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Temperature Effect in Adsorption of Blue HE-3R on *Calendula officinalis*: Isotherm, Kinetics and Thermodynamics

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Adsorption of a textile reactive dye blue HE-3R was carried out with a low-cost adsorbent material *i.e.*, *Calendula officinalis*. The batch adsorption experiment was done with respect to the effect of pH, concentration of dyes, adsorbent dose and contact time. All the experimental results were analyzed for the suitability of Isotherm models (Freundlich, Langmuir, Redlich-Peterson and Tempkin) and kinetic models (pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich). Adsorption process follows Redlich-Peterson isotherm and Pseudo-second order kinetics. The maximum adsorption quantity was found to be 17.85 mg g^{-1} for the adsorption of blue HE-3R on *Calendula officinalis*. The low temperature favours the adsorption process. The difference in the SEM image and changes in the group frequencies in FT-IR spectra supports the adsorption of Blue HE-3R on *Calendula officinalis* effectively.

Keywords: Textile dye, *Calendula officinalis*, Adsorption, Kinetics, Thermodynamics, Activation energy.

INTRODUCTION

The wastewater generated from the industries like textile, leather, plastic and many others introduces toxicity to the water bodies. The major source for colour pollution is textile industries in which reactive dyes are used due to their fast reactivity towards fibers. Hence it is necessary to treat the wastewater containing dyes. Many treatment methods has been used so far like, electrochemical [1,2], photochemical [3,4], membrane technique [5,6], Fenton-oxidation [7,8], ion-exchange methods [9,10], coagulation-flocculation [11,12], biological degradation [13,14], *etc*. Among these, the adsorption technique becomes a promising technology because of its simplicity of the experimental procedure. Many low-cost adsorbents such as bagasse [15], neem bark [16], *Hypharrhenia hirta* [17], wheat straw, mangrove bark, *Prosopis juliflora* pod [18] were tested for their adsorption efficiency with various dyes.

This paper presents the suitability of *Calendula officinalis* as an adsorbent towards the removal of an anionic textile dye, Blue HE-3R from an aqueous solution. A batch adsorption experiment was carried out with the effect of pH, adsorbent dose, dye concentration and contact time.

EXPERIMENTAL

An anionic dye Blue HE-3R (BHE3R) [λ_{max}: 571 nm] was used as received without further purification. A stock solution of 500 mg L^{-1} of Blue HE-3R was prepared and then diluted suitably to the required initial concentration. An adsorbent carbon prepared from *Calendula officinalis* (CO) as stated by Raman *et al.* [19]. The 50 mL of the dye mixtures of required concentration in mg L^{-1} was agitated in Orbital shaking incubator at the constant speed (150 rpm) with required adsorbent dosage. The colour removal percentage was determined by noting the absorption wavelength (λ_{max}) of dye solution before and after adsorption using UV spectrophotometer.

$$\text{Removal of dye (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

where, C_i and C_e are the initial and equilibrium concentrations of the dye in mg L^{-1}, respectively.

RESULTS AND DISCUSSION

Effect of pH: The equilibrium uptake of the 50 mg L^{-1} of Blue HE-3R with respect to pH of the medium was investigated

onto 1 g L^{-1} of *Calendula officinalis* by varying the initial pH from 1 to 6 at 303 K. The dye adsorbed on carbons was higher (50.67 %) at lower pH and it decreases (1.78 %) rapidly as the pH increases. As the pH of the solution increased, the dye adsorbed decreased considerably.

$$\text{Carbon (C)} + H_3O^+ \longrightarrow \text{C---}H^+ + H_2O$$

$$\text{C---}H^+ + \text{Dye}^- + H_2O \longrightarrow \text{C---Dye-} + H_3O^+$$

Effect of adsorbent dose: The adsorbent dose varied from 0.4 to 2 g/L for 50 mg/L of the dye solution at pH 2. The percentage removal was increased from 12.054 to 47.545 and the quantity of dye adsorbed was decreased from 15.65 to 11.886 mg/g respectively. At higher adsorbent dose the larger surface area available for the dye molecule, hence the number of molecules may adsorb on the available adsorbent.

Effect of initial concentration of dye: The quantity of dye adsorbed was measured in terms of initial dye concentration from 20 to 100 mg/L by 1 g/L of adsorbent at pH 2. The amount of dye adsorbed was found to be 8.686 to 17.268 mg/g as the concentration of dye increased from to 20 to 100 mg/L respectively. This may be explained, as the concentration of dye increases, the available dye molecule becomes larger; hence, a larger number of the molecule may adsorb on the constant surface area.

Effect of contact time: The percentage removal of dye with respect to contact time on varying concentration of dyes (20, 40, 60, 80 and 100 mg/L) was investigated. The adsorption trend was similar to all concentrations, almost 50-60 % of the adsorption was done within 5-10 min and equilibrium adsorption was reached in 1 h contact time. Adsorption was fast, as the fresh surface of adsorbent available initially; and it continues gradually from 10 to 60 min contact time. The equilibrium percentage removal of dye was found to be 43.43, 33.42, 23.46, 16.22 and 17.27 % for 20, 40, 60, 80 and 100 mg/L of dye solution respectively (Fig. 1).

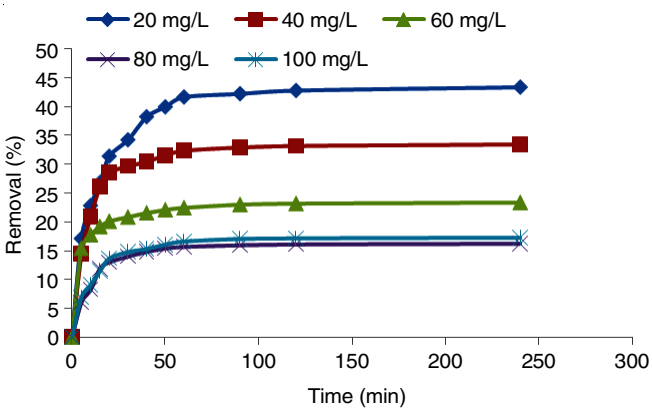

Fig. 1. Effect of contact time for Blue HE-3R on *Calendula officinalis* at 30 °C

Adsorption isotherms for Blue HE-3R on *Calendula officinalis*: The isotherm study was carried out at 303 K between 20-100 mg/L of Blue HE-3R on 0.05 g/50 mL of the adsorbent dose at pH 2.

Freundlich isotherm and Langmuir isotherm: The amount of solute adsorbed, Q_e is related to the equilibrium concentration of solute in solution, C_e by following Freundlich relation:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e$$

where, K_F is a constant for the system, related to the bonding energy. The values of K_F, related to bond energy and 1/n are determined from the intercept and slope of a linear plot between log (Q_e) and log (C_e) of Freundlich equation. As the value of K_F is 4.707, indicates the quantity of dye adsorbed onto *Calendula officinalis* is maximum with a larger number of bonding for a unit equilibrium concentration (a measure of adsorption capacity, mg/g). Also, the value of 1/n for *Calendula officinalis*, is between 0 to 1, that is 0.279 reveals that the surface of the carbon becomes homogeneous form heterogeneous.

The Langmuir isotherm applied to the sorption process can be represented by the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$$

where, C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g), Q_m (mg/g) and K_L (L/mg) is Langmuir constants related to adsorption capacity and energy of adsorption respectively. The values of Q_m and K_L were determined from the intercept and slopes of the linear plots of C_e/Q_e *vs.* C_e.

A separation factor R_L, explains the essential feature of Langmuir isotherm, which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_i}$$

where C_i is the initial dye concentration, mg/L. The R_L values very well lie between 0 and 1 and hence the adsorption process was favourable.

Tempkin isotherm and Redlich-Peterson isotherm: The linearized equation of Tempkin isotherm models is given as follows:

$$Q_e = \beta \ln K_T + \beta \ln C_e$$

where, K_T is an equilibrium constant of binding corresponding to the maximum energy of binding (mg/L) and the β is related to the heat of adsorption. Tempkin isotherm constants K_T and β were determined by the plot of Q_e *versus* ln C_e. The values of K_T, β and correlation coefficient, R^2 for Tempkin isotherm model are given in Table-1.

Redlich-Peterson isotherm can be applied either in the homogeneous or the heterogeneous system due to the high versatility of the equation. It can be stated by the following equation:

$$\log \frac{C_e}{Q_e} = \log K_R + \beta_R \log C_e$$

where, β is the desorption constant and K_R, is Redlich-Peterson isotherm constant in g/L (Fig. 2).

The experimental data and the correlation coefficients (R^2) values for Blue HE-3R on *Calendula officinalis* was 0.926, indicates the applicability of the Langmuir isotherm model. The adsorption efficiency with respect to monolayer adsorption capacity, Q_m is 17.855 mg/g, which are almost good in the quantity of adsorption. The monolayer adsorption capacities,

TABLE-1
ISOTHERM AND KINETIC PARAMETER FOR THE ADSORPTION OF BLUE HE-3R ON *Calendula officinalis*

Adsorption isotherms			Adsorption kinetics				
Isotherm	Parameter	*Calendula officinalis*	Kinetics	Parameter	303 K	313 K	323 K
				Q_e (exp)	13.369	11.304	9.457
	1/n	0.279	Lagergren's first-order model	Q_e (cal)	9.060	7.385	4.731
Freundlich	K_F	4.707		K_1	0.041	0.039	0.031
	R^2	0.795		R^2	0.991	0.970	0.924
	Q_m	17.855	Pseudo second-order model	Q_e (cal)	14.016	11.885	10.046
Langmuir	K_L	0.082		K_2	0.009	0.010	0.009
	R^2	0.926		R^2	0.999	0.999	0.994
	β	0.721		α	4.995	3.475	1.762
Redlich-Peterson	K_R	0.212	Elovich model	β	0.406	0.458	0.491
	R^2	0.963		R^2	0.896	0.899	0.946
	β	3.369		k_{id}	0.629	0.554	0.542
Tempkin	K_T	1.362	IPD	C_i	6.205	5.009	3.227
	R^2	0.769		R^2	0.684	0.674	0.695

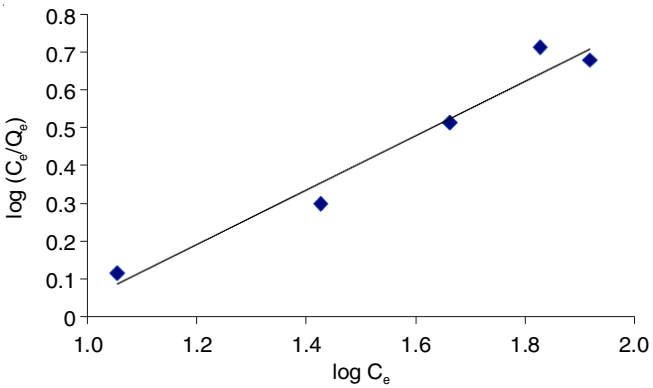

Fig. 2. Redlich-Peterson isotherm for the adsorption of Blue HE-3R on *Calendula officinalis*

Q_m of the various adsorbent for Blue HE-3R was presented in Table-1.

Adsorption kinetics for Blue HE-3R on *Calendula officinalis*: The adsorption kinetics was carried out at 303 K, 313 K and 323 K with the initial concentration of dye as 20, 40, 60, 80 and 100 mg/L of Blue HE-3R on 1 g/L of adsorbent dose at pH 2 for 3 h of contact time.

Lagergren's first-order and Pseudo-second order kinetics: The pseudo-first-order kinetic model of Lagergren is more suitable for lower concentration of solute and its linearized equation is:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t$$

where, Q_t (mg/g) is the amount of adsorbate adsorbed at time t (min); Q_e (mg/g) is the adsorption capacity in the equilibrium; k_1 (min^{-1}) is the rate constant of pseudo-first-order model. The values of k_1 and Q_e for the adsorption of Blue HE-3R dye onto *Calendula officinalis*, determined from the plot of log (Q_e-Q_t) *vs.* time.

Adsorption kinetics was explained by the pseudo-second-order model, expressed in the linear equation as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

where, k_2 is the second order rate constant (g/mg/min). The second order rate constant, k_2 values for Blue HE-3R on *Calendula officinalis* was calculated from the slopes of the respective linear plots of t/Q_t *vs.* t (Fig. 3).

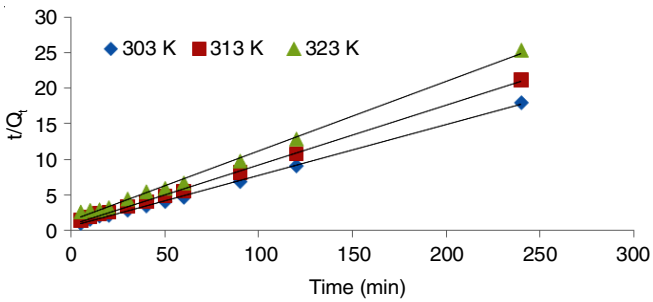

Fig. 3. Pseudo second-order kinetic model for the adsorption of Blue HE-3R on *Calendula officinalis*

Elovich and intra-particle diffusion kinetics: Elovich model suggests that the chemisorptions, *i.e.* a chemical reaction, is probably the mechanism that controls the rate of adsorption. This model can be applied with success in the liquid solution and the linear form of the Elovich equation is:

$$Q_t = \frac{1}{\beta}\ln \alpha\beta + \frac{1}{\beta}\ln t$$

where, α (mg/g) is the initial sorption rate and β (g/mg) is the desorption constant. The values of α and β can be calculated from the slope and intercept of the plot of Q_t *versus* ln t. As can be seen from the Table-1, the higher value of α and lower value of β for Blue HE-3R on *Calendula officinalis* at 303 K than at 313 K and 323 K presumes the higher initial adsorption with lower desorption rate, hence the lower temperature is preferred for the adsorption of Blue HE-3R on *Calendula officinalis*.

Intra-particle diffusion mechanism of an adsorption process was best explained by the Weber and Morris; the linearized equation is given as follows:

$$Q_t = k_{id}t^{0.5} + C_i$$

where, Q_t (mg/g) is the quantity of dye adsorbed at time t and k_{id} ($mg/gh^{0.5}$) is intra-particle diffusion constant. The value of k_{id} and C_i are calculated from the slop and intercept of a plot Q_t *versus* $t^{0.5}$, when adsorption follows intra-particle diffusion process. Value of C_i gives an idea of the thickness of the boundary layer. The C_i value for *Calendula officinalis* is 6.205,

5.009 and 3.227 at 303, 313 and 323 K respectively. Therefore the thickness of the adsorbed layer is higher at 303 K when compared with 313 and 323 K (Table-1). This may be due to coverage of surface layer first and then diffusion into the pores, which are the rate limiting step.

The correlation coefficients, R^2 were 0.999, 0.999 and 0.994 at 303, 313 and 323 K respectively (Table-1), suggest a strong relationship between the parameters and also explain that the process follows pseudo-second order kinetics. The calculated value of Q_e(cal) and the experimental value of Q_e(exp) were in good agreement for pseudo-second order kinetic model than those calculated for pseudo-first order. Thus, adsorption of Blue HE-3R onto *Calendula officinalis* adsorbent obeys the pseudo-second order kinetics.

Effect of temperature and thermodynamic studies: The effect of temperature for the adsorption of 40 mg/L of Blue HE-3R dye onto 1 g/L of adsorbent was studied between the ranges 298-323 K. Fig. 4 indicates the decreasing the percentage removal from 40.217 to 23.641 % as the temperature increases from 298 to 323 K. It can be explained as the increasing temperature increases the random motion of the adsorbate dye particle, hence the available number of dye particle near to the adsorbent decreases, hence the adsorption decreases.

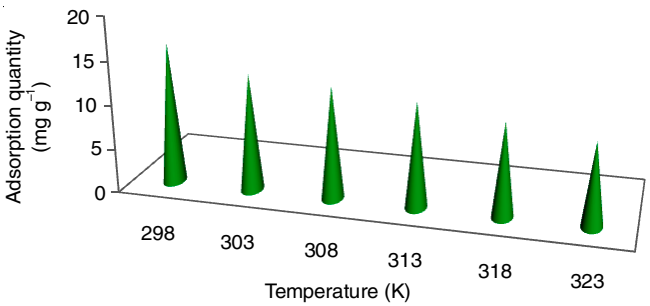

Fig. 4. Effect of temperature for Blue HE-3R on *Calendula officinalis*

The enthalpy change, entropy change and free energy change were determined for the adsorption of Blue HE-3R on *Calendula officinalis* with the help of the following relations:

$$\ln\left(\frac{Q_e m}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where, m is the dose of adsorbent in mg L^{-1}. Thermodynamic parameters such as ΔH°, ΔS° and ΔG° were determined from the slope ($-\Delta H^\circ/R$) and intercept ($\Delta S^\circ/R$) of the plots of ln ($Q_e m/C_e$) *vs*. 1/T. As can be seen from the Table-2, the enthalpy change (ΔH°) and the entropy change (ΔS°) are negative only at 298 K and not at 308 K or 318 K. It indicates the adsorption process is exothermic in nature and the randomness of solute molecule decreases during adsorption. Also, the free energy change is highly negative at lower temperature indicates the feasibility of adsorption, but at the higher temperature, the feasibility of the adsorption process becomes unfavourable as the free energy change becomes positive for Blue HE-3R on *Calendula officinalis*.

Therefore, all the thermodynamic factors such as the change in enthalpy (ΔH°), change in entropy (ΔS°) and change in free energy (ΔG°) favour the adsorption of dyes on the adsorbent at the lower temperature.

TABLE-2
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF BLUE HE-3R ON *Calendula officinalis*

ΔH° (kJ mol^{-1} K^{-1})	ΔS° (J mol^{-1} K^{-1})	Dye concentration: 20 mg/L		
		ΔG° (kJ mol^{-1} K^{-1})		
		298 K	308 K	318 K
-24.249	-81.209	-0.049	0.763	1.575

The idea of energy barrier is the key strength to describe the reaction nature, which can be determined by the linear form of Arrhenius equation. It relates the rate of the reaction and temperature, given as:

$$\ln k = \ln A - \frac{E_a}{RT}$$

where, k is the rate constant (form pseudo-second order kinetics); E_a, is activation energy (kJ mol^{-1}); A, is the Arrhenius factor (g mg^{-1} min^{-1}); R, is the gas constant and T is the temperature (K). The activation energy of the adsorption process was estimated from the slop of the plot ln k *vs*. 1/T. It was found to be 2.436 kJ mol^{-1} for Blue HE-3R. Since the activation energy barrier is lower in quantity, the adsorption is favourable.

FT-IR and SEM micrograph analysis: Fourier transform infrared spectroscopy (4000-400 cm^{-1}) is used to characterize the various functional groups present in the *Calendula officinalis* before and after adsorption of Blue HE-3R (Fig. 5). The peak at 752 and 765 cm^{-1} is for the presence of C-Cl (str) in both free *Calendula officinalis* and dye loaded *Calendula officinalis*. The presence of symmetric C-H and C-O (str) is evidenced by the peaks at 1245 and 1385 cm^{-1} in free *Calendula officinalis*, whereas it is observed at 1049 and 1217 cm^{-1} in dye loaded *Calendula officinalis*. The peaks at 1610 cm^{-1}, 1704 cm^{-1} in free *Calendula officinalis* and 1585 cm^{-1}, 1714 cm^{-1} in dye loaded *Calendula officinalis* indicates the presence of conjugated C=O (str). Around at 2350 cm^{-1} a peak found in both free *Calendula officinalis* and dye loaded *Calendula officinalis* is the characteristic for the N-H ion (str) in amine salts; also the peak at 3000 cm^{-1} is characteristic for O-H (str). A significant difference in surface texture is found in scanning electron micrography of free *Calendula officinalis* and dye loaded Blue HE-3R (Fig. 6).

Conclusion

The adsorption process follows Freundlich isotherm at low temperature, Langmuir isotherm at high temperature and pseudo-second order kinetics. The thermodynamic study showed the reaction favours at low temperature (298 K) as the value of ΔH° is -24.25 kJ mol^{-1} K^{-1}, ΔS° is -81.20 J mol^{-1} K^{-1} and the ΔG° is -0.049 kJ mol^{-1} K^{-1}. At the higher temperature such as 308 K and 318 K the free energy change was found to be 0.763 and 1.575 kJ mol^{-1} K^{-1} respectively. The adsorbent *Calendula officinalis* is an easily available low-cost material. Therefore it can be used for small scale dyeing industries.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

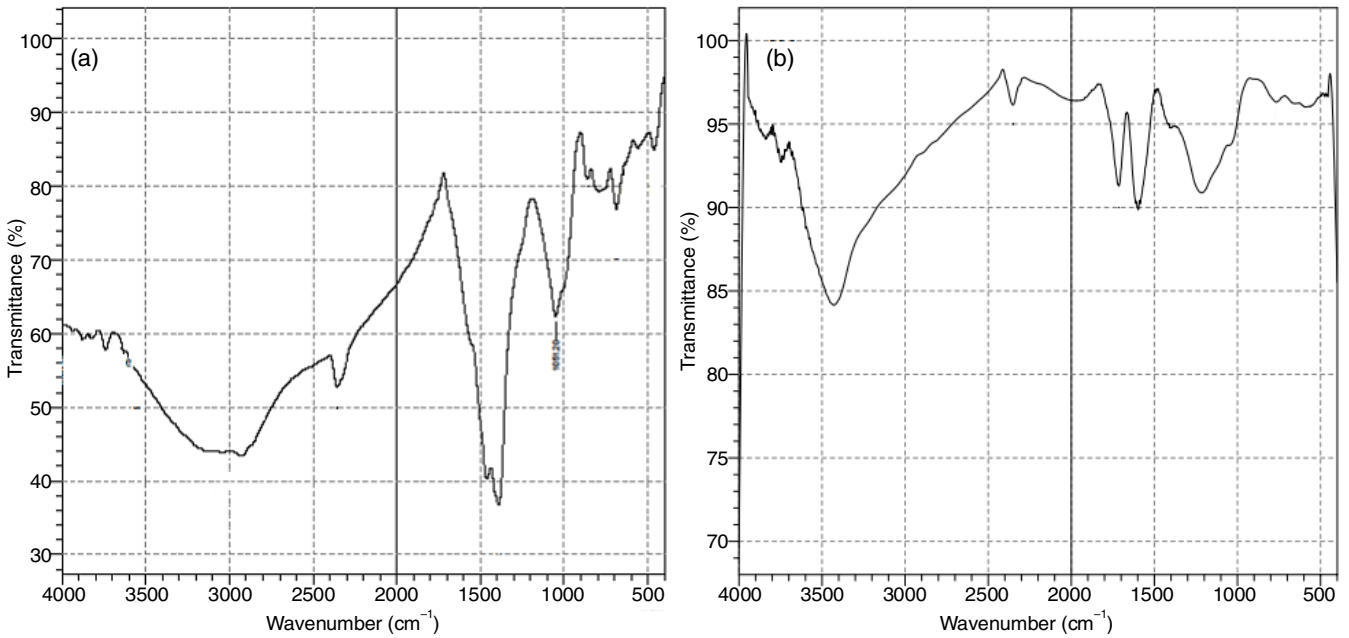

Fig. 5. FTIR spectrum of *Calendula officinalis* (a) before and (b) after adsorption of Blue HE-3R

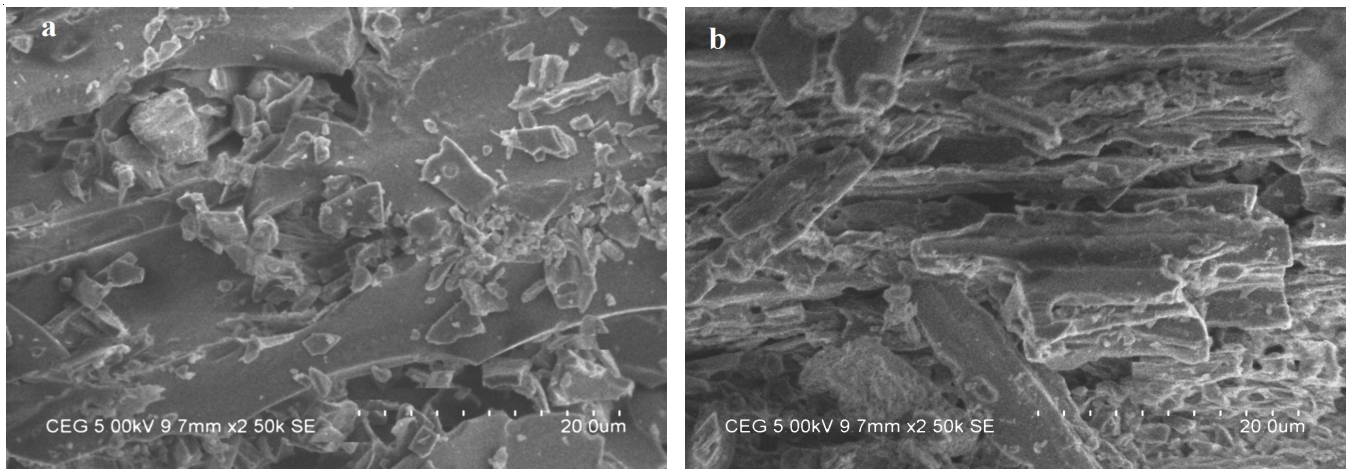

Fig. 6. SEM micrography of *Calendula officinalis* (a) before and (b) after adsorption of Blue HE-3R

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