



Efficient and Low-Cost Removal of Methylene Blue using Activated Natural Kaolinite Material

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Abstract

Clays are low-price and very useful material for water treatment purpose. In this work, we reported the application of activated natural kaolinite material which obtained from Wediombo beach, Yogyakarta for methylene blue adsorption. The natural kaolinite material was activated under an acidic condition to obtain the activated kaolinite material. The activated kaolinite material was characterized using Fourier transform infrared, X-ray diffraction, scanning electron microscope, and surface analysis. From the adsorption experiment, the activated kaolinite material gave moderate adsorption percentages for methylene blue. The adsorption kinetics followed the Ho and McKay kinetic model while the adsorption isotherm followed Langmuir model. The q_{\max} value for methylene blue adsorption using activated natural kaolinite material was at a moderate level (3.40 mg g^{-1}). The plausible adsorption mechanism of methylene blue on the surface of activated kaolinite material happened through hydrogen bondings and/or electrostatic interactions. These findings are important for a wastewater treatment using a low-cost adsorbent material.

Keywords: kaolinite, adsorption, methylene blue, Wediombo beach, acid activation

1. INTRODUCTION

Water pollution has reached alarming levels nowadays thus there is no option to neglect pollutant removal issue [1][2]. Among the harmful water pollutants, synthetic dyes are the most stable chemicals in the aquatic environment. Their stability is a very serious issue because it means their degradation process may take a very long period thus heightens the possibility to spread out and reach our food chain [3]. Methylene blue is a synthetic sulfur- and nitrogen-heterocyclic compound that widely used for textile and dye applications in our life. Unfortunately, methylene blue is a very toxic chemical for human health because it generates headache, nausea, skin irritation, respiratory infection and nervous disruption [4][5]. Because of that, effort on the removal of methylene blue shall be carefully considered.

Adsorption is the simplest removal technique of

methylene blue at room temperature and ambient pressure [6]. Hundreds of adsorbent materials have been designed and investigated for methylene blue removal, however, some of the adsorbent materials are expensive and they need a complicated preparation [7]-[12]. Clay materials are low-cost adsorbent materials because they are naturally abundant in Indonesia [13][14]. Activated montmorillonite and bentonite materials showed remarkable adsorption capability for methylene blue removal from the aqueous phase [15]-[17]. It was reported that natural kaolinite clay material was found at Wediombo beach, Yogyakarta [18], however, their application for methylene blue adsorption has not been reported yet. Therefore, an effort on the utilization of natural kaolinite material for an environmental remediation process is challenging for the researcher.

In the present work, we evaluated the application of activated kaolinite for methylene blue removal from the aqueous solution. The activated kaolinite material was characterized using Fourier transform infrared, X-ray diffraction, scanning electron microscope, and surface analysis. The adsorption kinetics and isotherm adsorption experiments of methylene blue adsorption using activated kaolinite materials will be discussed.

2. MATERIALS AND METHODS

2.1. Materials

Kaolinite material from Wediombo beach and

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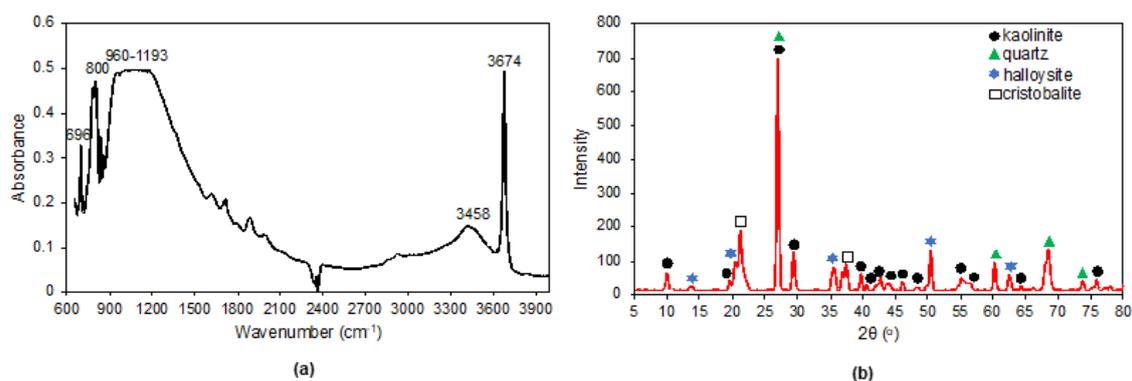


Figure 1. (a) FTIR spectrum and (b) XRD pattern of activated kaolinite material.

distilled water were purchased from Progo chemical distributor while methylene blue and concentrated sulfuric acid (98%) was purchased from Merck in pro analytical grade.

2.2. Instruments

The Fourier transform infrared (FTIR) of the material was measured by a Shimadzu IR Prestige-21 spectrophotometer while the morphological image of the material was recorded using a scanning electron microscope (SEM) JEOL JSM-6510. The X-ray diffractogram of the material was obtained using Shimadzu XRD S-6000. The surface analysis of the material was examined through a nitrogen adsorption-desorption method using a Quantachrome Nova station A apparatus. The concentration of methylene blue in the aqueous solution was measured from a standard curve with several concentration series (5, 10, 20, and 30 mg L⁻¹) using a double beam Shimadzu UV-Vis spectrophotometer UV-1800.

2.3. Methods

2.3.1. Activation of Kaolinite

Activation of kaolinite material was carried out

in a similar procedure previously reported by Kurniawan et al. [19]. Briefly, as much as 10 g of raw kaolinite material was added into 100 mL sulfuric acid 1.0 M. The mixture was refluxed at 350 K for 6 h. After the reaction, the mixture was filtrated and the residue was washed until neutral. The residue was dried at 330 K and characterized by FTIR, XRD, SEM, and surface analysis.

2.3.2. Adsorption of methylene blue

Methylene blue solution was prepared by dissolving 20 mg of methylene blue in 1 L of distilled water to obtain a concentration of 20 mg L⁻¹. As much as 200 mg of kaolinite material was added into 50 mL of methylene blue solution and then the mixture was stirred at 150 rpm. The concentration of methylene blue was measured using a UV-Vis spectrophotometer. The adsorption kinetic study was conducted by varying the adsorption time form 50 mL of methylene blue 20 mg L⁻¹ with 10 mg adsorbent material. Meanwhile, the adsorption isotherm study was evaluated by varying the methylene blue concentration as the aqueous solution.

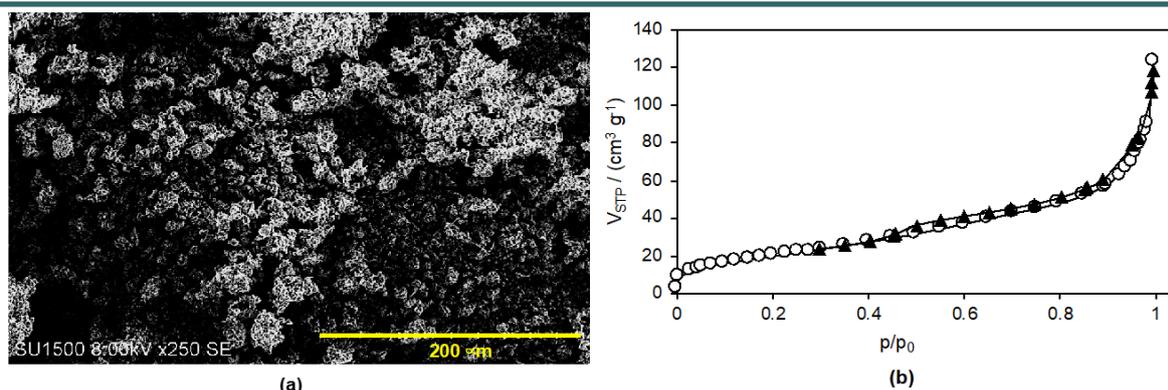


Figure 2. (a) SEM micrograph and (b) nitrogen adsorption-desorption isotherm plot of activated kaolinite material.

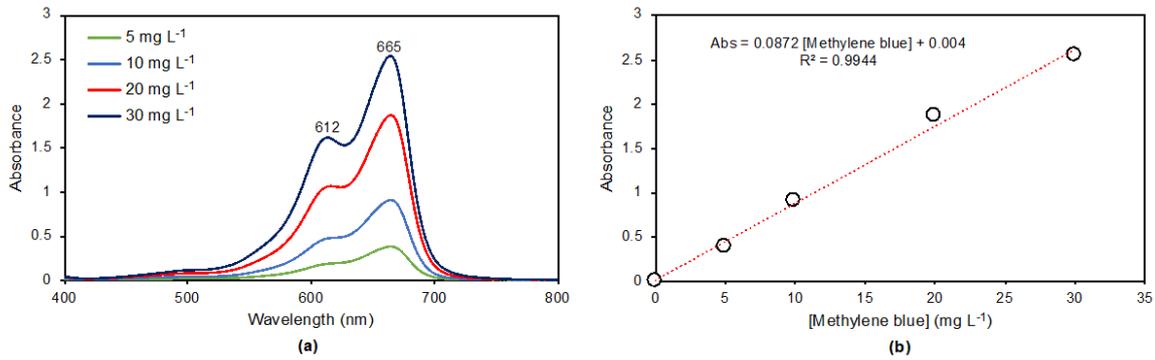


Figure 3. (a) Visible spectra and (b) calibration curve of methylene blue standard solution.

3. RESULTS AND DISCUSSIONS

3.1. Activation of kaolinite

Acidic activation of kaolinite material was carried out to remove the impurities from its three-dimensional structure [20]. The common impurities of clay materials are base metal ions that interacted with the tetrahedral silica and octahedral alumina framework through electrostatic interaction. The success of the activation process was elucidated using the FTIR spectroscopy. Figure 1(a) shows the FTIR spectrum of the activated kaolinite material from 600-4,000 cm^{-1} . It was found that the O-Si-O bending and Si-O stretching signals at 696 and 800 cm^{-1} appeared as a sharp signal. The AlO_6 and SiO_4 absorption signals appeared as a broad signal at 960-1,193 cm^{-1} . While the O-H and AlO-H functional groups are appeared as a broad signal at 3,458 cm^{-1} and a sharp signal at 3,674 cm^{-1} , respectively. These spectral characteristics were similar to the other reported literature thus proving that the activation of kaolinite material was successfully carried out [21][22].

The XRD pattern of activated kaolinite is displayed in Figure 1(b). Since the kaolinite material was obtained from Wediombobeach thus the several crystalline phases were found such as kaolinite (JCPDS 00-005-0143), quartz (JCPDS 00-046-1045), halloysite (JCPDS 00-029-1487), and cristobalite (JCPDS 00-039-1425). The diffractogram signals at $2\theta = 10.06, 19.46, 26.96, 29.42, 39.82, 40.76, 42.78, 43.92, 46.20, 48.44, 55.30, 56.56, 63.48,$ and 75.80 correspond to the kaolinite crystal phase with hkl plane of (0 0 1), (0 2 0), (1 1 1), (-1 1 2), (0 1 3), (-1 -3 2), (-1 -2 3), (-2 2 2), (-2 1 3), (1 4 1), (3 0 0), (-1 4 3), (-2 5 1), and (-2 -6 2), respectively. The diffractogram signals at $2\theta = 26.96, 60.32, 68.40,$ and 73.78 correspond to the quartz crystal phase with (1 0 1), (2 1 1), (3 0 1), and (1 0 4) hkl planes, respectively. The diffractogram signals at $2\theta = 13.66, 20.06, 35.15, 54.27,$ and 62.64 correspond to the halloysite crystal phase with hkl plane of (0 0 1), (1 0 0), (1 1 0), (2 1 0), and (3 0 0), respectively. Meanwhile, the diffractogram signals at $2\theta = 21.98$ and 36.56 correspond to the cristobalite crystal phase with (1

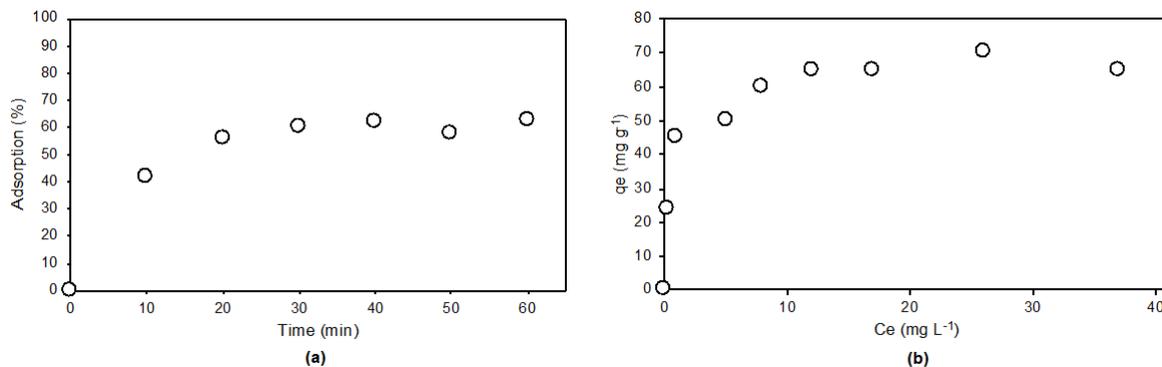


Figure 4. (a) Effect of adsorption time on the adsorption capability of activated kaolinite material. Mass of the adsorbent = 200 mg. Volume of the aqueous solution = 50 mL. [Methylene blue] = 20 mg L^{-1} . Shaking speed = 150 rpm. (b) Adsorption isotherm for methylene blue using activated kaolinite material. Mass of the adsorbent = 200 mg. Volume of the aqueous solution = 50 mL. Shaking speed = 150 rpm. Adsorption time = 30 min.

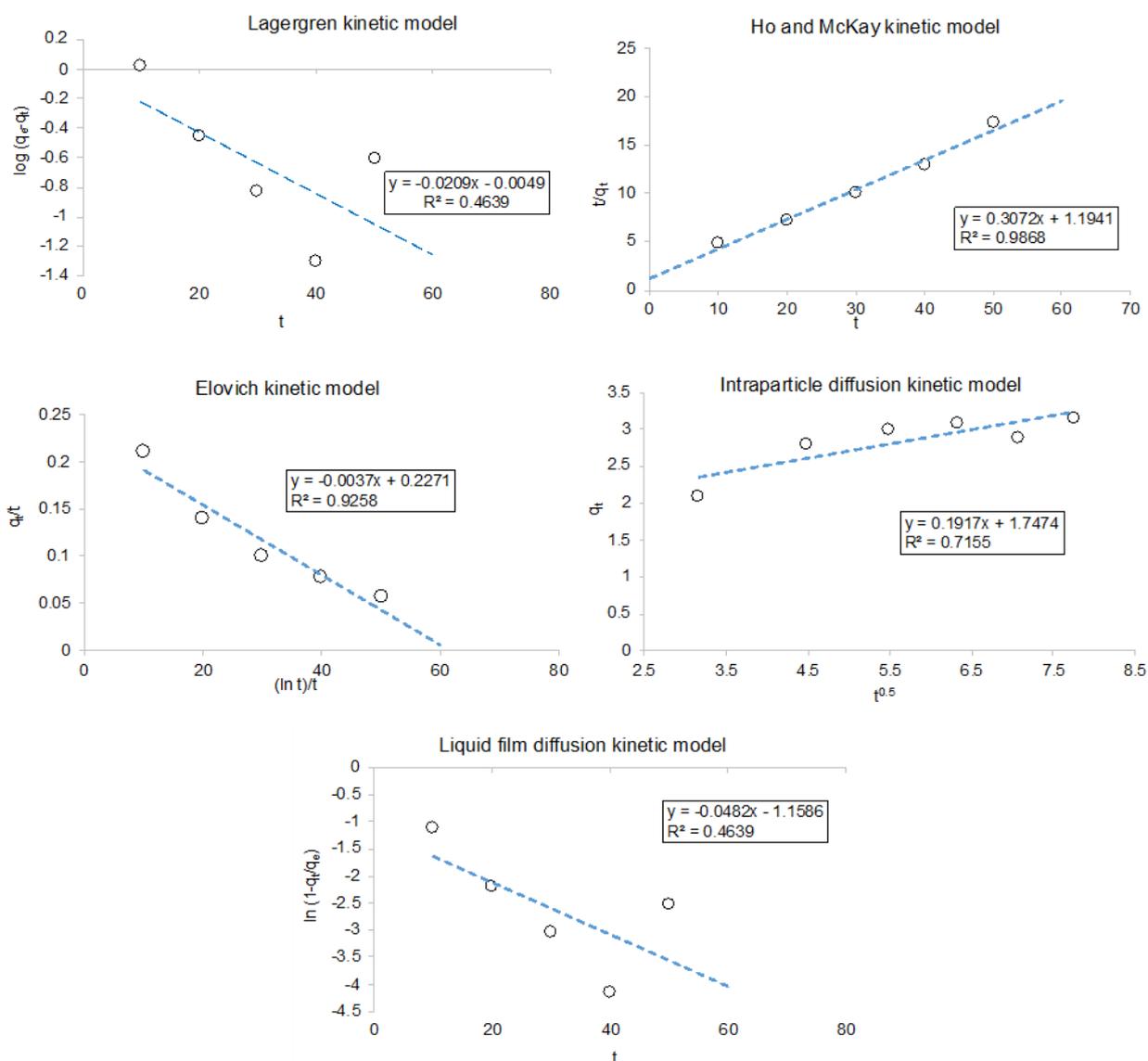


Figure 5. Kinetic models of methylene blue adsorption using activated kaolinite material. Mass of the adsorbent = 200 mg. Volume of the aqueous solution = 50 mL. [Methylene blue] = 20 mg L⁻¹. Shaking speed = 150 rpm.

0 1) and (2 0 0) hkl planes, respectively. From the spectral assignment, the activated kaolinite material was mainly composed of kaolinite crystal phase as previously described [23].

The SEM micrograph of activated kaolinite is shown in Figure 2(a) with a scale bar of 200 nm. The morphology of activated kaolinite material shows agglomerated crystal materials in micrometer size. This morphology supported the XRD data that the activated kaolinite material composed of several crystal phases. The nitrogen adsorption-desorption isotherm plot is shown in Figure 2(b). From the BET calculation, the activated kaolinite material has a surface area of 76.86 m² g⁻¹, a pore size of 8.39 nm, and a pore volume of 17.66 mL g⁻¹. The

activated kaolinite material has a higher surface area, a bigger pore size, and a larger pore volume than the un-activated kaolinite material, i.e. 61.13 m² g⁻¹, 7.72 nm, and 0.12 mL g⁻¹, respectively [15]. Because of that, the activated kaolinite material was further evaluated for methylene blue adsorption.

3.2. Adsorption of methylene blue using activated kaolinite material

Before the adsorption experiment, a series of methylene blue standard solution was prepared at 5, 10, 20, and 30 mg L⁻¹ concentration. The visible spectrum of a series of methylene blue standard solution is shown in Figure 3(a) while Figure 3(b) shows the calibration curve to calculate the

Table 2. Isotherm adsorption model of methylene blue using activated kaolinite material.

Kinetic model	Mathematical equation	R ²
Lagergren	$\log (q_e - q_t) = -0.0209 t - 0.0049$	0.4639
Ho-McKay	$t/q_t = 0.3072 t + 1.1941$	0.9868
Elovich	$q_t/t = -0.0037 (\ln t)/t + 0.2271$	0.9258
Intraparticle diffusion	$q_t = 0.1917 t^{0.5} + 1.7474$	0.7155
Liquid film diffusion	$\ln(1 - q_t/q_e) = -0.0482 t - 1.1586$	0.4639

concentration of methylene blue. Methylene blue has two adsorption signals at 612 and 665 nm as previously reported. The calibration curve gave the equation of $Abs = 0.0872 [Methylene\ blue] + 0.004$ with R² value of 0.9944.

The kinetic study of methylene blue adsorption using activated kaolinite material was evaluated and the results are shown in Figures 4(a) and 5, as well as Table 1. The required time to reach equilibrium was 20 min. From the kinetic models, it was found that the methylene blue adsorption followed Ho and McKay model with an R² value of 0.9868. The theoretical q_e (amount of methylene blue adsorbed per unit of activated kaolinite material) value (3.26 mg g⁻¹) was near to the experimental q_e value (3.15 mg g⁻¹) demonstrating the validity of Ho and

McKay model in the present study [24].

On the other hand, the adsorption isotherm of methylene blue adsorption was studied and the results are shown in Figures 4(b) and 6, as well as Table 2. The q_e value was reached a plateau at C_e = 12 mg L⁻¹. From the adsorption isotherm models, it was found that the methylene blue adsorption followed the Langmuir model with an R² value of 0.9961. According to the Langmuir model, the maximum adsorption capacity (q_{max}) and Langmuir constant (K_L) of 3.40 mg g⁻¹ and 1.36 L mg⁻¹, respectively. The separation constant (R_L) value was 0.035 demonstrating that the adsorption of methylene blue using activated kaolinite material was favorable (0 < R_L < 1) [24].

Table 3 shows the q_{max} values of several

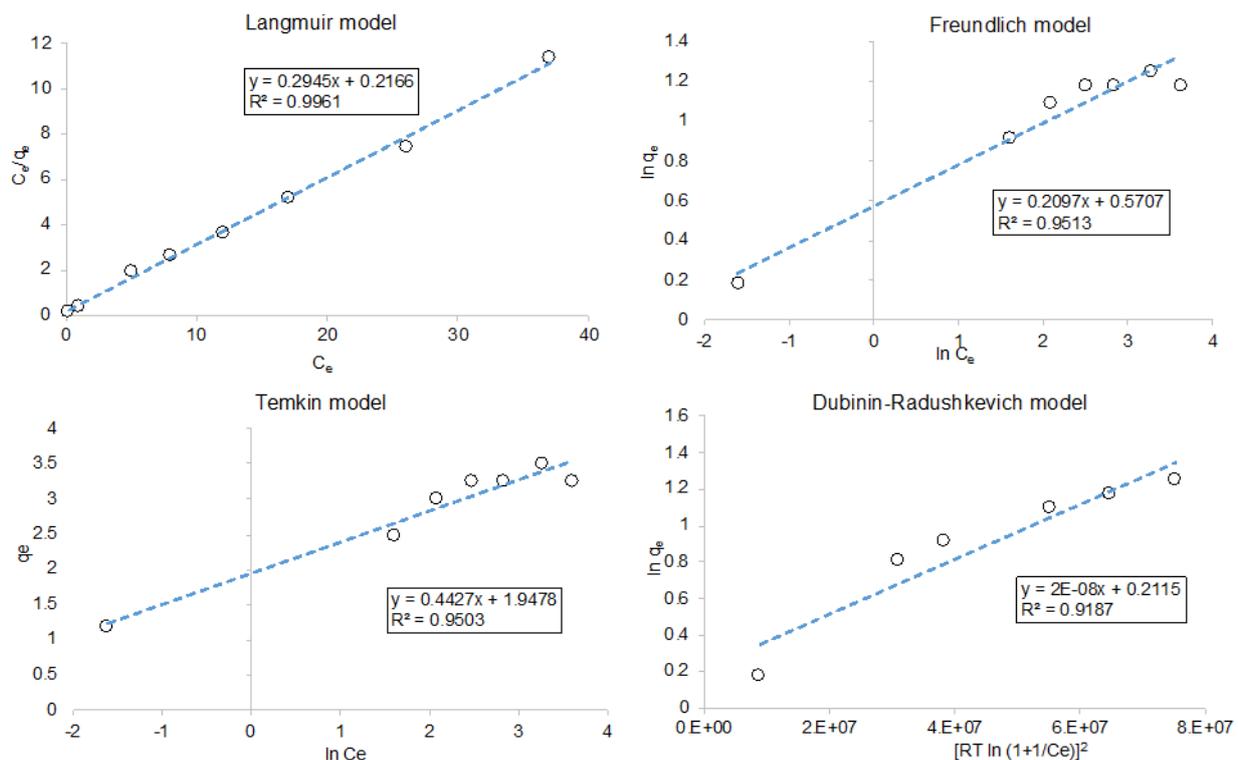


Figure 6. Adsorption isotherm models of methylene blue adsorption using activated kaolinite material. Mass of the adsorbent = 200 mg. Volume of the aqueous solution = 50 mL. Shaking speed = 150 rpm. Adsorption time = 30 min.

Table 2. Isotherm adsorption model of methylene blue using activated kaolinite material.

Isotherm adsorption model	Mathematical equation	R ²
Langmuir	$C_e/q_e = 0.2945 C_e + 0.2166$	0.9961
Freundlich	$\ln q_e = 0.2097 \ln C_e + 0.5707$	0.9513
Temkin	$q_e = -0.0037 \ln C_e + 1.9478$	0.9503
Dubinin-Radushkevich	$\ln q_e = 2 \times 10^{-8} [RT \ln(1 + 1/C_e)]^2 + 0.2115$	0.9187

adsorbent materials. A different source of kaolinite material gave different q_{\max} values (see Table 3 lines 1-4). This phenomenon may be caused by different geochemical environment and crystal phases. The q_{\max} value of Wediombo kaolinite was lower than Algerian and Indian kaolinites but still higher than Malaysian kaolinite. Furthermore, the q_{\max} value of Wediombo kaolinite was higher than other adsorbent materials, such as fly ash, red mud, glass wool, fine ground wheat straw, activated carbons, living biomass, eggshell, chrome sludge, and magnetic nanoparticles, which was remarkable (see Table 3 lines 5-15).

It was reported that clay-based materials consist of tetrahedral silica and octahedral alumina layers with both Bronsted and Lewis acid sites. Sandollah et al. reported methylene blue adsorption on activated kaolinite occurred through an ion-exchange reaction [3]. Meanwhile, Rida et al. reported that methylene blue was adsorbed on the activated kaolinite surface through hydrogen bonding and electrostatic interactions [15]. Therefore, the adsorption of methylene blue could happen through either hydrogen bonding or electrostatic interactions as shown in Figure 7. Such a moderate q_{\max} value (3.40 mg g^{-1}) may be caused by the agglomeration of several crystal phases as shown from the SEM image in Figure 2(a).

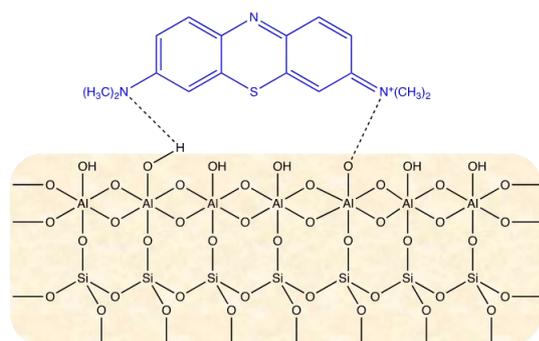


Figure 7. Plausible chemical interactions for methylene blue adsorption on the surface of activated kaolinite material.

4. CONCLUSIONS

Activation of Wediombo kaolinite using acidic condition yielded a low-cost activated kaolinite material with efficient adsorption capability for methylene blue removal. The success of the activation process was proved by the FTIR spectrum. The activated kaolinite contains kaolinite, quartz, halloysite, and cristobalite crystal phases as shown from the XRD data. The morphology of activated kaolinite material shows agglomerated crystal materials in micrometer size with high surface area and large pore volume. It was found that the methylene blue adsorption followed Ho and McKay model with q_e value of 3.15 mg g^{-1} . On the other hand, the adsorption isotherm of methylene blue adsorption followed the Langmuir model with q_{\max} , K_L , and R_L values of 3.40 mg g^{-1} , 1.36 L mg^{-1} , and 0.035 , respectively. The q_{\max} value of Wediombo kaolinite was higher than other adsorbent materials demonstrating that efficient methylene blue removal from the aqueous phase has been successfully achieved. Nevertheless, further modification of the kaolinite material is still required to improve its adsorption ability for a real commercial process.

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Tabel 3. Maximum adsorption capacities of several adsorbent materials for methylene blue.

Adsorbent material	q_{\max} (mg g ⁻¹)	Reference
Algerian kaolinite	13.99	[15]
Indian kaolinite	7.59	[25]
Wediombo kaolinite	3.40	Present work
Malaysian kaolinite	1.37	[3]
Fly ash	2.85	[26]
Red mud	2.49	[27]
Glass wool	2.24	[28]
Fine ground wheat straw	2.23	[29]
Almond shell based activated carbon	1.33	[30]
Fir wood based activated carbon	1.21	[31]
Living biomass	1.17	[32]
Corn cob based activated carbon	0.84	[33]
Eggshell	0.80	[34]
Chrome sludge	0.51	[35]
Magnetic nanoparticles	0.20	[36]

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