Removal of Indigo Carmine from Aqueous Solutions by Graphene Oxide: Kinetic and Equilibrium Studies

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ABSTRACT
In this study the GO was oxidized and applied as an adsorbent for the removal of indigo carmine (IC) molecules from aqueous solution. The GO was prepared starting with natural graphite powder using the Hummers method. The GO was characterized by scanning electron microscopy (SEM) measurements. Also X-ray powder diffractometer was performed to determine the crystallinity of GO. The effects of various parameters such as solution pH (2.0-10.0), adsorbent dose (0.001 g to 0.1 g), contact time (5.0-145 min), and temperature (25-40°C) were investigated. The results demonstrated that the maximum percentage of IC adsorption was found at pH 5.0 and 40 min contact time with 0.02 g GO. Kinetic adsorption data were analysed using the first-order model and the pseudo-second-order model. The regression results indicated that the adsorption kinetics was more accurately showed by the pseudo-second-order model. The equilibrium data in aqueous solutions were fitted to Langmuir and Freundlich isotherms and the equilibrium adsorption of IC was best described by the Langmuir model.

Keywords: Adsorption, Graphene oxide, Indigo carmine, Isotherms, Thermodynamics

INTRODUCTION
One of the most important industrial pollutants, especially in textile industries, is the dyes that even at low concentrations of one parts per million (ppm) are recognizable by naked eyes. The history of using the first industrial dye goes back to 1856. Since then, production and usage of this matter have increased and it is estimated that 7 × 10^5 tons of this material are produced every year. It is also estimated that about 10% of the produced dyes are annually entered into the environment, which causes problems for both humans and the wildlife. Indigo carmine, together with the indigo, is the most representative indigoid dye, and it is widely used in the textile industry for cotton cloths and other denim products. Indigo carmine one of the most hazardous substances in industrial wastewater that can cause severe health problems in human being, since they exhibit high biotoxicity and possible mutagenic and carcinogenic effects [1,2]. Thus, the removal of dye from colored sewage has attracted increasing attention. Various technologies containing coagulation/flocculation, biological treatment, chemical oxidation, adsorption, membrane separation and ion exchange have been developed [3-8].

Among these techniques, adsorption has been intended to be simple, ease of operation, and highly efficient. A wide variety of materials were reported for dye removal, including polymer, activated carbon, zeolite, clay, etc. [9-12]. Considering the pollutant control at present, it is still necessary for the development of new adsorbent materials with high adsorption capacities and removal efficiencies. Recently, Graphene and graphene oxide (GO), have been intensively developed, and found to exhibit a unique range of properties.

With its unique small bandgap, the preparation of a graphene oxide based semiconductor nanocomposite provides a highly efficient visible-light driven photocatalyst for wastewater treatment. Due to its high thermal, mechanical and optical properties, the addition of a graphene oxide to an inorganic semiconductor has the Inclination to Unveil synergism of properties of unique materials [13,14]. In comparison with carbon nanotubes, GO has the higher specific surface area and the sp2 hybrid carbon nanostructure that could easily obtained from natural graphite through a easy chemical oxidation-exfoliation-reduction procedure at a low cost [15,16]. In addition, through the chemical oxidation modification, many oxygen-containing functional groups appear in GO [17-19].
In the present study, graphene oxide (GO) was used for removal of indigo carmine molecules from aqueous solution. The effects of pH, GO dose, contact time, and temperature on adsorption capacity of GO have been investigated. Based on these studies, the Langmuir and Freundlich isotherm models were used to fit the equilibrium data. Finally, the adsorption kinetics was evaluated.

MATERIALS AND METHODS

Chemicals and reagents
All chemicals and reagents were purchased from Merck (Darmstadt, Germany). Double-distilled water was used in all experiments. All adsorption experiment was conducted in triplicates to assure the repeatability of our results.

Synthesis of graphene oxide (GO)
Graphite oxide (GO) was prepared starting with natural graphite powder using the Hummers method [20]. A mixture of graphite (2 g), NaNO₃ (1 g), and concentrated sulfuric acid (100 ml) was stirred for 30 min within an ice bath. Under vigorous stirring, KMnO₄ (8 g) was added slowly to the suspension. The rate of addition carefully controlled to keep the reaction temperature below 10 °C. Then the mixture was transferred to an ice bath to 35°C and stirred for three hours, and then 200 ml of H₂O was slowly added. The reaction temperature was rapidly increased to 98°C for 1 hour was fixed. At this stage, mixed color gradually became brown. Water (400 ml) added to the system. Then 30 ml of H₂O₂ (30%) to reduce the residual permanganate was used. Color dark brown mixture gradually changed into bright yellow. For purification, the mixture was washed by rinsing and centrifugation with 5% HCl then deionized (DI) water for several times until the water pH close to 7. After filtration and vacuum dried over night at room temperature, dry and solid graphene oxide (GO) was obtained [21].

Adsorption Experiments
For adsorption experiments solution with initial concentration of 40, 50 and 60 micro mol per liter of color indigo carmine prepared and pH of the solution using 0.5 M solutions of hydrochloric acid and/or sodium hydroxide in the range of 2 to 8 were set. Finally, by adding 0.02 grams of graphene oxide to soluble, samples for 10 minutes on shaker at 180 rpm at room temperature were placed. After completion of the shake and separate absorbent, the absorption rate of each solution by spectrophotometer readings and The sorption efficiency (%) and amounts of adsorbed IC (qe) by GO were calculated using Equations (1) and (2), respectively:

\[ \text{Sorption efficiency (\%)} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]  
\[ q_e = \left( \frac{(C_o - C_e)}{V} \right) m \]  
\[ R(\%) = \left( \frac{(C_o - C_e)}{C_o} \right) \times 100 \]

Where \( C_o \) and \( C_e \) (mg/L) are the concentrations of IC initially and at equilibrium, respectively. \( V \) is the volume of the solution (L), \( m \) is the weight of adsorbent (g) and \( q_e \) (mg/g) is the amount of adsorbed IC at equilibrium [22, 23]. Finally, the V(V) removal percent (R%) was calculated by Equation (3).

RESULTS AND DISCUSSION

Instrumentation
Unicom 5625 UV/Vis Spectrophotometer, Perkin Elmer, USA was used for the determination of IC at \( \lambda_{\text{max}} = 645 \) nm.

Graphene Oxide Characterization
Scanning electron microscopy (SEM) was employed to study the morphology of prepared samples. Figure 1 shows the typical SEM images of GO obtained by a Hummers method. The GO show the sheet-like structure with large thickness, wrinkled edge, and smooth surface. XRD pattern of GO nanosheets shown in Figure 2. The diffraction peak at 2θ=26.58 is indicated to the (002) planes of GO. Distances between the layers of GO possible due to formation of oxygen-containing functional groups, such as hydroxyl, epoxide and carboxyl. Thus, the XRD pattern it can be concluded that graphite powder is almost completely oxidized.

Optimization of adsorption
An initial study show that absorption efficiency is highly depends on the solution pH, contact time, GO dose and temperature.
Effect of pH

The initial pH of solutions in the whole adsorption process is an important variable because it can affect the dye adsorption process via changing the surface charge of an adsorbent and the ionization behavior of adsorbent and dye. The effect of pH on the adsorption of IC molecules was studied in the pH range of 2.0-10.0 with a stirring time of 90 min and IC concentration fixed at 40 mg L\(^{-1}\). The results are shown in Figure 3. According to it, the adsorption percentage of IC increased by increasing the pH of the aqueous solution from 1.0 to 5.0, and a maximum adsorption at pH 5.0 was achieved. When pH was further increased from 6.0 to 10.0, the adsorption percentage is reduced.

The dispersion property of the nanomaterial is severely affected by zeta-potential which was analyzed for prepared GO samples. P. Leroy et al. reported that the zeta-potential is one of the most important parameters of ion adsorption and electrostatic interaction between GO and dye [24]. The pH of point of zero charge (pHzpc) is important property and shows that the electrical neutrality of adsorbent and surface at a particular value of pH. pHzpc for the GO was determined around 3.3 that can continuously change to 7.5 by non-covalent electrochemical attachment [24,25]. When the pH is low (<pHzpc), the reduction in IC adsorption efficiency can be ascribed to the increase in the proton concentration. A proton could compete with the IC in absorption mechanism. Thus With increasing pH (>pHzpc), the
positive charge of the surface Reduced and the repulsion between the positive surface and IC molecules is reduced too much that leads to higher adsorption. When pH of the solution was higher than 5.0, reducing the adsorption efficiency of IC molecules might result from the other IC oxidation states that formed in high pH, which affected adsorption capacity on the oxidized IC. Thus, pH 5.0 was chosen as the optimum pH of the system. The results are in agreement with those reported in the literature [26,27].

**Effect of adsorbent dose**

The adsorbent dosage is an important factor for the sorption capacity of IC. The effect of amount of GO on the IC removal at 40 mg L⁻¹ for three concentration 0.01, 0.02 and 0.03 gr IC is shown in Figure 4. It was observed that the removal efficiency increases from 32.1% to 86.8% with an increase in adsorbent dose from 0.001 to 0.02 g and the maximum adsorption was observed at 0.02 g. This is because of the increase in the surface area and availability of more active sites for adsorption. Thus 0.20 g of adsorbent was choose as adsorbent dose for all latter experiments in this paper because of higher sorption efficiency and passable sorption capacity. The results are according to those reported in the literature [28,29].

**Effect of temperature**

To determine the effect of temperature, adsorption experiments were carried out at range 25°C to 45°C. The adsorption capacity decreases with increase in temperature. Which illustrates that the adsorption process of adsorption of IC molecules on GO is exothermic in nature. The decrease in the absorption rate with increased temperature may be attributed to the may be attributed to weaken the adsorption forces between the active sites of the adsorbents and adsorbate species as well as between the adjacent molecules of the adsorbed phases.

**Effect of time**

Equilibrium time is a major parameter in the design of economic systems used for wastewater treatment. The results showed that the adsorption of molecules IC molecules by GO enhancement with the increasing of time and reached equilibrium at about 35 min. The reason may access a high number of vacant binding active sites for dye at the
beginning and gradual covering of binding sites, that reduced the adsorption speed and in the end when the equilibrium was obtained.

**Adsorption kinetics**

In order to study the mechanism of adsorption, the first-order and pseudo-second order kinetics models were used to fit the experimental data. To investigate the kinetics of adsorption, three different initial concentrations of IC were selected 30, 40, and 50 mg L⁻¹. Linear form of the pseudo-first order rate equation by Lagergren [30] is given by Equation (4):

\[
\ln(q_e - q_t) = \ln(q_e) - k_1 t / 2.303
\]

Where \( q_e \) and \( q_t \) (mg g⁻¹) are the amounts of IC adsorbed per unit weight of the adsorbent at equilibrium and time \( t \), respectively, \( k_1 \) is the equilibrium rate constant of pseudo-first order (min⁻¹) and \( t \) is the contact time (min). Values of \( k_1 \) were obtained from the slopes of the linear plots of \( \ln(q_e - q_t) \) versus \( t \), as shown in Figure 5. This model is based on the assumption that the rate of absorption is proportional to the number of free sites available. The pseudo-second order kinetic rate equation [31] is based on the assumption, that the rate of absorption is proportional to the number of occupied sites. The linear form can be written as:

\[
t / q_t = 1 / k_2 q_e^2 + t / q_e
\]

Where \( k_2 \) (g mg⁻¹ min⁻¹) is the second order rate constant of adsorption. From the plots of \( t / q_t \) against \( t \), \( q_e \) and \( k_2 \) are evaluated. The constants of Equations (4) and (5) and correlation coefficients were obtained from Figure 5 at various concentrations and mentioned in Table 1. The calculated determination coefficients \( R^2 \) from the three initial dye concentrations of the pseudo-second order model were higher than that model. In addition to, the \( q_{cal} \) value for the pseudo-second order model is more similar to the experimental value \( q_{exp} \). The results demonstrate that pseudo-second-order model fitted the experimental data better. It can be used to describe adsorption kinetics. It also confirmed that the rate limiting step may include chemical absorption valence forces by sharing or exchanging of electrons between adsorbent and adsorbate. The \( k_2 \) values for IC adsorption were calculated to be 0.005, 0.011, and 0.006 mg⁻¹g⁻¹min⁻¹, respectively, for 30, 40, and 50 mg L⁻¹ IC desorption. The low value of rate constant \( k_2 \) proposed that the adsorption rate decreased with the increase in time and the adsorption rate was proportional to the number of unoccupied sites.

**Figure 5:** (a) First-order kinetic plot and (b) pseudo-second-order kinetic plot for the adsorption of IC onto GO at 25 WC.

\[
t / q_t = 1 / k_2 q_e^2 + t / q_e
\]

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<th>q (con)</th>
<th>k (min⁻¹)</th>
<th>R²</th>
<th>q (cal)</th>
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**Adsorption Isotherms**

The results of concentration optimization showed that adsorption of IC molecules by GO increased with the increasing of concentration and reached equilibrium at about 12 mol/L. The sorption isotherms reveal the special relation between equilibrium concentration of adsorbate in the bulk and the adsorbed value at the surface. Some adsorption isotherms equations are accessible which the two most used are Langmuir and Freundlich isotherms. The Langmuir adsorption
isotherm assumed that adsorption takes place at special homogeneous sites within adsorbent and has found successful use too many adsorption processes of monolayer sorption. The Langmuir isotherm can be written in the form:

\[ \frac{C_e}{q_e} = \left( \frac{C_e}{q_m} \right) + \left( \frac{1}{q_m b_1} \right) \]  

(6)

Where \( q_m \) (mg g\(^{-1}\)), \( q_e \) (mg/g) and \( C_e \) (mg/L) are the maximum adsorption capacity, the amount of dye adsorbed per unit of adsorbent at equilibrium concentration and equilibrium dye concentration, respectively. The essential features of the Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant separation factor \( R_L \) that is given by the following equation:

\[ R_L = \frac{1}{1 + b C_0} \]  

(7)

Where \( b \) (L mg\(^{-1}\)) is the Langmuir constant and \( C_0 \) (mg L\(^{-1}\)) is initial concentration of adsorbate. The value of \( R_L \) shows the type of the isotherm to be either irreversible (\( R_L = 0 \)), linear (\( R_L < 1 \)), unfavorable (\( R_L > 1 \)) and or favorable (\( 0 < R_L < 1 \)).

According to Table 2, the \( R_L \) values were in the range of 0-1 at 25\(^\circ\)C that indicating the sorption of IC molecules on GO is favorable under the conditions used in this study. Freundlich adsorption model takes the following form:

\[ \ln q_e = \left( \frac{1}{n} \right) \ln C_e + \ln K_f \]  

(8)

Where, \( K_f \) is the Freundlich constant (L/mg), and \( n \) is Freundlich constant depending on the intensity of adsorption. Values of \( n > 1 \) represent adsorption process is favorable [32]. As shown in Table 2, the calculated value of \( n \) was found 2.519. This implies that the adsorption of IC molecules on GO is favorable under the conditions used in this research.

Figure 6 shows the fitting curves to the experimental data and parameters calculated by the two models are summarized in Table 2. The correlation coefficients (R\(^2\)) for the Langmuir and Freundlich models were 0.990 and 0.972, respectively. It is clear that the adsorption curves fitted better with the Langmuir isotherm than Freundlich isotherm which these results are in agreement with those reported in the literature [33-35]. In our study, \( n \) value was higher than 1 that shows adsorption intensity was good. The high \( n \) and \( K_f \) values indicate that the IC molecules are favorably adsorbed on the GO as well as the easy separation of the IC from the aqueous solutions. The \( K_f \) value can be accepted and workable as a low-cost and new potential adsorption system. The results also indicate that adsorption of IC on GO is an exothermic process and the adsorption of IC by GO takes place in a monolayer adsorption manner.

![Figure 6: (a) Langmuir and (b) Freundlich isotherms for the adsorption of IC onto GO at 25\(^\circ\)C.](image)

### Table 2: Isotherm parameters of adsorption of IC onto GO

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<td>K(_f)</td>
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### CONCLUSION

The present research shows that graphene oxide (GO) is an effective adsorbent for the adsorption of indigo carmine from aqueous solutions. The GO was prepared starting with natural graphite powder using the Hummers method. The effects of adsorption parameters, such as the pH, amount of GO used, temperature, and contact time were studied and optimized. Kinetic studies revealed that pseudo-second-order model was better suitable than a pseudo-first-order model with the correlation coefficients >0.99. The higher correlation coefficients (R\(^2\)) of the Langmuir equation suggest that the Langmuir isotherm can be used to fit the experimental adsorption data and evaluate the maximum dye adsorption capacities of adsorbents.
REFERENCES


