

Full Length Research Paper

Sorption kinetics of methylene blue on adsorbents derived from *Delonix regia* seed pods and *Vigna subterranea* fruit hulls

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Kinetics of methylene blue adsorption on adsorbents prepared from *Delonix regia* seed pods (DRSP) and *Vigna subterranea* fruit hulls (VSFH) were investigated. Characterization of the adsorbents indicated that the points of zero charge (PZC) of DRSP and VSFH are 5.30 and 4.80 respectively. Optimum removal efficiencies of methylene blue by DRSP and VSFH occurred at pH of 8.00 and 11.00 respectively. For both DRSP and VSFH, equilibrium was attained after 4 hours of agitation time, leading to over 80% removal of methylene blue at ionic strength of 0.4 M and beyond. Among the kinetic models tested, the experimental data fitted well to pseudo- second order model ($R^2 = 0.996$ for DRSP and $= 0.998$ for VSFH), suggesting that the adsorption of methylene blue on DRSP and VSFH involves chemisorption. The study demonstrates that DRSP and VSFH can serve as alternative low-cost adsorbents for removing methylene blue from wastewater.

Key words: Adsorption, *Delonix regia*, kinetics, methylene blue, *Vigna subterranean*.

INTRODUCTION

In recent time, there is a growing interest and concern among scientists and the general public over increasing contamination of aquatic environment by chemical substances. This is partly due to the realization that the presence of certain chemical contaminants in aquatic environment is potentially damaging to both human and animal health. Methylene blue is a heterocyclic aromatic compound, known systematically as 3,7- bis(dimethylamino)-phenothiazin-5-iumchloride (Figure1).

In analytical chemistry, methylene blue is used for

spectrophotometric determination of hydrogen sulfide (Fogo and Popowsky,1949) and as redox indicator (Prasetyo and Mufakhir (2011)). It is also used in medicine for the treatment of refractory hypotension (Weissgerber, 2008) methemoglobinemia (Wendel, 1937; Etteldorf, 1951;Burke et al.,2013; Khanal et al.,2015), sepsis in immune suppressed patients (Ramamoorthy et al., 2013) and as antidote for cyanide antidote for cyanide poisoning (Hanzlik, 1933).However, in spite of its vast medical and scientific applications, consumption of

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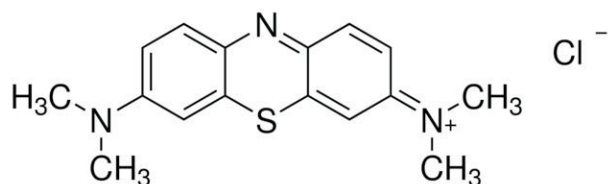


Figure 1. Structural formula of methylene blue.

excess amount of methylene blue has been shown to have neurotoxic effect on the central nervous system (Vutskits et al., 2008). Due to its widespread use, substantial quantity of methylene blue is released into aquatic environment during production, usage, and disposal and this may result in excess amount of methylene blue entering the food chain through bioaccumulation by aquatic biota. Besides its harmful impact on human health, contamination of aquatic environment by excess methylene blue (or any other dye) causes reduction in the growth of algae due to obstruction of light required for photosynthesis, which subsequently leads to ecological imbalance in the aquatic ecosystem (de Sousa et al., 2012).

In view of the adverse effects associated with contamination of aquatic environment by excess methylene blue, remediation techniques such as biodegradation (Ong et al., 2005; Ramamurthy and Umamaheswari, 2013), phytoremediation (Tan et al., 2016), adsorption (Rafatullah et al., 2010; Mikati et al., 2013) and advanced oxidation process (Houas et al., 2001; Madhu et al., 2009; Jian-Xiao et al., 2011; Ameta et al., 2013) have been studied for their viability in removing, decolorizing or degrading methylene blue in wastewater. Among these remediation techniques, removal of methylene blue (and other contaminants) by adsorption process is considered to be the safest because no toxic residue is left behind in the treated water. Although adsorbents such as clay minerals (Schoonheydt and Heughebaert, 1992; Ghosh and Bhattacharyya, 2002; Al-Wahbi and Dammag, 2001; Sarma et al., 2011) and commercial activated carbon (Al-Baidhany and Al-Salihy, 2016) have been employed for the removal of methylene blue from wastewater, research into the use of alternative low-cost adsorbents derived from agricultural wastes is steadily growing. Advantages of using adsorbents obtained from agricultural waste materials for the removal of toxic contaminants from wastewater include a partial reduction in the volume of solid waste materials in the environment and a cutback in the cost of wastewater treatment (Grassi et al., 2012).

Trees of *Delonix regia* (picture on the left of Figure 2) are planted mainly for ornamental purpose while *Vigna subterranea* (picture on the right of Figure 2) is cultivated mainly because of its high nutritional value. In northern

Nigeria, large quantities of *D. regia* seed pods (DRSP) and *V. subterranea* fruit hulls (VSFH) are usually disposed of as waste materials. Hence, the main focus of this paper is to study the kinetics of methylene blue adsorption on adsorbents derived from DRSP and VSFH with a view to finding out the suitability of removing methylene blue from wastewater by these adsorbents.

MATERIALS AND METHODS

Collection and preparation of adsorbents

D. regia seed pods were obtained from the main campus of Bauchi State University, Gadau, Bauchi State, Nigeria and *V. subterranea* fruit hulls were obtained from a farm in Darazo Local Government Area of Bauchi State, Nigeria. The seed pods and the fruit hulls were washed with water, air-dried, pulverized and sieved into fine particles as previously described (Sebata et al., 2013; Akinola et al., 2015). The fine particles derived from *D. regia* seed pods and *V. subterranea* fruit hulls were stored in air-tight containers and labeled DRSP and VSFH respectively.

Preparation of adsorbate and reagent solutions

Analytical grade reagents were used to prepare stock solutions containing 1000 mgL⁻¹ methylene blue, 2 moldm⁻³ KNO₃, 0.1 moldm⁻³ HNO₃ and 0.1 moldm⁻³ NaOH solutions using standard procedure (Mendham et al., 2000). This involves dissolution of appropriate amount of each reagent in doubly distilled water and diluting the resulting solutions in 1000 cm³ volumetric flasks. These stock solutions were later used in subsequent experiments described in this paper.

Determination of points of zero charge

The points of zero charge (PZC) of DRSP and VSFH were determined using solid addition method (Nidheesh et al., 2012). In this method, 1.0 g of DRSP or VSFH were added to ten 250 cm³ Erlenmeyer flasks containing 50 cm³ of aqueous solution each. Prior to transferring these aqueous solutions into the 250 cm³ Erlenmeyer flasks, the ionic strengths were adjusted to 0.1 moldm⁻³ by adding appropriate amount of 1.0 moldm⁻³ while the pH values were adjusted to values ranging from 2.00 to 10.00 by adding appropriate amounts of 0.1 moldm⁻³ HNO₃ solution or 0.1 moldm⁻³ NaOH solution. The flasks were then agitated at 200 rpm for 1 hour using WSZ series Orbital Shaker. Thereafter, the pH values of the supernatants were measured using JENWAY 3505 Ph meter. The difference between the initial and final pH was calculated using Equation 1. Plots of ΔpH against were constructed and the points of interception on the pH_i axes gave values of PZC for DRSP and VSFH.

$$\Delta pH = pH_f - pH_i \quad (1)$$

Effects of operating variables on removal efficiency

Effects of initial solution pH (in the range of 2.00 to 12.00), ionic strength (in the range of 0.2 to 1.6 M) and contact time (in the range



Figure 2. Pictures of *D. regia* seed pods (left) and *V. subterranea* fruit hulls (right).

of 20 to 480 min) on the removal efficiencies of methylene blue by DRSP and VSFH were investigated using a one-factor-at-a-time (OFAT) approach (Montgomery, 2013). This approach consists of selecting a baseline set of levels for each factor (pH = 2.00; ionic strength = 0.2 M; contact time = 300 min were selected as baseline set in this study), and then successively varying each factor over its range with the other factors held constant at the baseline level. For each treatment combination, 1.0 g of adsorbent was added to 50 cm³ of dye solution containing 50 mg/L methylene blue in 250 cm³ Erlenmeyer flask. The flasks were then agitated at 200 rpm for appropriate periods of time using WSZ series Orbital Shaker. The content of each flask was filtered and the residual concentrations of methylene blue in the flasks were determined at 664 nm using UNICO UV-2100 Spectrophotometer (UNICO Instrument Co., Ltd, Shanghai, China). The removal efficiencies of methylene blue (expressed as % removal) were then calculated using Equation 2. Optimum condition was selected for each operating factor by constructing a graph that indicates how the removal efficiencies are affected by varying the factor with all other factors held constant.

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100\% \quad (2)$$

Investigation of sorption kinetics

Experiment for sorption kinetic study was carried out by adding 1.0 g of DRSP or VSFH to nine 250 cm³ Erlenmeyer flasks containing 50 cm³ of dye solutions. The concentration of methylene blue in each flask was maintained at a value of 50 mg/L while the pH and ionic strength of each solution were adjusted to the requisite optimal values. The flasks were then agitated at ambient temperature (28°C) for specific periods of time (20, 40 60, 80, 100, 120, 140, 160 and 180 min) using WSZ series Orbital Shaker at 200 rpm. The content of each flask was filtered and the residual concentrations of methylene blue in these filtrates were determined at 664 nm using UNICO UV-2100 Spectrophotometer (UNICO Instrument Co., Ltd, Shanghai, China). The amount of methylene blue adsorbed onto the adsorbent at various time intervals was calculated using Equation 3. This experiment was carried out twice and the fitness of the average data obtained was tested using intraparticle diffusion model (Equation 4), pseudo-first order model

(Equation 5), pseudo-second order model (Equation 6) and Elovich equation (Equation 7)

$$q_t = \frac{v}{m} (C_i - C_t) \quad (3)$$

$$q_t = k_{int} t^{1/2} \quad (4)$$

$$\log (q_s - q_t) = \log q_s - \frac{k_1}{2.303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_s^2} + \frac{1}{q_s} t \quad (6)$$

$$q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \text{Int} \quad (7)$$

The point of zero charge (PZC) for DRSP and VSFH obtained from the plots of ζ pH against pH_i displayed in Figure 3 are 5.30 and 4.80 respectively. PZC is the pH at which the surface charge of a material is equal to zero at some ambient temperature, applied pressure, and aqueous solution composition (Sposito, 2004; Alvarez-Silva et al., 2010). At pH values below PZC, the surface charge on an adsorbent is negative but the surface charge becomes positive at pH values above PZC (Oluwaseye et al., 2011; Gusmao et al., 2013). PZC reported in literature for adsorbents prepared from other agricultural wastes are 7.10 for oil palm fruit fibre (Abia and Asuque, 2008), 5.00 for sugarcane bagasse (Zhang et al., 2011), 6.00 for watermelon shell (Banerjee et al., 2012), 4.18 for orange peel (De Souza et al., 2012) and 3.50 for groundnut shell (Akinola and Umar, 2015).

Optimum operating variables

Results showing the variation of percent removal of methylene blue by DRSP and VSFH as functions of initial solution pH, total ionic

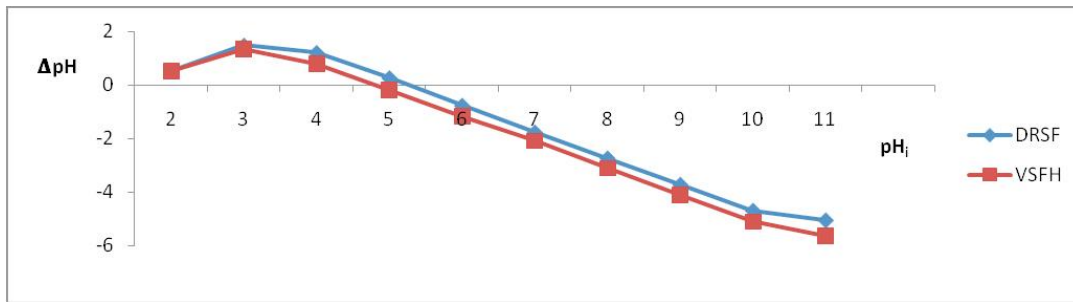


Figure 3. Plots of ΔpH against pH_i showing points of zero charge of DRSF and VSFH.

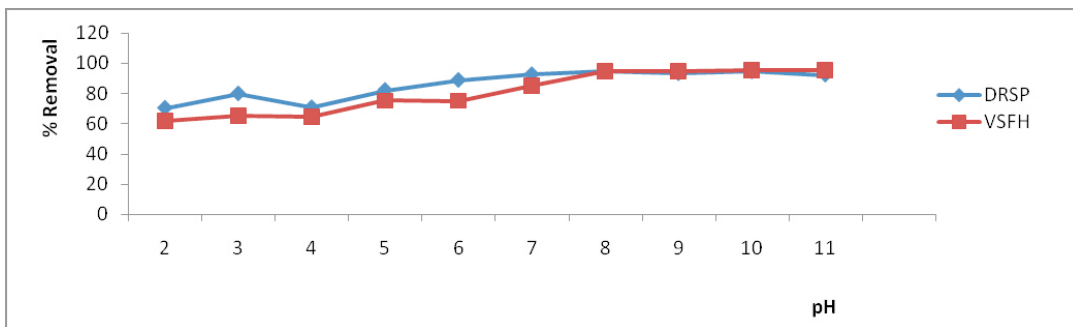


Figure 4. Plots of removal efficiencies against initial solution pH.

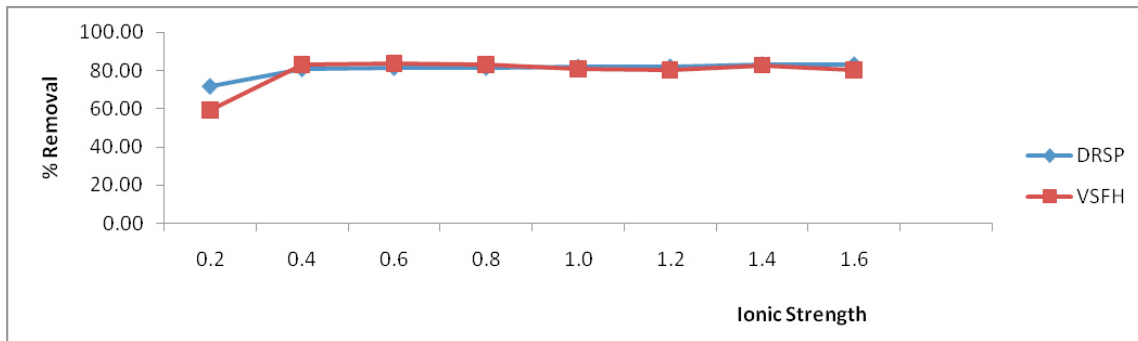


Figure 5. Plots of removal efficiencies against ionic strength.

strength of the solution and contact time are presented in Figures 4, 5 and 6 respectively. As shown in Figure 4, higher removal of methylene blue occurred at higher pH values, reaching maximum values of 94.72% at pH of 8.00 for DRSF and 95.70% at pH of 11.00 for VSFH. The increased removal efficiencies of methylene blue by the DRSF and VSFH at pH values above 5.30 (value of PZC for DRSP) and 4.80 (value of PZC for VSFH) is consistent with the fact that methylene blue molecules exist as positively charged ions in aqueous solution, and therefore exhibit enhanced electrostatic attractions for the adsorbents since the surface charges on the adsorbents are negative at pH values above their PZC. The plots presented in Figure 5 show that at ionic strength of

0.2 M, 71.88 and 59.38% of methylene blue were removed from aqueous solution by DRSF and VSFH respectively. However, beyond the ionic strength value of 0.2 M, adsorptions of methylene blue on both DRSF and VSFH increased slightly above 80.00% but remained essentially constant in solutions with ionic strength values ranging from 0.4 to 1.6 M. In Figure 6, the percent removal of methylene blue by DRSF increased gradually from 38.85% at 20 min to 89.22% at 240 min. Beyond 240 min, the removal efficiency of methylene blue by DRSF remained more or less constant. Similarly, Figure 6 also shows that percent removal of methylene blue by VSFH increased gradually from 29.09% at 20 min to 84.42% at 240 min, remaining roughly constant beyond 240

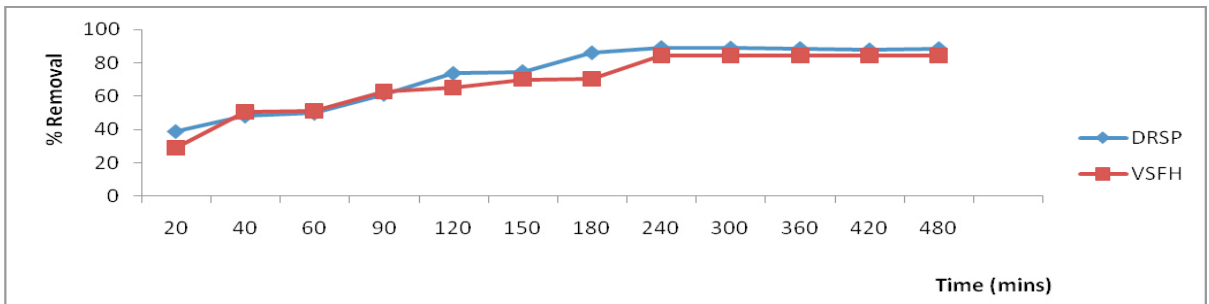


Figure 6. Plots of removal efficiencies against contact time.

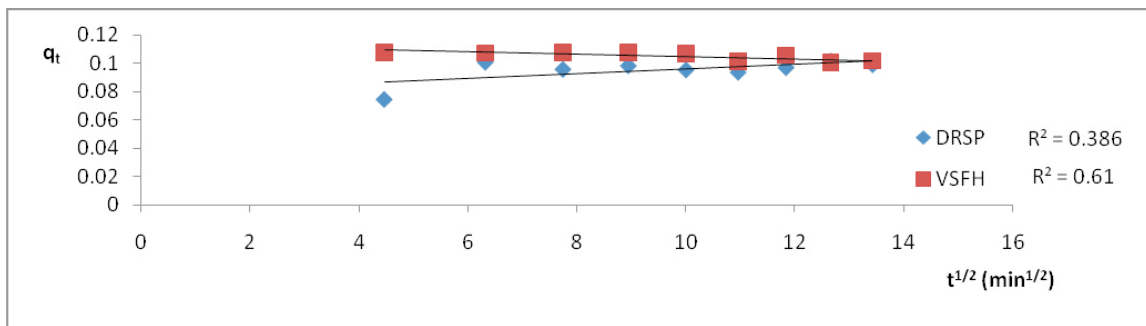


Figure 7. Intraparticle diffusion plots for methylene blue adsorption on DRSP and VSFH.

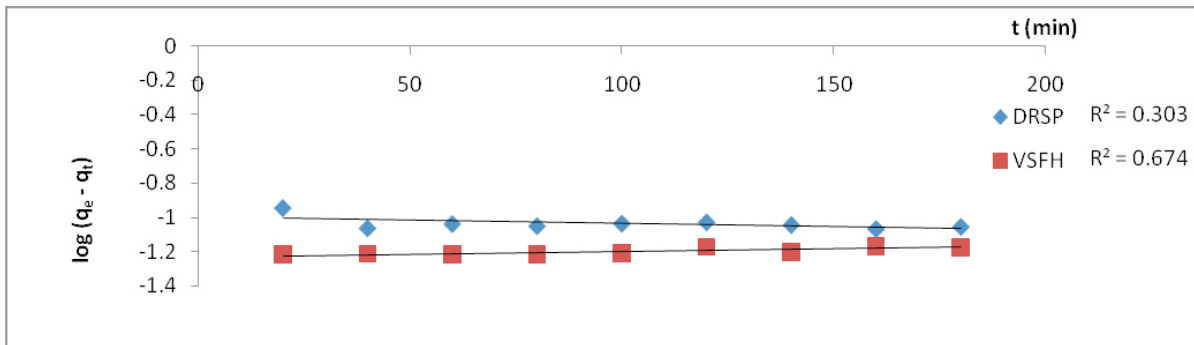


Figure 8. Pseudo-first order plots for methylene blue adsorption on DRSP and VSFH.

minutes. In view of these findings, the kinetic experiments involving DRSP and VSFH were carried out at pH values of 8.00 and 11.00 respectively. The ionic strengths of all solutions were adjusted to 1.0 M and all the kinetic data were collected within the first 3 h.

Sorption kinetics

The charts displayed in Figures 7, 8, 9 and 10 are plots of intraparticle diffusion model, pseudo-first order model, pseudo-second order model and Elovich model for testing the fitness of sorption kinetic data of methylene blue on DRSP and VSFH. The coefficients of determination (R^2 values) and the rate constants

obtained from these plots are presented in Table 1. Among the four kinetic models tested, the experimental data fitted well to pseudo-second order model for both DRSP and VSFH as indicated by the values of coefficients of determination ($R^2 = 0.996$ for DRSP and $= 0.998$ for VSFH in Table 1). Pseudo-second order model is based on the assumption that the adsorption process involves chemisorption, which requires sharing or exchange of valence electrons between the adsorbent and the adsorbate (Ho, 2006). The pseudo-second order rate constants obtained in the present study ($2.155 \text{ gm}^{-1}\text{min}^{-1}$ for DRSP and $2.873 \text{ gm}^{-1}\text{min}^{-1}$ for VSFH in Table 1) are several order of magnitude higher than $0.0059 \text{ gm}^{-1}\text{min}^{-1}$ reported for the adsorption of methylene blue on NaOH-modified dead leaves of plane trees (Gong et al., 2013), 0.0012

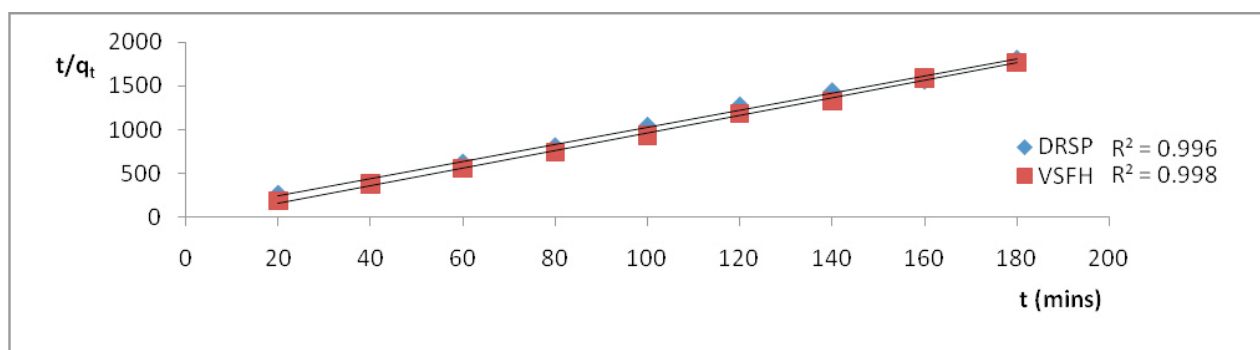


Figure 9. Pseudo-second order plots for methylene blue adsorption on DRSP and VSFH.

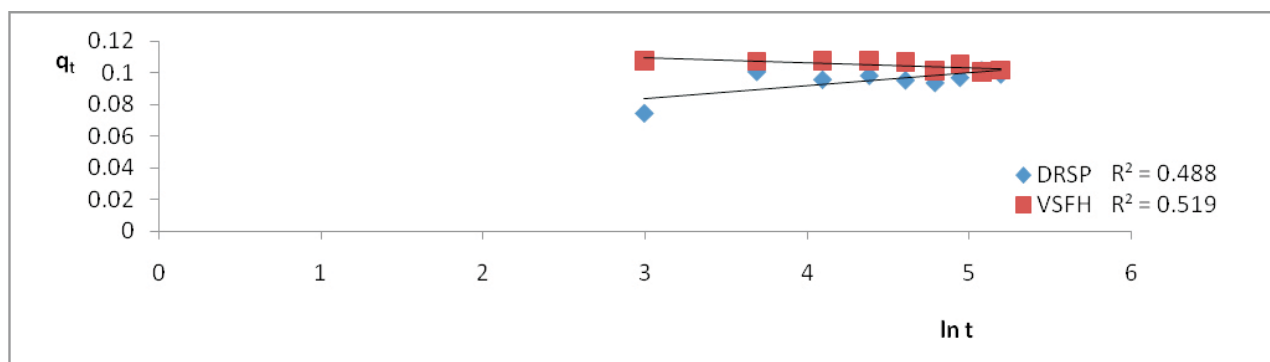


Figure 10. Elovich plots for methylene blue adsorption on DRSP and VSFH.

Table 1. Coefficients of determination and rate constants of methylene blue adsorption on DRSP and VSFH.

Adsorbent	Intraparticle diffusion model		Pseudo-first order model		Pseudo-second order model			Elovich model	
	R ²	k _{int}	R ²	K ₁	R ²	K ₂	R ²	á	?
DRSP	0.386	0.001	0.303	0.000	0.996	2.155	0.488	1.45×10 ²⁰	125.0
VSFH	0.610	0.000	0.674	0.000	0.998	2.873	0.519	2.49×10 ²⁰	-333.3

gmg⁻¹min⁻¹ reported for the adsorption methylene blue on NaOH-modified durian leaf powder (Hussin et al., 2015). The implication of these findings is that, the rates of removal of methylene blue from aqueous solution by DRSP and VSFH are faster than the rates of removal of methylene blue from aqueous solution by adsorbents derived from other agricultural waste materials in the literature cited.

Conclusion

The search for alternative low-cost adsorbents from locally-available agricultural waste materials provided the impetus for this research work. Adsorbents prepared from the seed pods of *D. regia* and the fruit hulls of *V.*

subterranea were characterized and the suitability of these adsorbents, *vis-à-vis* their ability to remove methylene blue from aqueous solution, were evaluated by studying the kinetic behaviors of the adsorption systems. Findings suggest that adsorptions of methylene blue on both adsorbents were adequately described by pseudo-second order model, suggesting that the adsorptions involve sharing or exchange of valence electrons between the adsorbents and the adsorbate. This study demonstrates that the adsorbents prepared from the seed pods of *D. regia* and the fruit hulls of *V. subterranea* may be suitable for removing methylene blue from contaminated wastewater.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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ABBREVIATIONS AND SYMBOLS

C_i = adsorbate initial concentration (mg/L); C_e = residual concentration of adsorbate in solution at equilibrium (mg/L); C_t = residual concentration of adsorbate in solution at time t (mg/L); K_{int} = intraparticle diffusion rate constant; K_1 = pseudo-first order rate constant; K_2 = pseudo-second order rate constant; m = mass of the adsorbent (g); pH_f = final pH of solution; pH_i = initial pH of solution; ΔpH = difference between final and initial pH PZC; PZC = point of zero charge; q_t = amount of adsorbate sorbed on the adsorbent at any time t (mg/g); q_e = amount of adsorbate sorbed on the adsorbent at equilibrium (mg/g); t = time of adsorption (minutes); V = volume of the adsorbate solution (L); \dot{a} = initial sorption rate of adsorbate; \dot{d} = desorption constant.

REFERENCES

- Abia AA, Asuque ED (2008). Sorption of Pb(II) and Cd(II) ions onto chemically unmodified and modified oil palm fruit fibre adsorbent: analysis of pseudo second order kinetic models. *Indian Journal of Chemical Technology* 15:341-348.
- Akinola LK, Umar AM (2015). Adsorption of crystal violet onto adsorbents derived from agricultural wastes: kinetic and equilibrium studies. *Journal of Applied Sciences and Environmental Management* 19(2):279– 288.
- Akinola LK, Ibrahim A, Chadi AS (2016). Kinetic and equilibrium studies of Congo red adsorption on adsorbent from bambara groundnut hulls. *Al-Hikmah Journal of Pure & Applied Sciences* 2(2):79-88.
- Al-Baidhany JH, Al-Salihy ST(2016). Removal of methylene blue dye from aqueous solution by using commercial granular activated carbon with different types of adsorbers. *Mesopotamia Environmental Journal* 2(2):1- 11.
- Alvarez-Silva M, Uribe-Salas A, Mirnezami M , Finch JA (2010). The point of zero charge of phyllosilicate minerals using the Mular-Roberts titration technique. *Minerals Engineering* 23:383-389.
- Al-Wahbi AAM, Dammag HAQ (2001). Removal of methylene blue from aqueous solutions using Yemen bentonite. *Diyala Journal of Engineering Sciences* 4(1):30-53.
- Ameta A, Ameta R, Ahuja M (2013). Photocatalytic degradation of methylene blue over ferric tungstate. *Scientific Review & Chemical Communications* 3(3):172-180.
- Banerjee K, Ramesh ST, Gandhimathi R, Nidheesh PV , Bharathi KS (2012). A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solution. *Iranica Journal of Energy and Environment* 3(2):143-156.
- Burke P, Jahangir K, Kolber MR (2013). Dapsone-induced methemoglobinemia: case of the blue lady. *Canadian Family Physician* 59(9):958-961.
- de Sousa ML, de Moraes PB, Lopes PRM, Montagnolli RN, de Angelis DF, Bidoie ED (2012). Contamination by remazol red brilliant dye and its impact in aquatic photosynthetic microbiota. *Environmental Management and Sustainable Development* 1(2):129-138.
- De Souza JVTM, Diniz KM, Massocatto CL, Tarley CRT, Caetano J, Dragunski DC (2012). Removal of Pb(II) from aqueous solution with orange sub-products chemically modified as biosorbent. *BioResources* 7(2):2300-2318.
- Etteldorf JN (1951). Methylene blue in the treatment of methemoglobinemia in premature infants caused by marking ink. *The Journal of Pediatrics* 38(1):24-27.
- Fogo JK, Popowsky M (1949). Spectrophotometric determination of hydrogen sulfide: methylene blue method. *Analytical Chemistry* 21(6):732-734.
- Ghosh D, Bhattacharyya KG (2002). Adsorption of methylene blue on kaolinite. *Applied Clay Science* 20(6):295-300.
- Gong L, Sun W, Kong L (2013). Adsorption of methylene blue by NaOH-modified dead leaves of plane trees. *Computational Water, Energy, and Environmental Engineering* 2:13-19.
- Grassi M, Kaykioglu G, Belgiorio V, Lofrano G (2012). Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process. In Lafrano, G. (Ed.) *Emerging Compounds Removal from Wastewater: Natural and Solar Based Treatment*, London, Springer, pp.15-37.
- Gusmao KAG, Gurgel LVA, Melo TMS, Gil LF (2013). Adsorption studies of methylene blue and gentian violet on sugarcane bagasse modified with EDTA dianhydride (EDTAD) in aqueous solutions: kinetic and equilibrium aspects. *Journal of Environmental Management* 118:135-143.
- Hanzlik PJ (1933). Methylene blue as antidote for cyanide poisoning. *The Journal of the American Medical Association* 100(2):357.
- Ho YS (2006). Review of second-order models for adsorption systems. *Journal of Hazardous Materials B* 136:681-689.
- Houas A, Lachheb H, Ksibi M, Elaloui E, Guillard C, Herrmann J (2001). Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B: Environmental* 31:145-157.
- Hussin ZM, Talib N, Hussin NM, Hanafiah MAKM, Khalir WKWM (2015). Methylene blue adsorption onto NaOH modified durian leaf powder: isotherm and kinetic studies. *American Journal of Environmental Engineering* 5(3A):38-43.
- Jian-Xiao LV, Ying C, Guo-hong X, Ling-yun Z, Su-fen W (2011). Decoloration of methylene blue simulated wastewater using a UV-H₂O₂ combined system. *Journal of Water Reuse and Desalination* 1(1):45-51.
- Khanal R, Karmacharya P, Pathak R, Poudel DR, Ghimire S, Alweis R (2015). Do all patients with acquired methemoglobinemia need treatment? A lesson learnt. *Journal of Community Hospital Internal Medicine Perspectives* 5(5):1-3.
- Madhu GM, ARaj MAL, Pai KVK (2009). Titanium oxide (TiO₂) assisted photocatalytic degradation of methylene blue. *Journal of Environmental Biology* 30(20):259-264.
- Mendham J, Denney RC, Barnes JD, Thomas MJK (2000). *Vogel's textbook of quantitative chemical analysis*, 6th ed., Prentice Hall, England P 315.
- Mikati FM, Saade NA, Slim KA, El-Jamal MM (2013). Biosorption of methylene blue on chemically modified *Chaetophora elegans* alga by HCl and citric acid. *Journal of Chemical Technology and Metallurgy*
- Montgomery DC (2013): *Design and analysis of experiments*, 8th ed., John Wiley & Sons Inc., Danvers P 4.
- Nidheesh PV, Gandhimathi R, Ramesh ST, Ananth-Singh TS (2012). Kinetic analysis of crystal violet adsorption onto bottom ash. *Turkish Journal of Engineering and Environmental Sciences* 36:249-262.
- Oluwaseye A, Uzairu A, Eddy NO (2011). Biosorption of Cr (VI) and Ni (II) from aqueous solution onto *Bacillus subtilis* immobilized in agarose gel. *Der Chemica Sinica* 2(5):173-188.
- Ong S , Toorisaka E, Hirata M, Hano T (2005). Biodegradation of redox dye methylene blue by up-flow anaerobic sludge blanket reactor.

- Journal of Hazardous Materials 124:88-94.
- Prasetyo E, Mufakhir FR (2011). Redox titration of iron using methylene blue as indicator and its application in ore analysis. Asian Transactions on Basic and Applied Sciences 1(5):1-9.
- Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010). Adsorption of methylene blue on low-cost adsorbents: a review. Journal of Hazardous Materials 177:70-80.
- Ramamoorthy S, Patel S, Bradburn E, Kadry Z, Uemura T, Janicki PK, Shah , Bezinover D (2013). Use of methylene blue for treatment of severe sepsis in an immunosuppressed patient after liver transportation. Case Reports in Transportation, Article ID 203791.
- Ramamurthy V, Umamaheswari G (2013). Biodegradation of synthetic dyes by *Aspergillus terreus* inoculated on solid media. International Journal of Innovative Research in Science, Engineering and Technology 2(12):7821-7827.
- Sarma GH, SenGupta S, Bhattacharyya KG (2011). Methylene blue adsorption on natural and modified clays. Separation Science and Technology 46(10):1602-1614.
- Schoonheydt RA, Heughebaert L (1992). Clay adsorbed dyes: methylene blue on laponite. Clay Minerals 27:91-100.
- Sebata E, Moyo M, Guyo U, Ngano NP , Nyamunda BC , Chigondo F, Chitsa V, Shumba M (2013). Adsorptive removal of atrazine from aqueous solution using bambara groundnut hulls. International Journal of Engineering Research and Technology 2(5):312-321.
- Sposito G (2004). The surface chemistry of natural particles. Oxford University Press, Oxford P 25.
- Tan KA, Morad N, Ooi JQ (2016). Phytoremediation of methylene blue and methyl orange using *Eichhornia crassipes*. International Journal of Environmental Science and Development 7(10):724-728.
- Vutskits L, Briner A, Klauser P, Gascon E, Dayer AG, Kiss JZ, Muller D, Licker MJ, Morel DR (2008). Adverse effects of methylene blue on central nervous system. Anesthesiology 108:684-692.
- Weissgerber AJ (2008). Methylene blue for refractory hypotension: a case report. AANA Journal 76(4):271-274.
- Wendel WB (1937). Use of methylene blue in methemoglobinemia from sulfanilamide poisoning. The Journal of the American Medical Association 109(15):1216-1218.
- Zhang Z, Moghaddam L, Hara IMO, Doherty WOS (2011). Congo red adsorption by ball-milled sugarcane bagasse. Chemical Engineering 178:122-128.