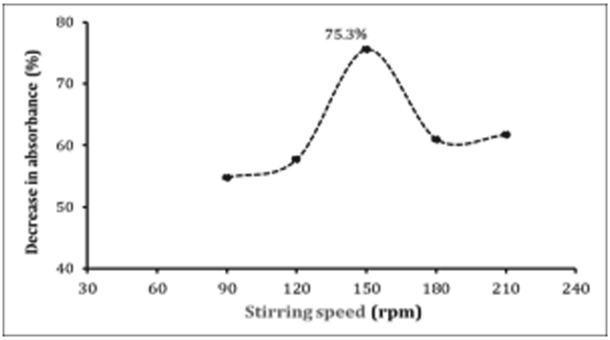

Fig. 4. Effect of stirring speed on the percentage decrease in the absorbance of peat water

4 Conclusion

From the results of the research that has been carried out, it can be concluded that peat water treatment using 400 °C calcined kaolin can adsorb organic matter in peat water by 75.53%. The optimum conditions for decreasing organic matter occurred in the adsorption process at pH = 4, stirring time of 1.5 h, kaolin mass of 500 mg per 50 mL of peat water and stirring speed of 150 rpm.

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