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ADSORPTION OF METHYLENE BLUE ON ADSORBENTS DERIVED FROM *DELONIX REGIA* SEED PODS AND *VIGNA SUBTERRANEA* FRUIT HULLS: A KINETIC STUDY

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ABSTRACT
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 indicates 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 R^2 = 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.

Keywords: Adsorption, *Delonix regia*, Kinetics, Methylene blue, *Vigna subterranean*

ABBREVIATIONS AND SYMBOLS

C_i	Adsorbate initial concentration (mg/dm^3)
C_e	Residual concentration of adsorbate in solution at equilibrium (mg/dm^3)
C_t	Residual concentration of adsorbate in solution at time t (mg/dm^3)
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	Point of zero charge
q_t	Amount of adsorbate absorbed on the adsorbent at any time t (mg/g)
q_e	Amount of adsorbate absorbed on the adsorbent at equilibrium (mg/g)
T	Time of adsorption (minutes)
V	Volume of the adsorbate solution (dm^3)
α	Initial sorption rate of adsorbate
β	Desorption constant

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-ium chloride (Fig. 1). 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 immunosuppressed patients (Ramamoorthy *et al*, 2013) and as antidote for cyanide poisoning (Hanzlik, 1933). However, in spite of its vast medical and scientific applications, consumption of 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; Al-Wahbi and Dammag, 2001; Ghosh and Bhattacharyya, 2002; 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* are planted mainly for ornamental purpose while *Vigna subterranea* is an edible fruit that is cultivated mainly because of its high nutritional value. In northern Nigeria, large quantities of *Delonix regia* seed pods (DRSP) and *Vigna 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.

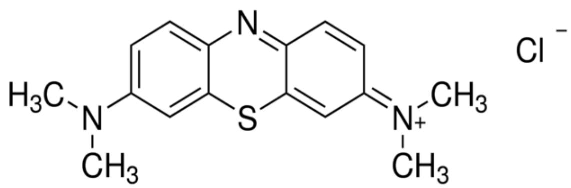

Fig. 1: Structural formula of methylene blue

MATERIALS AND METHODS

Collection and Preparation of Adsorbents

Delonix regia seed pods were obtained from the main campus of Bauchi State University, Gadau, Bauchi State, Nigeria and *Vigna 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*, 2016). The fine particles derived from *Delonix regia* seed pods and *Vigna 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 $moldm^{-3}$ KNO_3, 0.1 $moldm^{-3}$ HNO_3 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 cm^3 volumetric flasks. These stock solutions were 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 cm^3 Erlenmeyer flasks containing 50 cm^3 of aqueous solution each. Prior to transferring these aqueous solutions into the 250 cm^3 Erlenmeyer flasks, the ionic strengths were adjusted to 0.1 $moldm^{-3}$ by adding appropriate amount of 1.0 $moldm^{-3}$ KNO_3 while the pH values were adjusted to values ranging from 2.00 to 10.00 by adding appropriate amounts of 0.1 $moldm^{-3}$ HNO_3 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 pH_i were constructed and the points of intercept on the pH_i axes gave values of PZC for DRSP and VSFH.

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

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 of 20 to 480 minutes) 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 minutes 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 cm^3 of dye solution containing 50 mg/L methylene blue in 250 cm^3 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.

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

Investigation of Sorption Kinetics

Experiment for sorption kinetic study was carried out by adding 1.0 g of DRSP or VSFH to nine 250 cm^3 Erlenmeyer flasks containing 50 cm^3 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 minutes) 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)

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

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

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

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

$$q_t = \frac{1}{\beta} \ln(\alpha\boldsymbol{\beta}) + \frac{1}{\beta} \ln t \quad \ldots\ldots\ldots\ldots \quad (7)$$

RESULTS AND DISCUSSION

Points of Zero Charge

The points of zero charge (PZC) for DRSF and VSFH obtained from the plots of **Δ**pH against pH_i displayed in Fig. 2 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 positive but the surface charge becomes negative 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 strength of the solution and contact time are presented in Figs. 3, 4 and 5 respectively. As shown in Fig. 3, 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 Fig. 4 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 Fig. 5, the percent removal of methylene blue by DRSF increased gradually from 38.85 % at 20 minutes to 89.22 % at 240 minutes. Beyond 240 minutes, the removal efficiency of methylene blue by DRSF remained more or less constant. Similarly, Fig. 5 also shows that percent removal of methylene blue by VSFH increased gradually from 29.09 % at 20 minutes to 84.42 % at 240 minutes, remaining roughly constant beyond 240 minutes. In view of these findings, the kinetic experiments involving DRSF 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 hours.

Sorption Kinetics

The charts displayed in Figs. 6, 7, 8 and 9 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 R^2 = 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 $gmg^{-1}min^{-1}$ for DRSP and 2.873 $gmg^{-1}min^{-1}$ for VSFH in Table 1) are several order of magnitude higher than 0.0059 $gmg^{-1}min^{-1}$ reported for the adsorption of methylene blue on NaOH-modified dead leaves of plane trees (Gong *et al*, 2013), 0.0012 $gmg^{-1}min^{-1}$ reported for the adsorption of methylene blue on sugarcane bagasse modified with EDTA dianhydride (Gusmao *et al*, 2013) and 0.023 $gmg^{-1}min^{-1}$ 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.

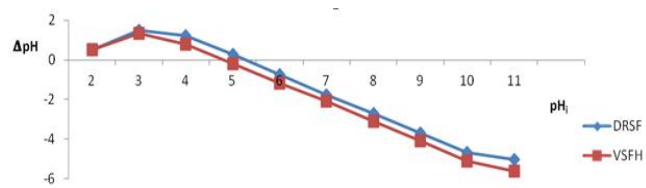

Fig. 2: Plots of **Δ**pH against pH_i showing points of zero charge of DRSF and VSFH

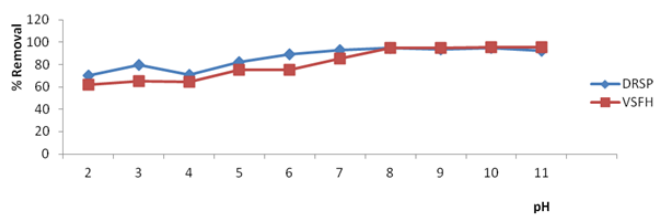

Fig. 3: Plots of removal efficiency against initial solution pH

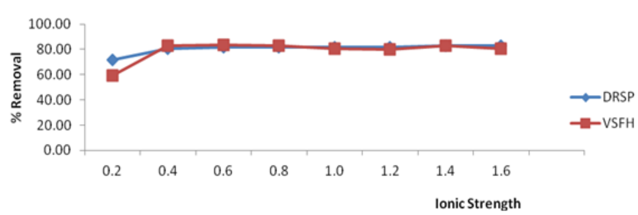

Fig. 4: Plots of removal efficiency against ionic strength

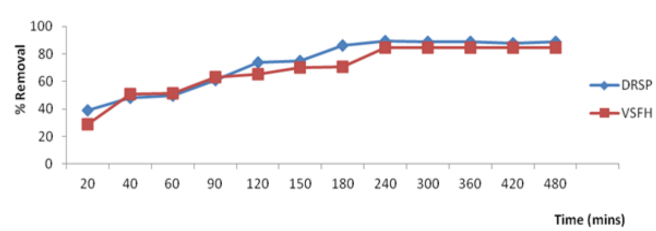

Fig. 5: Plots of removal efficiency against contact time.

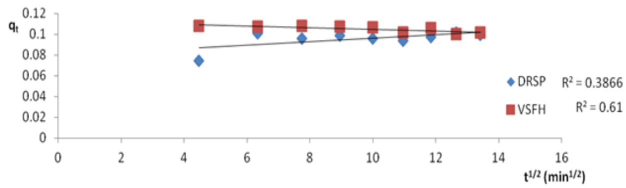

Fig. 6: Intraparticle diffusion plot for methylene blue adsorption on DRSP and VSFH

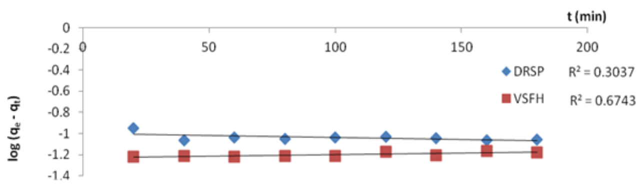

Fig 7: Pseudo-first order plot for methylene blue adsorption on DRSP and VSFH

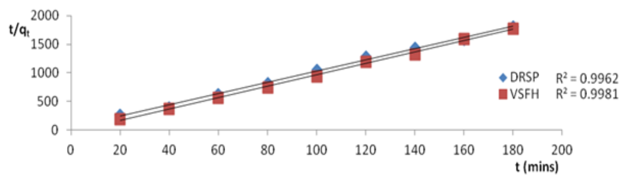

Fig. 8: Pseudo-second order plot for methylene blue adsorption on DRSP and VSFH

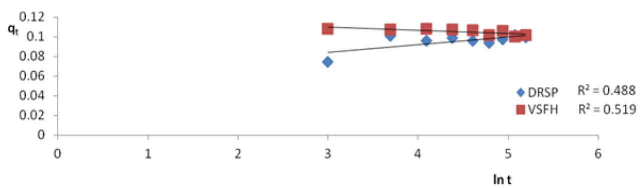

Fig. 9: Elovich plot for methylene blue adsorption on DRSP and VSFH

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	A	β
DRSP	0.386	0.001	0.303	0.000	0.996	2.155	0.488	1.45×10^{01}	125.0
VSFH	0.610	0.000	0.674	0.000	0.998	2.873	0.519	2.49×10^{-20}	-333.3

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 *Delonix regia* and the fruit hulls of *Vigna 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 indicate 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 *Delonix regia* and the fruit hulls of *Vigna subterranea* can serve as alternative low-cost adsorbents for removing methylene blue from contaminated wastewater.

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