Original Article

e-ISSN: 2581-0545 - https://journal.itera.ac.id/index.php/jsat/

Activated Cassava Leaves As Low-Cost Adsorbent to Remove Dyes From Water

Received 16th November 2021
Accepted 4th March 2022
Published 11th April 2022

Open Access

DOI: 10.35472/jsat.v6i1.771

Chairunnisa [a]*, Yuni Lisafitri [b] and Mariyam [a]

[a] Department of Chemistry, Institut Teknologi Sumatera, Lampung, Indonesia

[b] Department of Environmental Engineering, Institut Teknologi Sumatera, Lampung, Indonesia

Corresponding E-mail: chairun.nisa@ki.itera.ac.id

Abstract: In this study, activated cassava leaves were prepared using NaCl (CLN) and KOH (CLK) as novel and low-cost materials for removing dyes from water. The prepared materials were characterized using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The adsorption experiments were carried out under different conditions of initial dye concentration (50 – 600 ppm), pH solution (4 – 10), and contact time (1 – 180 min) under room temperature. The adsorption kinetics has been studied using the pseudo-first and pseudo-second-order. The equilibrium isotherms have been analyzed using the Langmuir and Freundlich models. The adsorption kinetics of methylene blue onto activated cassava leaves follows a pseudo-second-order model. According to the isotherm study, the Langmuir model shows the best fitting results with the maximum adsorption capacity of 217.39 mg/g and 416.66 mg/g for cassava leaves that were activated by NaCl and KOH, respectively.

Keywords: *adsorption, adsorbent, methylene blue, cassava leaves*

Introduction

The high industrial development has led to the environmental quality decline, mainly coming from the textile industry's waste. Textile industrial waste has been reported to pollute water bodies with harmful chemicals [1] such as organic dyes. The presence of dyes in water will cause harmful effects on living things [2], such as several severe health problems like diarrhea, typhoid, nerve disorder, and skin lesion [3]. Therefore, serious handling techniques of dyes in water are required. Some of the ways that have been used for pollutants removal are electrocoagulation [4], photocatalytic degradation [5], and adsorption [6]. One of the most cost-efficient methods to remove dyes from the water body is adsorption due to its simplicity and efficiency [7]. In order to reduce the cost of the adsorption process, low-cost materials are highly demanded. For this reason, several low-cost sorbents have been studied, such as chitin [8], vanillin biomass [9], and date tree leaves [10].

In recent years, the utilization of by-products of wastes from large-scale industrial operations and agricultural waste materials has gained more attention. Biomass waste possesses several advantages, such as its affordability, high efficiency, minimization of chemical or biological sludge, and the possibility of effluent recovery [11]. One of the most abundant biomass in Indonesia is cassava. Cassava is known as one major commodity of Indonesia. The use of cassava leaves as adsorbent for removing dyes was preliminarily studied before [12] and has been reported to their excellent ability for removing methylene blue (MB) from wastewater even by just treating the leaves with deionized water. The ability of cassava leaves strongly corresponds to the existence of several oxygen-based functional groups that can attract MB through electrostatic interaction.

According to that report, even though dry cassava leaves showed promising MB adsorption capacity, the enhancement of their capacity is necessary in order to minimize the amount of adsorbent used in the application. Based on those reasons, therefore, in this report, the continuation of the study using the same precursor (cassava leaves) with other simple activation methods was conducted to increase the adsorption capacity of cassava leaves so then the reliable alternative low-cost adsorbent material could be easily provided.

Method

Materials

Cassava (*Manihot esculenta*) leaves were taken from the cassava farm near Institut Teknologi Sumatera. The deionized water was purchased from Brataco. The HCl, NaCl,

Journal of Science and Applicative Technology Original Article

KOH, and methylene blue (MB) were purchased from Chemical Industry Indonesia.

Instrumentation

The morphologies and structure of activated cassava leaves were observed using scanning electron microscopy (SEM) (ZEISS EVO MA 10). Fourier transform infrared spectrometer (FTIR) (Agilent/carry 630) was used to investigate the surface's functional groups on activated cassava leaves. UV/Vis spectrophotometry (Genesys 150) was used to measure methylene blue concentration.

Procedure

Adsorbent preparation

The cassava leaves were pre-treated by washing and drying processes. The dried leaves were crushed by using a domestic blender. After that, some powder was activated with NaCl and KOH separately. The activation process was conducted by stirring the mixture of those solutions and cassava leaves for 1 hour. The activated cassava leaves are then separated from the solution. After that, cassava leaves that had been activated using NaCl and KOH were washed by using deionized water until the clear filtrate was obtained to remove the remained solution attached to the leaves. The washed cassava leaves were then dried using an oven at 100^{o}C for 5 hours. Finally, the dried activated cassava leaves that were activated by NaCl were labeled as CLN, while those that were activated by KOH were labeled as CLK. Those two types of adsorbent materials were then characterized and used in the adsorption study.

Adsorption behavior study

The effect of pH

A 10 mg of adsorbent was added into the 10 ml MB with a concentration of 50 ppm. The pHs used for this study were 4, 6, 8, and 10. All different pHs were obtained by adding NaOH and HCl solution into the MB solution. The mixture of adsorbent and dye solutions was then shaken for two hours. The MB concentration that remained in the solution was then measured using UV/Vis Spectrophotometry.

The effect of contact time

The effect of contact time on the adsorption of MB was conducted using 10 mg of activated cassava leaves that were individually placed in bottled vials containing 10 mL of 50 ppm of methylene blue solution. Adsorption kinetics study was conducted using 1 to 180 min contact time between adsorbent and adsorbate. After that, the methylene blue that remained in the solution was measured using UV/Vis Spectrophotometry.

The effect of initial concentration of methylene blue

Both kinds of activated cassava leaves were individually placed in bottled vials containing 10 mL solution of varying initial concentrations of MB (50 – 600 ppm). The initial pH of the solution was 6 (without adjustment). The mixture was shaken at room temperature with 100 rpm of speed and two hours of contact time. The amount of MB that remained in the solution was analyzed by UV/Vis Spectrophotometry.

The amount of MB absorbed onto each material is calculated based on the following equation:

$$\mathbf{qe} = \frac{\mathbf{(Co-Ce)V}}{\mathbf{m}} \quad \textbf{(1)}$$

where qe (mg dye/g adsorbent) is adsorption capacity of adsorbent at equilibrium state, Co and Ce are the initial and equilibrium concentrations of dye in the solution (mg L^{-1}), V is the volume of the solution (L), and m is the mass of dry adsorbent used (g). The percent of removed MB (%R) is calculated by using the following equation:

$$\%\mathbf{R} = \frac{\mathbf{(Co-Ce)}}{\mathbf{Co}}\mathbf{x100}\% \quad \textbf{(2)}$$

where %R is removal efficiency (%).

Results and Discussion

Characterization of Adsorbent

Fourier transform infrared spectrometer (FTIR) gives helpful information regarding the functional site of the material. The FTIR spectra (**Figure 1**) of CLN and CLK exhibit a broad peak at 3280 cm^{-1} responsible for O – H stretching vibration. Other peaks are shown at 2907 cm^{-1} and 2855 cm^{-1} that may be due to the C – H stretching of alkane and C – H and C = O stretching of carboxylic acid and ester, respectively. Peaks at 1021 cm^{-1} may correspond to the ester or ether's C – O stretching vibration [13]. The peaks at 1617 cm^{-1} may be due to the overlapping peak of the C – C stretching vibration of the aromatic ring and the N – H bending vibration [14]. Overall, there are no significant differences between before and after adsorption for both materials.

Based on the SEM results in **Figures 2 and 3**, both CLN and CLK have highly heterogeneous surfaces with different sizes and shapes of pores. The activation by using NaCl and KOH produces wide pores that may be caused by the electrolytic action of the activating agent. This activating agent then made the cellulose swell in the direction of the longitudinal axis remains unchanged as the lateral bonds are broken down with the result that intern and intra micelle voids increase [15]. Moreover, the activation by using KOH has

Published by: Lembaga Penelitian dan Pengabdian Masyarakat (LPPM)
Institut Teknologi Sumatera, Lampung Selatan, Indonesia

removed inorganic impurities in the cassava leaves [16]. As a consequence, bigger and more pores were produced.

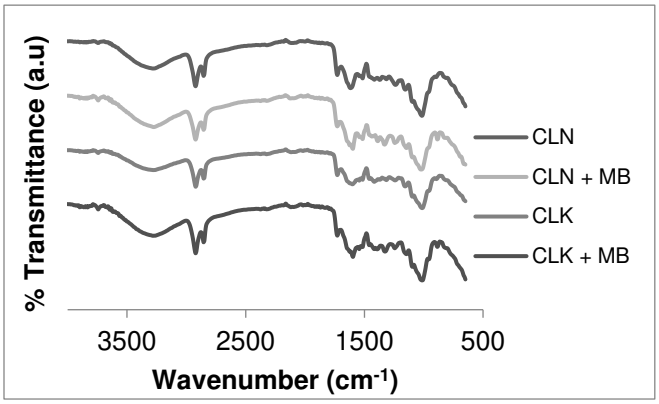

Figure 1. FTIR Spectra of CLN and CLK before and after adsorption

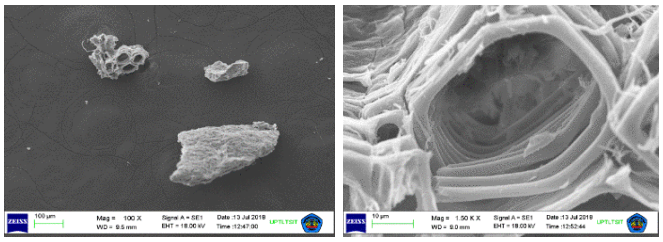

Figure 2. SEM image of the cassava leaves activated NaCl

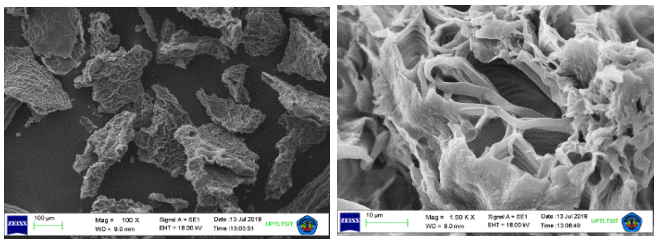

Figure 3. SEM image of the cassava leaves activated KOH

Adsorption Behaviour Result

Effect of Contact Time

In order to establish the equilibrium time and kinetics of MB adsorption on the activated cassava leaves, the effect of contact time (ranging from 1 to 180 minutes) was used. **Figure 4** shows that the removal efficiency of activated cassava leaves towards MB increases gradually with increasing contact time and reaches a constant value afterward. Rapid sorption of MB on the surface of activated cassava leaves represents an adsorbent's efficiency for wastewater treatment application. Based on data of MB sorption in **Figure 4**, these equilibrium times for both materials could be reached only using 10 minutes of contact time.

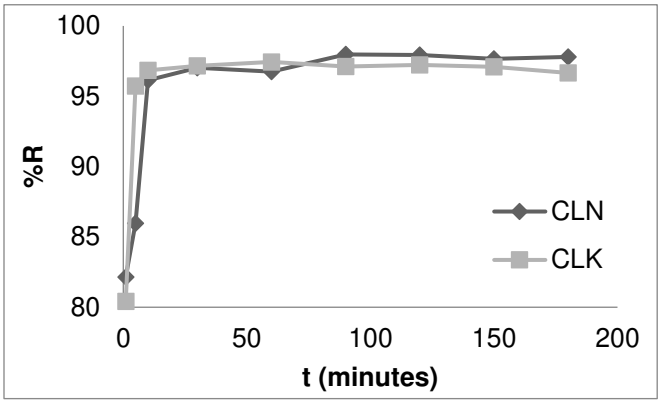

Figure 4. Effect of contact time on sorption of MB by activated cassava leaves

The Effect of Initial Concentration

Figure 5 shows that the adsorption capacity of activated cassava leaves increases as the higher the concentration of MB is used. The adsorption capacity of CLN reached the maximum value when it was used for the MB solution with the initial concentration (Co) of more than 300 ppm. On the other hand, for the CLK, that stagnant phase was reached when the initial concentration of MB solution was more than 500 ppm. Those stable uptake showed that the equilibrium had been reached, and both CLN and CLK could not adsorb more than their maximum capacity when they were used in the very concentrated solution.

From those findings, it can be assumed that CLK has more MB adsorption capacity than CLN because the equilibrium phase on CLK was reached on the higher concentration of MB. It has been known that KOH has a strong ability to enhance the nitrogen content on biomass which may attract more MB on the material [17].

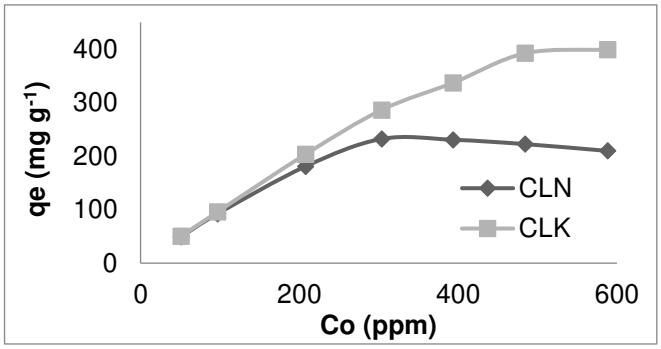

Figure 5. Effect of initial on sorption of MB by activated cassava leaves

Effect of pH

The medium's acidity is one of the essential factors in the adsorption study of water pollutants because this parameter can affect the solution chemistry of the pollutants. Acidity also strongly influences the ionic state of functional groups

on the surface of adsorbents [18]. The low values of cassava leave sorption capacity at pH less than 4 can be explained by the competition of protons with MB at the available sites on the surface of cassava leaves [19]. On the other hand, the adsorption capacity of activated cassava leaves increases when pH is higher than 2 then remains constant on the other pH, with a %R value up to 97%. This might be due to the deprotonation of functional groups on the surface of activated cassava leaves, so the adsorption sites increased, enhancing adsorption capacity. This result shows that activated cassava leaves can have a good adsorption ability to remove MB from water in a wide range of pH.

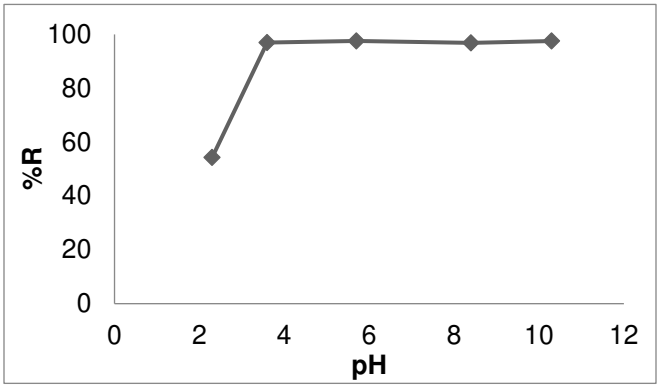

Figure 6. Effect of pH on Removal efficiency by CLN

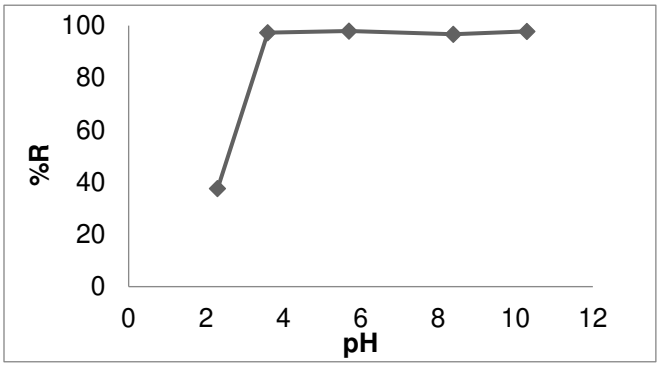

Figure 7. Effect of pH on Removal efficiency by CLK

Adsorption Kinetics Study

According to the previous report [20], there are consecutive steps that were taking place during the adsorption dye on the porous adsorbent:

1. Transport of the adsorbate ions to the external surface of the adsorbent (film diffusion)
2. Transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion)
3. Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent

In order to know the mechanism of MB adsorption onto activated cassava leaves, the kinetics study was conducted by using pseudo-first and pseudo-second-order models. The pseudo-first-order model is based on the approximation that the adsorption rate relates to the number of unoccupied adsorptive sites [21]. The pseudo-first-order kinetic model in its final form is described in the following equations:

$$\mathbf{ln(qe - qt) = ln\,qe - k_1 t} \quad \textbf{(3)}$$

where qe (mg g^{-1}) is the adsorption capacity at equilibrium, qt (mg g^{-1}) is the adsorption capacity at the time, k_1 (min^{-1}) is the pseudo-first-order rate constant, and t (min) is the contact time.

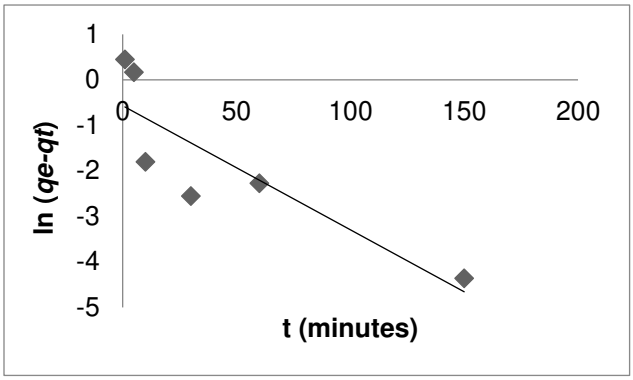

Figure 8. Pseudo-first-order model of MB sorption on CLN

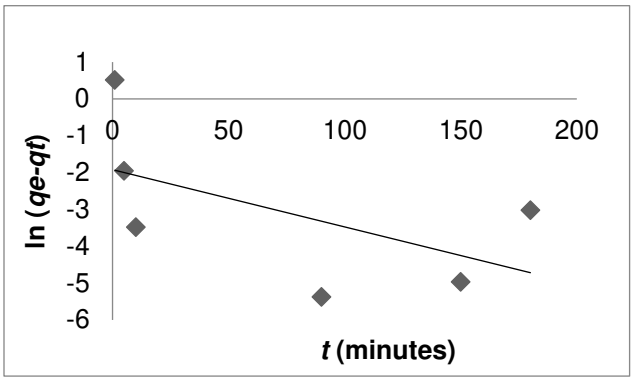

Figure 9. Pseudo-first-order model of MB sorption on CLK

The pseudo-second-order kinetic model was presented in the equation below:

$$\mathbf{qt} = \frac{\mathbf{k_2 q_{e^2}\, t}}{\mathbf{1 + k_2 q_e t}} \quad \textbf{(4)}$$

where qe (mg g^{-1}) is the adsorption capacity at equilibrium, qt (mg g^{-1}) is the adsorption capacity at the time, k_2 (g mg^{-1}

Published by: Lembaga Penelitian dan Pengabdian Masyarakat (LPPM)
Institut Teknologi Sumatera, Lampung Selatan, Indonesia

min^{-1}) is the pseudo-second-order rate constant, and t (min) is the contact time.

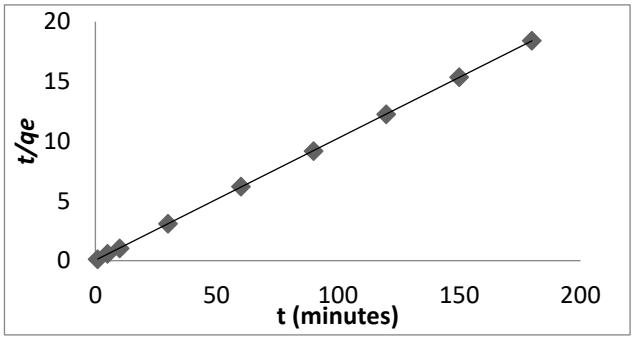

Figure 10. Pseudo-second-order of MB sorption on CLN

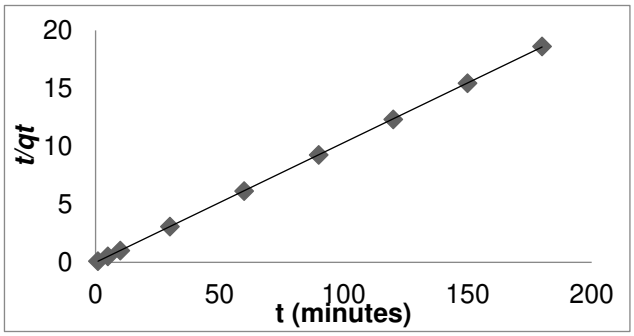

Figure 11. Pseudo-second-order of MB sorption on CLK

Tabel 1. Pseudo-second-order kinetic model rate constant of activated cassava leaves at room temperature.

Samples	*qe*	*k*	*h*	R^2
CLN	9,77	0,27	26,73	1
CLK	9,71	-2,30	217,39	1

Based on the kinetic study results, it is suggested that the pseudo-second-order model describes the adsorption kinetics of activated cassava leaves more appropriately than the pseudo-first-order.

Adsorption Isotherm

In the present study, the adsorption of MB onto the activated cassava leaves was calculated by using Langmuir and Freundlich isotherm equation. Langmuir isotherm is based on the monolayer sorption of MB on the surface of activated cassava leaves sites and is represented by the following equation:

$$\frac{Ce}{qe} = \frac{1}{bq_0} + \frac{Ce}{q_0} \quad \textbf{(6)}$$

where Ce (mg L^{-1}) is equilibrium concentration, qe (mg g^{-1}) is the equilibrium adsorption capacity, b (L mg^{-1}) is the equilibrium adsorption constant, and q_0 is the maximum adsorption capacity.

On the other hand, Freundlich's model assumes that the adsorption surface is heterogeneous, and the binding force decreases with the increased site occupation [21]. The following linear equation represents the Freundlich isotherm model:

$$\ln qe = \ln Kf + \frac{1}{n}\log Ce \quad \textbf{(5)}$$

where qe (mg g^{-1}) is the equilibrium adsorption capacity, Ce (mg L^{-1}) is equilibrium concentration, Kf and n are Freundlich constants which are related to the sorption capacity and the intensity of sorption [19]. K and n represent the adsorption capacity and measure of heterogeneity, respectively. The type of isotherm can be favorable if 1/n < 1 and unfavorable if 1/n > 1 [16].

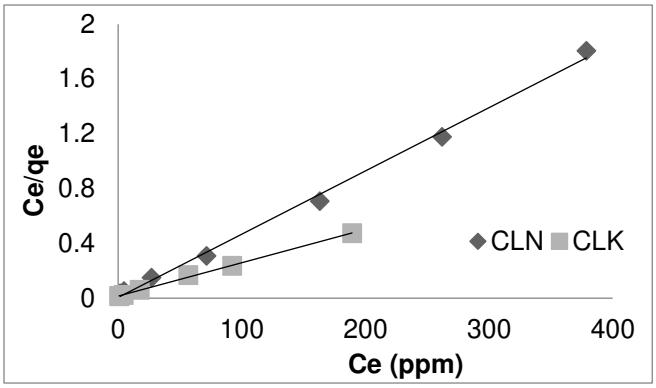

Figure 12. Langmuir isotherm of MB adsorption by activated cassava leaves

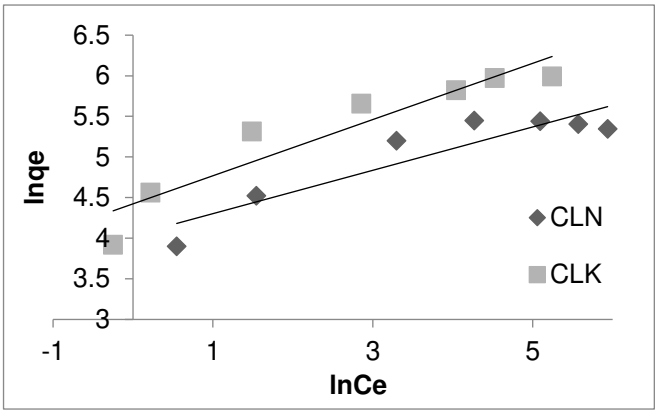

Figure 13. Freundlich isotherm of MB adsorption by activated cassava leaves

Table 2 shows that the adsorption of MB onto activated cassava leaves follows the Langmuir isotherm model, in which the R^2 value is 0.99 for both adsorbents. The value of q_m is 217.39 mg g^{-1} for CLN and 416.66 mg g^{-1} for CLK.

Table 2. Langmuir and Freundlich constants for the adsorption of MB on activated cassava leaves

Isotherm Models		Sample	
		CLN	CLK
Langmuir Model Parameters	q_m	217.39	416.66
	Kl	0.85	0.15
	R^2	0.99	0.99
Freundlich Model Parameters	$1/n$	0.26	0.34
	K_f	10886.79	26485
	R^2	0.84	0.88

The effect of the presence of salt in the target solution

The effect of salt studies shows that the presence of salt can decrease the adsorption capacity of activated cassava leaves towards MB. The adsorption capacity of activated cassava leaves decreased with the increase of salt concentration. This result might be due to the competition effect between MB and Na^+ ions from the salt for the sites available for the adsorption process. From this study, it can be assumed that the interaction between MB and cassava leaves is an electrostatic attraction between a negative surface site which comes from several functional sites that might present on cassava leaves such as -NH_2, -COOH, -OH, and cationic MB.

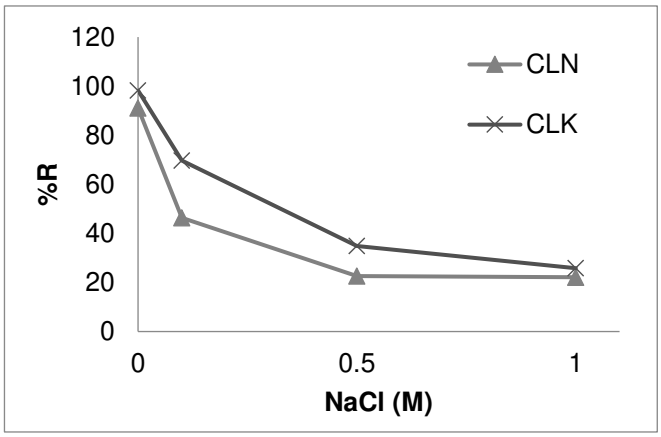

Figure 14. The effect of salt presence on the adsorption of MB onto activated cassava leaves

Table 3. Comparison of Monolayer Adsorption Capacities of Various Sorbents for MB Adsorption

Sorbent	Adsorption capacity (mg g^{-1})	Reference
Prickly bark of cactus fruit	222.22	[18]
Gulmohar plant leaf powder	177.9	[22]
Rejected Tea	147	[11]
Banana leaves	109.89	[23]
CL	178.5	[12]
CLN	217.39	This work
CLK	416.66	This work

Conclusions

The CLN and CLK were successfully developed. There are no characteristic peaks observed from both materials. The present study shows that activated cassava leaves can be used as adsorbents to remove MB from an aqueous solution. From the study effect of pH, from pH 4 to 10, %R values were more than 96%. The adsorption kinetics data fitted the pseudo-second-order model. The equilibrium time for both materials could be reached by only 10 minutes. The adsorption isotherm for CLN and CLK followed the Langmuir model. The maximum adsorption capacity value for CLN and CLK is 217.39 mg g^{-1}, and CLK is 416.66 mg g^{-1}, respectively. Overall, CLK has shown better performance than CLN on the adsorption of methylene blue.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

This work was financially supported by the grant of Institut Teknologi Sumatera, 134al/IT9.C1/PP/2018.

References

[1] R. Kant, "Textile dyeing industry an environmental hazard," *Nat. Sci.*, vol. 04, no. 01, pp. 22–26, 2012.

[2] G. Samchetshabam, A. Hussan, T. G. Choudhury, and S. Gita, "Impact of Textile Dyes Waste on Aquatic Environments and its Treatment Wastewater Management View project Tribal Sub Plan View project," *Environ. Ecol.*, vol. 35, no. September, pp. 2349–2353, 2017.

[3] F. Akarslan and H. Demiralay, "Effects of textile materials harmful to human health," *Acta Phys. Pol. A*, vol. 128, no. 2, pp. 407–408, 2015.

[4] M. Z. B. Mukhlish, M. M. R. Khan, A. R. Islam, and A. N. M. S. Akanda, "Removal of reactive dye from aqueous solution using coagulation-flocculation coupled with adsorption on papaya leaf," *J. Mech. Eng. Sci.*, vol. 10, no. 1, pp. 1884–1894, 2016.

[5] C. Xu, G. P. Rangaiah, and X. S. Zhao, "Photocatalytic degradation of methylene blue by titanium dioxide: Experimental and modeling study," *Ind. Eng. Chem. Res.*, vol. 53, no. 38, pp. 14641–14649, 2014.

[6] C. Shi, F. Tao, and Y. Cui, "Evaluation of nitriloacetic acid modified cellulose film on adsorption of methylene blue," *Int. J. Biol.*

Published by: Lembaga Penelitian dan Pengabdian Masyarakat (LPPM) Institut Teknologi Sumatera, Lampung Selatan, Indonesia

Macromol., vol. 114, pp. 400–407, 2018.

[7] Z. Heidarinejad, O. Rahmanian, M. Fazlzadeh, and M. Heidari, "Enhancement of methylene blue adsorption onto activated carbon prepared from Date Press Cake by low frequency ultrasound," *J. Mol. Liq.*, vol. 264, pp. 591–599, 2018.

[8] Y. L. Cao, Z. H. Pan, Q. X. Shi, and J. Y. Yu, "Modification of chitin with high adsorption capacity for methylene blue removal," *Int. J. Biol. Macromol.*, vol. 114, pp. 392–399, 2018.

[9] H. Zhang, X. Yong, J. Zhou, J. Deng, and Y. Wu, "Biomass Vanillin-Derived Polymeric Microspheres Containing Functional Aldehyde Groups: Preparation, Characterization, and Application as Adsorbent," *ACS Appl. Mater. Interfaces*, vol. 8, no. 4, pp. 2753–2763, 2016.

[10] F. Boudrahem, F. Aissani-Benissad, and A. Soualah, "Adsorption of lead(II) from aqueous solution by using leaves of date trees as an adsorbent," *J. Chem. Eng. Data*, vol. 56, no. 5, pp. 1804–1812, 2011.

[11] N. Nasuha, B. H. Hameed, and A. T. M. Din, "Rejected tea as a potential low-cost adsorbent for the removal of methylene blue," *J. Hazard. Mater.*, vol. 175, no. 1–3, pp. 126–132, 2010.

[12] Chairunnisa and Y. Lisafitri, "Preliminary studies of cassava leaves' ability to remove dyes from water," *J. Math. Fundam. Sci.*, vol. 52, no. 1, pp. 66–80, 2020.

[13] H. Pereira, D. Carvalho, J. Huang, M. Zhao, and G. Liu, "Improvement of Methylene Blue removal by electrocoagulation / banana peel adsorption coupling in a batch system," *Alexandria Eng. J.*, vol. 54, no. 3, pp. 777–786, 2015.

[14] D. Siswanta and A. Suratman, "Shirasu Balloons and Polydopamine-Modified Shirasu Balloons for Adsorption of Methylene Blue," *Water, Air, Soil Pollut.*, 2016.

[15] S. P. Patel, M. Thomas, A. V Patel, and J. V Patel, "Study of KOH Impregnated Jack Fruit Leaf Based Carbon as Adsorbent for Treatment of Wastewater Contaminated with Nickel," *Int. J. Recent Trends Eng. Res.*, vol. 02, no. July, pp. 219–229, 2016.

[16] R. Wang, P. Wang, X. Yan, J. Lang, C. Peng, and Q. Xue, "Promising porous carbon derived from celtuce leaves with outstanding supercapacitance and CO2 capture performance," *ACS Appl. Mater. Interfaces*, vol. 4, no. 11, pp. 5800–5806, 2012.

[17] Q. Li, Y. Hou, J. Wang, Y. Liu, N. Xiang, and Z. Huang, "Superiority of Raw Biomass and Potassium Hydroxide in Preparation of Ultrahigh Nitrogen Doping of Carbon for NH3-SCR Reaction," *ACS Sustain. Chem. Eng.*, vol. 8, no. 30, pp. 11308–11316, 2020.

[18] H. B. Z. Mohamad Zulfika, R. Baini, and N. S. Ahmad Zauzi, "Effect of pH, Dosage and Concentration on the Adsorption of Congo Red onto Untreated and Treated Aluminium Dross," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 205, no. 1, 2017.

[19] S. Abdelkarim, H. Mohammed, and B. Nouredine, "Sorption of Methylene Blue Dye from Aqueous Solution Using an Agricultural Waste," *Trends Green Chem.*, vol. 03, no. 01, 2017.

[20] A. Ebrahimian Pirbazari, E. Saberikhah, M. Badrouh, and M. S. Emami, "Alkali treated Foumanat tea waste as an efficient adsorbent for methylene blue adsorption from aqueous solution," *Water Resour. Ind.*, vol. 6, pp. 64–80, 2014.

[21] J. Yan, Y. Huang, Y. E. Miao, W. W. Tjiu, and T. Liu, "Polydopamine-coated electrospun poly(vinyl alcohol)/poly(acrylic acid) membranes as efficient dye adsorbent with good recyclability," *J. Hazard. Mater.*, vol. 283, pp. 730–739, 2015.

[22] V. Ponnusami, R. Madhuram, V. Krithika, and S. N. Srivastava, "Effects of process variables on kinetics of methylene blue sorption onto untreated guava (Psidium guajava) leaf powder: Statistical analysis," *Chem. Eng. J.*, vol. 140, no. 1–3, pp. 609–613, 2008.

[23] R. R. Krishni, K. Y. Foo, and B. H. Hameed, "Adsorptive removal of methylene blue using the natural adsorbent-banana leaves," *Desalin. Water Treat.*, vol. 52, no. 31–33, pp. 6104–6112, 2014.