

Decolorization and Removal of Reactive Red 198 by Nano-Magnetic Graphene Oxide

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In this research, a systematic study of the adsorption and decolorization process of reactive red 198 (RR198) onto Fe₃O₄-graphene oxide (Fe₃O₄-GO) was applied *via* various pH, sorption time and temperature. Investigation of reactive red 198 adsorption kinetics were satisfied by the pseudo-first and second order model. According to the kinetic examinations, the equilibrium reached within 15 min following the pseudo-second-order model. The sorption data have interpreted by the Langmuir model with the maximum adsorption of 357.14 mg g⁻¹ at 298 K and a rate constant of R² = 0.996. The mean energy of adsorption and thermodynamic parameters such as ΔH° , ΔS° and ΔG° values were determined which included the exothermic and spontaneous nature of the sorption process. The results indicated, reactive red 198 vigorously was adsorbed on the Fe₃O₄-GO surface *via* π - π interaction and cation- π bonding acid under UV Irradiation could degrade the reactive red 198 strongly and within 60 min the reactive red 198 totally disappeared.

Keywords: Fe₃O₄-graphene oxide, Reactive red 198, Decolorization, Kinetic, Thermodynamic models.

INTRODUCTION

Now-a-days the removal and recycling wastewater plays a significant role among industrial factories which are not only producing organic pigments and dyes but also making wastewaters which have toxic effects in environment [1]. Unfortunately, most of the synthesis and organic dyes withstand against microorganism in soil, sun emission and oxidizing agents, to be decomposed by them [2]. Scientists and researchers endeavor to control and attenuate the wastewaters toxic effects *via* designing some special methods and process in order to absorb these organic dyes and safe the environment from their destructive effects [3]. Currently, nanomaterials have been used by researchers to advance removal and treatment of industrial wastewaters. These nanomaterials are divided into two main categories such as nanometal [4] and none-nanometal materials such as Fe₃O₄-graphene oxide (Fe₃O₄-GO) and graphene oxide or nano-carbon families, respectively, which are powerful and remarkable nanomaterials that could be used as a strong absorbent *via* their great and enormous specific surface area and minor internal diffusion resistance [5]. On the other hand, researchers try to modify the structure of these nano magnetic materials in order to remove dyes and restored from aqueous solutions easily which could be used for several times and it's

not only remove dyes but also not damage the environment [6]. The magnetic materials could be used in two fundamental fields such as chemical and physical methods which are consecutively used in nanoparticles and coating [7] or chemical vapour deposition (CVD) to separate pollutants. Fe₃O₄ and graphene oxide have also been used to remove and adsorb a variety of organic substances and toxic elements such as tetracycline, reactive black [8] and copper ions [9]. Some materials like graphene oxide could be a brilliant choice to alter and adjust the magnetic nanoparticles for many reasons such as low price, wide range of sources and friendly for environment [10]. The Fe₃O₄-GO could remove and separate organic pollutant easily for many reasons such as graphene oxide has many benzoic rings on its surface and could charge Fe₃O₄ *via* these electrons of rings and leads Fe₃O₄ to adsorb organic azo dyes and intensify photocatalyst behaviours of Fe₃O₄-GO especially in decolorization process [11]. Based on previous papers the work on adsorption process by theoretical and experimental activities to discover best method to remove and adsorb pollutants from aqueous solutions *via* choosing appropriate adsorbents [12]. In present work, Fe₃O₄-GO was prepared to create a strong adsorbent with a low prices and simple synthesis procedure to adsorb and separate the reactive red 198 from aqueous solution. The characterization of Fe₃O₄-

GO nanocomposite was examined *via* FT-IR and UV-visible. The adsorption manner of reactive red 198 onto Fe_3O_4 -GO nanocomposite was explored and the main adsorption mechanisms were surveyed in different pH, time, concentrations and temperatures. The photocatalyst properties of Fe_3O_4 -GO were examined by decolonization processes which are performed under UV irradiation *via* assisting hydrogen peroxide.

EXPERIMENTAL

All chemicals used were of analytical reagent grade and used without further purification. Graphite flakes (150 μm flakes) were purchased from Sigma-Aldrich chemical Co. USA. Graphene oxide nanoparticles were manufactured by improved Hummers method [13] and reactive red 198 was purchased from Alvan Sabet Co. Iran.

FT-IR spectrum was recorded on a spectrum 100N Fourier transform infrared spectroscopy (Nicolet Magna IR 550) equipped with deuterated triglycine sulphate (DTGS) detector and KBr beam splitter. UV-Vis-NIR lambda 25 (Perkin Elmer Co. UK) was used to record the absorption spectra of reactive red 198, Fe_3O_4 -GO and Fe_3O_4 /GO-reactive red 198 complexes.

Preparation of graphene oxide: Graphene oxide was prepared from graphite powder using a modified Hummer's method. Firstly, a 9:1 mixture of concentrated H_2SO_4 : H_3PO_4 was added to a mixture of graphite flake (3 g, 1 wt equiv) and KMnO_4 (18 g, 6 wt equiv), producing a slight exothermal to 35–40 °C. The reaction was then washed and the residues were centrifuged (4000 rpm for 4 h) and the supernatant decanted away. The remaining material after multiple-wash process was mixed with 200 mL of diethyl ether. The obtained solid on filter was vacuum-dried overnight at room temperature [14].

Preparation of Fe_3O_4 -GO nanocomposite: Firstly 15 mL of graphene oxide (2.72 mg mL^{-1}) was dispersed into 40 mL ethanol with stirring. Then 0.9522 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.5228 mmol) and 1.0520 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (3.7842 mmol) were dissolved in 10 mL of distilled water under sonication and solution was injected drop wise into the graphene oxide suspension and stirred for 0.5 h. The resulting mixture was heated to 68 °C before ammonia solution was added to adjust the pH to 10. The mixture was stirred at 68 °C for 2 h and cooled to room temperature. The Fe_3O_4 -GO composite was separated from the mixture using a permanent magnet and rinsed two times with ethanol and distilled water, respectively before being dried at 65 °C for 12 h [15].

General adsorption experiments: To demonstrate the removal efficiency, the adsorption experiments were performed using a series of 100 mL flasks containing 150 mg L^{-1} Fe_3O_4 -GO and 100 mL (10–300 mg L^{-1}) reactive red 198 solution. The pH of the solutions were adjusted around 4 by adding concentrated HCl and NaOH solution. The mixtures of Fe_3O_4 -GO and reactive red 198 solutions were incubated for 3 h and used for determination by UV-visible absorbance at maximum wavelength of 518 nm.

To study the influence of pH on adsorption, Fe_3O_4 -GO (6 mL of 150.0 mg L^{-1}) and reactive red 198 solutions (2 mL of 200, 300 and 500 mg L^{-1}) were prepared. The pH of Fe_3O_4 -GO solutions were adjusted from 2 to 10 using NaOH and HCl aqueous solution then incubated for 3 h. The supernatant was collected for determination by UV-visible absorbance at 518 nm.

Decolonization: Decolonization experiments were conducted in a UV lamp, using a 50 W medium-pressure, 25 mW cm^{-2} Hg lamp (254 nm, Philips) placed inside a quartz tube as irradiation source. Concentration of reactive red 198 and hydrogen peroxide were 30 mg L^{-1} and 0.33 mM, respectively. In all experiments, the Fe_3O_4 -GO dosage was chosen 0.5 g L^{-1} . Finally samples were stirred at 300 rpm and aerated continuously.

RESULTS AND DISCUSSION

FT-IR: Fourier transform infrared (FTIR), measurements provide further evidence for the oxidation of Fe^{2+} into Fe_3O_4 by using graphene oxide as the oxidizing reagent. As shown in Fig. 2, the strong band at 580 cm^{-1} in the IR spectrum of the as-prepared Fe_3O_4 -GO is due to the Fe-O vibration of Fe_3O_4 nanoparticles, which indicated that Fe^{2+} has been oxidized into Fe_3O_4 nanoparticles by graphene oxide. The IR bands of hydroxyl (3400 cm^{-1}), along with oxygen groups (1228 cm^{-1}) and carbonyl (1731 cm^{-1}) groups, associated with graphene oxide were significantly reduced upon its reduction to produce Fe_3O_4 -GO. The FTIR spectrum of dye adsorption was shown in Fig. 2. The peaks of 1656 cm^{-1} (SO_3 : S=O), 1621 cm^{-1} , amine 1557 cm^{-1} (-CNH), 3437 cm^{-1} (amine: N-H) and 3261 cm^{-1} (hydroxyl: OH) represented the reactive red 198 peak (Fig. 1), which involved the functional group of amine group (NH_2), hydroxyl group (OH) reactive red 198. Accordingly, electrostatic interaction occurred between the protonated amine,

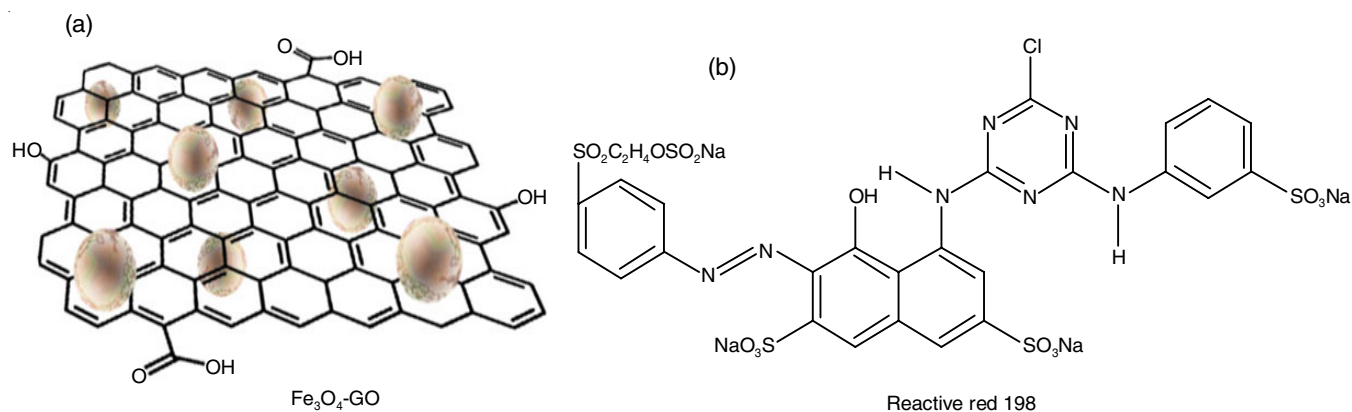


Fig. 1. (a) Fe_3O_4 -GO (b) Reactive red 198 structures

hydroxyl and sulfonate group of reactive dye. In Fig. 1, the peak of amine II, (-CHN) and amine were shifted to 1557, 1488 and 3438 cm^{-1} , respectively. Fig. 2, represented the FTIR spectra of Fe_3O_4 -GO/reactive red 198 around 2700 cm^{-1} started and ended till around 3600 cm^{-1} . It could be relevant to the interaction between Fe_3O_4 both hydroxyl and amine groups and at the result became very wide. The shifted amine group disappeared, which means Fe_3O_4 -GO could absorb these compounds. Furthermore, the flat peaks of Fe_3O_4 -GO did not change from original position and accepted the new peaks in 748 cm^{-1} and 860 cm^{-1} which are related to C-Cl and S-O of dye. It confirmed the attachment of dye onto the Fe_3O_4 -GO as shown in Fig. 2. Fe_3O_4 -GO and reactive red 198 stick to each other and form bundles, because of this process, water molecules could form H-bonds with functional groups on Fe_3O_4 -GO, which blocks the access of reactive red 198 molecules into the sorption sites [15].

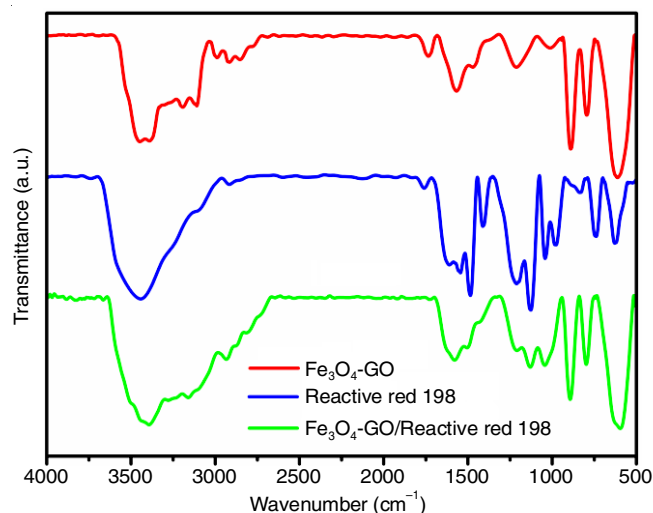


Fig. 2. FTIR of Fe_3O_4 -GO (Red), reactive red 198 (blue), Fe_3O_4 -GO/reactive red 198 (Green)

UV-visible measurements: The absorption spectra of Fe_3O_4 -GO, reactive red 198 and Fe_3O_4 -GO/reactive red 198 are shown in Fig. 3. The Fe_3O_4 -GO dispersion displays a maximum absorption at 221 nm, which is due to the π - π^* transition of aromatic C=C bands. Furthermore, a similar shoulder around 240 π - π^* and 300 nm is observed which could be attributed to π - π^* transitions of the carbonyl groups and oxygen groups on graphene oxide and Fe_3O_4 , respectively [16]. The reactive red 198 absorption bands are located at 234, 392, 518 nm and with the maximum wavelength on 518 nm. The adsorbed reactive red 198 onto Fe_3O_4 -GO represents on 392 and 518 nm which were decreased abruptly and shifted to 410 and 557 nm, respectively. The band of 234 nm is vanished and two shifted bands (392 and 518) are clearly demonstrated that these bands are the main sites of adsorption of reactive red 198 onto Fe_3O_4 -GO. The adsorption process is possibly the electrostatic-dispersion interaction between bulk systems on Fe_3O_4 -GO surface and reactive red 198 molecules contained both benzene rings and double bands (C=C, C=O and), or hydrophobic and π - π electron donor-accepter interaction between Fe_3O_4 -GO and reactive red 198. The cation- π bonding may happen

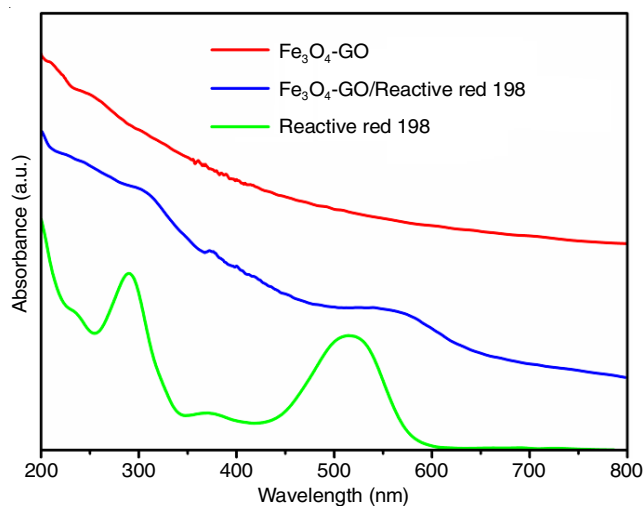


Fig. 3. UV-visible absorption spectra of Fe_3O_4 -GO, reactive red 198 and Fe_3O_4 -GO/reactive red 198

between the easily protonated azo groups which are adsorbed on the Fe_3O_4 -GO *via* π -electrons.

Effect of pH: In present research, different concentrations of reactive red 198 (6 mL to 200, 300 and 500 mg L^{-1}) were applied to examine the sorption manner of reactive red 198 on a constant concentration of Fe_3O_4 -GO (2 mL of 150 mg L^{-1}) at different pH values using UV-visible spectroscopy. The adsorption percentage (Ads. %) was considered based on the eqn. 1. Adsorption and removal percentage of dyes from aqueous solution in different amount of reactive red 198 concentrations were investigated and the initial concentration of dye was 200-500 mg L^{-1} for 180 min. It can be observed from Fig. 4 with the increase of concentrations, the percentage of adsorptions decrease. Minimum adsorption belonging to 500 mg L^{-1} with 56.4 %, 300 mg L^{-1} about 70.1 % and maximum of adsorption belonged to 200 mg L^{-1} with 78.6 %. The adsorption characteristic indicated a rapid uptake of the dye.

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

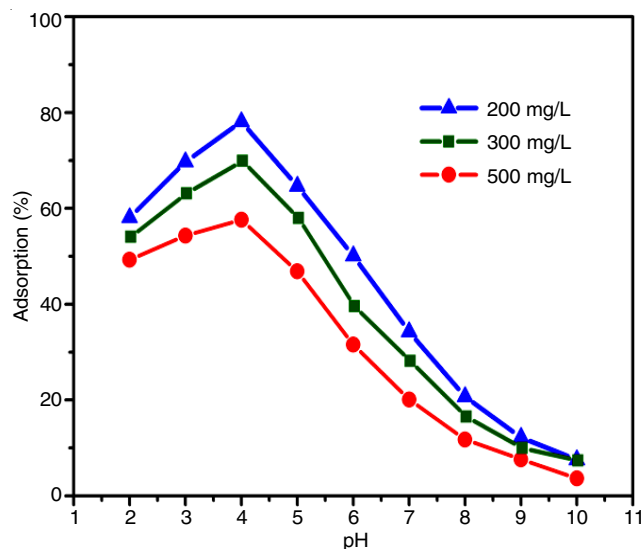
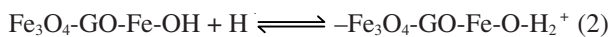


Fig. 4. Effect of pH on the adsorption efficiency of reactive red 198 (200-500 mg L^{-1}) on Fe_3O_4 -GO (150.0 mg L^{-1}); Temp. 25 ± 0.1 $^{\circ}\text{C}$

where, C_0 and C_t (mg L^{-1}) are the concentration of dye in the solution at initial and equilibrium time, respectively. According to Fig. 4, in solutions with pH 2.0 to 10 removal of reactive red 198 increases with increasing pH and a maximum value was found at pH 4. The observed trend can be explained by effect of surface charge of adsorbent depending on the solution pH, the adsorbent surface under Fe_3O_4 -GO protonation or deprotonating as shown by the eqn. 2:



At $\text{pH} < 7$, $\text{Fe}_3\text{O}_4\text{-GO-Fe-O-H}_2^+$ could be dominant species. These species have high positive charge density make the negative charged dye (reactive red 198) adsorption favourable due to electrostatic attraction. However, at $\text{pH} > 7$, $\text{Fe}_3\text{O}_4\text{-GO-Fe-OH}$ is the main species in $\text{Fe}_3\text{O}_4\text{-GO}$. Deprotonated species are under $\text{Fe}_3\text{O}_4\text{-GO}$ electrostatic repulsion for negative charged dye. This fact may causes a reduction on dye adsorption. Moreover, in this pH values, negative surface charge can be formed due to protonation of electron π - π rich regions on the surface of $\text{Fe}_3\text{O}_4\text{-GO}$. When pH increases, the carboxylic groups are ionized and the negative charge density on the surface increases, because of removal of dyes. The maximum sorption of reactive red 198 on $\text{Fe}_3\text{O}_4\text{-GO}$ was found at pH 4.0 according to Fig. 4, dye binding sites on the adsorbent were closely associated with H_3O^+ at lower pH, which cause an increase in the electrostatic attraction between positively charged sorbent surface and the negatively charged dye molecules. $\text{Fe}_3\text{O}_4\text{-GO}$ capacity of adsorption decreased when the pH of the solution increased from 4 to 10, also under alkaline conditions sorption capacity significantly decreased fewer than 20 %.

Adsorption isotherms: Different concentrations of reactive red 198 (6 mL to 20-300 mg L^{-1}) were used to examine the sorption condition of reactive red 198 on a constant concentration of $\text{Fe}_3\text{O}_4\text{-GO}$ (2 mL of 150 mg L^{-1}) at different pH values using UV-visible spectroscopy. Adsorption isotherms describe how solutes interact with sorbents. Adsorption isotherms and the equilibrium adsorption in different concentrations of reactive red 198 and $\text{Fe}_3\text{O}_4\text{-GO}$ as a function of equilibrium concentration of reactive red 198 are examined. The absorption data were fitted to Langmuir and somehow in Freundlich which are often pronounced by Equilibrium sorption isotherms model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (3)$$

where C_e is the equilibrium concentration of reactive red 198 (mg L^{-1}), q_m is the maximum monolayer adsorption (mg g^{-1}), q_e is the amount of reactive red 198 adsorbed per unit weight of $\text{Fe}_3\text{O}_4\text{-GO}$ at equilibrium concentration (mg g^{-1}) and b is

the Langmuir constant related to the affinity of binding targets (mg L^{-1}). The equilibrium concentration (C_e) of reactive red 198 was calculated for reactive red 198 calibration curve [17] in follow conditions: reactive red 198 (10-300 mg L^{-1}), $\text{Fe}_3\text{O}_4\text{-GO}$ (150 mg L^{-1}) and different temperatures of (298, 303, 308 and 313 K). On the other hand, the Langmuir-Freundlich isotherm constants were determined from the plots of C_e/q_e against C_e , $\ln q_e$ versus $\ln C_e$, respectively, at 298, 303, 308 and 313 K. The isothermal constants and the correlation coefficients are depicted in Table-1.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where, K_f and n are Freundlich constants indicating the sorption capacity (mg g^{-1}) and intensity, respectively. It is found that the adsorption of reactive red 198 on $\text{Fe}_3\text{O}_4\text{-GO}$ correlated well ($r > 0.99$) with the Langmuir equation as compared to the Freundlich equation ($r > 0.95$) in present concentration range. Therefore, the Langmuir isotherm fits appropriate compared with the Freundlich isotherm in all conditions according to the correlation coefficients r . The maximum adsorption capacity of reactive red 198 on $\text{Fe}_3\text{O}_4\text{-GO}$ was 357.14, 313.54, 161.29 and 136.98 mg g^{-1} at 298, 303, 308 and 313, respectively. The shape of the isotherm has been discussed in order to predict whether an adsorption system is desirable or undesirable. The vital property of the Langmuir isotherms can be expressed by means of ' R_L ', a dimensionless constant related to the separation factor or equilibrium parameter. R_L is calculated using the following equation [18]:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where, C_0 is the initial concentration (mg L^{-1}) of reactive red 198 and b is the Langmuir adsorption of equilibrium constant (L mg^{-1}). The calculated R_L values are recorded in Table-1. The equilibrium parameter R_L was existed to be between 0 and 1, hence the sorption process was favourable and the adsorbent employed to demonstrated $\text{Fe}_3\text{O}_4\text{-GO}$ potential for the sorption of reactive red 198. The differences of Polanyi potential with the concentration according to:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

where, R is the ideal gas constant and T is the temperature (K). A linear correlation is obtained by plotting $\ln q_e$ versus ϵ^2 (Table-1), indicating that reactive red 198 adsorption also obeys the D-R equation. The adsorption energy for reactive red 198 adsorption can be determined by the relation [19]:

$$E = (-2K)^{-1/2} \quad (7)$$

TABLE-1
LANGMUIR, FREUNDLICH AND DUBININ-RADUSHKEVICH (D-R) CONSTANTS AND CORRELATION COEFFICIENTS OF REACTIVE RED 198 ADSORPTION ONTO $\text{Fe}_3\text{O}_4\text{-GO}$ AT DIFFERENT TEMPERATURES

T (K)	Langmuir			Freundlich			(D-R)		
	q_m (mg/g)	R_L	r^2	K_f (mg/g)	n	r^2	q_m (mg/g)	E (kJ/mol)	r^2
298	357.14	0.3196	0.9969	1.4151	22.21	0.9975	1.05	7.35	0.9977
303	313.54	0.0683	0.9931	1.9183	25.06	0.9967	1.11	6.90	0.9988
308	161.29	0.0192	0.9911	1.4558	29.97	0.9915	1.02	8.05	0.9648
313	136.98	0.0153	0.9908	1.5238	35.75	0.9844	1.06	8.85	0.9700

The values of the adsorption energy in Table-1 were estimated as 7.35, 5.38, 8.85 and 8.079 kJ mol⁻¹ at 298, 303, 308 and 313 K, respectively, indicating that the values lie within the range of energy in physical adsorption, *i.e.*, < 8 kJ mol⁻¹ [20]. In other former study, Fe₃O₄-GO suspensions have a higher maximum adsorption capacity for reactive red 198 than other adsorbents. By comparing with the q_m value of various adsorbents for reactive red dye families as shown in Table-2, Fe₃O₄-GO is better than most adsorbents mentioned in Table-2. Considering the differences in the physical properties of adsorbents and experimental situations, it is arduous to obtain a reasonable evaluation through the data listed, even among our data still provide the useful information at least on the order of magnitude.

TABLE-2 MULTIWALLED CARBON NANOTUBES (MWNTS), POWDERED ACTIVATED CARBON (PAC), DEHYDRATED BEET PULP CARBON (DBPC), EGG SHELL COMPOSITE (ESC) POLYHEDRAL OLIGOMERIC SILSESQUOXANE (POSS) APPROXIMATE VALUE FROM THE LITERATURE FIGURE IN 25 °C			
Dye	Absorbents	q_m (mg g ⁻¹)	Ref.
RR195	<i>Pinus sylvestris</i> L.	8.425 (20 °C)	[37]
RR198	MWCNT	200	[38]
Remazol RR198	ESC	46.93 (22 °C)	[39]
RR120	Chitosan-Fe(III)	290.70	[40]
RR M-2BE	MWCNT	312.3	[41]
RR M-2BE	PAC	243.9	[42]
C.I. RR250	POSS	11.71	[43]
RR195	DBPC	45.24	[44]
RR198	<i>Potamogeton crispus</i>	17.51	[45]
RR198	Fe ₃ O ₄ -GO	357.14	Present work

RR = Reactive red

Adsorption kinetics: In order to explore the adsorption process of reactive red 198 onto Fe₃O₄-GO, pseudo-first-order and pseudo-second-order kinetics model were proposed (Fig. 5). Time has significant role which plays in kinetics investigations between adsorbate and adsorbant. The pseudo-first-order (a) and the pseudo-second-order (b) kinetics model for adsorption of reactive red 198 (40 mg L⁻¹) on Fe₃O₄-GO suspension (150 mg L⁻¹), pH = 4.6, T = 298, 303, 308 K.

Pseudo-first-order model: For finding out the adsorption behaviour of kinetic process, the kinetic parameters of the adsorption procedure were measured by means of pseudo-first-order and pseudo-second order kinetic paradigms. Lagergren is known as pseudo-first-order kinetic model. The pseudo-first-order equation is given as eqn. 8 [21].

$$\ln (q_1 - q_t) = \ln q_1 - k_1 t \quad (8)$$

where q_1 and q_t are the amount of dye molecules that adsorbed on the sorbent (mg g⁻¹) at equilibrium and at desired time t , respectively and k_1 is the rate constant of the first-order

adsorption (min⁻¹). The values of k_1 for reactive red 198 adsorption onto Fe₃O₄-GO were determined from the plot of $\ln (q_1 - q_t)$ against t (Fig. 4a). Furthermore, the values of k_1 and q_1 were depicted in Fig. 5a and are represented in Table-3. The value of the correlation coefficient (R_2) attained fairly well (0.985), suggesting the pseudo-first-order equation is relatively fit and suitable for the characterization of this adsorption process.

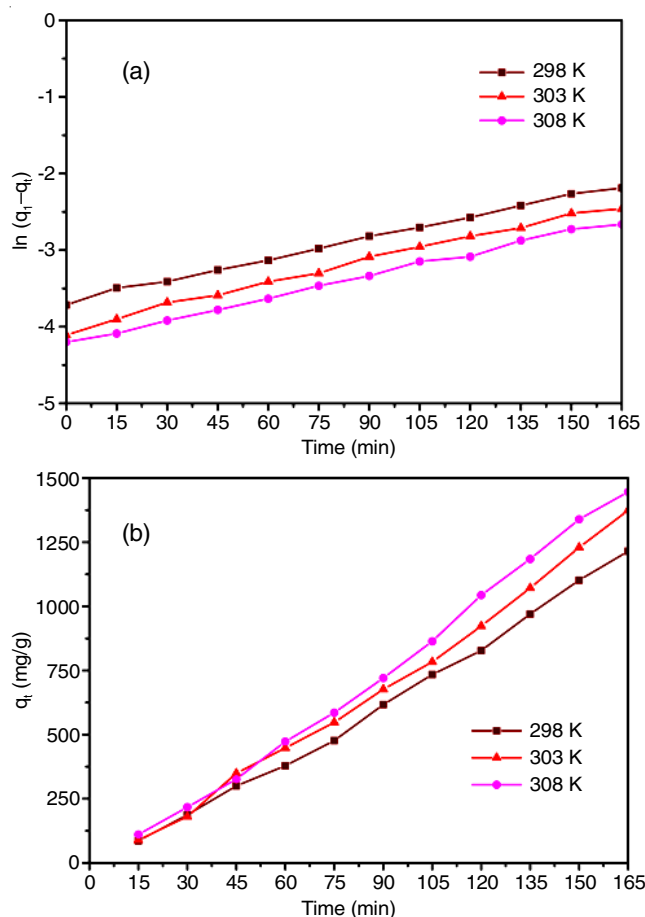


Fig. 5. Pseudo-first-order (a) and the pseudo-second-order (b) kinetics model for adsorption of reactive red 198 (40 mg L⁻¹) on Fe₃O₄-GO suspension 150.0 mg L⁻¹, pH = 4.3, T = 298, 303, 308 K

Pseudo-second-order hypothesis: The pseudo-second-order model is illustrated as eqn. 3 [22]. The straight-line plots of t/q_t versus t (Fig. 5b) have been verified to make rate parameters. The second-order rate constants were used to analyze the preliminary sorption rate h (mg g⁻¹ min⁻¹) [23], given by:

$$h = k_2 q_2^2 \quad (9)$$

The batch kinetic data based on our investigation were appropriately satisfying the condition of second-pseudo order models. In the present study, Ho's pseudo-second-order kinetics

TABLE-3 KINETIC PARAMETERS FOR REACTIVE RED 198 ADSORPTION ON FE ₃ O ₄ -GO AT A VARIETY OF TEMPERATURES							
T (K)	Pseudo-first-order model			Pseudo-second-order model			
	k_1 (min ⁻¹)	q_1 (mg g ⁻¹)	r_1	k_2 (mg g ⁻¹ min ⁻¹)	q_2 (mg g ⁻¹)	h (mg g ⁻¹ min ⁻¹)	r_2
298	0.57	1.01	0.985	0.028	466	6180	0.994
308	0.636	1.007	0.983	0.031	743	17142	0.991
318	0.756	1.003	0.951	0.033	801	18465	0.993

model was exploited to examine the fitness of the experimental data and to appraise the kinetics the adsorption of reactive red 198 on the Fe₃O₄-GO that was based on the assumption that the rate-limiting step includes chemisorption, which has been expansively applied to the sorption of contaminants from aqueous solutions in recent year [23]. So, only second-pseudo order models effectively described with the kinetic data at 95 % confidence level. The advantages of the kinetic parameters and assessed the primary sorption rate values are recorded in Table-3. In this part among three temperature 298, 303 and 308 the q_2 values were consecutively assessed q_2 (mg g⁻¹) 446, 743 and 801, k_2 (mg g⁻¹ min⁻¹) 0.028, 0.031, 0.028 and for h (mg g⁻¹ min⁻¹) 6180, 17142, 18456. Based on the correlation coefficients, the adsorption of reactive red 198 is finest described by the pseudo-second-order model. The initial adsorption rate increased with the augmentation of temperature in an expected adsorption system. Furthermore, it was feasible to calculate the activation energy (E_a) for the adsorption retaining the Arrhenius equation basically on k_2 values [24].

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

where A , E_a , R is the frequency factor (min⁻¹), the activation energy (kJ mol⁻¹), R the ideal gas constant (kJ mol⁻¹ K⁻¹) and T is the temperature (K) [24].

Eqn. 5 can be converted into eqn. 6 by taking logarithm:

$$\ln k = \ln A - E_a/RT \quad (11)$$

Therefore, E_a could be found from the slope of the line plotting $\ln k$ versus $1000/T$ and the estimated E_a for reactive red 198 adsorption on Fe₃O₄-GO was 4.469 kJ mol⁻¹. The chemisorption or physisorption mechanisms are often a significant indicator to describe the kind of interaction between dye and adsorbent. The physisorption processes typically have energies in the range of 4–40 kJ/mol, while higher activation energies (40–400 kJ/mol) suggest it for chemisorption. The lower the E_a was, the less sensitive the temperature influences the reaction of adsorption. It has been proved that the process could be easily conducted and it indicates that it was physisorption mechanism. The value of E_a was 4.469 kJ/mol. It indicates that this procedure run under physisorption mechanism [25].

Thermodynamic studies: The sorption behaviours in different concentrations of reactive red 198 onto Fe₃O₄-GO were critically discovered at 298, 303, 308 and 313 K, consecutively. Thermo-dynamic parameters were calculated from following equations:

$$\Delta G^\circ = -RT \ln K_c \quad (12)$$

where, R is the universal gas constant (8.314 kJ mol⁻¹ K⁻¹), T is the temperature (K) and K_c is the distribution coefficient. Gibbs free energy change of adsorption (ΔG°) was calculated by using $\ln K_c$ values for various temperatures. The K_c value was computed using following equation:

$$K_c = \frac{q_e}{C_e} \quad (13)$$

where, C_e is the equilibrium concentration of reactive red 198 and q_e is the amount of reactive red 198 adsorbed per unit weight of Fe₃O₄-GO at equilibrium concentration (mg g⁻¹).

The enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption were assessed from the following equation [26]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

According to eqn. 14, ΔH° and ΔS° factors can be calculated from the slope and intercept of plot of ΔG° against T , respectively. The thermodynamic parameters were presented in Table-4. Normally, the adsorption process is assigned to physisorption in nature since the ΔG° value is in the range of 0–20 to kJ mol⁻¹. Changing in free energy for adsorption of reactive red 198 onto Fe₃O₄-GO nanoparticles, which followed by decreases from 11.169 kJ/mol, -8.850, -4.878, -3.523 at 298.0 K, 303.0 K, 308.0 K, 313 K, respectively; with an initial concentration of 40 mg L⁻¹. Moreover, the enthalpy value for a sorption process can also be used to better understanding between chemical and physical sorption. For chemical sorption, values of enthalpy change in range of 83 to 830 kJ/mol, while for physical sorption range from 8 to 25 kJ/mol.

TABLE-4
THERMODYNAMIC PARAMETERS FOR THE
ADSORPTION OF REACTIVE RED 198 ON Fe₃O₄-GO

ΔG° (kJ/mol)				ΔH°	ΔS°
298 K	303 K	308 K	313 K	(kJ/mol)	(kJ/mol)
-11.169	-8.850	-4.878	-3.523	-90.03	-0.285

The value of ΔH° gives is clue that the interaction between reactive red 198 and Fe₃O₄-GO became decreases in adsorption *via* increasing adsorption temperature. Hence, this process can be considered as a physisorption process. The value of ΔG° is negative and the absolute value plummet with an increase in temperature, indicating that the adsorption of dye on the Fe₃O₄-GO is spontaneous. The negative value of change in enthalpy (ΔH°) demonstrates that the adsorption is exothermic in nature, which is in agreement with the consequences made from the adsorption equilibrium isotherms. Negative value of change in entropy (ΔS°) reflects the plunged randomness at the solid/solution interface during the adsorption process. According to the experimental results and previous report, the physisorption process can be expressed as follows: (1) opening up pores of Fe₃O₄-GO structure, (2) enhancing the mobility and range of penetration within the Fe₃O₄-GO and (3) overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion [27].

Decolorization: The photocatalytic activities of Fe₃O₄-GO composites were observed under UV and visible revion. The removal yields of reactive red 198 at various conditions are presented in Fig. 6. Approximately 100 % of reactive red 198 was degraded after 60 min in the presence of photocatalysts due to UV-induced with assist of hydrogen peroxide to photolysis of dye and a negligible decrease in dye concentration was obtained afterwards. Nearly 100 % of the dye was decolorized under UV exposure in different samples which were arranged to examine modificaion condition for decolorization. The reactive red 198 was examined by different conditions: reactive red 198/UV, Fe₃O₄-GO/UV, H₂O₂/UV, Fe₃O₄-GO/H₂O₂-UV and Fe₃O₄-GO/H₂O₂-visible light, Fe₃O₄-GO/visible light and H₂O₂-visible light. The Fe₃O₄-GO as a strong photocatalyst could create hole-electron and produce the free radical of hydroxyl

on its surface and assist to augment and intensify the effect of decolorization in aqueous solutions.

The degradation of reactive red 198 onto Fe₃O₄-GO nano-composite was represented in Fig. 6 which shows after UV-irradiation for 10 min, Fe₃O₄-GO/H₂O₂-UV and H₂O₂/UV have degraded the most reactive red 198 concentration approximately to near 100 % after 60 min. On the other hand, photodegradation of dyes in the presence of bare nanoparticles have already been reported [28]. The UV and H₂O₂/visible light conditions did not have any success performance to degradation of the reactive red 198 in this period of time. The samples of Fe₃O₄-GO/UV, Fe₃O₄-GO/H₂O₂-visible light and Fe₃O₄-GO visible light have some changes to effect on reactive red 198 and decolorize it partially after 10 min, but only Fe₃O₄-GO/UV in comparison with two other conditions in this part show some significant changes in its behaviour and after 10 min the Fe₃O₄-GO/UV has gradually decreases until 100 min. It shows that Fe₃O₄-GO could photolysis of aqueous solution and produce slightly OH[•]. When a catalyst is also added, H₂O₂ and UV irradiation are simultaneously photolysis of water or any aqueous solutions and produce hole-electron pairs on catalysts surface (eqn. 2). The hole-electron pairs can produce OH[•] radicals and superoxide anions [•]O₂⁻, which can decompose dyes to CO₂, H₂O and other residuals species (eqns. 1-7) [26,29].

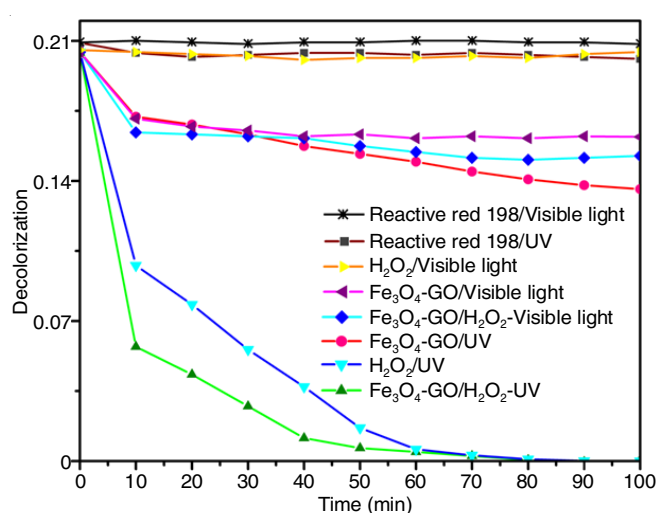
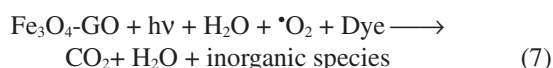
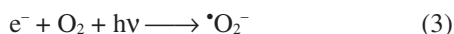
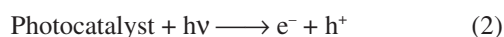
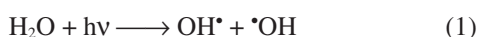


Fig. 6. Decolorization of reactive red 198 under various conditions during 100 min

The degradation of dyes in the presence of various condition during 100 min is shown in Fig. 6. It illustrates the corresponding temporal evolution of the UV-visible absorption

spectra of Fe₃O₄-GO as a strong catalyst. The degradation time of this dye in the presence of this composite was displayed appropriate catalytic activity rather than others. Because the dye is easily decolorized completely by Fe₃O₄-GO in only 1 h. For Fe₃O₄-GO as a powerful absorbent was also fabricated and used to test the catalytic activity and represent that could remove and degrade reactive red 198 in different conditions which is shown in Fig. 6 under UV irradiation with UV-visible spectroscopy.

The catalytic activity of the Fe₃O₄-GO composite is mainly enhanced the high efficiency of charge separation through the synergistic effect between graphene oxide and Fe₃O₄ [27]. The improved ability of the Fe₃O₄-GO composite to adsorb reactive red 198 compared with that of Fe₃O₄ can be described to formation of π - π stacking between reactive red 198 molecules and aromatic ring of graphene *via* van der Waals interaction. Graphene oxide acts as an electron acceptor to accelerate interfacial electron transfer from Fe₃O₄, significantly hindering the recombination of charge carriers and thus improving photocatalytic activity. The catalytic activity of this composite is determined by the amount of graphene oxide to transfer photo-induced electrons and the contact area between Fe₃O₄ and reactive red 198 [30].

As shown in Fig. 7, whole samples were alike, both the reactive red 198/UV and H₂O₂/visible light are in top with maximum absorbance approximately juxtapose to each other. The Fe₃O₄-GO/UV, Fe₃O₄-GO/H₂O₂-visible light and Fe₃O₄-GO samples showed some decreases in their absorbance paradigms and approximately near to each other, but Fe₃O₄-GO/UV could be success to more degradation of reactive red 198. The last samples Fe₃O₄-GO/H₂O₂-UV and H₂O₂/UV are existed at the lowest level of the diagram which are demonstrated that

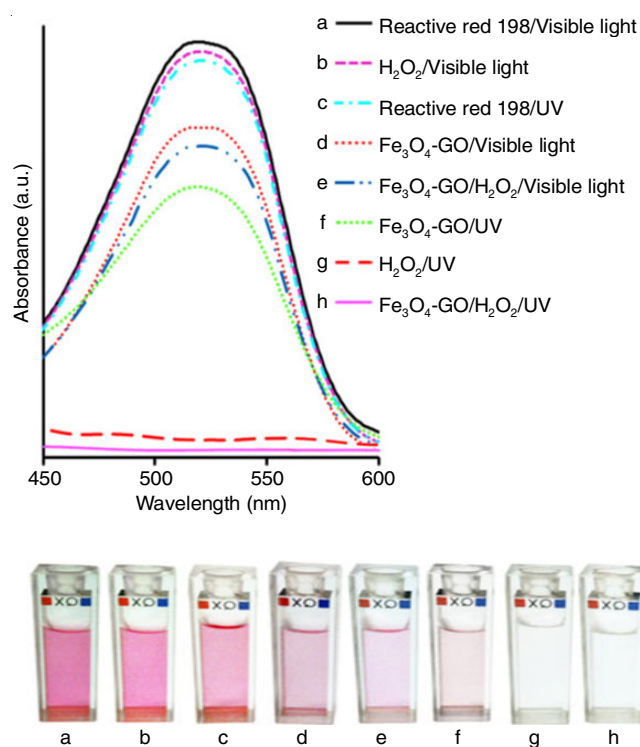


Fig. 7. UV-visible spectroscopy and degradation of reactive red 198 in different conditions

these two conditions have the most appropriate to vanish the colour of the dye and between $\text{Fe}_3\text{O}_4\text{-GO}/\text{H}_2\text{O}_2\text{-UV}$ and $\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe}_3\text{O}_4\text{-GO}/\text{H}_2\text{O}_2\text{-UV}$ has a great effect on degradation of reactive red 198. The key point of decolorization is reproducing $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ from H_2O_2 and aqueous solution as mentioned above could play a significant role among the samples which use absorbent under UV irradiation but the $\cdot\text{OH}$ could be created only on the powerful photocatalyst to produced more $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ to degraded a plethora of dyes in a short period time.

Conclusion

On account of the present adsorption results, $\text{Fe}_3\text{O}_4\text{-GO}$ has a high capacity for adsorption of reactive red 198. The adsorption mechanism is possibly non-electrostatic dispersion and hydrophobic interaction between reactive red 198 and $\text{Fe}_3\text{O}_4\text{-GO}$. The unsaturated bond and metal effect on the surface of $\text{Fe}_3\text{O}_4\text{-GO}$ facilitate omnipotent $\pi\text{-}\pi$ interaction between them. Cation- π bonding was likely happen between the azo group and benzoic rings on the reactive red 198 and $\text{Fe}_3\text{O}_4\text{-GO}$ π -electron-rich structures. $\text{Fe}_3\text{O}_4\text{-GO}$ can effectively absorb reactive red 198 in aqueous solution in extensive range of pH from 2 to 10. The percentage of degradation of reactive red 198 by $\text{Fe}_3\text{O}_4\text{-GO}$ can be reached to 99.8 %. According to kinetic studies the equilibrium is achieved in only 15 min and the pseudo-second-order model is followed. The adsorption isotherms could be well fitted by the Langmuir adsorption isotherm equation with the maximum adsorption capacity of 357.14 mg g^{-1} (298 K). On thermodynamic parameters suggest that the adsorption is a spontaneous, exothermic and physisorption process.

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