Graphene Oxide Decorated with Nickel Cobaltite Nanoparticles as an Adsorbent for Cationic Methyl Green Dye: Kinetic, Isotherm, and Thermodynamic Studies

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Abstract

In this study, graphene oxide (GO) flakes were embellished with NiCo$_2$O$_4$ (NC) nanoparticles by in situ deposition, and the produced composite (NC: GO) was utilized as an adsorbent to remove methyl green dye (MG) from aqueous solutions. The successful coating of graphene oxide with nickel cobaltite nanoparticles (NC) was verified using FT-IR, SEM and X-ray diffraction (XRD) studies. The crystalline particle sizes of NC nanoparticles and NC nanoparticles decorated GO were 10.53 nm and 9.30 nm respectively. The impact of several experimental factors, including time of contact, the dosage of adsorbent, and temperature were investigated. The optimal contact time and adsorbent dosage were 120 minutes and 3 mg/L, respectively. The adsorption data fitted better to Freundlich isotherm. Four kinetic models were used to track the adsorption process: a pseudo first-order equation, a pseudo second-order equation, an intraparticle diffusion equation, and the Boyd equation. Modeling of the experimental data revealed that the adsorption kinetics was well represented by the pseudo-second order model($R^2=0.9945$) with a rate constant of 3.2 ×10$^{-3}$ (g/mg. min). MG dye is gradually absorbed by the NC nanoparticles through intraparticle diffusion and is afterward held in smaller pores. The values of the thermodynamic analysis showed that the MG dye adsorption was an endothermic in nature, spontaneous and physisorption process.

Keywords: Boyd equation, Debye-Scherer equation, Intraparticle diffusion, Interplanar spacing, Pseudo first order model.

Introduction

Given the increased rate of pollution and depletion of natural resources, researchers and environmentalists are concerned about water contamination because of its negative effects on the ecosystem. Water can contain a variety of pollutants, including heavy metals, organic compounds, chemical waste, and dyes. Dyes are categorized as significant pollutants on humans and the environment. Many of them have a history of causing cancer or being toxic. Dye degradation is more challenging due to their xenobiotic characteristics, resistance to a variety of chemicals and oxidizing agents, and complicated aromatic structures. To treat dye-containing wastewater diverse techniques can be used, such as membrane filtration, coagulation, nano-filtration and flocculation, reverse and forward osmosis, biological treatments, nano-photocatalyst and advanced oxidative processes. However, several of these techniques have certain setbacks and are expensive and energy-intensive. Adsorption is still one of the best treatment alternatives due to its simplicity, ease of use, and low cost in contrast to other approaches.

Nano-adsorbents including oxides of transitional elements like Mn, Fe, Co, and Ni, bimetallic
oxides and graphene and its derivative are frequently used in the removal of various pollutants because of their roles in the adsorption process. Graphene oxide, one of the two-dimensional structures of carbon allotropes, is synthesized by chemically oxidizing the graphite layers. GO are widely used in wastewater treatment due to its large surface area, high water dispersibility, high mechanical strength, and decorated with reactive functional groups on the basal plane and the edge. Similarly, bimetallic oxides, cobaltite in particular, which has the general formula $\text{MC}_2\text{O}_4\text{O}_3$ (M = Zn, Mn, Cu, Fe, Ni, or Mg), has been suggested as a potential material to consider for adsorption performance due to its electrical and magnetic properties, availability in nature, low cost, less toxic, and environmentally friendly.

Materials and Methods

Graphite powder with an average size of 75 μm was purchased from Fluka. $\text{H}_2\text{SO}_4$ (98%), $\text{H}_2\text{O}_2$ (30%), NaNO$_3$, and KMN$_2$O$_4$ were supplied by Merck. HCl and NaOH were purchased from GCC Company. Co(NO$_3$)$_2$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O were supplied by BDH. Methyl green (MG) (Molecular Weight $\text{C}_{25}\text{H}_{30}\text{Cl}_2\text{N}_3$; maximum wavelength ($\lambda_{\text{max}}$=618 nm) supplied by wilmad-limited-United Kingdom, was used without further purification. The structural investigation and the average size of the prepared materials were studied by X-ray powder diffractometer (XRD). Shimadzu (Japan) profiles were registered using CuK$_\alpha$ (1.54060), Voltage: 40.0 kV and Current: 30.0 mA. The features of functional groups were examined by the FT-IR spectra on the Shimadzu, 8400s, (Japan) spectrophotometer.

Fabrication of Graphite Oxide (GTO) and Nickel Cobaltite-graphene Oxide

Nanocomposite (NC: GO)

The GTO was synthesized using Hummer method. A mixture of 10 g graphite and 5 g sodium nitrate was mixed vigorously with 230 mL of 98% sulphuric acid in an ice bath for half an hour. Then 30 g of potassium permanganate was added carefully and stepwise to prevent the temperature exceeding 20 °C. After that, the ice bath was removed and the temperature brought to 35 ± 3 °C and maintained for half an hour. The second step involved adding 460 mL of water to raise the temperature to 98 °C for 15 minutes. The color suspension was brown. The suspension was further diluted with 1400 mL of warm water. The colorless soluble manganese sulphate was obtained by treating the suspension with 30% hydrogen peroxide. Finally, the warm suspension was filtered and washed with 5% HCl solution and then with distilled water until pH reached 7. The obtained filter cake was dried in a vacuum oven for 48 hours. In the subsequent process, NC nanoparticles were in situ deposited on GO flakes. Firstly 0.05 g of GTO was dispersed in 10 mL distilled water using a probe ultrasonic for 1 hour. Then added slowly to a mixture of the same types and molarity solutions of Ni(NO$_3$)$_2$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O. The mixture's pH was raised to 9 gradually by adding 50 mL of 0.75 M NaOH under vigorous stirring. The temperature maintained between 50 – 60 °C. The formed gel was collected by centrifugation, washed, dried at 100 °C, and finally calcined at 300 °C for 2 hours. The resulting nanocomposite was denoted as NC: GO.

Calibration Curve of MG Dye

Prior to the adsorption procedure, standard solutions in the range of 1–15 mg/L were prepared daily by serial dilution from the MG stock solution, which was prepared by dissolving 0.1 g in 1000 ml of distilled water. The absorption was assessed using a UV-visible spectrophotometer at $\lambda_{\text{max}}$=618 nm. The calibration curve was created using the Beer-Lambert law by plotting the absorption results against the standard dye solution concentration. The determined slope served as a guide for determining
concentration in the remaining experiments. Fig. 1 displays the calibration curve.

![Calibration curve of MG dye solution](image)

**Figure 1. Calibration curve of MG dye solution.**

Adsortion Experiments

The adsorption experiments were carried out in a thermostatic shaking water bath with varying temperatures of 15, 25, and 35 °C and a constant rotational speed of 120 rpm. To identify the influence of NC: GO dosage on MG dye adsorption, different amounts of adsorbent NC: GO ranging from 1 mg to 4.5 mg (0.5 mg intervals) were introduced into 10 mL of fixed initial concentration of MG solution at 25 °C until the equilibrium time was reached. The adsorption process to reach equilibrium was studied, and 10 mL of MG aqueous solution was mixed with 3 mg of the adsorbent (NC: GO) at different periods (5 to 180 minutes). The initial MG concentration was 15 mg/L. The supernatant solution and adsorbent were separated by centrifugation at 5000 rpm for 10 minutes. The quantity of MG adsorbed onto NC: GO was calculated using the following Eq. 1.

\[
q_t = \frac{V(c_0 - c_t)}{m}
\]

Where \(c_0\) and \(c_t\) are the initial concentration and concentration at (t) time respectively, \(q_t\) is the amount of adsorbate MG (mg/g) at t time, \(V\) volume of MG dye solution (L), and \(m\) weight of adsorbent (g). To examine the impact of temperature, the temperature was held at a different range of temperatures (15– 25– 35 °C) with varying concentrations of MG dye. The amount of MG adsorption at equilibrium \(q_e\) (mg/g) was calculated using the above equation where \(q_t = q_e\) and \(c_t = c_e\). A spectrophotometric approach was used to measure the remaining final MG concentrations in the solution at a maximum wavelength \(\lambda_{\text{max}}\) of 618 nm.

Results and Discussion

Characterization

The XRD diffractogram of (GO), NC undoped, and NC doped with GO (NC: GO) are shown in Fig. 2. XRD patterns of GO show distinct diffraction peaks at 10.08 (d= 8.76 nm), the increasing interlayer space of GO, and the formation of a broad graphitic peak with lower intensity indicates intercalated many oxygen functional groups within the graphite Lattice. NC characteristic peaks and JCPDS (card no. 073-1702) are in good agreement. The matching in (d) and the small displacement change in (2θ) support the preparation of NC. Table 1 lists the prepared NC and the JCPDS interplanar spacing (d) and diffraction peak positions (2θ). The pattern of the nanocomposite (NC: GO) exhibits the same peaks that are attributed to NC. No peaks of GO were seen, which indicates that NC nanoparticles are coating the surface of GO nanosheets, or, to put it another way, that NC has virtually completely covered the GO surface.

![XRD patterns](image)

**Table 1. The interplanar spacing (d) and diffraction peak positions of NiCo_2O_4 compared with JCPDS (card no. 073-1702 and 00-020-0781).**

<table>
<thead>
<tr>
<th>Mille index</th>
<th>NiCo_2O_4 prepared</th>
<th>JCPDS (073-1702)</th>
<th>NiCo_2O_4 prepared</th>
<th>JCPDS (073-1702)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)(^a)</td>
<td>19.145°</td>
<td>18.928</td>
<td>4.63</td>
<td>-</td>
</tr>
<tr>
<td>(220)</td>
<td>31.261°</td>
<td>31.152°</td>
<td>2.85</td>
<td>2.87</td>
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<tr>
<td>(311)</td>
<td>36.849°</td>
<td>36.705°</td>
<td>2.43</td>
<td>2.45</td>
</tr>
<tr>
<td>(400)</td>
<td>44.792°</td>
<td>44.635°</td>
<td>2.02</td>
<td>2.03</td>
</tr>
<tr>
<td>(422)(^b)</td>
<td>55.066°</td>
<td>44.635°</td>
<td>1.65</td>
<td>-</td>
</tr>
<tr>
<td>(511)</td>
<td>59.231°</td>
<td>59.115°</td>
<td>1.55</td>
<td>1.56</td>
</tr>
<tr>
<td>(440)</td>
<td>65.022°</td>
<td>64.963°</td>
<td>1.43</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Using the Debye-Scherer equation shown below, the average crystallite size (d) in nanometers of the NC nanoparticles and NC: GO were determined.

\[
d = \frac{0.94 \lambda}{\beta D \cos \theta}
\]

\[\text{Table 1. The interplanar spacing (d) and diffraction peak positions of NiCo}_2\text{O}_4 \text{ compared with JCPDS (card no. 073-1702 and 00-020-0781).}\]
Where \( \lambda \) is the X-ray wavelength of Cu-K\( \alpha \) = 0.1542 nm, the diffraction peak's full width at half maximum (FWHM) is \( \beta_0 \) in radians, and the Bragg diffraction angle peak is \( \theta \). The calculated average crystallite size of NC and NC on the GO surface is 10.53 nm and 9.30 nm respectively. The reduction in crystallite size demonstrated that the inclusion of nanoparticles prevents the restacking of the GO layers in the composite and also minimizes particle agglomeration.

The FT-IR spectra of GO, NC, and NC: GO nanocomposite are displayed in Fig. 3. The stretching vibration at 1744 cm\(^{-1}\) is related to the C=O at the edge of GO sheets. Peaks at 1279 and 1073 cm\(^{-1}\) are associated to C-O stretching in epoxy groups\(^{26}\), while peaks at 1619 cm\(^{-1}\) and 1457 cm\(^{-1}\) are related to C=C stretching of aromatic rings\(^{27}\). 1153 cm\(^{-1}\) and 712 cm\(^{-1}\) attributed to stretching of tertiary OH and OH out of plane respectively\(^{28}\). The H-O-H bending vibration mode of NC indicated by the bands at 1508 cm\(^{-1}\) and 1371 cm\(^{-1}\). The weak bands at 662 cm\(^{-1}\) and 550 cm\(^{-1}\) were attributed to the stretching vibration of the Ni-O and Co-O, which were moved to 557 cm\(^{-1}\) and 655 cm\(^{-1}\) as in the case of NC: GO nanocomposite\(^{29}\). The wide band between 2500 and 3500 cm\(^{-1}\) caused by O-H stretching. The FT-IR fingerprints for both the NC and GO are present in the spectrum of the NC: GO nanocomposite, further supporting the composite's formation.
Figure 4. NC: GO nanocomposite analysis: SEM images in 35 kx, 70 kx and EDX.

Effect of Adsorbent Weight

Fig. 5 shows the impact of the adsorbent NC: GO dose on the adsorption of MG. With the increase of adsorbent weight, the percentage removal of MG increased, going from 41.7 at dose 1 mg/L to 47.59 at dose 3 mg/L. The percentage removal measurements tended to decrease with increasing dosage, the primary cause of this behavior is that during the adsorption process, adsorption sites stay unsaturated, although the number of accessible adsorption sites grows by raising the dosage of the adsorbent. The optimal and economical adsorbent dosage is 3 mg/L as shown in Fig. 5.

Figure 5. Effect of adsorbent dosage (NC: GO) on MG removal, (contact time 60 min, cₑ= 15 mg/L)

Effect of contact time

Equilibrium time is one of the most crucial equilibrium judgment criteria for the design of wastewater treatment systems or adsorption processes. The effect of contact time 5–180 min on the adsorption capabilities of MG over NC: GO at a concentration of 15 mg/L and NC: GO dose of 3 mg/L is shown in Fig. 6. According to Fig. 6, the presence of a very high number of active sites on the adsorbent NC: GO surface may be the reason why the adsorption capacity rose quickly until the contact duration reached 60 min. A plateau reached in contact time ≥ 100 may be due to decrease in the number of surface-active sites or an increase in the repulsive forces between the MG molecules on NC: GO surface and the bulk phase. Additionally, Fig. 6 demonstrates that when the temperature rises, the equilibrium adsorption capacity gradually increased, indicating that the adsorption process was preferred.

Figure 6. Contact time effect of MG adsorption on the 3 mg/10mL dose adsorbent NC: GO at different temperature

Effect of Temperature

By varying the temperatures from 288 to 308 K, the removal percentage (R%) of MG dye was determined using the following Eq. 3.

\[
R\% = \left( \frac{c_o - c_e}{c_o} \right) \times 100
\]

Where the initial and equilibrium concentrations of MG are denoted by \(c_o\) and \(c_e\), respectively. The adsorption of MG onto NC: GO nanocomposite increases as the temperature rises, as can be observed in Fig. 7. This indicates that the adsorption process is endothermic, or put another way, the MG adsorption onto NC: GO surface requires a significant amount of energy to move from the bulk solution to the surface. This behavior is the same as that of the majority of adsorption processes.
Removal (%)
Temperature (K)

Figure 7. The temperature effect on MG adsorption onto NC: GO nanocomposite at room temperature, Initial concentration 15 mg/L.

Adsorption Kinetic Study

The kinetics of the adsorption process was investigated by conducting a series of sorption experiments at a fixed temperature and tracking the amount adsorbed over time. There are multiple steps involved in the process by which an adsorbate binds to an adsorbent at the solid-liquid interface: internal (intraparticle) and external diffusion, in which the adsorbate diffusion from and across the liquid film to the surface of solid particles: Bulk diffusion, in which the adsorbate diffusion from the bulk of the solution to the liquid film encircling the solid: and interaction of the adsorbate with the surface sites through physical or chemical bonds. The study of the kinetics of the adsorption process has led to a considerable understanding of these mechanisms. Thus, the experimental data were represented by four models: the pseudo-first order model (PFO), the pseudo-second order model (PSO), the Weber & Morris kinetic model (intraparticle diffusion ID), and Boyd. The PFO model is usefully expressed in natural logarithmic form as follows:

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

Where the rate constant \( k_1 \) (1/min) and amounts of MG absorbed at equilibrium \( q_e \) (mg/g) can be found from the slope and intercept of the plot \( \ln (q_e - q_t) \) versus time respectively, see Fig. 8. The \( q_t \) (mg/g) represents the amounts of MG absorbed at a time \( t \) in min. The linearized forms of PSO kinetics can be defined according to Eq. 5

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \\
\]

A plot of \( \frac{t}{q_t} \) against time yields straight line then the rate constant \( k_2 \) (g/mg, min) and \( q_e \) can be calculated from the intercept and the slope respectively see Fig. 8. The kinetic parameters with the sum of squares errors (SSE) of PFO and PSO at different temperatures were obtained and summarized in Table 2.

Table 2. Parameters of the pseudo-first, second order kinetic and Weber and Morris kinetic of NC: GO towards MG dye at different temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>288</th>
<th>298</th>
<th>308</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_e, exp (mg/g)</td>
<td>27.57</td>
<td>34.22</td>
<td>39.41</td>
</tr>
<tr>
<td>q_e, cal (mg/g)</td>
<td>15.73</td>
<td>17.02</td>
<td>14.88</td>
</tr>
<tr>
<td>Ki (1/min)</td>
<td>0.0260</td>
<td>0.0378</td>
<td>0.0257</td>
</tr>
<tr>
<td>SSE</td>
<td>0.9474</td>
<td>1.5276</td>
<td>1.1138</td>
</tr>
<tr>
<td>R²</td>
<td>0.9419</td>
<td>0.9549</td>
<td>0.9308</td>
</tr>
<tr>
<td>q_e, cal (mg/g)</td>
<td>28.90</td>
<td>35.46</td>
<td>40.32</td>
</tr>
<tr>
<td>K_2 (g/mg min)</td>
<td>0.0032</td>
<td>0.0047</td>
<td>0.0042</td>
</tr>
<tr>
<td>SSE</td>
<td>0.2442</td>
<td>0.2524</td>
<td>0.0410</td>
</tr>
<tr>
<td>R²</td>
<td>0.9945</td>
<td>0.9991</td>
<td>0.9982</td>
</tr>
<tr>
<td>Weber and Morris model</td>
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<td></td>
</tr>
<tr>
<td>Ki</td>
<td>1.0449</td>
<td>1.1209</td>
<td>1.0356</td>
</tr>
<tr>
<td>c</td>
<td>14.452</td>
<td>21.275</td>
<td>26.569</td>
</tr>
<tr>
<td>R²</td>
<td>0.9628</td>
<td>0.9168</td>
<td>0.9704</td>
</tr>
</tbody>
</table>

Better fit of the kinetic model is shown by higher values of the correlation coefficient (R²) and lower values of the corresponding SSE value. The computed R² value of PSO was much higher than that of the PFO model as shown in Table 2.

Fig. 8 also further supports this model's superior linearity. In addition, the equilibrium capacity values \( q_e \) that were theoretically predicted using the PSO model fit were nearer to the experimental values. As a result, it has been demonstrated that MG adsorption on NC: GO followed PSO adsorption kinetics.
Figure 8. Kinetic models for the adsorption of MG dye onto the adsorbent NC: GO nanocomposite Pseudo-first-order and Pseudo-second-order.

Intraparticle Diffusion Model (ID)

To highlight the rate-limiting step, the Webber–Morris model (ID) was applied Eq. 6.

\[ q_t = k_i \sqrt{t} + C \]  \hspace{1cm} \text{Eq. 6}

From the plot amount adsorbed at t time (qt) against the square root of contact time (\( \sqrt{t} \)), the intraparticle diffusion rate constant \( k_i \) (mg/g.min\(^{1/2}\)) and C (mg/g) is estimated from the slope and intercept respectively see Table 2. The values of C are related to the thickness of the boundary layer. The larger C implies a greater effect on the boundary layer. As shown in Fig. 9, three steps were detected in the whole adsorption process: the initial fragment was ascribed to external diffusion and the second fragment was attributed to intraparticle diffusion, the third fragment may be due to diffusion of the adsorbate MG through smaller pores of adsorbent then followed by the equilibrium due to the low solute concentration of MG in solution. From Fig. 9, we can also observe the straight line fitted didn’t go through the origin sign that the intra-particle diffusion was not the only rate-controlling step\(^{33}\).

Figure 9. Kinetic plot of intra-particle diffusion model

To determine the true rate-controlling step for the adsorption of MG on CN: GO adsorbent Boyd equation\(^{34}\) has been used to analyze kinetic data. It is presented as the following

\[ -\ln(1 - F) = k_b t \]  \hspace{1cm} \text{Eq. 7}

Where \( k_b \) is Boyd constant (min\(^{-1}\)) and F is the fractional attainment of equilibrium can be defined by \( q_t/q_e \). Fig. 10 shows that there is a linear pattern with no zero intercept value, demonstrating the significance of both film diffusion and pore diffusion as regulatory processes for the MG mechanism adsorption on NC: GO\(^{35,36}\).

Figure 10. Boyd plot for MG adsorption onto NC: GO adsorbent

Adsorption Isotherms

The MG adsorption isotherms on NC: GO adsorbent at 288, 298, and 308 K are shown in Fig. 11 and demonstrate that the equilibrium uptake increased as the concentration of MG increased; this might be because there were more MG ions nearby the NC: GO active sites. The fact that the equilibrium adsorption increased with temperature further supports the endothermic nature of the MG adsorption on NC: GO adsorbent.
Figure 11. The effect of temperature on NC: GO ability to adsorb MG dye

The experimental data are generally shown graphically to further explain the interaction between the adsorbate and the adsorbent at a constant temperature. Langmuir and Freundlich's models were used to simulate the data from adsorption isotherms. Langmuir 1916 provided a model for chemical adsorption (chemisorption) 37. The following expression gives the Langmuir equation's linearized form.

\[
\frac{q_e}{c_e} = \frac{1}{q_{\text{max}}k_L} + \frac{c_e}{q_{\text{max}}} \quad \text{..................8}
\]

A plot of \(\frac{q_e}{c_e}\) versus \(c_e\) yields a straight line. The slope can be identified with the amount of MG dye needed to form a monolayer on the surface of NC: GO (\(q_{\text{max}}\) in mg/g) and the intercept with a constant affinity of the adsorption sites (\(k_L\) in L/mg). According to Hall et al 38, the essential characteristics of a Langmuir isotherm can be stated in terms of a dimensionless constant separation factor which is determined using the following equation 37

\[
R_L = \frac{1}{1 + k_Lc_e} \quad \text{..................9}
\]

Where \(c_o\) (mg/L) is the maximum MG dye concentration and \(k_L\) (L/mg) is the Langmuir constant. Table 3 includes the calculated values of \(R_L\) at 288, 298, and 308 K. The current adsorption process is favorable because the \(R_L\) values range from 0 to 1 38 40. An acceptable isotherm that can be utilized for adsorption from solution is the empirical isotherm of Freundlich. The Freundlich isotherm is the type of isotherm that is most appropriate for explaining electrostatic attraction, H-bonding and π-π interaction. The convenient way to write the logarithmic form is as follows:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \quad \text{..................10}
\]

Where \(K_f\) and \(n\) are the capacity adsorption, and intensity of adsorption respectively. The constants \(K_f\) and \(n\) can be concluded from the intercept and slope of the plot \(\ln q_e\) versus \(\ln c_e\). Table 3 summarizes the parameters and \(R^2\) of Langmuir and Freundlich adsorption isotherms. Comparison of the correlation coefficients of Langmuir and Freundlich equations demonstrates that the Freundlich equation fits MG adsorption better than Langmuir. The \(n\) values higher than 1 indicate that the adsorption process on NC: GO adsorbent is physical and has a high degree of heterogeneity 41,42.

### Table 3. Isotherm parameters and correlation coefficients for the adsorption of MG on NC: GO at different temperatures.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameters</th>
<th>Temperatures</th>
<th>288 K</th>
<th>298 K</th>
<th>308 K</th>
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</thead>
<tbody>
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<td>Langmuir</td>
<td>(K_L) (L/mg)</td>
<td>0.21</td>
<td>0.2808</td>
<td>0.2260</td>
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<tr>
<td></td>
<td>(q_{\text{max}}) (mg/g)</td>
<td>32.67</td>
<td>50.00</td>
<td>69.44</td>
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</tr>
<tr>
<td></td>
<td>(R_L)</td>
<td>0.22</td>
<td>0.18</td>
<td>0.21</td>
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</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9132</td>
<td>0.9145</td>
<td>0.9049</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>(K_f) (mg/g)/ (mg/L)^n)</td>
<td>6.18</td>
<td>10.77</td>
<td>12.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(n)</td>
<td>1.69</td>
<td>1.58</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9580</td>
<td>0.9545</td>
<td>0.9836</td>
<td></td>
</tr>
</tbody>
</table>

### Thermodynamic Analysis

To demonstrate how temperature affects the adsorption process of the MG dye on the NC: GO adsorbent, the standard entropy change (\(\Delta S^o\)), enthalpy change (\(\Delta H^o\)), and free energy change (\(\Delta G^o\)) were determined. The standard Gibbs energy change of the adsorption process can be calculated from the constant of the standard thermodynamic equilibrium (\(K_{eq}^o\)) according to Eq. 11

\[
\Delta G^o = -RT \ln K_{eq}^o \quad \text{...............11}
\]

Where \(R\) is the universal gas constant 8.314 J/mole K and \(T\) absolute temperature (K). By graphing \(\ln q_e/c_e\) vs \(q_e\) and extrapolating \(q_e\) to zero it is possible to determine the values of \(K_{eq}^o\) (L/g) 43 as illustrated in Fig. 12.

Figure 12. Plots of \(\ln (q_e/c_e)\) versus \(q_e\) for adsorption of MG on NC: GO adsorbent.
At a given temperature the $\Delta G^\circ$ can be deduced in term of the change in $\Delta S^\circ$ and $\Delta H^\circ$ according to Eq. 12 below

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \hspace{1cm} \ldots \ldots \ldots \ldots. 12$$

By substitution eq.12 in eq. 11 yield

$$\ln K^a = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \hspace{1cm} \ldots \ldots \ldots \ldots. 13$$

plotting $\ln K^a$ versus $(1/T)$ gives a linear relationship. The slope is equal to $-\Delta H^\circ/R$, and the intercept equal to $\Delta S^\circ/R$. The values of $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ are listed in Table 4. The spontaneous character $\Delta G^\circ < 0$ and $\Delta G^\circ < 20 \text{ KJ/mole}$ suggests that the molecules of MG dye are more responsive to NC: GO adsorb. The adsorption process can be categorized as an endothermic and physisorption process based on the magnitude of $\Delta H^\circ > 0$ and $\Delta H^\circ < 80 \text{ KJ/mol}$. Additionally, the positive $\Delta S^\circ$ value showed that the degrees of freedom at the solid-liquid interface expanded during the adsorption process 44.

### Table 4. Thermodynamic Parameters for adsorption of MG onto the NC: GO adsorbent

<table>
<thead>
<tr>
<th>T/K</th>
<th>$\Delta G^\circ$ (KJ/mol)</th>
<th>$\Delta S^\circ$ (J/mole.K)</th>
<th>$\Delta H^\circ$ (KJ/mole)</th>
<th>$E_a$ (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>-5.00</td>
<td>107.99</td>
<td>25.83</td>
<td>9.57</td>
</tr>
<tr>
<td>298</td>
<td>-6.89</td>
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<td></td>
</tr>
<tr>
<td>308</td>
<td>-7.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Conclusion**

NC: GO nanocomposite has been synthesized as adsorbent to remove MG dye from an aqueous solution by in situ deposition of nickel cobaltite on GO sheets. The XRD, SEM and FTIR analyses were used to investigate the physicochemical properties of GO, NC and NC: GO nanocomposite. XRD analysis showed a good agreement between NC characteristic peaks and JCPDS. Through this study, the optimum value of adsorbent dosage was obtained 3 mg and the contact time was 120 minutes. The equilibrium data have been examined utilizing the Langmuir and Freundlich isotherms. The isotherm's distinctive parameters and associated correlation coefficients have been identified. The Freundlich isotherm offers better correlation which means that the electrostatic interaction between the MG dye and the functional groups on the NC: GO adsorbent controls the dyes' ability to adsorb. The kinetic data were best represented by the pseudo-second order kinetic model. According to Boyd and Weber and Morris models the results indicated that both film diffusion and intraparticle diffusion are involved in the mechanism adsorption of MG. The calculation of thermodynamic parameters revealed that the adsorption of MG is a spontaneous, a physisorption process, and endothermic process.

Furthermore, the straight-line plot of $\ln K_2$ against $1/T$ Fig. 13 is used to compute the activation energy ($E_a$) from the slope using the Arrhenius formula as shown below

$$\ln k_2 = \ln A - \frac{E_a}{RT} \hspace{1cm} \ldots \ldots \ldots \ldots. 14$$

Where $A$ and $k_2$ are the Arrhenius factor and the PSO rate constant respectively. The magnitude of the activation energy gives a clue as to whether the adsorption is mostly chemical or physical. Higher activation energies (40–800 kJ/mol) imply chemisorption, while lower activation energies (5–40 kJ/mol) are typical of physisorption 43, 44. For the MG adsorption onto NC: GO, the outcome is 32.16 kJ/mol (see Table 4), suggesting that the adsorption has a low potential barrier and corresponds to a physisorption process 45-47.

![Figure 13. ln K2 versus 1/T](image-url)
Acknowledgment

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Authors’ Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Besides, the Figures and Images, which are not ours, have been given the permission for re-publication attached with the manuscript.

Authors’ Contribution Statement

M. A. A. and S. H. M. contributed to the design and implementation of the research. M. A. A. prepared GO, NC and its composite and performed the analysis of the results FT-IR, XRD. M. A. A. made the adsorption experiments. S. H. M. worked on the manuscript, designed the figures, and interpreted the results.

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تزيين أوكسيد الجرافين بدقائق كوبليت النيكل النانوية كسطح ماز للصبغة الميثيل الأخضر الكاتيونية: دراسات حركية، إيزيثيرمية، وديناميكية حرارية
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الخلاصة
تم في هذه الدراسة، تزيين دقاعات أكسيد الجرافين (GO) بجزيئات كوبليت النيكل النانوية (NC) باستخدام متراكم المحمض (NC: GO) كسطح ماز لإزالة صبغة الميثيل الأخضر (MG) عن طريق التنقية في المحلول المائي. تم التحقق من التغطية الناجحة لجزيئات كوبليت النيكل النانوية (NC) بواسطة دراسات FT-IR. كانت أحيان التجميد البلوري للNC و للمزئين GO والمزيج GO:NC قبل التوالي تم دراستها تأثير العديد من العوامل التيربية، بما في ذلك زمن التلامس، وكمية السطح المائي، ودرجة الحرارة. وكان وقت التلامس الأمثل 3 دقائق و 9 مليم / لتر على التوالي. تلائم بيانات الأمتارز بشكل أفضل مع نموذج Frendlich. تم استخدام أربعة نماذج حركة للعوامل التيربية: معادلة إمتساق من الدرجة الأولى، معادلة إمتساق من الدرجة الثانية، معادلة الانتشار داخل السطح، ومعادلة بو د. أظهرت نماذج الامتارز التي تم تطبيقها بشكل جيد، معادلة الانتشار الثانية الامتارز (R² = 0.9945) مع معدل ثابت سرعة يبلغ 3.2 × 10⁻⁹ (جم / مليم. دقيقة). تم امتصاص صبغة MG تدريجياً بواسطة الجسيمات النانوية من NC خلال الانتشار داخل الجسيمات وتم الاحتفاظ بها بعد ذلك في مسما أصغر. أظهرت قيم التحليل الديناميكي الحراري أن عملية الامتارز كانت ممتصة للحرارة بطيئاً، وتكاثرية وعملية الامتارز فيزيائية.

الكلمات المفتاحية: معادلة بو د، معادلة دميتراشر، الانتشار داخل الجسيمات، المسافات البينية، النموذج الامتاز من الدرجة الأولى.