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Composite of Kaolin/Sodium Alginate (SA) Beads for Methylene Blue Adsorption

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Dyeing industry is one of the fast-growing industries but at the same time has also brought us a big issue on environment pollution. Adsorption processes is the most effective method in dye removal compared to other methods of wastewater treatment. In recent years, there is an increasing interest in utilizing clay material such as kaolinite as an adsorbent to remove not only inorganic but also organic molecules. In this study, composite of kaolin-sodium alginate (SA) beads was synthesized by varying the weight of kaolin from 0.5 g to 2 g. XRD, FTIR, and surface area analyses were used to characterize the kaolin; while FTIR was used to characterize the composite where the functional groups of kaolin and SA are existing. The amount of 1 g kaolin in SA could improve the adsorption of methylene blue up to 78% of removal after 8 hours. The adsorption model fits pseudo second order kinetic and Langmuir isotherm.

Keywords: Adsorption, composite, kaolin, pollutant removal, sodium alginate

INTRODUCTION

The increased utilization of synthetic chemical dyes in industrial processes such as dyeing of cloth, paper and pulp manufacturing, leather treatment and printing in past few years has resulted in the release of dye-containing industrial effluents into the soil and aquatic ecosystems (Ejder Korucu et al. 2015). During the coloration process, a significant percentage of the dye does not bind to the fabric and is lost to the wastewater stream (Zaharia and Suteu 2012). The toxicity nature of most dyes caused major environmental concern for their presence in industrial effluents. Most of dyes might be carcinogenic and mutagenic, and equipped with other traits such as inert and non-biodegradable when discharged into waste streams (Zaharia and Suteu 2012). Moreover, the existence of dyes in water environment could induce the formation of colored wastewaters, which can hinder the penetration of sunlight and oxygen, as essentials for the survival of

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various aquatic forms (Buthelezi et al. 2012). Methylene blue is one of the common cationic dyes in the industries. It has wide applications such as coloring papers, dyeing cottons and silk (Chowdhury and Saha 2012). Methylene blue can cause some harmful effects such as heartbeat increase, vomiting, and shock in humans (Badis et al. 2016).

Various approaches covering physical and/or chemical processes have been applied in treatment of industrial wastewater containing dye, but the methods are still very costly and not environmentally safe. One of the most effective methods in wastewater treatment is adsorption process (Yagub et al. 2014). The adsorption process for dye removal by using kaolin has been used widely to remove methylene blue (Rida et al. 2013, Huang et al. 2016, Boukhemkhem and Rida 2017, He et al. 2018, Khairy et al. 2018, Mouni et al. 2018), acid red (Lawal and Moodley 2016), basic red 5 (Alam et al. 2014), brilliant green (Shirsath et al. 2013), rhodamine B (Tang et al. 2015), and malachite green (Caponi et al. 2017). The effective removal of dyes by using kaolin has shown its potential as low cost adsorbent (Boukhemkhem and Rida 2017, Khairy et al. 2018). The usage of adsorbent for wastewater treatment needs to be engineered to avoid the loss of adsorbent during the process. The pairing of kaolin with organic material such as graphene hybridized polydopamine (He et al. 2019), pineapple peel cellulose-g-acrylic acid hydrogel (Dai and Huang 2017), graphene-alginate (Nigiz 2019), alginate-polyvinyl alcohol (Abd El-Latif et al. 2010), and poly(sodium p-styrenesulfonate hydrate) (Huang et al. 2016) to form composite has been studied for the removal of dye from water environment. In this study, facile synthesis of kaolin composite in sodium alginate (SA) beads was performed as an approach to ease the recollection of adsorbent and avoid its lost. The variation of kaolin was performed from 0.5 g to 2 g to remove the methylene blue. The comparison of adsorption by using SA only, and kaolin was also performed in this study.

EXPERIMENTAL METHOD

Materials

Kaolin (Kaolin (M) Sdn. Bhd., Malaysia), sodium alginate and calcium chloride (Fisher Scientific (M) Sdn. Bhd., Malaysia), methylene blue (Bendosen, Malaysia). All chemicals were used as received.

Synthesis of kaolin/SA beads

To prepare adsorbents in a shape of beads, a fixed amount of kaolin was mixed with the 1% sodium alginate solution. The mixture was then dropped by using syringe into the calcium chloride with the concentration of 10 g/L. All the beads were filtered and being dried in an oven for 5 hours at 40°C.

Effect of contact time with a constant mass

For this experiment, kaolin beads were being prepared by fixing the mass of beads at 0.5 g. For the adsorbate, a 50 ml of 50 ppm methylene blue was prepared. The mixture of adsorbents and adsorbate was then placed on a shaker for a continuous shaking at 200 rpm. Samples

were taken at the time interval of 0 min, 30 mins, 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, and 6 hours. The experiment was repeated with a different kaolin contain of 0.5 g, 1 g, and 2 g. All solution samples were being tested using the UV-vis spectrophotometer to observe the removal (λ=646 nm).

Effect of methylene blue concentration

Based on the contact time experiments explained in previous section, 1 gr kaolin beads showed the highest rate of adsorption, hence it was used for further experiments on the effect of methylene blue concentration. Different concentration of methylene blue was prepared at 20, 40, 60, 80, and 100 ppm. All adsorbates were then being mixed together with the 0.5 g of 1 g-kaolin/SA beads as the adsorbents. Samples were taken at 0 min and 8 hours to indicate the initial and final concentration. All solution samples were being tested using the UV-vis spectrophotometer (Shimadzu UV-1800, Japan) to observe the removal (λ=646 nm).

Characterization

The crystallinity of kaolin was analyzed by using x-ray diffractometer (XRD) (Bruker D8, USA) using X'Pert3 Powder & Empyrean PANalytical with Cu Kα irradiation from 10° to 70° with step size of 0.01°/step and exposure time of 1s/step. The functional groups were analyzed by using Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum One, USA) with infrared scan from 4000 to 500 cm^{-1}. Surface morphologies were investigated using field emission scanning electron microscopy (FESEM) (Zeiss Supra 55 VP, Germany).

RESULTS AND DISCUSSION

Morphology and functional groups

Kaolin shows typical sheet morphology with randomly arranged-stacked layer of sheets as can be seen in Fig. 1a. The surface morphology of bead can be seen in Fig. 1b, where kaolin sheets are visible.

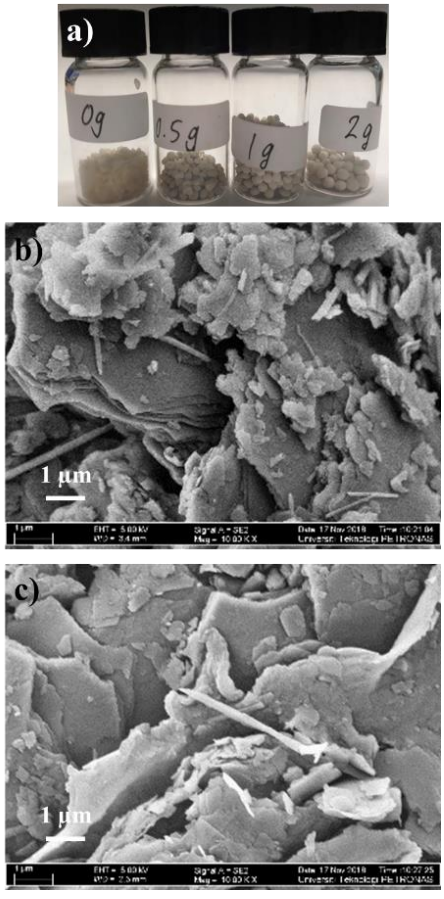

Fig. 1: a) Image of kaolin/SA beads (amount of kaolin: 0g, 0.5g, 1g, and 2g), SEM images of b) kaolin and c) kaolin/SA (1g of kaolin) bead surface

The XRD pattern of kaolin is shown in Fig. 2, where it consists of kaolinite,

muscovite, and quartz. The 2θ diffraction angles for kaolinite can be clearly seen at 12.2° and 24.8°; for muscovite at 17.7°, and for quartz at 26.6°. This result shows the same agreement with XRD pattern for clay in previous research by Hemra et al (Hemra and Aungkavattana 2016).

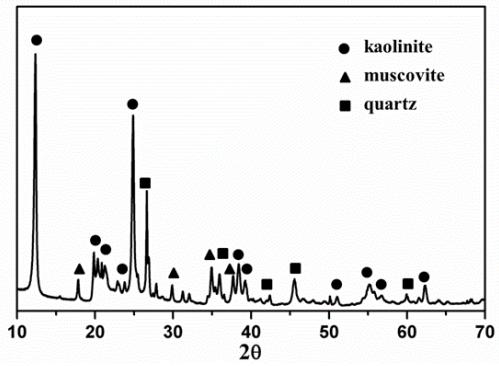

Fig. 2: XRD pattern of kaolin

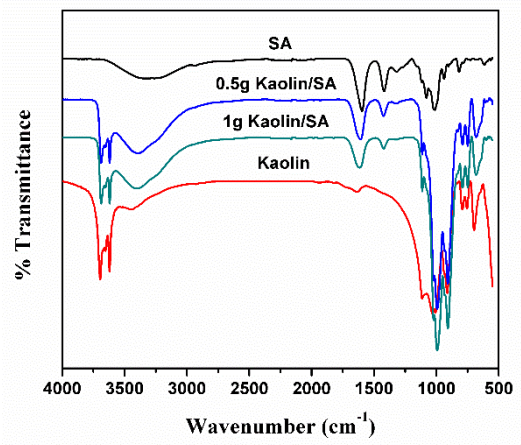

Fig. 3: FTIR spectra of composite kaolin/SA

The functional groups of kaolin/SA composite are shown in Fig. 3 to have the peaks belong to both kaolin and SA. The functional groups of kaolin for Si-O stretching vibration are visible at 697, 1002 and 1121 cm^{-1} (Panda et al. 2010, Štengl and Henych 2013). The peaks appearing at 753 and 799 cm^{-1} can be assigned to stretching vibration of Si-O-Al (Štengl and Henych 2013, Rekik et al. 2017). While the peaks at 900 and 3692 cm^{-1} can be attributed to Al-OH vibrations of the alumina sheets in kaolin (Panda et al. 2010, Naghsh and Shams 2017). The appearance of functional groups of SA can be seen at 1425 and 1609 cm^{-1} which are attributed to stretching vibrations of symmetric and asymmetric bands of carboxylate anions, respectively (Rao et al. 2013).

Methylene blue adsorption

The adsorption of methylene blue shows significant improvement of adsorption when the samples contain kaolin (Fig. 4a). The adsorption of methylene blue by using only SA can only remove 16% of methylene blue. When 0.5 g of kaolin is added into SA beads, the removal of methylene blue can be increased up to 22.7%, and increased further to 62% when 1 g of kaolin added into SA beads. Based on the removal result, it can be seen that 1 g of kaolin is the optimum amount in SA beads to remove methylene blue, since the addition of 2 g of kaolin caused decreasing of removal. Similar result was observed in previous study by Dai et al (Dai and Huang 2017), which further increasing in kaolin amount in composite did not improve the adsorption performance. The optimum performance was obtained at low amount of kaolin (Dai and Huang 2017). This can be caused by the agglomeration of kaolin at higher amount in beads which hinders the adsorption of methylene blue. Until certain amount, the increasing of adsorbent dosage has significant improvement in adsorption performance (Nigiz 2019), as can be seen by the increasing of kaolin from 0.5 g to 1 g in this study. This result is comparable to the

adsorption of methylene blue using only kaolin (Fig. 4b) which can remove around 68% of methylene blue.

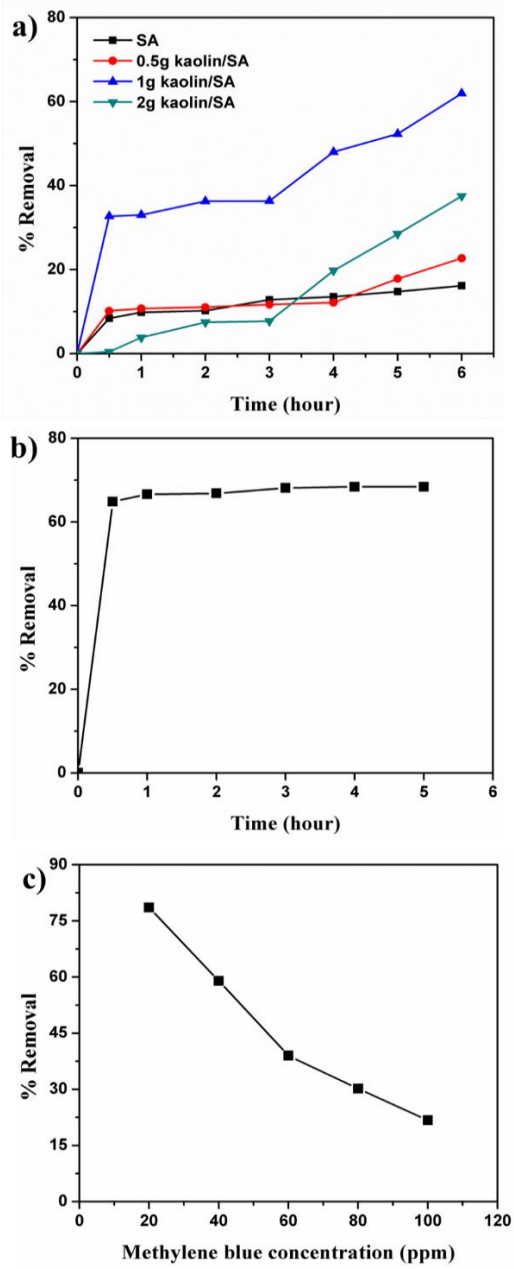

Fig. 4: Removal of methylene blue by using a) kaolin/SA composite beads, b) kaolin, and c) 1g-kaolin/SA at various concentrations of methylene blue

The adsorption of various concentration of methylene blue was performed by using 1g-kaolin/SA as the optimum sample (Fig. 4c), which by the increasing concentration of methylene blue, the adsorption by composite beads was found to be decreased.

Adsorption Kinetic

The adsorption for methylene blue fits the pseudo-second order model (Fig. 5) which follows Eq. (1).

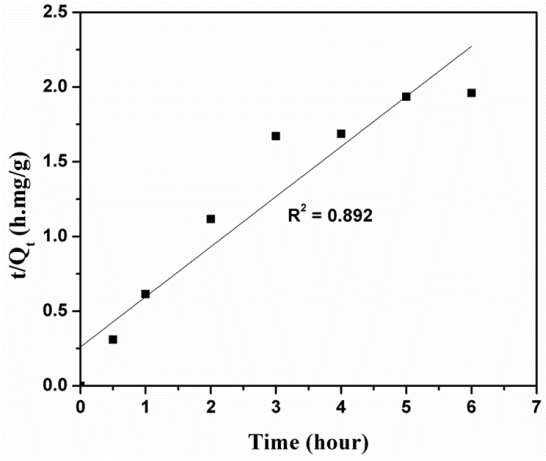

Fig. 5: Pseudo-second order kinetic of methylene blue adsorption by using 1g kaolin/SA

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad (1)$$

where t/Q_t was plotted against time, k_2 is pseudo-second order rate constants of adsorption, Q_e and Q_t are the amount of methylene blue adsorbed (mg/g) at equilibrium and time, t respectively, and time, t denotes the adsorption time (hour). The linearized model has been widely applied for solid-liquid adsorption system (Robati 2013). The kinetic process for methylene blue adsorption followed the characteristics of pseudo-second order model with R^2 of 0.892. The rate of adsorption increased around double throughout the time. In this type of adsorption, the rate-controlling step is the chemical reaction, and the pseudo-second

order chemical reaction kinetics shows the best fit of the experimental data.

Adsorption isotherms

Using the variation of methylene blue concentration, the isotherms were analyzed by fitting to Langmuir and Freundlich isotherm models as shown in Fig. 6. From the comparison of the isotherm models, the kaolin/SA beads used for the adsorption were best fit in Langmuir isotherm. Freundlich isotherm is applied for heterogeneous or complex system, and condensed adsorbent with highly interactive species on the surface (Khairy, Ayoub et al. 2018). Based on the linear regression (Fig. 6), the data do not show a good fit to Freundlich isotherm, which the adsorption might happen until the monolayer covered. There are few considerations of assumption that need to be taken for this isotherm. For examples, the sorption takes place at specific homogeneous sites within the adsorbent and there is no interaction between adsorbates in the plane of the surface and it is a monolayer type of adsorption (Santos, Costa et al. 2018). The Langmuir isotherm is valid for monolayer adsorption on a homogenous adsorbent surface containing a finite number of identical site and no interaction between adsorbate molecules (Khairy, Ayoub et al. 2018). The Langmuir isotherm is represented by linear equation, as can be seen in Eq. (2) (Khan, Dahiya et al. 2012).

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max}b} \quad (2)$$

where Q_{max} is the monolayer adsorption capacity (mg/g), b is the Langmuir constant (L/mg) related to the free energy of adsorption. From the data obtained, the maximum adsorption capacity obtained from the correlation is 2.145 mg/g.

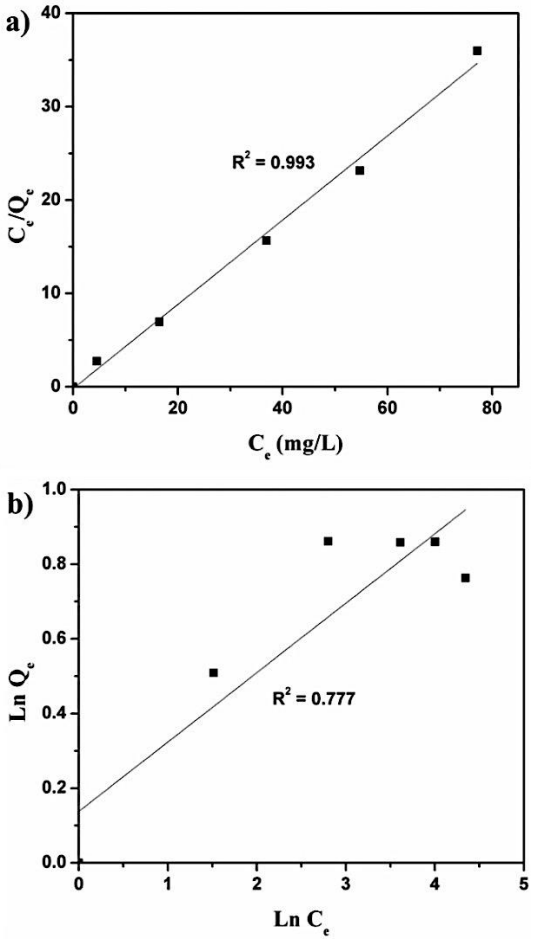

Fig. 6: a) Langmuir and b) Freundlich isotherm models of kaolin/SA adsorption

The comparison of kaolin composite in this study with previous works is presented in Table 1. The adsorption capacity is considered low, but the % removal of methylene blue shows promising result. Therefore, to improve the performance of kaolin/SA, functionalization and pre-treatment of materials need to be performed in the future to increase the adsorption sites.

Table 1: Kaolin composites performance for methylene blue removal

Material	% removal	Adsorption capacity (mg/g)	Reference
Poly(sodium p-styrenesulfonate hydrate)-modified kaolin	-	76	(Huang et al. 2016)
Alginate/polyvinyl alcohol-kaolin	92.7% after 6 hours	1.87	(Abd El-Latif et al. 2010)
Sodium alginate-kaolin	62% after 6 hours	2.145	This work
Graphene hybridized polydopamine-kaolin	90% after 12 hours	39.663	(He et al. 2019)
Pineapple peel cellulose-g-acrylic acid hydrogel-kaolin	-	153.85	(Dai and Huang 2017)
Graphene-kaolin-alginate	97% after 3 hours	-	(Nigiz 2019)

CONCLUSIONS

The composite beads of kaolin/SA could serve as alternative low cost adsorbent for dye removal. The layered stacks of kaolin nano-sheets can be observed on the surface of kaolin/SA beads by using FE-SEM analysis. The existence of functional groups of kaolin and SA can be revealed by using FTIR analysis. In this study, the removal of methylene blue could reach 62% after 6 hours of adsorption by using 1g-kaolin/SA beads, which is in comparison with the adsorption using kaolin that can reach 68%. The kinetic of adsorption fits pseudo-second order where the adsorption is governed by chemisorption.

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