Graphene Oxide/Co$_3$O$_4$ Nanocomposite: Synthesis, Characterization, and Its Adsorption Capacity for the Removal of Organic Dye Pollutants from Water

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Abstract

In this work, graphene oxide/Co$_3$O$_4$ nanocomposite was synthesized via hydrothermal decomposition of [Co(en)$_3$](NO$_3$)$_3$ complex onto graphene oxide nanosheets. The as-prepared nanocomposite (denoted as GO/Co$_3$O$_4$) was structurally characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopies (TEM and SEM), energy dispersive X-ray (EDX) spectroscopy, magnetic measurements, and N$_2$ adsorption–desorption analysis. The results demonstrated successful immobilization of Co$_3$O$_4$ nanoparticles with an average diameter size of around 12.5 nm on the surface of graphene oxide nanosheets. The adsorption performance of GO/Co$_3$O$_4$ nanocomposite was investigated towards different organic dyes in aqueous solutions. The results displayed that the adsorption rate of the GO/Co$_3$O$_4$ nanocomposite was 98% for methylene blue (MB) in 12 min, and 66% and 45% for Rhodamine B (RhB) and methyl orange (MO) in 40 min, respectively. The effects of various important parameters including adsorbent dosage, contact time, pH, and temperature on the adsorption process were investigated in detail. The equilibrium adsorption data were better fitted by Langmuir isotherm. Adsorption kinetics is well-modeled using pseudo-second-order model. Different thermodynamic parameters indicated that the adsorption process was physisorption and spontaneous. The findings of the present work highlighted facile fabrication of GO/Co$_3$O$_4$ and its application for rapid and efficient removal of MB from wastewater.

Keywords: Graphene oxide nanosheets, Co$_3$O$_4$ nanoparticles, Hydrothermal decomposition, Nanocomposite, Adsorption performance, Organic dyes.

1. Introduction

Many chemical industries such as paper, plastics, cosmetics, leather, printing, food, textile, etc. use dyes for coloring their products and release the various types of dyes into water bodies which prevent the penetration of sunlight, retard the photosynthetic reactions, and affect aquatic life.$^{1-4}$ Most dye molecules have aromatic rings in their structures, which make them highly toxic, non-biodegradable, carcinogenic, and mutagenic to both human being and aquatic life.$^5$ Hence, it is essential to remove or minimize dyes to permissible levels, without disturbing the quality of water to be able to use it in diverse industrial and agricultural applications.$^6$ A wide array of wastewater treatment techniques including membrane filtration, centrifugation, photodegradation, chemical coagulation, and adsorption have been developed for removing dyes from wastewater. Among these technologies, adsorption is the most widely used method due to its versatility, wide applicability, and economic feasibility.$^7$ Activated carbon, clays, zeolites, polymeric materials, etc. have been applied to adsorb dyes from wastewater. However, these adsorbents suffer from either low adsorption capacities or separation problem. Hence, the adsorbent having both mentioned characteristics is immensely desired in both science and technology societies.$^8$ In material science research, a great deal of attention has been focused on graphene, a carbon allotrope with a two-dimensional sheet-like structure with many unique features such as high electrical conductivity, mechanical flexibility, chemical and thermal stability, high surface functionality, and large surface area.$^7$ Due to strong interplane interactions, graphene and its derivatives tend to aggregate in a layer-by-layer manner which, as a result, a significant part of their surface area is lost. The use of the
dispersion of single-layered GO as an absorbent allows one to utilize the surface area to the utmost extent, but these GO sheets are difficult to collect from water. This problem can be solved via chemical modification of graphene by the process of attaching organic groups or inorganic particles onto graphite oxide (GO) surfaces which can result not only in physical separation of the resultant functionalized graphene sheets but also in the possible formation of a stable dispersed phase of graphene in the synthesis process\textsuperscript{10-12} and keep the surface area and pore volume at high levels which is required for applications such as adsorption processes and photocatalysis.\textsuperscript{13}

In recent years, various transition metal oxides nanoparticles such as \(\text{Fe}_2\text{O}_3\), \(\text{ZnO}\), \(\text{Fe}_3\text{O}_4\), \(\text{TiO}_2\), etc., have been deposited on GO nanosheets. For instance, Amino-functionalized \(\text{Fe}_3\text{O}_4\) (\(\text{NH}_2\text{-Fe}_3\text{O}_4\)) particles were deposited on graphene oxide sheets and were used to adsorb Methylene Blue (MB) and Neutral Red (NR) from aqueous solution by Xie et al.\textsuperscript{14} The adsorption test of dyes demonstrated that it only took 30 min for MB and 90 min for NR to reach equilibrium. Luo et al. fabricated magnetic cyclodextrin/graphene oxide (MCGO) materials and investigated their application as excellent adsorbents for methylene blue.\textsuperscript{15} MCGO demonstrated extremely fast MB-removal from wastewater with high removal efficiency within 50 min. Li et al. prepared a magnetic \(\text{CoFe}_2\text{O}_4\)-functionalized graphene sheet (\(\text{CoFe}_2\text{O}_4\)-FGS) nanocomposite via a facile hydrothermal method and used it to adsorb methyl orange.\textsuperscript{16} The observed maximum adsorption capacity at 10 mg L\textsuperscript{-1} initial concentration was 71.54 mg g\textsuperscript{-1}. In another study, Fan et al. prepared a magnetic chitosan-GO (MCFO) nanocomposite through covalent bonding of chitosan to the surface of \(\text{Fe}_3\text{O}_4\) nanoparticles followed by covalent functionalization of GO with magnetic chitosan which acted as a good adsorbent to adsorb MB from aqueous solutions.\textsuperscript{17} Yao et al. also fabricated \(\text{Fe}_3\text{O}_4\)/SiO\(_2\)/GO nanocomposite through a covalent bonding technique and used it as an adsorbent for the removal of MB from aqueous solution.\textsuperscript{18} Maximum MB adsorption capacities were 97, 102.6, and 111.1 mg g\textsuperscript{-1} at 25, 45, and 60 °C, respectively.

Spinel-type cobalt oxide (\(\text{Co}_3\text{O}_4\)) is an important magnetic p-type semiconductor oxide and its synthesis and properties have attracted considerable attention owing to its prominent applications in heterogeneous catalysis, energy storage and conversion, sensors, devices, etc.\textsuperscript{19-25} For this reason, various nanostructures of \(\text{Co}_3\text{O}_4\) such as nanoparticles, nanoplates, nanorods, nanotubes, nanodiscs, nanoflowers, nanocubes and hollow microspheres structures have been prepared by using different synthesis methods.\textsuperscript{26-33} To the best of our knowledge, the investigation of adsorption properties of GO/\(\text{Co}_3\text{O}_4\) nanocomposites has not been reported yet. In this study, we presented a solvothermal approach for the production of GO/\(\text{Co}_3\text{O}_4\) nanocomposite. The resulting products was characterized by FT-IR, XRD, Raman, FE-SEM, EDX, TEM, and VSM techniques and its adsorption properties in removing dye molecules from aqueous solutions were investigated.

2. Experimental

2.1. Materials

Methyl orange (\(\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}\), MO), methylene blue (\(\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\), MB), Rhodamine B (\(\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3\)), RhB), Cobalt (II)-chlorid hexahydrate, and all other materials and solvents were purchased from Merck chemical Co (Germany). All chemical materials were of analytical grade and were used as received without further purification.

2.2. Synthesis of \(\text{Co}_3\text{O}_4\) Nanoparticles

First, \([\text{Co(en)}_3]([\text{NO}_3]_3\) complex was prepared via the simple reaction of an aqueous solution of \([\text{Co(en)}_3]\text{Cl}_3\) with concentrated nitric acid according to the reported method.\textsuperscript{34} To prepare \(\text{Co}_3\text{O}_4\) nanoparticles, \([\text{Co(en)}_3]\) (\(\text{NO}_3\))\(_3\) complex was decomposed at 250 °C for 1 h in an electric furnace under ambient air. The decomposition product was collected for characterization.

2.3. Synthesis of Graphene Oxide/\(\text{Co}_3\text{O}_4\) Nanocomposite (GO/\(\text{Co}_3\text{O}_4\))

Graphene oxide (GO) was prepared by the oxidation of graphite powder under acidic conditions according to modified Hummers method using a mixture of \(\text{H}_2\text{SO}_4\), \(\text{NaNO}_3\), and \(\text{KMnO}_4\).\textsuperscript{35,36} For the synthesis of GO/\(\text{Co}_3\text{O}_4\) nanocomposite, 50 mg GO was dispersed into 20 mL deionized water by sonication for 1 h to achieve a uniform dispersion of GO. 100 mg as-prepared \(\text{Co}_3\text{O}_4\) nanoparticles were dispersed in deionized water for 15 min and were gradually added into GO suspension. The mixture was sonicated for 30 min and transferred into an autoclave for hydrothermal treatment at 180 °C for 24 h. The resultant product was separated by centrifugation and washed with deionized water, and dried in an oven at 60 °C for 12 h.

2.4. Methods of Characterization

Fourier-transform infrared spectra were obtained on Shimadzu FT-IR 8400S (Japan) with temperature controlled high sensitivity detector (DLATGS detector) in the scan range of 500–4000 cm\textsuperscript{-1} using KBr pellet. The XRD patterns were obtained on a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Ka radiation (\(\lambda = 1.5406\) Å) for phase determination samples. Optical absorption spectra of dyes were obtained on a Cary 100 UV-Vis spectrophotometer in the wavelength range of 200–800 nm. A vibrating sample magnetometer (VSM, Magnetic Daneshpajoh Kashan Co., Iran) was employed to measure magnetic parameter at room temperature. Particle size was ob-
served by a transmission electron microscope (Philips CM120) at the accelerating voltage of 100 kV. SEM images were obtained on MIRA3 TESCAN Field Emission Scanning Electron Microscope equipped with Energy Dispersive X-ray (EDX) analyzer for the elemental analysis of the sample. N$_2$ adsorption-desorption measurements were performed at 77 K (Micromeritics Tristar ASAP 3000) using Brunauer-Emmett-Teller (BET) method.

2.5 Adsorption Tests

Adsorption experiments were performed by using 30 ml solution with known MB concentration and varying the amount of GO/Co$_3$O$_4$ as the adsorbent from 10 to 30 mg in 40 min. The initial pH of MB solution was adjusted in the range of 4–12 by dropwise adding 0.1 mol/L NaOH or 0.1 mol/L HCl solutions. After adsorption was completed, the solution was separated from the precipitate by centrifugation at 5000 rpm for 5 min. The concentrations of the dye in the solutions after different time intervals were determined with a UV-visible spectrophotometer at the wavelength of 664 nm ($\lambda_{\text{max}}$). The amount of MB adsorbed onto GO/Co$_3$O$_4$ nanocomposite ($q_t$) and its removal rate ($R\%$) were calculated by the following equations:

$$q_t = (C_0 - C_t)\frac{V}{m}, \quad R\% = \frac{(C_0 - C_t)100}{C_0} = \frac{(A_0 - A_t)100}{A_0}$$  \hspace{1cm} (1)

where $C_0$ and $C_t$ (mg/L) are liquid-phase concentrations of dye at initial and at time $t$, respectively. $V$ (L) is the volume of the solution and $m$ (g) is the mass of the used adsorbent. $A_0$ and $A_t$ are the absorbance of MB before and after the adsorption, respectively.

3. Results and Discussion

3.1 Characterization of the GO/Co$_3$O$_4$ Nanocomposite

The FT-IR spectra of the samples are shown in Figure 1. For the starting [Co(en)$_3$][NO$_3$]$_2$ complex, the characteristic stretching bands of NH$_2$, CH$_2$, NO$_3$ were appeared at about 3100–3400, 2951 and 1380 cm$^{-1}$, respectively.$^{37}$ As can be seen in the spectrum of Co$_3$O$_4$ (Figure 1(b)), almost all bands associated with the complex obviously disappeared when the complex was decomposed at 250 °C and only two strong bands at 569 and 663 cm$^{-1}$ were observed which confirmed the spinel structure of Co$_3$O$_4$. The former band was attributed to the stretching vibration mode of Co(III)–O and the latter band could be assigned to Co(II)–O bond.$^{38}$ The formation of Co$_3$O$_4$ from the [Co(en)$_3$][NO$_3$]$_2$ complex can be related to the explosive decomposition of the complex via an intramolecular redox process occurring between the ethylenediamine (en) ligands and NO$_3^-$ ions as reducing and oxidizing agents, respectively. This reaction resulted in the formation of solid Co$_3$O$_4$ and gaseous products i.e. CO$_2$, H$_2$O and NO (NO, N$_2$O and NO$_2$).$^{38}$ Although the exact reaction is unclear and intermediates and gaseous products had not been identified directly, the formation of Co$_3$O$_4$ can be expressed as follows: [Co(en)$_3$][NO$_3$]$_2$ (s) → Co$_3$O$_4$(s) + CO$_2$(g) + H$_2$O(g) + NO (NO(g) + N$_2$O(g) + NO$_2$(g)). In FT-IR spectrum of GO (Figure 2(c)) obvious characteristic peaks of GO could be seen, including C=O stretching vibrations of COOH groups (1726 cm$^{-1}$), graphitic C=C stretching vibrations (1618 cm$^{-1}$), O-H deformation vibrations of tertiary C-OH (1398 cm$^{-1}$), C-O stretching vibrations of epoxy/alkoxy groups (1026 cm$^{-1}$) and O-H stretching vibrations ( 3100–3700 cm$^{-1}$).$^{39}$ However, as can be seen in Figure 2(d), after hydrothermal treatment the band of C=O was disappeared and the intensity of O-H and C-O bands were decreased, which indicated the removal of oxygen-containing functional groups and reduction of GO. This finding confirms the formation of reduced graphene oxide (rGO) in the composite and the restoration of a graphitic structure in graphene.$^{40}$ Moreover, the two strong absorption peaks in the spectrum of GO/Co$_3$O$_4$ at lower

![Figure 1. FT-IR spectra of (a) [Co(en)$_3$][NO$_3$]$_2$ complex, (b) Co$_3$O$_4$, (c) GO, and (d) GO/Co$_3$O$_4$.](image-url)
frequencies (in the 400–600 cm⁻¹ range) could be assigned to the stretching vibrations of Co-O bonds of Co₃O₄ phase. This result confirmed the formation of GO/Co₃O₄ nanocomposite.

In order to further identify the chemical composition and structure of the prepared samples, powder X-ray diffraction (XRD) was conducted. Figure 2 displays the XRD patterns of Co₃O₄ and GO/Co₃O₄ nanocomposite. The diffraction patterns in Figures 2(a) and (b) are similar and can be indexed to the Co₃O₄ phase (JCPDS No. 78-1970). Moreover, no characteristic diffraction peaks for GO were observed in the pattern indicating that GO nanosheets were not stacked during the synthesis process. The reason can be attributed to the fact that Co₃O₄ nanoparticles anchored on the surfaces of GO prevented the exfoliated GO nanosheets from restacking. However, a broad characteristic peak for graphene nanosheets at about 2θ = 23° appeared, suggesting that GO was reduced to graphene during the formation of the nanocomposite. The average domain size of Co₃O₄ nanoparticles was calculated to be approximately 13 nm by the Scherrer formula: \[ D_{\text{XRD}} = \frac{0.9\lambda}{\beta \cos \theta}, \]

where \( D_{\text{XRD}} \) is average crystalline size; \( \lambda \), \( \beta \), and \( \theta \) are wavelength of Cu Kα radiation, full width at half maximum of the diffraction peak, and Bragg angle, respectively.⁴¹

Compared to GO, it was clear that D and G bands of GO/Co₃O₄ were down shifted by 10 cm⁻¹. The red shifts of D and G bands for GO/Co₃O₄ provided evidence for charge transfer between GO and Co₃O₄, which indicated a strong interaction between them. Raman spectra further confirmed the successful synthesis of GO/Co₃O₄ composite.

SEM images indicating the microstructural features of GO, Co₃O₄, GO/Co₃O₄ nanocomposite are shown in Figure 4. SEM image of pure GO in Figure 4(a) shows layered structure of GO having large stacks, possibly consisting of hundreds of graphene oxide nanosheets. It should also be noted that the surfaces of GO sheets were quite flat and smooth. Figure 4(b) shows SEM micrograph of sphere-like Co₃O₄ nanoparticles. The SEM images of GO/Co₃O₄ in Figures 4(c) and (d) clearly show graphene oxide nanosheets were successfully decorated with Co₃O₄ nanoparticles. It can be clearly seen that the Co₃O₄ nanoparticles were well deposited on GO which were a flexible interleaved structure. Some wrinkles are found on the surface, which may be important for preventing aggregation of GO and maintaining high surface area, which could be a great benefit to its adsorption ability. On the contrary with pure GO sheets, the surfaces of GO nanosheets in the nanocomposite were rough, and the edges were highly crumpled.

The morphologies and microstructures of the as-prepared Co₃O₄ and GO/Co₃O₄ samples were further

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Figure 4. SEM images of (a) GO, (b) Co$_3$O$_4$, and (c,d) GO/Co$_3$O$_4$.

Figure 5. TEM images of (a,b) Co$_3$O$_4$, and (c,d) GO/Co$_3$O$_4$ nanocomposite.
analyzed by TEM. Figures 5(a) and (b) show the typical TEM images of the Co$_3$O$_4$ displaying that the product consists of a large quantity of nearly uniform monodispersed spheres with the diameter size in the range of 10–25 nm which loosely aggregated. As can be seen in Figures 5(c) and (d), the almost aggregated graphene sheets are fully exfoliated and decorated homogeneously with sphere-like Co$_3$O$_4$ nanoparticles having an average diameter of 12 nm in consistent with the average particle size calculated from Debye-Scherer formula. No obvious aggregation was seen in Figures 5(c) or 4(d). The GO sheets could not only prevent agglomeration of the Co$_3$O$_4$ nanoparticles and enable a good dispersion of these spherical particles, but also substantially enhance the specific surface area of the composite.

Further investigation was carried out by energy dispersive X-ray spectroscopy (EDX) to characterize the composition of the as-prepared GO/Co$_3$O$_4$ nanocomposite as shown in Figure 6. The presence of C, O and Co elements in the composites could be proven by the EDX elemental spectrum of GO/Co$_3$O$_4$. The inset of Figure 6 shows a representative SEM image of the nanocomposite with corresponding EDX elemental mappings. As presented in the inset of Figure 6, the distribution of corresponding elemental mappings confirmed the existence of C, O, and Co. From the maps, it can be seen that the elements were uniformly distributed over the nanocomposite, confirming the homogeneity of the sample. The results further indicated that Co$_3$O$_4$ nanocrystals had been successfully loaded on the surface of GO.

The magnetization curves of Co$_3$O$_4$ and GO/Co$_3$O$_4$ samples were measured at room temperature, as shown in Figure 7. Obviously, the shape of magnetic hysteresis loop of Co$_3$O$_4$ sample shows a ferromagnetic behavior. The fine hysteresis loop of GO/Co$_3$O$_4$ nanocomposite exhibited a typical weak ferromagnetic behavior at room temperature. The saturation magnetization (Ms) of Co$_3$O$_4$ nanoparticles sample is 1.3 emu g$^{-1}$. In contrast, the GO/Co$_3$O$_4$ nanocomposite has smaller Ms value (0.18 emu g$^{-1}$), due to the presence of non-magnetic GO component, weakening its magnetic property.

Nitrogen adsorption experiments were used to evaluate the pore size and structure of samples. Figure 8 shows the nitrogen adsorption–desorption isotherms and the corresponding pore size distributions curves (the insets) for GO, Co$_3$O$_4$ and GO/Co$_3$O$_4$ samples. The isotherms in Figure 8(a)–(c) can be classified to type IV with H4 hysteresis loop for GO and H3-hysteresis loops for Co$_3$O$_4$ and GO/Co$_3$O$_4$ samples (according to the IUPAC classification), which indicate the presence of mesopores. The interconnected porous network could mainly contribute to the formation of mesopores of GO and the aggregation of GO nanosheets could result in the formation of the mesopores. Some textural properties of the samples were listed in Table 1. As shown in Table 1, the materials were mesoporous. The BET surface area and pore volume of GO/Co$_3$O$_4$ were higher than the values of GO. It can be concluded that the addition of Co$_3$O$_4$ had a great effect on the structure of GO, greatly increasing the surface area and pore volume, which were all favorable factors for improving the adsorption performance.

![Figure 6. EDX spectrum of GO/Co3O4 nanocomposite. The inset shows the corresponding EDX elemental mappings.](image)

![Figure 7. Magnetic hysteresis loops of (a) Co3O4 nanoparticles and (b) GO/Co3O4 nanocomposite.](image)

| Entry | Sample  | $S_{BET}$ (m$^2$/g) | $V_p$ (cm$^3$/g) | $D_p$ (nm) |
|-------|---------|---------------------|-----------------|------------|
| 1     | GO      | 79.15               | 0.126           | 1.26       |
| 2     | Co$_3$O$_4$ | 103.67          | 0.338           | 1.27       |
| 3     | GO/Co$_3$O$_4$ | 107.27          | 0.336           | 1.27       |

$S_{BET}$: BET surface area. $V_p$: Total pore volume. $D_p$: Average pore diameter calculated using BJH method.
3.2. Adsorption Studies

The adsorption activity of GO/Co$_3$O$_4$ was examined by dispersing composite powder (30 mg) into an aqueous solution (30 ml, 25 mg L$^{-1}$) of organic dyes (MB, RhB, and MO), and the concentrations of the dye solutions were determined at given intervals by UV-vis absorption spectra. From Figure 9, it can be clearly seen that GO/Co$_3$O$_4$ had different adsorption abilities towards MB, RhB, and MO. The removal percentage of MB of up to 98% could be achieved in 12 min, while only 66% and 45% of RhB and MO were removed within 40 min. To better understand adsorption ability of the nanocomposite, MB was chosen as the removal target to study the adsorption performance in more detail, including adsorption kinetic parameters, adsorption isotherms, and thermodynamic parameters.

Figure 10 shows the adsorption abilities of pure Co$_3$O$_4$ and GO samples toward MB, RhB, and MO dyes under our reaction conditions. By using Co$_3$O$_4$ alone, it is clear from Figure 10(a)–(c) the decrease in intensities of characteristic UV-Vis absorption bands of these dyes is almost negligible within 40 min, indicating that it has no ability to adsorb dyes even after long contact times. Figure 10(d)–(f) shows that the GO sample has different adsorption ability towards the dyes. It can be seen that the intensity of the absorption bands of MB and RhB decreases with increasing contact time. The adsorption efficiencies of GO nansheets sample toward these two dyes are about 90% and 50%, respectively, albeit after long adsorption times of 40 min (Figure 10(d) and (e)). On the other hand, as can be seen in Figure 10 (f), the decrease in intensity of characteristic absorption band of MO dye is trace within 40 min. In Figure 10 (g) the adsorption abilities of Co$_3$O$_4$, GO and GO/Co$_3$O$_4$ samples toward MB, RhB, and MO dyes were compared. The removal percentages of three dyes in the presence of Co$_3$O$_4$ sample as an adsorbent were almost negligible (less than 5%) in 40 min. The removal rates of GO sample for MB and RhB cationic dyes are 90 and 50% after long adsorption time of 40 min and the removal of
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Figure 9. The adsorption capability of GO/Co₃O₄ nanocomposite toward different dyes: (a) MB; (b) RhB and (c) MO. (d) The removal efficiency of MB, RhB, and MO dyes.

Figure 10. The adsorption capabilities of (a)–(c) Co₃O₄ nanoparticles and (d)–(f) graphene oxide (GO) nanosheets toward MB, RhB, and MO dyes. (g) Adsorption efficiency (%) of the dyes in the presence of different adsorbent samples.
MO dye is almost negligible at the same time. It is clear that with respect to the removal percentages and adsorption times, the GO/Co$_3$O$_4$ nanocomposite is more suitable and superior. It is suggested that the well dispersed Co$_3$O$_4$ nanoparticles on the graphene surface could act as spacers and thus prohibit the graphene sheets to restack. This directly results in significant increase of the geometry surface area of graphene, which can be of great benefit to adsorption processes. This result is consistent with BET surface area data in Figure 8.

3.3 Kinetic Studies and Effects of Contact Time

Figure 11 shows the effect of GO/Co$_3$O$_4$ adsorbent dosage on the removal of MB. It is obvious that the percentage of dye removed by the adsorbent increased during the initial stage due to the highest amount of available vacant surface sites and was then slow for all samples until a state of equilibrium was reached after 12 min. It is also observed in Figure 11 that the percentage of the adsorbed dye at equilibrium increased sharply from 43% to 98% with increasing adsorbent dosage from 10 to 30 mg that could be attributed to increase of contact area and availability of more adsorption sites.

Meanwhile, to further investigate the adsorption behavior of GO/Co$_3$O$_4$, pseudo-second-order kinetics model was applied. The pseudo-second-order kinetic model is expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

(2)

where $k_2$ is rate constant of the pseudo-second-order model (g mg$^{-1}$ min$^{-1}$), $q_e$ and $q_t$ (mg g$^{-1}$) are the amounts of the dye adsorbed at equilibrium and at various times t (min), respectively. The values of $k_2$ and $q_e$ at different amount of adsorbent can be determined from the intercept and slope of plots of $t/q_t$ versus t (Figure 12), respectively, and the results are given in Table 2. It is observed that the experimental adsorption capacity ($q_{exp}$: 24.63) value was close to the calculated adsorption capacity ($q_{cal}$: 26.31). Also, large correlation coefficients ($R^2 = 0.998$) suggested that the adsorption kinetic followed the pseudo-second-order model. The values of $q_{cal}$ were increased from 26.31 to 38.46 mg g$^{-1}$, when the initial amount of adsorbent was decreased from 30 mg to 10 mg, due to the affinity for the adsorption surface sites at lower adsorbent concentration.

The comparative removal efficiency of MB with different adsorbents in the aqueous medium is presented in Table 3. It was observed that in term of removal efficiency (%) and contact time, GO/Co$_3$O$_4$ nanocomposite was the most efficient adsorbent (98% adsorption of methylene blue) compared to other reported adsorbents. This may be
due to the fact that, in the case of GO/Co₃O₄ nanocomposite, the main driving force for adsorption was electrostatic forces of attraction between cationic MB molecules and negatively charged oxygen-containing surface groups along with π–π interaction between localized π electrons in the conjugated aromatic rings of the adsorbent and adsorbate which is comparatively stronger than π−π interaction, electrostatic attraction, van der Waals interaction, and hydrogen bonding alone.⁴³,⁴⁴

3. 4. Adsorption Isotherm

An adsorption isotherm declares the relationship between the mass of dye adsorbed at a given temperature under equilibrium conditions per unit mass of adsorbent (qe, mg g⁻¹) and the liquid phase dye concentration (Ce, mg L⁻¹).⁴⁵ In this study, to investigate the nature of electrostatic interaction of dye molecules with GO/Co₃O₄ nanocomposite, Langmuir and Freundlich models were applied, in which the experiments were conducted by varying the amount of adsorbent from 10 to 25 mg at 25 °C while keeping the concentration of methylene blue solution constant (25 mg L⁻¹). Langmuir adsorption model supposes that maximum adsorption occurs on a saturated monolayer of solute molecules and all adsorption sites on the adsorbent surface are homogeneous and is given by the following equation:⁴⁶

\[
\frac{c_e}{q_e} = \frac{1}{k_L q_m} + \frac{c_e}{q_m}
\]

(3)

where \(k_L\) is Langmuir adsorption constant, \(c_e\), \(q_e\), and \(q_m\), are MB concentration at equilibrium (mg L⁻¹), the amount of MB adsorbed at equilibrium (mg g⁻¹), and the maximum adsorption capacity (mg g⁻¹), respectively. The values of \(q_m\) and \(k_L\) are computed from the slope and intercept of the linear plot of \(c_e/q_e\) versus \(c_e\). The separation factor (RL) is used to evaluate the favorability adsorption on the adsorbent, which is defined by the following equation:⁴⁷

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

(4)

The parameter can show that the isotherm is irreversible \((R_L = 0)\), favorable \((0 < R_L < 1)\), linear \((R_L = 1)\) or unfavorable \((R_L > 1)\). In this work, the value of RL calculated for the initial concentrations of MB was 0.11, which illustrated that the adsorption of MB onto GO/Co₃O₄ was favorable. Freundlich model is based on the assumption that the multilayer of the adsorption process occurs on a heterogeneous surface and is given by the following equation:⁴⁷

\[
R_L = 1/(1 + k_L C_0)
\]

(3)

Figure 13. Adsorption isotherm plots for the adsorption of MB onto GO/Co₃O₄ nanocomposite: (a) Langmuir isotherm, (b) Freundlich isotherm.

Table 3. The comparative removal efficiency of MB with different adsorbents.

| Entry | Adsorbent material efficiency (%) | Removal | Cₘₙ (mg L⁻¹) | Time (min) | Ref. |
|-------|----------------------------------|---------|--------------|-----------|------|
| 1     | G–CNT hybrid                     | 97      | 10           | 180       | [40] |
| 2     | H₃P₂[W₆O₁₆] /MOF-5               | 97      | 10           | 10        | [49] |
| 3     | M-MWCNTs                         | 82      | 20           | 120       | [51] |
| 4     | (4-Hap)₈[Mo₃O₁₂]₈ hybrid         | 100     | 10           | 120       | [54] |
| 5     | H₃PW₈O₄₀@MIL-101                | 97.5    | 20           | 30        | [55] |
| 6     | GO/Co₃O₄ nanocomposite           | 98      | 25           | 12        | This work|
log\(q_e\) = \(1/n \log c_e + \log k_f\) \hspace{1cm} (5)

where \(K_f\) is a Freundlich constant and \(n\) is the heterogeneity factor. The isotherms based on the experimental data are shown in Figures 13(a) and (b), and the parameters obtained from linear regression are summarized in Table 4. According to the obtained data, correlation coefficient \(R^2\) in Langmuir model (0.973) was higher than that of Freundlich model (0.910), which exhibited that Langmuir model was suitable for describing the adsorption equilibrium of MB on GO/Co\(_3\)O\(_4\) nanocomposite.

### 3.5. Effect of pH

The effect of pH on the adsorption process of dyes is important because industrial dyes are discharged in wastewaters at a pH different from the environmental pH.\(^46\) In general, the solution pH can affect the surface charge of the adsorbent, the degree of ionization/dissociation of dye molecules as well as dissociation of functional groups on the active sites of the adsorbent.\(^49,50\) Figure 14 shows the effect of initial solution pH on MB adsorption onto GO/Co\(_3\)O\(_4\). Both, the adsorption capacity and removal rate of MB became significant with increasing solution pH from 4 to 12. This phenomenon can be explained by the fact that at higher pH values, the surface of GO/Co\(_3\)O\(_4\) may become negatively charged, which can attract positively charged MB cations through electrostatic forces. A similar trend was observed for the adsorption of methylene blue onto magnetic cyclodextrin/graphene oxide,\(^35\) or polydopamine microspheres,\(^47\) magnetite-loaded multi-walled carbon nanotubes,\(^51\) and magnetic graphene oxide.\(^52\)

### 3.6. Thermodynamic Parameters

Thermodynamic studies for the adsorption of MB onto GO/Co\(_3\)O\(_4\) were carried out at different temperatures. Thermodynamic parameters, namely, Gibbs free energy (\(\Delta G^o\)), enthalpy (\(\Delta H^o\)) and entropy (\(\Delta S^o\)) were calculated using following equations:

\[
\ln K_L = -\Delta H^o/(RT) + \Delta S^o/R
\]
\[
\Delta G^o = -RT \ln K_L
\]
\[
\ln K_f = \ln A - \frac{E_a}{RT}
\]

where \(K_L\) (L/g) is Langmuir constant, \(R\) is universal gas constant (8.314 J mol\(^{-1}\) K) and \(T\) is absolute temperature (in Kelvin). Plotting \(\ln K_L\) versus \(1/T\) gave a straight line with slope and intercept equal to \(-\Delta H^o/R\) and \(\Delta S^o/R\), respectively (Figure 15). The positive value of \(\Delta H^o\) (Table 5) showed endothermic nature of adsorption process that it was in accordance with increasing adsorption capacity collaborated with the increase of temperature. The negative value of \(\Delta G^o\) for different temperatures showed the feasibility and spontaneous nature of adsorption. The activation energy, \(E_a\), was calculated by using Arrhenius equation:

\[
\ln k = \ln A - \frac{E_a}{RT}
\]
where k is pseudo-second-order rate constant, $E_a$, A, R, and $T$ are activation energy, Arrhenius factor, universal gas constant, and temperature in Kelvin, respectively. The linear plot of lnk against 1/T provided slope equal to $-E_a/R$. The value of $E_a$ ranging from 5 to 40 kJ mol$^{-1}$ are characteristic for physisorption while ranging from 40 to 800 kJ mol$^{-1}$ indicates chemisorptions.\(^{53}\) The activation energy for the adsorption of MB onto GO/Co$_3$O$_4$ nanocomposite was found to be 7.37 kJ mol$^{-1}$, which indicated that the process was governed by physical adsorption.

### Table 5. Thermodynamic parameters for the adsorption of MB onto GO/Co$_3$O$_4$.

| T (K) | $\Delta G^\circ$ (KJ/mol) | $\Delta H^\circ$ (KJ/mol) | $\Delta S^\circ$ (J/mol k) |
|-------|--------------------------|--------------------------|---------------------------|
| 298   | $-2.96$                  | 13.01                    | 53.62                     |
| 308   | $-3.49$                  | $-$                      | $-$                       |
| 318   | $-4.03$                  | $-$                      | $-$                       |

## 3. 7. Recyclability of GO/Co$_3$O$_4$ Nanocomposite

Recovery and regeneration ability of the adsorbent, that can reduce the cost of the treatment process, is crucial for its practical application. For this purpose, the used adsorbent was regenerated with ethanol solution, and the absorption-desorption cycle was repeated four times and the obtained results are shown in Figure 16. In the first three cycles, the removal efficiencies were 98%, 95%, and 93%, respectively, and then remained at 90% at the fourth cycle. These results show that the adsorbent had the potential of reusability.

### Figure 16. Effect of recycle times of GO/Co$_3$O$_4$ on MB removal rate.

## 4. Conclusion

GO/Co$_3$O$_4$ nanocomposite was synthesized successfully by a hydrothermal route. The results obtained from XRD, FTIR, FESEM, EDS, and TEM techniques showed that Co$_3$O$_4$ nanoparticles were deposited onto GO nanosheets. Compared with Co$_3$O$_4$ nanoparticles, GO/Co$_3$O$_4$ nanocomposite showed weaker ferromagnetic behavior. The results revealed that GO/Co$_3$O$_4$ nanocomposite demonstrated rapid uptake of cationic methylene blue (MB) and the adsorption process followed pseudo-second-order kinetic model as well as Langmuir isotherms. Rapid adsorption rate was mainly attributed to the electrostatic interaction of oppositely charged adsorbate−adsorbent species along with their π−π interaction. Thermodynamic parameters showed that the adsorption was spontaneous. Recyclability tests indicated that GO/Co$_3$O$_4$ nanocomposite could be recycled and utilized several times without losing adsorption capacity.

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## 6. References

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Povzetek
Nanokompozit grafenovega oksida (GO)/Co3O4 smo sintetizirali s hidrotermalnim razpadom spojine [Co(en)3(NO3)2] na nanoplasteh grafenovega oksida. Tako pripravljen nanokompozit (GO/Co3O4) smo karakterizirali z infrardečo spektroskopijo (FT-IR), rentgensko praškovno difrakcijo (XRD), ramansko spektroskopijo, vrstično in presevno elektronsko mikroskopijo (TEM, SEM), energijsko disperzivno rentgensko spektroskopijo (EDX), magnetnimi meritvami in N2 adsorpcijsko – desorpcijsko analizo. Rezultati so pokazali, da so se nanodelci Co3O4 s povprečnim premerom 12,5 nm pripeli na plasti grafenovega oksida. Adsorpcijsko učinkovitost GO/Co3O4 smo preučevali napram različnim organskim barvilom v vodnih raztopinah. Rezultati adsorpcijske učinkovitosti nanokompozita GO/Co3O4 so: metilen modro: 98 % v 12 minutah; rodamin B 66 % v 40 minutah, metiloranž 45 % v 40 minutah. Podrobno smo preučevali vplive različnih parametrov kot so množina adsorbenta, čas, pH vrednosti in temperatura na adsorpcijski proces. Podatki adsorpcijskega ravnotežja najbolje sledijo Langmuirjevi izotermi, adsorpcijsko kinetiko pa lahko opišemo s psevdo modelom drugega reda. Različni termodinamski parametri kažejo na to, da je proces adsorpcije spontan. Poudarimo lahko tudi lažjo pripravo nanokompozita GO/Co3O4 in njegovo uporabo pri odstranjevanju barvila metilen modro iz odpadnih vod.