

PAPER • OPEN ACCESS

Congo red dye reduction mediated by the electron (e^-) transfer route of BH_4^- ions using synthesized $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanosheets

To cite this article: Varadhi Govinda *et al* 2024 *Mater. Res. Express* **11** 065003

View the [article online](#) for updates and enhancements.

You may also like

- [Transition metal dichalcogenide \(TMDs\) electrodes for supercapacitors: a comprehensive review](#)
Shweta Tanwar, Anil Arya, Anurag Gaur et al.
- [One-dimensional architecture with reduced graphene oxide supporting ultrathin \$\text{MoO}_3\$ nanosheets as high performance anodes for lithium-ion batteries](#)
Yanqi Feng and Hui Liu
- [Coupling Enhanced Oxygen Reduction Reaction Activity from Ag Nanorods-rGO Hybrids](#)
Dong-Xiang Zhu, Shuai Chen, Jian-Li Mi et al.

Materials Research Express



PAPER

OPEN ACCESS

RECEIVED

15 November 2023

REVISED

9 May 2024

ACCEPTED FOR PUBLICATION

21 May 2024

PUBLISHED

4 June 2024

Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](#).

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Congo red dye reduction mediated by the electron (e^-) transfer route of BH_4^- ions using synthesized $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanosheets

Varadhi Govinda¹, Subba Reddy A² , Cheera Prasad³, Sangaraju Sambasivam⁴, Indra Bahadur⁵, Lebogang Maureen Katata-Seru⁵ , Faruq Mohammad⁶, Oyirwoth P Abedigamba^{7,*} and Hyeong Yeol Choi^{3,*}

¹ Department of Chemistry, Gayatri Vidya Parishad College for Degree and PG Courses (A), Rushikonda Campus, Visakhapatnam – 530045, India

² Analytical Development Laboratory, Apicore LLC, NJ 08873, United States of America

³ Department of Fashion Design, Dong-A University, Busan 49315, Republic of Korea

⁴ National Water and Energy Center, United Arab Emirates University, Al Ain-15551, United Arab Emirates

⁵ Department of Chemistry, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

⁶ Department of Chemistry, College of Science, King Saud University, PO Box 2455, Riyadh, 11451, Saudi Arabia

⁷ Department of Physics, Kyambogo University, PO Box 1, Kyambogo, Uganda

* Authors to whom any correspondence should be addressed.

E-mail: oyigamba@kyu.ac.ug and spaachoi@dau.ac.kr

Keywords: congo red, $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid composite, x-ray diffraction, FTIR, TEM

Abstract

The treatment of toxic organic pollutants is extremely important for the conservation of clean air, soil, and water. In this study, (reduced graphene oxide) $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite was prepared by a facile hydrothermal technique and employed for organic dye adsorption from wastewater. The synthesized $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite was studied using FTIR, XRD, SEM, TEM, BET, Raman spectroscopy, and UV–visible. The physical characterizations prove the deposition of NiCo_2O_4 particles on the rGO surface. The transmission electron microscope image demonstrated that the NiCo_2O_4 particles with an average size of ~ 46 nm was dispersed on the rGO surface. The obtained nanoparticles show a higher specific surface area of $56.4 \text{ m}^2 \text{ g}^{-1}$. Adsorption dynamics as investigated by time and concentration variation show that the adsorption data follows pseudosecond order kinetics and the Langmuir isotherm model, with a maximum adsorption capacity of 106.2 mg g^{-1} , indicating homogeneous physiochemical adsorption of CR dye on the adsorbent surface. Besides, the catalytic effectiveness of synthesized nanocomposite towards Congo red (CR) dye reduction mediated by the electron (e^-) transfer route of BH_4^- ions was explained in detail. The electrostatic interaction used between the $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid composite and Congo red increased the adsorption ion effectiveness of the dye sample.

1. Introduction

Nowadays, water contamination by the dye is one of the major threats to human health and the environment [1]. Commercial dyes are normally described by their structural and color stability, high degree of aromaticity and widely conjugated chromophores. There are presently around 10,000 various types of synthetic dyes, and more than 10×10^5 tons of them are formed yearly all over the world, with a high percentage of them being azo dyes [2]. Meanwhile, dyes are a major class of synthetic organic compounds generated from a variety of sources, such as leather, plastics, textile industry plants, paper, the food and pharmaceutical industries, others in to the ecosystem [3]. Moreover, Congo Red (CR) dye, also known as Direct Red 28, is a synthetic azo dye that has been widely used in the textile industry to color garments. Mutagenicity refers to a substance's ability to cause genetic mutations, which can lead to negative health effects such as cancer. Exposure during pregnancy or to developing organisms can cause developmental defects and reproductive harm. Congo Red can irritate the skin and eyes when in touch. People who touch or come into contact with items containing Congo Red may develop skin

irritation, redness, and itching. The release of Congo Red into the environment, particularly aquatic bodies, might have negative consequences [3]. It may contribute to water contamination, harming aquatic ecosystems. So, the removal of these organic dyes is essential.

To solve the problem of water pollution, extensive techniques have been utilized, including Fenton, surface adsorption, chemical precipitation, flocculation, coagulation, photocatalysis, biological treatment, ozonation, membrane filtration, advanced oxidation processes, and zonal filters [4]. Nevertheless, the majority of these techniques suffer from some drawbacks, such as insensitive reaction conditions, high expenditure, and phase transfer of contaminants. Therefore, there is an essential requirement for the growth of an efficient handling process for the removal of these organic dyes from the environment. To facilitate, the removal of organic contaminants from the pollutant water, the removal procedure of organic dyes by various kinds of samples has fascinated growing concentrations during the past decades. NaBH_4 is a well-known reducing agent. Removal of organic dyes by NaBH_4 in the nonexistence of an adsorbent is kinetically not easy but thermodynamically favorable [5]. As a possible alternative, adsorption of organic pollutants was employed with nanoparticles such as Fe_3O_4 , Ag and Cu nanoparticles due to their cost efficiency [6–10]. The major complexity in their application includes nanoparticle agglomeration which can result in the deactivation of nanocatalysts and their removal from the reaction medium, therefore making revival and renewal hard. Consequently, there is a need for an increase in environmentally benevolent techniques for the synthesis of heterocomposites through the immobilization of nanoparticles on/into solid supports [11–13].

Among different solid support components, graphene oxide (GO) and reduced graphene oxide (rGO) are well-recognized as they offer practical benefits over other supports such as improved specific surface area, good thermal/chemical stability, good mechanical strength, high structural flexibility, ease of work-up, handling and separation of products, non-toxic nature and high adsorption efficiency [14]. Moreover, rGO forms a nanocomposite sample with inorganic and polymer components due to its acquisition of many unique features, such as good thermal conductivity, more charge carriers and planar structure. Reduced graphene oxide and plenty of its composites are extensively employed in optical, optoelectronic, bioengineering, catalytic, biosensor, magnetic, electrochemical sensor and energy storage [15–30]. Moreover, rGO based samples act as efficient adsorbents for organic pollutants such as dyes, pesticides, and antibiotics [31–33]. The rGO based samples were utilized as a support for many catalysts such as ZnO, Pt, Au, and Fe_3O_4 [11]. Due to their intriguing electronic conductivity, high adsorption capacity, and large surface area, many explorers also employed rGO-based components as electron acceptors and supporting matrix for catalyst particles to develop the effectiveness of the removal of dyes. Moreover, Nickel cobaltite (NiCo_2O_4) has been investigated for its possible use in adsorption applications, including the removal of dyes such as Congo Red from aqueous solutions. When NiCo_2O_4 is utilized as a composite material or in conjunction with other substances (for example, graphene oxide), synergistic effects can improve overall adsorption performance.

In this work, we have discussed the synthesis and characterization of a NiCo_2O_4 /rGO hybrid nanocomposite with stability and good catalytic properties. Moreover, NiCo_2O_4 nanoparticles and the high adsorption capacity of the rGO/ NiCo_2O_4 hybrid nanocomposite were prepared through a facile hydrothermal method. And nanocomposite was studied for its applicability in the removal of Congo red dye in aqueous solutions. The amount of dye reduction has been examined using UV–visible spectroscopy.

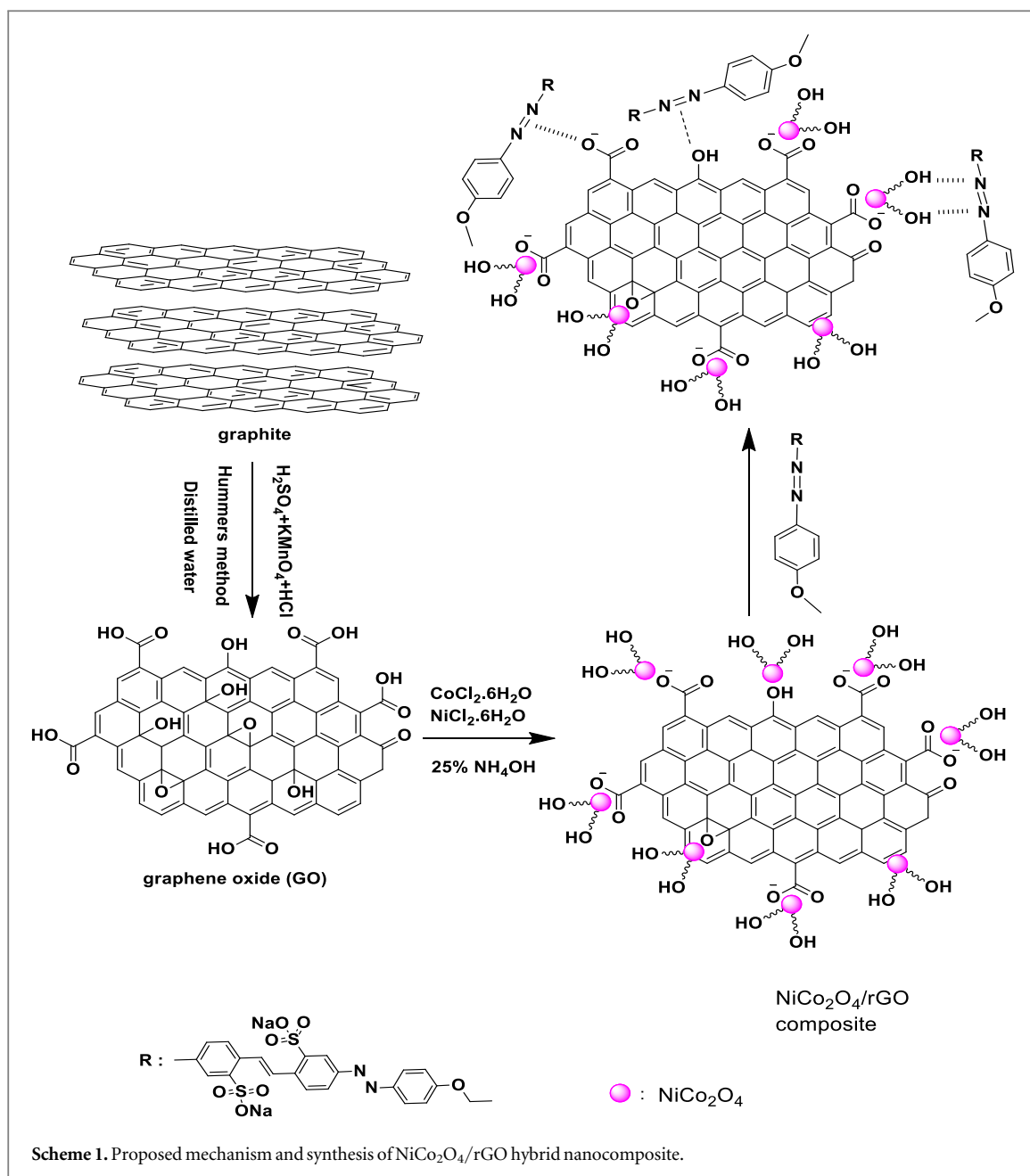
2. Materials and methods

2.1. Materials

Graphite powder, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, KMnO_4 , HCl, NaOH, NaNO_3 , H_2SO_4 , H_2O_2 and NH_4OH have been procured from Sigma Aldrich. Deionized water was utilized throughout this study.

2.2. Synthesis of GO

To make graphene oxide, a modified Hummers process was used [34]. In this technique, 34.5 ml of concentrated H_2SO_4 was added to 1.5 g of graphite powder and 0.75 g of NaNO_3 , and the resulting mixture was cooled to 0 °C in an ice bath. Slowly adding 4.5 g of solid KMnO_4 while keeping the reaction temperature below 20 °C. The reaction was carried out at 35 °C for 7 h with magnetic stirring after the addition of KMnO_4 . A further 4.5 g of KMnO_4 was added, and the mixture was stirred for 12 h at 35 °C. After cooling to room temperature, the reaction mixture was poured into 200 ml of cold water and 1.5 ml of 30% H_2O_2 . Finally, the mixture was centrifuged and rinsed multiple times with water, 30% HCl, and ethanol. The resulting product was dispersed in water, sonicated for 30 min, filtered, and then vacuum-dried overnight at 60 °C.



2.3. Synthesis of $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite

The preparation of the $\text{rGO}/\text{NiCo}_2\text{O}_4$ hybrid sample is shown in scheme 1. A modified Hummers method was utilized to prepare graphene oxide. The $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite has been prepared through a hydrothermal process [35]. 20 mg of graphene oxide were added to 35 ml of de-ionized water by ultrasonication for 20 min. After that, 0.119 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.273 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dispersed in 15 ml of de-ionized water. The above synthesized solution was slowly mixed into the solution of GO over 1 h under strong stirring to obtain a homogeneous solution. Next, NH_4OH (25%) was dissolved into the above synthesized sample under a constant rate of stirring to maintain the pH of the sample at ~ 11 . After stirring for 8 h, the as-synthesized solution was transferred into a 100 ml autoclave. The reaction was carried out at 150°C for 20 h. The resultant product was washed with ethanol, water and further dried at 70°C in the oven for 10 h. The resultant sample was further calcined at 400°C for 5 h under Ar atmosphere at a rate of 3°C min^{-1} employing a muffle furnace, to get the final product, which is $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite. The pure NiCo_2O_4 was synthesized by the same process without mixing GO.

2.4. Catalytic reductions of congo red

The Congo red adsorption tests were conducted by stirring 150 mg of $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite in 25 ml of Congo red (200 mg l^{-1}) at room temperature. 30 ml of newly synthesized aqueous NaBH_4 solution

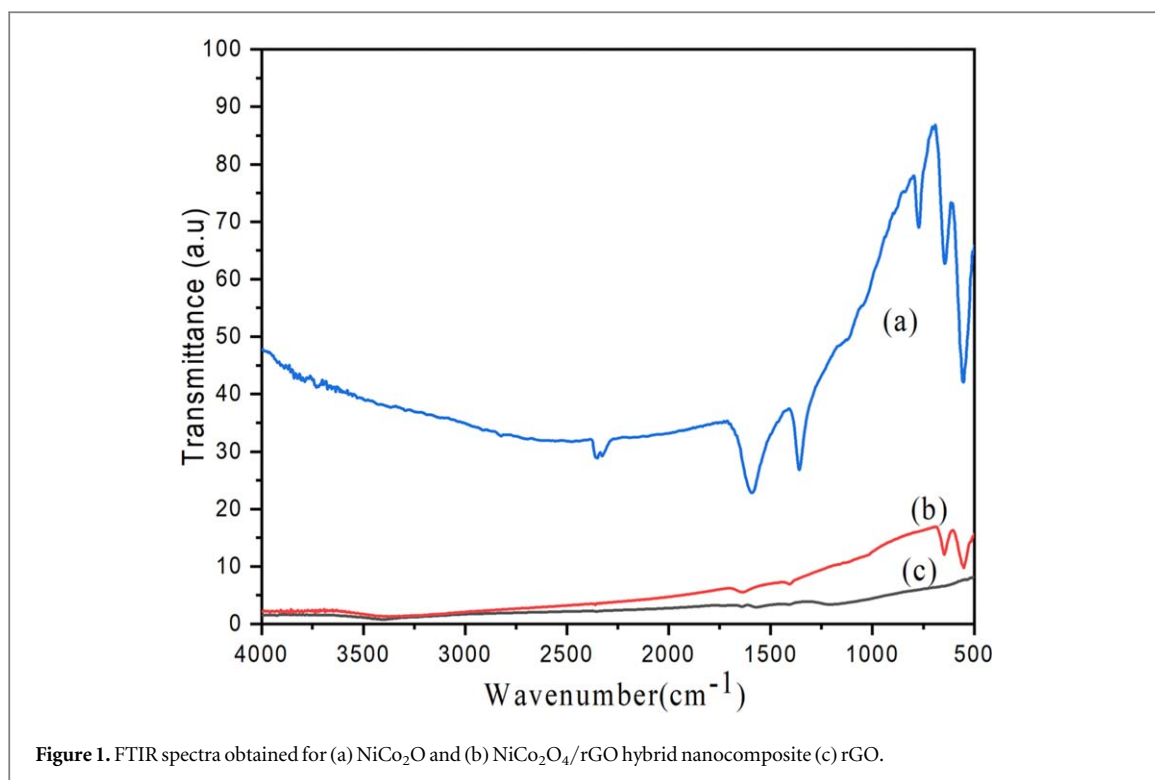


Figure 1. FTIR spectra obtained for (a) NiCo₂O₄ and (b) NiCo₂O₄/rGO hybrid nanocomposite (c) rGO.

(3.5×10^{-3} M) has dissolved, and the above solution was vigorously stirred at room temperature. UV-vis spectroscopy was used to determine the concentration of the leftover dye solution by measuring absorbance at the maximum absorption wavelength of $\lambda_{\text{max}} = 493$ nm for CR. If the pH needs to be lowered, sulfuric acid (H₂SO₄) can be added. These acids donate protons, decreasing the pH of the solution. Moreover, if the pH needs to be raised, sodium hydroxide (NaOH) can be added. These bases accept protons, increasing the pH of the solution. The following adsorption conditions were used in the experiment: an adsorbent dosage of 150 mg; solution volume of 25 ml; and a temperature of 25 °C. Equation (1) was used to get the dye adsorption percentage.

$$\text{Adsorption \%} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Equation (1) was used to compute the rGO/NiCo₂O₄ composite's equilibrium adsorption capacity (Q_e).

$$Q_e = \frac{(C_i - C_e)V}{M} \quad (2)$$

Where C_i is the initial concentration of Congo red solution (mg/l), C_e is the dye concentration at close to equilibrium, V is the volume of dye solution (L), and M is the dosage of the composite (g).

2.5. Characterization techniques

Molecular structure was examined by FTIR measurements (Thermo Nicolet FTIR – 200). The x-ray diffraction (XRD) analysis of the sample was carried out on an x-ray powder diffractometer Bruker AXS D8 advanced diffractometer). Morphological structure was studied by field emission scanning electron microscopes (SEM, FEI, and Quanta 400). The microstructure and morphology were explored by TEM (JEOL JEM-3010 machine operated at 200 kV). The specific surface area has been explored employing the Brunauer–Emmet–Teller (BET) technique. Raman analysis of the obtained product was explored on (Horiba HR 800UV confocal Raman spectrometer).

3. Results and discussions

3.1. Characterization of NiCo₂O₄/rGO hybrid nanocomposite

The FTIR spectrum has been explored in the frequency range 4000–400 cm^{−1} to recognize the chemical bonding states between the GO and NiCo₂O₄. Figure 1, exhibits the FTIR spectrum of rGO, pristine NiCo₂O₄ and rGO/NiCo₂O₄. The FTIR spectrum of rGO represents the characteristic peaks at 3300–3600, 1644, 1278 cm^{−1}

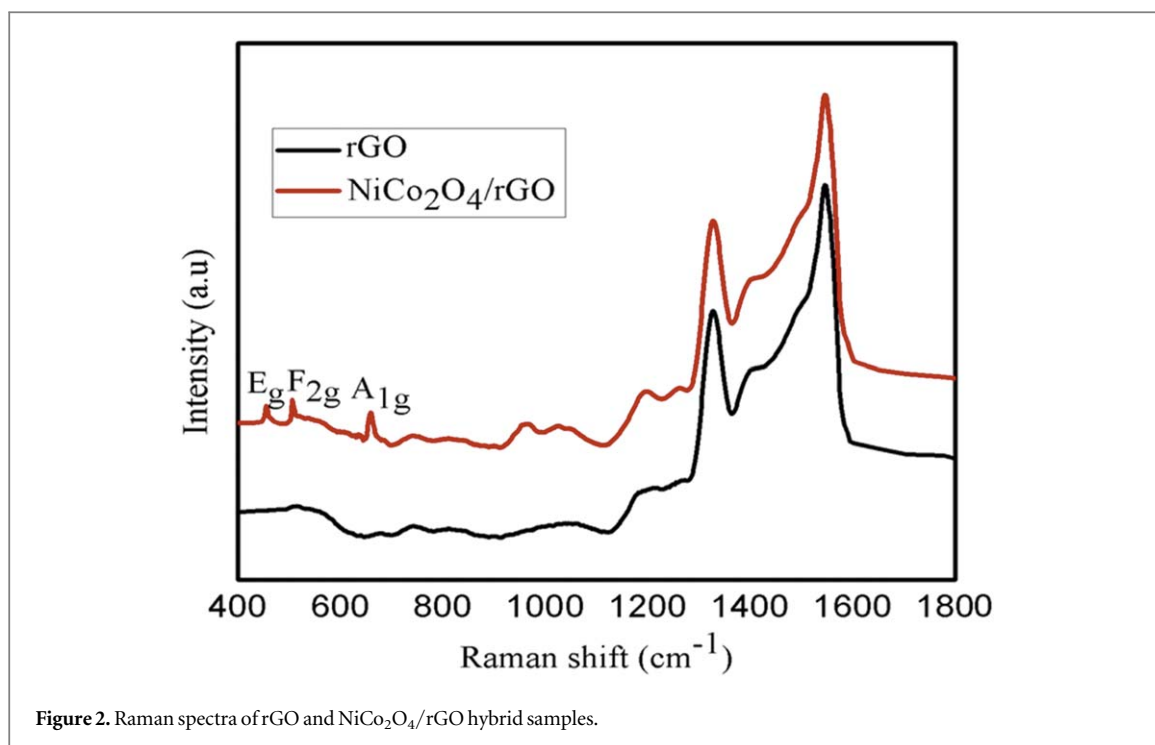


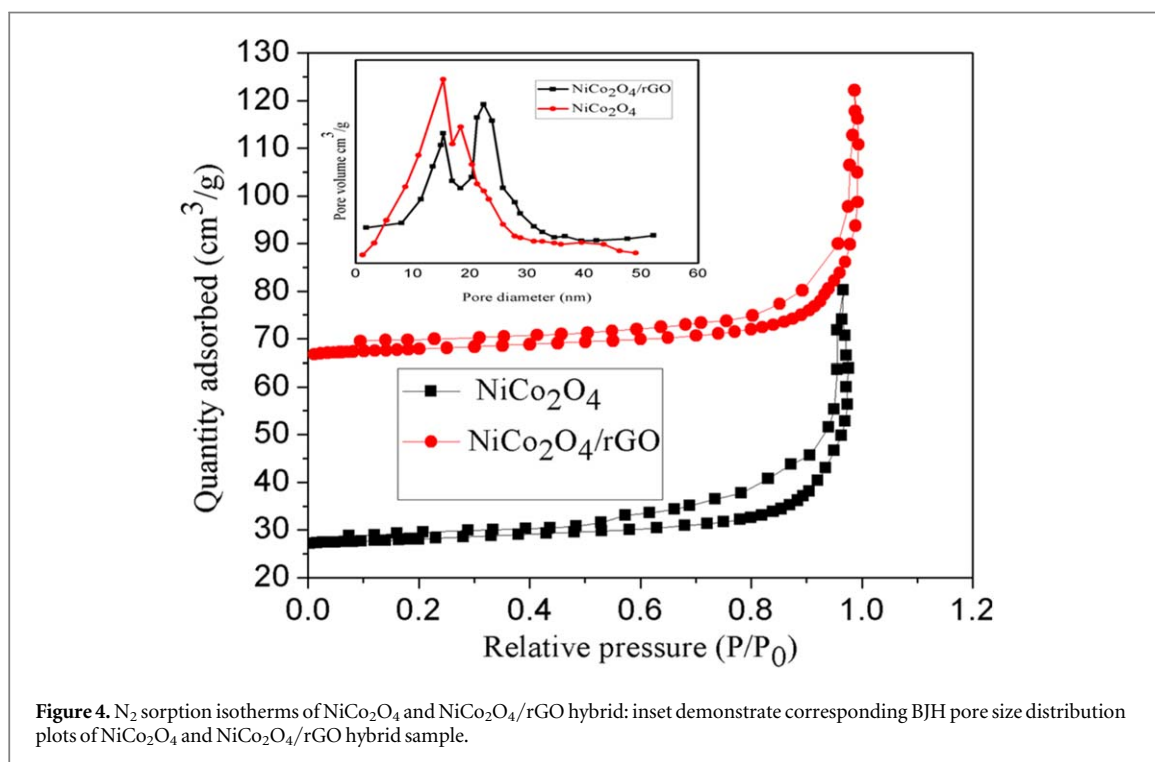
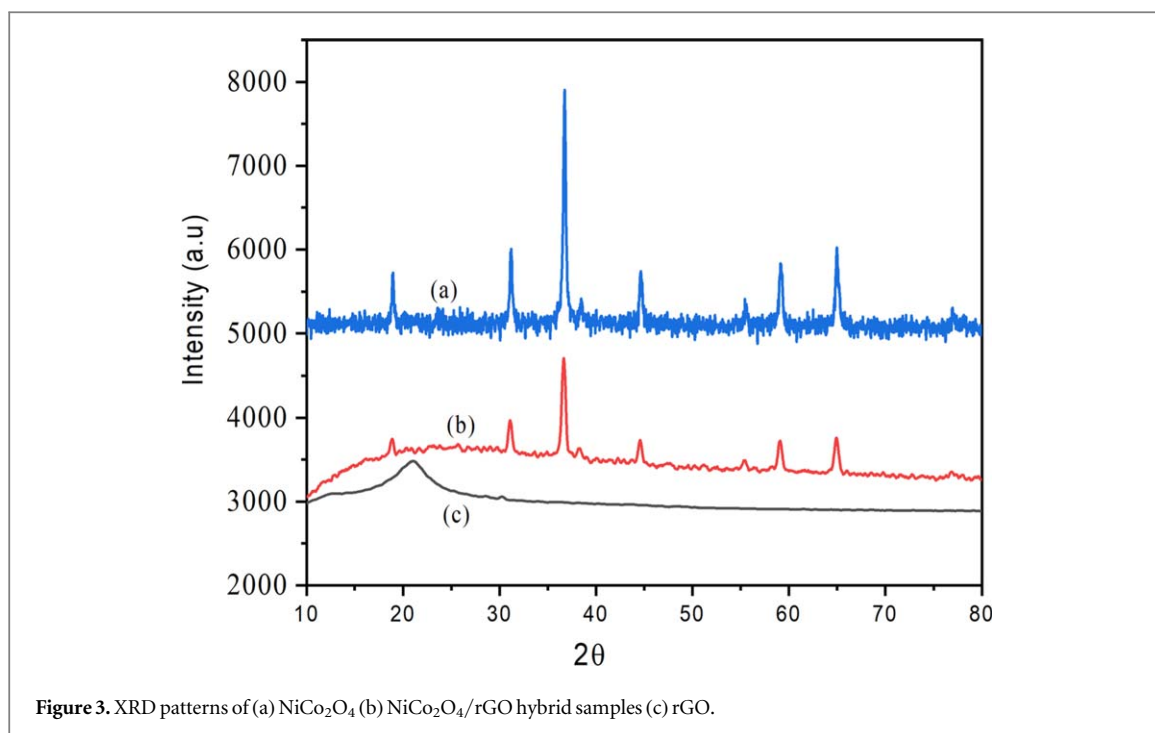
Figure 2. Raman spectra of rGO and NiCo₂O₄/rGO hybrid samples.

which correspond to functional groups –OH, C = O, C–O–C bonds with stretching vibrations (figure 1(c)) [36, 37]. The NiCo₂O₄/rGO hybrid nanocomposite spectrum demonstrates two intense bands at 548 and 650 cm^{−1} owing to the metal oxygen vibrations of NiCo₂O₄ and along with the other bands in the range of 315–3600 cm^{−1} 1636 cm^{−1} have identified in the case of NiCo₂O₄/rGO hybrid nanocomposite (figure 1(b)) [38]. Moreover, figure 1(a) shows the FT-IR spectra of the NiCo₂O₄ material. The strong peaks at 556 and 651 cm^{−1} are caused by Ni–O and Co–O stretching vibrations, which result in the development of the spinel NiCo₂O₄ nanostructure.

The Raman spectrum of rGO is usually depicted by two definite characteristics such as the G and D modes which are shown to the E_{2g} phonon of sp² carbon atom and breathing mode of the k point photons of A_{1g} symmetry, respectively. Figure 2, demonstrates the Raman spectra of rGO and NiCo₂O₄/rGO hybrid nanocomposite materials. Both NiCo₂O₄/rGO hybrid nanocomposite and rGO materials exhibit two broad peaks at about 1328 cm^{−1} (D band) and 1547 cm^{−1} (G band). In the Raman spectra of NiCo₂O₄/rGO hybrid nanocomposite peaks observed at around 454, 502 and 656 cm^{−1} could be ascribed E_g, F_{2g} and A_{1g} of the phonon modes of NiCo₂O₄ which are related to the vibrations of Co–O and Ni–O bonds. A similar phenomenon was also shown in the literature [39, 40].

In order to examine the influence of surface structure on catalytic performance, the crystal structure of rGO, pure NiCo₂O₄ and NiCo₂O₄/rGO hybrid nanocomposite was characterized by XRD technique, the results are given in figure 3. GO reveals a diffraction peak at 10.4° corresponding to the (002) plane, after removing oxygen functional groups, interlayer spacing decreased and the peak shifted to 22.1°. Furthermore, the XRD patterns of pure NiCo₂O₄ samples are presented in figure 3(a). Pristine NiCo₂O₄ samples exhibit significant diffraction peaks corresponding to cubic spinel NiCo₂O₄ (JCPDS no. 73–1702). Disorderedly stacked rGO nanosheets exhibit less diffraction than well-crystalline NiCo₂O₄. The lower crystallite size of NiCo₂O₄ in NiCo₂O₄-rGO hybrid nanocomposite is due to the great dispersing action of rGO sheets, which prevents NiCo₂O₄ nanoparticle aggregation. As presented in figure 3, NiCo₂O₄/rGO hybrid nanocomposite demonstrates clear diffraction peaks at 18.76, 31.25, 36.25, 44.19, 59.35 and 65.23° corresponding to (111), (220), (311), (400), (422), (511) and (440) plane reflections of the spinel crystalline structure of NiCo₂O₄/rGO hybrid nanocomposite (JCPDS Card No:20–0781) [41].

The BET specific surface area of NiCo₂O₄ and NiCo₂O₄/rGO hybrid nanocomposite has been explored employing the liquid N₂ sorption isotherm. Figure 4, depicts BET adsorption and desorption isotherms of the NiCo₂O₄/rGO hybrid nanocomposite material, which represent ‘type IV’ isotherms, with the characteristics of a mesoporous sample. The BET surface areas for NiCo₂O₄/rGO hybrid nanocomposite and pure NiCo₂O₄ materials are 56.4 m² g^{−1} and 42 m² g^{−1}. The mesoporous nature of NiCo₂O₄/rGO hybrid nanocomposite was proved by the BJH pore size distribution analysis and BET specific surface area. The average diameter of these materials is found to be in mesoporous region, with the bi-modal for NiCo₂O₄/rGO hybrid nanocomposite and



NiCo_2O_4 . Nevertheless, the pore size distribution maxima are located at 15.4 and 22.5 nm for $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite, whereas those in pure NiCo_2O_4 material are at 15.3 nm and 18.3 nm. These mesoporous $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite have budding application in organic dyes from the environment and the removal of toxic metals.

The microstructure and morphology of the $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite were explored by SEM and TEM. Figure 5(a), shows the SEM image of the $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite. The SEM image attained for $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite exhibits that it has a sheet-like morphology. A closer look reveals that tiny NiCo_2O_4 nanocrystals are uniformly packed over the surface of the rGO nanosheets. TEM images of RGO sheets consist of few layers stacked each other with less wrinkles and folding, indicative of the reduction process from graphene oxide and the formation of defects. The edges may appear more electron-

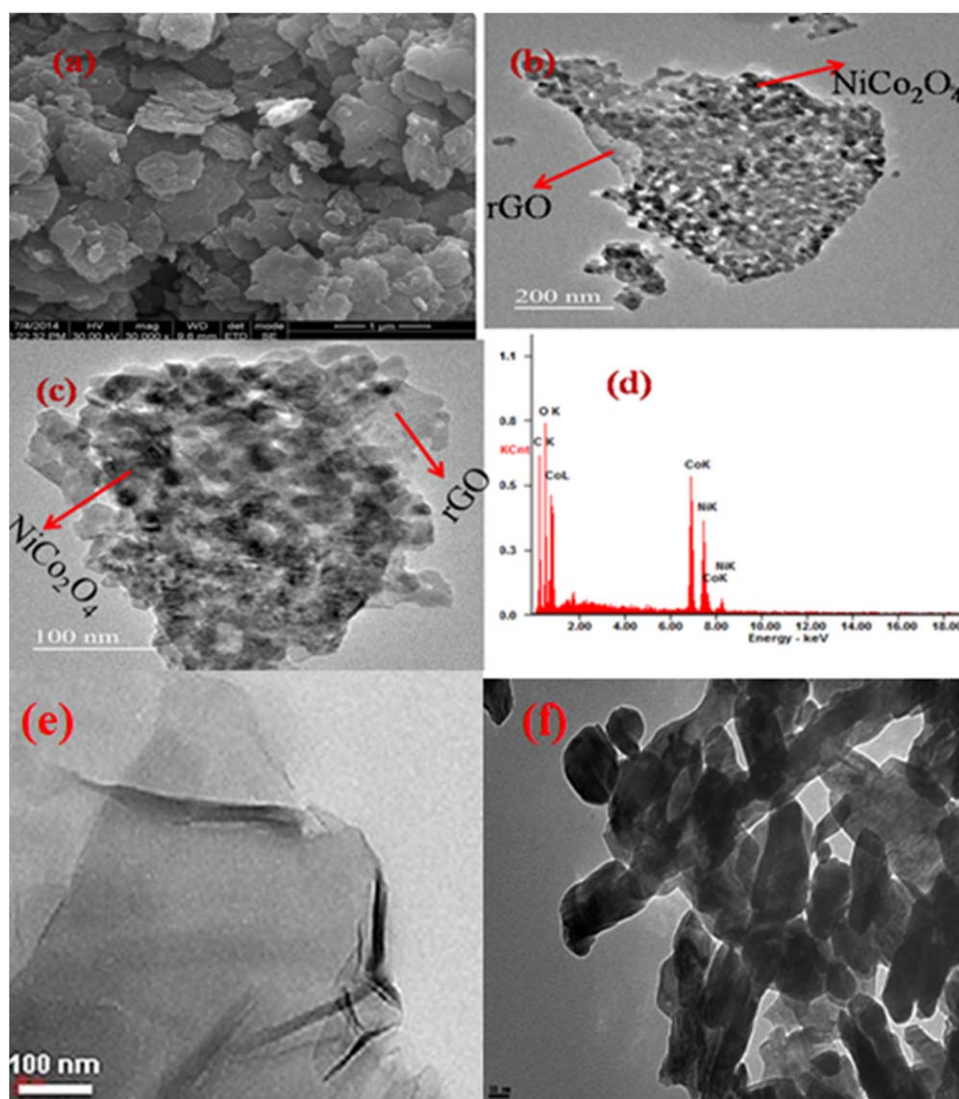


Figure 5. (a) SEM image of NiCo₂O₄/rGO hybrid sample (b and c) TEM images of NiCo₂O₄/rGO hybrid sample at different magnification (d) EDS analysis of NiCo₂O₄/rGO hybrid sample (e) TEM image of rGO (f) TEM image of NiCo₂O₄.

dense due to the presence of oxygen-containing functional groups, which are reduced during the synthesis process. Moreover, TEM images of the as-prepared pure NiCr₂O₄ sample are shown in figure 5. The TEM pictures of NiCr₂O₄ nanostructures clearly show that they were constructed from numerous nanoparticles of uniform size. In figures 5(b) and (c) TEM images of NiCo₂O₄/rGO hybrid nanocomposite showed important changes in the surface morphology and roughness, visually representing the presence of NiCo₂O₄ nanoparticles. The shape of the as-prepared NiCo₂O₄ sample is quasi-spherical with an average size of ~46 nm. A close examination of the SEM micrographs of the NiCo₂O₄/rGO hybrid nanocomposite demonstrates the random distribution of quasi-spherical NiCo₂O₄ samples on the rGO surface. The results of EDS analysis were demonstrated in figure 5(d), which obviously indicates the presence of Ni, Co and C in the resulting sample. To prove the whole sample which contains Ni, Co, O, and C, no other elements were seen.

3.2. The effect of different parameters on removing Congo red dye

3.2.1. Effect of initial pH

The effect of initial pH on CR adsorption has been explored over the pH range of 3–9. As depicted in figure 6(a) the effectiveness of removing CR by NiCo₂O₄/rGO hybrid nanocomposite decreased when the pH range increased from 3–9. This is due to the active sites of the NiCo₂O₄/rGO hybrid nanocomposite converting from a positive to a negative charge when the pH range increased, resulting in the presence of electrostatic repulsion between the NiCo₂O₄/rGO hybrid nanocomposite and CR dye as CR molecule is an intrinsically anionic dye. It was observed that the adsorption is enormous in an acidic medium. This is owed to the increases in the number

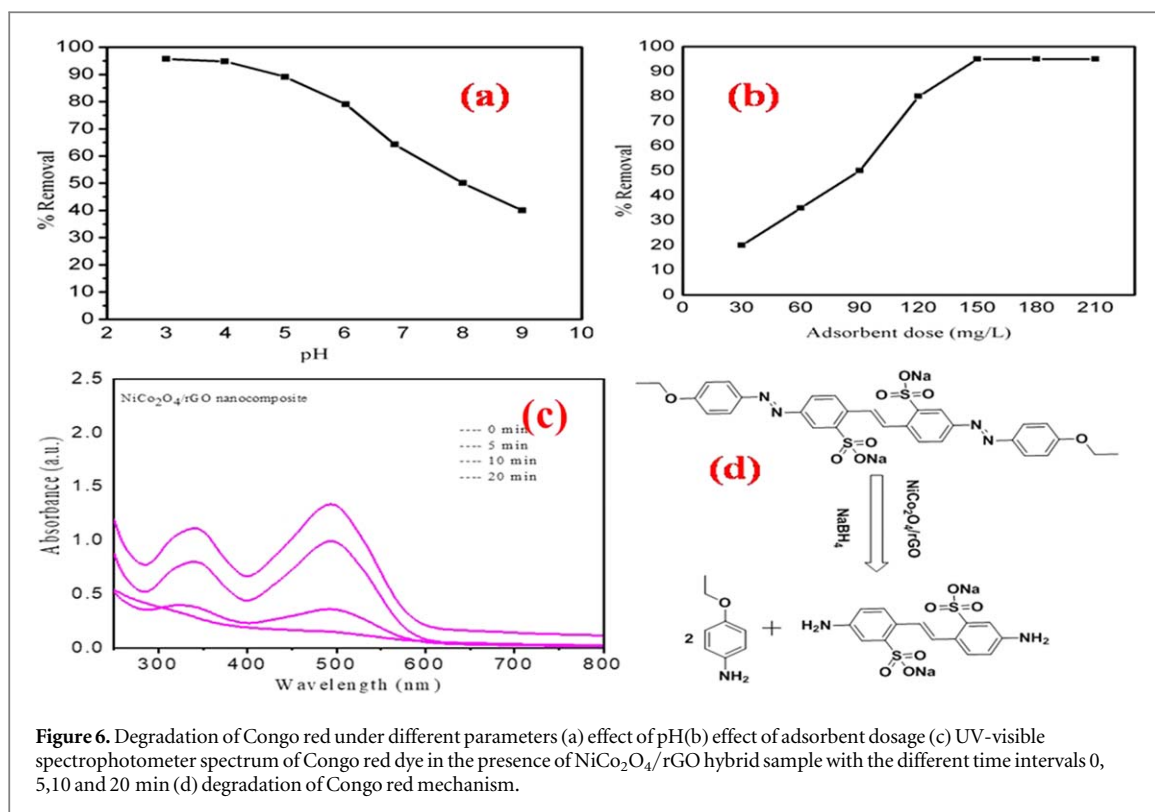


Figure 6. Degradation of Congo red under different parameters (a) effect of pH (b) effect of adsorbent dosage (c) UV-visible spectrophotometer spectrum of Congo red dye in the presence of $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid sample with the different time intervals 0, 5, 10 and 20 min (d) degradation of Congo red mechanism.

of positively charged sites with decreasing pH values, which favor the electrostatic attractions between $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite and CR dye.

3.2.2. Effect of the adsorbent dose

The effect of $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite concentration on the adsorption of Congo red by the $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid sample is shown in figure 6(b), where we can study that increasing the concentration of the adsorbent range from 30, 60, 90, 120, 150, 180 and 210 mg L^{-1} improved the dye adsorption effectiveness. This may be attributed to the larger $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite surface area and more available adsorption active sites. The removal effectiveness of Congo red dye is not extensively affected by a further increase in adsorbent amount over 150 mg/l . This shows that a part of the $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite surface remains uncovered, due to the aggregation of the adsorbent particles at the higher adsorbent dose.

3.2.3. Effect of congo red initial concentration

As the CR concentration increases from 200, 250, and 300 mg L^{-1} , the percentage of CR adsorbed by $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite declines from 95.7%, 65%, and 46%. The removal effectiveness of CR dye decreased when dye concentration increased due to fewer surface-active sites for constant adsorbent dosage.

3.2.4. Adsorption study

NiCo_2O_4 has a strong catalytic activity because of its distinct electrical structure and surface characteristics. The synergy of nickel and cobalt ions in the oxide lattice improves catalytic activity. This degradation process frequently results in the formation of reactive oxygen species on the catalyst's surface, which can oxidize and degrade dye molecules. NiCo_2O_4 nanoparticles can also act as photocatalysts, degrading Congo Red dye in response to solar or visible light exposure. This photocatalytic activity is related to NiCo_2O_4 's semiconductor nature, which allows for light absorption and the formation of electron-hole pairs, thereby initiating redox reactions with dye molecules. NiCo_2O_4 catalysts are normally quite stable and can be reused several times without losing important catalytic activity. This is useful in practical applications since it eliminates the requirement for regular catalyst replacement.

Further, the catalytic activity of the as-prepared $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite was employed to examine its application in organic dye adsorption experiments. The catalytic activity of the $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid nanocomposite has been studied with the catalytic reduction of Congo red by NaBH_4 in water treatment. The reduction reaction can be simply examined with UV-vis spectroscopy. The figure 6(c) demonstrates that CR solution revealed the typical band at 496 nm and demonstrates the absorbance's changes calculated at different

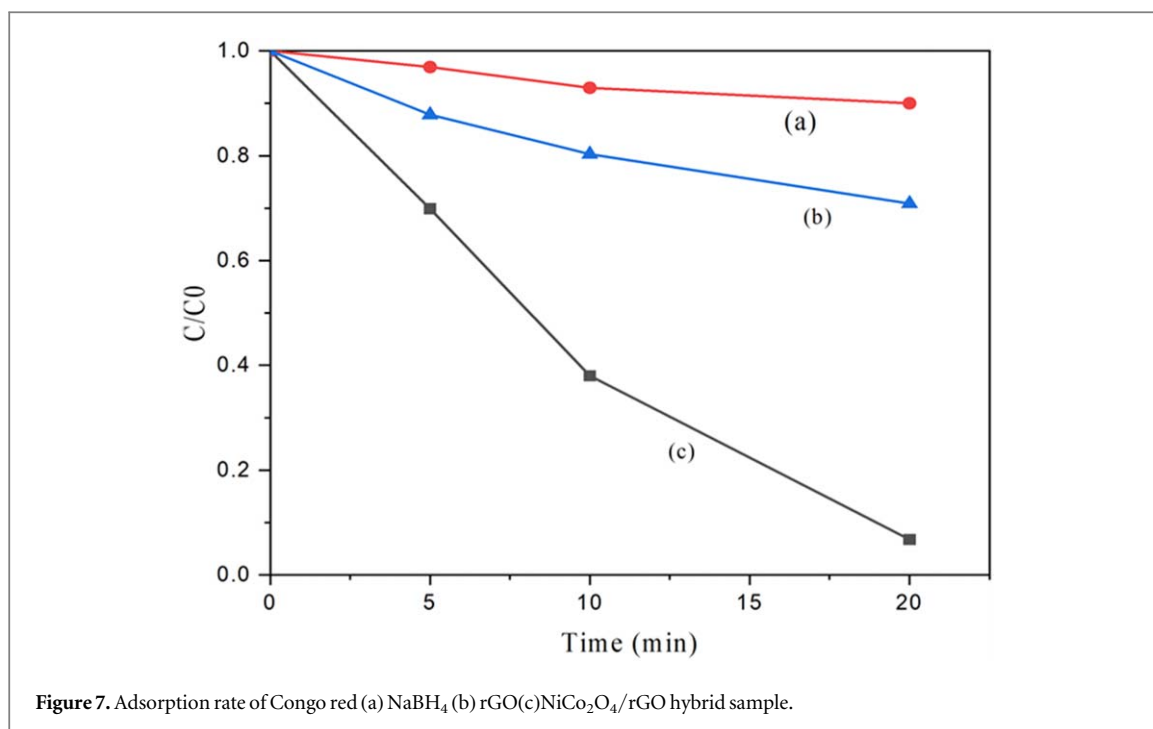


Table 1. Comparison of various catalysts in the reduction of Congo red.

S. N	Adsorbent	Time	References
1	Fe ⁰ /polyaniline nanofibers	30 min	[42]
2	ZnFe ₂ O ₄ /SiO ₂ /TG nanocomposite	60 min	[43]
3	Fe ₃ O ₄ -TSPED-Tryptophan	10 min	[44]
4	ZnO/MWCNTs	50 min	[45]
5	Bentonite/ chitosan@Co ₃ O ₄	480 min	[46]
6	MgO/GO composite	3 h	[47]
7	ZnO-Al ₂ O ₃ microspheres	40 min	[48]
8	rGO/NiCo ₂ O ₄ hybrid nanocomposite	20 min	Present work

time intervals during the NaBH₄ reduction of CR in the presence of NiCo₂O₄/rGO hybrid nanocomposite at room temperature. The catalytic adsorption studies have been conducted in the absence and presence of a NiCo₂O₄/rGO hybrid nanocomposite. The reduction of Congo red by NaBH₄ in aqueous solution happened very slowly without any catalyst other than proceeds quickly with NiCo₂O₄/rGO hybrid nanocomposite. To begin with, adding NaBH₄ alone to the organic dye did not decrease dispersion, however NiCo₂O₄/rGO hybrid nanocomposite removal dye within 20 min. The catalytic activity of the prepared NiCo₂O₄/rGO hybrid nanocomposite is related to the earlier reported nanoparticles for the removal of Congo red by NaBH₄ [42–48].

In addition, the catalytic mechanism for removal of Congo red relies on the e[−] move from the BH₄[−] donor to the acceptor Congo red by adsorption of the reactant molecules on to the catalyst surface [49]. The NiCo₂O₄/rGO hybrid nanocomposite can provide a good substrate for the e[−] transfer reaction from BH₄[−] donor to Congo red. It recommends the catalytic adsorption of CR dye, and the catalytically active NiCo₂O₄/rGO hybrid composite was chosen as a model to improve the dye adsorption rate, because of its unique features, such as its reactive surface and large specific area [50]. The presence of hydroxyl groups over the surface of the NiCo₂O₄/rGO hybrid composite interact with the CR dye through hydrogen bonding and electrostatic interactions, helping the adsorption of the CR dye. The catalytic performance of the present NiCo₂O₄/rGO hybrid nanocomposite is compared with that reported for other samples in table 1, demonstrating that it has a better removal performance than other composite materials for the removal of Congo red. This phenomenon is clearly clarified in figure 6(d). After 20 min at room temperature and in the presence of NaBH₄ and NiCo₂O₄/rGO hybrid nanocomposite materials, 95.7% of total CR has been successfully degraded from the solution (See figure 7). These are much better than the rGO and NaBH₄ materials (removed only 28% and 9%). After the completion of four cycles, there is a small decrease (~90%) in the catalytic

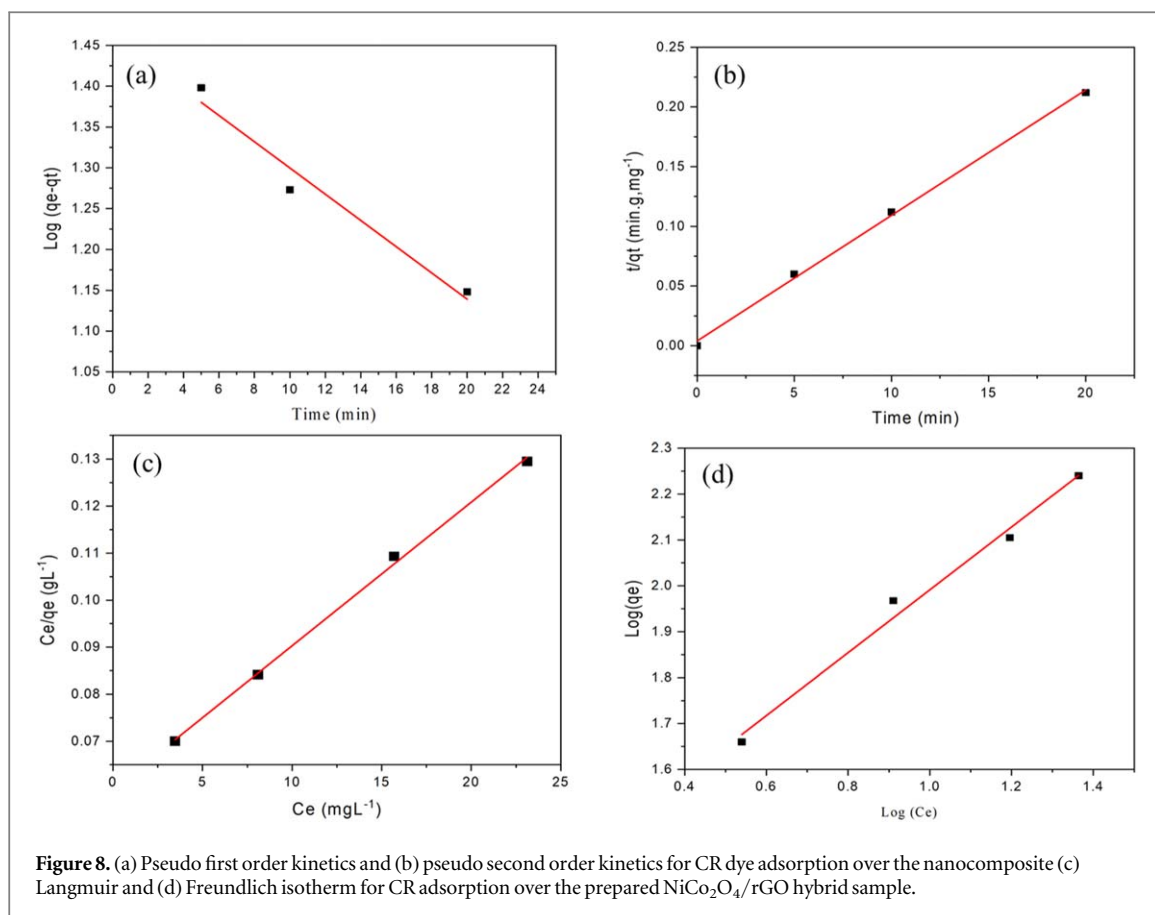


Table 2. Kinetic model parameters for CR adsorption over NiCo₂O₄/rGO hybrid nanocomposite.

Pseudo first order			Pseudo second order		
$K_1 \text{ min}^{-1}$	$q_e \text{ (mg g}^{-1}\text{)}$	R^2	$K_2 \text{ (g/mg. min)}$	$q_e \text{ (mg/g)}$	R^2
0.037	4.82	0.9642	0.027	95.60	0.9983

adsorption percentage. The result revealed that the NiCo₂O₄/rGO hybrid nanocomposite has reasonable stability in the adsorption reaction media.

3.2.5. Adsorption kinetics

The dye adsorption data were examined using the pseudo first-order and pseudo-second-order, which are discussed below, in order to understand the CR adsorption process on NiCo₂O₄/rGO hybrid nanocomposite, particularly the potentially rate-controlling stage. Lagergren proposed the pseudo-first-order kinetic model for the adsorption of solid/liquid systems, and its formula is as follows [51–54]:

$$\ln(q_e - q_t) = \ln q_e - \frac{K_1}{2.303} t \quad (3)$$

where q_t (mg/g) and q_e (mg/g) signify the quantity of dye adsorbed at any time t (min) and at the equilibrium time, respectively, and k_1 (1/min) is the rate constant of pseudo-first-order adsorption. k_1 is determined by plotting $\log(q_e - q_t)$ versus t . The estimated and experimental q_e values, however, do not agree (table 2), and the pseudo-first-order kinetic model does not adequately represent the CR adsorption on NiCo₂O₄/rGO hybrid nanocomposite. The pseudo-second-order kinetic model's linear form can be written as [55, 56]:

Table 3. Adsorption isotherm parameters for CR adsorption by NiCo₂O₄/rGO hybrid nanocomposite.

Langmuir			Freundlich		
qm (mg/g)	b (L/mg)	R ²	K _F (mg/g)	n	R ²
106.28	1.12	0.9982	6.7842	1.460	0.9888

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 (g/(mg min)) is the rate constant of pseudo-second order adsorption calculated using linear plots of t/q_t against t (table 2). The experimental and predicted values for q_e were close; additionally, by comparing the correlation coefficients (R^2) values obtained for pseudo-second order and pseudo-first-order kinetics, the adsorption process can be determined to be a pseudo second-order reaction, as shown in figures 8(a) and (b).

3.2.6. Adsorption isotherms study

The initial concentrations of Congo red solutions were varied to study adsorption isotherms. The adsorption isotherm data of Congo red onto composites was fitted with two classic isotherm models, namely, Langmuir (equation (5)) and Freundlich (equation (6)), which are expressed by the equation:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (5)$$

Where C_e (mg.L⁻¹) represents the equilibrium concentration of CR dye, q_e (mg/g) represents the equilibrium adsorption capacity, q_m (mg/g) represents the maximum adsorption capacity, and b (L/mg) represents the Langmuir constant. The Freundlich adsorption isotherm model, on the other hand, posits a heterogeneous surface with adsorption sites with unequal energies. This may be represented using equation (6) as follows:

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (6)$$

Where K_F (mg.g⁻¹) denotes the Freundlich constant and $(1/n)$ denotes the adsorption extent. Figures 8(c) and (d), shows the linear plots of the Freundlich and Langmuir isotherms. According to table 3, the determination coefficients (R^2) for Langmuir were found to be 0.9982, while those for Freundlich were found to be 0.9888, demonstrating that both models can adequately represent the adsorption of CR onto NiCo₂O₄/rGO hybrid nanocomposite. Furthermore, the Freundlich n value is 1.460, indicating a significant affinity between the CR and the NiCo₂O₄/rGO hybrid nanocomposite ($n > 1$). According to the Langmuir isotherm, the maximal CR adsorption capacity onto NiCo₂O₄/rGO is 106.28 mg g⁻¹. Furthermore, the maximal adsorption capacity of CR onto NiCo₂O₄/rGO hybrid nanocomposite was compared to that of previously described adsorbents [56]. This is most likely due to the fact that NiCo₂O₄/rGO hybrid nanocomposite can interact with CR in a variety of ways, including (i) electrostatic attraction between CR and NiCo₂O₄/rGO hybrid nanocomposite and (ii) conjugation between the benzene rings of NiCo₂O₄/rGO hybrid nanocomposite and aromatic CR. (iii) hydrogen bonding between CR and NiCo₂O₄/rGO hybrid nanocomposite.

4. Conclusions

In summary, we studied a facile hydrothermal method for the synthesis of NiCo₂O₄/rGO hybrid nanocomposite. The prepared NiCo₂O₄/rGO hybrid nanocomposite has been proven by FTIR and Raman scattering measurements. The NiCo₂O₄/rGO hybrid nanocomposite crystal structure and phase were investigated employing XRD and the quasi-spherical morphology was resolved by TEM analysis. The BET investigation recommended that the accumulation of rGO to NiCo₂O₄ was the reason for the significant increase in the catalytic performance with a surface area value of 56.4 m² g⁻¹. Moreover, the NiCo₂O₄/rGO hybrid nanocomposite demonstrates strong catalytic activity towards Congo red dye adsorption. Enhanced adsorption activity of NiCo₂O₄/rGO compared to NaBH₄ was seen owing to the presence of more surface area rGO nanosheets. The important advantages of this methodology are mild reaction conditions, a short reaction time and the elimination of hazardous materials. The Langmuir isotherm model fit the adsorption equilibrium data well, but the pseudo-second-order model fit the kinetic data well. Therefore, our results prove that the NiCo₂O₄/rGO sample exhibits tremendous adsorption performance towards the removal of organic contaminants and can be an appropriate candidate for different eco-friendly environmental applications.

Therefore, we suppose that this nanocomposite has extensive applications in catalysis and has demonstrated its suitability as a nanocomposite for the handling of polluted water with organic dyes.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Funding

This research was supported by Outstanding scientist at a local university through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2022R1I1A3066142). KSU author acknowledges the funding from Researchers Supporting Project number (RSP2024R355), King Saud University, Riyadh, Saudi Arabia.

Ethics declarations

Not applicable.

Ethical approval

Not applicable.

Competing interests

The authors declare no competing interests.

ORCID iDs

Subba Reddy A  <https://orcid.org/0000-0002-6291-5420>

Lebogang Maureen Katata-Seru  <https://orcid.org/0000-0002-7228-305X>

Oyirwoth P Abedigamba  <https://orcid.org/0000-0002-9755-9112>

References

- [1] Chawla S, Uppal H, Yadav M, Bahadur N and Singh N 2017 Zinc peroxide nanomaterial as an adsorbent for removal of congo red dye from water *Ecotoxicol. Environ. Saf.* **135** 68–74
- [2] Kant R 2012 Textile dyeing industry an environmental hazard *Nat. Sci.* **4** 22–6
- [3] Acemioglu B 2004 Adsorption of congo red from aqueous solution onto calcium-rich fly ash *J. Colloid Interface Sci.* **274** 371–9
- [4] Rahimi R, Kerdari H, Rabbani M and Shafiee M 2011 Synthesis, characterization and adsorbing properties of hollow Zn-Fe₂O₄ nanospheres on the removal of Congo red from aqueous solution *Desalination* **280** 412–8
- [5] Dutta S, Gupta B, Kumar Srivastava S and Gupta A K 2021 Recent advances on the removal of dyes from wastewater using various adsorbents: a critical review *Mater. Adv.* **2** 4497
- [6] Prasad C, Yuvaraja G and Venkateswarlu P 2017 Biogenic synthesis of Fe₃O₄ magnetic nanoparticles using Pisumsativum peels extract and its effect on magnetic and Methyl orange dye degradation studies *J. Magn. Magn. Mater.* **424** 376–81
- [7] Prasad C, Karlapudi S, Venkateswarlu P, Bahadur I and Kumar S 2017 Green arbitrated synthesis of Fe₃O₄ magnetic nanoparticles with nanorod structure from pomegranate leaves and Congo red dye degradation studies for water treatment *J. Mol. Liq.* **240** 322–8
- [8] Prasad C, Karlapudi S, Narasimha Rao C, Venkateswarlu P and Bahadur I 2017 A highly resourceful magnetically separable magnetic nanoparticles from aqueous peel extract of Bottle gourds for organic dyes degradation *J. Mol. Liq.* **243** 611–5
- [9] Prasad C, Gangadhara S and Venkateswarlu P 2016 Bio-inspired green synthesis of Fe₃O₄ magnetic nanoparticles using watermelon rinds and their catalytic activity *Appl. Nanosci.* **6** 797–802
- [10] Yuvaraja G, Prasad C, Vijaya Y and Venkata Subbaiah M 2018 Application of ZnO nanorods as an adsorbent material for the removal of As (III) from aqueous solution: kinetics, isotherms and thermodynamic studies *International Journal of Industrial Chemistry.* **9** 17–25
- [11] Prasad C, KrishnaMurthy P, HariKrishna R, SreenivasaRao R, Suneetha V and Venkateswarlu P 2017 Bio-inspired green synthesis of RGO/Fe₃O₄ magnetic nanoparticles using Murrayakoenigii leaves extract and its application for removal of Pb(II) from aqueous solution *J. Environmental Chem. Eng.* **5** 4374–80
- [12] Prasad C, Tang H and Liu W 2018 Magnetic Fe₃O₄ based layered double hydroxides (LDHs) nanocomposites (Fe₃O₄/LDHs): recent review of progress in synthesis, properties and applications *J. Nanostructure in Chemistry.* **8** 393–412
- [13] Prasad C, Karlapudi S, Sellola G and Venkateswarlu P 2017 Bio inspired green synthesis of Ni/Fe₃O₄ magnetic nanoparticles using Moringaoleifera leaves extract: a magnetically recoverable catalyst for organic dye degradation in aqueous solution *J. Alloys and Compounds.* **700** 252–8

- [14] Afkhami A, Saber-Tehrani M and Bagheri H 2010 modified maghemite nanoparticles as an efficient adsorbent for removing some cationic dyes from aqueous solution *Desalination* **263** 240–8
- [15] Aradhya M et al 2019 Comparative electrochemical analysis of rGO-FeVO₄ nanocomposite and FeVO₄ for supercapacitor application *Appl. Surf. Sci.* **488** 221–7
- [16] Majeed Khan M A, Wasi K, Maqsood A and Abdulaziz N A 2019 Investigation on the structure and physical properties of Fe₃O₄/RGO nanocomposites and their photocatalytic application *Mater. Sci. Semicond. Process.* **99** 44–53
- [17] Baoshan H and Xiaohai Y 2019 A 'signal-on' voltammetric aptasensor fabricated by hcPt@AuNFs/PEI-rGO and Fe₃O₄NRs/rGO for the detection of zeaxenone *Sensors Actuators B* **290** 477–83
- [18] Lirong X, Ruiying L, Fang W, Xu G, Xianghui Z, Lianjie Q and Jiaqin Y 2019 In-situ synthesis of porous organic polymer on rGO for high-performance capacitive energy storage *Journal of Energy Storage* **25** 100873
- [19] Mahdi H, Nima N, Benyamin Y, Alireza K and Parvaneh S 2018 Enhanced optical properties of ZnS–rGO nanocomposites for ultraviolet detection applications *Ceram. Int.* **44** 17878–84
- [20] Yibing M, Yaya Z, Youyi S, Chen H, Zhiyuan X, Xiaolin L, Luyan S and Yaqing L 2019 Tunable magnetic properties of Fe₃O₄/rGO/PANI nanocomposites for enhancing microwave absorption performance *J. Alloys Compd.* **796** 120–30
- [21] Lin P, Shen J, Prasad C, Tang H, Liu Q and Zhang M 2019 the synergetic effect of carbon nanotubes and MoS₂ as co-catalysts for enhancing the photocatalytic oxygen evolution of Ag₃PO₄, *Ceram. Int.* **45** 21120–6
- [22] Prasad C, Tang H, Liu Q, Zulfiqar S, Shah S and Bahadur I 2019 An overview of semiconductors/layered double hydroxides composites: Properties, synthesis, photocatalytic and photoelectrochemical applications *J. Molecular Liquids* **289** 111114
- [23] Prasad C, Tang H and Bahadur I 2019 Graphitic carbon nitride based ternary nanocomposites: From synthesis to their applications in photocatalysis: a recent review *J. Molecular Liquids* **281** 634–54
- [24] Prasad C, Liu Q, Tang H, Yuvaraja G, Long J, Rammohan A and Zyryanov G V 2020 An overview of graphene oxide supported semiconductors based photocatalysts: properties, synthesis and photocatalytic applications *J. Mol. Liq.* **297** 111826
- [25] Mohammad B A, Amirhosro B, Majid S, Seyed M R and Parisa S 2019 Fe₃O₄@MoS₂/RGO as an effective nano-electrocatalyst toward electrochemical hydrogen evolution reaction and methanol oxidation in two settings for fuel cell application *J. Colloid and Interface Science* **537** 186–96
- [26] Prasad C, Madkhali N, Lee B-M, Kang C S and Choi H Y 2023 Recent developments in GO/Cellulose based composites: properties, synthesis, and its applications *Polymer* **270** 125786
- [27] Cheng Z, Xinpei G, Shaolong T, Mingsen D and Youwei D 2017 NiCo₂O₄@rGO hybrid nanostructures on Ni foam as high-performance supercapacitor electrodes *J. Mater. Chem. A* **5** 5912–9
- [28] Cheng Z, Chenglong L, Chao C, Shaolong T, Mingsen D, Yuliang L and Youwei D 2018 Interface polarization matters: Enhancing supercapacitor performance of spinel NiCo₂O₄ nanowires by reduced graphene oxide coating *Electrochim. Acta* **260** 814–22
- [29] Salarizadeh P, Askari M B, Seifi M and Rozati S M 2019 MoS₂ coating on different carbonaceous materials: Comparison of electrochemical properties and hydrogen evolution reaction performance *J. Electroanalytical Chemistry* **847** 113198
- [30] Cheng Z, Ye H, Shaolong T, Mingsen D and Youwei D 2017 High-energy all-solid-state symmetric supercapacitor based on Ni₃S₂ mesoporous nanosheet-decorated three-dimensional reduced graphene oxide *ACS Energy Lett.* **24** 759–68
- [31] Barqi J, Masoudpanah S M, Hasheminasari M and Liu X 2023 Nanoribbon-like NiCo₂O₄/reduced graphene oxide nanocomposite for high-performance hybrid supercapacitor *J. Alloys and Compounds* **930** 167509
- [32] Manalu A, Tarigan K, Humaidi S, Ginting M, Sebayang K, Hamid M and Sebayang P 2023 Study and characterizations of NiCo₂O₄/rGO as candidate of supercapacitor electrodes material performance *In AIP Conference Proceedings* **2480** 020001
- [33] Wei Z, Guo J, Qu M, Guo Z and Zhang H 2020 Honeycombed-like nanosheet array composite NiCo₂O₄/rGO for efficient methanol electrooxidation and supercapacitors *Electrochim. Acta* **362** 137145
- [34] Hummers W and Offeman R 1958 Preparation of graphene oxide *J. Am. Chem. Soc.* **80** 1339
- [35] Kumar Das A, Layek R K, Kim N H, Jung D and Lee J H 2014 Reduced graphene oxide (RGO)-supported NiCo₂O₄ nanoparticles: an electrocatalyst for methanol oxidation *Nanoscale* **6** 10657
- [36] Kumar A, Sadanandhan A M and Jain S L 2019 Silver doped reduced graphene oxide as a promising plasmonic photocatalyst for oxidative coupling of benzylamines under visible light irradiation *New J. Chem.* **43** 9116
- [37] Page A J, Chou C-P, Pham B Q, Witek H A, Irle S and Morokuma K 2013 Quantum chemical investigation of epoxide and ether groups in graphene oxide and their vibrational spectra *Phys. Chem. Chem. Phys.* **15** 3725–35
- [38] Li L, Peng S, Cheah Y, Teh P, Wang J, Wee G, Ko Y, Wong C and Srinivasan M 2013 Electrospun porous NiCo₂O₄ nanotubes as advanced electrodes for electrochemical capacitors *Chem. Eur. J.* **19** 5892–8
- [39] Lazarevic Z Z, Jovalekic C, Milutinovic A, Sekulic D, Ivanovski V N, Recnik A, Cekic B and Romcevic N Z 2013 Nanodimensional spinel NiFe₂O₄ and ZnFe₂O₄ ferrites prepared by soft mechanochemical synthesis *J. Appl. Phys.* **113** 187221
- [40] Jacintho G V, Brolo A G, Corio P, Suarez P A and Rubim J C 2009 Structural investigation of MFe₂O₄ (M = Fe, Co) magnetic fluids *J. Phys. Chem. C* **113** 7684–91
- [41] Al-Rubaye S, Rajagopalan R, Dou S X and Cheng Z 2017 Facile synthesis of reduced graphene oxide wrapped porous NiCo₂O₄ composite with superior performance as an electrode material for supercapacitors *J. Mater. Chem. A* **5** 18989–97
- [42] Das R, Bhaumik M, Giri S and Maity A 2017 Sonocatalytic rapid degradation of Congo red dye from aqueous solution using magnetic Fe⁰/polyaniline nanofibers *Ultrason. Sonochem.* **37** 600–13
- [43] Etemadinia T, Barikbin B and Allahresani A 2019 Removal of congo red dye from aqueous solutions using ZnFe₂O₄/SiO₂/Tragacanth gum magnetic nanocomposite as a novel adsorbent *Surfaces and Interfaces* **14** 117–26
- [44] Sahoo J K, Paikra S K, Mishra M and Sahoo H 2019 Amine functionalized magnetic iron oxide nanoparticles: Synthesis, antibacterial activity and rapid removal of Congo red dye *J. Mol. Liq.* **282** 428–40
- [45] Seyed Arabia S M, Lalehlooa R S, Olyai M R, Ali G A and Sadegh H 2019, Removal of congo red azo dye from aqueous solution by ZnO nanoparticles loaded on multiwall carbon nanotubes *Physica E* **106** 150–5
- [46] Abukhadra M R, Adlii A and Mohamed Bakry B 2019 Green fabrication of bentonite/chitosan@ cobalt oxide composite (BE/CH@Co) of enhanced adsorption and advanced oxidation removal of Congo red dye and Cr (VI) from water *Inter. J. Biol. Macromol.* **126** 402–13
- [47] Xu J, Xu D, Zhu B, Cheng B and Jiang C 2018 Adsorptive removal of an anionic dye Congo red by flower-like hierarchical magnesium oxide (MgO)-graphene oxide composite microspheres *Appl. Surf. Sci.* **435** 1136–42
- [48] Lei C, Pi M, Xu D, Jiang C and Cheng B 2017 Fabrication of hierarchical porous ZnO-Al₂O₃ microspheres with enhanced adsorption performance *Appl. Surf. Sci.* **426** 360–8
- [49] Jacob B, Mohan M, Dhanyaprabha K C and Thomas H 2022 NiCo₂O₄ nanoparticles anchored on reduced graphene oxide with enhanced catalytic activity towards the reduction of p-Nitrophenol in water *Colloids Surf., A* **643** 128717

- [50] Saleh Katubi K M, Akbar S, Zulfiqar S, Shahid M, Irshad A, Alrowaili Z A, Al-Buriahi M S and Cochran E W 2024 Synthesis of rGO-Supported $\text{NiCo}_2\text{O}_4/\text{NiS}$ nanocomposite for effective degradation of diclofenac and bromophenol blue *Ceram. Int.* **50** 22109–22
- [51] Kiriarachchi H D, Abouzeid K M, Bo L and Samy M 2019 El-Shall, growth mechanism of sea urchin ZnO nanostructures in aqueous solutions and their photocatalytic activity for the degradation of organic dyes *ACS Omega*. **4** 14013–20
- [52] Al-Rawashdeh N A F, Allabadi O and Aljarrah M T 2020 Photocatalytic activity of graphene oxide/zinc oxide nanocomposites with embedded metal nanoparticles for the degradation of organic dyes *ACS Omega*. **5** 28046–55
- [53] Abu-Dalo M, Jaradat A, Albiss B A and Al-Rawashdeh N A F 2019 Green synthesis of TiO_2 NPs/Pristine pomegranate peel extract nanocomposite and its antimicrobial activity for water disinfection *J. Environ. Chem. Eng.* **7** 103370
- [54] Debnath S, Maity A and Pillay K 2014 Impact of process parameters on removal of Congo red by graphene oxide from aqueous solution *J. Environ. Chem. Eng.* **2** 260–72
- [55] Kumar Sahoo S, Kumar Sahoo J, Kumar Panigrahi G, Kumar Pattanayak D, Sundar Rout A and Lenka A 2020 Preparation of graphene oxide from bio-soot wastes: as an efficient adsorbent for highly noxious congo red dye *Flat Chem.* **24** 100198
- [56] Zourou A, Ntziouni A, Adamopoulos N, Roman T, Zhang F, Terrones M and Kordatos K 2022 Graphene oxide- CuFe_2O_4 nanohybrid material as an adsorbent of Congo red dye *Carbon Trends*. **7** 100