THERMODYNAMIC AND KINETIC ANALYSIS OF BASIC GREEN-4 DYE REMOVAL FROM AQUEOUS SOLUTIONS USING ADSORPTION TECHNIQUE

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Abstract

In this work, a local sunflower husk (SFH) was used as a natural surface for removing Basic Green-4 (BG4) dye, as a water-soluble pollutant. The effect of initial concentration, contact time, the mass of surface of the dye with the SFH as well as the medium temperature was studied.

The application of Langmuir, Freundlich isotherms on the collected data of the adsorption process found to harmonize to Freundlich equation more than that of Langmuir. However, the adsorbed mass of BG4 dye showed a direct increase with the increase of SFH mass and equilibrium was achieved within a 60min window.

The interaction of BG4 with SFH surface was spontaneous and exothermic. The empirical kinetic outcomes at ambient temperatures were applied to pseudo 1st and 2nd order equations. However, the process has found to follow the rate of pseudo 2nd order, while the intraparticle diffusion was considered as a step in the mechanism of adsorption.

Key words: Sunflower husk, Green-4 dye, Freundlich, adsorption, Langmuir

Introduction

Wastewater is a major source of water pollution since it contains different kinds of environmental, and industrial pollutants (Al-Janabi et al., 2011; Crini and Lichtfouse, 2019). One of the most common environmental pollutants is dyes which are widely spread and commonly be found in industries discharges (Al-Janabi et al., 2012) like paper rubber, textile, dye, motor oils (Abdul Kareem and Al-Janabi, 2018) and plastic manufacturing industries (Ramaraju, Manoj Kumar Reddy and Subrahmanyam, 2014; Teng, San Wong and Low, 2014). The chemical nature and the type of functional groups of dyes, make them carcinogenic and mutagenic agents for the environment and the aquatic habitat even when they exist in low concentrations (Jain et al., 2007). The origin of synthesis and the complex chemical structure of dyes make the process of dye removal from water resources as a complicated process (Elmoubarki et al., 2015).

Different techniques were used for the treatment and control of chemical pollutants (Al-Janabi, 2016), not limited to; sedimentation, coagulation, ion exchange, oxidation, foam flotation, and adsorption techniques (Franca et al., 2010; Sharma, Saikia and Das, 2014). The adsorption techniques are considered one of the most preferred approaches used in the treatment of water pollution, due to the simplicity of the method, equipment that used, affordability, as well as the availability of adsorption surfaces locally (Kar, Smith and Subramanian, 2009). The widely used surface in wastewater treatment is activated carbon prepared from different natural sources. Other types of cheap and natural adsorption surfaces were also used, like, wheat husk (Sivakumar et al., 2012), palm leaf (Uddin et al., 2009), coconut shells (Ardejani et al., 2008; Tanyildizi, 2011), lemon peel, date waste and coffee waste(Liang et al., 2014).

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The aim of this research is to work out the capacity of the SFH sorbent to seize aqueous pollution such as Basic Green-4 dye (BG4). Thermodynamic and kinetic parameters were studied in addition to the mechanism of the adsorption.

**Materials and Methods**

UV-Vis. Spectrophotometer, Shimadzu. PC 1650, Japan.

Malachite Green (Basic Green-4) (BG4) dye, Henan DaKen Chemical Co. (99%), China (Fig. 1).

*Standard solutions of BG4 dye*: A set of BG4 dye standard solutions of different concentrations (10–200 ppm) were prepared in distilled water.

*Preparation of SFH sorbent bed*: SFH powder was washed with distilled water and dried for 2 hr under sunlight then overnight in an oven at 60°C.

**Effect of mass**

An exact mass of the SFH in the range of (0.05-0.2g) were mixed with a 10ml of BG4 solution (100 ppm), were used and the adsorption experiment was done at 25°C.

**The adsorption isotherm**

The isotherms of BG4 adsorption was performed by shaking 0.05g of SFH into 10ml dye in the concentrations of (10–200 ppm). After 60 min of shaking at pH = 5.4, the mixture was centrifuged for 30min at about 3000 rpm and the supernatant analyzed spectrometrically at l_{max} = 617 nm to quantify BG4 dye (Fig. 2).

The amount of BG4 adsorbed was obtained using equation (1) (Bencheikh Lehocine, 1989; M. Dharmendirakumar, G.Vijayakumar et al., 2015):

\[
q_e = \frac{V}{m} \left( \frac{C_o}{C_e} \right)
\]

Where; q_e is the adsorbed mass of the dye (mg/g) on a certain mass of the sorbent bed of SHF m (g), V (L) is the volume of BG4 solution, while C_o and C_e (µg/ml) is the startup concentration of BG4 and at equilibrium, respectively.

The adsorption process and the value estimation of the thermodynamic functions were performed at temperatures ranging from 25 to 45°C.

**Kinetic Studies**

The contact time of the adsorption process was tested on a thermostatic shaker by mixing 0.05g of SFH into 10 ml BG4 solutions (100 ppm), at 25°C. The residual concentration of dye was determined at different durations, the removal dye percentage was calculated as follows (Blázquez et al., 2010):

\[
\% \text{Removal} = \frac{C_o}{C_e} \times 100
\]

**Effect of ionic strength**

Different concentrations of sodium chloride (0.05-0.25µg/mg) were used to determine the influence of the ionic-strength on the adsorption of BG4 dye.

**Results and Discussion**

**Effect of SFH mass**

The influence of SFH mass on the quantity of BG4 adsorbed was studied. It was shown that the quantity adsorbed decreased, as the mass of SFH increased from 0.01 to 0.2g, (Fig. 3). The surface area of any surface, so the sum of active sites that is free for adsorption is increased as the mass of surface increased (Lakshmipathy and Sarada, 2015). While (Fig. 4) showing the adsorption of BG4 onto SFH at 25°C.

The amount of BG4 adsorbed on the SFH surface, increased as the concentration of dye increased. The driving force of concentration gradually proportional directly with increasing the concentration of dye and hence increase the mobility of the molecules in the liquid phase

![Chemical structure of BG4](Fig. 1: The chemical structure of the BG4.)

![UV-Vis Spectrum of BG4 dye exhibit an absorbance maximum at l_{max} = 617 nm.](Fig. 2: UV-Vis Spectrum of BG4 dye exhibit an absorbance maximum at l_{max} = 617 nm.)
where: $K_f$ and $n$ are the experimental constants of Freundlich.

The Freundlich constants and the correlation coefficient ($K_f = 21.37$, $n = 2.74$, $r^2 = 0.983$), were obtained from linear plot, (Fig. 5).

**Thermodynamic of the adsorption process**

A decrease in the adsorption of BG4 on SFH with increasing the heat from 25°C to 45°C, means it is an exothermic adsorption process (Fig. 6). This is expected as an increase in temperature weakens the attraction forces of BG4 molecules with the sorbent surface (Suteu and Malutan, 2012).

The equations (4-6) were used to calculate the functions of ($\Delta H$, $\Delta G$, and $\Delta S$)

$$\ln X_m \propto \frac{RT}{\ln C_0 - \ln q_e}$$

$$G = RT \ln K$$

$$H = T \Delta S$$

The adsorption of BG4 dye on SFH has a negative value of free energy and entropy (Table 1). This refers to the spontaneity of the adsorption process and to the uniform distribution of dye molecules on the SFH surface (Valizadeh et al., 2016).

**Kinetic analysis**

The rate of BG4 removal increase with time as appears from Figure 7.

Adsorption process on the solid surfaces occurs firstly on the adsorbent external surface until equilibria. The removal rate of the dye out of the aqueous medium is governed by a molecular diffusion of BG4 on the adsorbent internal surface. While the inner side has higher attraction towards adsorbent molecules. Thus, the content of BG4 adsorbed by the SFH surface is increased (Alghamdi et al., 2019).
The adsorption mechanism and kinetics of dye were evaluated by applying pseudo 1st order and pseudo 2nd order equations. The pseudo 1st order kinetics is given by the (equation 7) (Hsieh et al., 2004).

\[ \ln q_t = \ln q_e - k_1 t \]  

As: \( q_e \) and \( q_t \) were the amount in (mg/g) of BG4 that adsorbed at equilibria and at the time t (min.) respectively, \( k_1 \) is the rate constant of the pseudo 1st order model.

\( k_1 \) for the adsorption of BG4 dye on SFH was worked out from the slope of the plot in equation (7) and (Fig. 8).

The linear form of the pseudo-second-order model is (Hsieh et al., 2004):

\[ \frac{t}{q_t} = \frac{1}{q_e h} + \frac{1}{q_e} t \]  

As: \( h \) is the rate of startup adsorption as \( h = k_2 q_e^2 \), \( k_2 \) is the rate constant of pseudo 2nd order.

A straight line resulting from plotting \( \frac{t}{q_t} \) versus t

Fig. 8: Linear plot of pseudo 1st order kinetic of BG4 adsorption.

![Fig. 8: Linear plot of pseudo 1st order kinetic of BG4 adsorption.](image)

Table 1: Thermodynamic functions of BG4 adsorption on SFH.

<table>
<thead>
<tr>
<th>( \Delta H(\text{kJ/mol}) )</th>
<th>( \Delta G(\text{kJ/mol}) )</th>
<th>( \Delta S(\text{J/(mol.K)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-29.323</td>
<td>-41.594</td>
<td>-41.190</td>
</tr>
</tbody>
</table>

Table 2: Kinetic constants for adsorption of BG4 dye on SFH at 25°C.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Pseudo 1st order</th>
<th>Pseudo 2nd order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( q_e ) (mg/g)</td>
</tr>
<tr>
<td>298</td>
<td>0.117</td>
<td>1.115</td>
</tr>
</tbody>
</table>

Fig. 7: The relation between the removal percentage of BG4 and time of contact at 25°C.

Fig. 9: Pseudo 2nd order kinetic of BG4 adsorption.

![Fig. 9: Pseudo 2nd order kinetic of BG4 adsorption.](image)

The experimental kinetic data were analyzed by intraparticle diffusion kinetics to calculate the rate-determining step of adsorption process.
As: \[ q_t = k_d t^{1/2} \] is the rate constant of intraparticles.

The correlation of \( q_t \) against \( t^{1/2} \) exhibited high linearity (Figure 10). However, \( k_d, C \) and \( r^2 \) were 0.174, 18.467 and 0.953, respectively. Nevertheless, the trend line does not go through the point of origin which conclude that the step of intraparticle diffusion might not be the controlling step in the adsorption mechanism. In addition, the adsorption process may include boundary layer effect as appear from the value of constant \( C \) (Mohammadi, Daemi and Barikani, 2014; AL-TAWEEL, 2014; NAS, 2019; Sarma, Gupta and Bhattacharyya, 2019).

**Effect of ionic strength**

The results (Fig. 11) show that the quantity of BG4 adsorbed was decreased with increasing the quantity of NaCl which can be attributed to the competition of Na\(^+\) ions with dye on the active sites of SFH surface (Veli and Alyüz, 2007).

**Conclusion**

SFH surface has a high capacity to capture BG4 molecules from their aqueous solutions. The adsorption outcome of BG4 dye was well obeyed Freundlich isotherm and the thermodynamic parameters exhibited that adsorption of BG4 dye by SFH was spontaneous and exothermic in nature. The adsorption process follows Pseudo second-order kinetics at 25°C, and the intraparticle diffusion kinetics shows that more rate-controlling steps that control the adsorption process.

**References**


