Applicability of Tempkin Equilibrium and Elovich Kinetics for Chemisorption of Brown HE-2G on Calendula Officinalis

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A B S T R A C T

Calendula officinalis is a low-cost material used as adsorbent for the removal of textile dye, Brown HE-2G. The effect of pH, concentration of dyes, adsorbent dose and contact time were obtained by batch adsorption technique. The results were analyzed by adsorption isotherm models (Freundlich, Langmuir, Redlich-Peterson and Tempkin). The results were in good agreement with Langmuir model and the Redlich-Peterson isotherm models. The Langmuir monolayer adsorption quantity was found to be, 76.56 mg g^{-1} Brown HE-2G. Pseudo-first-order, pseudo-second-order, Intraparticle diffusion and Tempkin kinetic models were used to fit the experimental data, it was well fitted into pseudo second order kinetics. FT-IR and SEM analysis have effectively supported the adsorption of Brown HE2G on the adsorbent.

INTRODUCTION

The discharge of effluent from the tannery, plastic, textile, painting, leather etc., industries leads to water pollution by introducing toxicity to the water bodies and the dyes used were carcinogenic in nature [1, 2]. Dyes of different kinds such as reactive, acidic, basic and non-ionic dyes are commercially used. Reactive dyes especially react with textile fiber to form dye-fiber bond [3]. Though many wastewater treatment processes such as electrocoagulation [4], chemical oxidation, photochemical degradation, biological degradation [5], membrane separation technique and liquid-liquid extraction [6] were successfully applied for the wastewater treatment. Adsorption technique was a powerful tool for the economical treatment of textile effluent. In recent days, low cast adsorbent such as sawdust [7], bagasse [8, 9], orange peel carbon [10], agricultural waste [11, 12] plays a vital role in adsorption technique than commercial activated carbon.

Calendula officinalis (Figure 1) is a culturally important ornamental flower; especially in Hindu culture. It has been generated as waste every day, thrown into a wasteland or in water bodies and leads to bio-degradable pollution. We tried to find the efficiency of this waste as a natural adsorbent for the color removal of Brown HE-

2G. A batch adsorption technique was carried out to find the efficiency of *Calendula officinalis* with respect to the pH, adsorbent dose, dye concentration and contact time. The experimental results were analyzed by kinetic models, equilibrium models and by thermodynamic studies.

Figure 1. *Calendula officinalis*

MATERIAL AND METHODS

Preparation of dye solution
The dye Brown HE2G (BHE2G) [λ_{max}: 471 nm] was obtained from cotton dyeing industry, Thiruvallur District, Tamil Nadu. It was used as received without

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further purification. A stock solution of 500 mgL^{-1} of BHE2G was prepared and then diluted suitably to the required initial concentration.

Adsorbent preparation

Calendula officinalis was collected from wasteland in Thiruvallur District, Tamil Nadu. It was washed several times with distilled water; dried in sunlight, then ground well and soaked in sodium hydroxide solution [13] for five days to remove coloring matters from *O. officinalis.* It was dried in sunlight and then in the hot air oven at 104±2 ºC after washed with distilled water. A portion of a dried sample was taken in a china dish, covered with thin aluminium sheet and carbonized. The carbonization was carried out in the muffle furnace for one hour at 200 ºC. It was ground well and the portion between 0 and 100 μm sieves was stored in desiccators and used for the adsorption experiments.

Method of Equilibrium Studies

A 50 mL of dye mixture of concentration between 20–150 mgL^{-1} was shaken at the constant agitation speed (150 rpm) in orbital shaking incubator (Remi Elektrotechnik Limited) with adsorbent dosage between 0.4–2 g L^{-1} was carried out at the temperature (30 ± 1ºC) using batch adsorption technique for a specific period of contact time (300 min) in an orbital shaker, after noting down the initial pH of the solution. The supernatant liquid was collected by filtering out the solid phase using 0.45μm filter paper and the residual concentration of dye present in the supernatant was determined by UV spectrophotometer (Shanghai Mapada Instruments Co. Ltd., Model: UV 1100). The percentage removal of dye was calculated using the following relationship:

$$\% \; Removal \; of \; dye = \frac{C_i - C_e}{C_i} X \; 100$$

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

RESULTS AND DISCUSSION

Effect of pH on dye mixture

A 50 mg/L of dye solution was taken and subjected to the effect of pH on 1 g/L of adsorbent between 1-6 pH. Initially, the percentage removal of dye was 90.03% and it decreases gradually as the pH increases, reached to 13.90% at pH 6 (Figure 2). Since the dye is anionic in nature, it has a greater affinity to H$^+$ at lower pH as the concentration of H$^+$ ion is more. On increasing pH, desorption is possible as the H$^+$ ions decrease. The possible mechanism is given as follows:

Carbon (C) + H$_3$O$^+$ ⟶ C---H$^+$ + H$_2$O
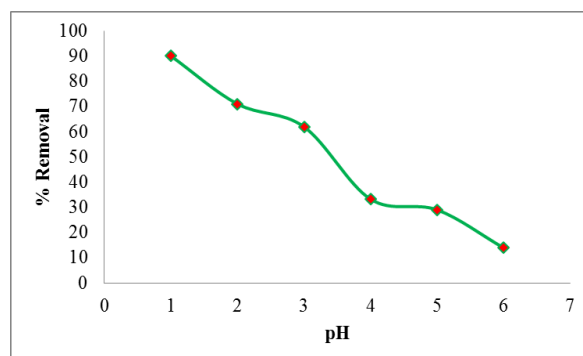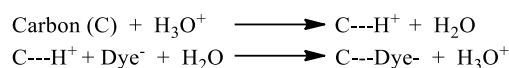C---H$^+$ + Dye$^-$ + H$_2$O ⟶ C--Dye- + H$_3$O$^+$

Figure 2. pH dependence of BHE2G on *O. officinalis* at 30ºC.

Effect of adsorbent dose on BHE2G dye solution

The adsorbent dose is 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 45.32 to 74.92 and the quantity of dye adsorbed was decreased from 56.65 mg/g to 18.73 mg/g respectively (Figure 3). This may due to increasing dose of adsorbent increases the surface area; hence, more number of molecules may adsorb on the available adsorbent.
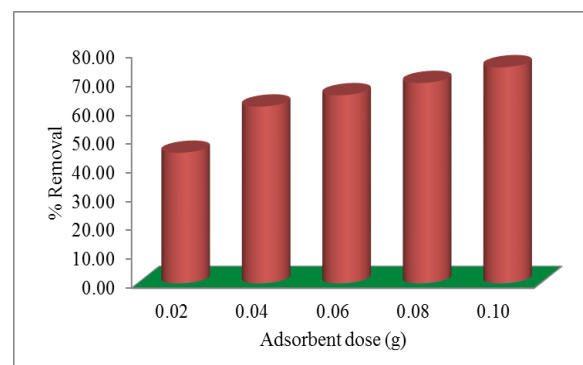

Figure 3. Effect of *O. officinalis* dose for the adsorption of BHE2G

Effect of initial dye concentration on *O. officinalis*

The quantity of dye adsorbed was measured in terms of initial dye concentration from 20 mg/L to 150 mg/L in 1 g/L of adsorbent at pH 2. The amount of dye adsorbed was found to be 15.71 to 65.04 mg/g as the concentration of dye increased from to 20 mg/L to 150 mg/L respectively (Figure 4). 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.
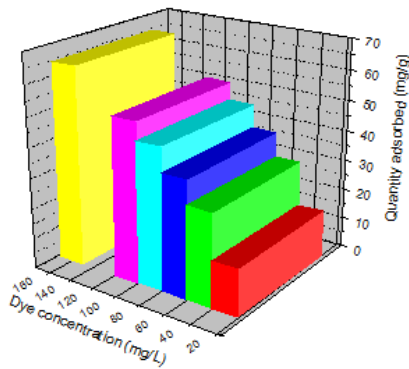
Figure 4. Effect of initial dye concentration of BHE-2G on *O. officinalis* at 30ºC.

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% of the adsorption was done within 10 minutes and equilibrium adsorption was reached in one hour contact time. Adsorption was fast, as the fresh surface of adsorbent available initially; and it continues gradually from 10 to 60 minutes contact time. The equilibrium percentage removal of dye was found to be 78.57, 76.40, 64.19, 57.98 and 52.32% for 20, 40, 60, 80 and 100 mg/L of dye solution, respectively (Figure 5).
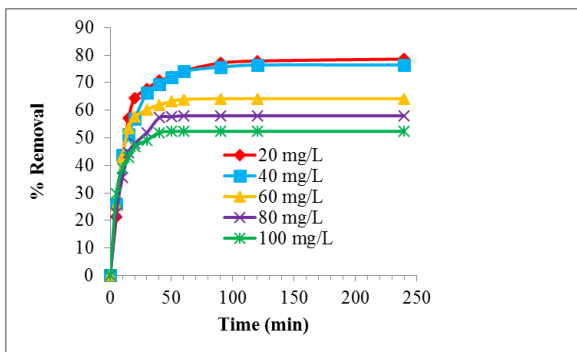

Figure 5. Effect of contact time for BHE-2G on *O. officinalis*

Isotherm Models

Freundlich and Langmuir Isotherm models were utilized to analyze the experimental condition. By using the following Freundlich relation [14]:

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

K_F, the adsorption energy was calculated. Also, the value for $1/n$ is obtained as fraction indicates the applicability of Freundlich adsorption model. Langmuir Isotherm model was applied to study the monolayer adsorption capacity of adsorbent using the relation [15]:

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

The monolayer adsorption capacity (Q_m) was found to be 76.56 mg/g (Figure 6). K_L value obtained by above relation was used to find R_L factor which described as $0< R_L<1$; favorable, $R_L>1$; unfavorable, $R_L=1$; linear and $R_L=0$ for the irreversibility of the adsorption process.

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

Since the R_L values calculated is lie between 0 to1 (Table 1), the adsorption is favorable between 20-150 mg/L.
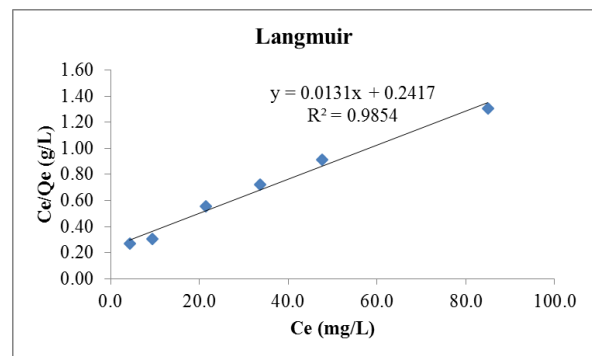

Figure 6. Langmuir adsorption isotherm for BHE-2G on *O. officinalis*

TABLE 1. R_L Values

C_i (mg/L)	R_L
20	0.481
40	0.316
60	0.236
80	0.188
100	0.156
150	0.110

The linearized equation of Redlich-Peterson (R-P) isotherm describes the homogeneous and heterogeneous nature of adsorption reaction [16]:

$$log \frac{C_e}{Q_e} = log \, K_R + \beta \, log \, C_e$$

where, β is the desorption constant and K_R is R-P isotherm constant (g L^{-1}). The isotherm constants β, K_R and the correlation coefficients, R^2 for the R-P isotherm are listed in Table 2. Tempkin isotherm describes the adsorbent-adsorbate interactions [17]. Generally, Tempkin isotherm has been used in the linearized and rearranged form as following:

$$Q_e = \beta \, lnK_T + \beta \ln C_e$$

where, K_T is the maximum energy of binding at an equilibrium (mg L^{-1}) and the β is adsorption heat. Figure 7 of Q_e vs ln C_e, is used for the determination of the constants K_T and β (Table 2).
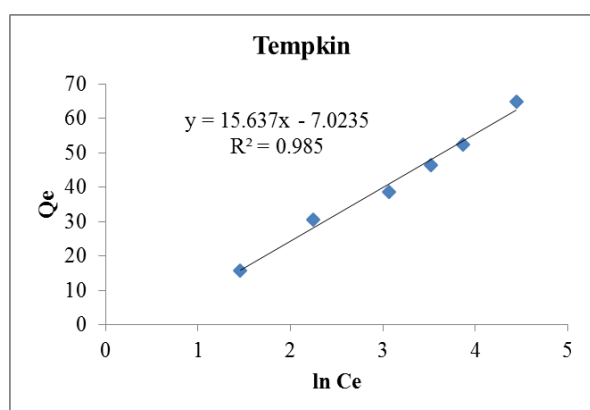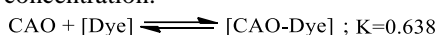
Figure 7. Tempkin isotherm model for the adsorption of BHE-2G on *O. officinalis* at 30ºC.

The results of each model for the adsorption of BHE-2G on *O officinalis* are presented in Table 2. The correlation coefficient, R^2, value of each model was compared for the adsorption process. As from the Table 2, Langmuir and Tempkin model have higher R^2 value. According to Tempkin, the following equilibrium has proposed for the adsorption; the equilibrium constant indicates the favorability of adsorption by decreasing the initial dye concentration.

CAO + [Dye] ⇌ [CAO-Dye] ; K=0.638

The high heat of adsorption (β = 15.637) from the tempkin model and high monolayer adsorption capacity (Q_e = 76.560 mg/g) from Langmuir model indicates the nature of adsorption was chemisorptions.

TABLE 2. Isotherm parameter for the adsorption of BHE2G on *O. officinalis* at 30ºC

Isotherm model	Parameter	BHE2G
Freundlich	1/n	0.448
	K_F	9.433
	R^2	0.957
Langmuir	Q_m	76.560
	K_L	0.054
	R^2	0.985
R-P	β	0.552
	K_R	0.106
	R^2	0.971
Tempkin	β	15.637
	K_T	0.638
	R^2	0.985

Kinetics of adsorption process

The suitability of first order and second order kinetic model for the experimental condition were analyzed. The pseudo-first-order rate constant and amount of dye adsorbed were calculated from the Lagergren kinetic model [18], which is applicable for a lower concentration of solute.

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

The following pseudo-second-order model [19] was used to calculate the quantity of dye adsorbed as well as second order rate constant.

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

A graph of Time Vs t/Q_t is drawn at 303, 313 and 323K (Figure 8). The experimentally obtained value of Q_e, 15.71 mg/g, 11.429 mg/g and 7.714 mg/g is in good agreement with the calculated value of second order kinetics as 16.21 mg/g, 12.504 mg/g and 8.530 mg/g at 303K, 313K and 323K respectively (Table 3). It shows the adsorption of dye on adsorbent follows second order kinetics over pseudo-first order kinetics. Also, it is well understood by the R^2 values [20].
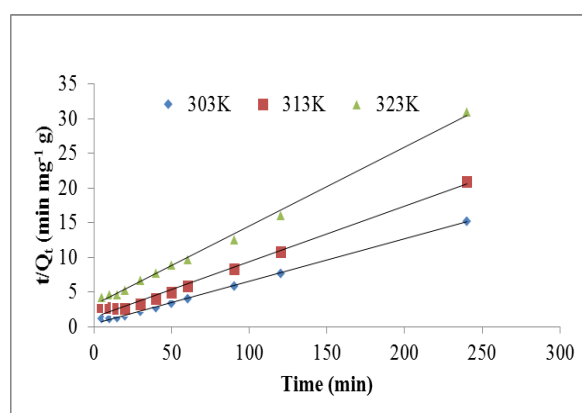

Figure 8. Pseudo second order kinetics of BHE-2G on *O. officinalis*

Elovich kinetic model

According to Elovich, the chemisorptions mechanism controls the rate of adsorption. The linear form of the Elovich equation for the liquid solution 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 slope and intercept of the plot of Q_t versus ln t, gives the value of α and β (Figure 9). As can be seen from the table 3, the higher value of sorption constant, α = 4.806, 1.569 and 0.934; the lower value of desorption constant, β = 0.316, 0.369 and 0.609 at 303K, 313K and 323K respectively favours the adsorption mechanism of BHE-2G on *O. officinalis* as chemisorptions [21]. The difference between adsorption and desorption constants decreases as the temperature increases (Figure 10). At the temperature 303K, desorption rate is higher compared to the adsorption constant. Therefore the lower temperature 303K is better for adsorption of BHE2G on *O. officinalis* than the higher temperature such as 313K and 323K according to the present work.
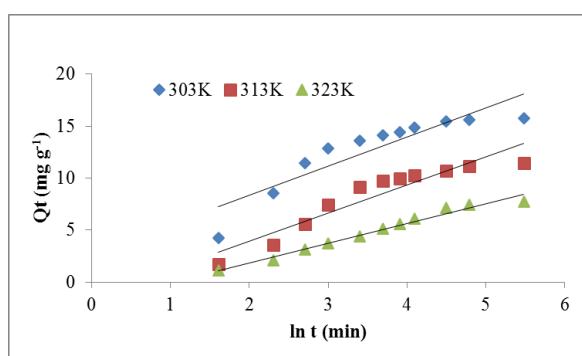
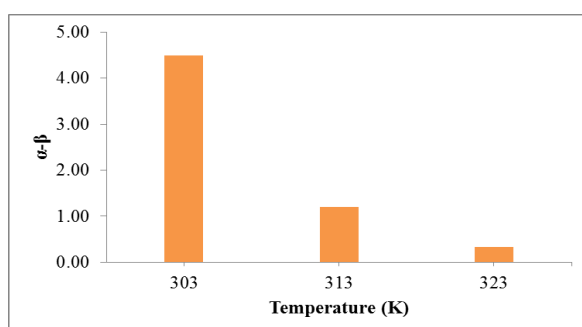**Figure 9.** Elovich model for dye adsorption on *O. officinalis*

Figure 10. Favorability of Chemisorption (α-β) with Temperature.

Intra-particle diffusion model

The Intra-particle diffusion of adsorbate on the adsorbent can be best explained by Weber and Morris [22] is as follows:

$$Q_t = k_{id}\, t^{1/2} + C_i$$

where, Q_t (mg g^{-1}) is the quantity of dye adsorbed at time t and k_{id} (mg g^{-1}min$^{-1/2}$) is intra-particle diffusion constant. The constant, k_{id} and C_i are obtained from the slope and intercept of the plot Q_t versus $t^{1/2}$ respectively (Table 3). Value of C_i gives an idea of the thickness of the adsorbed layer. Also, it is evident from the figure, there are two straight lines are obtained, in which the first line for surface adsorption and the second line is for the adsorption due to diffusion into the pores.

TABLE 3. Kinetic parameters for the adsorption of BHE2G on *O. officinalis* at different temperature

Kinetic model	Parameter	303K	313K	323K
	$Q_{e\,(exp)}$	15.7143	11.4286	7.7143
Lagergren's first order	$Q_{e\,(cal)}$	5.1637	8.5073	8.2536
	K_1	-0.0395	-0.0047	0.0002
	R^2	0.5627	0.5622	0.0003
Pseudo second order	$Q_{e\,(cal)}$	16.2137	12.5045	8.5300
	K_2	0.0105	0.0056	0.0062
	R^2	0.9978	0.9911	0.9848
	α	4.8063	1.5693	0.9342
Elovich	B	0.3159	0.3689	0.6089
	R^2	0.9025	0.8879	0.9580
	k_{id}	0.9448	0.6856	0.5593
IPD	C_i	5.7308	3.4917	0.9204
	R^2	0.6329	0.6616	0.8749

Thermodynamic Studies

Adsorption of the dye BHE-2G on *O. officinalis* is studied at 303, 313 and 323K, with the help of the following relations:

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

where, m is the dose of adsorbent (mg L^{-1}), C_e is the equilibrium concentration (mg L^{-1}) and Q_e is the amount of adsorption (mg g^{-1}) at equilibrium. T is the temperature (K) and R is the gas constant (8.314 J K^{-1} mol^{-1}). The slope (-$\Delta H°$/R) and intercept ($\Delta S°$/R) of the plots ln (Q_em/C_e) vs 1/T (figure 11) is used to determine the thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ are change in free energy (kJ mol^{-1}), change in enthalpy (kJ mol^{-1}) and change in entropy (J mol^{-1} K^{-1}), respectively.

TABLE 4. Thermodynamic parameter

Dye	$\Delta H°$(kJ/mol)	$\Delta S°$(kJ/mol)	$\Delta G°$(kJ/mol)		
			303K	313K	323K
BHE2G	-71.881	-0.227	-3.191	-0.924	1.343

The enthalpy change ($\Delta H°$), entropy change ($\Delta S°$) and free energy change ($\Delta G°$) values from the table 4, indicates the adsorption of BHE-2G on *O. officinalis* follows the exothermic, decreasing randomness and feasibility of chemisorptions at the lower temperature. As the temperature increases as 303K, 313K and 323K, free energy change becomes -3.191, -0.924 and 1.343 in kJ/mol respectively. Also, the adsorption quantity changes as 15.71 mg/g, 11.429 mg/g and 7.714 mg/g at 303K, 313K and 323K, respectively. It may due to decreasing availability of dye molecule near the adsorbent as the kinetic motion increases at higher temperature. Therefore, the above points reveal that the adsorption process is feasible at lower temperature and not at higher temperature.

FT-IR and SEM micrography analysis

The various functional groups present on the *O. officinalis* before adsorption and after adsorption of dye mixture were studied by Fourier transform infrared spectroscopy within 400-4000 cm^{-1} range. The peaks at 1704 cm^{-1} and 1610 cm^{-1} is characteristic for the presence of C=O (str) and conjugated C=O (str) which were present only in dye adsorbed *O. officinalis* and not in free *O. officinalis*. Fermi resonance of sym-C-H (bend) at 1385 and 1245 cm^{-1} with equal intensity also present for dye loaded *O. officinalis* and not in *O. officinalis*. The peaks centered at 3000 and 3250 cm^{-1} are characteristic for the presence of O-H (str) and N-H (str), also the peaks at 2350 cm^{-1} are for amine salt containing N-H ion (str) in both *O. officinalis* before and after adsorption. Other peaks between 850-500 cm^{-1} are having a significant

difference in *O. officinalis* and *O. officinalis* after adsorption (Figure 11). The Scanning Electron Microscopy was used to analyze the surface texture of *O. officinalis.* Figure 12a) indicates the presence of porous texture on *O. officinalis* and Figure12b) shows the different surface texture after adsorption of Brown HE-2G on *O. officinalis.*

TABLE 5. FT-IR spectroscopy of BHE2G loaded *O. officinalis*

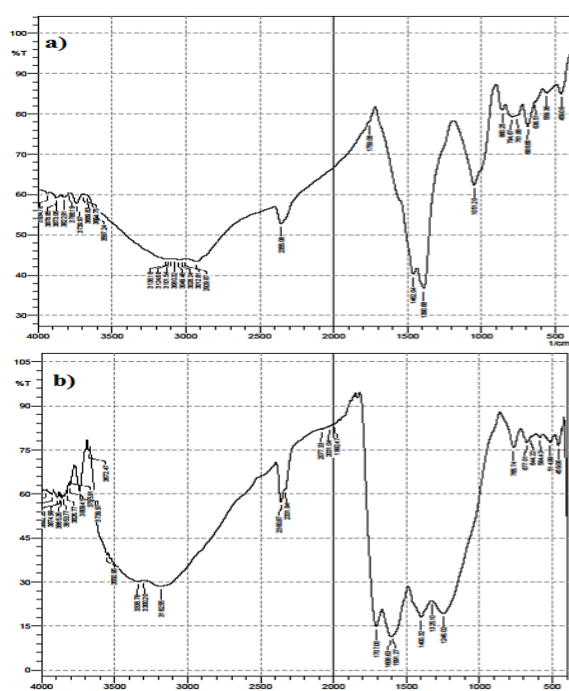| Functional groups	Frequency in cm^{-1}
C=O – str	1610
	1704
sym-C-H (Fermi resonance)	1245
	1385
O-H – str	3000
N-H – str	3250
N-H ion - str, amine salt	2350

Figure 11. FTIR spectrum of *O. officinalis* a) before and b) after adsorption of BHE-2G
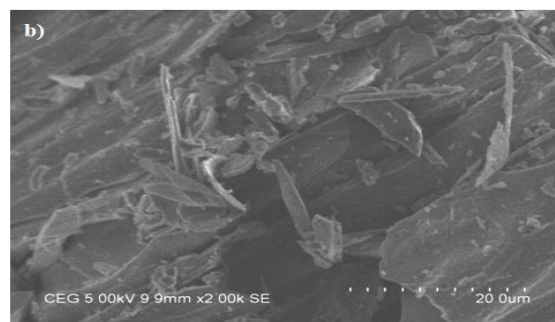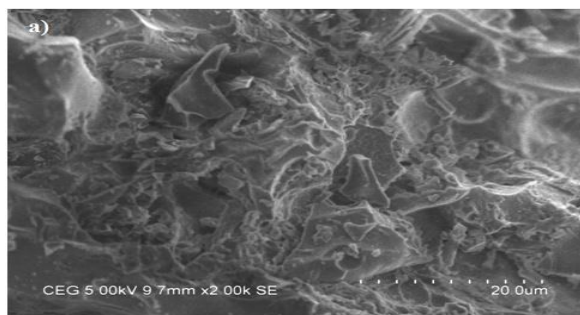

Figure 12. SEM microscopy of *O. officinalis* a) before and b) after adsorption of BHE-2G

CONCLUSION

- *Calendula officinalis* was identified as new adsorbent and studied their adsorption efficiency by Brown HE-2G, a commercial anionic dye.
- The Langmuir monolayer adsorption capacity was found to be 76.56 mg/g; the adsorption process follows pseudo second-order kinetics.
- The reaction favored at low temperature as the process is exothermic, decreasing entropy and the change in free energy is negative.
- Tempkin equilibrium studies and Elovich kinetic model proves the adsorption mechanism follows Chemisorption.
- Application**:** Since the used adsorbent is natural and easily available; it can be applied to small-scale dyeing industries.

Acknowledgement

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Persian Abstract

چکیده

Calendula officinalis یک ماده کم هزینه است که به عنوان جاذب برای حذف رنگ نساجی، Brown HE-2G استفاده می شود. اثر pH، غلظت رنگ، دوز جاذب و زمان تماس با روش جذب دسته ای به دست آمد. نتایج با استفاده از مدل های ایزوترم جذب (Freundlich، Langmuir، Redlich-Peterson و Tempkin) مورد تجزیه و تحلیل قرار گرفت. نتایج به دست آمده در توافق خوب با مدل لانگمیور و مدل ایزوترم Redlich-Peterson مطابقت داشت. مقدار جذب یکنواختی لنگمیر به ترتیب ۷۶,۵۶ میلی گرم بر گرم گرم برنز HE-2G بود. به ترتیب شبه مرتبه اول، مرتبه شبه دوم، انتشار دیفرانسیل داخل و مدل های جنبشی تمپکین برای تطابق با داده های تجربی مورد استفاده قرار گرفت. سینتیک شبه مرتبه دوم بستگی دارد، به خوبی به سینتیک شبه مرتبه دوم بستگی دارد. تجزیه و تحلیل FT-IR و SEM به طور موثر جذب Brown HE2G در جاذب را پشتیبانی می کند.