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# Potential of Dimethyl Sulfoxide Modified Kaolin and Cetyl Trimethylammonium Bromide as Amoxicillin Adsorbent

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## Abstract

The large use of amoxicillin allows this antibiotic to enter the environment in large quantities and cause pollution. The adsorption technique can be used as a method to remove amoxicillin contaminants in wastewater by utilizing kaolin as an adsorbent. This study aims to determine the characteristics of kaolin as an adsorbent and determine the ability of kaolin to adsorb amoxicillin. Kaolin was activated with hydrochloric acid and modified using Dimethyl sulfoxide (DMSO) and cetyl trimethylammonium bromide (CTAB). The results showed that the characteristics of DMSO and CTAB-modified kaolin showed a new peak which was an O-H bending vibration in functional group analysis using FTIR. X-ray diffraction results show that the distance between planes in the kaolin structure is larger. Meanwhile, the results of the SEM analysis showed that the surface morphology of kaolin had a higher level of crystallinity than before which proved an increase in the adsorption capacity of kaolin. The adsorption kinetics follows the Santosa kinetic equation model with an adsorption rate of 0.004 $min^{-1}$ and an equilibrium constant value of 0.007 $L.mol^{-1}$. The adsorption isotherm test follows the Freundlich isotherm equation model with an adsorption constant value of 561.694 $L.mg^{-1}$ and an empirical constant value of 0.270.

*Keywords: Antibiotics, Adsorption, Batch, Isotherms, Kinetics*

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## Abstrak (Indonesian)

Penggunaan amoksisilin yang banyak membuat antibiotik ini dapat masuk ke lingkungan dalam jumlah besar dan menyebabkan pencemaran. Teknik adsorpsi bisa digunakan sebagai metode untuk menghilangkan kontaminan amoksisilin dalam limbah cair dengan memanfaatkan kaolin sebagai adsorben. Penelitian ini bertujuan untuk mengetahui karakteristik kaolin sebagai adsorben dan mengetahui kemampuan kaolin menyerap amoksisilin. Kaolin diaktivasi dengan asam klorida dan dimodifikasi menggunakan Dimethyl sulfoxide (DMSO) dan Cetyl trimethylammonium bromide (CTAB). Hasil penelitian menunjukkan bahwa karakteristik kaolin modifikasi DMSO dan CTAB menunjukkan adanya puncak baru yang merupakan vibrasi tekukan O-H pada analisis gugus fungsi menggunakan FTIR. Hasil difraksi sinar X menunjukkan jarak antar bidang pada struktur kaolin menjadi lebih besar. Sementara itu, hasil analisis SEM menunjukkan morfologi permukaan kaolin yang memiliki tingkat kristalinitas lebih tinggi dari sebelumnya yang membuktikan adanya peningkatan kemampuan adsorpsi pada kaolin. Kinetika adsorpsi mengikuti model persamaan kinetika Santosa dengan nilai laju adsorpsi sebesar 0,004 $min^{-1}$, dan nilai konstanta kesetimbangan sebesar 0,007 $L.mol^{-1}$. Pengujian isoterm adsorpsi mengikuti model persamaan isoterm Freundlich dengan nilai konstanta adsorpsi sebesar 561,694 $L.mg^{-1}$ dan konstanta empiris senilai 0,270.

*Kata Kunci: Antibiotik, Adsorpsi, Batch, Isoterm, Kinetika*

## INTRODUCTION

Pollution that occurs in the aquatic environment has now become a serious threat to human health, so it is necessary to make efforts to reduce pollutants from the water matrix. One type of pollutant that often contaminates water resources is organic pollutants, also known as "emerging pollutants". These pollutants consist of drugs, hormones, pesticides, and so on [1].

Antibiotics are products that are often used to treat a disease caused by a bacterial infection [2]. One type of antibiotic that is often used is amoxicillin. Antibiotics from the penicillin class are usually used to treat various types of infections and are one of the most widely used types of antibiotics because they have a broad antibacterial spectrum, have high oral bioavailability and are relatively inexpensive [3]. However, along with the many uses of amoxicillin, this antibiotic can enter the aquatic environment through the pharmaceutical industry, hospital waste, urine, and feces. This causes pollutants from amoxicillin waste to contaminate sewers, ground surfaces, drinking water, and groundwater, thereby posing a threat to the environment [1]

Among the technologies for reducing the content of antibiotics in wastewater, the adsorption technique is one method that is often used. The use of clay or kaolin can be chosen as an adsorbent for amoxicillin. That is because both of them are common silicate natural minerals that have the characteristic phyllosilicate crystal structure and are categorized into seven main groups which are studied extensively as adsorbents [4]

The adsorption capacity of kaolin on amoxicillin can be increased by activating it with hydrochloric acid. Activation using acidic compounds will produce kaolin with an active site and greater surface acidity. The addition of hydrochloric acid will make the kaolin surface acidic so that the conductivity value can be increased. Thus, kaolin can be produced which has a higher adsorption capacity than before the activation [5]

Kaolin can be modified using dimethyl sulfoxide (DMSO) and cetyl trimethylammonium bromide (CTAB) so that it has a very high adsorption capacity compared to most other kaolin-based adsorbents [6]. This study aims to see the absorption ability of kaolin modified with DMSO and CTAB against amoxicillin.

The adsorption system can be carried out by two methods, namely the static method (batch) and the dynamic method (continuous or column). However, the most common and easy-to-use method is batch. Adsorption in the batch method is an adsorption process in which the adsorbent is mixed with a solution in a fixed amount and changes in quality are observed within a certain time interval [7].

## MATERIALS AND METHODS

### *Materials*

The kaolin materials were purchased from PT. Yudian Friend of Minerals (Yukami). Chemicals and reagents used included amoxicillin (Sigma-Aldrich), hydrochloric acid, sodium chloride, methanol, CTAB, DMSO, and distilled water.

### *Kaolin activation using hydrochloric acid*

Kaolin is heated in an oven at 100 °C until dry. The refined kaolin was weighed as much as 10 grams and put into a 100 mL beaker. The 100 mL of 0.25 M HCl was added and the mixture was stirred at 200 rpm for 120 minutes. Then, the kaolin was separated from the HCl solution by filtering using a vacuum. The remaining kaolin on the filter paper is washed with distilled water and then put in the oven to dry [5].

### *Modification of kaolin with DMSO and CTAB*

Modification step was carried out by dispersing 5 g of kaolin powder in 10 mL of DMSO solution (the ratio of DMSO to water was 10:1) while stirring for about 24 hours. Kaolin and DMSO were separated and washed extensively with methanol five times. After that, 3 g of the resulting methoxy kaolinite was mixed with 100 mL of CTAB solution and stirred for 12 hours. Samples were washed with distilled water and methanol and then stored in tubes. The samples were characterized using FTIR, SEM, and XRD [6].

### *Analysis of effect of amoxicillin contact time with adsorbents*

A total of 20 mg of sample was added to 100 mL of 15 ppm Amoxicillin solution and stirred with an orbital shaker at 100 rpm. The solution was filtered by the filtrate for analysis using a UV-Vis Spectrophotometer at the maximum wavelength. Variations in contact time are 15, 30, 45, 60, and 75 minutes. The test was repeated three times [8].

### *Analysis of the effect of amoxicillin concentration*

A total of 20 mg of sample was added to 100 mL of Amoxicillin solution with various concentrations of 5, 7.5, 10, 12.5, and 15 ppm and stirred with an orbital shaker at 100 rpm. The solution was filtered by filtrate and analyzed with a UV-Vis Spectrophotometer at the maximum wavelength. The test was repeated three times [8].

### *Determination of the crystallinity degree of the adsorbent*

A Bruker XRD D2 Phaser Powder X-ray Diffractometer was used to record the diffractogram of

the adsorbent sample. Determination of the crystallinity degree ($C$) by this instrument uses the equation (1).

$$C = \frac{A_c}{A_c + A_a} \times 100\% \quad (1)$$

$A_a$ represents the diffractogram's amorphous peaks and $A_c$ represents the area of the crystalline peaks. This technique, known as Hinrichen's method, uses gaussian functions to fit the diffractogram and do calculations[9].

***Determination of the percent adsorption of amoxicillin by adsorbent***

The amount of amoxicillin that is adsorbed is usually called the percent adsorbed. The percent adsorbed was obtained by comparing the adsorbate concentration that was successfully absorbed by the adsorbent with the initial concentration of the adsorbate before the adsorption process. Mathematically it can be written as in equation (2).

$$Percent\ adsorbed = \frac{C_a - C_0}{C_0} \times 100\% \quad (2)$$

Where $C_a$ is the adsorbate concentration after the adsorption process, while $C_0$ is the initial adsorbate concentration before adsorption [10].

## RESULTS AND DISCUSSION

***Results of kaolin activation with hydrochloric acid***

Activation of kaolin using 0.25 M Hydrochloric Acid aims to increase the adsorption capacity of kaolin to be able to absorb Amoxicillin. Hydrochloric acid is a strong acid with a high $H^+$ equivalent number and is an effective compound for removing impurities contained in kaolin. By decreasing the level of impurities, a space will form on the kaolin surface which allows Amoxicillin to be absorbed optimally during the adsorption process [5].

The addition of hydrochloric acid also functions to activate the Bronsted site found in the kaolin aluminosilicate structure. Hydrochloric acid can completely dissociate in water and form $H^+$ and $Cl^-$ ions. However, the concentration of hydrochloric acid used must be precise and not too high so as not to cause the dealumination of the kaolin. The activated kaolin is washed with aqua de mineral to remove $Cl^-$ ions from the acid [11].

***Results of kaolin modification with DMSO and CTAB***

Kaolin can be modified by adding DMSO and CTAB solutions to increase its adsorption capacity. Kaolin has very strong hydrogen bonds and is composed of closely packed layers. Therefore, DMSO, which has a small and very polar molecule, could be a candidate to release the hydrogen bond [4]. DMSO intercalation will produce long-lasting modifications. Meanwhile, CTAB is a cationic surfactant that can form a structure on kaolin, where this structure can increase the adsorption ability of kaolin [12].

***Kaolin functional group***

The modification processes the functional group prediction results did not appear to show a significant difference compared to pure kaolin (**Figure** 1). The hydroxyl group was still shown at wave numbers 3687 $cm^{-1}$ and 3621 $cm^{-1}$ for activated kaolin and at wave numbers 3688 $cm^{-1}$, 3621 $cm^{-1}$, 3687 $cm^{-1}$, and 3549 $cm^{-1}$ for kaolin DMSO-CTAB. Wave numbers 1114 $cm^{-1}$ and 1113 $cm^{-1}$ indicate the presence of siloxane functional groups (Si-O-Si), while Al-OH and silanol groups (Si-OH) are indicated by wave numbers 993 $cm^{-1}$ and 994 $cm^{-1}$, and 907 $cm^{-1}$ and 908 $cm^{-1}$ in activated kaolin and DMSO-CTAB kaolin. The Si-O-Al groups can be seen at wave numbers around 789-788 $cm^{-1}$ respectively. Meanwhile, new peaks appeared indicating the presence of Si-O groups in the area 681 $cm^{-1}$, 665 $cm^{-1}$, and 654 $cm^{-1}$ in activated kaolin and the area 749 $cm^{-1}$, 671 $cm^{-1}$, 654 $cm^{-1}$ in kaolin DMSO-CTAB.

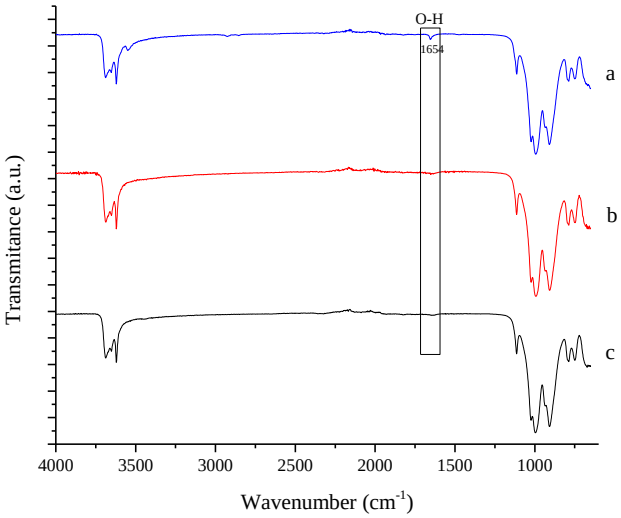



**Figure 1.** Kaolin FTIR Analysis Results: (a) Pure Kaolin, (b) Activated Kaolin, (c) DMSO-CTAB Modified Kaolin.

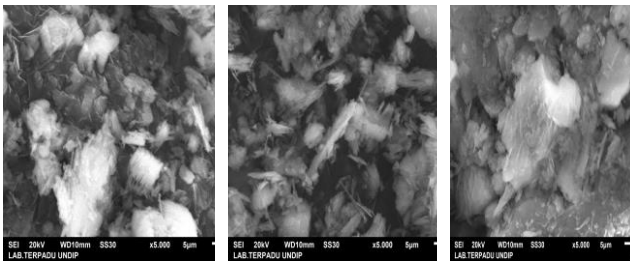
On the other hand, a new peak appeared in the modified kaolin, namely at wave number 1653 $cm^{-1}$ which was designated as the O-H functional group. The appearance of this new peak comes from the O-H bending vibrations due to the presence of water

molecules in the kaolin interlayer space after modification [4].

***Kaolin surface morphology***

The surface morphology of the adsorbent was analyzed using SEM. In the SEM results of kaolin shown in **Figure** 2, it can be seen that kaolin has a morphology in the form of layers or sheets. This structure comes from the main mineral content of kaolin, namely kaolinite which consists of sheets or thin layers composed of layers of silica ($SiO_2$) and alumina ($Al_2O_3$) [13].

In pure kaolin, it can be seen that there are still impurities scattered on the surface. In contrast to kaolin which has been activated with HCl which shows a cleaner morphology, where the kaolinite layer is more clearly visible. Meanwhile, in modified kaolin, it can be seen that the surface is increasingly closed which indicates higher kaolin crystallinity.



**(a)** **(b)** **(c)**

**Figure 2.** SEM results at 5000x magnification (a) Pure Kaolin (b) Activated Kaolin (c) DMSO-CTAB Kaolin

***Kaolin crystallinity***

The diffraction pattern of the modified kaolin was interpreted using X-ray diffraction (XRD) with Cu-Kα radiation (λ = 1.5406 Å). The range 3° to 90° is used as the scanning angle range.

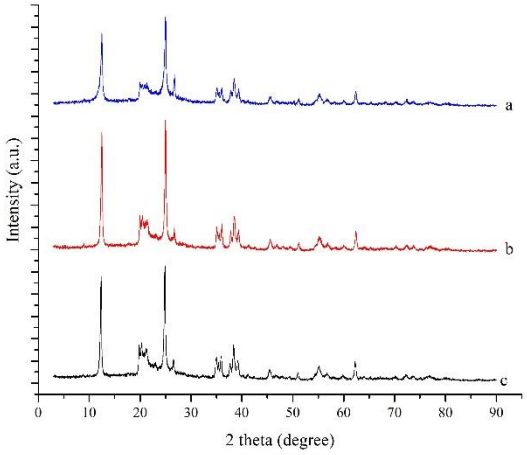



**Figure 3.** Kaolin XRD spectra: (a) Pure Kaolin, (b) Activated Kaolin, (c) DMSO-CTAB Modified Kaolin

Based on the resulting XRD diffractogram (**Figure** 3), kaolin has high crystallinity with its main peaks in the 2θ region, namely 12.293°, 20.337°, 24.853°, and 38.382°. After kaolin was activated and modified, the diffraction peak shifted to the left with a smaller value of 2θ. An angle shift of 2θ to the left will result in a larger distance between the planes [14].

XRD analysis also produces the crystallinity value of kaolin. Where pure kaolin has a crystallinity of 74.1%, activated kaolin is 83.3%, and DMSO-CTAB-modified kaolin has the highest crystallinity value, which is 98.9%. The higher the crystallinity value of kaolin, the more regular and denser the crystal structure. High crystallinity results in a rougher surface on kaolin so that it can provide more adsorption sites available to interact with amoxicillin [15].

***Effect of amoxicillin contact time with adsorbents***

Contact time is one of the most important parameters in the adsorption process. The contact time is related to the rate of reaction which is expressed as the change in concentration over time. The results of the adsorbed amoxicillin levels at various contact times of 15-75 minutes are shown in **Figure** 4.

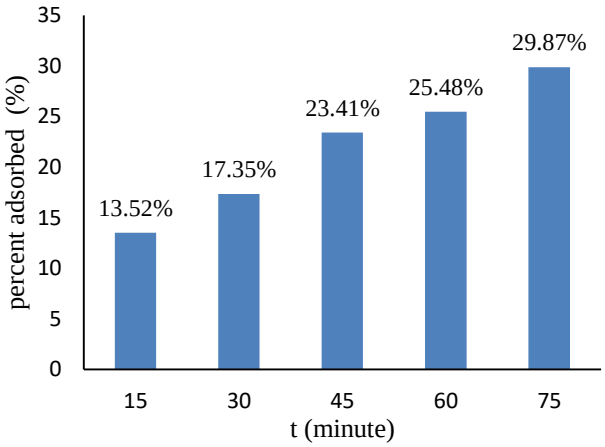



**Figure 4.** Effect of variation in contact time between amoxicillin and adsorbent

Based on **Figure** 4, it can be seen that the longer the contact time between the adsorbate and the adsorbent, the more amoxicillin levels are adsorbed. This was shown by the adsorption efficiency which increased over time and reached its peak in the 75th minute with an adsorption efficiency value of 29.87%. The data obtained from this variation can be used to determine the adsorption kinetics model that occurs during the adsorption process, including the Lagergreen kinetic equation model, the Ho kinetic equation model, and the Santosa kinetic equation model.

Adsorption kinetics states that there is a process of absorption of a substance by an adsorbent as a function of time. The characteristics of the adsorbent's absorption ability towards adsorbate can be seen from the adsorption rate. The adsorption rate can be determined from the adsorption rate constant ($k$) and the reaction order resulting from an adsorption kinetics model [16].

A pseudo-first order kinetic model is derived based on the Lagergren reaction rate equation. Lagergren's pseudo first order equation is given in equation (3).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where $q_t$ is the amount of adsorbate absorbed at time $t$ (mg.g$^{-1}$), $q_e$ is the equilibrium adsorption capacity (mg.g$^{-1}$), and $k_1$ is the rate constant of the lagergreen pseudo first order equation (min$^{-1}$).

The pseudo second order kinetic model (Ho) can be expressed as in equation (4).

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}\mathrm{t} \quad (4)$$

Where $k_2$ is the second order pseudo model rate constant (g.mg$^{-1}$.min$^{-1}$).

Santosa is based on the adsorbate concentration in the solution with the assumption that the adsorption is first order adsorption which reaches equilibrium. Mathematically it can be written as equation (5).

$$\frac{\ln(\frac{C_o}{C_a})}{C_a} = k\frac{t}{C_a}K \quad (5)$$

Where $k$ is the adsorption rate (min$^{-1}$), and $K$ is the equilibrium constant (L.mol$^{-1}$). The parameter results of the adsorption kinetics equation are presented in **Table** 1.

**Table 1.** Adsorption Kinetic Parameters of Lagergreen, Ho, and Santosa

| Kinetic Models | Parameter | Value |
|---|---|---|
| Lagergreen | $R^2$ | 0.976 |
| | $K$ | 0.031 g.mg$^{-1}$.min$^{-1}$ |
| | $qe$ | 20.710 mg.g$^{-1}$ |
| Ho | $R^2$ | 0.954 |
| | $K$ | 0.001 g.mg$^{-1}$.min$^{-1}$ |
| | $qe$ | 32.787 mg.g$^{-1}$ |
| Santosa | $R^2$ | 0.989 |
| | $K$ | 0.007 L.mol$^{-1}$ |
| | $k$ | 0.004 min$^{-1}$ |

**Table** 1 shows that the adsorption of amoxicillin by the adsorbent follows the Santosa kinetic model with the largest and best determination coefficient ($R^2$) compared to other kinetic models. Santosa kinetics assumes that the initial concentration of the adsorbate ($C_0$) does not affect the course of the reaction rate and what does affect it is the concentration of the adsorbate at $a$ certain $t$ state ($C_a$) [17]. In addition, a value of the adsorption rate ($k$) is comparable to the slope value on the Santosa kinetics graph, which is 0.004 min$^{-1}$. That is, the rate of adsorbent in adsorbing is 0.004 ppm per minute. Meanwhile, the value of the equilibrium constant (K) obtained is 0.007 L.mol$^{-1}$.

***Effect of amoxicillin concentration on absorption***

Determination of the optimum concentration or adsorption isotherm aims to see the absorption mechanism of the adsorbent in the adsorption process [18]. **Figure** 5. shows the results of adsorption efficiency with variations in the concentration of the adsorbate, namely 5, 7.5, 10, 12.5, and 15 ppm.

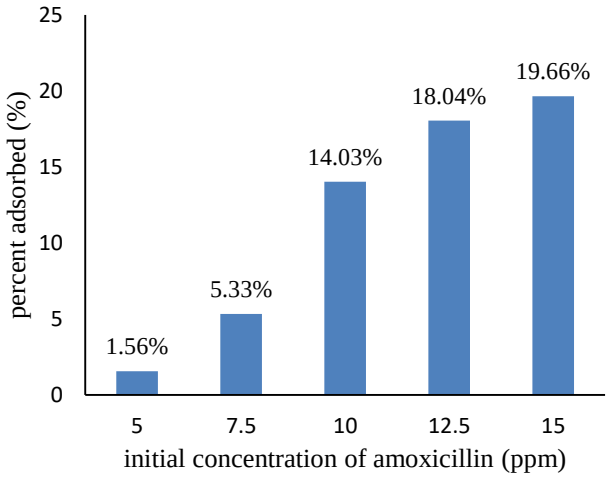



**Figure 5.** Amoxicillin Adsorption Efficiency with Variation of Adsorbate Concentration.

In determining the effect of concentration in the adsorption process, it was stated that the higher the adsorbate concentration, the more amoxicillin was adsorbed [19]. In modified kaolin with varying concentrations of Amoxicillin, there was an increase in adsorption efficiency at each concentration, with the highest efficiency being obtained, which was 19.65% at a concentration of 15 ppm.

The equilibrium relationship between the concentration in the liquid phase and the concentration in the adsorbent particles at a certain temperature can be determined using the adsorption isotherm. The adsorption isotherm takes place at a fixed temperature. The most common and widely used adsorption isotherm models in adsorption are the Langmuir isotherm model and the Freundlich isotherm model. [16].

Adsorption of adsorbate with the adsorbent used can be evaluated based on equation (6). Equation (6) is also called the Langmuir equation.

$$q_e = q_m \times K_l \frac{C_a}{1+K_l.C_a} \quad (6)$$

Where $q_m$ is the maximum adsorption capacity (mg.g$^{-1}$), $C_a$ is the concentration of solute in the solution after equilibrium occurs, and $K_l$ is the Langmuir adsorption constant (L.mg$^{-1}$).

Apart from using the Langmuir equation, the evaluation of adsorbate adsorption with adsorbents can also be done using the Freundlich equation (equation (7)).

$$q_e = k_F.C_a^{\frac{1}{n}} \quad (7)$$

Where $q_e$ is the amount of substance adsorbed per gram of adsorbent (mg.g$^{-1}$), $C_e$ is the concentration of solute in the solution after equilibrium occurs, and $k_F$ and $n$ are the adsorption capacity and intensity respectively.

The results of the isotherm parameter analysis using the Freundlich and Langmuir isotherm equation models are presented in **Table** 2.

**Table 2.** Freundlich and Langmuir Adsorption Isotherm Parameters

| Isotherm Models | Parameter | Value |
|---|---|---|
| Freundlich | $R^2$ | 0.970 |
| | $K$ | 561.694 L.mg$^{-1}$ |
| | $n$ | 0.270 |
| Langmuir | $R^2$ | 0.957 |
| | $Kl$ | 11.547 L.mg$^{-1}$ |
| | $qm$ | 0.091 mg.g$^{-1}$ |

**Table 3.** Adsorption of Amoxicillin using Several Adsorption

| Adsorbent | Adsorption Capacity | References |
|---|---|---|
| Zr-MOFs nanoparticle (UiO-66-H) | 2.3 ± 0.4 mg.g$^{-1}$ | [21] |
| *Pragmites australis* carbon | 110 mg.g$^{-1}$ | [22] |
| Acid-activated carbon from *Propolis juliflora* | 714.29 mg.g$^{-1}$ | [23] |
| Bentonite-chitosan composite | 66.1 mg.g$^{-1}$ | [24] |
| $MnO_2$ nanosheets | 16.094 mg.g$^{-1}$ | [25] |
| Activated carbon based on olive biomass | 166.96 mg.g$^{-1}$ | [26] |
| DMSO-CTAB kaolin | 561.694 L.mg$^{-1}$ | This Research |

It can be seen that Amoxicillin adsorption follows the Freundlich isotherm model with a larger $R^2$ value and close to 1 compared to the Langmuir isotherm model, which is 0.970 with a constant value adsorption ($K$) of 561.694 L.mg$^{-1}$ and empirical constant ($n$) of 0.270. So it can be assumed that the surface of kaolin as an adsorbent is heterogeneous and each molecule has a different adsorption capacity [20]. The comparison of the results obtained in this research with previous research is listed in **Table** 3.

## CONCLUSION

Kaolin which has been modified using DMSO and CTAB has a higher adsorption capacity than pure kaolin. The results of the modified kaolin characterization using DMSO-CTAB showed a new peak at wave number 1653 cm$^{-1}$ which is an O-H bending vibration in functional group analysis using FTIR. The results of X-ray diffraction show a shift in the value of 2θ to the left which indicates the distance between the planes becomes larger. Meanwhile, the results of SEM analysis showed that the surface morphology of kaolin was increasingly closed. Testing the modified kaolin adsorption kinetics using DMSO-CTAB on amoxicillin follows the Santosa kinetic equation model with an $R^2$ value of 0.989, an adsorption rate value ($k$) of 0.004 min$^{-1}$, and an equilibrium constant value ($K$) obtained of 0.007 L.mol$^{-1}$. Meanwhile, the adsorption isotherm test follows the Freundlich isotherm equation model with an $R^2$ value of 0.970, an adsorption constant ($K$) value of 561.694 L.mg$^{-1}$, and an empirical constant ($n$) of 0.270.

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