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Graphene Oxide/Co₃O₄ Nanocomposite: Synthesis, Characterization, and Its Adsorption Capacity for the Removal of Organic Dye Pollutants from Water

Kolsoum Pourzare, Saeed Farhadi* and Yaghoub Mansourpanah

Department of Chemistry, Lorestan University, Khoramabad 68151-44316, Iran

* Corresponding author: E-mail: sfarhadi1348@yahoo.com

Tel: +98 06633120611, fax: +98 06633120618.

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Abstract

In this work, graphene oxide/Co₃O₄ nanocomposite was synthesized via hydrothermal decomposition of [Co(en)₃](NO₃)₃ complex onto graphene oxide nanosheets. The as-prepared nanocomposite (denoted as GO/Co₃O₄) 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 N₂ adsorption–desorption analysis. The results demonstrated successful immobilization of Co₃O₄ nanoparticles with an average diameter size of around 12.5 nm on the surface of graphene oxide nanosheets. The adsorption performance of GO/Co₃O₄ nanocomposite was investigated towards different organic dyes in aqueous solutions. The results displayed that the adsorption rate of the GO/Co₃O₄ 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/Co₃O₄ and its application for rapid and efficient removal of MB from wastewater.

Keywords: Graphene oxide nanosheets, Co₃O₄ 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.⁹ 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^{10–12} and keep the surface area and pore volume at high levels which is required for applications such as adsorption processes and photocatalysis.¹³

In recent years, various transition metal oxides nanoparticles such as Fe_2O_3 , ZnO , Fe_3O_4 , TiO_2 , etc., have been deposited on GO nanosheets. For instance, Amino-functionalized Fe_3O_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.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.¹⁵ MCGO demonstrated extremely fast MB-removal from wastewater with high removal efficiency within 50 min. Li et al. prepared a magnetic CoFe_2O_4 -functionalized graphene sheet ($\text{CoFe}_2\text{O}_4\text{-FGS}$) nanocomposite via a facile hydrothermal method and used it to adsorb methyl orange.¹⁶ The observed maximum adsorption capacity at 10 mg L^{-1} initial concentration was 71.54 mg g^{-1} . In another study, Fan et al. prepared a magnetic chitosan-GO (MCFO) nanocomposite through covalent bonding of chitosan to the surface of Fe_3O_4 nanoparticles followed by covalent functionalization of GO with magnetic chitosan which acted as a good adsorbent to adsorb MB from aqueous solutions.¹⁷ Yao et al. also fabricated $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{GO}$ nanocomposite through a covalent bonding technique and used it as an adsorbent for the removal of MB from aqueous solution.¹⁸ Maximum MB adsorption capacities were 97, 102.6, and 111.1 mg g^{-1} at 25, 45, and 60°C , respectively.

Spinel-type cobalt oxide (Co_3O_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.^{19–25} For this reason, various nanostructures of Co_3O_4 such as nanoparticles, nanoplates, nanorods, nanotubes, nanodiscs, nanoflowers, nanocubes and hollow microspheres structures have been prepared by using different synthesis methods.^{26–33} To the best of our knowledge, the investigation of adsorption properties of $\text{GO/Co}_3\text{O}_4$ nanocomposites has not been reported yet. In this study, we presented a solvothermal approach for the production of $\text{GO/Co}_3\text{O}_4$ 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)-chloride 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 Co_3O_4 Nanoparticles

First, $[\text{Co}(\text{en})_3](\text{NO}_3)_3$ complex was prepared via the simple reaction of an aqueous solution of $[\text{Co}(\text{en})_3]\text{Cl}_3$ with concentrated nitric acid according to the reported method.³⁴ To prepare Co_3O_4 nanoparticles, $[\text{Co}(\text{en})_3](\text{NO}_3)_3$ 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/ Co_3O_4 Nanocomposite ($\text{GO/Co}_3\text{O}_4$)

Graphene oxide (GO) was prepared by the oxidation of graphite powder under acidic conditions according to modified Hummers method using a mixture of H_2SO_4 , NaNO_3 , and KMnO_4 .^{35,36} For the synthesis of $\text{GO/Co}_3\text{O}_4$ 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 Co_3O_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 $500\text{--}4000 \text{ cm}^{-1}$ using KBr pellet. The XRD patterns were obtained on a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) for phase determination samples. Optical absorption spectra of dyes were obtained on a Cary 100 UV-Vis spectrophotometer in the wavelength range of $200\text{--}800 \text{ nm}$. 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. N₂ 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/Co₃O₄ 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 ($\lambda_{\max}$). The amount of MB adsorbed onto GO/Co₃O₄ nanocomposite (q_t) and its removal rate (R%) were calculated by the following equations:

$$q_t = (C_0 - C_t)V/m, R\% = (C_0 - C_t)100/C_0 = (A_0 - A_t)100/A_0 \quad (1)$$

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/Co₃O₄ Nanocomposite

The FT-IR spectra of the samples are shown in Figure 1. For the starting [Co(en)₃](NO₃)₃ complex, the characteristic stretching bands of NH₂, CH₂, NO₃ were appeared at about 3100–3400, 2951 and 1380 cm⁻¹, respectively.³⁷ As can be seen in the spectrum of Co₃O₄ (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 Co₃O₄. 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 Co₃O₄ from the [Co(en)₃](NO₃)₃ complex can be related to the explosive decomposition of the complex via an intramolecular redox process occurring between the ethylenediamine (en) ligands and NO₃⁻ ions as reducing and oxidiz-

ing agents, respectively. This reaction resulted in the formation of solid Co₃O₄ and gaseous products i.e. CO₂, H₂O and NO_x (NO, N₂O and NO₂).³⁸ Although the exact reaction is unclear and intermediates and gaseous products had not been identified directly, the formation of Co₃O₄ can be expressed as follows: [Co(en)₃](NO₃)₃(s) → Co₃O₄(s) + CO₂(g) + H₂O(g) + NO_x (NO(g) + N₂O(g) + NO₂(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/Co₃O₄ at lower

Figure 1. FT-IR spectra of (a) [Co(en)₃](NO₃)₃ complex, (b) Co₃O₄, (c) GO, and (d) GO/Co₃O₄.

frequencies (in the 400–600 cm^{-1} range) could be assigned to the stretching vibrations of Co–O bonds of Co_3O_4 phase. This result confirmed the formation of $\text{GO}/\text{Co}_3\text{O}_4$ 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 Co_3O_4 and $\text{GO}/\text{Co}_3\text{O}_4$ nanocomposite. The diffraction patterns in Figures 2(a) and (b) are similar and can be indexed to the Co_3O_4 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 Co_3O_4 nanoparticles anchored on the surfaces of GO prevented the exfoliated GO nanosheets from restacking. However, a broad characteristic peak for graphene nanosheets at about $2\theta = 23^\circ$ appeared, suggesting that GO was reduced to graphene during the formation of the nanocomposite. The average domain size of Co_3O_4 nanoparticles was calculated to be approximately 13 nm by the Scherrer formula: $D_{\text{XRD}} = 0.9\lambda/(\beta \cos \theta)$, where D_{XRD} is average crystalline size; λ , β , and θ are wavelength of Cu K α radiation, full width at half maximum of the diffraction peak, and Bragg angle, respectively.⁴¹

Figure 2. XRD patterns of (a) Co_3O_4 and (b) $\text{GO}/\text{Co}_3\text{O}_4$ nanocomposite.

Raman spectroscopy is a powerful tool to characterize significant structural changes of GO during the composite synthesis. Figure 3 presents the Raman spectra of GO and $\text{GO}/\text{Co}_3\text{O}_4$ nanocomposite. According to the Raman spectrum of GO in Figure 3(a), the obvious peaks at 1318 and 1584 cm^{-1} can be attributed to the disordered structure (D band, sp^3 carbon atoms of disorders and defects) and graphite structure (G band, sp^2 carbon atoms in graphitic sheets) of GO, respectively.⁴² In the spectrum of $\text{GO}/\text{Co}_3\text{O}_4$, D and G peaks still exist, while other two obvious peaks at 477 and 683 cm^{-1} can be attributed to

Figure 3. Raman spectra of (a) GO and (b) $\text{GO}/\text{Co}_3\text{O}_4$ nanocomposite.

Co_3O_4 . Compared to GO, it was clear that D and G bands of $\text{GO}/\text{Co}_3\text{O}_4$ were down shifted by 10 cm^{-1} . The red shifts of D and G bands for $\text{GO}/\text{Co}_3\text{O}_4$ provided evidence for charge transfer between GO and Co_3O_4 , which indicated a strong interaction between them. Raman spectra further confirmed the successful synthesis of $\text{GO}/\text{Co}_3\text{O}_4$ composite.

SEM images indicating the microstructural features of GO, Co_3O_4 , $\text{GO}/\text{Co}_3\text{O}_4$ 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 Co_3O_4 nanoparticles. The SEM images of $\text{GO}/\text{Co}_3\text{O}_4$ in Figures 4(c) and (d) clearly show graphene oxide nanosheets were successfully decorated with Co_3O_4 nanoparticles. It can be clearly seen that the Co_3O_4 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 Co_3O_4 and $\text{GO}/\text{Co}_3\text{O}_4$ samples were further

Figure 4. SEM images of (a) GO, (b) Co₃O₄, and (c,d) GO/Co₃O₄.

Figure 5. TEM images of (a,b) Co₃O₄, and (c,d) GO/Co₃O₄ nanocomposite.

analyzed by TEM. Figures 5(a) and (b) show the typical TEM images of the Co_3O_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 transparent graphene sheets are fully exfoliated and decorated homogeneously with sphere-like Co_3O_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_3O_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_3O_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_3O_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_3O_4 nanocrystals had been successfully loaded on the surface of GO.

Figure 6. EDX spectrum of GO/ Co_3O_4 nanocomposite. The inset shows the corresponding EDX elemental mappings.

The magnetization curves of Co_3O_4 and GO/ Co_3O_4 samples were measured at room temperature, as shown in Figure 7. Obviously, the shape of magnetic hysteresis loop

Figure 7. Magnetic hysteresis loops of (a) Co_3O_4 nanoparticles and (b) GO/ Co_3O_4 nanocomposite.

of Co_3O_4 sample shows a ferromagnetic behavior. The fine hysteresis loop of GO/ Co_3O_4 nanocomposite exhibited a typical weak ferromagnetic behavior at room temperature. The saturation magnetization (M_s) of Co_3O_4 nanoparticles sample is 1.3 emu g^{-1} . In contrast, the GO/ Co_3O_4 nanocomposite has smaller M_s 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_3O_4 and GO/ Co_3O_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_3O_4 and GO/ Co_3O_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_3O_4 were higher than the values of GO. It can be concluded that the addition of Co_3O_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.

Table 1 Textural properties of GO, Co_3O_4 and GO/ Co_3O_4 samples.

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_3O_4	103.67	0.338	1.27
3	GO/ Co_3O_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.

Figure 8. N_2 adsorption–desorption isotherms of (a) GO, (b) Co_3O_4 and (c) $\text{GO}/\text{Co}_3\text{O}_4$ samples. The insets show the corresponding pore size distribution curves.

3. 2. Adsorption Studies

The adsorption activity of $\text{GO}/\text{Co}_3\text{O}_4$ 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 $\text{GO}/\text{Co}_3\text{O}_4$ 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_3O_4 and GO samples toward MB, RhB, and MO dyes under our reaction conditions. By using Co_3O_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 nanosheets 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_3O_4 , GO and $\text{GO}/\text{Co}_3\text{O}_4$ samples toward MB, RhB, and MO dyes were compared. The removal percentages of three dyes in the presence of Co_3O_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

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/Co₃O₄ nanocomposite is more suitable and superior. It is suggested that the well dispersed Co₃O₄ 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/Co₃O₄ 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/Co₃O₄, pseudo-second-order kinetics model

Figure 11. The effect of with different dosages of GO/Co₃O₄ on the removal of MB

was applied. The pseudo-second-order kinetic model is expressed by the following equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

where k_2 is rate constant of the pseudo-second-order model ($\text{g mg}^{-1} \text{min}^{-1}$), 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 ($q_{e,\text{exp}}$: 24.63) value was close to the calculated adsorption capacity ($q_{e,\text{cal}}$: 26.31). Also, large correlation coefficients ($R^2 = 0.998$) suggested that the adsorption kinetic followed the pseudo-second-order model. The values of $q_{e,\text{cal}}$ 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.

Figure 12. Pseudo-second-order kinetics plot of MB adsorption on GO/Co₃O₄ nanocomposite.

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/Co₃O₄ nanocomposite was the most efficient adsorbent (98% adsorption of methylene blue) compared to other reported adsorbents. This may be

Table 2. Adsorption kinetic parameters for the adsorption of MB onto GO/Co₃O₄.

Adsorbent dosage (mg)	$q_{e,\text{exp}}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) ^a	$q_{e,\text{cal}}$ (mg g^{-1})	R^2
30	24.63	0.05159	26.31	0.998
20	25.15	0.0371	28.57	0.994
10	32.52	0.0193	38.46	0.989

^aPseudo-second-order kinetics

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

Entry	Adsorbent material efficiency (%)	Removal	C _{MB} (mg L ⁻¹)	Time (min)	Ref.
1	G–CNT hybrid	97	10	180	[40]
2	H ₆ P ₂ W ₁₈ O ₆₂ /MOF-5	97	10	10	[49]
3	M-MWCNTs	82	20	120	[51]
4	(4-Hap) ₄ [Mo ₈ O ₂₆]hybrid	100	10	120	[54]
5	H ₃ PW ₁₂ O ₄₀ @MIL-101	97.5	20	30	[55]
6	GO/Co ₃ O ₄ nanocomposite	98	25	12	This work

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 (q_e , mg g⁻¹) and the liquid phase dye concentration (C_e , 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 ad-

sorbent surface are homogeneous and is given by the following equation:⁴⁶

$$c_e/q_e = 1/k_L q_m + c_e/q_m \quad (3)$$

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 (R_L) is used to evaluate the favorability adsorption on the adsorbent, which is defined by the following equation:⁴⁷

$$R_L = 1/(1 + K_L C_0) \quad (4)$$

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 R_L 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

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

Table 4. Isotherm parameters for the adsorption of MB onto GO/Co₃O₄.

Langmuir isotherm				Freundlich isotherm		
K_L (L mg ⁻¹)	q_m (mg g ⁻¹)	R_L	R^2	K_F (mg g ⁻¹ (L mg ⁻¹) ^{1/n})	n	R^2
0.32	40	0.11	0.973	16.36	3.98	0.910

$$\log q_e = 1/n \log c_e + \log k_f \quad (5)$$

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/Co₃O₄ 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.⁴⁸ 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/Co₃O₄. 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/Co₃O₄ 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,¹⁵ 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/Co₃O₄ were carried out at different temperatures. Thermodynamic parameters, namely, Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using following equations:

$$\begin{aligned} \ln K_L &= -\Delta H^\circ/(RT) + \Delta S^\circ/R \\ \Delta G^\circ &= -RT \ln K_L \end{aligned} \quad (6)$$

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 $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively (Figure 15). The positive value of ΔH° (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 ΔG° for different temperatures showed the feasibility and spontaneous nature of adsorption. The activation energy, E_a , was calculated by using Arrhenius equation:

$$\ln k = \ln A - E_a/RT \quad (7)$$

Figure 14. Effect of initial pH on adsorption capability and removal of MB with GO/Co₃O₄ nanocomposite. **Figure 15.** Van't Hoff plots for the adsorption of MB onto GO/Co₃O₄.

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 $\ln k$ 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/Co₃O₄ 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/Co₃O₄.

T (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol K)
298	-2.96	13.01	53.62
308	-3.49	–	–
318	-4.03	–	–

3. 7. Recyclability of GO/Co₃O₄ 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/Co₃O₄ on MB removal rate.

4. Conclusion

GO/Co₃O₄ nanocomposite was synthesized successfully by a hydrothermal route. The results obtained from XRD, FTIR, FESEM, EDS, and TEM techniques showed

that Co₃O₄ nanoparticles were deposited onto GO nanosheets. Compared with Co₃O₄ nanoparticles, GO/Co₃O₄ nanocomposite showed weaker ferromagnetic behavior. The results revealed that GO/Co₃O₄ 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/Co₃O₄ nanocomposite could be recycled and utilized several times without losing adsorption capacity.

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6. References

1. C. A. Demarchi, M. Campos and C. A. Rodrigues, *J. Environ. Chem. Eng.* **2013**, 1, 1350–1358. DOI:10.1016/j.jece.2013.10.005
2. J. Wang, C. Zheng, S. Ding, H. Ma and Y. Ji, *Desalination* **2011**, 273, 285–291. DOI:10.1016/j.desal.2011.01.042
3. F. Marahel, M. A. Khan, E. Marahel, I. Bayesti and S. Hosseini, *Des. Water Treat.* **2015**, 53, 826–835.
4. N. M. Julkapli, S. Bagheri and S. B. A. Hamid, *Scientific World J.* **2014**, 2014. DOI:10.1080/19443994.2013.846240
5. H. Hou, R. Zhou, P. Wu and L. Wu, *Chem. Eng. J.* **2012**, 211, 336–342. DOI:10.1016/j.ces.2012.09.100
6. A. K. Sarkar, A. Pal, S. Ghorai, N. Mandre and S. Pal, *Carbohydr. Polym.* **2014**, 111, 108–115. DOI:10.1016/j.carbpol.2014.04.042
7. M. Yusuf, F. Elfighi, S. A. Zaidi, E. Abdullah and M. A. Khan, *RSC Adv.* **2015**, 5, 50392–50420.
8. L. Zhou, C. Gao and W. Xu, *ACS Appl. Mater. Interfaces.* **2010**, 2, 1483–1491. DOI:10.1021/am100114f
9. Y. Chen, L. Chen, H. Bai and L. Li, *J. Mater. Chem. A.* **2013**, 1, 1992–2001. DOI:10.1039/C2TA00406B
10. S. Park and R. S. Ruoff, *Nat. nanotechnol.* **2009**, 4, 217–224. DOI:10.1038/nnano.2009.58
11. X. Wang, X. Li, L. Zhang, Y. Yoon, P. K. Weber, H. Wang, J. Guo and H. Dai, *Sci.* **2009**, 324, 768–771. DOI:10.1126/science.1170335
12. T. Ramanathan, A. Abdala, S. Stankovich, D. Dikin, M. Herrera-Alonso, R. Piner, D. Adamson, H. Schniepp, X. Chen and R. Ruoff, *Nat. Nanotechnol.* **2008**, 3, 327–331. DOI:10.1038/nnano.2008.96
13. B. Li and H. Cao, *J. Mater. Chem.* **2011**, 21, 3346–3349. DOI:10.1039/C0JM03253K

14. G. Xie, P. Xi, H. Liu, F. Chen, L. Huang, Y. Shi, F. Hou, Z. Zeng, C. Shao and J. Wang, *J. Mater. Chem.* **2012**, 22, 1033–1039. DOI:10.1039/C1JM13433G
15. L. Li, L. Fan, H. Duan, X. Wang and C. Luo, *RSC Adv.* **2014**, 4, 37114–37121.
16. N. Li, M. Zheng, X. Chang, G. Ji, H. Lu, L. Xue, L. Pan and J. Cao, *J. Solid State Chem.* **2011**, 184, 953–958. DOI:10.1016/j.jssc.2011.01.014
17. L. Fan, C. Luo, X. Li, F. Lu, H. Qiu and M. Sun, *J. Hazard. Mater.* **2012**, 215, 272–279. DOI:10.1016/j.jhazmat.2012.02.068
18. Y. Yao, S. Miao, S. Yu, L. P. Ma, H. Sun and S. Wang, *J. Colloid Interface Sci.* **2012**, 379, 20–26. DOI:10.1016/j.jcis.2012.04.030
19. F. Jiao and H. Frei, *Angew. Chem.* **2009**, 121, 1873–1876. DOI:10.1002/ange.200805534
20. H. Sun, H. Tian, Y. Hardjono, C. E. Buckley and S. Wang, *Catal. Today.* **2012**, 186, 63–68. DOI:10.1016/j.cattod.2011.09.001
21. J. A. Koza, Z. He, A. S. Miller and J. A. Switzer, *Chem. Mater.* **2012**, 24, 3567–3573. DOI:10.1021/cm3012205
22. Z. Wang and L. Zhou, *Adv. Mater.* **2012**, 24, 1903–1911. DOI:10.1002/adma.201200469
23. G. Wang, H. Liu, J. Horvat, B. Wang, S. Qiao, J. Park and H. Ahn, *Chem. Eur. J.* **2010**, 16, 11020–11027. DOI:10.1002/chem.201000562
24. T. Zhu, J. S. Chen and X. W. Lou, *J. Mater. Chem.* **2010**, 20, 7015–7020. DOI:10.1039/c0jm00867b
25. L. Jin, X. Li, H. Ming, H. Wang, Z. Jia, Y. Fu, J. Adkins, Q. Zhou and J. Zheng, *RSC Adv.* **2014**, 4, 6083–6089.
26. S. Farhadi and K. Pourzare, *Mater. Res. Bull.* **2012**, 47, 1550–1556. DOI:10.1016/j.materresbull.2012.02.028
27. S. Farhadi, K. Pourzare and S. Bazgir, *J. Alloys Compd.* **2014**, 587, 632–637. DOI:10.1016/j.jallcom.2013.10.259
28. L. Wang, J. Deng, Z. Lou and T. Zhang, *Sens. Actuators B Chem.* **2014**, 201, 1–6. DOI:10.1016/j.snb.2014.04.074
29. J. Xu, L. Gao, J. Cao, W. Wang and Z. Chen, *Electrochim. Acta.* **2010**, 56, 732–736. DOI:10.1016/j.electacta.2010.09.092
30. D. Vickers, L. Archer and T. Floyd-Smith, *Colloids Surf. A Physicochem. Eng. Aspects*, **2009**, 348, 39–44. DOI:10.1016/j.colsurfa.2009.06.025
31. J. S. Chen, T. Zhu, Q. H. Hu, J. Gao, F. Su, S. Z. Qiao and X. W. Lou, *ACS appl. mater. interfaces.* **2010**, 2, 3628–3635. DOI:10.1021/am100787w
32. S. Farhadi, Z. Heydari-Chegeni and M. Mousavi, *J. Alloys Compd.* **2017**, 692, 923–933. DOI:10.1016/j.jallcom.2016.09.136
33. F. Hong, Y. Ni, Y. Zhong, H. Wu, *J. Alloys Compd.* **2016**, 659, 112–121. DOI:10.1016/j.jallcom.2015.11.049
34. G. S. Girolami, T. B. Rauchfuss, R. J. Angelici, *Synthesis and technique in inorganic chemistry: a laboratory manual*, University Science Books, Sausalito, CA, **1999**.
35. Y. Yao, Z. Yang, H. Sun and S. Wang, *Ind. Eng. Chem. Res.* **2012**, 51, 14958–14965. DOI:10.1021/ie301642g
36. P. Bradder, S. K. Ling, S. Wang and S. Liu, *J. Chem. Eng. Data.* **2010**, 56, 138–141. DOI:10.1021/je101049g
37. K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, Wiley Online Library, **1986**.
38. S. Farhadi, M. Javanmard and G. Nadri, *Acta Chim. Slov.* **2016**, 63, 335–343. DOI:10.17344/acs.2016.2305
39. B. Pejova, A. Isahi, M. Najdoski and I. Grozdanov, *Mater. Res. Bull.* **2001**, 36, 161–170. DOI:10.1016/S0025-5408(00)00479-7
40. L. Ai and J. Jiang, *Chem. Eng. J.* **2012**, 192, 156–163. DOI:10.1016/j.cej.2012.03.056
41. H. P. Klug and L. E. Alexander, *X-ray diffraction procedures*, Wiley New York. **1954**.
42. Y. Zhao, S. Chen, B. Sun, D. Su, X. Huang, H. Liu, Y. Yan, K. Sun and G. Wang, *Sci. Rep.* **2015**, 5, 7629–7635. DOI:10.1038/srep07629
43. P. Sharma and M. R. Das, *J. Chem. Eng. Data.* **2012**, 58, 151–158. DOI:10.1021/je301020n
44. Y. Li, Q. Du, T. Liu, X. Peng, J. Wang, J. Sun, Y. Wang, S. Wu, Z. Wang and Y. Xia, *Chem. Eng. Res. Des.* **2013**, 91, 361–368. DOI:10.1016/j.cherd.2012.07.007
45. L. Sun, S. Hu, H. Sun, H. Guo, H. Zhu, M. Liu and H. Sun, *RSC Adv.* **2015**, 5, 11837–11844.
46. L. Yao, S. K. Lua, L. Zhang, R. Wang and Z. Dong, *J. Hazard. Mater.* **2014**, 280, 428–435. DOI:10.1016/j.jhazmat.2014.08.026
47. J. Fu, Z. Chen, M. Wang, S. Liu, J. Zhang, J. Zhang, R. Han and Q. Xu, *Chem. Eng. J.* **2015**, 259, 53–61. DOI:10.1016/j.cej.2014.07.101
48. X. Rong, F. Qiu, C. Zhang, L. Fu, Y. Wang and D. Yang, *Powder Technol.* **2015**, 275, 322–328. DOI:10.1016/j.powtec.2015.01.079
49. X. Liu, W. Gong, J. Luo, C. Zou, Y. Yang and S. Yang, *Appl. Surf. Sci.* **2016**, 362, 517–524. DOI:10.1016/j.apsusc.2015.11.151
50. Z. Chen, J. Zhang, J. Fu, M. Wang, X. Wang, R. Han and Q. Xu, *J. Hazard. Mater.* **2014**, 273, 263–271. DOI:10.1016/j.jhazmat.2014.03.053
51. L. Ai, C. Zhang, F. Liao, Y. Wang, M. Li, L. Meng and J. Jiang, *J. Hazard. Mater.* **2011**, 198, 282–290. DOI:10.1016/j.jhazmat.2011.10.041
52. J. H. Deng, X.-R. Zhang, G.-M. Zeng, J.-L. Gong, Q.-Y. Niu and J. Liang, *Chem. Eng. J.* **2013**, 226, 189–200. DOI:10.1016/j.cej.2013.04.045
53. A. Farghali, M. Bahgat, W. El Roubay and M. Khedr, *J. Alloys Compd.* **2013**, 555, 193–200. DOI:10.1016/j.jallcom.2012.11.190
54. Y. Q. Zhang, C.-C. Wang, T. Zhu, P. Wang and S.-J. Gao, *RSC Adv.* **2015**, 5, 45688–45692.
55. T. T. Zhu, Z.-M. Zhang, W.-L. Chen, Z.-J. Liu and E.-B. Wang, *RSC Adv.* **2016**, 6, 81622–81630.

Povzetek

Nanokompozit grafenovega oksida (GO)/Co₃O₄ smo sintetizirali s hidrotermalnim razpadom spojine [Co(en)₃](NO₃)₃ na nanoplasteh grafenovega oksida. Tako pripravljen nanokompozit (GO/Co₃O₄) smo karakterizirali z infrardečo spektroskopijo (FT-IR), rentgensko praškovo 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 najboljše 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.