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OPTIMIZATION FOR COLOUR REMOVAL PROPERTY OF PREPARED REDUCED GRAPHENE OXIDE (rGO)

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Abstract

In this study, the modified Hummer process was used to synthesize graphene oxide (GO) from graphite powder. Later, GO was chemically reduced to form reduced graphene oxide (rGO) nanoparticles using hydrazine hydrate as the reducing agent. Techniques such as XRD, FT IR, UV-visible, SEM, and EDX were used to characterize the prepared rGO. Malachite green (MG), a cationic dye, was employed as a model dye contaminant to study the colour removal efficiency of rGO. In order to assess the optimal values of the important parameters, including the initial dye concentration, pH, contact time, and rGO dosage, batch adsorption tests were conducted. For the purpose of removing the colour of malachite green utilizing synthesized rGO, the optimum conditions were found to be 10 ppm of MG concentration, pH 4, 60 min of contact time, and 0.06 g of adsorbent dosage.

Keywords: graphite, reduced graphene oxide, modified Hummer process, hydrazine hydrate, malachite green

Introduction

Dye and pigment pollution has been a significant problem on a global scale and is likely to get worse in the environment. Dyes are coloured, toxic, and non-biodegradable. They affect humans and other living beings when they enter the food chain (Hassan and Nemr, 2017). To treat this effluent, several physical, chemical, and biological decolourization methods are employed. Among them, adsorption gives the best result for removing coloured materials. Recently, graphene oxide (GO) and reduced graphene oxide (rGO) have been employed for the removal of organic pollutants and dyes from industrial effluents (Yusuf *et al.*, 2015). Graphite, one of many allotropes of carbon, can provide great potential in many applications, such as electronic and functional nanocomposites (Hidayah *et al*., 2017). A single atomic plane layer of graphite is called graphene. Graphene can be produced from graphite using chemical vapour deposition (CVD) and mechanical or chemical methods (Zaaba *et al*., 2017). Graphene Oxide (GO) is prepared from the oxidation of graphite powder by Modified Hummer’s Method (Mindivan, 2016). The oxidation of graphite in protonated solvents leads to graphite oxide, which consists of multiple stacked layers of graphene oxide. GO has a similar hexagonal carbon structure to graphene but also contains hydroxyl, alkoxy, carbonyl, carboxylic acid, and other oxygen-based functional groups (Smith *et al*., 2019). GO was synthesized and characterized using various analytical techniques and exploited as an adsorbent for rapid removal of malachite green dye from the aqueous solution (Mohamadi *et al*., 2016). These are usually considered one kind of chemically derived graphene, just like GO. Hydrazine hydrate ($H_2NNH_2.H_2O$), one of the reducing agents used in the chemical reduction of exfoliated graphene oxide sheets, was found to be the most effective in synthesizing extremely thin graphene-like sheets. As oxygen atoms are taken out, the rGO becomes less hydrophilic and precipitates. The main objective of the research was to prepare reduced graphene oxide from graphite and examine how effectively it adsorbed the cationic dye malachite green after being exposed to it.

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Materials and Methods

Sample Collections

In this research, graphite powder (extra pure, purchased from China Aladdin Industry Corporation), sodium nitrate ($NaNO_3$), sulphuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide(H_2O_2), and hydrochloric acid (HCl) were procured from BDH. The chemicals used were of analytical reagent grade.

Synthesis of Graphene Oxide

A modified Hummer process was used to make graphene oxide from powdered graphite. Briefly, 120 mL of concentrated sulphuric acid was mixed with 5 g of graphite and 5 g of $NaNO_3$. Using an ice bath, the mixture was kept cool-about 5 °C-while being ultrasonically processed for an hour. After that, 15 g of KMnO4 was slowly added to the mixture. For a homogenous mixture, the mixture was then ultrasonically agitated for 1 h in an ultrasonic bath. The mixture was then progressively given 250 mL of distilled water, and it was ultrasonically processed for an hour. The mixture was then brown in colour. The colour of the mixture changed to a light brown hue. The mixture was then given an additional 100 mL of deionized water, and it was agitated for 1 h at 90 °C. To produce a pale-yellow suspension, 50 mL of hydrogen peroxide and 100 mL of purified water were mixed. The remaining $KMnO_4$ and MnO_2 produced in the solution were also converted to colourless soluble salts when hydrogen peroxide was added, changing the colour of the solution from brown to light yellow.

Synthesis of Reduced Graphene Oxide (rGO)

To synthesize rGO 100 mL of distilled water were mixed with 0.1 g of GO. The mixture was heated at 95˚C for 12 h with 1 mL of hydrazine hydrate. The rGO was obtained from the mixture as a black powder after filtering. Multiple repetitions of distilled water washing were performed on the finished product.

Characterization of Reduced Graphene Oxide

Modern methods were used to characterize the reduced graphene oxide. The presence of the crystalline phase in the sample was evaluated by X-ray Diffraction (XRD, Rigaku, /max 2200, Japan). In order to identify the functional groups, present in the sample, a Fourier Transform Infrared (FT IR) spectrometer was used. Scanning Electron Microscopy (SEM, JOEL-JSM-5610, Japan, Ion Sputter-JEC-1600) was employed for the morphological examination. The relative elemental abundance was determined using the Energy Dispersive X-Ray (EDX) method. UV-visible spectrophotometer (Shimadzu: UV-1800) was used to measure the absorbance of dye solutions.

Colour Removal of Malachite Green Dye Solution by the Prepared Reduced Graphene Oxide

In this study, the effectiveness of colour removal by reduced graphene oxide was examined. Malachite green (MG) (1000 ppm) stock solution was made in distilled water. Serial dilution was used to create a series of standard MG solutions. A spectrophotometer was used to measure the absorbance of dye solutions between the wavelengths of 400 and 800 nm. Plotting the absorbance against the concentration of the malachite green solution allowed for the construction of the standard calibration curve.

Determination of the Optimum Conditions for Colour Removal of MG Dye

Effects of initial dye concentration, pH, contact time, and dosage of adsorbent on colour removal of MG dye were studied utilizing the prepared rGO. The following equation was used to determine the percentage of MG that was coloured and removed by rGO.

$$\text{Colour removal percent} = \frac{C_o - C_t}{C_o} \times 100$$

where C_o and C_t are concentrations of MG at initial and at time t, respectively.

Effect of Initial Concentration of Malachite Green

In separate conical flasks, precisely weighed samples (0.06 g each) were placed. Each conical flask was then filled with 50 mL of a dye solution with concentrations of 10, 20, 30, 40, and 50 ppm. The mixtures were shaken for 120 min, after which the sampling mixture was immediately centrifuged for 20 min at 200 rpm. After the removal of the dye solution, the remaining absorbance of the malachite green solution was measured at 617 nm by using a spectrophotometer.

Effect of pH on the Removal of Malachite Green

In the pH range of 2 to 10, the impact of pH on the adsorption capacity of rGO was determined by the initial pH value of the solution (10 ppm), which was adjusted with 0.1 M HCl or 0.1 M NaOH using a pH meter. In separate conical flasks, precisely weighed samples (0.06 g each) and 50 mL of dye solutions were added to each conical flask and agitated using an electric shaker. After 20 min, the mixture was immediately centrifuged at 200 rpm for 20 min. The absorbance of malachite green was measured at 617 nm by using a spectrophotometer.

Effect of Contact Time on the Removal of Malachite Green

In separate conical flasks, precisely weighed samples (0.06 g each) were placed. Then 50 mL of 10 ppm dye solution were added to each conical flask and agitated using an electric shaker at intervals of 30 min, 60 min, 90 min, 120 min, and 150 min, respectively. The sample mixture was immediately centrifuged at 200 rpm for 20 min. A spectrophotometer was used to measure the absorbance of the residual dye solution.

Effect of Dosage of Reduced Graphene Oxide for the Removal of Malachite Green

Different masses (0.02, 0.04, 0.06, 0.08, and 0.10) of the prepared rGo sample were placed in the conical flasks, and 50 mL each of 10 ppm malachite green solutions were added. The mixture were agitated using an electric shaker for 1 h at room temperature in order to achieve perfect equilibrium. Centrifugation was used to separate the sample solutions from the sorbent for 20 min at 200 rpm. The absorbance of the residual malachite green solution was determined at 617 nm by the spectrophotometer.

Results and Discussion

X-ray Diffraction (XRD) Analysis

With an interlayer distance of 0.334 nm, the strong and distinct diffraction peak (002) of graphite powder was seen at a 2θvalue of 26.52° (Figure 1). It is found in Figure 2 that the distinctive diffraction peak (001) of GO was displaced to a 2θ value of 10.48°, indicating that the graphite was completely oxidized into GO (Cui *et al*., 2011). When graphite oxidizes and transforms into GO, the XRD peak should change from 2θ value of 26^o to 11^o (Zaaba *et al*., 2017).

With a d-spacing of 0.84 nm, the GO interlayer distance also increased. When compared to the graphite sample, the XRD pattern of the rGO sample in Figure 3 shows dominating and broad peaks at around 2θ value of 25.14° and a d-spacing of about 0.35 nm, which suggests a small difference (0.334 nm). These results showed that after the reduction process used to synthesize few-layer graphene, the crystalline structure could be retained (Jiao *et al.*, 2017).

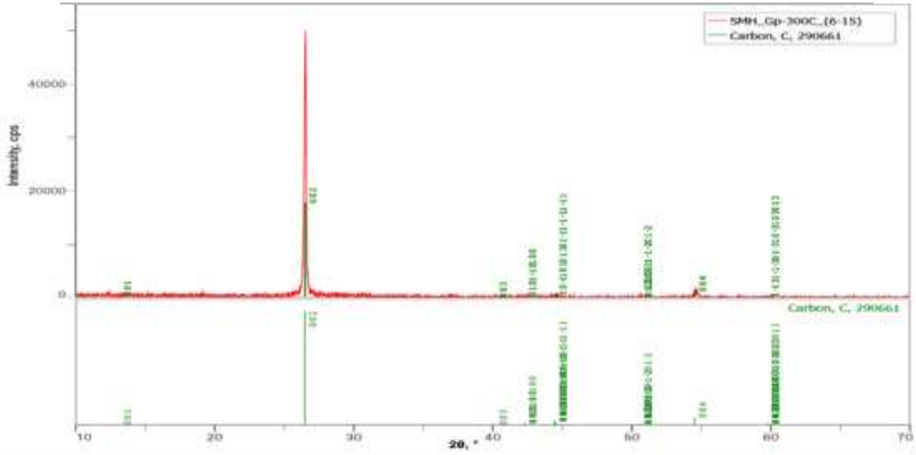

Figure 1. X-ray diffractogram of graphite powder

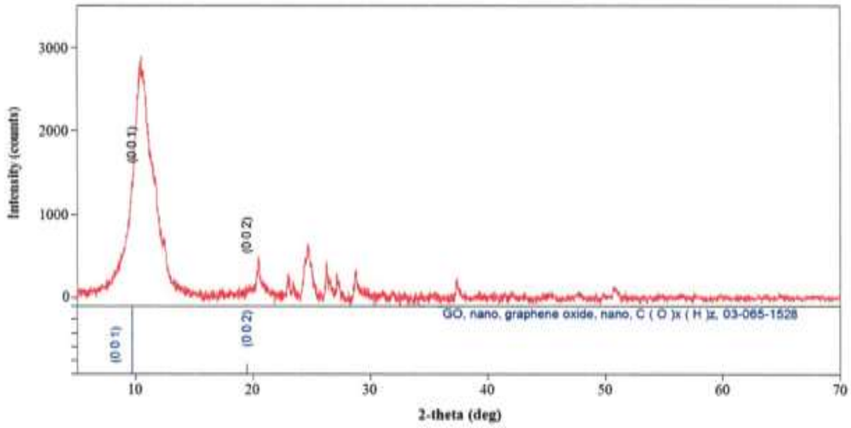

Figure 2. X-ray diffractogram of prepared GO

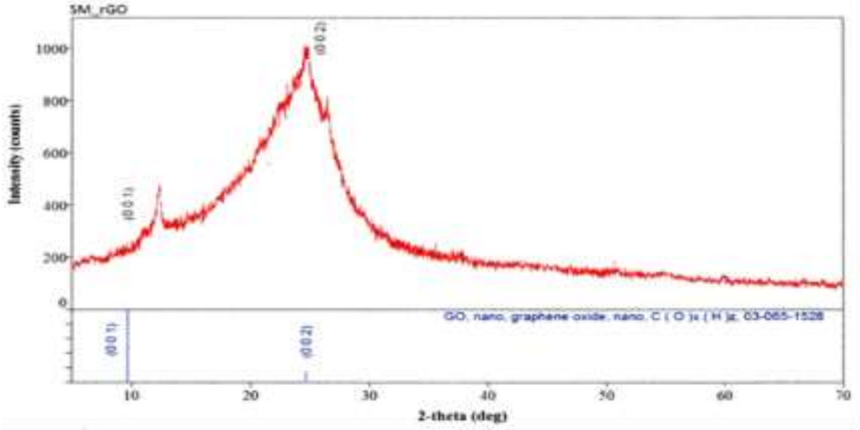

Figure 3. X-ray diffractogram of prepared rGO

Fourier Transform Infra-Red (FT IR) Analysis

The FT IR spectrum of rGO is presented in Figure 4. The spectrum shows no sharp peaks, confirming the efficient reduction of rGO. The peak at 1555 cm^{-1} corresponds to the aromatic C=C stretching of rGO (Ickecan *et al.*, 2017). The procedure of hydroxyl and carboxyl functionality removal could be efficiently facilitated by chemical reduction.

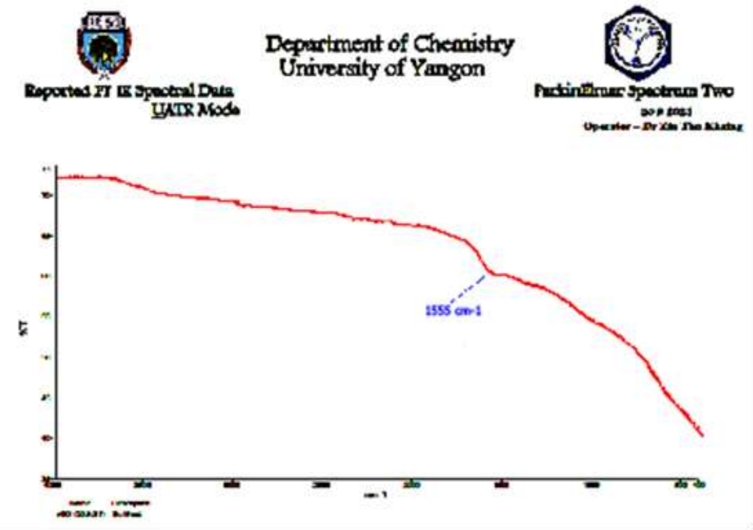

Figure 4. FT IR spectrum of reduced graphene oxide

UV Spectroscopic Measurement

The UV spectroscopic measurement was performed between 200 and 400 nm (Figure 5). The rGO absorption peak was found at 280 nm, which was in accordance with the literature value of 279 nm (Hidayah *et al*., 2017). Li *et al*. (2008) reported that the absorption peak of GO was 238 nm. After the reduction of GO, there was a redshift towards a higher wavelength of 280 nm. The shift was due to the π-π* transition of the graphitic C-C ring (Low *et al*., 2015).

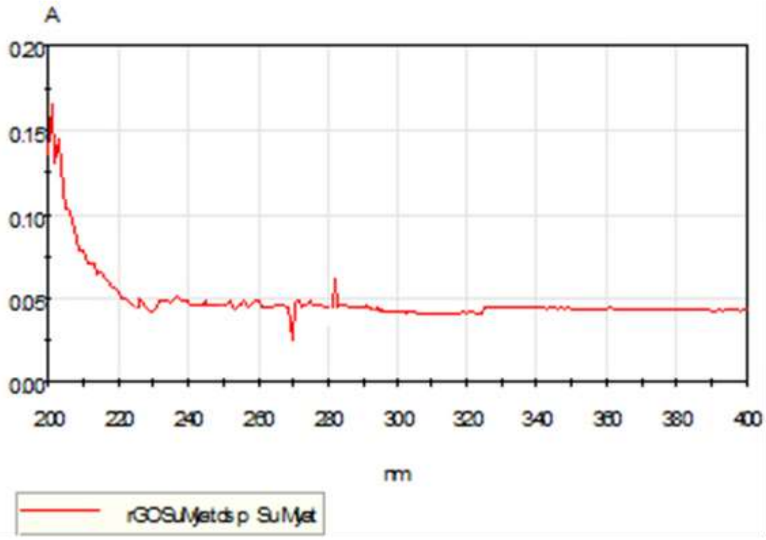

Figure 5. UV absorption spectrum of rGO

Scanning Electron Microscopic (SEM) Analysis

The SEM measurement was carried out to analyze the morphology of the prepared rGO (Figure 6). The SEM micrograph produced a substantially enlarged image of a surface of material. Graphene oxide that has undergone chemical reduction using hydrazine hydrate is seen in the micrograph. Sheets that had been crumpled and piled on the rGO surface formed disordered structural material.

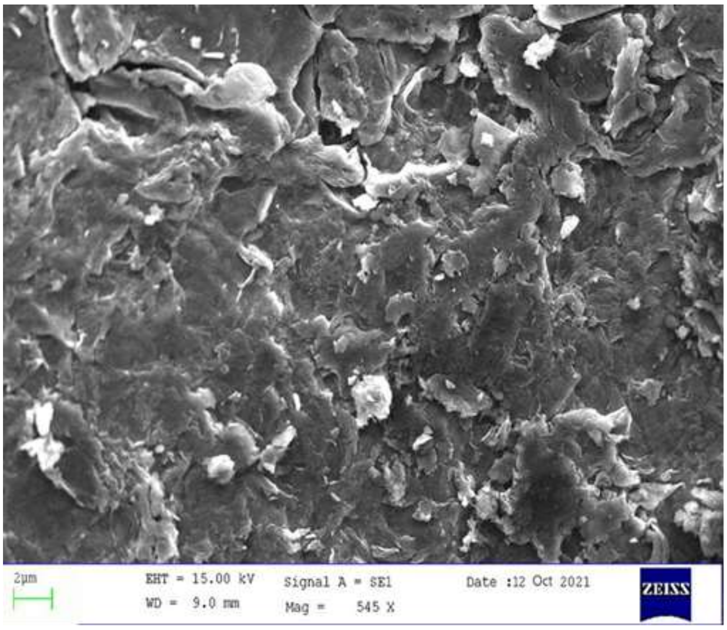

Figure 6. SEM micrograph of reduced graphene oxide (rGO)

Energy Dispersive X-Ray (EDX) Analysis

The Energy Dispersive X-Ray (EDX) spectrometer was used to determine the elements that made up the prepared rGO (Figure 7 and Table 1). According to EDX analysis, the elemental composition of carbon and oxygen in rGO was determined to be 86.65% and 13.35%, respectively. After GO was reduced, the carbon to oxygen atomic ratio was 6.4, with 13.35% of oxygen still present.

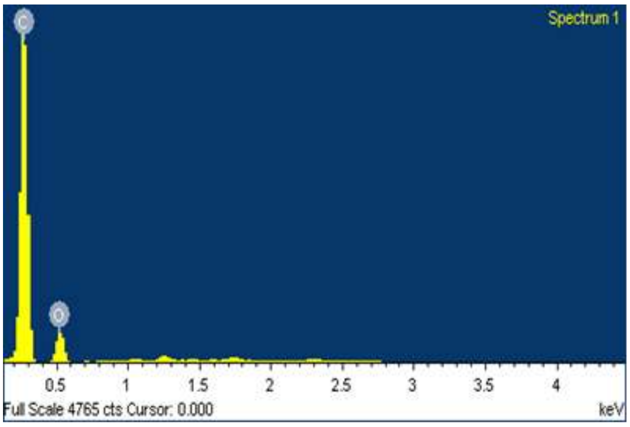

Figure 7. EDX spectrum of reduced graphene oxide (rGO)

Table 1. The Elemental Compositions in Graphene Oxide

Element	Weight %	Atomic %
C	86.65	89.63
O	13.35	10.37

The Wavelength of Maximum Absorption of Malachite Green

In this work, the absorption spectra of MG Dye at various concentrations were recorded in the wavelength range of 400-800 nm. It was observed that the wavelength of maximum absorption of MG dye solution was 617 nm (Figure 8).

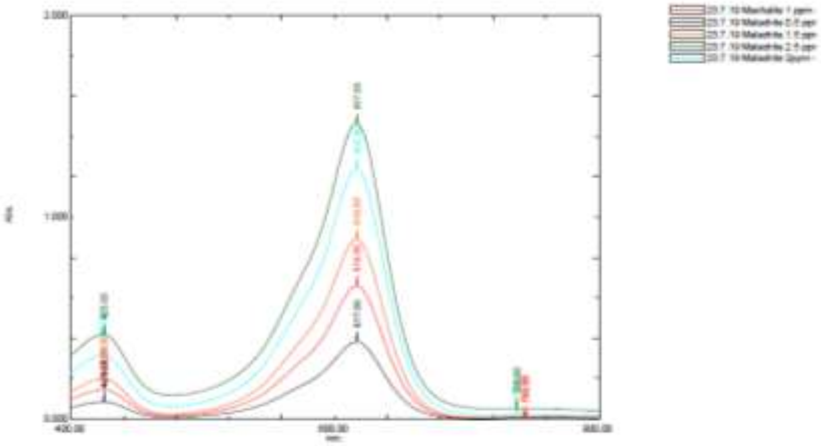

Figure 8. Wavelength of maximum absorption of malachite green

The Optimum Conditions for Colour Removal of MG Dye using Prepared rGO

Effect of initial concentration

The effect of the initial concentration of MG dye on the adsorption process was well studied. The initial concentration of MG dye in the solution was varied such as, 10, 20, 30, 40, and 50 ppm at pH 7 in the experiment using 0.06 g of prepared rGO. The maximum colour removal efficiency was obtained at the initial concentration of MG dye (10 ppm). The removal percent decreased from 90.66 % to 89.37 % as the concentration of MG increased from 10 to 50 ppm (Figure 9 and Table 2).

Table 2. Effect of Initial Concentration of Malachite Green

	Concentration (ppm)	Percent Removal (%)
1	10	90.66
2	20	90.46
3	30	89.99
4	40	89.86
5	50	89.37

The volume of dye solution = 50 mL
Weight of sample (GO) = 0.06 g
Contact Time = 60 min
Temperature = room temperature
pH = 7

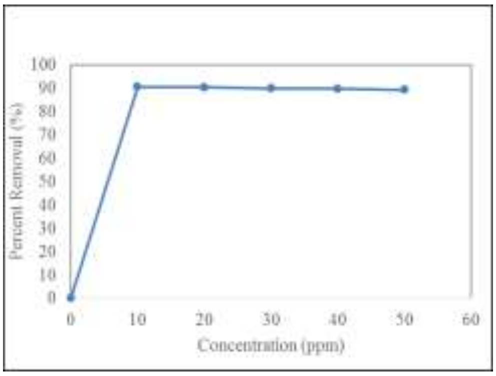

Figure 9. Effect of initial concentration of malachite green

Effect of pH

The effect of pH (2, 4, 6, 8, and 10) on the removal of MG dye by using prepared rGO was carried out for 60 min at room temperature. The maximum colour removal efficiency was obtained at pH 4 by using 0.06 g of prepared rGO (Figure 10 and Table 3).

Effect of contact time

The effect of contact time on dye by rGO was studied by varying the contact time to 30, 60, 90, 120, and 150 min on a rotary shaker. Rapid adsorption took place within the first 30 min of contact time, and the colour removal of 92.26 % was achieved using 0.06 g of prepared rGO at room temperature and pH 7 (Figure 11 and Table 4). After 60 min, the highest colour removal percent of 95.47 % was attained, followed by a slight decrease in colour removal percent of 94.00 % after 90 min.

Table 3. Effect of pH on the Removal of Malachite Green

No.	pH	Percent removal (%)
1	2	90.83
2	4	94.56
3	6	91.66
4	8	90.42
5	10	89.99

The volume of dye solution = 50 mL
Concentration = 10 ppm
Weight of sample = 0.06 g
Contact Time = 60 min
Temperature = room
temperature

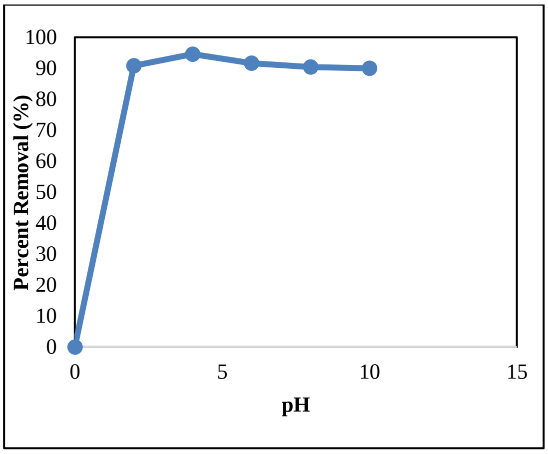

Figure 10. Effect of pH on the removal of malachite green

Table 4. Effect of Contact Time on the Removal of Malachite Green

No.	Time (min)	Percent removal (%)
1	30	92.26
2	60	95.47
3	90	94.00
4	120	91.23
5	150	90.41

The volume of dye solution = 50 mL
The concentration of dye solution = 10 ppm
Weight of sample = 0.06 g
Temperature = room temperature
pH = 7

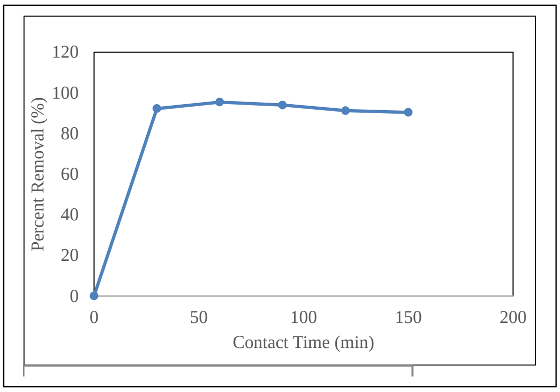

Figure 11. Effect of contact time on the removal of malachite green

Effect of dosage

The dosage of the adsorbent was varied in the range of 0.02 to 0.10 g (0.02, 0.04, 0.06, 0.08, and 1.00 g) while keeping the initial concentration of 10 ppm of MG at 60 min. The removal efficiency of MG increased from 90.10 to 96.05 % by an increase of rGO from 0.02 g to 0.06 g due to the increase in the adsorption sites. However, a further increase in the mass of rGO decreased the colour removal percent due to the desorption of the MG dye molecule from the adsorbent surface. The maximum colour removal percent was observed at a dosage of 0.06 g of prepared rGO (Figure 12 and Table 5).

Table 5. Effect of Dosage of Reduced Graphene Oxide for Removal of Malachite Green

No.	Dosage (g)	Percent removal (%)
1	0.02	90.10
2	0.04	92.23
3	0.06	96.05
4	0.08	94.41
5	0.10	92.88

Volume of dye solution = 50 mL
Concentration of dye solution = 10 ppm
Time = 60 min
Temperature = room temperature
pH = 7

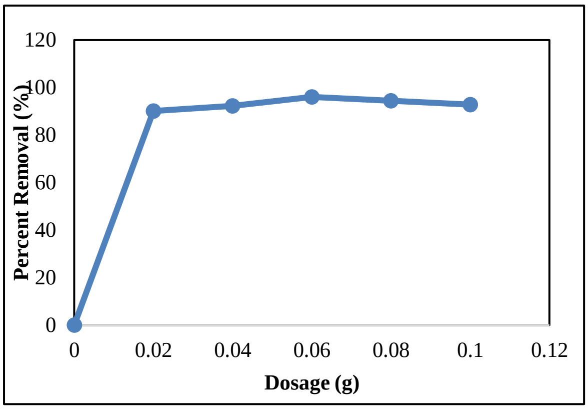

Figure 12. Effect of Dosage of Graphene Oxide for Removal of Malacchite Green

Conclusion

Reduced graphene oxide was successfully prepared by oxidizing graphite by modified Hummer's method followed by reduction with hydrazine hydrate. The prepared rGO was characterized by XRD, FT IR, SEM, UV-visible spectroscopy, and EDX. The dominant and broad peak at an approximately 2θ value of 25.14° in the XRD pattern, the absence of epoxy and alkoxy groups in the FT IR spectrum, and the appearance of the UV absorption peak at 280 nfm confirmed the prepared sample as rGO. The removal of malachite green dye from the aqueous solutions by adsorption with rGO has been experimentally determined. The effects of the initial concentration of MG dye, pH, contact time, and adsorbent dose on the removal of MG by prepared rGO were investigated.The maximum removal percent of MG by prepared rGO was found to be 96.05% at pH 7 for 60 min and initial concentration of 10 ppm MG and 0.06 g of prepared rGO. Due to these unique properties, reduced graphene oxide, meets the needs of various applications.

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