



ADSORPTION AND DESORPTION STUDIES OF DYES ONTO PYROLYSED CHEMICALLY ACTIVATED SHEA BUTTER (*Vitellaria paradoxa*) LEAVES

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ABSTRACT

The present study explains the preparation and application of Vitellaria paradoxa Activated Biomass (VPAB) as a new low-cost adsorbent for the removal of Methylene Blue (MB) and Rhodamine B (RhB) dye from its aqueous solution. pH_{pzc} determines the pH at which the adsorbent surface has net electrical neutrality. The effects of operating parameters such as contact time, adsorbent dosage, pH and particle sizes were investigated for the removal of MB and RhB dyes using VPAB. The maximum adsorption of MB and RhB dye onto VPAB took place in the following experimental conditions: pH of 6, contact time of 60min and pH of 7 contact of time 80 mins. The adsorption kinetic results showed that the pseudo-second order model was more suitable to explain the adsorption of MB and RhB dye onto VPAB.

Keywords: Activated Biomass, Desorption, Methylene Blue and Rhodamine B Chloroquine

INTRODUCTION

Background

Large amounts of dye 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 (Dubey *et al.*, 2010) and even soils through irrigation (Topaç *et al.*, 2009; Zhou & Wang 2010). Presences 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 & 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 (RhB) is basic dye 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 (Ghaly *et al.*, 2014). 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 (Orfanos *et al.*, 2016). 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, RB can cause skin and eye irritation with redness and pain, irritation to the respiratory tract and gastro-intestinal tract (Shakir *et al.*, 2010). 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 (Gurses *et al.*, 2006), leaf powder (Bhattacharyya & Sharma 2005), activated carbon from oil palm wood (Ahmad *et al.*, 2007) etc. have been studied for adsorption of dye from aqueous solutions. Compared to *Vitellaria Paradoxa* leaves may be utilized as a potentially low-cost and effective adsorbent.

The production of biochar needs higher temperature and additional activation process. A few studies have been reported on removal of dyes on using *Vitellaria paradoxa* seed as adsorbent.

Batch Adsorption Studies

The effect of the following process parameters was studied during the adsorption process

Contact time, Dosage, pH of solution, Particles size

Batch adsorption study was carried out by varying all the parameters one by one keeping the rest of the parameters constant. The amount of adsorbate adsorbed at equilibrium was calculated by using the following equations:

$$q_e = \frac{(C_0 - C_e)}{m} V \dots\dots\dots 1$$

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

$$q_t = \left(\frac{C_0 - C_t}{m} \right) \cdot V \dots\dots\dots 2$$

Where;

q_e = adsorption capacity (solid phase concentration of adsorbate on the adsorbent) (mg g^{-1}), C_0 = initial concentration of adsorbate (mg L^{-1}), C_e = concentration of adsorbate at equilibrium (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)

Pseudo-first order kinetic model

The liner form of pseudo-first order kinetic model described

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

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 $\ln(q_e - q_t)$ 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 $q_{e,\text{exp}}$ and the calculated equilibrium adsorption capacity $q_{e,\text{cal}}$, 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 as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots 4$$

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 ($\text{gmin}^{-1}\text{mg}^{-1}$), t = time (min)

The equilibrium adsorption capacity (q_e), and the constant k_2 can be determined experimentally from the slope and intercept of plot t/q_t 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 $q_{e,\text{exp}}$ and the calculated equilibrium adsorption capacity $q_{e,\text{cal}}$, 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 as:

$$q_t = k_{id} t^{\frac{1}{2}} + C_i \dots\dots\dots 5$$

Where; k_{id} = intra-particle diffusion rate constant ($\text{mg min}^{-1/2}\text{g}^{-1}$), C_i = 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 vs $t^{1/2}$. 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_i to this linear plot is a measure of thickness of the boundary layer (mg g^{-1}). A value of C_i close to zero indicates that diffusion is the only rate limiting step (Ahmed and Dhedan, 2012). Moreover, the larger the intercept C_i , the greater is the contribution of surface sorption in rate determining step.

MATERIALS AND METHODS

MATERIALS

Methylene Blue (C.I. 52015) and Rhodamine B (C.I. 45170) were purchased from Sigma-Aldrich, Co., USA. *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. The dried leaves were pulverised to smaller pieces

using pestle and mortar and then kept for further use.

METHODS

The preparation of the NaOH *Vitellaria Paradoxa* Activated Biomass (VPAB) was largely guided by the method described by Wang *et al.* (2014), using a two-step chemical activation technique. The *Vitellaria paradoxa* leaves (VPL) was carbonized at 200°C in a muffle furnace for 15min. The carbonized sample was then crushed and sieved through a 200 micrometer sieve. The carbonized VPAB powder (50 g each) 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 will then be left to dry in an oven overnight at 100°C for 12 hours. The activated carbon obtained was washed severally first with 250mL 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.

The desorption efficiency of MB and RhB-loaded VPAB was evaluated in the presence of different desorbing agents; hydrochloric acid (HCl), sodium hydroxide (NaOH) and distilled water. The loaded adsorbent was washed with distilled water to remove traces of unadsorbed MB and RhB. Desorption solution (50 cm³) were added to a set of flasks containing 0.1 g of the MB and RhB-loaded adsorbent, followed by agitation at 200 rpm for 60 min. The best desorbing agent was further explored for the effect of contact time (10- 60 min) on desorption efficiency. All analytical methods are the same as above. FT-IR Characterization of the VPAB was done before and after MB and RhB adsorption, over the wave number range of 4000-650 cm⁻¹ and pH at point of zero charge was determined where by a known volume (50ml) of 0.1M NaCl was taken in different Erlenmeyer flask. pH of the solutions were adjusted to 2, 3, 4, 5, 6, 7, 8, 9 and 10 using 0.1M HCl and 0.1M NaOH. The adsorbent (0.1 g) was added to all pH ranges separately and the flasks content were allowed to stir for 6h. The final pH of the solutions was noted after filtration. A graph was plotted between the initial pHi and change in pH (Δ pH) to obtain point of zero charge.

Contact Time

Equilibrium time is the state of the adsorption process, where maximum adsorption capacity or removal of the adsorbate is attained at given conditions. Adsorbate solution (100mg/l for MB; 100mg/l for RhB, 50ml each) was taken in different Erlenmeyer flasks and marked as 1, 2, 3, and so on. A fixed amount of adsorbent was added to each flask and allowed to stir for

varying time period. For instance, the flask number 1 was removed from the top of orbital shaker after 20min; flask number 2 was removed after 40min and so on for all the flasks with 20min interval. The contents of all flasks removed after varying time of contact will be filtered and subjected to analysis.

Dosage

Adsorbate solution (100mg/l for MB; 100mg/l for RhB, 50ml each) was taken in 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) will be added to flask number 1, 2, 3, and so on, respectively. The contents of the flasks were allowed to shake using orbital shaker for a predefined time and at constant agitation speed (200 rpm).

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 (Ushakumary and Madhu, 2014). Adsorbate solution (100mgL⁻¹ for MB; 100mgL⁻¹ for RhB, 50ml each) were taken in different Erlenmeyer flasks and marked as 1, 2, 3, and so on. 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, 0.1M). 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 be filtered after completion of the time period and remnant concentration of the adsorbate was determined.

Particle size

The effect of particle size of the any adsorbent played a significant role in determining adsorption capacity and adsorption rate, 0.1g of adsorbent was added to 50ml of adsorbate in Erlenmeyer flask in conjunction with T = 30°C, C₀ = 100mg/g, at optimized value was placed on an orbital shaker at constant agitation speed of 200rpm.

Kinetic studies

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 (50ml), fixed amount of adsorbent was added and the system will be kept in contact on an orbital shaker. After a predefined time intervals (10min), the flask contents will be filtered and filtrates will be subjected to analysis by the appropriate technique. The data thus obtained will be used to check the goodness of fit for Elovich model, pseudo-first order and pseudo-second order kinetic model. This eventually will give an idea about the mechanism of the process. Intra-particle diffusion model will also be employed on the kinetic data in order to have an idea about the possible rate determining step during the process.

RESULTS AND DISCUSSION

BATCH EXPERIMENT

Effect of contact time on MB and RhB

The effect of contact time on adsorption of MB and RhB with VPAB was studied. From the experimental data, the process of adsorption reaches the equilibrium state after 60 mins in MB while 80 mins in RhB respectively. The reaction rate was fast at first 20 mins 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.

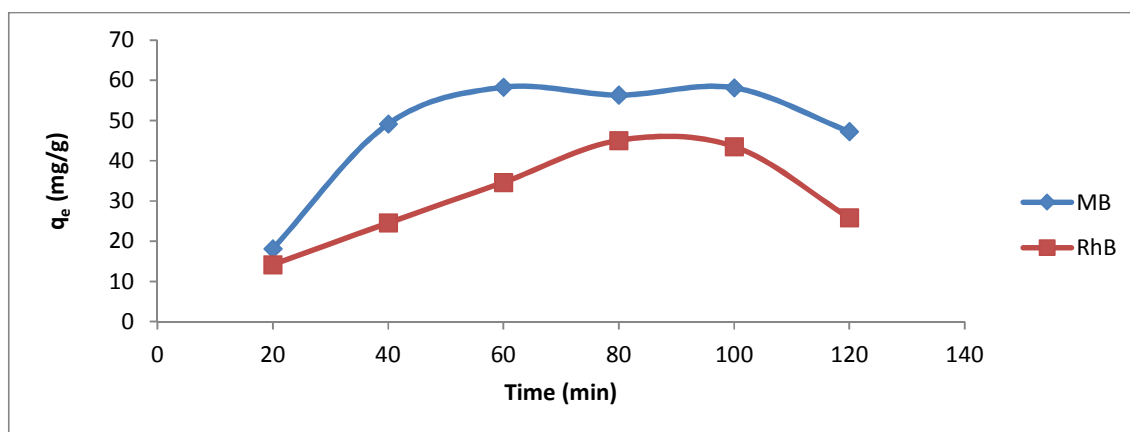


Fig 1: Effect of contact time on the Adsorption capacity of MB and RhB onto VPAB

Effect of Adsorbents Dosage on MB and RhB

The effect of Adsorbents Dosage of VPAB on the dye removal was studied. The determination of VPAB dosage is important because it determines the efficiency of dye removal and may also be used to predict the cost of VPAB per unit of

solution to be treated. As expected, the efficiency of dye removal increases significantly as adsorbent dosage decreases. The graph indicates that, there was rapid removal at 0.1 g with efficiency capacity of 48.10mg/g for MB and 40.87 mg/g for RhB. Similarly trend reported by (Abdul Salam and Adekola2018).

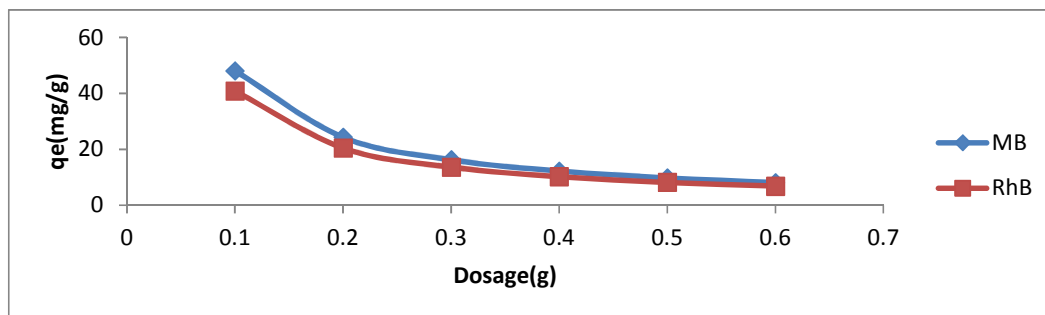


Fig 2: Effect of adsorbent dosage on the Adsorption capacity of MB and RhB onto VPAB

Effect of pH on adsorption of MB and RhB

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 MB it was maximum at pH = 6 with

adsorption capacity of 49.271 mg/g in case of RhB the pH was greater at 7 with adsorption capacity of 36.05 mg/g. Generally adsorption found to decrease with increase in pH of solution.

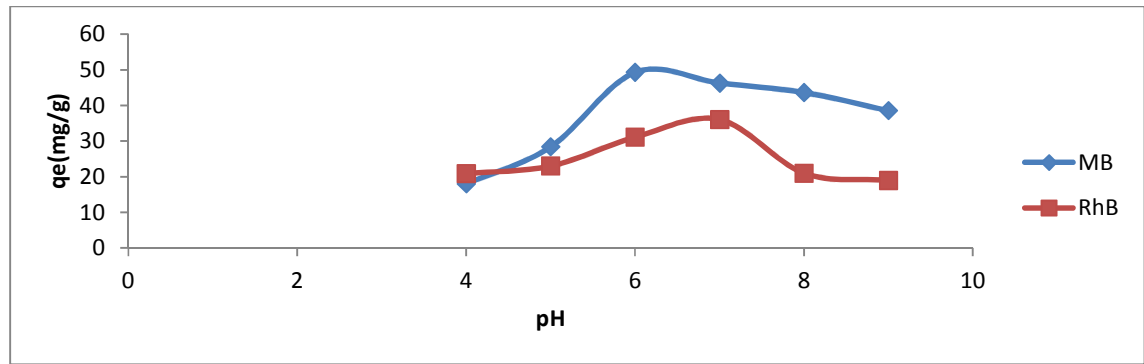


Fig 3: Effect of pH on the Adsorption capacity of MB and RhB onto VPAB

Effect of particle size of MB and RhB

Adsorption of MB and RhB on five different sized particles (200, 300, 450, 600, and 1000 μ m) was studied. The results of variation of these particle sizes on dye adsorption are shown in fig. 4. It can be observed that as the particle size increases the adsorption of the dye decreases

and hence the adsorption capacity of dye 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 internal surface of the particle may not be utilized for adsorption and so the amount of dye adsorbed is small.

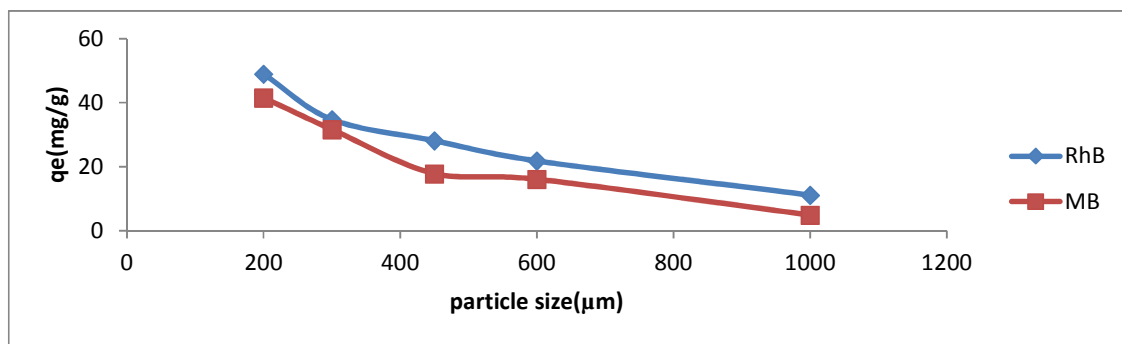


Fig. 4: Effect of particle size on the Adsorption capacity of MB onto VPAB

pH point at zero charge (pHpzc)

The determination of pH_{PZC} was carried out to determine the value of pH for which the surface of VPAB bears a net charge of zero. pH_{pzc} plays vital role in surface characterization as it

determines how easily an adsorbent can bind potentially harmful ions. The point of zero charge for VPAB was found to be 6.0. The result indicated that the pH_{ZPC} of VPAB depended on the raw material and the activated agency.

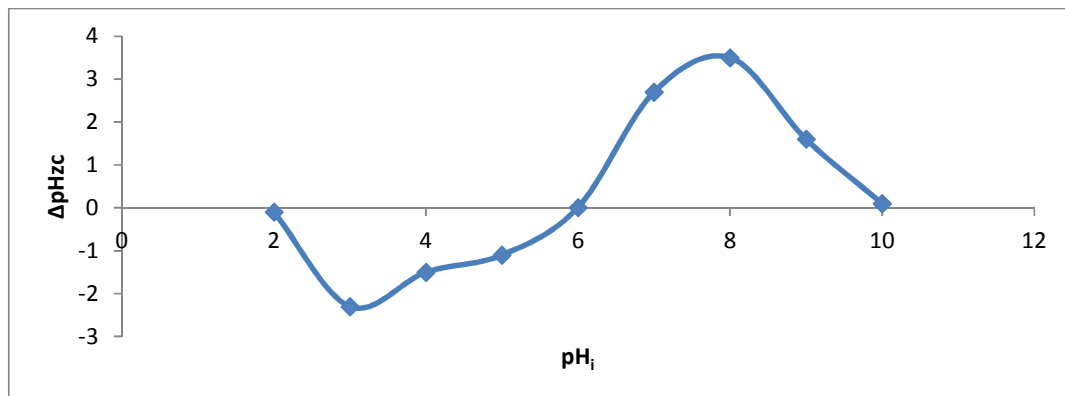


Fig 5: pH at point of zero charge

Adsorption Kinetics

The kinetics studies of any adsorption system describe the rate of adsorbate uptake on adsorbent, and it controls the equilibrium time. The mechanism and the rate determining step of an adsorption reaction can be determined by modeling into kinetic model. The pseudo-first order, pseudo-second order and Elovich models were used to determine the rate constant for adsorption of MB and RhB onto VPAB. An intra-particle diffusion model was also applied to get some hints about the mechanism of reaction. As can be seen in Table 2 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 VPAB 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 MB and RhB onto VPAB. The experimental values were 49.092 mg/g and 49.508 mg/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 2 were 0.8480mg/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 2, 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 2 indicate that the intra particle diffusion model is not applicable in MB and RhB removal by VPAB. 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 2: kinetics models for adsorption of MB and RhB onto VPAB

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

Desorption kinetics

Selection of Best Desorbing agent

To investigate the possibility of regeneration of MB and RhB adsorbent, desorption studies was carried out using two regenerants (HCl and

NaOH). Meanwhile, the results obtained indicated that HCl gave best desorption in both MB (28.61%) and RhB (18.56%). Similar experiment was conducted by (Neupane *et al.*, 2014).

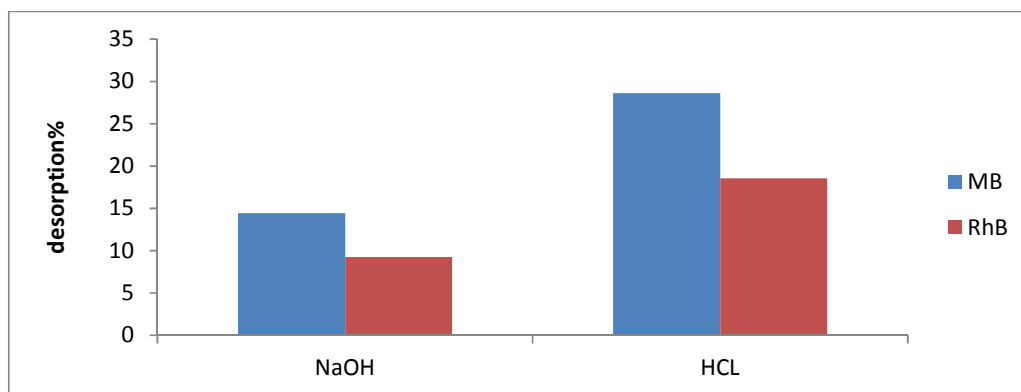


Fig 7: Selection of desorbing medium

Effect of Contact Time on MB

Desorption experiments were carried out for varying time intervals and the result was presented in Fig. 8. It was observed that desorption was rapid in the first 10 min in MB

while fast after 20min in RhB, decreased gradually and reached equilibrium after 30 min in MB, but 40min in RhB. This indicated that the desorption is quite fast.

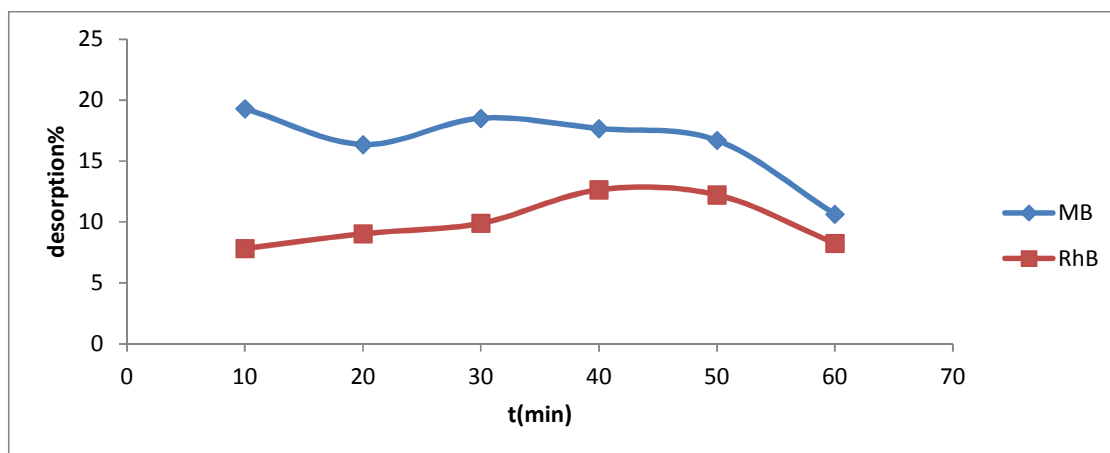


Fig. 8: Effect of contact Time on the Desorption of MB and RhB From Spent Biosorbent

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