

Adsorption of Anionic Dye from Aqueous Solution Using Activated Montmorillonite/Graphene Oxide/Gelatin Composites

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ABSTRACT: *The present work describes the adsorption of the anionic dye Congo Red (CR) by materials based on Activated Montmorillonite (AM), graphene oxide (GO), and gelatin (G). The materials were prepared and characterized by X-Ray Diffraction (XRD), infrared spectroscopy (FT-IR), and thermal analysis (ATG/DTG) in the previous study. Adsorption experiments of CR dye on GO/AM at different ratios of GO were performed to evaluate the adsorption efficiencies. The maximum adsorption capacity of anionic dye (CR) onto (GO / AM10%) composite was insufficient. To improve the adsorption capacity, a cationic-charged component such as gelatin was added to obtain a new composite (GO/AM/G). Therefore, the effects of several factors on the adsorption capacity of (GO/AM/G) composite, such as the pH of dye solution, adsorbent dosage, contact time, initial dye concentrations, temperature, and regeneration, were investigated. In addition, the kinetics of dye adsorption followed the pseudo-second-order model, and the adsorption isotherm was very well described by the Freundlich model. Afterward, the study of the temperature's effect on the adsorption rate indicated that the reaction was exothermic with the medium disorder. The values of the free energy showed that the nature of the adsorption was physisorption. The reusability of the composites using 0.1N HCl for over six cycles indicated the economic significance of these materials as adsorbents. The fast removal rate in a wider range of pH and the easy reusability and regeneration make the composite (GO/AM/G) a prospective material for dye adsorption from aquatic environments.*

KEYWORDS: *Activated montmorillonite; Biopolymer; Adsorption capacity; Anionic dyes.*

INTRODUCTION

Industrial wastewater treatment is a process that separates and removes contaminants containing oils, dissolved heavy metals, dyes, suspended solids, and organic compounds. Physico-chemical and biological treatment processes using conventional chemicals such as metal formulations based on aluminium or iron and synthetic polymers are certainly effective and economically viable but they cause serious environmental and health

issues [1]. Recently, it has been shown that the water protection of the organic coatings can be highly improved through nanoparticles that are renewable, environmentally friendly, and biodegradable [2]. Clay minerals have been adapted to the field of nanocomposites due to their small particle size, high chemical stability, high ion exchange capacity, and intercalation properties, especially in the application of reinforcement materials with polymers.

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Montmorillonite is clay that has a crystalline structure composed of an octahedral layer of aluminum hydroxide between two tetrahedral layers of silica. These clays interact with organic compounds such as graphene oxide to form complexes with various properties [3]. Multiple modifications of clays have been synthesized through physical grinding, heat, acid treatments, ion exchange, pillaring reactions [4], polymer reactions, and micro/nanocomposites formation [3].

Graphene Oxide (GO) adds an organic modification on the montmorillonite due to its hydrophilic and hydrophobic functional groups. It has shown many interesting properties citing a strong affinity, high mechanical strength, biodegradability, large specific surface area, high thermal conductivity and high cation-exchange amount [5]. Note that there is a weak chemical interaction between the graphene oxide and the montmorillonite mineral due to their electronegativities, so it is imperative to add another component to strengthen the bond between them. Moreover, other modifications can improve their adsorption capacities by the use of cationic polymers or surfactants which generate some interactions between the cationic species and the adsorbents [6].

Due to their low-cost, their particular polymeric structure, biopolymers such as gelatin represent an interesting and attractive alternative as adsorbents in the elimination of contaminants [7]. Gelatin (G) is a natural fibrous protein polymer, non-toxic, anti-carcinogenic, biocompatible and biodegradable. It has excellent physical and chemical properties such as biodegradability, hydrophilicity, biocompatibility and reactivity of side-chain radical which gives it an excellent potential in a wide field of application. It is obtained by partial hydrolysis of the triple helix structure of collagen which can be easily obtained by extraction from animal tissue [8].

In a previous work [9], we studied the preparation and the characterisation of (GO/AM/G) composites. In the present study, our main objective is to investigate the possibility to combine activated montmorillonite, graphene oxide, hexadecyltrimethylammonium bromide (HDTMA) as intercalation agent and gelatin to obtain GO/AM/G material. HDTMA was introduced into AM and GO suspensions as a crosslinker and to increase the layer spacing of the prepared nanocomposite [9].

GO/AM/G composite was used as an adsorbent for the removal of an anionic dye, namely Congo Red (CR),

from aqueous solutions. The optimization of the adsorption conditions was performed by investigating the influence of different parameters. Adsorption kinetics, equilibrium isotherms, and thermodynamic studies were also conducted.

EXPERIMENTAL SECTION

Materials

Raw montmorillonite (RC) was supplied by a local company known as ENOF. Graphite powder, Hexadecyltrimethylammonium bromide (HDTMA-Br), gelatin, sodium nitrate, sulphuric acid, potassium permanganate and hydrogen peroxide were purchased from Sigma-Aldrich (99 % purity) and used without other purifications.

All solutions were prepared using bidistilled water.

The activation of the montmorillonite (AM)

Activation of raw montmorillonite (RM) was carried out according to the method described in our earlier work.

Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesized from graphite powder by a modified Hummers method [9, 10].

Synthesis of GO/AM/G composite

To obtain graphene oxide/activated montmorillonite (GO/AM) composite with different ratios (GO/AM) (w/w) of 5%, 10% and 20%, 500 mg of AM powder was mixed with a solution containing 25 mg, 50 mg and 100 mg of GO. 0.17g of hexadecyltrimethylammonium bromide (HDTMA-Br) was separately dissolved in 20 mL of distilled water, and then added drop-wise to the suspension of GO/AM 10% (the other ratios of GO/AM were not used because of their low efficiency in dye adsorption). The suspension was refluxed at 80 °C for 4 h to obtain (GO/AM/HDTMA) composite.

Afterwards different amounts of gelatin have been added to the previous solution by continuously stirring for 120 min to obtain composites labelled GO/AM/G1, GO/AM/G2, GO/AM/G3 according to the amounts of gelatin (125 mg, 60 mg and 30 mg) respectively. The suspension was then centrifuged at 4000 rpm for 30 min. The supernatant was discarded, and the product was washed using bidistilled water for three times. Finally, the prepared composites were dried for 24 h at 80 °C.

Characterization

The XRD patterns of the samples were obtained with X-ray diffractometer ULTIMA IV (Rigaku, Tokyo, Japan), operating with Copper K α radiation ($\lambda=1.54 \text{ \AA}$) at 40 kV and 30 mA. All experiments were carried out at ambient temperature with 2θ varying between 2 and 40°, a scan speed of 2°/min and a step size of 0.02°.

Thermogravimetric analyses of the samples were obtained using High-resolution TGA (TA Instruments Q Series Q600 SDT). 10 mg of finely ground sample was heated in an open platinum crucible with a heating rate of 10 °C/min and temperature from 50 to 800 °C under a nitrogen atmosphere flow rate of 100 mL/min.

Infrared (IR) spectra of the samples were obtained using an Agilent Cary 600 Series FT-IR Spectrometer equipped with DRIFT (Diffuse Reflectance Infra-red Fourier Transform) accessories. Spectra over the 4,000 - 400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s .

Adsorption studies of anionic dye by different composite

A series of activated montmorillonite/graphene oxide (GO/AM) composites labelled GO/AM5% GO/AM10% and GO/AM20%, GO/AM/HDTMA and GO/AM/G were tested for their efficiencies in adsorption of anionic dye Congo Red (CR) at different pH range in batch experiment. The pH of solutions was varied from 2 to 10 by the addition of NaOH (0.1M) or HCl (0.1M). 20 mg of the adsorbents were added in a volume of 40 mL and concentration 50 mg/L of CR solution.

The effects of adsorbent dosage, ranging from 10 to 100 mg with varying contact time from 5 min to 4 hours on the adsorption capacity of congo red were studied for GO/AM/G composite. Adsorption isotherm was released at different dye concentrations between 10 and 300 mg/L with a volume of 40 mL at pH = 6 by using 40 mg of adsorbents. At the same operative conditions (volume 40 mL, concentration 50 mg/L and pH = 6 and 40 mg of adsorbent dose), the effect of temperature was studied by monitoring the adsorption kinetics for 10 to 180 min at four different temperatures 293 K, 308 K, 318 K and 328 K.

The reusability of the adsorbent was studied by six cycles of continuous adsorption-desorption. 200 mg of adsorbent was mixed with 100 mL of CR dye solution of concentration of 50 mg/L for 1 hour. The loaded adsorbent

was desorbed in HCl solution (100 mL, 0.5 N) for 60 min. The sample was then placed in NaOH solution (100 mL, 0.5 N) and shaken at 25 °C for 60 min to neutralize the residual hydrochloric acid. Finally, the adsorbent is sufficiently washed with distilled water for a new adsorption-desorption cycle. The adsorbent was finally dried in oven at 80 °C for 24 hours.

The conical flasks were agitated at 400 rpm and made to react under a certain time interval. To separate solid and liquid phases, the suspension solution was centrifuged at 4000 rpm for 20 min, then the supernatant was analysed by UV-Vis spectrophotometry (OPTIZEN 1412 UV/VIS). Congo red (CR) was determined by measuring its absorbance at their maximum wave lengths ($\lambda_{\text{max}}=557 \text{ nm}$ in pH acidic range (pH < 5.5) and at $\lambda_{\text{max}}=505 \text{ nm}$ in pH basic range (pH > 5.5)). Structures of CR dye is represented in Fig.1.

The adsorption capacity was calculated according to the following Equation (1):

Where q_e is the equilibrium adsorption capacity of adsorbent (mg/g), C_0 and C_e are the initial and equilibrium concentration of the CR solution, respectively (mg/L). m is the weight of the adsorbent (mg), and V is the volume of the CR solution (mL).

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

RESULTS AND DISCUSSION

Characterization

In a previous work [11], we have studied the synthesis and the characterisation of used composites, the essential characterization remarks that must be remembered are the following:

X-Ray Diffraction (DRX)

X-Ray diffraction patterns of the activated montmorillonite (AM) showed the shift of the first characteristic peak from 13.68 Å to 10.9 Å suggesting a parallel arrangement of the mineral montmorillonite layers. No predominant GO peak was observed in GO/AM spectrum, indicating the homogenous distribution of GO on AM structure. The disappearance of montmorillonite peak at $2\theta = 8.1^\circ$ indicates that the reactants on the GO/AM surfaces have been able to separate away. This phenomenon might indicate the possibility of the formation of an exfoliated structure.

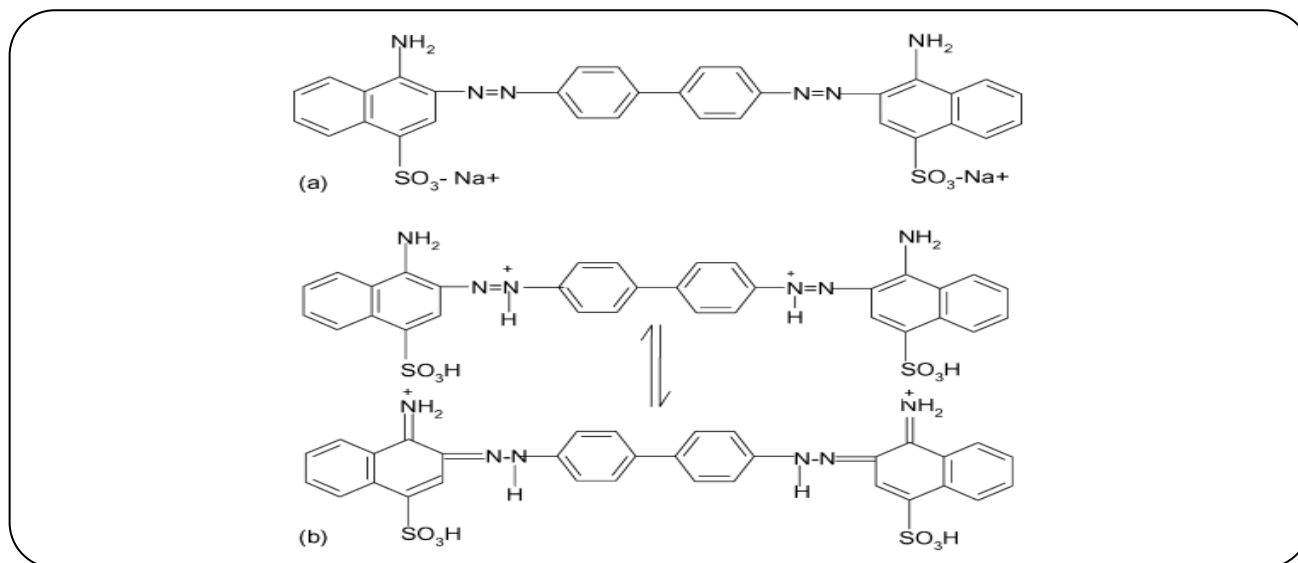


Fig. 1: Structure of CR at: (a) pH > 5.5 and (b) pH < 5.5 [10].

X-Ray diffraction patterns of modified montmorillonite GO/AM/HDTMA exhibited an interlayer spacing of 19.4 Å. This increase in the basal spacing for the modified montmorillonite demonstrates that at least a fraction of the cationic surfactant has replaced the hydrated interlayer cations and a nanocomposite was prepared.

Indeed, XRD patterns of composites (GO/AM/G) changed distinctly compared to AM. The interlayer spacing increased from 19.4 to 23.5 Å due to the insertion of gelatin molecules into the sheets of GO/AM/HDTMA

Thermal analysis

The TG and DTG results obtained, indicate that the activated montmorillonite (AM) exhibited a mass loss of 1.36 % at 54 °C, corresponding to the loss of the interlayer water. A second mass loss of 2.14% between 170 °C and 450 °C was related to the dehydroxylation of montmorillonite structure. The mass loss between 450 °C and 650 °C was attributed to the dehydroxylation of the aluminosilicate groups in montmorillonite structure. The TG and DTG curves of GO/AM exhibited more weight loss than AM of 6% at around 200°C to 400°C might be due to the decomposition of GO in the impregnated catalyst. Hence, it showed that GO/AM has good thermal stability.

The TG and DTG curves of GO/AM/ HDTMA exhibited an important weight loss occurred between 340 and 450°C was certainly due to the decomposition of cationic surfactants intercalated within the AM layers.

The last weight loss occurred between 480 and 600°C it related to the dehydroxylation of the aluminosilicates. These findings indicate that the surfactant molecules adsorbed onto the external surface of the AM sample and intercalated in the interlayer spaces helped to improve the thermal stability of the corresponding composites.

The TG and DTG curves of (GO/AM/G) composite showed a new weight loss at 323 °C related to the gelatin molecules. Comparing with TG and DTG curves of GO/AM/HDTMA sample, the thermograms showed the same weight losses for GO, AM, and HDTMA molecules.

Infrared analysis

AM was characterized by the two broad bands at 3630 and 3440 cm⁻¹, which were attributed to the -OH stretch of the lattice hydroxyl and the -OH stretch from free H₂O, respectively. In addition, the Si-O stretching vibration band appeared at 1032 cm⁻¹.

For GO/AM composite, all the peaks of GO and AM were appeared, and the bands of peaks belonging to GO became weak. These results illustrated that GO had been composited with AM.

The FT-IR spectrum of GO/AM/HDTMA showed, a new intense bands appeared at 2928 cm⁻¹ and 2852 cm⁻¹ which characterized the presence of a symmetric (ν_s(CH₂)) and asymmetric (ν_{as}(CH₂)) vibration of methylene groups on the carbon chain of surfactant. The IR spectrum of GO/AM/G gathered all the previous peaks, the intensity of

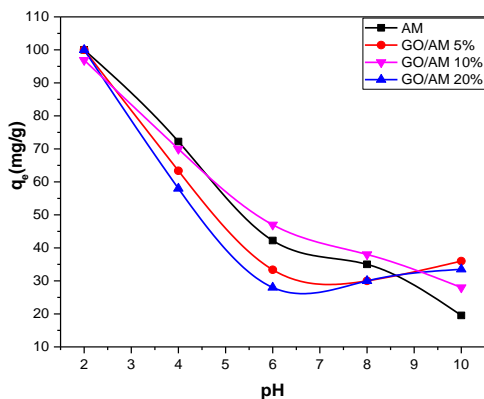


Fig. 2: Adsorption capacities of CR by different adsorbents.

the band attributed the N-H stretching vibration (3419 cm^{-1}) of gelatin, was ameliorated through combination with absorption bonds of O-H, indicating the interaction between GO/AM/HDTMA and gelatin.

Adsorption studies

pH effect

The pH value effect on the adsorption capacities of CR by different adsorbents (AM, and GO/AM for different percentage of graphene oxide (5%, 10% and 20%) are presented in Fig.2

The pH study presented in Fig. 2 showed that the adsorption capacity of anionic dye (CR) on AM and GO/AM at different ratio decreased when the pH increased from 2 to 10. This result is certainly due to electrostatic repulsion between surface negative charges of the adsorbent and anionic dye molecules [12].

The effect of pH on the adsorption capacity is shown in Fig. 3

The maximum adsorption capacities of CR on different adsorbents were compared. Results indicated that the adsorption performance of the GO/AM/G composite toward CR was higher than the other adsorbents. The addition of surfactant HDTMA to the GO/AM10% composite improved clearly the adsorption capacity of CR for pH values between 2 and 10. This result is certainly due to the contribution of positive charges of HDTMA surfactant on the composite GO/AM/HDTMA structure. In this case the adsorption was favorable by hydrophobic interactions and strong electrostatic interactions between $-N^+(\text{CH}_3)_3$ groups and anionic dye molecules [6].

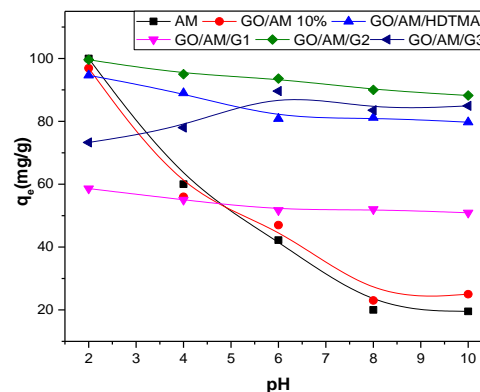


Fig. 3: The adsorptive capacities of CR by AM, GO/AM10%, GO/AM/HDTMA, GO/AM/G1, GO/AM/G2, GO/AM/G3.

To improve more the adsorption capacities, we added gelatin as a biopolymer. The results showed that the composite GO/AM/G which contains 10% (w/w%) of gelatin was the most performed adsorbent of anionic dye molecules comparing with the other adsorbents. When the mass fraction of gelatin was higher than 10%, the adsorption capacity decreased. This result is certainly explained by the saturation of montmorillonite surface by gelatin molecules.

The presence of positive charge of gelatin increased the adsorption efficiency in all pH range (Fig. 3). In acidic medium, the high concentration of H^+ ions promoted the protonation of functional groups such as amide and hydroxyl. Consequently, GO/AM/G was charged positively which increased the electrostatic attractions with negative charges of dye anions (CR). While, at higher pH, negative charges of activated montmorillonite deprotonated amino groups and ionized carboxylic groups of gelatin led to a decrease in adsorption capacities[13].

Adsorbent dose effect

The influence of adsorbent dosage on the removal efficiency (q_e) of CR by GO/AM/G was studied, and the results are plotted in Fig.4.

The adsorption percentage increased with adsorbent dose.

Adsorption capacity decreased with increasing adsorbent dose. Its suggest overlapping between the active sites which have decreased during adsorption process [14].

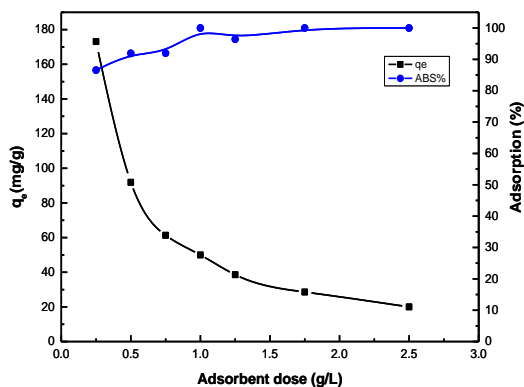


Fig. 4: Effect of the adsorbent dose on the adsorbed amount of CR dye by GO/AM/G.

Effect of contact time

Equilibrium time is the most important factor used to obtain a practical view of CR migration into adsorbent. Effect of contact time of CR adsorption on GO/AM/G was showed in Fig. 5.

To describe the adsorption kinetics, several models were developed. In this study, pseudo first, pseudo second order, and the intraparticle diffusion models were used [15].

The pseudo-first and pseudo second order are represented by Equations (2) and (3) respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

The intraparticle diffusion model was also tested. The initial rate of the intraparticle diffusion is the Equation is (4).

$$q_t = \left(k_{id} * t^{\frac{1}{2}} \right) + C \quad (4)$$

k_1 (min^{-1}), k_2 ($\text{g/mg} \cdot \text{min}$) and k_{id} ($\text{mg/g} \cdot \text{min}^{1/2}$) are the adsorption rate constants of the pseudo first, pseudo second order and the intraparticle diffusion models respectively and were determined graphically by plotting $\ln(q_e - q_t) = f(t)$, $t/q_t = f(t)$ and $q_t = f(t^{1/2})$ respectively.

The adsorption kinetic plots were shown in Fig.6 (a,b and c). The results of three models were summarized in Table1. It can be concluded from Table 1, that pseudo-second-order equation provides the best correlation coefficient and agreement between calculated q_e values and the experimental data, whereas the pseudo-first-order, the intraparticle diffusion equations do not give a good fit to

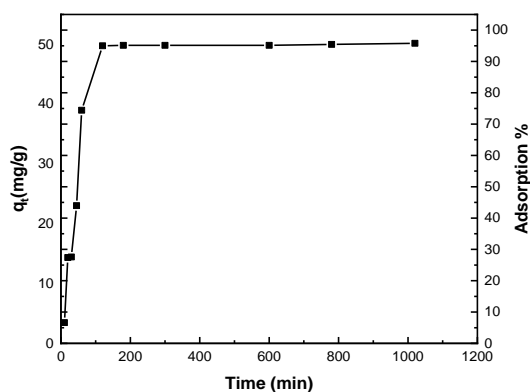


Fig.5. Effect of contact time on the adsorption of CR onto GO/AM/G composite.

the experimental data for the adsorption of CR. This suggests the chemical adsorption is the rate limiting step. The reaction mechanism may be partly a result of two steps. The first one was a rapid fixation of CR molecules at the most reactive sites, while the second one was a slow fixation on weak energy sites.

The intraparticle diffusion model was considered as an efficiency method to the further elaboration of determining the diffusion mechanisms and identify the possible rate controlling procedure[16].

The first slope of GO/AM/G (Fig. 10.c) represented the shortest step in which the adsorption was instantaneously done on the external surface of the adsorbent. While, the second one represented the intraparticle diffusion which limited the adsorption mechanism. The diffusion rate constant (k_{d1}) in the first step was higher than the second one (k_{d2}). This phenomenon can be explained by the adsorption of CR dye on the outer surface which was very high. Once the outer surface was completely saturated, CR molecules were adsorbed on the inner surface of the adsorbent. When the dye molecules diffused through the inner pores or along the pore surface wall into the particles, the diffusion resistance increased. Consequently, the diffusion rate decreased[17].

Effect of initial dye concentration

Generally, the adsorption capacity depends on the initial concentration of the dye. To reveal the effect of the concentration of CR on adsorption, experiments were carried out at different dye solutions concentrations from 10 to 250 mg/L (Fig. 7).

Table 1: The kinetics parameters for the adsorption of CR on GO/AM/G.

Adsorbent	q_e (mg/g)	Pseudo- first-order equation			Pseudo- second- order equation			Intraparticle- diffusion equation			
		$k_1 \cdot 10^2$ (min^{-1})	q_e (cal) (mg/g)	R^2	$k_2 \cdot 10^4$ (g/mg.min)	q_e (cal) (mg/g)	R^2	k_{d1} ($\text{mg/g} \cdot \text{min}^{1/2}$)	K_{d2} ($\text{mg/g} \cdot \text{min}^{1/2}$)	C (mg/g)	R^2
GO/AM/G	50.17	3.35	76.24	0.923	4.90	52.35	0.995	0.657		2.843	0.940
									$3.86 \cdot 10^{-4}$	49.71	0.988

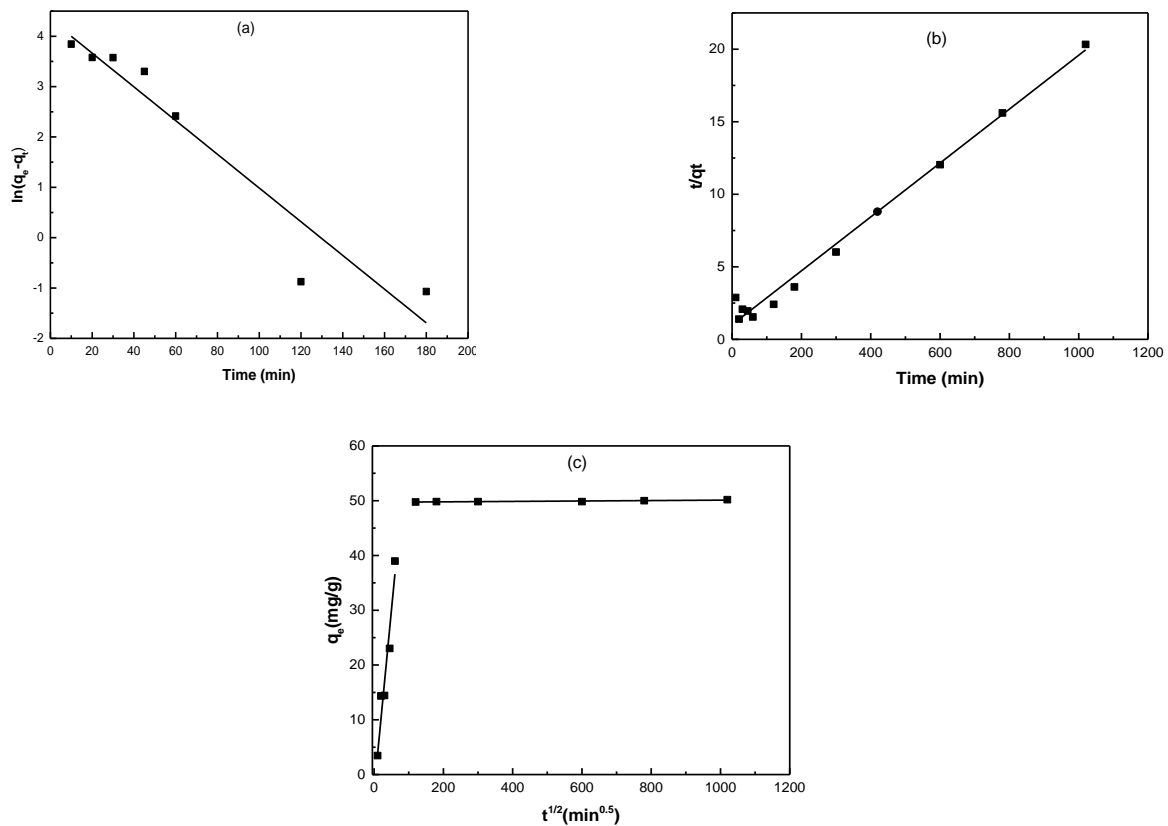


Fig. 6: Kinetics models for the adsorption of CR on GO/AM/G composite pseudo-first order (a) pseudo-second order (b) intra-particles diffusion (c).

Fig.7 showed the adsorption isotherm of CR using GO/AM/G composite. The equilibrium adsorption capacity (q_e) increased along with the dye concentration. A multilayer or mesopore adsorption has taken place followed by capillary condensation, resulting in isotherms of type IV[18].

In this study the BET- Langmuir–Freundlich isotherm equations[19] [20] were used for modeling the experimental data (Fig.8).

The Langmuir isotherm was calculated according to the following equation:

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

q_m is the maximum adsorption capacity and k_L equilibrium constant

In case of liquid adsorption (dye), the BET isotherm was expressed in the following equation

$$\frac{C_e}{(C_i - C_e) \cdot q_e} = \frac{1}{B \times q_m} + \left(\frac{B - 1}{B \times q_m}\right) \times \frac{C_e}{C_i} \quad (6)$$

B is the BET constant expressive of the energy of interaction. The slope of this line is $\frac{1}{B \times q_m}$ and the intercept

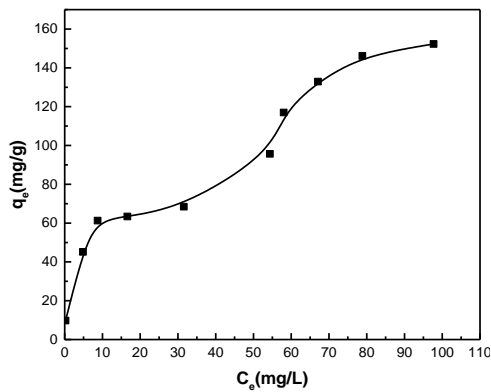


Fig.7: Effect of initial dye concentration on the adsorption of CR on GO/AM/G composite.

on the Y-axis is $\frac{B-1}{B \cdot q_m}$. The Combination of slope and intercept gives $q_m = 1/(\text{slope} + \text{intercept})$. Hence, after knowing the intercept and slope values, the values of q_m and B are determined [18].

The Freundlich isotherm was calculated according the following equation:

$$q_e = k_F * C_e^n \quad (7)$$

k_F is Freundlich constant and n is Freundlich's energy parameter

The Langmuir–Freundlich isotherm plots were shown in Fig.8 (a, b) and the obtained results of these models are summarized in Table 2.

Table 2 results showed that the Freundlich model fits experimental data more suitable ($R^2 = 0.970$) than the Langmuir and BET models, thus indicating that the adsorption of CR on GO/AM/G is a multilayer process [21].

Effect of temperature

The thermodynamic model of CR adsorption on GO/AM/G was evaluated by the thermodynamic parameters including the changes in free energy (ΔG), entropy (ΔS), and enthalpy (ΔH)[22]. All of the thermodynamic parameters were calculated using to the following Equations:

$$\ln(k_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G = -RT \ln(k_d) \quad (9)$$

Where R (8.314 (J/mol.K)) is the ideal gas constant,

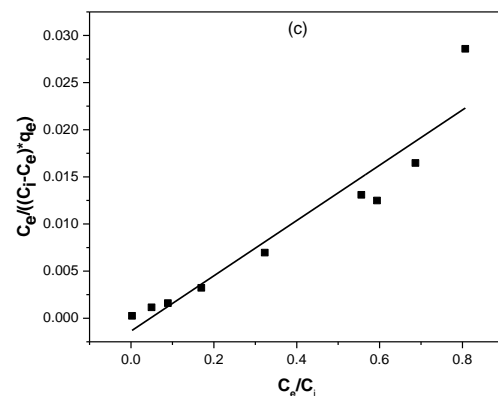
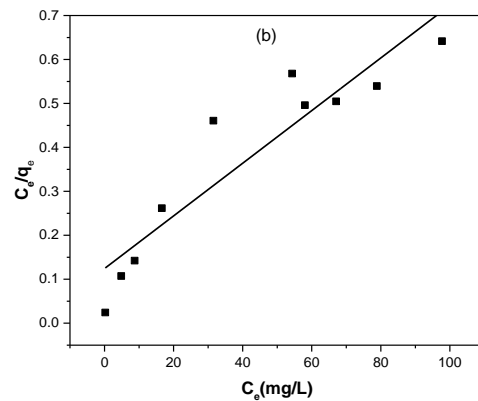
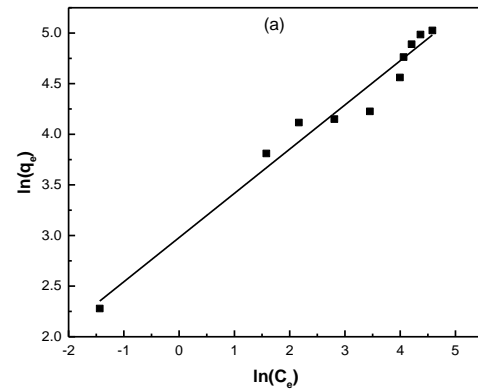


Fig. 8: Freundlich (a) Langmuir (b) and BET (c) isotherms sorption analysis on GO/AM/G.

T is temperature (K), and k_d is the distribution coefficient (mL/g). Values of ΔH , ΔS and ΔG were determined graphically by plotting $\ln(K_d) = f(1000/T)$ in Fig. 9.

The thermodynamic parameters were summarized in Table 3

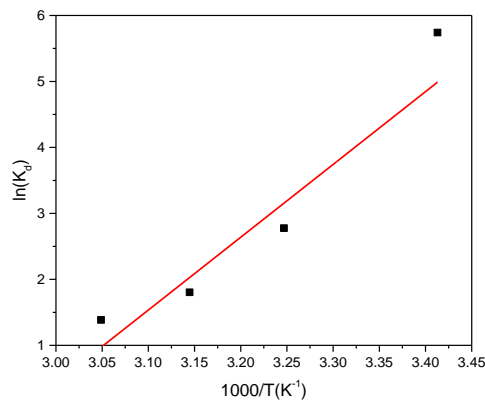
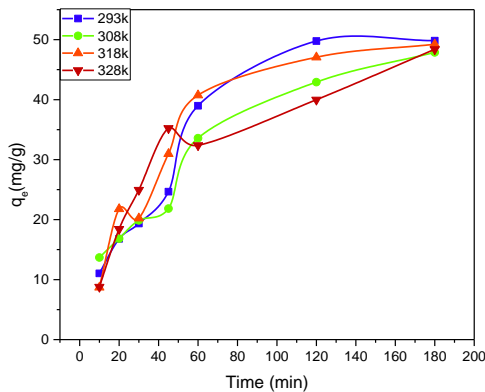
The negative value of ΔH ($\Delta H < 84$ kJ / mole) suggested that the adsorption process was probably

Table 2: Freundlich and Langmuir and BET coefficients.

Adsorbent	Langmuir				Freundlich			BET		
	q_m (mg/g)	k_L (L/mg)	R_L	R^2	K_F (L/g)	n	R^2	q_m	B	R^2
GO/AM/G	166.66	0.048	0.175	0.863	19.66	2.289	0.970	35.84	19.92	0.905

Table 3: Thermodynamic parameters of dye adsorption on GO/AM/G composite.

Adsorbent	Température (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K.mol)	E_a (Kj/mol)
GO/AM/G	293	-13,983	-101.43	-301.54	8.3
	308	-7.109			
	318	-4,766			
	328	-3,774			

**Fig .9: Van't Hoff plot for the adsorption of CR.****Fig .10: Kinetics of Congo Red adsorption on the GO/AM/G at different température (■) $T=293K$, (●) $T=308K$, (▲) $T=318K$, (▼) $T=328K$.**

exothermic due to the physisorption [23]. While, the negative value of ΔS suggested a decrease in randomness at the solid/liquid interface during the adsorption of CR on

GO/AM/G in the aqueous solution. Indeed, the negative value of ΔG ($\Delta G < 0$) for GO/AM/G indicated that the adsorption process led to an increase of free energy and a spontaneity of the process[24].

Activation energy

The effect of contact time on CR adsorption by GO/AM/G composite at different temperatures was plotted in Fig.10.

Adsorption kinetics data were measured under different temperatures (298, 308, 318 and 328 K), then the activation energy (E_a) was calculated according to the Arrhenius Equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (10)$$

The activation energy (E_a) of the adsorption of Congo red onto GO/AM/G was found to be 8.3 kJ/mol (Table. 3) as calculated from the slope of the Arrhenius plot. The low value of E_a suggested that the adsorption was governed by physisorption process, which is in agreement with previous results [25].

Regeneration study

The results of reusability of GO/AM/G composite in CR dye solution adsorption were shown in Fig.11.

GO/AM/G was reused more than six times with a decrease in adsorption capacity after the second use as shown in Fig.11. These results could be explained by the good chemical stability of the polymer on the surface of the clay. They could also indicate the excellent regeneration performance of our composite which can be

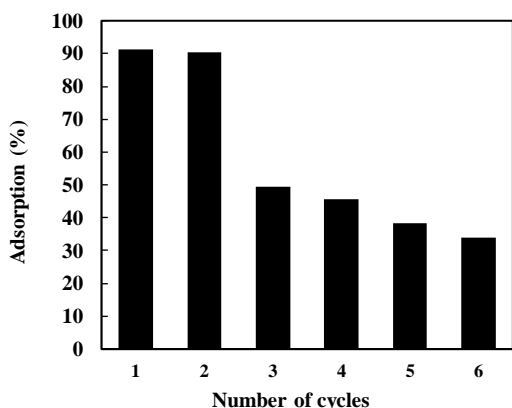


Fig. 11: Regeneration of GO/AM/G composite in CR dye solution.

an economic advantage in several applications especially in the industrial field[26].

CONCLUSIONS

In this study, GO/AM, GO/AM/HDTMA, and GO/AM/G composites were prepared by the modification of Activated Montmorillonite (AM) with Graphene Oxide (GO) as an organic base, HDTMA surfactant and gelatin.

Performance comparison of different adsorbents was evaluated to remove CR dye from water. The pH effect showed that, the composite that contain GO (50mg), AM, HDTMA and gelatin (60mg) showed a higher removal capacity of CR dye compared to the other composites.

The adsorption capacity of GO/AM/G was highly dependent on other operating parameters, like: contact time, adsorbent dose, initial concentration, temperature and regeneration. From the obtained results, the adsorptive behavior of CR using the GO/AM/G composite can be well described by the Freundlich model and pseudo-second-order model. Thermodynamics studies indicated that adsorption of Congo red on GO/AM/G composite was stable over an extensive range of temperature; it was also exothermic and spontaneous. The values of the free energy showed that the nature of the adsorption was physisorption. Regeneration of the composite was carried out for over six cycles and made the composite GO/AM/G a prospective material for dye adsorption from aquatic environments, indicating the economic significance, the good durability as well as good efficiency for repeated use.

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