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Microwave-assisted synthesis of graphene and its application for adsorptive removal of malachite green: thermodynamics, kinetics and isotherm study

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ABSTRACT

Recently, much attention has been given to water pollution as its overall impact is much higher in comparison with air and soil pollution. In this context, dyes are considered as an important and common pollutant in water bodies because of their recalcitrant properties which render them difficult to degrade. Dyes adversely affect flora and fauna by imposing carcinogenic and mutagenic effects on them. In this study, graphene (GR) nanosheets synthesized using modified Hummer's method were used as nanoadsorbent material for the removal of malachite green (MG) from solution. The best suited condition for maximum adsorption was found at pH 8, temperature 313 K, adsorbent dose of 0.5 g/L, and percentage maximum removal of MG was found as 79% with a maximum adsorption capacity of 23.8095 mg/g. The adsorbent was also found to possess a good regenerative property. Equilibrium adsorption data recorded were subjected to Langmuir, Freundlich, Temkin and DR-isotherms and was found to best fit the Langmuir isotherm model. DR model and ΔH° analysis revealed that the process under observation was physico-chemisorptions in nature. The kinetics of adsorption was found to follow pseudo-second-order model. The rate constant was determined to increase with a corresponding rise in temperature indicating endothermic character of adsorption which was also supported by the thermodynamic analysis. Hence, it could be concluded that application of GR nanosheets resulted in efficient removal of MG from its aqueous solutions.

Keywords: Adsorption; Dyes; Graphene; Malachite green; Kinetics; Thermodynamics

1. Introduction

Dyes from different industrial sources such as textiles, paper and pulp mills, dyes synthesis, printing, food and cosmetics are considered as one of the major water pollutants. The rate of natural dye degradation is very slow because of its biorecalcitrant nature. Dyes have been reported to possess tumour enhancing, mutagenic and carcinogenic properties and therefore express detrimental effect on flora and fauna alike [1–8]. Malachite green (*n*-methyl *di*-amino *tri*-phenyl methane) (MG) is one of the most widely used dye for

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manufacture of ink, dyeing of different items of cotton, silk, paper, leather, etc. Exposure to this dye results in decreased food intake capacity, retarded growth and fertility rates, damage to liver, spleen, kidney and heart, lesions on skin, eyes, lungs and bones, etc.

Through ages, MG has been widely used as bacteriocidal, antifungal, ectoparasital (in aquaculture of fisheries) as well as dyeing agent. For the removal of such dyes from aqueous environment, the process of adsorption has been established as the most suitable and eco-friendly in comparison with other conventional technologies such as microbial degradation, absorption and reverse osmosis. in terms of large-scale application, cost efficiency and minimum manpower [9,10]. Many existing studies have focused on preparation of adsorbents from agro-industrial waste materials because of their inexpensive, eco-friendly and renewable nature. Several materials used for successful adsorbent preparation include orange peels, mango seed husks, pineapple stems, coconut bunch waste, pumpkin seeds, cotton plant waste etc. [11–13].

Graphene (GR) consists of one-atom-thick sheets of sp^2 hybridized carbon atoms arranged in a honeycomb-like fashion [14]. GR exhibits very high surface area, electrochemical properties [15,16], exceptional thermal conductivity and has very high young's modulus and electron mobility. GR has also been used in various fields for preparation of nanoelectronics, hydrogen storage, polymer composites, solar cell, field-effect transistors, biosensors, electrodes for super capacitors and batteries [17,18].

Previous studies report GR synthesis by different methods such as chemical vapour deposition, exceptional growth on electrically insulating surface, electrical arch discharge, direct sonication, chemical reduction of graphene oxide (GO) as well as exfoliation of pure graphite. However, the chemical method ranks higher than other methods for large-scale industrial production. Different reducing agents used to reduce GR are hydrazine, vitamin C, sodium borohydride, hydroquinone, sodium carbonate, glucose, etc. [18,19]. A recent report narrates the implementation of GR as an adsorbent for the removal of heavy metals like Pb^+, Cd^+ and Cu^+ from effluents [20]. In this study, GR nanosheets synthesized from GO were used as adsorbent for the successful removal of MG from its aqueous solutions.

2. Experimental procedure

2.1. Materials

All chemicals used were of analytical grade. Graphite fine powder was purchased from Sigma–Aldrich, USA. Other reagents were supplied by Merck, India. Chemical reagents are used directly without further purification.

2.2. Synthesis of GO

GO was synthesized by the Hummer's method with modifications [21]. Sulphuric acid and potassium permanganate were slowly added to graphite powder taken in a conical flask. The mixture was kept under stirring for 150 min at a temperature of 45˚C. After cooling to room temperature, distilled water was added. Finally, hydrogen peroxide was added very slowly to the solution which turned yellow in colour. The product solution was then sonicated and filtered by vacuum filtration unit and followed by repeated washing with water and hydrochloric acid. The cake deposited on the filter paper was dried at 55˚C, crushed and stored in an airtight container for future use.

2.3. Synthesis of GR

The GR used for MG removal was synthesized from the GO prepared earlier by chemical reduction of the same using hydrazine hydrate (H_2O_4) [22]. GO solutions in distilled water were prepared and heated it to a temperature of 45˚C in a microwave digester. Hydrazine hydrate was then added to the solution, and the colour changes its colour from brown to black. The solution was kept with shaking at 120 rpm, for 150 min at 35˚C. After this, the solution was sonicated followed by vacuum filtration. The residue obtained was dried at 60˚C, crushed and stored for further experiments.

2.4. Measurement and characterization

The prepared samples were characterized by scanning electron microscopy (SEM), XRD, FTIR and Raman Spectroscopy. SEM analysis was carried out to study the changes in surface textures such as smoothness and roughness of the GR nanosheets. The XRD analysis was done to investigate the interlayer spacing of the prepared sample. The surface functional groups of the prepared sample of GR and GO were detected by FTIR spectroscopy. The spectra were recorded from 4,000 to 400 cm^{-1}. Raman spectroscopy (Model: T64000, Make: J-Y Horiba) was done to evaluate the degree of structural deformations and number of layers in GR and GO.

2.5. Adsorption experiment

All the batch adsorption studies were carried out in 250-mL conical flasks with continuous stirring and constant temperature. The initial concentration of MG varied from 5 to 25 mg/L, while the adsorbent doses selected were in the range of 0.1–1 g/L.

The stock solution of the dye was prepared separately for each set of experiment. Sampling was done at regular time intervals, and the concentration of MG remaining in the liquid phase was determined by centrifuging the sample to settle down particles and recording the absorbance (λ-max) of the solution using a spectrophotometer at a wavelength of 616 nm. The amount of dyes adsorbed per unit mass of the adsorbent was calculated using the mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q (mg/g) was the amount adsorbed per gram of adsorbent, C_0 and C_e were the initial and equilibrium concentration of MG in the solution (mg/L), respectively, m was the mass of the adsorbent used (g), and V (L) was the initial volume of the MG in the solution.

3. Results and discussions

3.1. Characterization of GR

SEM analysis was performed to investigate the morphological features (roughness and smoothness) of the prepared samples of GR and GO. From Fig. 1, it was observed that GO consisted of thin wrinkled paper-like structures, a typical feature of GO reported in previous studies [23,24]. On the other hand, the figures showed that GR possessed a flaky texture which reflected by its layered microstructure.

The XRD analysis were performed to investigate the interlayer spacing of the prepared GO and GR. A broad peak of 2θ at 24.95 and 43.10 with an interlayer spacing of 0.356 and 0.2097 nm was observed which could be indexed to the characteristic peaks of (0 0 2) and (1 0 0) plane reflections, respectively, of GR nanosheet [25] which was much lower than that of GO (0.796 nm) (Figure not shown).

FTIR spectra analysis had been used to detect the presence of functional groups and also quantitative measure of the deoxygenating reaction on GO and GR. GO showed the strong peaks at 3,368 cm^{-1} resulting from the presence of—OH (stretching vibration) groups as well as peaks at 1,718, 1,685, 1,617 and 1,054 cm^{-1} which were assigned to the C=O, COOH, C=C groups and the C–O–C groups, respectively, (Figure not shown). After reducing with hydrazine hydrate, the peak at 1,718, 1,616 and 1,056 cm^{-1} almost disappeared and the peak for OH stretching bonds at 3,368 cm^{-1} weakened indicating that oxygen containing functional groups were removed from GO after reduction with hydrazine hydrate [24–28].

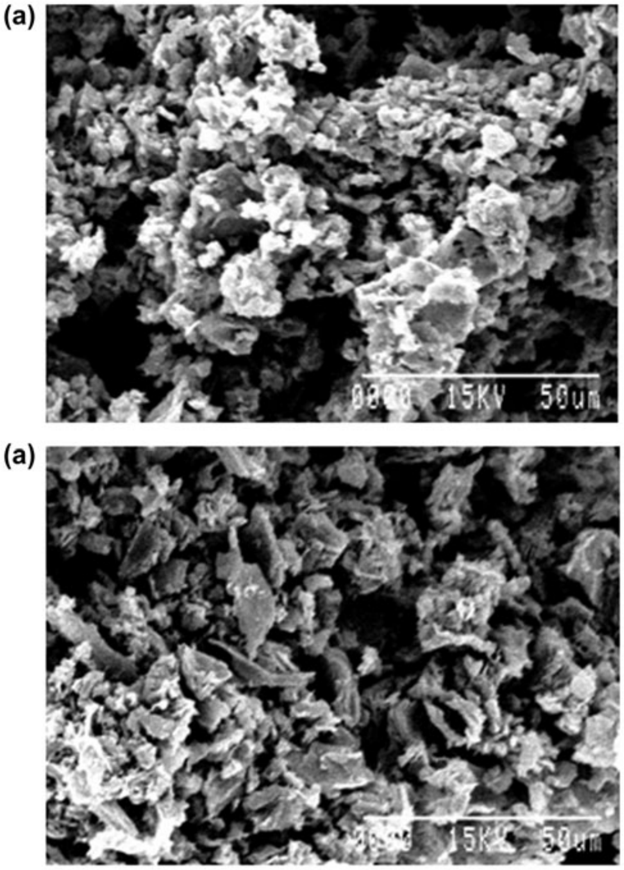

Fig. 1. SEM of (a) GO nanosheet and (b) GR nanosheet.

Raman spectroscopy was done to evaluate the degree of structural deformations and number of layers in the GO and GR samples. From the resultant spectra, it was clear that there were three typical modes related to graphite-like structure: a G band, a D band and a 2D band. The D and G bands were at 1,350, 1,597 cm^{-1} for GO and 1,346, 1,583 cm^{-1} for GR in the prepared samples, respectively. According to the position and intensity of 2D band (2D$_1$ and 2D$_2$), the number of layers in GR could be determined. Increase in the number of layers leads to an increase in the intensity of the 2D$_2$ peak and blue shift of the 2D peak, while a single layer of GR showed a single 2D band at around 2,600 cm^{-1} (Figure not shown). In this study, GR showed a 2D peak at 2,665 cm^{-1} which was the characteristic feature of three to five layer of GR nanosheet [14,27].

3.2. Effect of pH on MG removal

pH is the most important factor influencing any adsorption as it influences the surface charge of the adsorbent, degree of ionization of material present in the solution, dissociation of functional group on the adsorbent and dye chemistry. The effect of pH on the removal of MG was studied at pH 2–9 by keeping constant dose of adsorbent at 0.5 g/L. Results are shown in Fig. 2. Significant removal of MG was observed when the pH increased from 2 to 8 and after that there was no significant change observed with further rise in the pH range. The maximum adsorption removal of MG was at pH 8, and percentage removal was 79%. Therefore, the further experiments were carried out at pH 8. MG is a basic dye which existed in solution as positively charged species so that the degree of its adsorption on GR was primarily influenced by the surface charge of the GR which in turn influenced by the solution pH. At low pH, all the sites were occupied by the H^+ ions and little sites were available for dye adsorbed, but as pH increased, there will be less H^+ and more and more surface area for dyes and maximum removal was observed at basic pH range.

3.3. Effect of initial concentration and contact time on MG removal

It is essential to evaluate the effect of initial concentration and contact time for the adsorption of dye from the aqueous solution. The effect of contact time with different initial concentration is shown in Fig. 3. The rate of adsorption was a function of initial concentration of adsorbate, which made it an important factor to be considered for effective adsorption. It was observed that as the initial concentration of MG increased, the adsorption capacity of GR increased because the initial concentration of dye increased the overall driving force of mass transfer. However, at the same time, percentage removal of dye decreased from 94.6 to 49% with increased in MG concentration from 5 to 25 mg/L. This showed that the surface of adsorbent possessed specific number of sites for adsorption, which became saturated after certain time and then there was no adsorptive removal. It is clear that by increasing the contact time, removal percentage increased but there was not a significant change after adsorption capacity reached to 23.17 mg/g (see Fig. 3).

3.4. Adsorption isotherm of MG removal

For this study, four isotherms namely Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) model had been used to fit the equilibrium data for MG adsorption on GR at three different temperatures 303, 308 and 313 K. The results obtained are shown in Table 1. The Langmuir adsorption isotherm was based on the assumption that adsorption took place on homogenous surface. The Langmuir equation was given by following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{2}$$

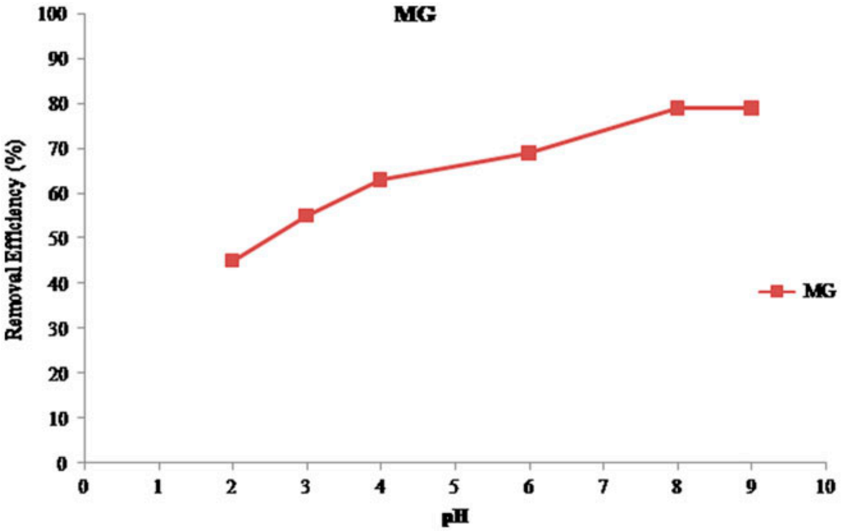

Fig. 2. Effect of pH on the adsorption of MG on GR nanosheet.

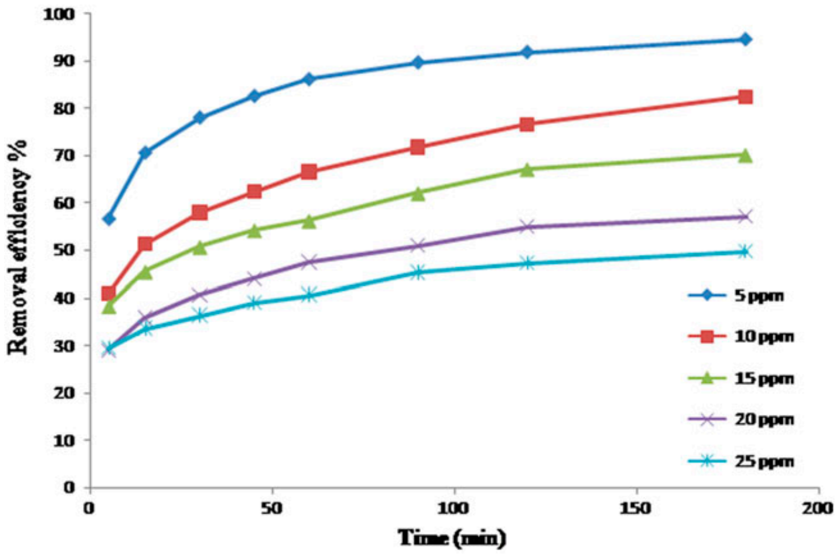

Fig. 3. Effect of initial concentration and contact time of dye on adsorption of MG using GR (condition: weight of adsorbrnt = 0.5 g/L, stirring = 140 rpm, temperature = 313 K, contact time = 180 min, and pH = 8).

Table 1
Parameter of Langmuir, Freundlich, Temkin and D–R isotherm models for MG adsorbed by GR (condition: weight of adsorbrnt = 0.5 g/L, stirring = 140 rpm, temperature = 313 K, contact time = 180 min, and pH = 8)

Langmuir isotherm	Value	Freundlich isotherm	Value	D–R model	Value	Temkin	Value
q_m (mg/g)	23.809	K_f (mg/gm)	18.578	β	5x105 × 10^{-3}	B_T	2.0
K_L (L/mg)	0.0238	$1/n$ $(\text{L/mg})^{1/n}$	0.124	q_m	22.443	K_T	18.034
R^2	0.996	R^2	0.967	E	10	R^2	0.954
				R^2	0.922		

where q_m (mg/g) was the maximum amount of dye per unit weight of adsorbent for complete monolayer coverage, and K_L was Langmuir adsorption constant (L/mg). A plot of C_e/q_e vs. C_e should be linear if adsorption followed Langmuir behaviour [29,30].

Freundlich adsorption equation was given by:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log\ C_e \tag{3}$$

where K_f was Freundlich constant, and n was heterogeneity factor.

The D–R isotherm model was given by the following formula.

$$\ln q_e = q_m - \beta\varepsilon^2 \tag{4}$$

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{5}$$

where q_m was the maximum adsorption capacity, β was a coefficient related to the mean free energy of adsorption (mmol^2 J^{-2}), ε was the Polanyi potential (Jmmol^{-1}), R was the gas constant (8.314 Jmol^{-1} K^{-1}), T was the temperature (K), and C_e was the equilibrium adsorbate concentration (mg L^{-1}). The D–R constants, q_m and β, were determined from the intercept and slope of the plot between lnq_e and ε^2. The constant gave an idea about the mean free energy E (kJ mol^{-1}) of adsorption per mole of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and was calculated using the relationship.

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

Magnitude of E between 8 and 16 kJ mol^{-1} renders the sorption process as chemisorptions, while the values of $E < 8$ kJ mol^{-1} indicated the sorption process to be physical in nature.

The Temkin isotherm model was given by the following equation [31–33].

$$q_e = B \ln A_T + B \ln C_e \tag{7}$$

$$B = \frac{RT}{b_T} \tag{8}$$

where A_T was Temkin isotherm equilibrium binding constant (L/g), b_T was Temkin isotherm constant, R denoted the universal gas constant (8.314 J/mol/K), T was temperature at 298 K, and B was a constant related to heat of sorption (J/mol).

Table 1 and Fig. 4 summarizes the corresponding constants for all the isotherms. R^2 value of Langmuir isotherm model (0.996) was greater than that of Freundlich (0.967), D–R isotherm (0.922), Temkin model (0.954) suggesting that MG adsorption on GR followed Langmuir isotherm the best. This also suggested that the surface of GR behaved homogeneous for MG adsorption. Adsorption capacity increased with the increase in temperature indicating that the process was endothermic in nature. In Table 2, the comparison of adsorption capacity ofthis study with other reported adsorbents had been mentioned and it was found that the GR had the potential to act as adsorbent for the dye removal study.

3.5. Adsorption kinetics of MG removal

To understand the controlling mechanism and kinetics of adsorption, two kinetic models, namely pseudo-first-order (Lagergren) and pseudo-second-order equations, were applied.

First-order rate equation is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{9}$$

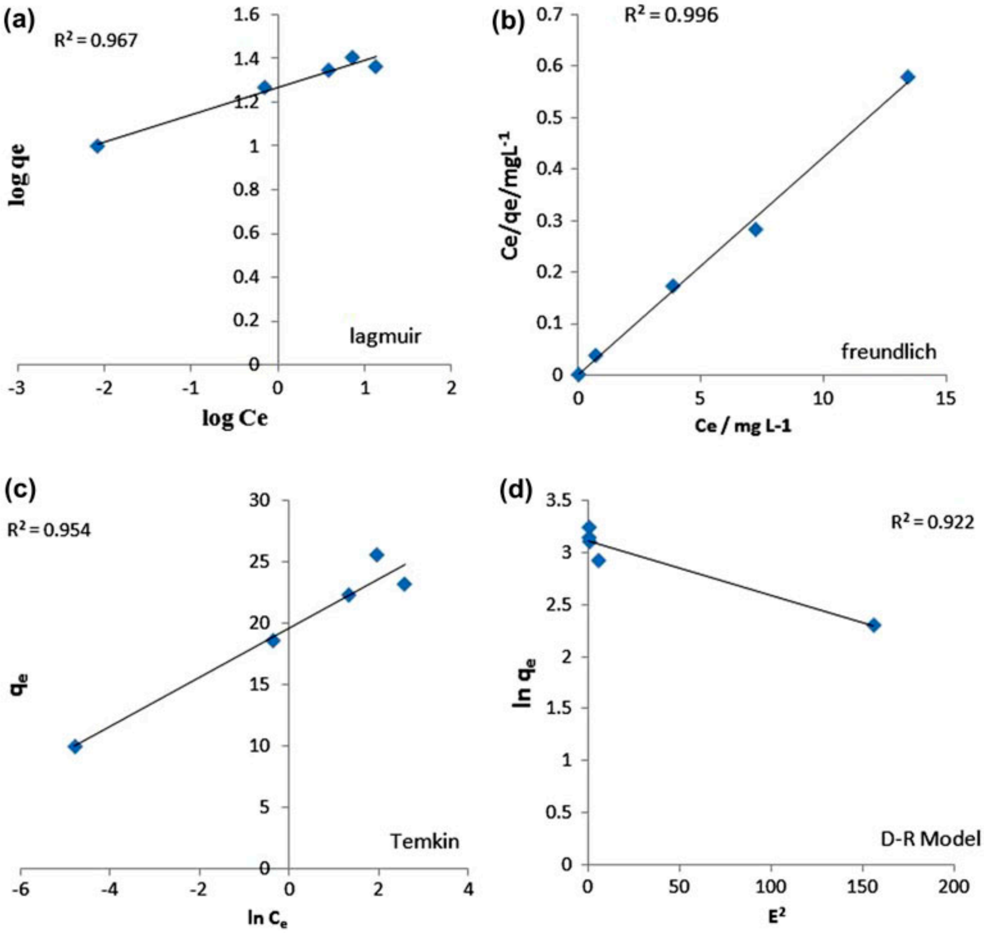

Fig. 4. (a) Langmuir, (b) Freundlich, (c) Temkin and (d) D–R model for adsorption isotherms of MG onto GR nanosheet.

Table 2
Comparison of adsorption capacities of MG onto various adsorbents

Adsorbents	q_m (mg/g)	References
Arundo donax root carbon	8.69	[34]
Hen feathers	2.82	[35]
Rice husk	76.92	[36]
Activated charcoal	0.18	[37]
Bentonite clay	7.72	[38]
Activated slag	74.2	[39]
Sugarcane dust	4.88	[40]
Activated carbon	8.27	[41]
GR	23.809	This study

where q_e and q_t were the amount of dye adsorbed (mg/g) at equilibrium and after time t (min), and k_1 was the rate constant of adsorption (min^{-1}). The plot of $\log(q_e - q_t)$ against t gave a linear relationship from which k_1 and q_e were determined using the slope and intercept of the plot [30,31].

The pseudo-second-order kinetic model was given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

where k_2 was the rate constant for the pseudo-second-order adsorption process (g/mg min). The value of k_2 and q_e was determined from the intercept and slope of the plot of t/q_t against t. The validity of each kinetic model was analysed by comparing the expected and calculated values of q_e and coefficient of determination R^2. The value of R^2 for 15, 20 and 25 mg/L of MG concentration were 0.987, 0.991 and 0.982, respectively. The corresponding k_2 values were 0.002, 0.0022 and 0.0016, while the calculated q_e (mg/g) was 24.390, 25 and 27.78, respectively. The coefficient of determination R^2 for pseudo-second-order was higher than pseudo-first- order process. R^2 for MG and the experimental values of q_e being approximately in the range of calculated q_e illustrated that the adsorption of MG onto GR followed pseudo-second-order model (Fig. 5).

The intraparticle diffusion equation is given by the following equation [6]

$$q_t = k_i t^{0.5} \tag{11}$$

The plot of q_t vs. $t^{0.5}$ gave a straight line with slope k_i, when only the intraparticle diffusion worked alone as a rate limiting step. In case of film diffusion, the intercept gave an idea of the thickness of the boundary layer. The present finding of adsorption of MG on GR at different temperatures implied that though the intraparticle diffusion was involved in the adsorption process, it was not the overall rate-controlling step as some other mechanisms were also playing an important role (Fig. 5).

3.6. Thermodynamic study

In order to determine whether the reaction is favourable or not, the thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) had to be considered.

Here, all the parameters are calculated using the following equations [30–41]:

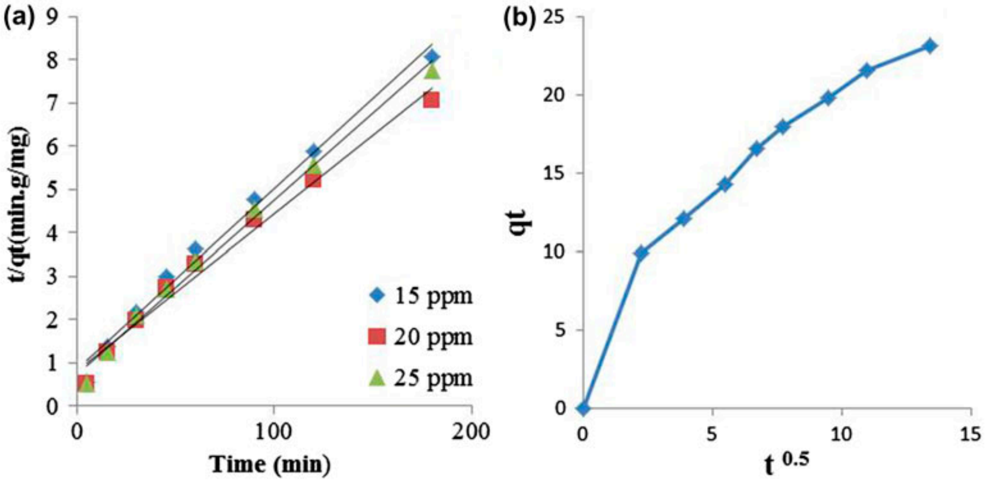

Fig. 5. (a) Pseudo second order kinetics plot and (b) Intra particle diffusion model for the adsorption of Malachite Green.

Table 3
Thermodynamic parameters for MG onto GR

Dye	Temperature	ΔG° (J/mol)	ΔH° (KJ/mol)	ΔS° (J/mol K)	R^2
MG	303	−2,465.301	22.47274	82.35	0.9950
	308	−2,919.305			
	313	−3,287.957			

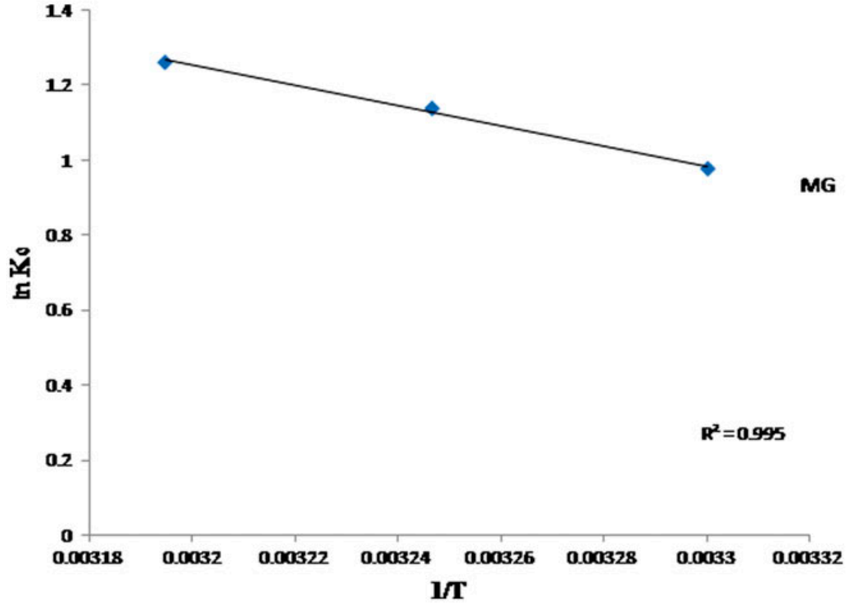

Fig. 6. Plot of ln K_c verses $1/T$ of MG adsorption, initial MG conentration is 20 mg/L, GR is 0.5 g/L.

$$\Delta G^\circ = -RT \ln K_C \tag{12}$$

$$K_C = \frac{C_a}{C_e} \tag{13}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

where R was the universal gas constant (8.314 J/mol K), K_c was the distribution coefficient, ΔG°, ΔH°, ΔS° and T represented Gibbs free energy change, enthalpy, entropy and temperature, respectively.

The Gibbs free energy (ΔG°) for adsorption of MG onto GR obtained at temperature 303, 308, 313 K was listed in Table 3. ΔH° and ΔS° were determined by the slope and intercept from the plot of ln K_c vs. $\frac{1}{T}$ (Fig. 6). The values of ΔG° were negative at all temperatures confirming the feasibility of the process and the spontaneous nature of MG adsorption onto GR. The increase in the absolute value of ΔG° with rise in temperature indicated that the affinity of MG on GR was higher at high temperature. The positive value of ΔH° (22.473 kJ mol^{-1}) confirmed that the adsorption process was endothermic in nature. Based on the results of D–R model, the adsorption of MG on the GR nanosheet was found to be chemisorptions in nature, but for chemisorptions, the magnitude of ΔH° generally remained between of 80 and 200 kJ, but here it was found to be 22.47274 kJ mol^{-1}, indicating that the adsorption of MG onto GR followed physico-chemical adsorption process instead of chemisorptions alone. The positive value of ΔS° (82.35 J mol^{-1} K^{-1}) reflected the affinity of the GR on MG and an increased randomness at the solid–liquid interface during adsorption.

4. Conclusion

An eco-friendly method for the exfoliation of graphite into mono-atom-thick or oligo-atom-thick sheet of GR and GO has been successfully developed in this study. The obtained nanosheet was also productively applied as a good adsorbent for removal of basic dyes such as MG from its aqueous solution. The adsorption process was found to follow pseudo-second-order kinetics, and the process was analysed to be endothermic in nature. This study inaugurates the possibility of preparing different types of GR/GO based nanocomposites for better and effective adsorption of dyes, organic/inorganic pollutants, metals and other such contaminants.

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