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Aqueous Phase Adsorption of Dyes onto Activated Carbon Prepared from *Vitellaria Paradoxa* (Shea Butter) Leaves: Kinetic and Thermodynamic Studies

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ABSTRACT

The present study explains the preparation and application of *Vitellaria paradoxa* activated carbon (VPAC) as a potential low-cost adsorbent in the removal of Methylene Blue (MB) and Rhodamine B (RhB) dyes from aqueous solution, Scanning electron Microscope (SEM) showed surface morphology with depositions of adsorbed dyes in smooth regular formation on the surface. The effects of operating parameters such as contact time, adsorbent dose, pH, temperature, and particle size were investigated for the removal of MB and RhB dyes using VPAC. The adsorption process follows pseudo-second order kinetic model as the calculated and experimental values of the adsorption capacities are in close agreement, Q_{exp} = 49.092mg/g, Q_{cal} = 49.505mg/g for MB while Q_{exp} = 49.508mg/g, Q_{cal} = 49.011mg/g for RhB respectively, with R^2= 0.999 in each case. The adsorption mechanism results showed that the adsorption process was controlled by both the internal and external diffusion of the dyes. The values for free energy change (ΔG), and enthalpy change (ΔH) for MB and RhB were found to be; -2.3314 $kJmol^{-1}$ and -7.2125 $kJmol^{-1}$; and -3.4302 $kJmol^{-1}$ and -2.1340 $kJmol^{-1}$ respectively, which indicated the spontaneous, feasible, and exothermic nature of the adsorption process.

Keywords: Activated Carbon, Adsorption, Methylene Blue, Monolayer, Rhodamine B

INTRODUCTION

Dyes are complex chemical substances that bear stable aromatic rings synthesized to impart strong and persistent colour that does not degrade on exposure to light (Ibrahim and Sani 2014). Large amounts of dyes effluents are annually discharged by textile, cosmetics, paper, leather, pharmaceutical, food and other industries (Safarikova *et al.*, 2005; Mahvi 2008). A significant amount of these effluents is released into environment untreated thus causing pollution of surface water (Mahvi *et al.*, 2008; Carneiro *et al.*, 2010), ground water and even soils through irrigation (Topaç *et al.*, 2009; Zhou and Wang 2010). The Presence of low concentration (>1 ppm) of dyes are highly visible and can adversely affect the aquatic environment by preventing light penetration. Some dyes and their degradation products are found to be toxic, mutagenic and carcinogenic in nature (Keharia and Datta 2003). Thus, the removal of dyes from effluents has been given utmost importance. Synthetic dyes are resistant to natural degradation and pose numerous environmentally-oriented drawbacks when released into natural water bodies. Methylene blue (MB) and Rhodamine B (RhB) are basic dyes used extensively in dyeing of various products including cotton, silk, paper, bamboo, weed, straw and leather (Shakir *et al.*, 2010). Basic dyes are also considered as cationic dyes because they form a colored cationic salt when dissolved in water. Cationic dyes are considered more toxic than the anionic dyes, because they can easily interact with the negatively charged surface of cell membranes, and can enter into the cells. MB can cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, nausea, vomiting, and diarrhea (Senthilkumaar *et al.*, 2015). Similarly, RhB can cause skin and eye irritation with redness and pain, irritation to the respiratory tract and gastro-intestinal tract. There are several treatment processes for effluent containing dyes including biodegradation, chemical oxidation, foam flotation, electrolysis, photocatalysis, electro-coagulation, and adsorption (Mohammed, 2014).

Adsorption is one of the most efficient and attractive methods for removing pollutants from wastewater because of its easy process control, low cost and minimal energy requirements (Yang *et al.*, 2014). Various adsorbents, such as activated bituminous coal (El-Qada *et al.*, 2006), clay, leaf powder, activated carbon from oil palm wood (Ahmad *et al.*, 2007) etc. have been studied for adsorption of dyes from aqueous solutions.

Compared to *Vitellaria paradoxa* leaves (Raw and Activated carbon) may be utilized as a potentially low-cost and effective adsorbent. The production of activated carbon needs higher temperature and additional activation process. A few studies have been reported on removal of dyes on using *Vitellaria paradoxa* as adsorbent. This includes effect of cooking on moisture sorption isotherms of *Vitellaria paradoxa Gaertn*. Kernels: Evidence from light and scanning electron microscopy (Divine *et al*., 2012) and Sorption Study of Cd(II) from aqueous solution using activated carbon prepared from *Vitellaria paradoxa* shell (Jimoh *et al*., 2015).

MATERIALS AND METHODS

Materials

Vitellaria paradoxa leaves were obtained from Borgu local Government in New Bussa town, Niger state. The leaves were thoroughly washed to get rid of surface adhered particles, followed by air drying for 48h. Methylene Blue and Rhodamine were obtained from E. Merck (Mumbai, India). All reagents that were used are of analytical grade. Distilled water was used for the preparation of all solutions and adsorption experiments, 1000ppm of MB and RhB was prepared using distilled water which were kept as the stock solution and each experiment desired solution was diluted. Solutions were adjusted to desired pH using 0.1M NaOH and or HCl.

Methods

Preparation of Activated Carbon

The dried leaves were reduced to smaller particle size (<200µm) using pestle and mortar and then subsequently kept in an air tight container for further use. The *Vitellaria paradoxa* leaves (VPL) was carbonized at 200^{o}C in a muffle furnace for 15min. The carbonized sample was then crushed and sieved through a 200µm.The carbonized VPL powder (50g each) was impregnated with 50% (w/w) NaOH with the ratio of the activating agent and the precursor of 1:1. The impregnated samples were then left to dry in an oven overnight at 100^{0}C for 12 hours. The activated carbon obtained was washed severally first with 0.1M HCl solution and then with distilled water until a neutral pH is attained.

Batch Adsorption Techniques

The effect adsorbent dosages, contact time, pH of solution, temperature of solution, particles size were studied during the adsorption process.

Batch adsorption study was adopted in this study. As a general methodology, a known amount of adsorbent was added in specified volume of adsorbate solution. One of the aforementioned parameters was varied with pre-defined values while the other parameters kept constant. In each step of the study, one parameter was optimized and used in the rest of the steps. After adsorption in each step, the solution contents were filtered. After filtration, the residual concentration of MB and RhB was measured by a UV–VIS spectrophotometer (Perkin Elmer model) at pre-optimized wavelength. The adsorption capacity at any given time (q_t) and at equilibrium (qe) were calculated by using equations 1 and 2.

$$qe = \left(\frac{Co - Ce}{m}\right)V \qquad (1)$$

$$qt = \left(\frac{Co - Ct}{m}\right)V \qquad (2)$$

Where q_e = adsorption capacity (mg g^{-1}), C_o = initial concentration of adsorbate (mg L^{-1}), C_e = equilibrium concentration of adsorbate (mg L^{-1}), C_t = concentration of adsorbate at time t (mg L^{-1}), V = initial volume of adsorbate solution (L), m = mass of the adsorbent (g).

Contact Time

Equilibrium time was investigated using 100 mg/L for MB; 100 mg/L for RhB, 50mL each were measured into different Erlenmeyer flasks and marked as 1, 2, 3, and so on. A fixed amount of adsorbent (0.1g) was added to each flask and allowed to stir for varying time period of 10, 20, 30, 40, 50 and 60 mins.

Adsorbent Dosage

Adsorbate solution containing 100 mg/L for MB; 100 mg/L for RhB and 50 mL each was separately measured into different Erlenmeyer flasks and marked as 1, 2, 3, and so on. Different amounts of adsorbent (0.1g, 0.2g, 0.3g and so on) was added to the flask number 1, 2, 3, and so on, respectively. The contents of the flasks were agitated using orbital shaker for a predefined time of 60mins for MB and 80mins for RhB and at constant agitation speed (200 rpm). After the completion of time, the flask contents were filtered and subjected to analysis.

pH of Solution

The effect of pH was investigated by measuring 100 mg/L for MB; 100 mg/L for RhB and 50 mL each into different Erlenmeyer flasks marked as 1, 2, 3, and so on. The pH of the flask number 4 was adjusted to 5 using hydrochloric acid (HCl, 0.1M) and sodium hydroxide (NaOH, 0.1M). The pH of the second flask was adjusted to 6 and so on. After pH adjustment, a fixed amount of adsorbent was added and allowed to stir for a pre-defined period of time. The flask content was then filtered after completion of the time period and remnant concentration of the adsorbate was determined.

Temperature

The effect of the temperature was studied. Adsorbate solution containing 100 mg/L for MB; 100 mg/L for RhB and 50 mL each was added to different Erlenmeyer flasks and marked as 1, 2, 3, and so on. The pH of solutions was adjusted to optimum value of pH 6 and 7 for MB and RhB. To each flask, a pre-determined optimum amount of adsorbent was added and allowed to stir for an optimum period of time at different temperatures (303, 313,323 and 333 K). The flask contents were then filtered and analyzed for equilibrium phase adsorbate concentration.

Particle size

The effect of particle size of adsorbent played a significant role in determining adsorption capacity and adsorption rate, 0.1g of adsorbent was added to 50mL of adsorbate solution containing 100 mg/L in Erlenmeyer flask with T = 25^0C and 30^0C, for MB and RhB and C_o = 100 mg/g was placed on an orbital shaker at constant agitation speed of 200rpm.

Kinetic studies

To a specified 50 mL adsorbate solution, 0.1g of adsorbent was added and the system was agitated on an orbital shaker for time intervals of 10, 20, 30, 40, 50 and 60mins. The contents of each flasks was filtered and the filtrates were subjected to analysis by the appropriate technique. The data thus obtained was used to check the goodness of fit for Elovich model, pseudo-first order and pseudo-second order kinetic model. This eventually was given an idea about the mechanism of the process. Intra-particle diffusion model was also employed on the kinetic data in order to have an idea about the possible rate determining step during the process.

Thermodynamic studies

To a 50mL, fixed amount of adsorbent (0.1g) was added. The system was kept in contact on an orbital shaker for a pre-optimized period of time of 60 and 80mins at optimum pH of 6 and 7 of MB and RhB at different temperatures (30-60^{o}C). After the completion of time period the solution was filtered and analyzed for remnant concentration. The data thus obtained was used to determine the values of thermodynamic parameters including standard enthalpy change (ΔH^o), standard Gibb's free energy (ΔG^o) and standard entropy change (ΔS^o).

Scanning Electron Microscopy

Surface morphology of the adsorbents was examined by SEM. The sample was placed on brass stubs using adhesive tape on both sides. SEM micrographs were taken at various magnifications.

RESULTS AND DISCUSSION

Effect of contact time on MB and RhB onto VPAC

The effect of contact time on adsorption of MB and RhB with VPAC was studied. From the experimental data, the process of adsorption reaches the equilibrium state after 60mims in MB while 80mins in RhB. The reaction rate was fast at first 20mins in MB, which indicate that the rate of adsorption of MB was higher than RhB. Further, the adsorption proceeds at low rate and finally no significant adsorption are beyond equilibrium point. Similar finding were reported by Abdus-salam and Adekola (2018); Swarnabala and Rajesh (2017).

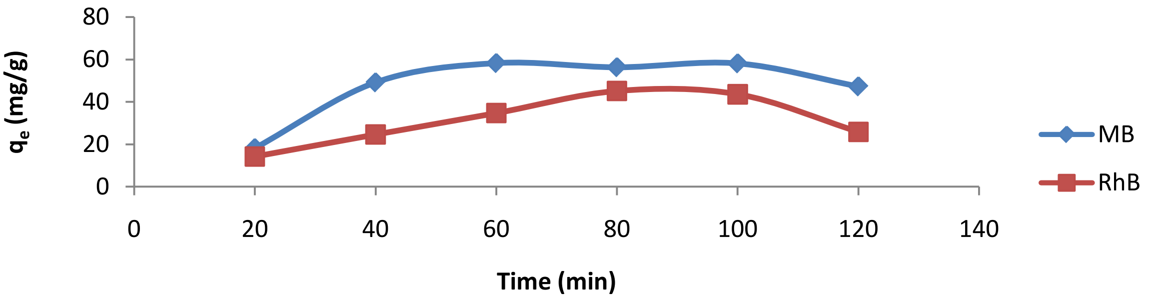


Fig. 1: Effect of contact time on adsorption of MB and RhB onto VPAC

Effect of Adsorbents Dosage on MB and RhB

The effect of adsorbents dosage of VPAC on the dyes removal was studied. The determination of VPAC dosage is important because it determines the efficiency of dyes removal and may also be used to predict the cost of VPAC per unit of solution to be treated. The adsorption capacity of dyes removal increases significantly as adsorbent dosage decreases. The graph indicates that, there was rapid removal at 0.1g with adsorption capacity of 48.10mg/g for MB and 40.87mg/g for RhB. May be due to increase in unsaturation of adsorption sites or particle interaction, such as aggregation which results as sorbent concentration increases, thereby leading to decrease in total surface area of the adsorbent (Ibrahim and Jimoh, 2008).

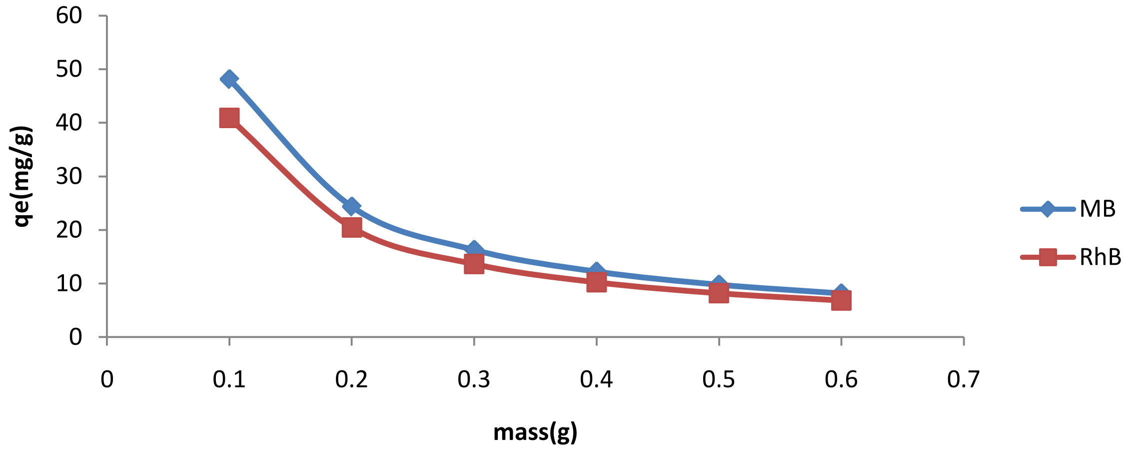


Fig. 2: Effect of adsorbent dosage on adsorption of MB and RhB onto VPAC

Effect of pH on adsorption of MB and RhB

The effects of pH on the adsorption of the dyes were investigated by varying the pH of the adsorbate solutions from 4 to 9. At pH 4 the removal was minimum, but it increased along with increasing pH of dyes solution. For MB it was maximum at pH = 6 with adsorption capacity of 49.271mg/g, while in case of RhB the adsorption was higher at pH 7 with adsorption capacity of 36.05mg/g. However, further increase in pH leads to decrease in the adsorption capacity.

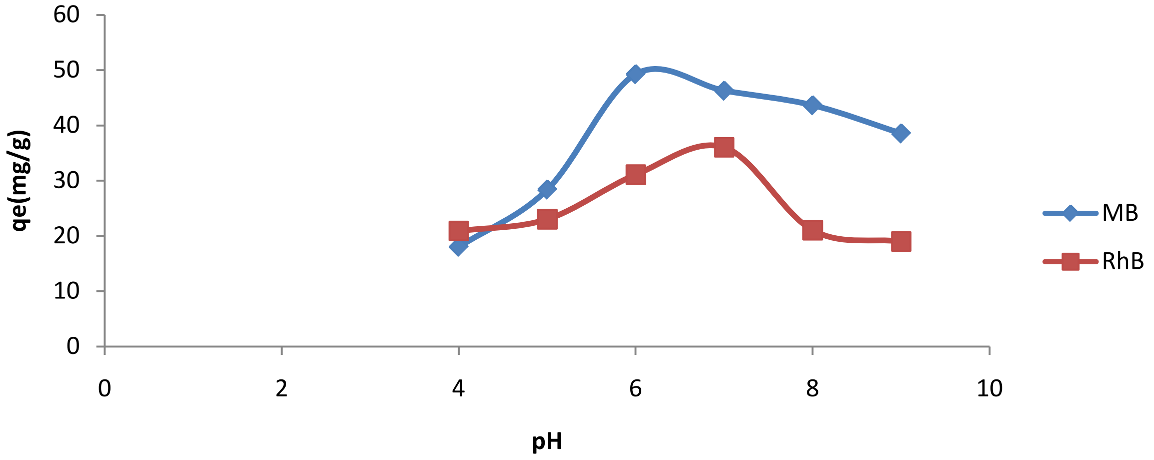


Fig. 3: Effect of pH on adsorption of MB and RhB onto VPAC

Effect of Temperature on adsorption of MB and RhB

The effect of temperature on adsorption of MB and RhB on *Vitellaria paradoxa* (Fig. 4) was investigated under temperature range of 35°C-60°C. At low temperatures, adsorption capacities of 28.44 mg/g and 10.78 mg/g were observed for MB and RhB respectively. This according to Ahmad *et al*. (2016), might be attributed to the participation of active sites with low activation energy in adsorption process. Further increase in temperature leads to increase in the adsorption capacities to maximum values of 48.77 mg/g and 40.98 mg/g at 50°C for MB and RhB respectively. Similar phenomenon was also reported by Parasanthi *et al*. (2016) for the adsorption of Crystal Violet by clay and Malachite Green by activated carbon.

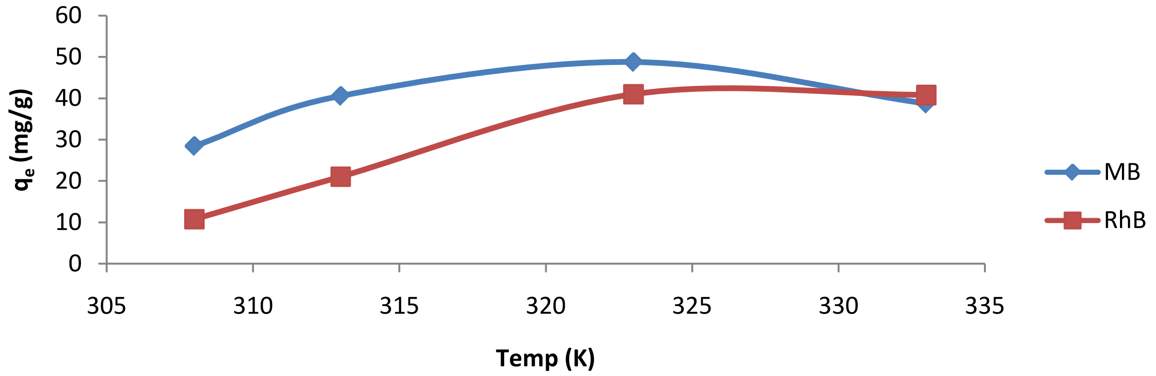


Fig. 4: Effect of Temperature on adsorption of MB and RhB onto VPAC

Effect of particle size of MB and RhB

Adsorption pattern of MB and RhB on five different particle sizes (200, 300, 450, 600, and 1000µm) of the adsorbent were as depicted in Fig. 5. It can be observed that as the particle size increases the adsorption of the dyes decreases and hence the adsorption capacity of dyes also decreases. This is due to the decrease in the available surface area. For larger particles, the diffusion resistance to mass transfer is high and most of the internal surface of the particle may not be utilized for adsorption and so the amount of dyes adsorbed is small.

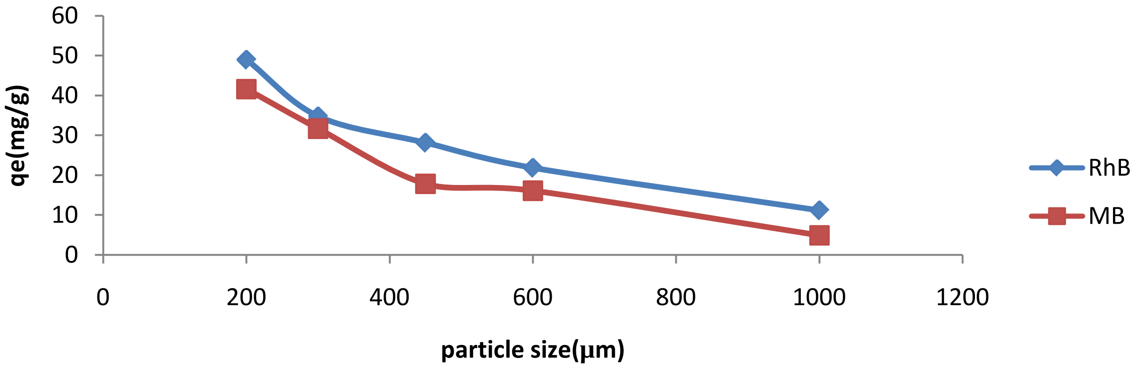
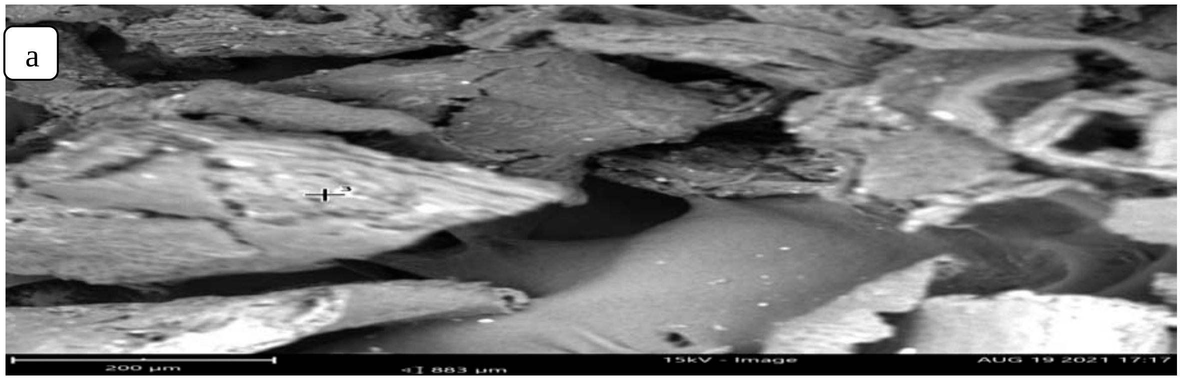


Fig. 5: Effect of particle size on adsorption of MB onto VPAC

Scanning Electron Microscopy

SEM micrographs of VPAC before and after adsorption of MB and RhB are shown in Fig. 6 (a – c). The micrograph of VPAC before adsorption (Fig. 6a) shows a moderately smooth surface which is devoid of cracks and cavities with presences of adhering particles which may be dust or salt. The micrographs of VPAC after adsorption of MB and RhB (Fig. 6: *b* and *c*) shows depositions of adsorbed dyes in smooth regular formation on the surface.

It is clear that the surfaces of VPAC moderately are smooth and contains cavities and pores which may enhance adsorption and intra particle diffusivity (Wahab *et al*., 2012). The porous structures have been filled after adsorption of the dyes MB and RhB.



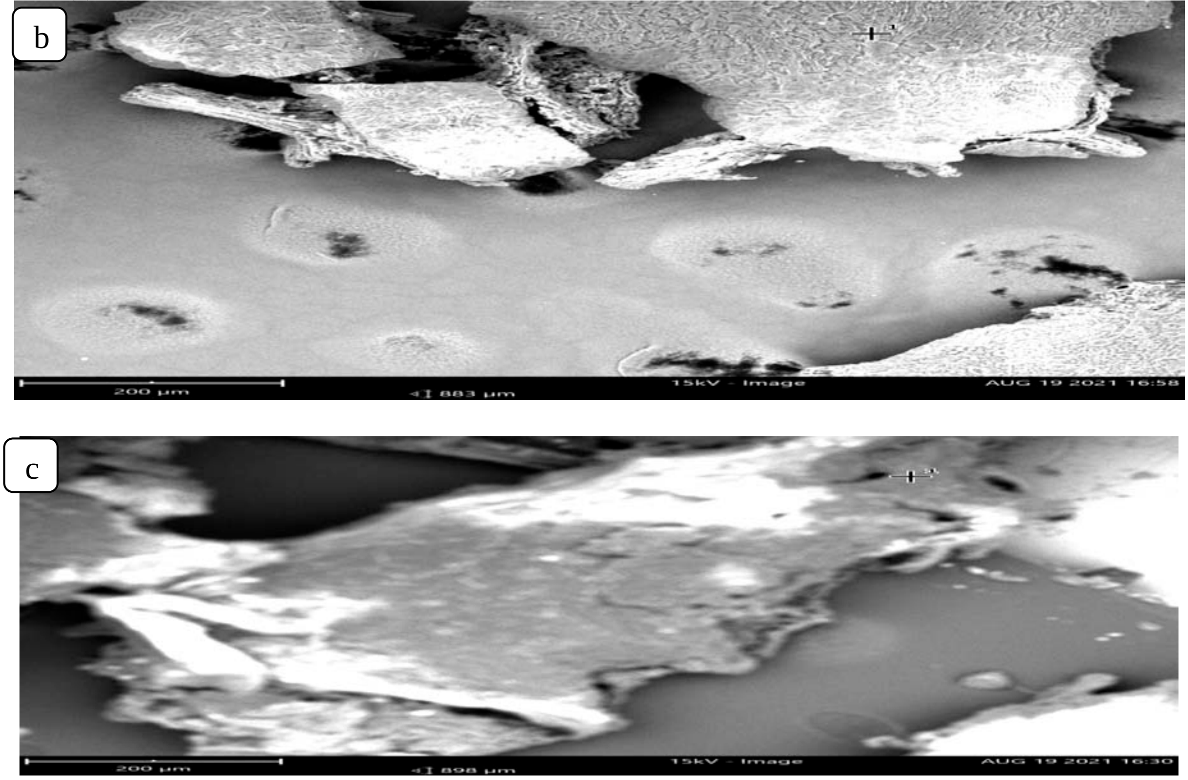


Fig. 6: SEM micrographs for VPAC (a) before adsorption, (b) after adsorption of MB and (c) after adsorption of RhB

KINETIC STUDIES

The kinetic studies of any adsorption system describe the rate of adsorbate uptake by adsorbent, and it controls the equilibrium time. The kinetic parameters are helpful in providing information about uptake rate, which gives important information for designing and modelling the adsorption processes. Pseudo-first order, pseudo-second order and Elovich models were used to determine the rate constant for adsorption of VPAC onto MB and RhB. An intra-particle diffusion model was also applied to get some hints about the mechanism of reaction.

Pseudo-first order kinetic model

The liner form of pseudo-first order kinetic model is as presented by equation 3;

$$ln(q_e - q_t) = lnq_e - k_1 t \qquad (3)$$

Where; q_e= equilibrium amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})
q_t = amount of adsorbate adsorbed per unit mass of adsorbent at time *t* (mg g^{-1})
k_1 = pseudo-first order adsorption rate constant (min^{-1})
t = time (min)

A linear plot of ln (qe–qt) against time allows one to obtain the rate constant as slope while the intercept gives equilibrium adsorption capacity. If the plot was found to be linear with good correlation coefficient, it indicates that Lagergren's equation is appropriate for the adsorbate-adsorbent system. Also, the experimental equilibrium adsorption capacity $q_{e,exp}$ and the calculated equilibrium adsorption capacity $q_{e,cal}$, must be in agreement with high values of correlation coefficient R^2.

Pseudo-second order kinetic model

Pseudo-second order kinetic model is based on the assumption that chemisorption is the rate-limiting step. Its linear form as described by Ho and McKay (1999) is represented by equation 4;

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \qquad (4)$$

Where; q_e = equilibrium amount of adsorbate adsorbed per unit mass of the adsorbent (mg g^{-1})
q_t = amount of adsorbate adsorbed per unit mass of adsorbent at time t (mg g^{-1})
k_2 = pseudo second order adsorption rate constant ($gmin^{-1}mg^{-1}$)
t = time (min)

The equilibrium adsorption capacity (qe), and the constant k_2 can be determined experimentally from the slope and intercept of plot t/qt versus t. The slope gives the equilibrium adsorption capacity q_e and the intercept k_2. If the adsorption process follows pseudo-second-order kinetics, then the experimental equilibrium adsorption capacity $q_{e,exp}$ and the calculated equilibrium adsorption capacity $q_{e,cal}$, must be in agreement with high values for the correlation coefficient R^2.

Intra-particle diffusion model

Intra particle diffusion model is based on the theory proposed by Weber and Morris (1963) who explains the mechanism of adsorption through diffusion and mathematically expressed by equation 5;

$$q_t = k_{id} t^{\frac{1}{2}} + \mathrm{C} \qquad (5)$$

Where; k_{id} = intra-particle diffusion rate constant (mg $min^{-1/2}g^{-1}$), C = constant
q_t = amount of adsorbate adsorbed per unit mass of adsorbent at time t (mg g^{-1}), t = time (min)

The intra-particle diffusion constant k_{id} can be obtained from the slope of the plot of q_t against $t^{1/2}$. If the linear plot of intra-particle diffusion model does not pass through the origin, this means that the intra-particle diffusion was not the rate-limiting step of adsorption process and indicates some degree of boundary layer control. This deviation from the origin may be due to difference in the rate of mass transfer in the initial and final stages of adsorption. The intercept C, to this linear plot is a measure of thickness of the boundary layer (mg g^{-1}). A value of C close to zero indicates that diffusion is the only rate limiting step. Moreover, the larger the intercept C, the greater is the contribution of surface sorption in rate determining step.

Elovich Isotherm

This model is based on a kinetic principle which assumes that adsorption sites increase exponentially with adsorption; this signifies a multilayer adsorption (Gubernak *et al.*, 2003). The linear form of the Elovich model is represented by equation 6 (Kumara *et al.*, 2010);

$$\mathbf{ln}qeCe = \mathbf{ln}Keqm - qeqm \ldots (6)$$

Where Ke and qm are Elovich constant and maximum adsorption capacity respectively and can be obtained from the linear plot represented by equation 6.

It can be seen in Table 1 the pseudo-first order equation did not agree with the calculated q_t from the linear plots. This shows that the adsorption of MB and RhB onto VPAC did not follow first order kinetics indicating that the adsorption was not diffusion controlled and adsorption was not preceded by diffusion through a boundary. The pseudo-second order kinetic model fits the experimental data quite well; the correlation coefficients values, R^2 all up to almost unity, and the experimental and theoretical uptakes are in good agreement. This indicates the applicability of the pseudo-second order kinetic model to describe the adsorption process of MB and RhB onto VPAC. The experimental values were 49.092 mg/g and 49.508mg/g respectively, while the calculated values were 49.505 and 49.011 mg/g. Elovich model gives useful information on the extent of both surface and activity and activation energy for physiosorption process. The obtained R^2 values of this model from Table 1 were 0.8480 mg/g and 0.7644 mg/g for MB and RhB respectively. This great deviation from linearity reflects that this model suggested by Elovich does not fit kinetic data. From Table 1, the constant C was found to increase from 46.602 in MB to 186.45 in RhB. These changes in C values belongs to increase in thickness of the boundary MB and RhB layer and decrease the chance of external mass transfer. The values of k_d obtained from the plots and given in Table 1 indicate that the intra particle diffusion model is not applicable in MB and RhB removal by VPAC. Since the plots of q_t versus $t^{1/2}$ do not pass zero and depending on the poor determination coefficients, R^2, it can be concluded that the intra particle diffusion is not rate determining step of adsorption mechanism.

Table 1: kinetics models for adsorption of MB and RhB onto VPAC

Kinetic Models	**Dyes**	**Parameters**			
		q_{eExp}(mg/g)	**q_{eCal}(mg/g)**	**$K_1(min^{-s})$**	**R^2**
Pseudo first order	MB	49.092	1.341	0.0222	0.6026
	RhB	49.508	1.335	0.0021	0.0617
		q_{eExp}(mg/g)	**q_{Cal}(mg/g)**	**$K_2(gmg^{-1}min-^{1})$**	**R^2**
Pseudo second order	MB	49.092	49.505	0.0408	0.9999
	RhB	49.508	49.011	0.0416	0.9999
				$K_d(min^{-s})$	**R^2**
Elovich	MB			0.6211	0.8480
	RhB			0.7644	0.7644
Intra particle Diffusion	MB				0.8142
	RhB				0.0039

THERMODYNAMIC STUDIES

These parameters are the actual indicator for practical application of the adsorbate adsorption process (Gardazi *et al.*, 2016).ΔG indicates the feasibility of the process, ΔH determines the exothermic and endothermic nature of the adsorption reaction and ΔS reveals the high or lower degree of disorder at solid-liquid interface during adsorption reaction. Thermodynamic parameters were determined using equations 7 – 10;

$$K_c = \frac{Co - Ce}{Ce} \quad (7)$$

$$\Delta G^o = -RTlnK_c \quad (8)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (9)$$

$$lnKc = -\frac{\Delta Ho}{RT} + \frac{\Delta S^o}{R} \quad (10)$$

Where;

ΔG° = Gibbs free energy change (kJ mol^{-1}), ΔH° = enthalpy change (J K^{-1} mol^{-1}), ΔS° = entropy change (J K^{-1} mol^{-1}), Kc = equilibrium constant, R = gas constant (8.314 J K^{-1} mol^{-1}) and T = temperature (K).

The values of ΔH° and ΔS° were calculated from the slope and intercept of lnKc versus 1/T plot.

In general, the negative values of ΔG show spontaneous feasible adsorption process and the decrease in its value by rising temperature shows the physical nature adsorption. The magnitude of ΔH describes the type of adsorption. All results obtained in this study is the normal consequence of the physical adsorption, which takes place through electrostatic interactions and is further confirmed by the free energy, ΔG that is conducted. This is in agreement with the work of Hussain (2010) on the adsorption of cadmium (Cd) onto watermelon rind under microwave radiation and Itodo (2021) on cowpea husk as a potential adsorbent for the removal of crystal violet and Congo Red dyes from aqueous solution.

Considering the correlation between van't Hoff plot and thermodynamic nature of the adsorption processes, a van't Hoff plot with positive slope indicates exothermic nature of a thermodynamic system. This was observed for MB and RhB onto VPAC in Table 2. Since for exothermic process, $\Delta H < 0$, thus the slope of the plot is greater than zero ($\Delta H > 0$). This implies decrease in equilibrium constant with an increase in temperature.

Table: 2 Thermodynamic parameters for adsorbate on adsorbents

Adsorbent	adsorbate	T(K)	Kc	ΔG(J/mol)	ΔH(J/mol)	ΔS(J/molK^{-1})
VPAC	MB	308	3.1005	-2.3314	-7.2125	5.228
		313	3.3949	-2.3575		
		323	3.9770	-2.4099		
		333	3.7759	-2.4621		
	RhB	308	4.4250	-3.4302	-2.1340	1.183
		313	4.5970	-3.4893		
		323	4.5410	-3.6076		
		333	4.4370	-3.7259		

CONCLUSION

The results obtained shows that *Vitellaria paradoxa* activated carbon can be used as a low cost adsorbent for removal of dye Methylene blue and Rhodamine B. The two dyes were found to be well adsorbed by VPAC under tested experimental conditions and the mechanism of the adsorption process was proposed to be physiosorption through electrostatic interaction between the surface of the adsorbent and functional group contained in the dyes.

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