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Original Article

Recovery of Cationic Dyes Bearing Wastewater Using Shea Butter Leaves: Kinetic Adsorption, Desorption and Reusability Studies

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ABSTRACT

The present study explains the preparation and application of *Vitellaria paradoxa* Activated Carbon (VPAC) as a new low-cost adsorbent in the removal of methylene blue and rhodamine B dye from its aqueous solution. SEM showed surface morphology, EDX disclosed elemental composition while pHpzc determines the pH at which the adsorbent surface has net electrical neutrality. The effects of operating parameters such as contact time, adsorbent dose, initial dye concentration, pH, temperature and competition were investigated for the removal of methylene blue and rhodamine B dyes using VPAC. VPAC was maximum at pH of 6 contact time of 60min and pH of 7 contact of time 80min respectively. The adsorption kinetic results showed that the pseudo-second order model was more suitable to explain the adsorption of methylene blue and rhodamine Bdye onto VPAC, because the calculated and experimental are in agreement. In VPAC, Q_{exp} = 49.092mg/g, Q_{cal} = 49.505mg/g and R^2= 0.999 for methylene blue while Q_{exp} = 49.508mg/g, Q_{cal} = 49.011mg/g and R= 0.999 for rhodamine B. The adsorption mechanism results showed that the adsorption process was controlled by both the internal and external diffusion of methylene blue and rhodamine B dye molecules. Desorption studies for reusability revealed that HCl offered the best recovery.

1. Introduction

The pollution of precious water sources with potentially harmful substances via natural and anthropogenic activities has become a global phenomenon requiring pressing scientific attention. In particular, the indiscriminate release of industrial effluent laden with synthetic dyes into water systems has become an alarming issue in recent years [1]. Synthetic dyes are extensively utilized in various application contexts, such as textiles, cosmetics, leather, pharmaceuticals, food processing, petroleum, rubber and printing [2]. Indeed, large amount of water is used in industrial operations leading to the released of contaminated water, and specifically dye-bearing wastewater. The synthetic dyes are considered unique among different water pollutants in the sense that they are noticeable to the bare eye even at low concentration [3]. Among all synthetic dyes used by the textile industry, cationic dyes are the brightest class with obvious coloration observed even at concentration as low as 1 ppm [4]. The stable structure and synthetic origin of most dyes confers high photostability and thus making their decolorization and degredation difficult [5]. The existence of these substances in aqueous systems has a major implication
On their toxicity, carcinogenicity and mutagenicity severely affect human health and the aquatic environment

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[6]. Therefore, the removal of dyes from effluents is essential to lessen their deleterious impacts on humans and the environment. To date, several treatment approaches like chemical precipitation, adsorption, memethylene blue rane filtration, evaporation, reverse osmosis, ion exchange and coagulation have been explored for remediation of wastewater [7]. Among the aforementioned techniques, adsorption has gained prominence in wastewater treatment because of it operative and economic advantages [8]. A wide range of adsorbent materials have been explored for dye removal such as activated carbon [9], nanoparticles [10], layered double hydroxides [11] and polymer composite [12]. Activated carbon is the most prominent adsorbent and has been recognized as one of the best available alternatives in the evacuation of pollutants from wastewater [13]. Due to its distinct properties, activated carbon exhibit extremely high adsorption efficiency for many adsorbates including cationic dyes. However, its large-scale application in wastewater treatment is hampered by its relatively high cost [14]. In the search for low cost adsorbents, intensive efforts have been made in the fabrication of activated carbon from renewable, low-cost and locally available resources like waste materials *Vitellaria paradoxa* Leaves are in dense clusters, spirally arranged at the end of stout twigs. They are covered by thick bark showing numerous leaf scars. Petioles 5-15cm long, leaves oblong. Juvenile leaves rust-red and pubescent, later coriaceous, glabrous and dark green, shining, 12-25 cm long and 4-7 cm wide, leaf margin wavy and bent [15]. The purposes of the present study were divided into five parts: (i) prepare activated carbon from VPL using a sodium hydroxide (NaOH) (ii) scanning electron microscopy (SEM), (iii) energy dispersive x ray (EDX) and pH at point of zero charge (pHpzc) analysis; (iv) assess its removal performance for methylene blue and rhodamine B from their respective individual and combined aqueous solutions; (v) investigate the kinetics, desorption and reusability study.

2. Materials and Methods

2.1 Materials

Methylene blue and rhodamine B dye (purity = 99%) were obtained from E. Merck (Mumbai, India). All other reagents used were of analytical grade. Distilled water was used throughout for the preparation of stock and experimental solutions. Methylene blue and rhodamine B stock solution was prepared at 1000 mg dm^{-3} using distilled water and diluted to the desired concentration for each experiment. Solutions were adjusted to desired pH using 0.1 M NaOH or HCl. *Vitellaria paradoxa* leaves were obtained from Borgu local Government in New Bussa town, Niger state.

2.2 Methods

The preparation of the NaOH activated carbon was largely guided by the method described by [16], using a two-step chemical activation technique. The carbonized VPL powder (50 g) was impregnated with 50% (w/w) NaOH to the ratio of the weight of the activating agent and the precursor is 1:1. The impregnated samples was then left to dry in an oven at 100^0C for 12 hours. The activated carbon obtained was washed severally first with 250 ml of 0.1M HCl and then with distilled water until a neutral pH is attained. It was finally dried in an oven and then stored in air tight containers for further application.

2.3 Batch Adsorption Studies

Batch adsorption study was carried out by varying all the parameters one by one keeping the rest of the parameters constant. As a general methodology, a known amount of adsorbent was added in specified volume of adsorbate solution. One of the above 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 methylene blue and rhodamine B was measured by a UV–VIS spectrophotometer (Perkin Elmer model) at pre-optimized wavelength. The extent of adsorbate adsorption was represented by adsorption capacity (q_e). The amount of dyes adsorbed at equilibrium was calculated by using the following equations:

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

The adsorption capacity at any given time (q_t) was calculated by using the following equation

$$qt\ (\frac{Co - Ct}{m}).V \quad \text{.....2}$$

Where;

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

2.3.1 Contact Time

A 50 ml of each of the dye solution were measured into a 100 ml flask and contacted with 0.1 g of the adsorbent at room temperature. The flasks were labelled for time difference of 20, 40, 60, 80 100 and 120 minutes and flasks were tightly covered and agitated for the appropriate time using incubator shaker. At the end of the timing scheduled each of the flasks were brought out and suspensions were filtered using Whatman No.1 filter paper. The un-adsorbed dye was determined with UV–VIS spectrophotometer (Perkin Elmer model) at pre-optimized wavelength. The quantity adsorbed was calculated from Eqn. 1.

2.3.2 Dosage

Adsorbate solution (100 mg/l for methylene blue; 100 mg/l for rhodamine B, 50 ml) was taken in different Erlenmeyer flasks and marked as 1, 2, 3, 4 and 5. A different amount of adsorbent (0.1g, 0.2g, 0.3g and so on) was added to flask number 1, 2, 3, 4 and 5 respectively. The contents of the

flasks were allowed to shake using orbital shaker for a predefined time and at constant agitation speed (200 rpm). After the completion of time, the flask contents were filtered and subjected to analysis.

2.3.3 pH of Solution

The pH of the solution is a crucial factor, which can influence the adsorption process. The variation in pH can affect the adsorbent surface by increasing, decreasing or neutralizing the positive or negative charges. The change in the surface negativity or positivity can, respectively, enhance or hinder the adsorption of adsorbate molecules on the surface of adsorbent [17]. Adsorbate solution ($100mgL^{-1}$ for methylene blue; $100mgL^{-1}$ for rhodamine B, 50 ml each) were taken in different Erlenmeyer flasks and marked as 1, 2, 3, 4 and 5. The pH of the flask number 4 was adjusted to 5 (as precise as possible) using hydrochloric acid (HCl, 0.1M) and sodium hydroxide (NaOH, 0.1 M). The pH of the second flask was adjusted to 6 and so on. After pH adjustment, a fixed amount of adsorbent (0.1 g) 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.

2.3.4 Initial Concentration

Effect of initial concentration was investigated by a fixed volume (50 ml) of the adsorbate solutions of varying concentration (20, 40, and 60… 120mg/l methylene blue) and (20, 40, 60… 120 mg/l rhodamine B) in different Erlenmeyer flasks. The solutions were adjusted to optimum pH value. To each flask, a fixed amount of adsorbent was added and allowed to stir for predefined optimum period of time. The solutions were then filtered and analyzed for residual concentration.

2.3.5 Temperature

The process of adsorption may be endothermic or exothermic, depending upon the temperature of the system. The adsorption reaction for any specific contaminant can be endothermic if the q_e of the adsorbent is raised with rise in temperature, and exothermic if the conditions are reversed. The quantitative effect of the temperature can vary for adsorbents [18]. Adsorbate solution (100 mg/l for methylene blue; 100 mg/l for rhodamine B, 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 pre-determined optimum value. 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 remaining adsorbate concentration.

2.3.5 Competition

Effect of competition was checked by fixed amount of volume (50 ml) of the adsorbate solutions. This was done by mixing two adsorbate in Erlenmeyer flask in the ratio of 1:1 shake thoroughly until is homogeneous. Different amounts of adsorbent (0.1g, 0.2g, 0.3 g and so on) were added to flask number 1, 2, 3, and so on, respectively. The contents of the flasks were allowed to shake using orbital shaker for 2 hours at 30^0C and at constant agitation speed (200 rpm). After the completion of time, the flask contents were filtered and subjected to analysis.

2.4 Kinetic Study

Kinetic models were used to determine the rate of the adsorption process. The kinetic data for the various adsorbate-adsorbent systems studied in the present work was analyzed in the light of four different kinetic models, namely, pseudo-first order, pseudo-second order, intra particle diffusion and Elovich. To a specified volume of adsorbate solution (50 ml), fixed amount of adsorbent (0.1 g) was added and the system was kept in contact on an orbital shaker. After a predefined time intervals (10 min), the flask contents was be filtered and filtrates was 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.

2.4.1 Pseudo-first order kinetic model

The liner form of pseudo-first order kinetic model described

$$ln(q_e - q_t) = lnq_e - k_1 t \quad \text{.....3}$$

Where; q_e= equilibrium amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})

q_t is amount of adsorbate adsorbed per unit mass of adsorbent at time t (mg g^{-1})

k_1 is pseudo-first order adsorption rate constant (min^{-1}), t is 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.

2.4.2 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 [19] is represented as:

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \quad \text{.....4}$$

Where; q_e is equilibrium amount of adsorbate adsorbed per

unit mass of the adsorbent (mg g^{-1}), q_t is 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

2.4.3 Intra-particle diffusion model

Intra particle diffusion model is based on the theory proposed [20] that explains the mechanism of adsorption through diffusion and mathematically expressed as:

$$q_t = k_{id} t^{\frac{1}{2}} + C \quad \ldots\ldots 5$$

Where; k_{id} is 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 qtvs $t^{1/2}$. 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.

Results and Discussion

3.1 Scanning Electron Microscopy

The SEM is an important technique for examining the surface texture and porosity of the adsorbent material. The SEM of VPAC before adsorption in Fig. 7a shows a moderately smooth surface which is devoid of cracks and cavities with presences of adhering particles which may be dust or salt. Hence, proper and more vigorous washing of leaf biomass is needed before application in adsorption [21]. The micrograph of VPAC after adsorption of methylene blue and rhodamine B in Fig. 7(b-c) shows depositions of adsorbed dyes in smooth regular formation on the surface

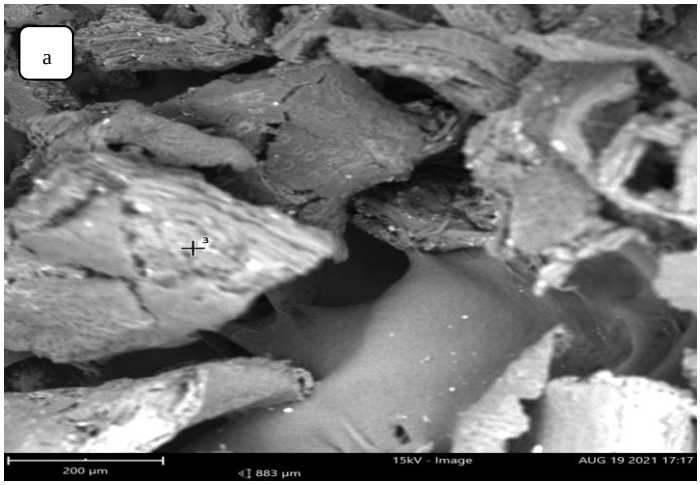

Fig. 7a SEM micrographs before adsorption

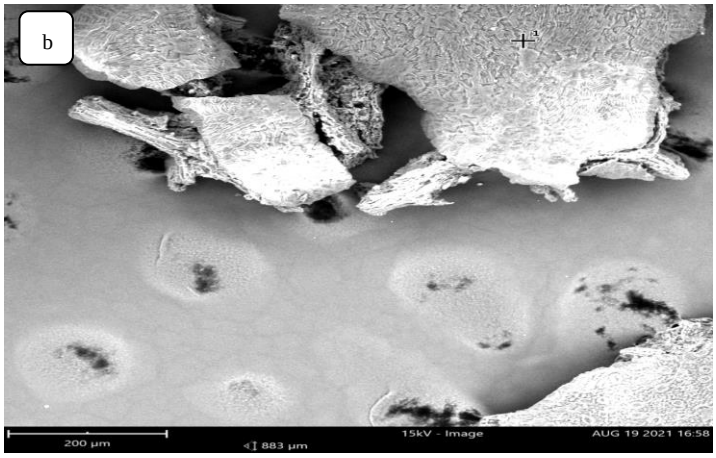

Fig. 7b SEM micrographs for VPAC after adsorption of methylene blue

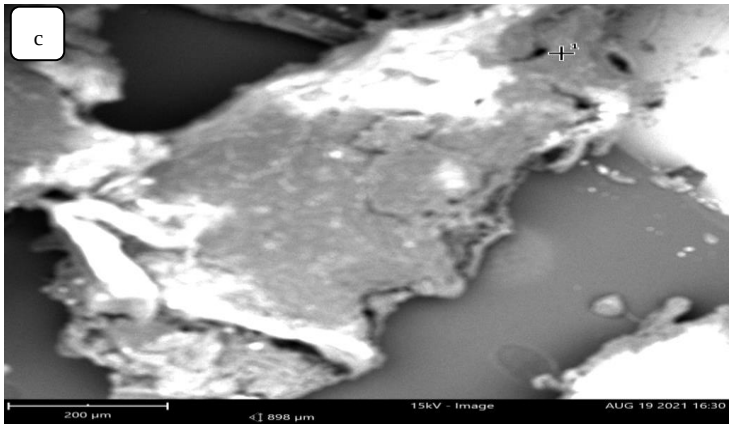

Fig. 7c SEM micrographs for VPAC after adsorption of rhodamine B

3.2 Elemental Dispersed X-Ray (EDX)

The EDX determine the composition of the small particles observed in the SEM micrographs Fig. 8(a-c), the elemental analysis was determined by EDX

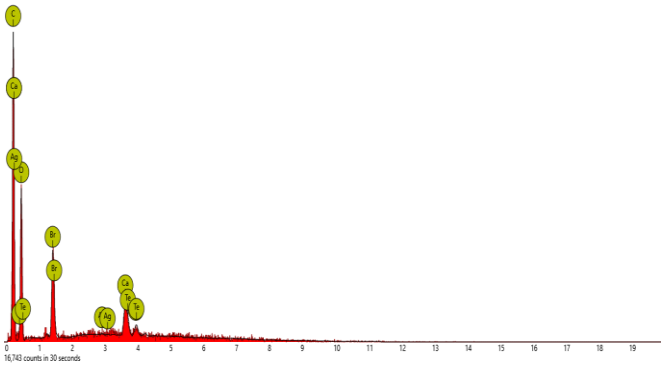

Fig. 8a EDX spectra for VPAC before adsorption

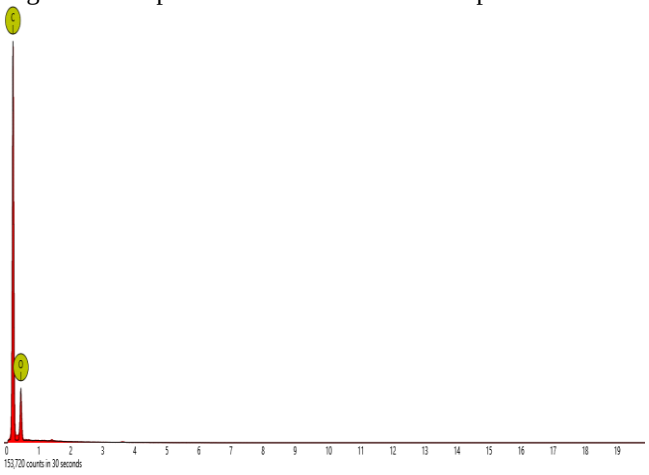

Fig. 8b EDX spectra for VPAC after adsorption of methylene blue

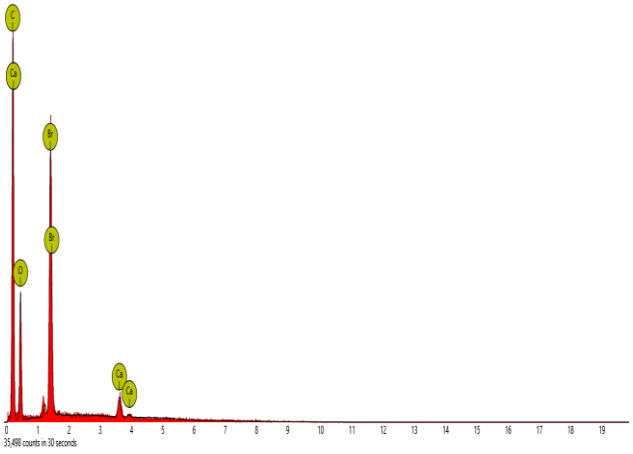

Fig. 8c EDX spectra for VPAC after adsorption of rhodamine B

3.3 pH at point of zero charge (pHpzc)

The determination of pH_{PZC} was carried out to determine the value of pH for which the surface of VPAC bears a net charge of zero. pHpzc plays vital role in surface characterization as it determines how easily an adsorbent can bind potentially harmful ions. The point of zero charge for VPAC was found to be 6.0. The result indicated that the pH_{ZPC} of VPAC depended on the raw material and the activated agency.

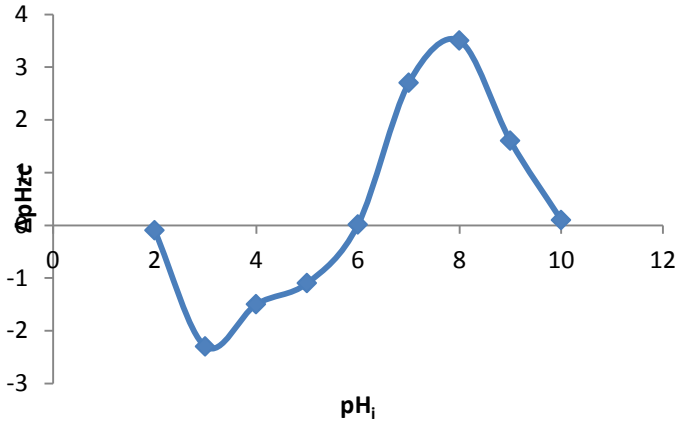

Fig. 9 at pH at point of zero charge

3.4 batch Adsorption Studies

3.4.1 The Effect of Contact Time

The effect of contact time on adsorption efficiency of methylene blue and rhodamine B onto VPAC was assessed by varying the contact from 20-120 min (20 min interval) with other parameters kept constant is given in Fig. 1, it is evident that the rate increased quickly with time, and then reached equilibrium. The contact time to reached equilibrium was 60min for methylene blue and 80min for rhodamine B. The adsorption capacity of methylene blue and rhodamine B onto the adsorbent significantly increased during the initial adsorption stage, and then the equilibrium was nearly reached. At this time, adsorption capacity reached was 49.78mg/g and 40.98mg/g for methylene blue and rhodamine B respectively. Hence, in the present work, 60min was chosen for methylene blue while 80min for rhodamine B as the equilibrium time. However, the removal of absorbate was fast initially, but gradually decreased with time until it reaches equilibrium. This can be due to the fact a large number methylene blue of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are not easy to be occupied as a result of forces between the solute molecules on the solid bulk phases. Similar finding was reported [22], [23]

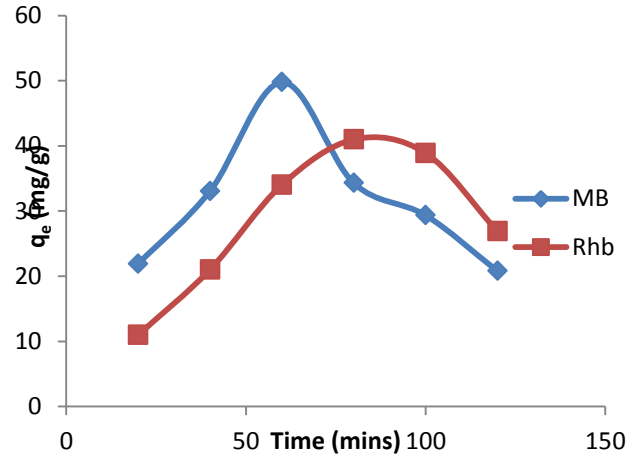

Fig. 1 Effect of contact time on adsorption of methylene blue and rhodamine B onto VPAC

3.4.2 Effect of Adsorbent Dosage.

The influence of adsorbent dose on methylene blue and rhodamine B removed at a fixed initial concentration of 0.1mg/L and pH 7 is shown in Figure 2. It was noticed that adsorption capacity of methylene blue and rhodamine B increased with an increase in adsorbent dose from 0.1 to 0.6 g/L. This was attributed to increased carbon surface and availability of more adsorption sites. From the result it is evident that optimum dosage of 0.1g/100 mL is required for appreciable removal of methylene blue and rhodamine B. Hence, this amount is employed as a dose for further studies [24].

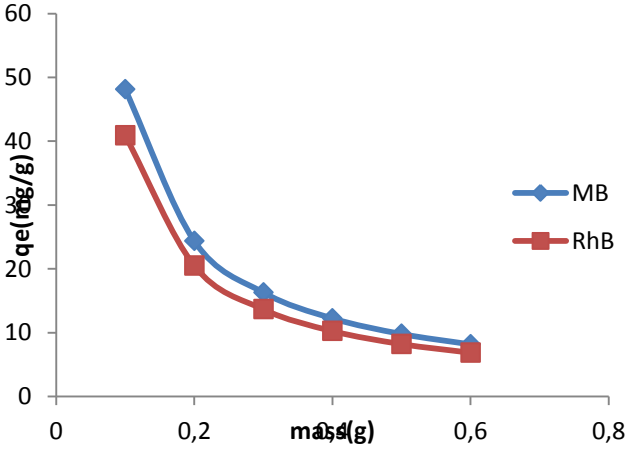

Fig. 2 Effect of dosage on adsorption of methylene blue and rhodamine B onto VPAC

3.4.3 The Effect of Initial Concentration

It was observed that at low concentration, the available driving force for movement of methylene blue and rhodamine B onto the adsorbent particles was low, while at high concentration, there was a corresponding increase in the driving force, thereby enhancing the interaction between the methylene blue and rhodamine Bin the aqueous solution phase and the active sites of adsorbents. As a result of this, there was uptake of methylene blue and rhodamine B dye molecules. At high concentration methylene blue and rhodamine B saturates the adsorbent sites quickly, thereby decreasing the overall amount of the dye removal [25]. Therefore, there was an increased in the quantity of dye adsorbed with an increase in the initial concentration. Hence, the increasing value of adsorption capacity q_e is not directly proportional to the increasing initial concentration.

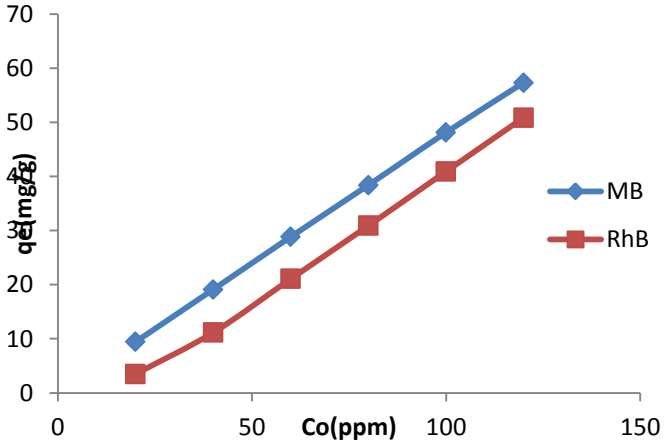

Fig. 3 Effect of initial conc. on methylene blue and rhodamine B onto VPAC

3.4.4 Effect of pH

The effects of pH on dye solution of two dyes removal were investigated by varying the pH from 4 to 9. At pH 4 the removal was minimum, but it increased along with increasing pH of dye solution. For methylene blue, it was maximum at pH = 6 with adsorption capacity of 49.271mg/g as we see in the Fig. 4.11 in case of rhodamine B the pH was greater at 7 with adsorption capacity of 36.05mg/g. Generally, adsorption found to decrease with increase in pH of solution. The adsorption of these positively charged dye groups on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH. The result showed that availability of negatively charged groups at the adsorbent surface is necessary for the adsorption of basic dyes to proceed which we see at pH 4 is almost unlikely as there is a net positive charge in the adsorption system due to the presence of H_30^+. Thus as the pH increased, more negatively charged surface was available thus facilitating greater dye removal. We see that the trend is increasing with increasing pH.

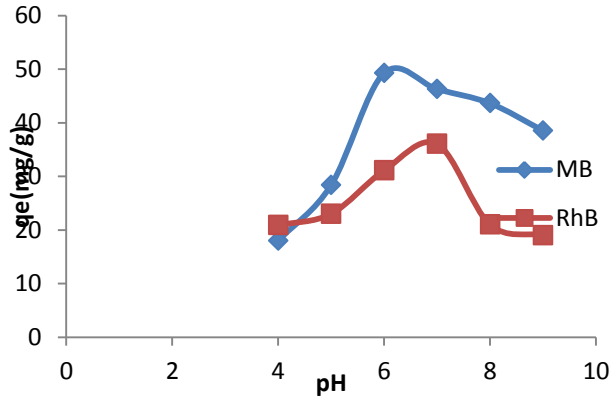

Fig.4 Effect of pH on adsorption of methylene blue and rhodamine B onto VPAC

3.4.5 Effect of Temperature

It was observed that the temperature was raised. This might probably due to variations in the activation energies of the adsorbent active sites. Hence, at low temperature, Rhodamine B (40.98mg/g) active sites with low activation energy participated in adsorption, while methylene blue with higher activation energy participated only at elevated temperature (48.77 mg/g). The higher removal due to increasing temperature may be attributed to chemical reaction taking place between the functional groups of the adsorbent and the dye [26]. Another reason for the improved adsorption at higher temperature is the increase in the kinetic energy of the sorbate molecules which enhance their collision frequency and mobility within the pores of the adsorbent [27]. Similar phenomenon was also observed for adsorption of CV by clay and MG by activated carbon [28]

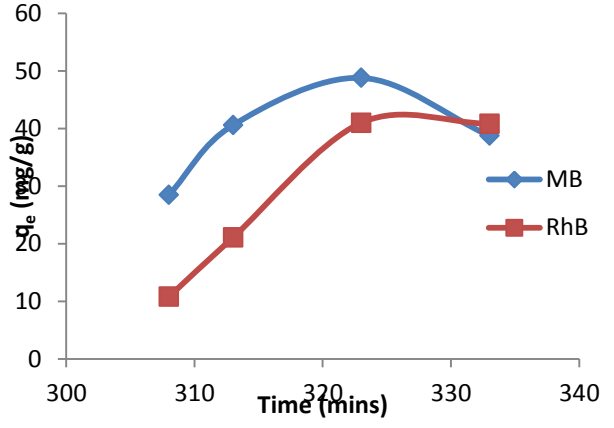

Fig.5 Effect of Temperature on adsorption of methylene blue and rhodamine B onto VPAC

3.4.6 Effect of Competition

The mixture of two basic dyes was done using activated carbon and compared with a single dye system [29]. A competitive adsorption between the two cationic dyes was observed and the result indicated the adsorption capacity of the mixture was 48.58mg/g which is high in the mixture compared to single dye with adsorption capacity of 42.65mg/g.

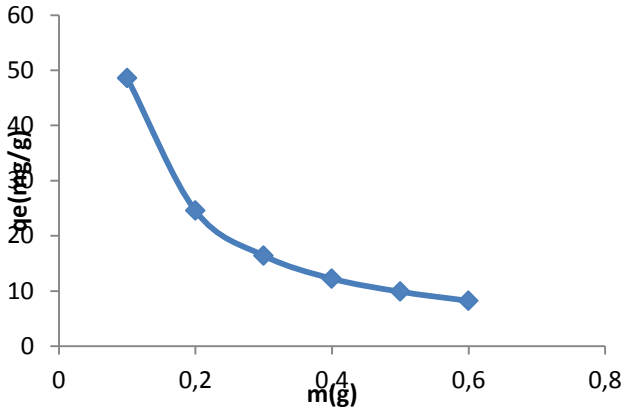

Fig.6 Effect of competing dyes on adsorption of methylene blue and rhodamine B onto VPAC

3.5 Kinetic Studies

The kinetics studies of any adsorption system describe the rate of adsorbate uptake on adsorbent, and it controls the equilibrium time. The kinetic parameters are helpful to give information about uptake rate, which gives important information for designing and modelling the adsorption processes.

The mechanism and the rate determining step of an adsorption reaction can be determined by modelling into kinetic model. The pseudo-first order, pseudo-second order and Elovich models were used to determine the rate constant for adsorption of VPAC onto methylene blue and rhodamine B. An intra-particle diffusion model was also applied to get some hints about the mechanism of reaction. 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 methylene blue and rhodamine B onto VPAC did not follow first order kinetics indicating that the adsorption was not diffusion controlled and adsorption was not proceeded 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 methylene blue and rhodamine B onto VPAC. The experimental values were 49.092mg/g and 49.508mg/g respectively, while the calculated values were 49.505 and 49.011mg/g. Elovich model gives useful information on the extent of both surface and activity and activation energy for physiosorption process with the values of R^2 obtained from this model in Table 1 as 0.8480mg/g and 0.7644mg/g for methylene blue and rhodamine B 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 methylene blue to 186.45 in rhodamine B. These changes in C values belong to increase in thickness of the boundary methylene blue and rhodamine B 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 methylene blue and rhodamine B 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.

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

kinetic models	**Dyes**	**parameter**			
		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

3.6 Desorption Studies

3.6.1 Selection of Best Desorbing agent

To investigate the possibility of regeneration of methylene blue and rhodamine B adsorbent, desorption studies was carried out using two regenerants (HCl and NaOH). Meanwhile, the results obtained indicated that HCl gave best desorption in both methylene blue (28.61%) and rhodamine B (18.56%). Similar experiment was conducted by [30].

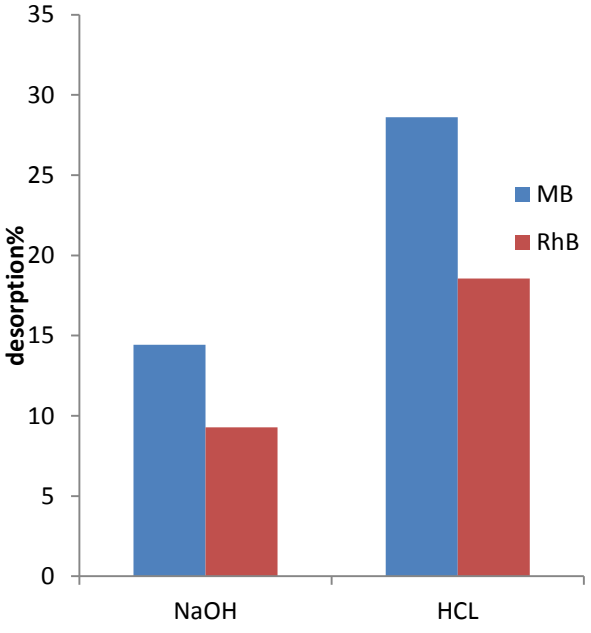

Fig.10 Selection of desorbing medium

3.6.2 Effect of Concentration on Methylene blue and Rhodamine B

The effect of concentration on desorption of Methylene blue and Rhodamine Bloaded adsorbents was investigated by varying the concentration of HCl (0.05, 0.1, 0.5 and 1). The variation in desorption percentage as a function of concentration of HCl is given in Fig. 10 was observed that desorption in both adsorbates increased with the increase in concentration of HCl. The highest desorption was obtained using 1.0M of HCl at 57.25% and 32.00% for methylene blue and rhodamine B respectively. At higher concentration, the amount of H^+ is adequate to replace the methylene blue and rhodamine B molecules from the loaded adsorbent. Similar trend was observed in the desorption of MG using concentrations of HCl [31].

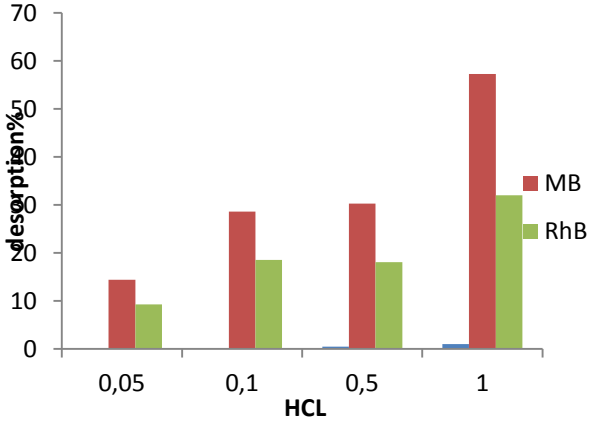

Fig.11 Effect of concentration of desorbing solution

3.6.3 Effect of Contact time on methylene blue and rhodamine B

Desorption experiments were carried out for varying time intervals and the result was presented in Fig. 12. It was observed that desorption was rapid in the first 10 min in methylene blue while fast after 20min in rhodamine B, decreased gradually and reached equilibrium after 30 min in METHYLENE BLUE , but 40min in Rhodamine B. This indicated that the desorption process was quite fast.

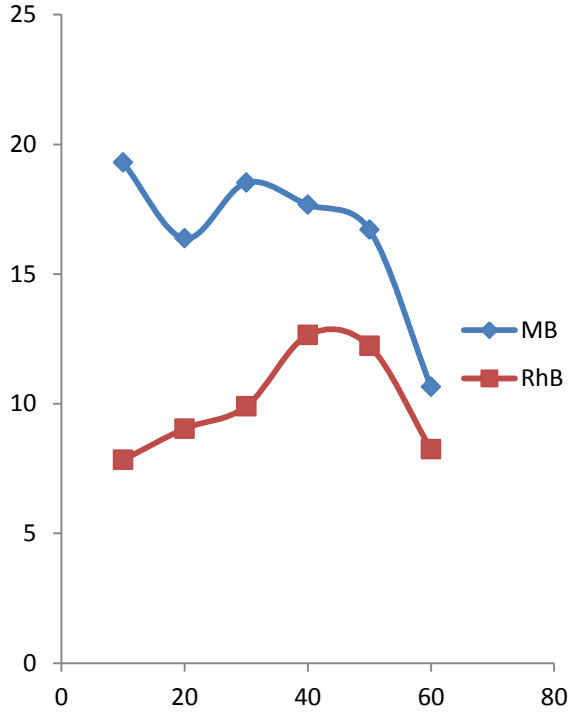

Fig.12 Effect of contact time on methylene blue and rhodamine B

Table: **2 Kinetic parameters for desorption of dyes onto VPAC**

Kinetic models	**parameters**	**Values**
Methylene blue		
Pseudo-first order	k_1	0.0144
	q_{dexp}	45.185
	q_{dcal}	1.0020
	R^2	0.646
Pseudo-second order	K_2	32.289
	q_{dexp}	45.185
	q_{dcal}	38.462
	R^2	0.9954
Intra particle	K_{id} ($mgg^{-1}min^{-1/2}$)	0.4794
	C	40.193
	R^2	0.4827
Elovich	β ($g\ mg^{-1}$)	0.0794
	R^2	
Rhodamine B		
Pseudo-first order	k_1	0.0019
	q_{dexp}	46.369
	q_{dcal}	1.446
	R^2	0.0244
Pseudo-second order	K_2	0.0222
	q_{dexp}	46.369
	q_{dcal}	45.045
	R^2	0.9994
Intra particle	K_{id} ($mgg^{-1}min^{-1/2}$)	0.3408
	C	47.281
	R^2	0.5839
Elovich	β ($g\ mg^{-1}$)	0.9138
	R^2	0.6377

3.6.4 Reusability Study

The efficiency of the regenerated adsorbent after five different adsorption/desorption cycles is presented in Fig. 13. It is seen that the adsorption/desorption efficiency decreases in the first cycle to the fifth cycle. This hinted that the adsorbent can be successively used for the removal methylene blue and rhodamine B from wastewater. The reason for the reduction in efficiency is because the active sites become fewer after every adsorption/desorption cycle.

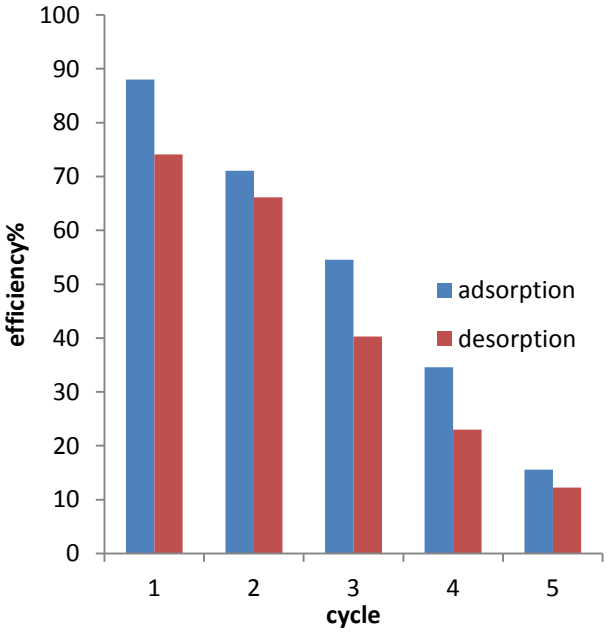

Fig.13 Efficiency of regenerated adsorbent for five cycles

Conclusion

The preparation of VPAC was achieved through two-step chemical activation technique. The dyes uptake increased

with increasing agitation time, concentration and temperature. The kinetic data obtained from this study showed good correlation coefficient for a pseudo-second order kinetic models. Desorption studies for reusability revealed that HCl offered the best recovery with 74.12% and the process follow pseudo-second-order kinetics. The conducted reusability test revealed the decline of the adsorbent performance.

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Conflict of Interest

The authors declare that they have no conflict of interest

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