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

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ABSTRACT

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 nonionic 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) (λmax: 471 nm) was obtained from cotton dyeing industry, Thiruvallur District, Tamil Nadu. It was used as received without
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 °C 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 °C. 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 ± 1°C) 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:

\[
\text{% Removal of dye} = \frac{C_i - C_e}{C_i} \times 100
\]

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:

\[
\text{Carbon (C) + H}_2\text{O}^+ \rightarrow \text{C--H}^+ + \text{H}_2\text{O}
\]

\[
\text{C--H}^+ + \text{Dye}^- + \text{H}_2\text{O} \rightarrow \text{C--Dye}^- + \text{H}_3\text{O}^+
\]

![Figure 2. pH dependence of BHE2G on *O. officinalis* at 30°C.](image)

**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](image)

**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 on *O. officinalis*](image)
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).

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 to 1 (Table 1), the adsorption is favorable between 20-150 mg/L.

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, \( \beta \) is the desorption constant and \( K_R \) is R-P isotherm constant (g L\(^{-1}\)). The isotherm constants \( \beta \), \( K_R \) 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:

\[ Q_e = K_T C_e + \beta \ln C_e \]

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

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.

$$\text{CAO} + [\text{Dye}] \rightleftharpoons [\text{CAO-Dye}] ; K_{eq}=0.638$$

The high heat of adsorption ($\beta = 15.637$) from the tempkin model and high monolayer adsorption capacity ($Q_e = 76.560 \text{ mg/g}$) from Langmuir model indicates the nature of adsorption was chemisorptions.

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

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameter</th>
<th>BHE2G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/n</td>
<td>0.448</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>9.433</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.957</td>
</tr>
<tr>
<td></td>
<td>$Q_m$</td>
<td>76.560</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$K_L$</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>0.552</td>
</tr>
<tr>
<td>R-P</td>
<td>$K_R$</td>
<td>0.106</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.971</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>15.637</td>
</tr>
<tr>
<td>Tempkin</td>
<td>$K_T$</td>
<td>0.638</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.985</td>
</tr>
</tbody>
</table>

**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.

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{t}{Q_e}$$

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].

**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:

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

where, $a$ (mg/g) is the initial sorption rate and $\beta$ (g/mg) is the desorption constant. The slope and intercept of the plot of $Q_t$ versus $\ln t$, gives the value of $a$ and $\beta$ (Figure 9). As can be seen from the table 3, the higher value of sorption constant, $a = 4.806$, 1.569 and 0.934; the lower value of desorption constant, $\beta = 0.316$, 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.
The adsorption process is feasible at lower temperature and decreasing availability of dye molecule near the adsorbent. 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 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

**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:

\[
\ln \left( \frac{Q_{eq}}{C_e} \right) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \\
\Delta G^o = \Delta H^o - T\Delta S^o
\]

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 (-\(\Delta H^o/R\)) and intercept (\(\Delta S^o/R\)) of the plots \(\ln (Q_e m/C_e)\) vs \(1/T\) (figure 11) is used to determine the thermodynamic parameters such as \(\Delta G^o\), \(\Delta H^o\) and \(\Delta S^o\) 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**

<table>
<thead>
<tr>
<th>Dye</th>
<th>(\Delta H^o) (kJ/mol)</th>
<th>(\Delta S^o) (kJ/mol)</th>
<th>(\Delta G^o) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHE2G</td>
<td>-71.881</td>
<td>-0.227</td>
<td>-0.0105</td>
</tr>
<tr>
<td></td>
<td>303K</td>
<td>1.191</td>
<td>0.924</td>
</tr>
<tr>
<td></td>
<td>313K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The enthalpy change (\(\Delta H^o\)), entropy change (\(\Delta S^o\)) and free energy change (\(\Delta G^o\)) 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. 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 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

**Intra-particle diffusion model**

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

\[
Q_t = k_id \cdot t^{1/2} + C_i
\]

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**

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameter</th>
<th>303K</th>
<th>313K</th>
<th>323K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagergren’s first order</td>
<td>(Q_{(exp)})</td>
<td>15.7143</td>
<td>11.4286</td>
<td>7.7143</td>
</tr>
<tr>
<td></td>
<td>(Q_{(cal)})</td>
<td>5.1617</td>
<td>8.5073</td>
<td>8.2536</td>
</tr>
<tr>
<td></td>
<td>(K_1)</td>
<td>-0.0395</td>
<td>-0.0047</td>
<td>0.0002</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.5627</td>
<td>0.5622</td>
<td>0.0003</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>(Q_{(exp)})</td>
<td>16.2137</td>
<td>12.5045</td>
<td>8.5300</td>
</tr>
<tr>
<td></td>
<td>(K_2)</td>
<td>0.0105</td>
<td>0.0056</td>
<td>0.0062</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9997</td>
<td>0.9911</td>
<td>0.9848</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>4.8063</td>
<td>1.5693</td>
<td>0.9342</td>
</tr>
<tr>
<td>Elovich</td>
<td>(B)</td>
<td>0.3159</td>
<td>0.3689</td>
<td>0.6089</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9025</td>
<td>0.8879</td>
<td>0.9580</td>
</tr>
<tr>
<td></td>
<td>(k_e)</td>
<td>0.9448</td>
<td>0.6856</td>
<td>0.5593</td>
</tr>
<tr>
<td></td>
<td>(C_i)</td>
<td>5.7308</td>
<td>3.4917</td>
<td>0.9204</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.6329</td>
<td>0.6616</td>
<td>0.8749</td>
</tr>
</tbody>
</table>
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*

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Frequency in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O – str</td>
<td>1610</td>
</tr>
<tr>
<td></td>
<td>1704</td>
</tr>
<tr>
<td></td>
<td>1245</td>
</tr>
<tr>
<td>sym-C-H (Fermi resonance)</td>
<td>1385</td>
</tr>
<tr>
<td>O-H – str</td>
<td>3000</td>
</tr>
<tr>
<td>N-H – str</td>
<td>3250</td>
</tr>
<tr>
<td>N-H ion - str, amine salt</td>
<td>2350</td>
</tr>
</tbody>
</table>

![Figure 11. FTIR spectrum of *O. officinalis* a) before and b) after adsorption of BHE-2G](image1)

**CONCLUSION**

- *Calendula officinalis* was identified as a 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**

The authors are thankful to Sri Sairam Engineering College to carry out this research work.

**REFERENCES**


Persian Abstract

چکیده

یک ماده کم هزینه است که به عنوان جاذب برای حذف رنگ نساجی Calendula officinalis استفاده می‌شود. pH فلکت که برابر 8.5 می‌باشد. با استفاده از آزمایشگاهی Brown HE-2G مورد قرار گرفت. تجزیه و تحلیل قرار گرفت، نتایج به دست آمده در توافق جذب با مدل لانگمیور و مدل ایزوتوپ می‌باشند. جذب به دست آمده در توافق خوب با مدل ایزوتوپ و مدل همکاری اند. فناوری که در این مطالعه مورد استفاده قرار گرفت به ترتیب 56.81 میلی گرم بر گرم بر می‌رود. به دست آمده در توافق خوب با مدل لانگمیور و مدل ایزوتوپ می‌باشد. به سویی که در این مطالعه مورد استفاده قرار گرفت، به خوبی به سیستم شبه حرارتی دوم یک Tip می‌گردد. تجزیه و تحلیل به طور مولکول جذب HE2G در جاذب را پیشنهاد می‌کنند.