

MODIFIED KAOLIN WITH CATIONIC SURFACTANT FOR GIBBERELIC ACID CARRIER MATERIALS

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ABSTRACT

Synthesis of surfactant modified kaolin from natural kaolin from Tatakan, Tapin, South Kalimantan and its application for carrier material of gibberellic acid have been conducted. The kaolin modification was done by surface engineering using cationic surfactant cetyltrimethylammonium bromide (C₁₆TMABr). The characterizations of kaolin and surfactant modified kaolin were carried out by XRF, SEM, XRD, FTIR and TGA/DTA. The adsorption capacity of kaolin was determined by Langmuir adsorption isotherm model. The result showed that kaolin from Tatakan, South Kalimantan consist of kaolinite, halloysite, quartz, chlorite, and christobalite. Surface modification using cationic surfactant showed that increasing surfactant content onto kaolin was proportional to the amount of surfactant loaded. Gibberellic acid was partitioned into the organic phase created by the surfactant tails of the C₁₆TMA⁺ modified kaolin. The calculations result by Langmuir adsorption isotherm model showed that the highest increasing adsorption capacity occurred on surfactant modified kaolin with surfactant/CEC ratio of 2.0, with the adsorption capacity of 28.41 mg/g.

Keywords: natural kaolin, cationic surfactant, gibberellic acid

INTRODUCTION

Immobilization techniques of chemical substances such as proteins, enzymes, fertilizer, pesticide, hormones and other organic molecules have started to emerge at around 1980s. Since then, immobilization techniques have been developed in wide areas of industry producing medicine, food, health and agricultural products [1-2]. Some materials have been proven to be promising as carrier materials for immobilization of organic molecules, as these materials are able to enhance the mechanic and thermal stability of the molecules being carried. There are also some findings showing that these materials enhance the resistance of molecules towards attacks from microorganism and organic solvents [3]. Bindings of bioactive species on inorganic substances as their supportive materials also offer some advances as they enhance the safety of users and untargeted organism. Moreover, this method can also be alternatives to reduce environmental problems [4]. Recently, researches to develop controlled release technology on chemical substances used in agricultural sector are mainly focused on formulation of the carrier material. Some of it is kaolin [5], hydrotalcite [4], zeolites [6], clay minerals [7-8], polymer matrixes [9] and combination between clay and polymer [10].

Applications of clay materials and modified clay as carrier material are done on the basis of some advantageous properties of them. Clay owns a relatively wide surface area, a high adsorption capacity, favorable rheology properties, high stability which is followed with a low toxicity [11]. Interactions between clay and organic molecules are dependent on properties and type of the clays. In addition, the interactions will also be influenced by characteristics of the adsorbate, which include size, shape, solubility and hydrophobicity of the adsorbate.

Recently, to enhance the capacity of clay minerals, either to adsorb or immobilize hydrophobic organic molecules, researchers have tried to modify the properties of clays' surface in order to adjust it with the adsorbate properties. Modification of clay's surface by using cationic surfactants (quaternary ammonium cation) has been proven to have the ability of enhancing clay's capacity in adsorbing organic molecules. For example, this kind of modification has been used to adsorb industrial waste, or contaminants in water and soil, such as chromate, nitrate, naphthalene, and phenol [12-15]. Other applications of this modification are immobilization of pesticide onto clay's surface [16-18], reducing pesticide from water bodies [19-20], developing formulas for slow-released

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pesticides [21-22], and adsorbing a number of dyestuffs [23-24].

Gibberellic Acid ($C_{19}H_{22}O_6$) or *2,4a,7-trihydroxy-1 methyl-8-methylenegibb-3-ene-1,10-dicarboxylic acid* is one of the most attractive plant growth regulators hormone that regulates the growth of plants, including triggering seed germination [25]. The objective of this study was to compare the gibberellic acid sorption capacities of kaolin and kaolin modified with cethyltrimethylammoniumbromide ($C_{16}TMABr$) surfactant.

EXPERIMENTAL SECTION

Materials

Materials used in this study were natural kaolin obtained from Tatakan, Tapin, at the province of South Kalimantan, Indonesia. The chemical reagents used were NaOH, HCl, $C_{16}TMABr$ (Cethyltrimethylammonium-bromide), gibberellic acid and ethanol were purchased from Merck (Germany).

Instrumentation

Instruments used in this study were (X-ray fluorescence) XRF Philips PW 1480, (Fourier transform infrared) FTIR Spectrophotometer Shimadzu Prestige-21, X-ray Diffractometer Shimadzu XRD-6000, (Scanning electron microscope) SEM JEOL JSM-6360LA, UV-Visible spectrophotometer Shimadzu Model 1661, and (Thermo gravimetric analyzer) TGA instrument from Seiko.

Procedure

Kaolin Preparation

Kaolin sample from Tatakan, South Kalimantan was oven-dried at 80 °C for 24 h. The dried kaolin was then pulverized by using mortar and sieved through 200-mesh sieve. The purification method was carried out through sedimentation with reference to previous study [5]. Purified kaolin was then redried at 100 °C for overnight.

Kaolin Modification Using Cationic Surfactant $C_{16}TMA^+$

Fifty milliliters of $C_{16}TMABr$ was prepared. Ratio between amount of the surfactant towards the Cation Exchange Capacity (CEC) were varied to be 0.5; 1.0 and

2.0. Ten grams of kaolin were slowly added into the surfactant solution, and then continuously stirred for 24 h at room temperature. The suspension was then filtered to separate the precipitated kaolin. The precipitated kaolin was then washed using aquabidest until no bromide anion detected with $AgNO_3$. The modified kaolin's resulted were then labeled as Kao-CTMA-0.5; Kao-CTMA-1.0 and Kao-CTMA-2.0, in accordance with the ratio of surfactant's amount/CEC for each type of modified kaolin.

Adsorption of Gibberellic Acid

As much as 0.5 g modified kaolin prepared through procedures described in previous section was used to adsorb 25 mL gibberellic acid solution. The gibberellic acid solution used in this study was in various concentration, 100; 150; 200; 250 and 300 mg/L. The adsorption process was carried out in a batch system, by using rotary shaker. Conditions of the process were set at the optimum pH and time of contact, with reference to the previous study [5]. The amount of gibberellic acid which was not absorbed by the adsorbent was determined through Langmuir approach for isotherm adsorption. Langmuir equation for isotherm adsorption can be written as follows [26]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

The equation can be rewritten as a linear equation as follow:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} + \frac{1}{C_e}$$

q_m (adsorption capacity) represent the maximum amount of adsorbate that can be binded by the adsorbent's surface (mg/g), while K_L stands for Langmuir constants (L/mg or mL/mg), q_e represents the amount of adsorbate being adsorbed when adsorption process has reached its equilibrium, while C_e is the concentration of the solution at the point of adsorption equilibrium. The value of K_L and q_m can be determined by drawing a graph of $1/C_e$ versus $1/q_e$.

According to Vimonses et al. [27], the appropriateness of this Langmuir isotherm pattern can be represented by using RL at the parameter of equilibrium which is an undimensional separation factor, mathematically written as:

$$R_L = \frac{1}{1 + K_L C_i}$$

Table 1. Chemical composition of kaolin sample

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI
wt. %	43.09	38.49	1.12	0.0437	0.140	0.443	0.710	1.04	14.71

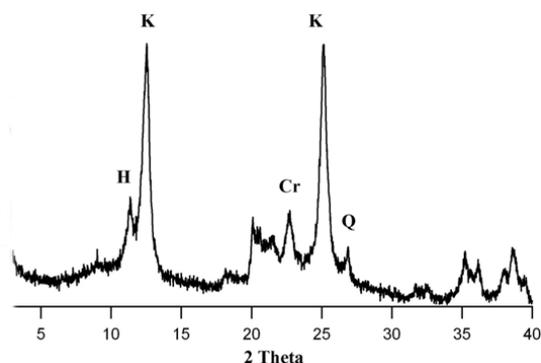
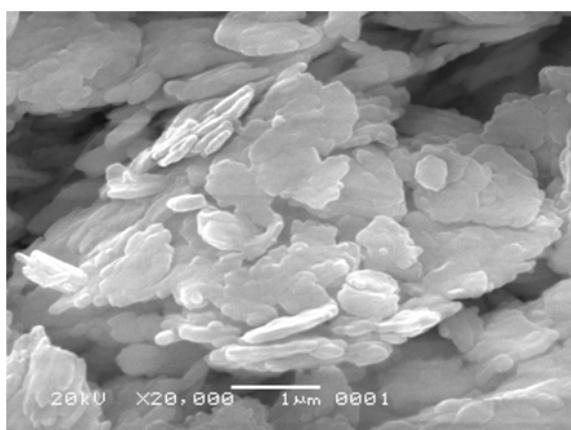
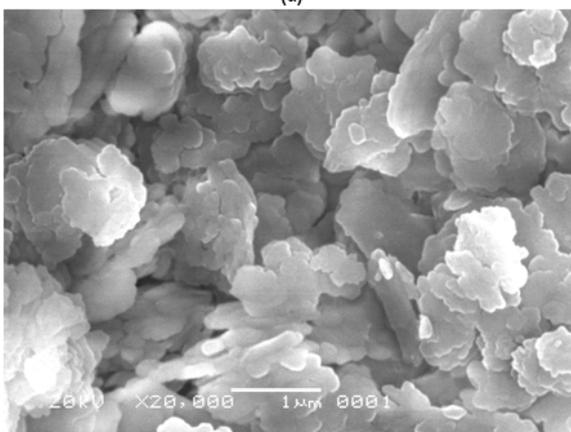


Fig 1. XRD pattern of kaolin from Tatakan. South Kalimantan. Indonesia (H=halloysite. K=kaolinite. Q=Quartz. Cr=Crysthobalite)



(a)



(b)

Fig 2. SEM of (a) kaolin and (b) modified kaolin with surfactant/CEC ratio 0.5

The value of R_L indicate the pattern of isotherm adsorption that occurred. When the value of $R_L > 1$, the type of adsorption is not appropriate. While the value of $R_L = 1$ indicates that it is a linear type, $0 < R_L < 1$ indicates that it is an appropriate type of isotherm, while $R_L = 0$ means the adsorption process is reversible.

RESULT AND DISCUSSION

Characterization of the kaolin

Kaolin used was rich in SiO_2 (~43.09%) and in Al_2O_3 (~38.49%) and contained small only small amount of Ca^{2+} , Mg^{2+} , Na^+ , Fe^{2+} , K^+ , Ti^{2+} ions (Table 1). Loss on ignition (LOI) was 14.71%. The XRD pattern of Tatakan kaolin is shown on Fig. 1. The kaolin samples showed diffraction patterns where the peak position of diffraction intensity at 2θ are 12.14; 12.42; 18.91; 19.98; 20.96; 21.38; 24.09; 25.02; 26.72 and 35.12. Diffraction peaks for each clay mineral are characteristic, where the 2θ angle of diffraction is highly interrelated with the crystal lattice of the minerals being analyzed. Through the identification done by observing the 2θ value ($^\circ$) of the crystals, Tatakan kaolin showed the presence of kaolinite, halloysite, quartz, and crystoballite. The micrographs of both kaolin (a) and kaolin modified with surfactant (b) are shown in Fig. 2, indicated a dominance of the characteristic morphology of both kaolin and modified kaolin, which has a layered group of hexagonal sheets. According to Murray [28], kaolin has layered pseudo-hexagonal structures as thick as 1-10 μm . Each layer consists of 10 to 50 sheets. SEM image of kaolin sample that has gone through the preparation process. Kaolin can be identified as groups of layered pseudo-hexagonal sheets. The surface morphology of modified kaolin (Fig. 2b) was smoother than that of unmodified kaolin with smaller fragments and a clearer sheet structure.

Modification of Kaolin Using Cationic Surfactants

In this study, the kaolin was modified by using $\text{C}_{16}\text{TMA}^+$ cationic surfactant with variations in the ratio of the surfactant amount and the CEC of kaolin. FTIR spectrum of kaolin and kaolin modified with cationic surfactant were shown in Fig. 3. From Fig. 3, it can be observed that here is a significant difference between the spectrum of kaolin before and after it is being treated with $\text{C}_{16}\text{TMA}^+$ surfactant. A significant difference that can be noticed is the appearance of new peaks at 2924.09 and 2854.65 cm^{-1} . These peaks come from the stretching vibration of aliphatic-C from the $\text{C}_{16}\text{TMA}^+$ surfactant [14]. Based on that FTIR spectrum, apparently there is an increase in the sharpness of the peak along with the increase of surfactant's concentration. This is an indication that there is a higher amount of surfactant being bounded to the kaolin's surface.

The widening of absorption peaks of the surfactant-modified kaolin also signifies that there have been changes taking place in the mineral's environment. At 1000 cm^{-1} , the peak become wider and

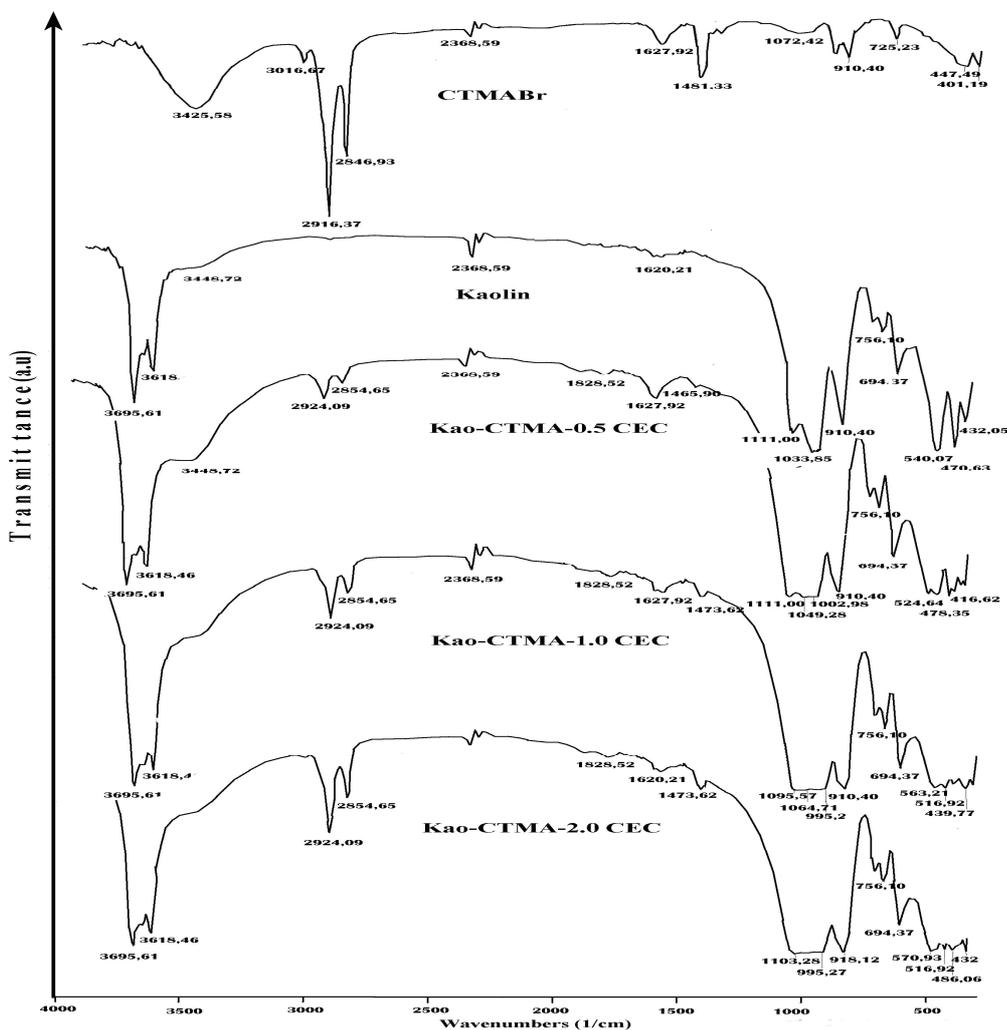


Fig 3. FTIR spectra of kaolin and surfactant modified kaolin

shifted from 1033.85 cm^{-1} to 995.27 cm^{-1} . Absorption peak in this area is characteristic for Si-O absorption of kaolinite materials. The widening and shifting of absorption bands were also detected at the area $400\text{--}500\text{ cm}^{-1}$. Absorption taking place at this range comes from stretch vibration of Si-O. This change implies that the modification with surfactant has altered the silicate environment of the kaolin. It is very likely that this change happened because the positively charged head-part of the cationic surfactant was attached to the surface of the surfactant, which is negatively charged. This comes in relevance with the conclusion stated by Zaman et al. [29] from their study about polyacrylic acid absorption on kaolin.

A semi-quantitative analysis was carried out through TGA. In this analysis, the amount of surfactant attached on the kaolin surface was estimated based on the mass reduction, shown in Table 2. To simplify the analysis, the temperature range was categorized into

three groups of range. All of the samples showed a relatively similar pattern at the range $28\text{--}200\text{ }^\circ\text{C}$. At this range of temperature, the process taking place is dehydration process, along with vaporization of other volatile substances from kaolin surface.

At the next stage of heating within the range $200\text{--}400\text{ }^\circ\text{C}$, there was a significant difference between the unmodified kaolin with the one modified with surfactant. At this range of temperature, the surfactant-modified kaolin appeared to undergo a substantial reduction of its mass. This mass reduction did not happen for the unmodified kaolin. It can be predicted that the mass reduction came as a result from the mass loss of organic molecules of the surfactant, which start to decompose at around $200\text{ }^\circ\text{C}$ [30-31].

At the next stage of heating ($400\text{--}500\text{ }^\circ\text{C}$), all samples (unmodified and modified kaolin) showed a significant mass reduction, implying that all of kaolin minerals have been dehydroxylated. The measurement

Table 2. Decreasing (%) of sample mass according to TGA

Sample	Decreasing mass (%)			
	T (°C) 28 - 200	T (°C) 200 - 400	T (°C) 400 - 500	T (°C) Σ 28 - 500
Kaolin	3.13	0.00	7.88	11.00
Kao-CTMA 0.5 CEC	2.50	1.88	7.88	12.25
Kao-CTMA 1.0 CEC	2.50	3.75	7.88	14.13
Kao-CTMA 2.0 CEC	2.50	6.88	7.88	17.25

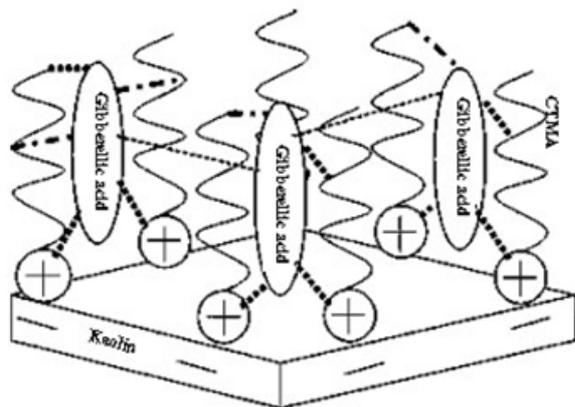


Fig 4. A schematic representation of configurations of adsorption of gibberellic acid onto modified kaolin (the dotted line represents hydrogen bonding; the dash and dot line represents hydrophobic interaction)

of weight loss on heating the unmodified and modified kaolin show that it losses ~7.88% weight in the 400–500 °C which is mostly due to combined water in the structure of kaolin mineral. This dehydroxylation is followed with process of decomposition into metakaolin [32-33]. It is reported that metakaolin has a structure containing ~11% of the total hydroxyls in the clay over most of its stability range [32]. According to Dion et al. [34] who studied dehydroxylation of kaolin, this process started to occur at 400 °C. The starting of the process is often signaled with lesser population of aluminium in the kaolin structure, due to the destructions of hydrogen bonding between the silica layers.

Based on the data, the highest percentage of mass reduction at 28–500 °C heating was observed to happen for the surfactant-modified kaolin with 2.0 ratio of surfactant/CEC. This fact suggests that a higher amount of surfactant being used to modify kaolin will be followed with a higher amount of surfactant being adsorbed.

Study of Gibberellic Acid Adsorption

Isotherm adsorption is an approach commonly used to determine adsorption capacity. In addition, this approach is also often used to draw a relationship between the weight of adsorbent and the amount of substances being adsorbed in an equilibrium state. In this study, Langmuir equation on isotherm adsorption

was used with reference to previous studies suggesting that adsorption of organic molecules onto kaolin surface fits Langmuir theory [14,26-27,35-36]. The adsorption process was carried out by varying gibberellic acid's concentration. In this study, the concentration was varied into 100, 150, 200, 250 and 300 mg/L. The condition was set at pH 7, while the time of contact between the adsorbent and gibberellic acid was set for 4 h. This condition was in accordance with the optimum condition suggested by the previous study [5]. The pattern of gibberellic acid adsorption by surfactant-modified kaolin as approached by Langmuir's theory. Table 3 leads to a deduction that the adsorption process of the adsorbents tended to suit the Langmuir theory of isotherm adsorption. Table 3 showed that $R^2 > 0.9$ for all adsorbents, making it possible to determine the adsorption capacity for each adsorbent by using Langmuir model of isotherm adsorption. How the adsorption pattern fits the Langmuir model can also be assessed by considering the separation factor constants, or Langmuir equilibrium parameters. To satisfyingly fits the Langmuir model, it is expected that $0 < R_L < 1$ [27].

As for this study, the values of q_m , R_2 and R_L are listed in Table 3. The result tabulated in this table leads to a conclusion that modification of kaolin using cationic surfactant is able to enhance the adsorption capacity of natural kaolin. This result some in accordance with studies done by Li and Bownman [12], and Khrisna et al. [13], Lee and Kim [14]. Those studies also come with a conclusion that modification of kaolin by using surfactant enhances kaolin's capacity in adsorbing organic molecules and inorganic anions, especially when the amount of surfactant is twice as much from the CEC value of kaolin. The increase in adsorption capacity of kaolin is possibly due to the change of properties of the surface from hydrophilic to be more hydrophobic.

The surface property of modified kaolin plays a key role in gibberellic acid adsorption performance which depends upon the way kaolin is modified with $C_{16}TMA$. A complete organic monolayer surface coverage by $C_{16}TMA$ means that electrostatic interaction, ligand exchange and cation bridging could not be the predominant mechanism. Considering the variability and numerous function groups of gibberellic acid molecules and the unique properties of surface of

modified kaolin we propose that multiple mechanisms are involved in the sorption of gibberellic acid by modified kaolin. Hydrophobic interaction and hydrogen bonding are suggested to be the major mechanism in gibberellic acid adsorption by modified kaolin. Adsorption by kaolin surface is relatively unimportant, presumably because of the strong dipole interaction between kaolin and solvent, which excludes organic solutes from this portion of the kaolin. After kaolin was modified with C₁₆TMA, hydrophobic organic monolayer surface coverage by C₁₆TMA would induce more contact and interaction with soluble gibberellic acid and then enhance the adsorption of gibberellic acid by van der Waals interactions. A large number of hydrogen bonds between C or N of C₁₆TMA and hydroxyl groups, carboxylic groups and phenolic groups of gibberellic acid additionally guarantee the effective adsorption of gibberellic acid. All of this could make up a complicated three-dimensional structure (Fig. 4). This change enhances the ability of modified kaolin to interact with gibberellic acid. The interaction between organic molecules and organoclays through hydrophobic interaction has been discussed quite comprehensively by Carrizosa et al. [21], based on their study about the interaction between organoclays with bentazon and dicamba.

CONCLUSION

The ratio between the amount of surfactant and CEC of the kaolin holds an important role in determining the amount of surfactant being attached onto the kaolin surface, and how surfactant is being distributed on the surface. This ratio also affects the capacity of adsorbent in adsorbing gibberellic acid. In this study, kaolin which was modified with C₁₆TMABr offered the most satisfying result of modification when the surfactant/CEC ratio was 2.0. In this composition, the adsorbent showed the highest adsorption capacity (28.41 mg/g) among adsorbents with other ratio compositions of surfactant and CEC.

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