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Synthesis and Characterization of rGO/Co₃O₄ composite as nanoadsorbent for Rhodamine 6G dye removal

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ABSTRACT

In this paper, Co₃O₄ nanoparticles are loaded onto rGO sheet by the hydrothermal method and used as a surface to absorb the cationic dye (Rhodamine 6G). They are characterized using X-ray diffraction, Field Emission Scanning Electron Microscopy, Transition Electronic Microscopy (TEM), UV-Vis Spectroscopy, Fourier Transform-Infrared Spectroscopy, Energy Dispersion X-ray and Zeta potential. The results indicated that there was heterogeneous distribution of Co₃O₄ nanoparticles (45 nm in size) on rGO sheets. The rGO/Co₃O₄ nanocomposite showed adsorption capacity with 122.4 mg/g for Rh. 6G dye. Additionally, the factors affecting the process of adsorption that include equilibrium time, temperature, pH solution, ionic intensity and adsorbent dose were studied. The equilibrium removal efficiency was studied using Langmuir, Freundlich and Temkin isotherm models. The kinetic data were analyzed with two different kinetic models and pseudo first-order kinetic model was found to be the best model for our adsorption experiment. The thermodynamic parameters including Gibbs free energy (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated for the adsorption process.

Keywords: Adsorption, Graphene oxide, Kinetic, Nanocomposite, Rhodamine 6G

1. INTRODUCTION

Presently, water pollution with dyes has become an environmental problem that adversely affects human health. Dyes are the most common contaminants available in wastewater [1]. Many industries produce dyes for example textiles, paper, plastics, leather, food, cosmetics, etc. [2]. In addition, dyes pose a deadly hazard to humans because of its bioaccumulation properties. Therefore, the processes for treatment of dye waste-water has made many researchers interested in this area and the use of various techniques to reduce that problem [3]. To eliminate contamination problem-with dyes, scientists resort to use various techniques for example adsorption, coagulation [4], chemical oxidation [5], membrane filtration [6], ion exchange [7] and photocatalysis [8]. Adsorption is one of the best prominent technologies mentioned above in water treatment because it is highly efficient, easy to operate and cost effective [9]. After the

invention of graphene, its application was not only in electronic and energy industry, but also in the scope of environmental remediation [10, 11]. Graphene single-layer material of the carbon allotropes possesses a two-dimensional lattice form of C atoms with sp^2 hybridization. The reason for the usage of graphene is often due to its excellent properties such as great surface area, which provides good adsorption capacity and good mechanical strength, an outstanding thermal stability, excellent optical and electrical properties [12]. After the treatment of the graphite, using strong oxidizing factors according to the modified Hummer's method, graphene oxide was produced [13]. The process showed the introduction of functional oxygen groups like hydroxyl, epoxy, and carboxyl on the surface of the graphite and then dispersing the layers using ultrasonication. It was observed that the oxygen-containing groups were able to form chemical bonds with the dyes to be suitable for final removal of dyes from wastewater etc [14]. Graphene oxide (GO) is an excellent precursor of reduced graphene oxide (rGO) that can be found using green reduction of exfoliated GO. Furthermore, the remaining oxygen-containing groups allow the addition of chemical modifications on the rGO surface [15]. It has been recently reported that graphene incorporated with nanoparticles, such as TiO_2 [16], Co_3O_4 [17], SnO_2 [18], ZnO [19], show high activities in adsorption, electrochemical catalysis, capacitors, photocatalytic degradation, etc. Since rGO hybrids can exhibit enhanced performance, it has become a priority for researchers to prepare these nanocomposites. Among the reported transition metal oxides, the cobalt (II, III) oxide (Co_3O_4) has delivered the promising electrochemical performance as an anode material for lithium-ion batteries [20] and superior specific capacitance for supercapacitors [21]. The synthesis of nanocrystalline Co_3O_4 has been carried out with various methods to obtain nanosize Co_3O_4 of different designs, such as nanotubes [20], nanoparticles [22], nanorods [23], and hollowed spheres [24]. To raise the efficiency of the adsorbent materials, rGO papers should be decorated with Co_3O_4 nanoparticles to give a composite form that possesses wonderful properties for example high conductivity, great surface area, speedy electronic transfers, excellent mechanical flexibility and good chemical stability [25, 26]. The process of loading nanoparticles on the rGO sheet also prevents the conglomeration of individual nanopapers and nanomaterials [27]. The previous research in this regard has shown rather effective results. Encouraged by these studies efforts have been made to prepared rGO/ Co_3O_4 nanocomposite [28-31].

In the current paper, the rGO/ Co_3O_4 nanocomposite was prepared and used to remove Rhodamine 6G dye from the contaminated water. Batch studies were performed by varying the contact time, temperature, pH solution and ionic intensity. The following is a description of the characterization of rGO/ Co_3O_4 nanocomposite using various techniques listed below to define the nanosize, thermal stability and determining the quality of active groups.

2. MATERIALS AND METHODS

2.1. Chemicals

Graphite precipitate, 97% H₂SO₄, 37% HCl, H₃PO₄, NaOH, and Ethanol were obtained from B.D.H Company and used directly without primary purification. 30 % H₂O₂, NaCl and NaOH were supplied from Scharlau. KMnO₄, NaNO₃ were supplied from Merck. Rhodamine 6G was obtained from chem-supply. Ascorbic acid, L-tryptophan, CoCl₂ and CoNO₂ were supplied from B.D.H Company. Deionized (DI) water was used as the solvent in all the experiments.

2.2. Instruments

The crystalline character of the solid has been identified by X-ray diffraction (XRD) analysis using a D/Max 2550 V diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) (Rigaku, Tokyo, Japan), and the XRD data were 60 collected at a scanning rate of 0.03°s^{-1} for 2θ in a range from 5° to 80° . Fourier Transform Infrared Spectroscopy (FT-IR) analysis was accomplished by a Nicolet Nexus 670 FT-IR instrument with KBr tablets as sample holders in the $4000\text{-}400 \text{ cm}^{-1}$ region. The UV-Visible tests were accomplished by Cary 300 Bio UV-Visible spectrometer in the wavelength range $200\text{-}900 \text{ nm}$, using 10 mm path length cuvette. The morphology of prepared materials was noted by Field Emission scanning electron microscopy (FE-SEM, JEOL, JSM-6701F, Japan) operated at an acceleration voltage of 8.0 kV and Transmission electron microscopy (TEM) notes were performed using Joel 2100 TEM under an accelerating voltage of 200 kV . The Zeta potentials of prepared materials were measured using laser Doppler electrophoresis with a Zetasizer Nano-ZS (Malvern Instruments Ltd., Worcestershire, United Kingdom) HCl and NaOH (0.1M) were used to regulate the acidic function.

2.3. Preparation of GO, rGO, Co₃O₄ and rGO/Co₃O₄ composites

Graphene Oxide was prepared by oxidation of pristine graphite powder via the Improved Hummer's method [32]. The rGO was prepared by mixing 0.1 mg/mL graphene oxide with 5.0 mg/mL L-ascorbic acid as a reducing agent and L-tryptophan as a stabilizing agent with a strong base (NaOH), where the solution is mixed into the sonication bath for 30 min . After the previous step, a mixture was left under reaction at a temperature $80 \text{ }^\circ\text{C}$ for 24 h . At the end of the time, the solution was cooled to room temperature and then returned to the sonication bath for 1h . Then, resulting solution was washed with deionized (DI) water and separated using a centrifuge (6000 rpm) for 10 min to obtain a black powder to guide the reduction of the GO. In the end, the powder was dried in an oven at $50 \text{ }^\circ\text{C}$ for one day to get rGO nanosheets [33]. In contrast, cobalt oxide nanoparticles were prepared by the solvothermal method. The cobalt (II) nitrate (Co(NO₃)₂·9H₂O) was mixed with sodium dodecyl benzene sulfonate (SDBS). Such solution, was dissolved in 40 mL absolute ethanol and inserted it into the sonication bath for 30 min to obtain a dark green solution. The resultant mixture is transferred into a 100 mL sealed Teflon-lined autoclave and kept at $180 \text{ }^\circ\text{C}$ for 6 h . After cooling the autoclave to room temperature, the dark precipitate was obtained, filtered, washed with

distilled water, and afterwards with absolute ethanol to eliminate any alkaline salt and surfactant that remained in the final product, and dried at 90 °C for 6 h under vacuum. The obtained powder was calcined at 400 °C for 3 h, and a black crystalline precipitate evidently formed Co₃O₄ nanoparticles were obtained [34, 35]. Finally, rGO/Co₃O₄ nanocomposite was prepared using the hydrothermal process which involves dissolution of 0.1 g of graphene oxide in 200 mL deionized distilled water by inserting it into the sonication bath for 1 h to obtain GO suspension. Then 1.4 g cobalt chloride (CoCl₂. 6H₂O) was dissolved in 10 mL of water and then the mixture was stirred for 2 h to complete the ion exchange process. After that, 10 mL sodium hydroxide (1 equivalent) in the form of drops was added with the solution was stirred for 1h. 1.5 mL of 30 % H₂O₂ was added to the mixture, inserted it into the Teflon-lined stainless steel autoclave and heated at 100 °C for 4 h. Next, 0.25 g of reduced agent L-ascorbic acid was added and transferred into autoclave heated again at 120 °C for 4 h. The powder yield was collected by a centrifugal method, washed with deionized water and then dried to obtain black powder rGO/Co₃O₄ nanocomposite calcined at 150 °C for 4 h [36].

2.4. Adsorption Experiments

2.4.1. Batch Adsorption Experiments

The Stock solution of 100 mg/L Rh.6G solution was prepared by dissolving 0.1 g Rh.6G powder in 100 mL of water. An aqueous solution (10 mL) with 1 mg nanocomposite and a suitable concentration of Rh.6G was shaken by a thermostatic reciprocating shaker at 120 rpm at 25 °C. After removal of the nanocomposite by filtration through a centrifuge of 6000 rpm, the dye concentrations in the supernatant were determined by a UV-Visible spectrophotometer.

The adsorption capacity (q_t, mg/g) and the removal percentage (%) were calculated from the following equation [37]:

$$q_t = \frac{V_{sol}(C_o - C_e)}{m} \dots\dots\dots (1)$$

$$Removal\% = \frac{(C_o - C_e)}{C_o} * 100 \dots\dots\dots (2)$$

Where C_o and C_t are the initial and final concentrations of dye in the solution (mg/L), respectively, V is the volume of the solution (mL), and m is the mass of nanocomposite (mg).

2.4.2. Effect of Adsorbent Dose

The effect of surface mass (rGO/Co₃O₄) on the process of adsorption of the dyes was studied using different weights (0.001, 0.002, 0.003, 0.06, 0.01 g) per 10 mL of dye solution. This factor requires the stabilization of all conditions (dye concentration, temperature and acid function). The dye solution was mixed with the adsorbent surface and placed in a water bath shaker for 6 h. The samples were then centrifuged at a speed of 6000 rpm to remove the adsorbent and the residual dye concentration was measured using a UV-Vis spectrophotometer.

2.4.3. Effect of Temperature

The adsorption procedure was repeated in the same manner at temperatures of 10, 20, 30 and 35 °C in a range of concentrations between 5 and 200 mg/L to estimate the basic thermodynamic functions.

2.4.4. Effect of pH

The effect of the acidic function was studied in the adsorption process. All conditions were stabilized at temperature 25 °C and concentration 100 mg/L. The weight (0.01 g) of the nanocomposite (rGO/Co₃O₄) was used and the dye solutions were added at different pH values (2.0-12.0) and the pH values were regulated with diluted HCl and NaOH solutions (0.1M). The pH solution at the beginning of the adsorption was measured using a pH-meter. The results were presented by drawing the amount of the adsorbed substance versus the value of the acidic function and its effect on the adsorption process.

2.4.5. Effect of Ionic Strength

The effect of ionic strength was measured using different weights of NaCl (0.001, 0.01, 0.05, 0.1, 0.15, 0.2, 0.3 and 0.4 g). A constant concentration of dye solutions was added to volumetric flasks containing 0.01 g of the nanocomposite (rGO/Co₃O₄). Then, the solutions were agitated using a water bath shaker at 120 rpm and 25 °C. When equilibrium was achieved, a centrifuge with 6000 rpm separated the adsorbate and the residual dye concentration was measured.

3. RESULTS AND DISCUSSION

3.1. Characterization of rGO/Co₃O₄ nanocomposite

Fig. 1. shows the XRD pattern of pure graphite displaying a sharp peak at $2\theta \approx 26.5^\circ$, which corresponds to d-spacing of 3.36 Å. After oxidation process, the formation of GO shows the appearance of a new peak, which is a diffraction peak at around 11.6 Å, which corresponds to an interlayer d-spacing of 7.60 Å. The rGO displays a broad diffraction peak at 25.7° , corresponding to an interlayer d-spacing of 3.49 Å [38]. In contrast, the XRD pattern of Co₃O₄ nanoparticles display the diffraction peaks ($2\theta = 19.09^\circ, 31.35^\circ, 36.92^\circ, 38.62^\circ, 44.87^\circ, 55.71^\circ, 59.42^\circ$ and 65.30°). All diffraction peaks of cobalt oxide can be indicated to cubic spinel Co₃O₄ crystal phase. The very sharp diffraction peaks and high intensity propose the high crystallization of the Co₃O₄ nanoparticles. The XRD pattern of rGO/Co₃O₄ nanocomposite display diffraction peaks at ($2\theta = 19.03^\circ, 31.63^\circ, 36.71^\circ, 38.51^\circ, 45.34^\circ, 56.36^\circ, 59.34^\circ$ and 65.07°) indicating the cubic spinel Co₃O₄. An additional small broad diffraction peak displaying at ($2\theta = 24.5-29.5^\circ$) corresponding to the irregular accumulate graphene sheets, while the diffraction peak of GO sheet approximately disappeared. The peak positions can be completely indicated to the face-centered cubic [39].

Fig. 2 shows the FTIR spectrum of pristine graphite which has two peaks at approximately 1668 cm^{-1} due to the skeletal vibration from graphite field (the sp² aromatic C=C) and a vibration band at 3444 cm^{-1} probably related to adsorbed water

molecules. After oxidation process, O-H stretching vibrations ($3100\text{-}3500\text{ cm}^{-1}$), alkoxy stretching vibrations ($1040\text{-}1170\text{ cm}^{-1}$), O-H (C-O) distortion peaks ($1300\text{-}1400\text{ cm}^{-1}$) and the stretching vibration of epoxy (C-O-O) groups ($1000\text{-}1280\text{ cm}^{-1}$) appeared. Significantly, the aromatic C=C peak could be identified between 1600 and 1650 cm^{-1} . After reducing with ascorbic acid, the peak at 1700 , 1330 , 1226 cm^{-1} almost disappears and the peak for OH stretching bonds at 3490 cm^{-1} weakens obviously. This evidently prove the effective removal of oxygen from the sheets. Furthermore, it exhibits new band in the region of 2410 cm^{-1} associated to the presence of -CH_2 stretching vibrations [40]. In contrast, FTIR spectrum of Co_3O_4 nanoparticles before adsorption shows two strong absorption bands at 663.4 and 570.8 cm^{-1} . This proves the formation of the spinel network of Co_3O_4 while $\text{rGO}/\text{Co}_3\text{O}_4$ composite displays strong absorption bands at 663.4 and 570.8 cm^{-1} are attributed to the presence of Co_3O_4 . It was observed that these functional groups were almost removed through the way of thermal treatments, and thus the GO is transformed into rGO. Furthermore, an appearance of a new absorption band at about 1511 cm^{-1} may be attributed to the skeletal vibration of the rGO sheets. After Rh.6G dye adsorption, there is remarkable shift in the positions of - OH, C=O group peaks. Fig. 2 also exhibits the characteristic stretching peaks of saturated C-H(CH_3) at 2932 cm^{-1} , stretching vibration of C-N at 2338 cm^{-1} and the peak related to the vibration of the aromatic ring at 1600 cm^{-1} is very prominent, which showed that the Rh.6G has been anchored on the surface of adsorbent after the adsorption. It is worth nothing that the carboxyl (C=O) peak shifted to 1719 cm^{-1} in Fig. 2, due to the reaction between carboxyl functional groups and Rh.6G. This can be explained by the following reason: Rh.6G is a kind of cationic dye, which can be adsorbed easily by electrostatic forces on negatively charged surfaces [38, 41].

The absorption spectrum of graphene oxide in Fig. 3 shows two absorption peaks at 229 nm which can be returned to the $\pi\text{-}\pi^*$ transition of aromatic (C=C) bonds and at 300 nm associated to the $n\text{-}\pi^*$ transition of the carbonyl groups (C=O) bonds. The rGO obtained the red shift up to 280 nm owing to the restoration of the sp^2 hybridized carbon grid due to the removal of the oxygen bearing functional groups [42, 43]. UV-vis spectra of the Co_3O_4 nanoparticles shows two wide absorption peaks in the wavelength ranges of $230\text{-}380\text{ nm}$ and $420\text{-}630\text{ nm}$ can be attributed to the formation of cobalt oxide. In contrast, UV-vis spectra of the $\text{rGO-Co}_3\text{O}_4$ nanocomposite contain three peaks. The two peaks at the wavelength 340 and 545 nm assigned Co_3O_4 nanoparticles and the absorption peak at 270 nm attributed to $\pi\text{-}\pi^*$ transitions of the aromatic C=C of rGO sheet [44, 45].

The morphologies of the prepared nanomaterials were studied by FE-SEM and TEM. Fig. 4 shows FE-SEM analysis of GO nanosheets tend to congregate together to form multilayer agglomerates. The individual nanosheets have sizes extending from tens to several hundreds of square nanometers [46]. However, reduced graphene oxide had a wrinkled paper-like morphology with severely folded lines [47]. The FE-SEM image of Co_3O_4 nanoparticles shows a sphere like morphology and is composed of agglomerated assembled spheres indicate a uniform homogeneity and good connectivity between the nanoparticles [48].

The surface morphology of the nanocomposite before and after Rh.6G dye adsorption was observed using FE-SEM analysis. There are significant changes to the surface morphology of the nanocomposites, as well as the formation of discrete aggregates on their surfaces following Rh.6G dye adsorption. The FE-SEM image of rGO/Co₃O₄ nanocomposite before adsorption shows rough surface and Co₃O₄ distributed as bright dots uniformly on the surface of the rGO nanosheets. These observations demonstrate the presence of both rGO and Co₃O₄. After Rh.6G dye adsorption as presented in Figure 4, nanocomposite displayed a dense and porous surface texture. Interaction of rGO/Co₃O₄ with Rh.6G dye has resulted in the formation of flake-like deposits on its surface [15].

The EDX analysis and the Elemental maps show that the prepared rGO/Co₃O₄ composite includes only cobalt, carbon, and oxygen, similar to the chemical composition of the nanocomposite. The appearance of the carbon signal in the spectrum is associated to the rGO network (Fig. 4). After Rh.6G dye adsorption a new peak appeared assigned to present nitrogen.

TEM analysis can be used to identify the morphology of prepared nanoparticles by passing a beam of electrons through the sample to give a picture on a phosphor screen, so that it can be different from SEM [49]. TEM image of GO shows silk waves, transparent and exhibit a very stable nature under the electron beam [50]. TEM image of the rGO sheet demonstrate a wrinkled paper-like structure. This is due to the chemical bonding of carbon atoms in either a single layer or multi layers [51]. TEM image of Co₃O₄ nanoparticles explain semi-spherical, porous texture, a uniform distribution and very homogeneous surface [52]. TEM image of rGO/Co₃O₄ nanocomposite displays uniform size of spindle-like Co₃O₄ nanoparticles distributed in a homogeneous and dense manner on rGO surface. The inclusion of Co₃O₄ nanoparticles between the interlayers of the graphene nanosheets was observed, suggesting a relatively strong interaction between rGO and Co₃O₄ particles. This prevents accumulation of the Co₃O₄ nanoparticles through thermal treatment (Fig. 5) [53, 54].

The zeta potential is a physical property exhibited by any material in dispersion and is an important parameter used for characterizing the electrical properties of interfacial layers in suspension. The GO solution would be stabilized when the zeta potential value becomes -46 mV in the pH range of 9-12 (Fig. 6). The negative zeta potential value of GO is due to the presence of electronegative functional groups formed at the graphite lattice during the oxidation (55). Zeta potential of rGO solution is up to +8.85 mV. The positive zeta potential values of rGO at pH < 5 are attributed to adsorption of positively charged ions (e.g. H⁺, Na⁺) in the aqueous solution [56]. Zeta potential of Co₃O₄ solution up to +23.1mV is attributed to the surface of the metal oxide is more positive and this leads to electrostatic interference between the metal and the rGO network. Finally, the zeta potential of the rGO/Co₃O₄ nanocomposite around -48.8 mV and shows that the surface of the composite is more stable in the alkaline medium and has a negative charge that can directly attract the cationic dye [57].

The specific surface area is calculated by employing the Brunauer-Emmett-Teller (BET) method and the pore size distributions (PSD) is obtained by means of the Barrett-Joyner-Halenda (BJH) method equation using the adsorption isotherm branch, which are shown in Fig. 7. The BET specific surface area and the pore diameter of rGO/Co₃O₄ nanocomposite before adsorption were found to be 82.202 m²/g and 4.61 nm, respectively. The value of the pore diameter suggested that rGO/Co₃O₄ nanocomposite was a mesoporous material. The isotherms exhibit a typical type-V shaped curve and a H2 hysteresis loop at a relative pressure of 0.98, indicating the presence of slit-shaped pores between the parallel layers of nanocomposite. After Rh.6G dye adsorption, the specific surface area and the pore diameter of nanocomposite 41.296 m²/g and 2.71 nm, respectively. The results show a significantly decrease in the surface area after Rh.6G dye adsorption as shown in Table 1. This indicates an interaction between dye and nanocomposite [58].

3.2. Adsorption Experiments

3.2.1. Effect of Adsorbent Dosage

An adsorption experiment of Rhodamine 6G dye removal is performed using different weights (0.001-0.01 g) of the nanocomposite. Note that dye increase the removal percentage with increasing weight of the nanocomposite. This can be attributed to the greater surface area of nanocomposite and the increase in the available active sites for Rh.6G dye adsorption. Consequently, the uptake of Rh. 6G reaches a saturation level at 0.01 g nanocomposite as the active sites present on the surface of rGO/Co₃O₄ become saturated with Rh. 6G. For subsequent experiments, 0.01 g of sorbent dose was selected (Fig. 8a) [59].

3.2.2. Effect of Contact Time and Kinetics of adsorption

The study of adsorption dye at different times (1-600 min) after the stabilization of all conditions affecting. In Rhodamine 6G dye adsorption capacity was increased with increasing the time to its maximum value (saturation state) but sometimes the adsorption capacity decreases with increasing time due to a desorption process (Fig. 8b) [60].

In order to investigate the mechanism of adsorption and potential rate controlling steps, two kinetic models, namely, pseudo-first-order and pseudo-second-order equation models were analyzed. The pseudo-first-order equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \dots\dots\dots (3)$$

Where k_1 is the rate constant of adsorption (1/min). The plot of $\log (q_e - q_t)$ against t gives a linear relationship from which k_1 and q_e are determined from the slope and intercept of the plot, respectively.

The pseudo-second-order model can be represented by the following linear form:

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

where k_2 is the pseudo second-order rate constant of adsorption (g/mg min). The values of q_e and k_2 are determined from the slope and intercept of the plot of t/q_t against t .

The validity of each kinetic model was checked by the fitted straight lines and depicted in Fig. 9. The corresponding kinetic parameters and the correlation coefficients are summarized in Table 2. The value of the correlation coefficient obtained from the linear plot of pseudo-second-order model is $R^2 = 0.614$, suggesting that the applicability of this model to the adsorption processes of Rh. 6G adsorption by the nanocomposite is unfeasible. The high R^2 value is obtained for pseudo-first-order model, indicating that the experimental data are well described by pseudo-first-order model.

3.2.3. Effect of pH

The pH of the aqueous solution is an important factor to affect the dye adsorption process through changing the surface charge of an adsorbent and the ionization behavior of adsorbent and dye. The influence of the solution pH on Rh. 6G removal by the rGO/Co₃O₄ was shown in Fig. 10. It can be seen that the dye removal efficiencies by the nanocomposite increase with increasing pH in pH range of 2.0-12.0. The observed lower adsorption capacity at lower pH value could be attributed to the protons competition with the cationic Rh.6G for the available adsorption sites on the rGO/Co₃O₄ surface. However, the surface of the rGO/Co₃O₄ may get negatively charged when the pH value increases to a certain extent. The electrostatic attraction between the negatively charged rGO/Co₃O₄ and the Rh.6G cation would lead to the increase in adsorption capacity [61].

3.2.4. Adsorption Isotherm Models

Three classic adsorption models, Langmuir, Freundlich and Temkin were used to describe the adsorption equilibrium. The mathematical representations of the Langmuir, Freundlich, and Temkin models are given below:

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

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots\dots\dots (6)$$

$$q_e = B \ln K_T + B \ln C_e \quad \dots\dots\dots (7)$$

where q_m is the theoretical maximum adsorption capacity per unit weight of the adsorbent (mg g⁻¹), K_L , K_F , K_T are adsorption constants of Langmuir, Freundlich and Temkin models, respectively, and n is the Freundlich linearity index. Langmuir model is an ideal model, which possesses perfect adsorbent surface and monolayer molecule adsorption. As an empirical model, Freundlich model is used widely in the field of chemistry. Temkin model is a proper model for the chemical adsorption based on the strong electrostatic interaction between positive and negative charges [62].

The results of fitting of these models are shown in Fig. 11 and the suitable parameters for Rh.6G dye are listed in Table 3. The lower correlation coefficients R^2 of the Langmuir and Temkin point out that the isotherm data do not fit the Langmuir and Temkin models. The higher correlation coefficient $R^2 = 0.910$ of the Freundlich model point out that the Freundlich equation can be used to fit the experimental adsorption data and evaluate the maximum dye adsorption capacity of the nanocomposite. The results suggest that the adsorption of Rh.6G by the nanocomposite take place in a multilayer adsorption behavior.

3.2.5. Effect of Temperature and Thermodynamic study

Temperature is a very important parameter controlling the adsorption process. It can modify the equilibrium capacity of the adsorbent for a particular adsorbate. Therefore, the effect of temperature on Rh.6G adsorption by rGO/Co₃O₄ was examined within a temperature range of 10-35 °C. Fig. 12 displays the increase in removal percentage of Rh.6G with the rise in temperature. The highest removal percentage occurring at 35 °C after an equilibrium period of 360 min. Nevertheless, other increase in temperature showed a decrease in the sorption process which may have resulted from the weakening of the physical bonds between the Rh.6G molecules and the active site of the adsorbent. The increase in removal percentage of Rh.6G with a corresponding rise in temperature may have resulted from an increase in the rate of diffusion of Rh.6G molecules neighboring the external surface and internal pores of the rGO/Co₃O₄ [63].

Thermodynamic parameters involving Gibbs free energy (ΔG°), enthalpy change (ΔH°) and change in entropy (ΔS°) are obtained at different temperatures according to the following formulas:

$$\Delta G = -RT \ln K \quad \dots\dots\dots (8)$$

$$\Delta G = \Delta H - T \Delta S \quad \dots\dots\dots (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad \dots\dots\dots (10)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \dots\dots\dots (11)$$

where R (8.314 J/mol K) is the ideal gas constant, T (K) is the absolute temperature, and k is Langmuir constant. ΔH° and ΔS° are calculated from the slope and intercept of van't Hoff plots of $\ln K$ versus T^{-1} . All these thermodynamic parameters are listed in Table 4.

The obtained value of energy ΔG° is -1.002. The negative values at three tested temperatures reveal that the adsorption process is feasible and spontaneous, and the adsorption is a physisorption and chemisorption process simultaneously. According to the positive value of ΔH° , it infers that the adsorption reaction is endothermic in nature and the adsorption process is energetically stable. The positive ΔS° values suggest the increased randomness at the solid/solution interface during the adsorption process [64].

3.2.6. Effect of Ionic Strength

The effect of solution ionic strength on adsorption of Rh.6G by rGO/Co₃O₄ was investigated by a series of experimental studies constructed by varying weights of NaCl from 0.001 to 0.4 g. As depicted in Fig. 13, It can be seen that the adsorption capacities decrease with the addition of NaCl due to the electrostatic repulsion effect. In previous studies, competition between Rh.6G species and Na⁺ ions for the adsorbent surface decrease of the adsorption capacity [65].

4. CONCLUSIONS

In this work, rGO/Co₃O₄ nanocomposite was prepared by the hydrothermal method. This method leads to a uniform distribution of Co₃O₄ nanoparticles on rGO sheets. The rGO/Co₃O₄ nanocomposite has great potential as an effective absorbent for removing Rh.6G in aqueous solution. The morphology and XRD studies indicate that Co₃O₄ nanoparticles with a size of about 49.45 nm are homogeneously dispersed on graphene sheets. The Rh.6G adsorption follows the pseudo first-order kinetics and the equilibrium data can be well fitted with the Freundlich isotherms. Thermodynamic parameters are calculated for the removal of dye and their values indicated that the process of removal is spontaneous and endothermic.

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Table 1: The specific surface areas, average pore diameters (BJH) and total pore volumes of rGO/Co₃O₄ nanocomposite before and after adsorption Samples

Samples	Specific surface Area (m ² g ⁻¹)	pore diameter (nm)	Total pore Volume (cm ³ g ⁻¹)
Before	82.202	4.61	0.188
After	41.296	2.71	0.068

Table 2: Adsorption kinetics parameters of adsorption of Rh.6G

Dye	Pseudo-first order			Pseudo-second order			
	k_1	q_e	R^2	k_2	q_e	h	R^2
Rh.6G	0.0105	97.582	0.950	4.467	140.845	0.886	0.614

Table 3: Langmuir, Freundlich and Tempkin isotherm constants for Rh.6G dye uptake by rGO/Co₃O₄ nanocomposite.

Dye	Langmuir equation			Freundlich eq.			Tempkin eq.		
	K_L	q_m	R^2	K_F	n	R^2	K_T	B	R^2
Rh.6G	0.256	88.495	0.665	11.148	2.195	0.910	288.43	0.045	0.763

Table 4: Thermodynamic parameters of adsorption of Rh.6G

Dye	ΔH (kJ.mol ⁻¹)	ΔG (kJ.mol ⁻¹)	ΔS (J.mol ⁻¹ .K ⁻¹)	Equilibrium Constant (K)
Rh.6G	+14.468	-1.002	+52.800	1.509

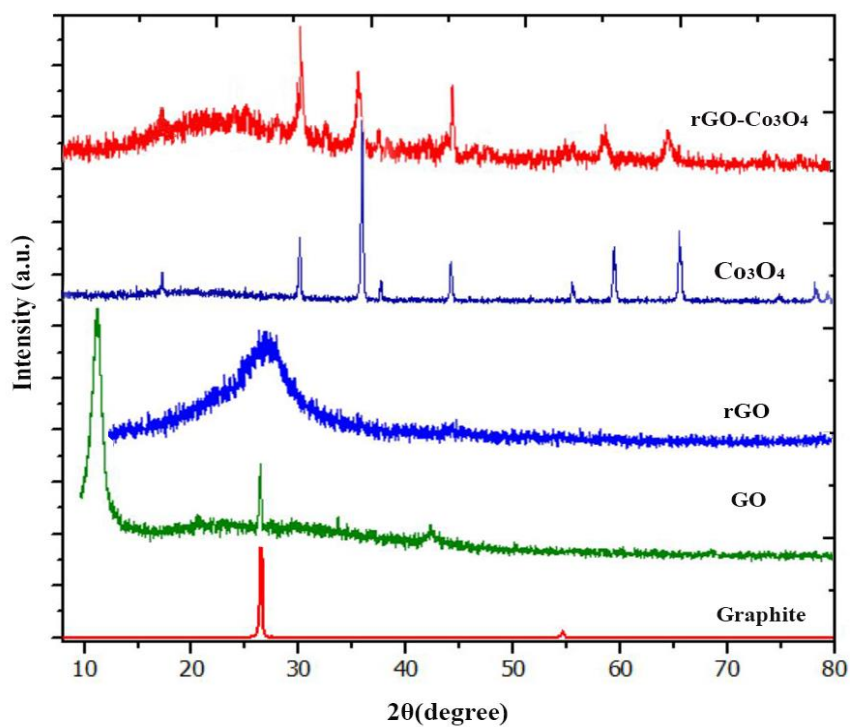


Fig. 1. XRD spectra of Gr, GO, rGO, Co_3O_4 and rGO/ Co_3O_4

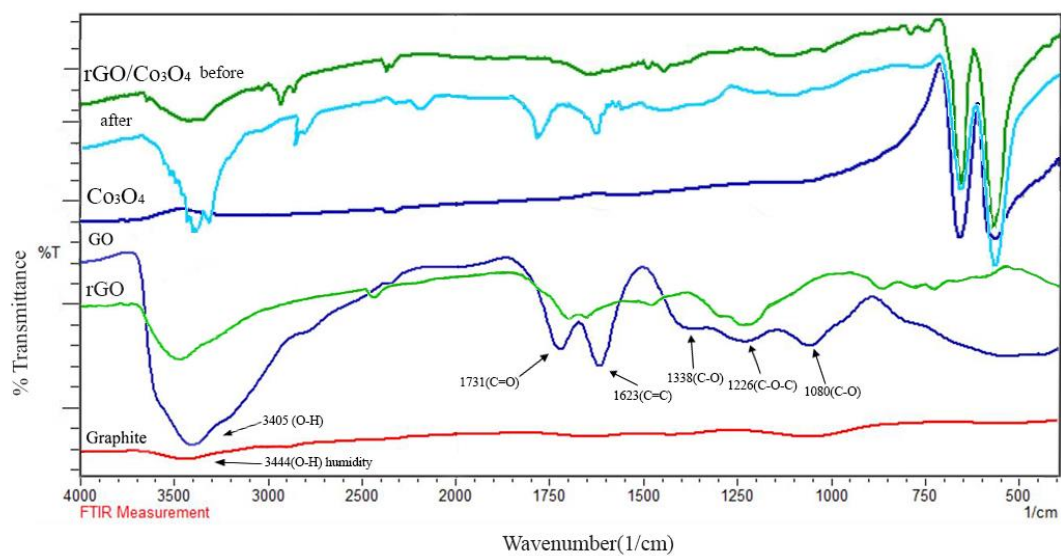


Fig. 2. FTIR analysis of G, GO, rGO, Co_3O_4 and rGO/ Co_3O_4 before and after adsorption

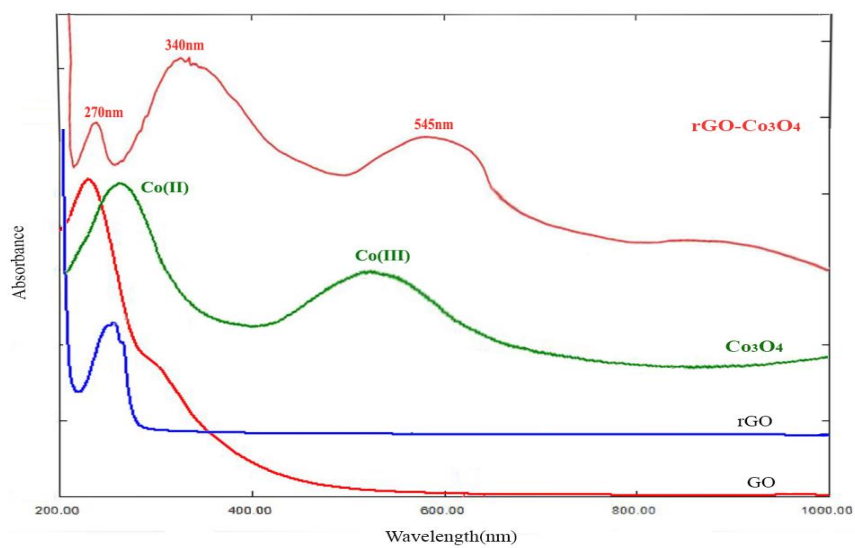
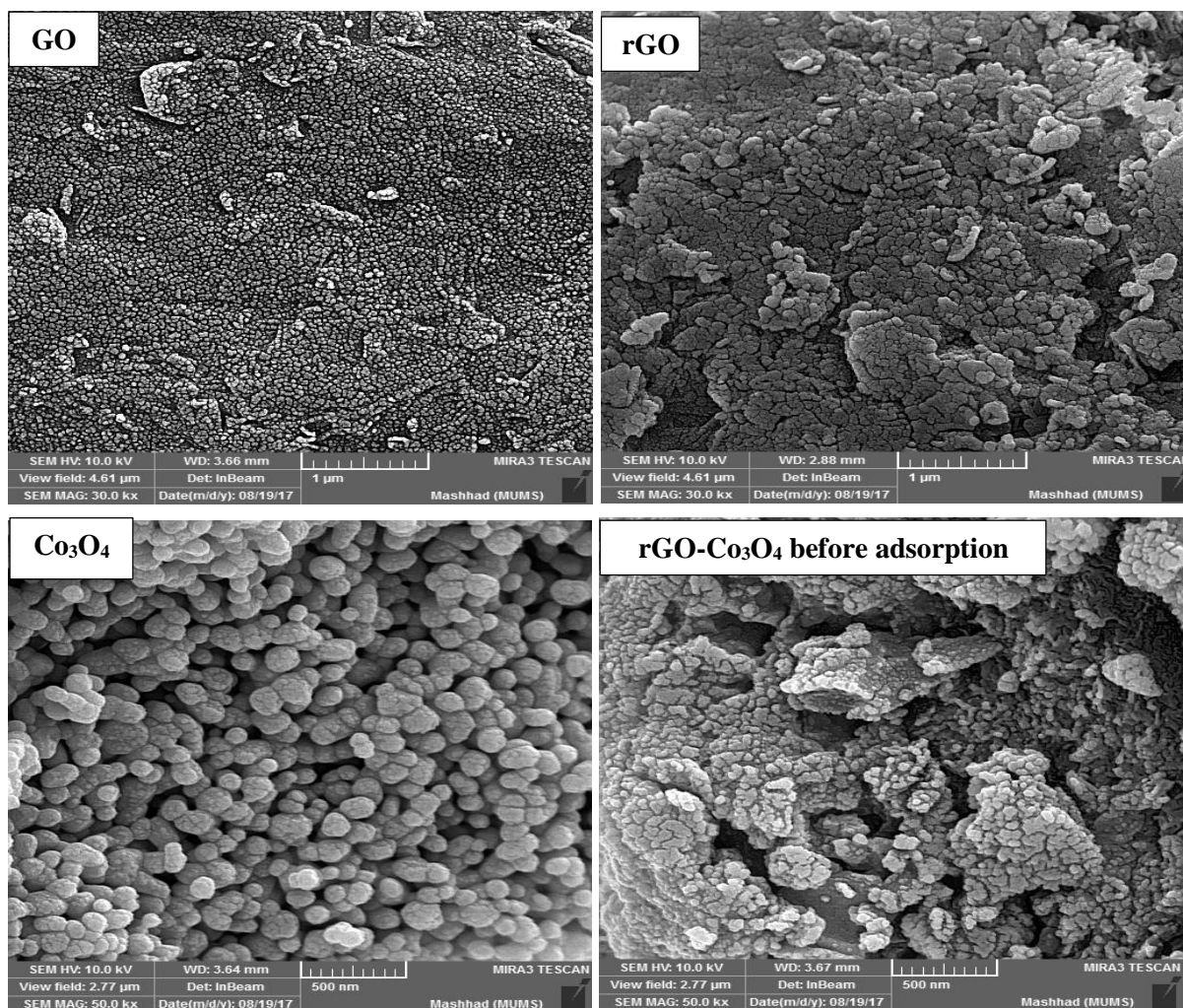


Fig.3 . UV-Vis analysis of GO, rGO, Co₃O₄ and rGO-Co₃O₄



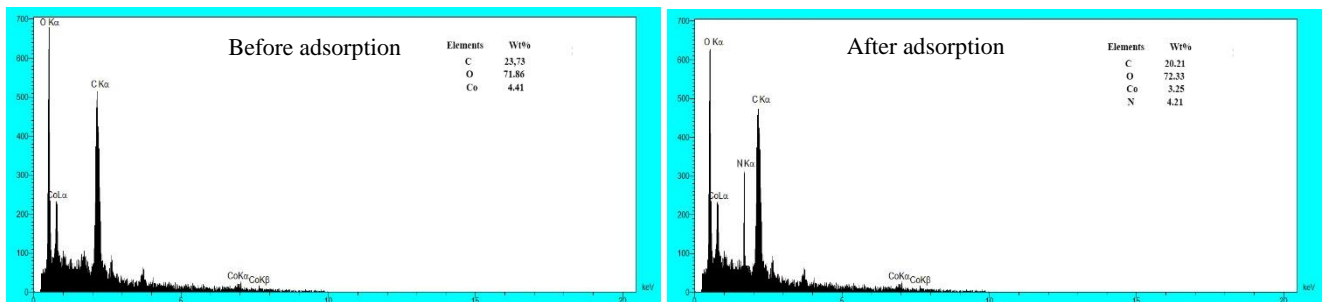
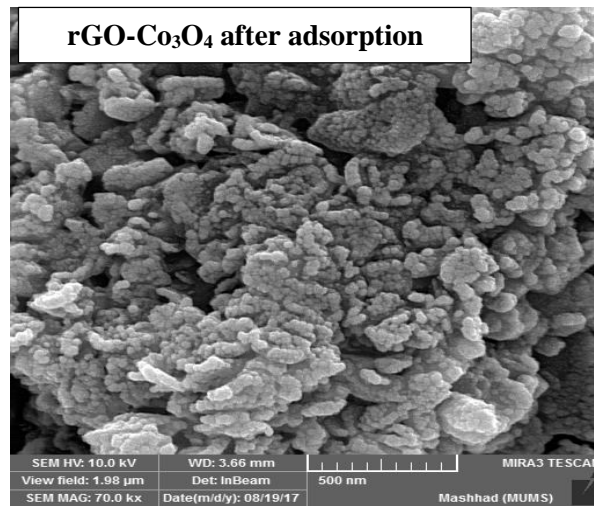
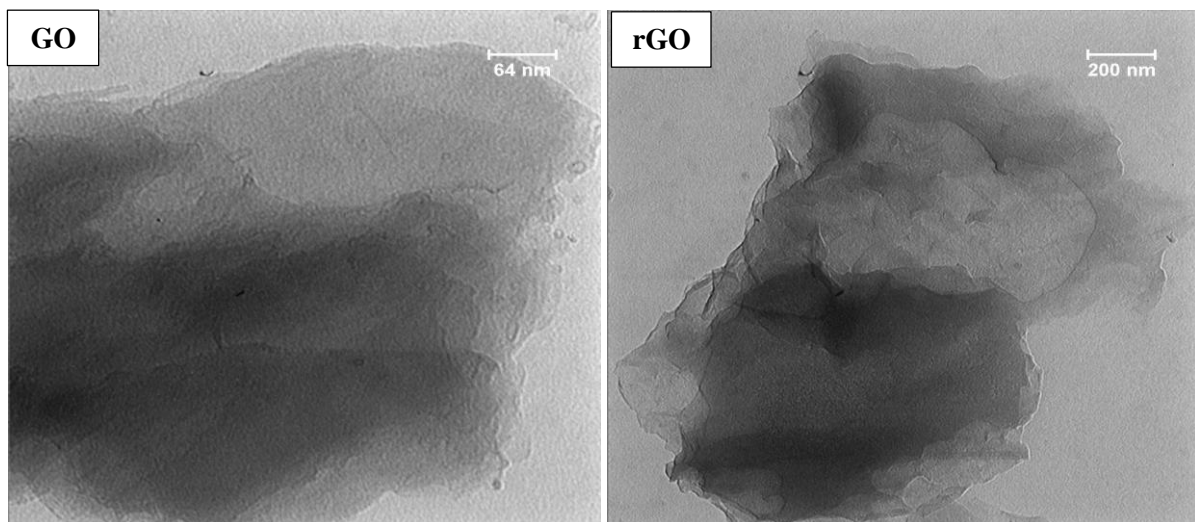


Fig. 4. FE-SEM analysis of GO, rGO, Co₃O₄ and rGO/Co₃O₄ and EDX analysis of rGO/Co₃O₄ before and after adsorption



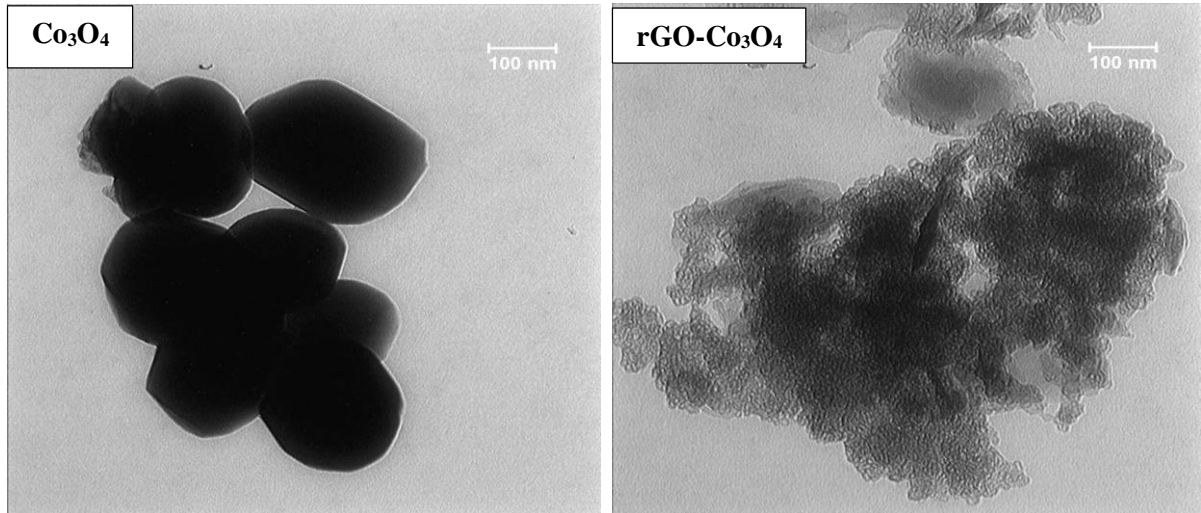


Fig. 5. TEM analysis of GO, rGO, Co_3O_4 and rGO/ Co_3O_4

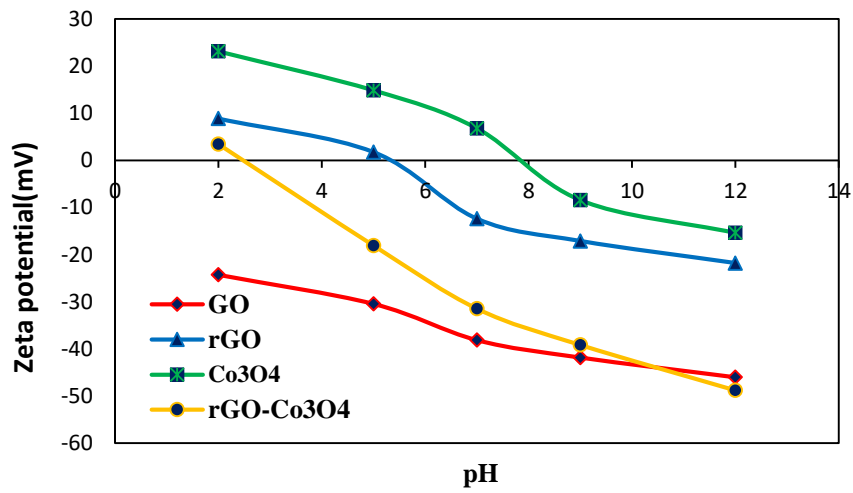
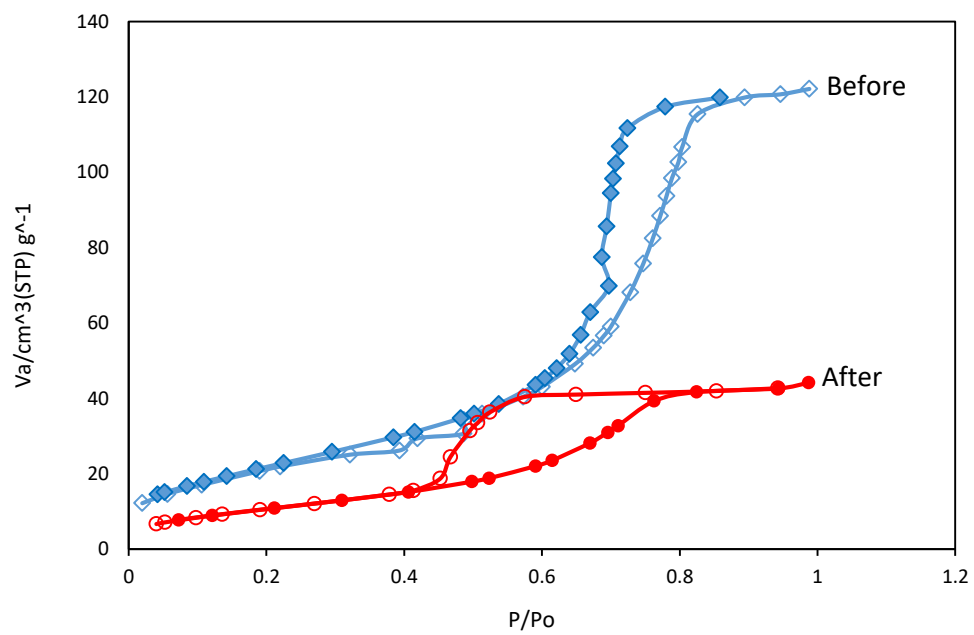


Fig. 6. Zeta potential of GO, rGO, Co_3O_4 and rGO/ Co_3O_4



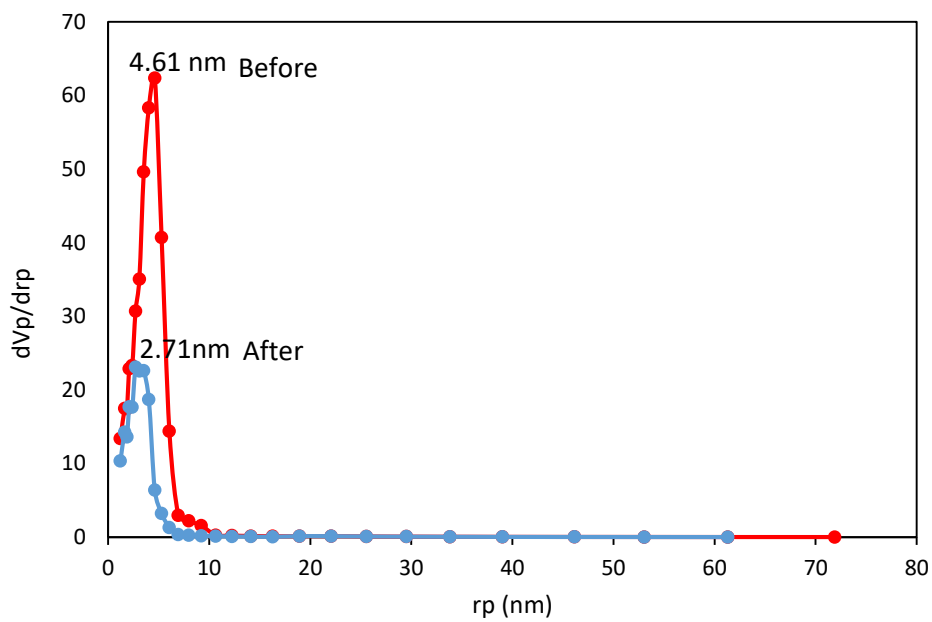


Fig. 7. N₂ adsorption and desorption curves and pore size distributions of rGO/C₀₃O₄ before and after adsorption

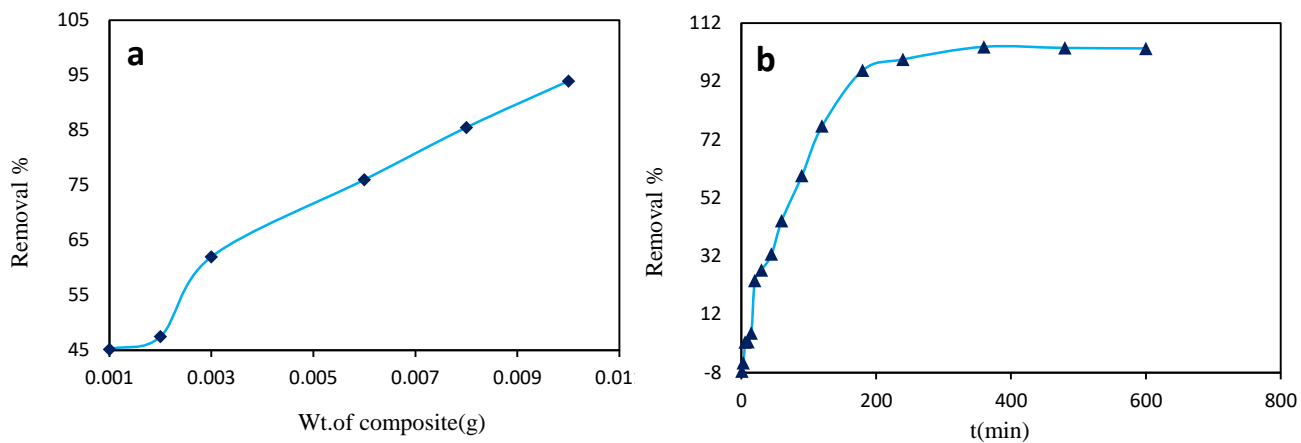


Fig. 8. Effect of (a) adsorbent dose, (b) reaction time on the removal percentage of Rh.6G dye

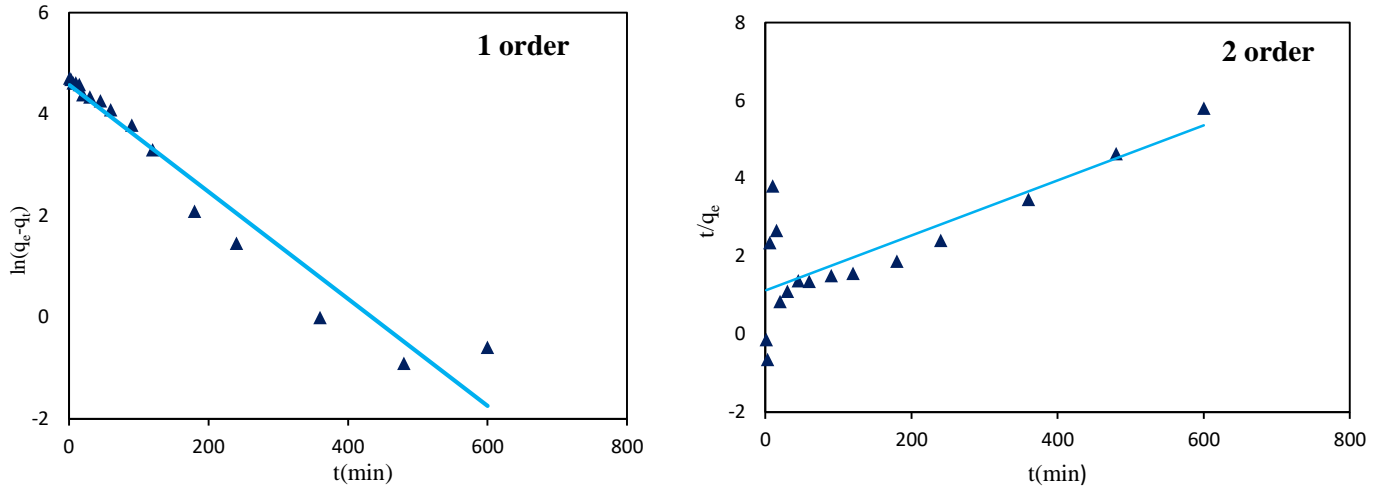


Fig. 9: Pseudo-first and Pseudo-second order kinetics for adsorption of Rh.6G dye

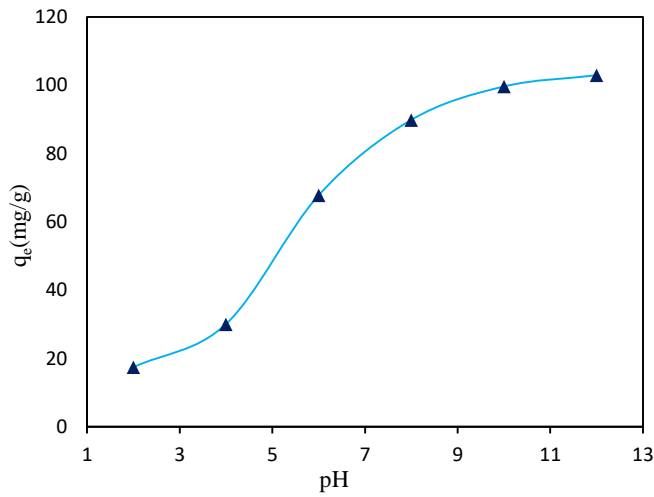
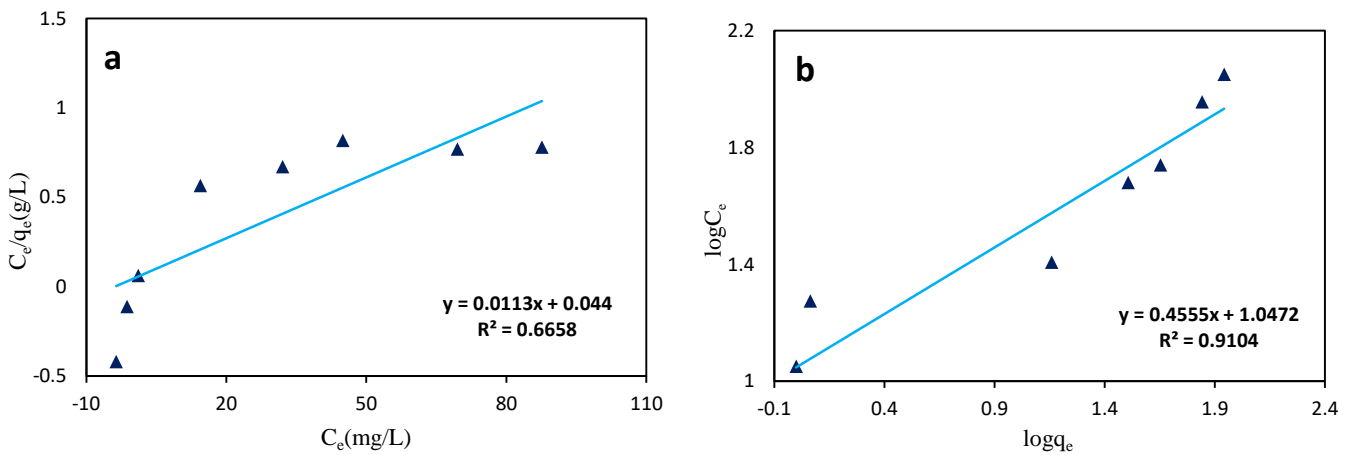


Fig.10. Effect of pH solution on adsorption Rh.6G dye on nanocomposite



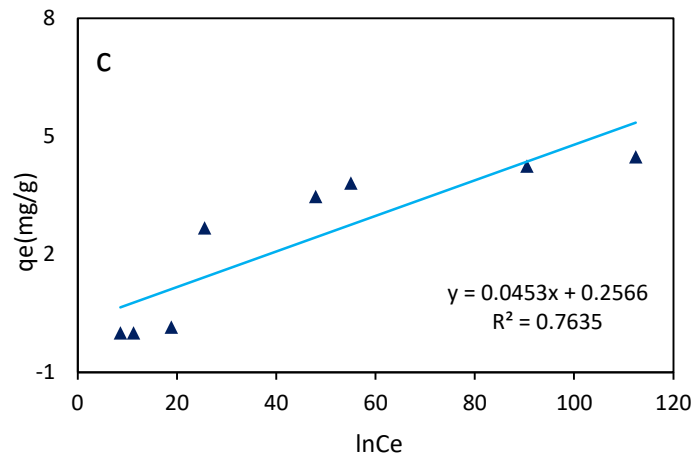


Fig. 11. Linearized form of (a) Langmuir model, (b) Freundlich model, (c) Tempkin model of Rh.6G dye

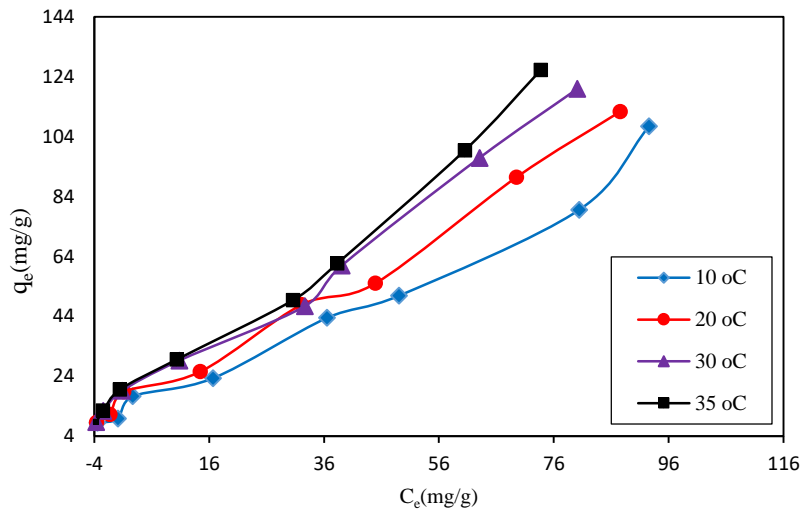


Fig. 12. Effect of temperature on the adsorption capacity of Rh.6G dye

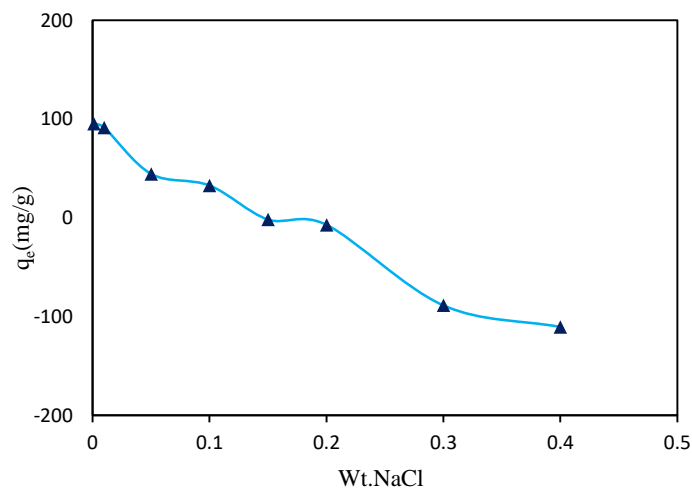


Fig.13. Effect of ionic strength on adsorption Rh.6G dye on nanocomposite