Isotherm and kinetics of methylene blue removal by *Musa acuminata* peel adsorbents

Nurul Huda Mohd Noor[a], Muhammad Abbas Ahmad Zaini[a,b*], Mohd Azizi Che Yunus[a,b]

[a] School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.
[b] Centre of Lipids Engineering & Applied Research, Ibnu-Sina Institute for Scientific & Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
* Corresponding author e-mail: abbas@cheme.utm.my

DOI: 10.2478/acmy-2021-0009

Abstract:
Adsorbents were derived from banana peel through chemical treatment using phosphoric acid, potassium hydroxide, and sodium hydroxide to adsorb methylene blue from water. The adsorption of methylene blue was performed at varying concentrations and contact times. The equilibrium data fitted well with Langmuir equation, with a maximum monolayer adsorption capacity of 99.28 mg/g (28%). Phosphoric acid-treated adsorbent exhibits a greater capacity despite a lower affinity than the other adsorbents. A two-stage batch adsorber model was developed to optimize the adsorbent dosage for performance evaluation. Banana peel is a promising resource of adsorbent for wastewater treatment.

Keywords: Activated carbon, adsorption, banana peel, two-stage adsorber, methylene blue

1.0. Introduction

Rapid expansion in the global population has resulted in an immense rise in industrialization. Dyes are broadly used in various industries such as textile, paint, paper, food processing and cosmetic, and have resulted in serious water pollution due to lack of awareness and inadequate waste management facilities. A huge volume of dye effluent is discharged into the streams without proper treatment, subsequently damaging the ecosystem and food chain [1]. Considering the negative implications, it is crucial for the dyes to be removed from the effluent prior to be released into the water bodies [2]. The existing techniques to treat dye-containing wastewater include coagulation, flocculation, chemical oxidation, ozonation, ultrafiltration, photochemical degradation, and biological degradation. However, the above-mentioned methods often bear some limitations, such as high cost, generation of secondary pollutants, and intensive energy requirement [3]. Among others, adsorption is a preferable treatment process for dye removal due to its simplicity, efficient and cost-competitive [4]. Adsorption is a process in which the dye molecules are accumulated on the surface of adsorbent. In the treatment process, less sludge is produced when compared with coagulation and precipitation [5].

Carbon-based adsorbent is commonly used for the removal of organic pollutants and dyes in wastewater treatment [2,6]. The adsorbent derived from the industrial and agricultural wastes is an indispensable replacement for the non-renewable and expensive commercial adsorbents. The quest has continued to strive for similar or better adsorption performance. The exploitation of natural residues such as coconut shells, bamboo, corn stalks, rice husk, and coffee husks, etc. for activated carbon/adsorbent production has been reported in much of published literature [7]. Among others, banana peel is also a promising carbon-based adsorbent candidate for water pollutants removal. Banana is an important fruit crop, globally cultivated in more than 130 countries. The peel contains large amount of pectin, cellulose, hemicelluloses, lignin, and oligosaccharides. The innovative conversion of banana peel into adsorbent turns not only the low-value and abundant agricultural waste into valuable and useful adsorbent for wastewater treatment but also improves the economics of banana-processing enterprises [8]. Considering such potential, and to widen the body of present knowledge, this work was aimed to evaluate the methylene blue removal by carbon-based adsorbents from Saba banana (*Musa acuminata*). The findings were discussed from the viewpoints of kinetics, equilibrium, and two-stage batch adsorber design to shed some light into practical applications in wastewater treatment.

2.0. Materials and methods

2.1. Materials

Musa acuminata peel was collected from a local food stall in Johor state of Malaysia. Potassium hydroxide, phosphoric acid and methanol were supplied by R&M Chemicals. Sodium hydroxide and hydrochloric acid were supplied by QRec (Asia) and VChem Laboratory Chemicals, respectively. Methylene blue ($C_{16}H_{18}ClN_3S$, mw = 319.85 g/mol) was supplied by HmBG Chemicals. All chemicals are of analytical reagent grade.

2.2. Preparation of adsorbent

Banana peel was cut into smaller pieces of ± 3 cm and was oven-dried at 110 °C for 24 h. It was treated using NaOH, H_3PO_4, and KOH at a fixed mass ratio of 1:1. A 25 g of dried banana peel was soaked into the activator solution, and the mixture was homogeneously stirred for 3 h at 80 °C. Then, it was completely dried in an oven overnight at 110 °C. The impregnated material was heated in a furnace under anoxic environment at 500 °C for 1.5 h. The samples were labelled as OBP (original banana peel char), H-AC (activated by H_3PO_4), N-AC (activated by NaOH) and K-AC (activated by KOH). H-AC was soaked in 0.1 M of HCl, while OBP, N-AC and K-AC in methanol, for 24 h. Then, they were washed with distilled water to remove residual chemicals. The materials were oven-dried at 110 °C for 24 h and stored in a sample vial for further analysis. The yield of OBP is 23.4 %, while that of chemically treated adsorbents are 31.8 %, 11.4 % and 11.8 % for H-AC, N-AC and K-AC, respectively.

2.3. Adsorption studies

Equilibrium and kinetic studies provide insight into the mechanisms and rate-controlling steps in the adsorption process. The adsorptive properties were evaluated at different dye concentrations and contact times using bottle-point technique. A 50 mg of adsorbent was brought into intimate contact with 50 mL of methylene blue solution. The concentration was fixed at 27 mg/L, and the residual concentration was measured at different time intervals. The adsorption capacity at time t, q_t (mg/g) was calculated as,

$$q_t = \frac{V}{m}(C_o - C_t) \quad (1)$$

where, V (L) is the volume of methylene blue solution, m (g) is the mass of activated carbon, C_o (mg/L) is the initial concentration and C_t (mg/L) is the concentration at time, t. The kinetic data were analyzed using intraparticle diffusion, pseudo-first-order and pseudo-second-order models (Table 1). The parameters, k_1 (min^{-1}) is the pseudo-first-order rate constant, k_2 (g/mg.min) is the pseudo-second-order rate constant, k_d ($mg/g.min^{-0.5}$) is the rate constant for intraparticle diffusion. For equilibrium adsorption, 50 mg of activated carbon was added into 50 mL of methylene blue solution of varying concentrations (5–300 mg/L). The mixture was allowed to equilibrate for 12 days. The residual concentrations were measured using a UV-Vis

spectrophotometer (Spectrumlab 752 Pro) at a wavelength of 580 nm. The calibration standard was determined as, a.u. = 0.0277 × concentration, for $0 < C_o < 25$ mg/L with $R^2 = 0.985$. The adsorption capacity, q_e (mg/g) was calculated as,

$$q_e = \frac{V}{m}(C_o - C_e) \quad (2)$$

where, C_e (mg/L) is the equilibrium concentration. The equilibrium data were analyzed using Langmuir, Freundlich and Redlich-Peterson models (Table 1). The parameters, Q_m (mg/g) is the monolayer adsorptive capacity, b (L/g) is the adsorption affinity, K_F and $1/n$ are the Freundlich constants, and K_R, α_R and β are Redlich-Peterson constants. The models were solved by non-linear regression using *Solver* of MS Excel by minimizing the sum-of-squared-error (SSE) to yield an optimum regression coefficient, R^2.

Table 1: Kinetic and isotherm models.

Model		Expression	
Kinetic	Pseudo-first-order	$q_t = q_e[1 - \exp(-k_1 t)]$	(3)
	Pseudo-second-order	$q_t = k_2 q_e^2 t/(1 + k_2 q_e t)$	(4)
	Intraparticle diffusion	$q_t = k_d t^{1/2} + C$	(5)
Isotherm	Langmuir	$q_e = (Q_m b C_e)/(1 + bC_e)$	(6)
	Freundlich	$q_e = K_F (C_e)^{\frac{1}{n}}$	(7)
	Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}}$	(8)

2.4. Two-stage adsorber design

The two-stage adsorber design is aimed to optimize the adsorbent dosage in achieving the desired removal performance in adsorption. The schematic representation of two-stage batch adsorption process is shown in Figure 1.

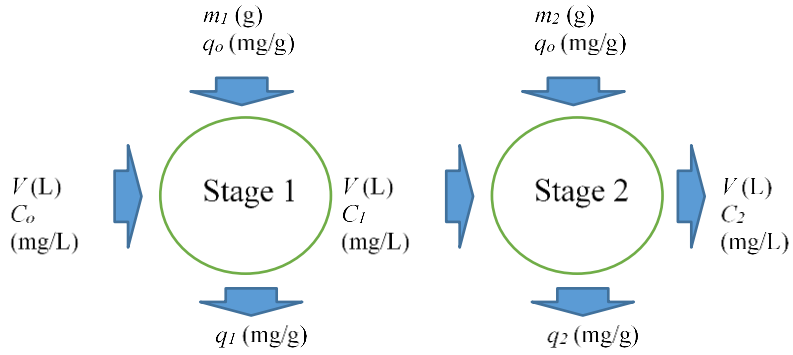

Figure 1: Two-stage adsorber design.

The following expression for adsorbent mass was obtained by combining the adsorption capacity in Equation (2) with Langmuir model.

$$m = \frac{V}{Q_m b C_e}(C_o - C_e)(1 + bC_e) \quad (9)$$

For a two-stage process, the total mass is,

$$m_1 + m_2 = \frac{V}{Q_m b C_1}(C_o - C_1)(1 + bC_1) + \frac{V}{Q_m b C_2}(C_1 - C_2)(1 + bC_2) \quad (10)$$

where, C_1 is the concentration leaving stage 1 and becomes the feed for stage 2, and $C_2 = C_e$. The optimum mass can be calculated by differentiating Equation (10) with respect to C_1.

$$\frac{d(m_1 + m_2)}{dC_1} = 0 \quad (11)$$

Solving,

$$C_1 = (C_o C_2)^{0.5} \quad (12)$$

The performance of two-stage adsorber can be calculated as,

$$Removal\ (\%) = \frac{C_o - C_2}{C_o} \times 100 \quad (13)$$

3.0. Results and discussion

3.1. Adsorption kinetics

Figure 2 shows the kinetic of methylene blue removal by *Musa acuminata* peel adsorbents. The initial adsorption stage is rapid due to the overwhelming interaction between dye molecules and plentiful active sites. A slow adsorption rate with increasing contact time is attributed to the slow diffusion of

molecules into the porous structure of adsorbent as the available external active sites depleted. Finally, the adsorption rate subsides to zero indicating the equilibrium state. For the concentration studied, the capacity at equilibrium increased in the order OBC < H-AC < K-AC < N-AC. It implies the effect of chemical treatment in enhancing the removal of methylene blue from water. Also, N-AC demonstrates a relatively fast dye removal compared to the other counterparts.

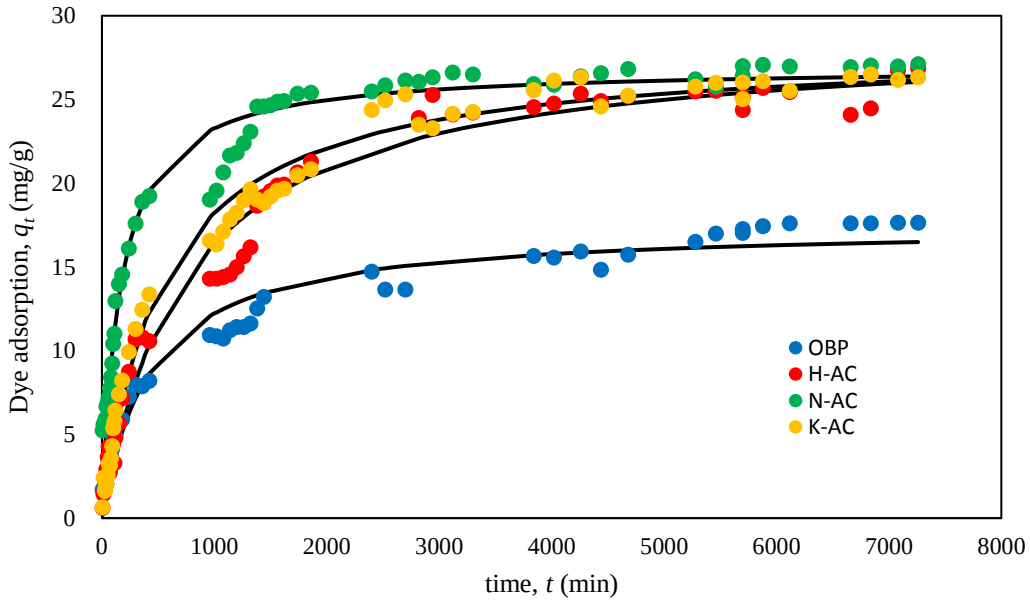

Figure 2. Kinetic of methylene blue adsorption by *Musa acuminata* peel adsorbents.

The constants of kinetic models are listed in Table 2. The pseudo-first-order model describes the initial phase as the adsorption progresses, while the pseudo-second-order model is often associated with chemisorption that controls the speed of this process. From Table 2, the pseudo-second-order model shows a better fit with the kinetic data than the pseudo-first-order model. The fact that the process could be accurately described by pseudo-second-order model further indicates that the film diffusion, intraparticle diffusion, and surface adsorption co-existed in the mass transfer process [9]. For the intraparticle diffusion model, the positive *C* value indicates that the intraparticle diffusion is not the only rate-determining step in dye adsorption. The magnitude also signifies a greater degree of boundary layer that resists the diffusion of dye molecules into the solid surface [10].

Table 2. Constants of kinetic models.

	OBP	H-AC	N-AC	K-AC
$q_{e,exp}$ (mg/g)	17.7	26.9	27.1	26.3
Pseudo-first-order				
$k_1 \times 10^3$ (min^{-1})	1.48	0.980	4.96	1.23
q_e (mg/g)	16.0	25.3	25.1	25.2
SSE	127	134	239	155
R^2	0.949	0.980	0.936	0.977
Pseudo-second-order				
$k_2 \times 10^3$ (g/mg.min)	0.133	0.046	0.233	0.066
q_e (mg/g)	17.5	28.8	27.0	28.1
SSE	52.5	89.2	102	55.4
R^2	0.972	0.982	0.972	0.989
Intraparticle diffusion				
$k_d \times 10^3$ (mg/g.min)	193	324	259	323
C	3.04	2.89	9.81	3.95
SSE	85.9	384	669	487
R^2	0.940	0.910	0.790	0.889

3.2. Equilibrium adsorption

Figure 3 shows the equilibrium data for methylene blue removal by banana peel adsorbents. Dye adsorption gradually increased with increasing concentration to a point of surface saturation that gives the maximum removal capacity. As the equilibrium concentration increases, the dye removal began to level off at 21 mg/g for OBP. K-AC and N-AC exhibit a strong intensity (steep gradient) at low concentration, which signifies a favourable adsorption with maximum capacities of 71 mg/g and 73 mg/g, respectively. Meanwhile, H-AC continued to demonstrate a gradual increase with a higher uptake of 99 mg/g. H-AC exhibits a better performance than the other adsorbents, even though it possesses a slow adsorption rate.

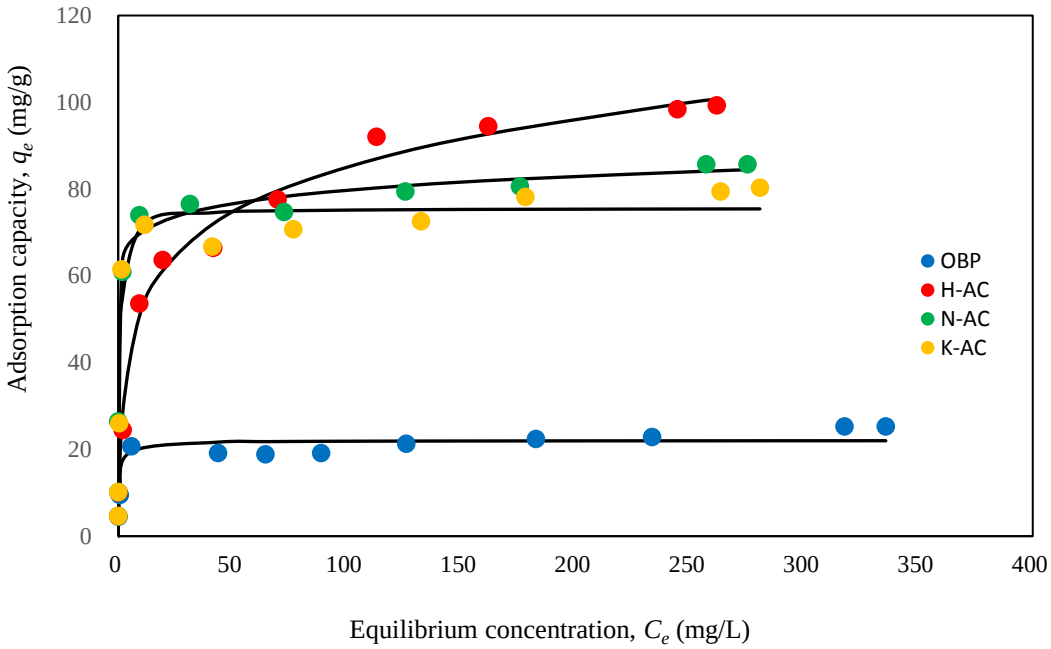

Figure 3. Equilibrium of methylene blue adsorption by *Musa acuminata* peel adsorbents.

Adsorption isotherm describes the interaction mechanism between dye molecules and adsorbent [11]. The isotherm constants are summarized in Table 3. The equilibrium data obeyed Langmuir model with $R^2 > 0.88$. The highest maximum capacity, Q_m of 99.3 mg/g was calculated for H-AC, which is in close agreement with the experimental value. The adsorption is assumed as a monolayer coverage of methylene blue molecules onto the homogeneous adsorbent surface [12]. The Langmuir constant, b is a measure of dye affinity towards the adsorbent, whose magnitude represents a favourable adsorption at low concentration.

Freundlich isotherm describes a multilayer adsorption on the heterogeneous adsorbent surface. The parameters, K_F and n represent the capacity and intensity of the system. All n values are higher than unity, signifying that the adsorption is favourable. The Redlich-Peterson isotherm combines the features of Langmuir and Freundlich models. The model becomes Langmuir isotherm when $\beta = 1$ and reduces to Freundlich isotherm (Henry's Law) at $\beta = 0$ [13]. From Table 3, $\beta \rightarrow 1$ signifies that the monolayer coverage is more dominant in methylene blue adsorption. Table 4 shows the comparison between H-AC and other methylene blue adsorbents in literature. H-AC demonstrates a better removal capacity than some similar activated carbons reported in literature.

Table 3. Constants of isotherm models.

	OBP	H-AC	N-AC	K-AC
C_o (mg/L)				
$Q_{m,exp}$ (mg/g)	25.3	99.3	85.7	80.3
Langmuir model				
Q_m (mg/g)	22.0	97.0	80.9	75.6
b (L/mg)	1.33	0.107	1.53	1.76
SSE	48.2	483	917	375
R^2	0.884	0.971	0.962	0.96
Freundlich model				
K_F (mg/g) $(L/mg)^{1/n}$	11.0	27.3	61.3	47.7
n	7.13	4.14	17.6	10.6
SSE	64.2	359	877	759
R^2	0.846	0.973	0.966	0.917
Redlich-Peterson model				
K_R	46.9	38.3	128	145
α_R	2.91	0.931	1.69	2.03
β	0.935	0.837	0.985	0.987
SSE	33.5	152	895	369
R^2	0.919	0.989	0.966	0.964

Table 4. Methylene blue removal by some activated carbons.

Adsorbent source	Q_m (mg/g)	Reference
Banana peel	99.3	This work
Ficus carica bast	47.6	[14]
Coconut leaves	66.0	[15]
Cashew nut shell	68.7	[16]
Black wattle bark	98.6	[17]
Coffee ground	182	[18]

3.3. Two-stage adsorber design

A two-stage adsorber design was proposed for H-AC to optimize the dosage in evaluating the adsorption performance. Figures 4 and 5 illustrate the effects of removal performance on intermediate adsorber concentration and total adsorbent dosage required at various influent concentrations. From Figure 3, the relationship between C_1 and C_o is linear. At any C_o, more driving force (concentration gradient) is needed in adsorber stage-1 to meet the desired removal efficiency. Also, the greater the performance, the higher the concentration difference in stage-1. Hence, more adsorbent dose would be required in stage-1 than that in stage-2. This is visualized in Figure 4. For example, to achieve 99 % of methylene blue removal, minimum doses of 112 mg and 392 mg are required for influent concentrations of 50 mg/L and 600 mg/L, respectively. The variation in adsorbent mass is significant when the removal percentage or target effluent concentration is high, and the influent concentration is low [19]. It is also useful and important to know the extent of treatment in each of the two stages.

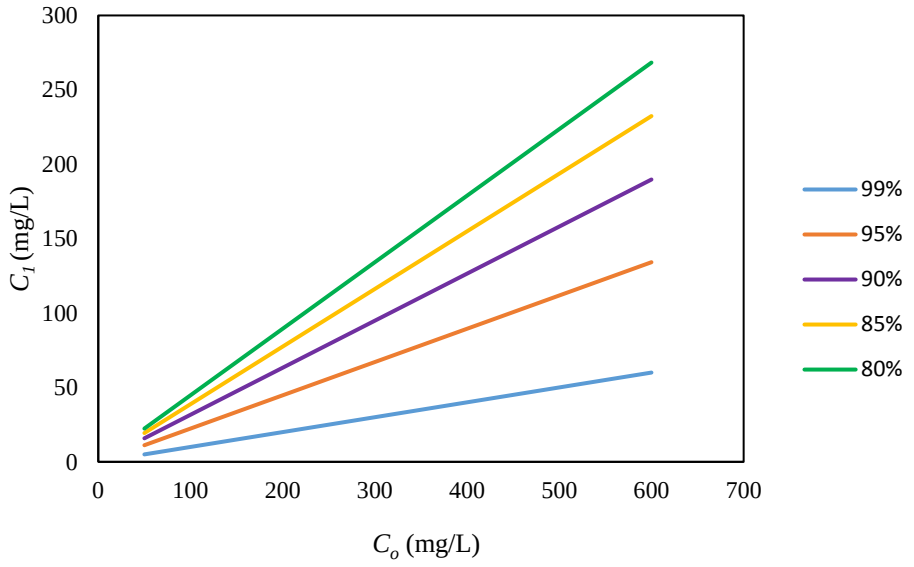

Figure 4. Effect of removal performance on intermediate adsorber concentration at various influent concentrations.

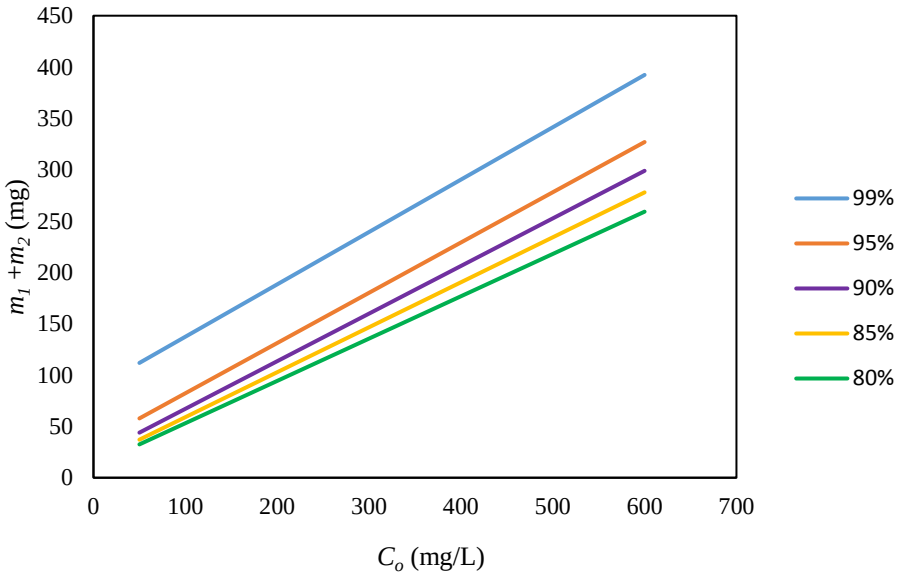

Figure 5. Effect of removal performance on total dosage required to achieve the separation at various influent concentrations.

4.0. Conclusion

Carbon-based adsorbents were prepared from *Musa acuminata* peel by chemical treatment. Equilibrium and kinetic of methylene blue adsorption revealed a maximum capacity of 99.3 mg/g by phosphoric acid treatment. The dye removal process could be best described as monolayer adsorption onto homogeneous adsorbent surface. In two-stage adsorber design, a high dosage is needed in stage-1, while the second stage is necessary to accomplish the process with a minimum dosage. The findings suggest that the laboratory made adsorbent from the banana peel could be successfully applied for the removal of dye in wastewater treatment.

5.0. Acknowledgement

This work was funded by UTM-ICONIC Grant No. 09G54.

6.0. References

[1] M.T. Amin, A.A. Alazba, M. Shafiq, "Comparative study for adsorption of methylene blue dye on biochar derived from orange peel and banana biomass in aqueous solutions", Environmental Monitoring and Assessment, Vol. 191, No. 12, Pp. 735, 2019.

[2] W. Astuti, M.A. Mahardhika, D.A. Putri, et al., "Application of kepok banana peel activated carbon prepared by conventional and microwave heating for malachite green adsorption", Materials Science and Engineering, Vol. 625, No. 1, Pp. 012025, 2019.

[3] J. Ma, D. Huang, J. Zou, L. Li, Y. Kong, and S. Komarneni, "Adsorption of methylene blue and Orange II pollutants on activated carbon prepared from banana peel", Journal of Porous Materials, Vol. 22, No. 2, Pp. 301-311, 2015.

[4] N.K. Mondal, and S. Kar, "Potentiality of banana peel for removal of Congo red dye from aqueous solution: Isotherm, kinetics and thermodynamics studies", Applied Water Science, Vol. 8, No. 6, Pp. 157, 2018.

[5] R.S. Ingole, D.H. Lataye, and P.T. Dhorabe, "Adsorption of phenol onto banana peels activated carbon", KSCE Journal of Civil Engineering, Vol. 21, No. 1, Pp. 100-110, 2017.

[6] R.K. Liew, E. Azwar, and P.N.Y. Yek, et al., "Microwave pyrolysis with KOH/NaOH mixture activation: a new approach to produce micro-mesoporous activated carbon for textile dye adsorption", Bioresource Technology, Vol. 266, Pp.1-10, 2018.

[7] V. Viena, M. Nizar, and S. Wardani, "Preparation of activated carbons from banana (Musa acuminate L.) peels for carbon monoxide adsorption", MICoMS 2017, Emerald Publishing Limited.

[8] E. Kusrini, M. Aulia, A.B. Widiantoro, Y. Nurani, and M. Mamat, "Synthesis and characterization of natural, pectin and activated carbon as low-cost potential adsorbents from kepok banana peels (Musa paradisiaca L.)", Material Science and Engineering, Vol. 440, No. 1, Pp. 1-7, 2018.

[9] J.R. Guarín, J.C. Moreno-Pirajan, L. Giraldo, "Kinetic study of the bioadsorption of methylene blue on the surface of the biomass obtained from the Algae D. antarctica", Journal of Chemistry, 2018, DOI: 10.1155/2018/2124845.

[10] J.O. Amode, J.H. Santos, Z.M. Alam, A.H. Mirza, C.C. Mei, "Adsorption of methylene blue from aqueous solution using untreated and treated (Metroxylon spp.) waste adsorbent: Equilibrium and kinetics studies", International Journal of Industrial Chemistry, Vol. 7, No. 3, Pp. 333-345, 2016.

[11] M. Khodaie, N. Ghasemi, B. Moradi, M. Rahimi, "Removal of methylene blue from wastewater by adsorption onto ZnCl2 activated corn husk carbon equilibrium studies", Journal of Chemistry, 2013, DOI: 10.1155/2013/383985.

[12] C. Patawat, K. Silakate, S. Chuan-Udom, N. Supanchaiyamat, A.J. Hunt, Y. Ngernyen, "Preparation of activated carbon from Dipterocarpus alatus fruit and its application for methylene blue adsorption", RSC Advances, Vol. 10, No. 36, Pp. 21082-21091, 2020.

[13] Y. Liu, X. Luo, Z. Zhang, P. Zhou, Z. Yang, "Modeling and thermodynamics of methylene blue and acid blue 80 adsorption onto potato residue based activated carbon", Chemical Research in Chinese Universities, Vol. 31, No. 4, Pp. 627-632, 2015.

[14] D. Pathania, S. Sharma, P. Singh, "Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast", Arabian Journal of Chemistry, Vol. 10, S1445-S1451, 2017.

[15] R. Abd-Rashid, A.H. Jawad, et al., "FeCl3-activated carbon developed from coconut leaves: Characterization and application for methylene blue removal", Sains Malaysiana, Vol. 47, No. 3, 603-610, 2018.

[16] P.S. Kumar, S. Ramalingam, K. Sathishkumar, "Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent", Korean Journal of Chemical Engineering, Vol. 28, No. 1, Pp. 149-155, 2011.

[17] S.F. Lütke, A.V. Igansi, L. Pegoraro, G.L. Dotto, L.A. Pinto, T.R. Cadaval Jr, "Preparation of activated carbon from black wattle bark waste and its application for phenol adsorption", Journal of Environmental Chemical Engineering, Vol. 7, No. 5, Pp. 103396, 2019.

[18] A. Reffas, V. Bernardet, B. David, L. Reinert, M.B. Lehocine, et al., "Carbons prepared from coffee grounds by H3PO4 activation: Characterization and adsorption of methylene blue and Nylosan Red N-2RBL", Journal of Hazardous Materials, Vol. 175, No. 1-3, Pp. 779-788, 2010.

[19] M. Hijab, J. Saleem, P. Parthasarathy, H.R. Mackey, G. McKay, "Two-stage optimisation for malachite green removal using activated date pits", Biomass Conversion and Biorefinery, Pp. 1-14, 2020.