



Kinetics Removal of Cationic Dyes in Aqueous Solution using Agricultural Waste

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Abstract: The low availability of water resources and the difficulty of access to drinking water are of increasing concern. To face this problem, it is important to improve the quality and quantity of this resource by fighting mainly against its pollution. Thus, it has become necessary to treat the wastewater of industries. In this work we studied the adsorption of Rhodamine B and Methylene blue onto the *vitellaria paradoxa* leaves with the aim of valorizing the natural biomass. To understand the adsorption process of raw *vitellaria paradoxa* (RVP) powder various studies were performed. Most characterizations of adsorbent like scanning electronic microscopy (SEM). The effects of parts of adsorbent, contact time, adsorbent dose and pH of solution on the batch adsorption of Rhodamine B Methylene blue on raw *vitellaria paradoxa* were studied. The maximum adsorption of MB and RhB dye onto RVP took place in the following experimental conditions: pH of 6.0 contact time of 60min and pH of 8.0, contact time of 100mins. The adsorption kinetic results showed that the pseudo-second order model was more suitable to explain the adsorption of MB and RhB dye onto RVP, because the calculated and experimental are in agreement where $Q_{exp} = 49.511\text{mg/g}$, $Q_{cal} = 48.544\text{mg/g}$ and $R = 0.999$ for MB while $Q_{exp} = 41.385\text{mg/g}$, $Q_{cal} = 41.494\text{mg/g}$ and $R = 0.999$ for RhB. The adsorption mechanism results showed that the adsorption process was controlled by both the internal and external diffusion of MB and RhB dye molecules

1. Introduction

With the rapid development of human society, harmful dyes are becoming the primary source of water pollution and represent a significant environmental concern (Smith *et al.*, 2016). Dyes are an essential source of water pollution. They are used in many areas such as textile, tannery, paper pulp, cosmetics, plastics, leather, printing, rubber, food, and pharmaceutical industries (Zhou *et al.*, 2019; González *et al.*, 2015; Barford *et al.*, 2009; Mittal *et al.*, 2009; El Messaoudi, *et al.*, 2016). These dyes are allergic substances, carcinogenic, and toxic for the health of humans and animals, and aquatic life, and the environment (El Messaoudi *et al.*, 2021; Afroze *et al.*, 2016; Azzaz *et al.*, 2016; Pandian *et al.*,

2017; Bentahar *et al.*, 2018; Valarmathi *et al.*, 2013). Methylene blue and Rhodamine B are cationic dyes; they are water-soluble dye with high chromaticity, extensively used in chemical indicators, dyes, biological stains, and drugs (Salem *et al.*, 2015; Sarıcı and Özdemir, 2019; Adeogun, 2020; El Messaoudi *et al.*, 2021; Aadouz *et al.*, 2023). It is pretty visible and stable in water at room temperature (Russo *et al.*, 2016). Adsorption is the most effective method used to remove dyes from aqueous solution compared to other techniques (coagulation, photocatalysis, flocculation, hydrogenperoxide, adsorption, oxidation, irradiation, ion exchange, reverse osmosis, advanced oxidation, membrane filtration, precipitation) due to their ease of operation, high efficiency, low-energy requiring technology, availability of different adsorbents, effectiveness in regeneration and reuse of the adsorbent (Ali *et al.*, 2012; El Messaoudi *et al.*, 2016; Akpomie and Conradie, 2020; Bentahar *et al.*, 2017; Chandane, and Singh, 2016; El Messaoudi *et al.*, 2021). In this context, many researchers developed low-cost materials such as agricultural solid wastes to minimize the pollution of wastewaters. Agricultural solid wastes contain main components : cellulose, lignin, hemicelluloses, lipids, proteins, etc. (Ashrafi *et al.*, 2016; Dbik, *et al.*, 2020). Besides are available and abundant in large quantities and have high potential sorbents due to the variety of functional groups ($-OH$, $-C=O$, $-C-O$, $-NH_2$) on their surfaces (Ghorbani *et al.*, 2020; El Messaoudi *et al.*, 2021). As a result, agricultural solid wastes can be used as an economical and eco-friendly adsorbent since they are abundant and renewable sources (Abbas and Ahmed 2016). Many agricultural solid wastes are used for the removal of dyes from an aqueous solution, such as date stones (*Phoenix dactylifera*) (Messaoudi *et al.*, 2017), jujube shells (*Ziziphus lotus*) (Messaoudi *et al.*, 2017), shell Argan nuts (Khomri *et al.*, 2020), *Clitoria fairchildiana* (Silva *et al.*, 2020), Olive pomace (salahat *et al.*, 2023; Rizzi *et al.*, 2017), Leaves of *Platanus* (Kong *et al.*, 2020), Walnut shell (Uddin and Nasar, 2020) Jojoba residues (Al-Zoubi *et al.*, 2020), *Calotropis procera* (Kaur and Kaur, 2017), Mandarin Peel (Unugul and Nigiz, 2020), Banana peel (Mondal and Kar, 2018) *Eragrostis plana* Nees (Filho *et al.*, 2017), and waste of citrus sinesis (Asgher and Bhatti, 2012). The *vitellaria paradoxa* leaves are agricultural solid waste abundant and available in Nigeria. The Leaves are in dense clusters, spirally arranged at the end of stout twigs, 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 (Orwa *et al.*, 2009) reference and selection guide version, the *vitellaria paradoxa* leaves was used to remove methylene blue and Rhodamine B from an aqueous solution. The prepared adsorbent was characterized by scanning electron microscope (SEM). Furthermore, the fundamental parameters affecting the dye adsorption, such as contact time, adsorbent dose, initial dye concentration and pH of solution were optimized.

2. Methodology

2.1 Sourcing of *Vitellaria paradoxa* leaves

Vitellaria paradoxa leaves were obtained from Borgu local Government in New Bussa town, Niger state. The cationic dyes, methylene blue ($C_{16}H_{18}ClN_3S$) and Rhodamine B ($C_{28}H_{31}ClN_2O_3$) used in this study were purchased from Sigma Aldrich. All reagents that were used are of analytical grade.

2.1.1 Preparation of Raw Sample

Vitellaria paradoxa leaves were prepared from agricultural wastes that had collected from agricultural fields. It was leached with double distilled water to eliminate dust contaminations. Afterward, it was dried in an open air for 48 h. The dried leaves were crushed into smaller pieces with the help of pestle and mortar to produce powder form. The resulting leaves media were then sieved by passing it through

standard sieves with mesh size of 200 μm . The leaves powder was kept in air tight plastic stacks for future use (Oznur *et al.*, 2013). Distilled water was used for the preparation of all solutions and adsorption experiments, 1000 ppm 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.

2.2 Batch Experiments

Batch experiments were 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 (0.1g) was added in specified volume of adsorbate solution. One of the 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 extent of adsorbate adsorption was represented by adsorption capacity (q_e). The amount of adsorbate adsorbed at equilibrium was calculated by using the following equations:

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

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}), V = initial volume of adsorbate solution (L), m = mass of the adsorbent (g)

2.2.1 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 (100 mg/l for MB; 100 mg/l for RhB, 50 ml 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 40 min and so on for all the flasks with 20 min interval. The contents of all flasks removed after varying time of contact was filtered and subjected to analysis.

2.2.2 Adsorbent Dose

Adsorbate solution (100 mg/l for MB; 100 mg/l for RhB, 50 ml each) was taken in different Erlenmeyer flasks and marked as 1, 2, 3, and so on. A different amount of adsorbent (0.1 g, 0.2 g, 0.3 g and so on) was 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). After the completion of time, the flask contents were filtered and subjected to analysis.

2.2.3 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 (Ushakumary and Madhu, 2014). Adsorbate solution (100 mgL⁻¹ for MB; 100 mgL⁻¹ for RhB, 50 ml 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, 0.1 M) 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 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.

2.2.4 Kinetic studies

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 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.

Pseudo-first order kinetic model

The liner form of pseudo-first order kinetic model described

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots\dots\dots 2$$

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 $q_{e,exp}$ and the calculated equilibrium adsorption capacity $q_{e,cal}$, must be in agreement with high values of correlation coefficient R².

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)

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \dots\dots\dots 3$$

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)

explains the mechanism of adsorption through diffusion and mathematically expressed as:

$$q_t = k_{id}t^{\frac{1}{2}} + C \dots\dots\dots 4$$

Where;

k_{id} = intra-particle diffusion rate constant ($\text{mg min}^{-1/2}\text{g}^{-1}$), 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 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 , 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.

2.2.5 Characterization of Selected Adsorbents

After screening, the selected adsorbents were subjected to characterization using analytical tools as given below:

Scanning Electron Microscopy

Similarly, surface morphology of the selected adsorbents was studied by SEM. The sample was placed on brass stubs using adhesive tape on both sides. SEM micrographs were taken at various magnifications.

3.0 Results and Discussion

3.1 Batch Experiments

3.1.1 Effect of contact time on MB and RhB

The effect of contact time on adsorption of MB and RhB with RVP was studied at 100 mg/l concentration at 0.1g of adsorbent and at 30°C respectively. When the system reaches adsorption equilibrium; no further net adsorption occurs and the rates of adsorption and desorption was equal. The time at which adsorption equilibrium occurs was determined from the plot of dyes uptake versus contact time (min). From the experimental data, the process of adsorption reaches the equilibrium state after 60 min in MB while 100 min in RhB respectively. The reaction rate was fast at first 40min of MB and 80 min of RhB, which indicate that the rate of adsorption of MB was also double than RhB. Further, the adsorption proceeds at low rate and finally no significant adsorption are beyond 100 min for both dyes. In industry, this contact time is very important for process optimization. The fast sorption of MB and RhB at the beginning can be attributed to the availability of a large number of vacant sites on the adsorbent surface, which was filled up by MB and RhB molecules.

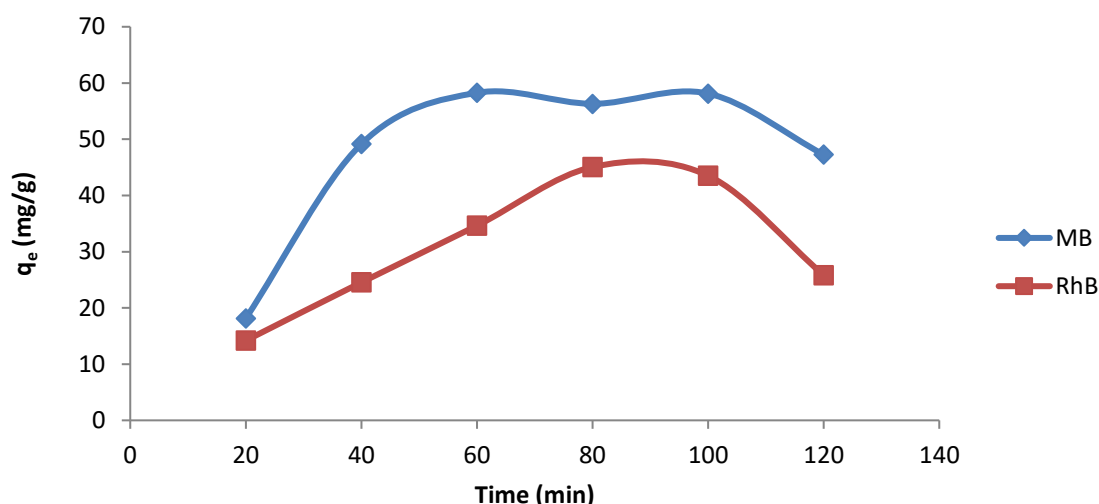


Fig. 1 Effect of contact time on Adsorption of MB and RhB onto RVP

3.1.2 Effect of Dosage on MB and RhB

The effect of the quantity of RVP used on the adsorption of MB and RhB dyes were studied, in which the amount of adsorbent was varied from 0.1 to 0.6 g while the dyes concentration was fixed at 100 mg/l. The net quantity of adsorbate removed increased with increasing mass of RVP which is attributed to an increase in the sportive surface area and the availability of more active binding site. The net equilibrium amount adsorbed however is an expression of the efficiency of an adsorbent which may not show increase in the amount adsorbed per unit mass as adsorbate dose increases (Nasuha *et al.*, 2010). The amount of MB and RhB dyes adsorbed per unit mass of RVP decreased as the RVP dosage was increased from 0.1 to 0.6 g, this may be due to the inaccessibility of active sites and partly to overlapping or aggregation of adsorption sites as the adsorbate dose increases (Akar *et al.*, 2008). Thus, with increasing adsorbent mass, the amount of dye adsorbed on the unit mass of adsorbent gets reduced, thus causing a decrease in adsorption capacity (q_e) value with increasing adsorbent mass concentration.

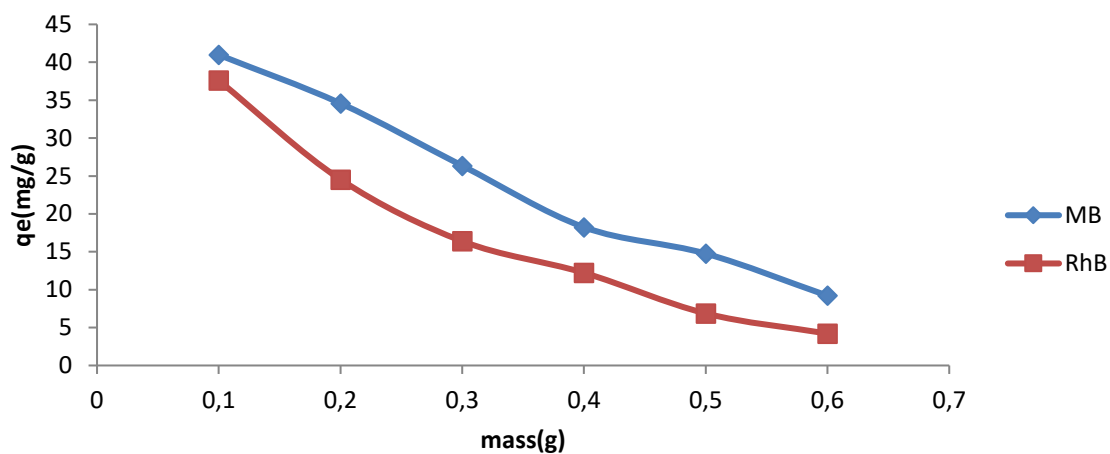


Fig. 2 Effect of dosage on Adsorption of MB and RhB onto RVP

3.1.3 Effect of pH on MB and RhB

The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. pH of solution not only affecting the surface charge of adsorbent, the degree of ionization of the dyes present in the solution and dissociation of functional group on the active sites of the adsorbent. The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. It is commonly known fact that the anionic dyes are favorably adsorbed by the adsorbent at lower pH values due to the presence of H^+ . At high pH values, cationic dyes are adsorbed due to negatively charged surface sites of RVP. In the present adsorption capacity system, the adsorption capacity of MB and RhB are 6 and 8 respectively with maximum adsorption capacity of 49.45 mg/g and 49.09 mg/g as shown in Fig. 3 this is agreement on the work of adsorption dyes by (Gupta *et al.*, 2010).

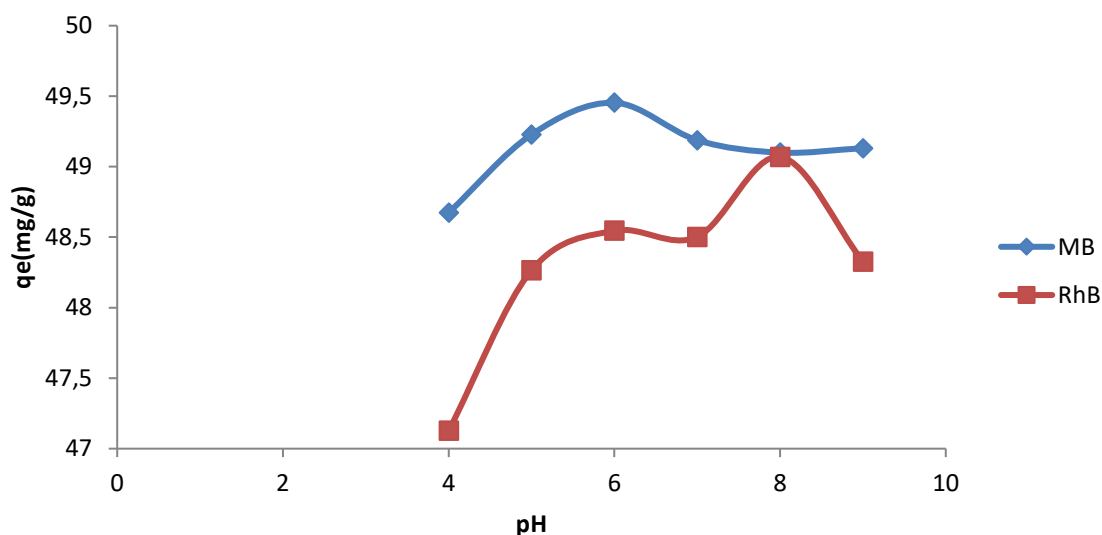


Fig.3. Effect of pH on Adsorption of MB and RhB onto RVP

3.1.4 Kinetic Studies

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 RVP onto MB and RhB. 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 MB and RhB onto RVP 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 RVP. The experimental values were 49.511 mg/g and 41.358 mg/g respectively, while the calculated values were 48.544 and 41.494 mg/g. Elovich model gives useful information on the extent of both surface and activity and activation energy for physisorption process. The obtained R^2 values of this model from Table 1 were 0.2149 mg/g and 0.1418mg/g for MB and RhB respectively. This great deviation from linearity reflects that this model suggested by Elovich does not fit kinetic data. 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 RVP. 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: Kinetic models for adsorption of MB and RhB onto RVP

Kinetic models	Dyes	parameters			
		$q_{eExp}(mg/g)$	$q_{eCal}(mg/g)$	$K_1(\text{min}^{-s})$	R^2
Pseudo first order	MB	49.511	0.411	0.0068	0.4739
	RhB	41.385	0.380	0.0011	0.0121
Pseudo second order		$q_{eExp}(mg/g)$	$q_{eCal}(mg/g)$	$K_2(\text{gmg}^{-1}\text{min}^{-1})$	R^2
	MB	49.511	48.544	0.133	0.9997
	RhB	41.385	41.494	0.0581	0.9998
Elovich		A	B	$K_d(\text{min}^{-s})$	R^2
	MB			0.6181	0.2149
	RhB			0.0906	0.1418
Intra particle Diffusion		A	B		R^2
	MB				0.159
	RhB				0.1324

3.1.5 Scanning Electron Microscopy

The SEM of RVP before adsorption in Fig. 4a 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. The micrograph of RVP after adsorption of MB and RhB in Fig. 4(b) and (4c) shows depositions of adsorbed dyes in smooth regular formation on the surface.

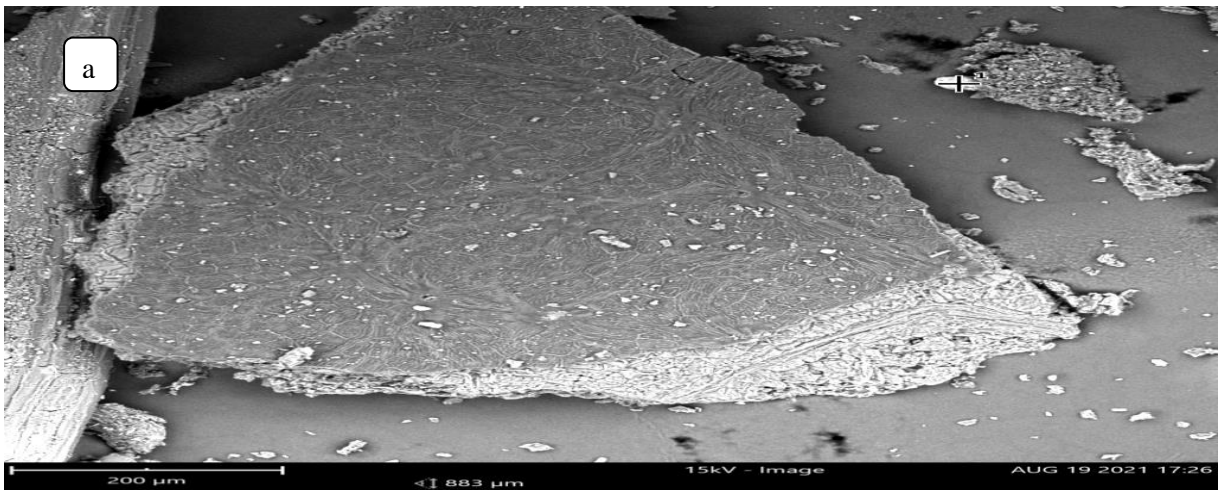


Fig. 4(a) SEM micrographs for RVP before adsorption

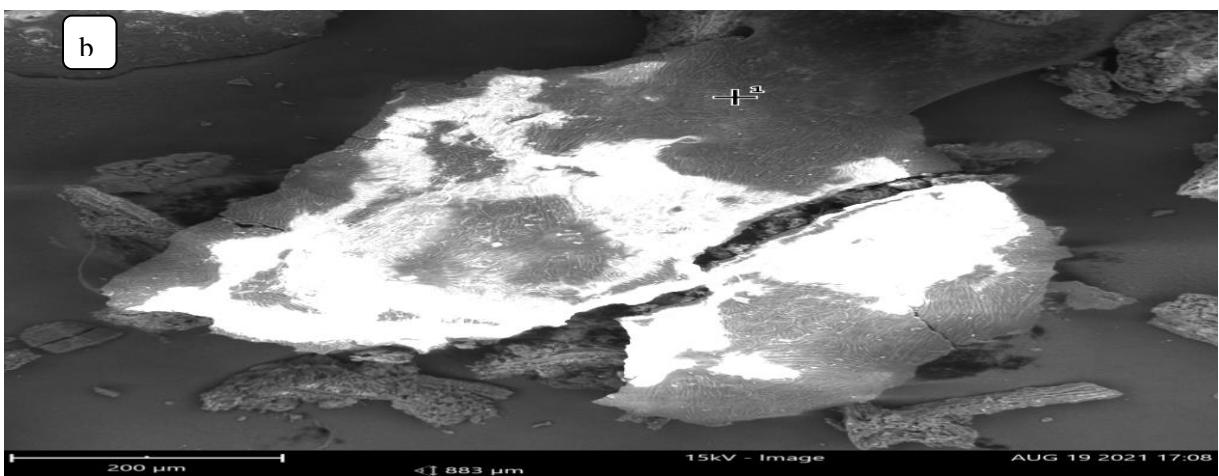


Fig. 4(b) SEM micrographs for RVP after adsorption of MB

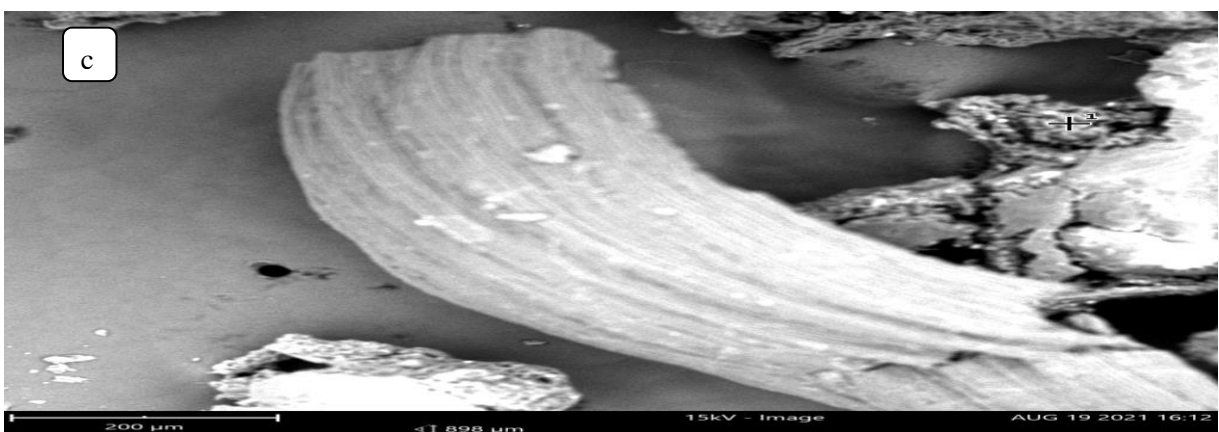


Fig. 4(c) SEM micrographs for RVP after adsorption of RhB

Conclusion

The study established that adsorbents derived from *vitellaria paradoxa* leaves can be effectively used for the removal of basic dyes. Experimental kinetic data correlate well with pseudo-second-order rate equation for all the adsorbates used in the present study, suggesting therefore, a chemisorption

mechanism. The findings clearly indicate that adsorbent derived from *vitellaria paradoxa* leaves has a promising potential in environmental applications such as removing hazardous substances from industrial wastewater.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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