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ORIGINAL ARTICLE

Removal of Toxic Congo Red Dye from Aqueous Solution Using a Graphene Oxide/Poly (Acrylamide-Acrylic acid) Hydrogel: Characterization, Kinetics and Thermodynamics Studies

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KEYWORDS

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ABSTRACT: This research studies the removal of textile dye (Congo red (CR)) from aqueous solution via using low-cost adsorbent prepared from GO/P (AA-co-AM) composite. Batch adsorption experiments were conducted to estimate the influence of several factors like pH solution, the concentration of CR dye, equilibrium time, adsorbent amount, and temperature solution. The top result correlation was found via the Langmuir model, and the best adsorption efficiency was 52.55 mg g^{-1} for CR dye. Thermodynamic studies appear that the adsorption of CR dye was feasible, endothermic, and spontaneous. Through the results, the prepared surface has very high efficiency in removing textile dyes and is environmentally friendly, inexpensive.

INTRODUCTION

Pollution is one of the utmost significant and most serious problems facing us at present, especially water pollution with dyes. Because of the many uses of these dyes in many industries, they are considered one of the most dangerous pollutants. There are many modern, easy, and inexpensive ways to get rid of pollutants, one of which is adsorption[1]. The adsorption of a component is often a surface phenomenon that refers to concentrating the component at an interface, or other bulk Atoms and molecules (sometimes) may be similarly adsorbed onto a surface [2]. The thermodynamic and molecular characteristics of adsorption (e.g. affinity, isotherm, isotherm, and enthalpy) are essential to explain binding processes and provide evidence of selectivity and toxicity control. However, for many processes, adsorption is important [3]. All these steps of gas separation and adsorption occur on solid surfaces (such as activated charcoal, clays, and hydrogels). Researchers have used a variety of biodegradable and effective adsorbents derived from natural resources to remove a variety of dyes from aqueous solutions under a variety of operating conditions. A special emphasis has been put on composite (GO/hydrogels)[4, 5]. Composite are three-dimensional cross-linked polymer networks composed of flexible chains capable of absorbing and retaining water and solute molecules. The composite structure's higher water content and porous structure networks allow for dyes diffusion [6-9]. This study aimed to develop a new absorbent composite from graphene oxide (GO), acrylamide (AM) and acrylic acid (AA). The sorption capacities and kinetics of composite was investigated for the removal of GR dye.

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MATERIALS AND METHODS

Chemicals

All chemicals utilized in this research were obtained from Sigma Aldrich Company and are of high purity and were prepared using distilled water.

Preparation of graphene oxide/poly (acrylamide-acrylic acid) hydrogel

Two grams of Graphene Oxide was dispersed deionized water in 1000 mL. The dispersion (0.002 g mL^{-1}) was undergone Sonication oscillations for 12 hr before utilize. A certain amount of Acrylamide-Acrylic acid that partially neutralized by 25% solution of NaOH was put in to a three-necked flask equipped through a thermometer, and nitrogen line. The quantity of a GO and AM dispersion additional in to flask. The mixing and stirred vigorously of 40 minute before put in to bath water at temp.50°C. The solution of (0.005 g mL^{-1}) MBA was dropped in to the flask under N2. After stirring of 40 min at temp. 50°C the bath water was little by little taken to to 65°C. Solution of KPS (0.05 g mL^{-1}) was dropped in to the flask. The mixture was allowed to react for about 2 hour until a black gel was formed. After being cooled down to room temp., the hydrogels were washed in deionized water for several times and cut in to small pieces, dry, and then ground and utilize Figure1.

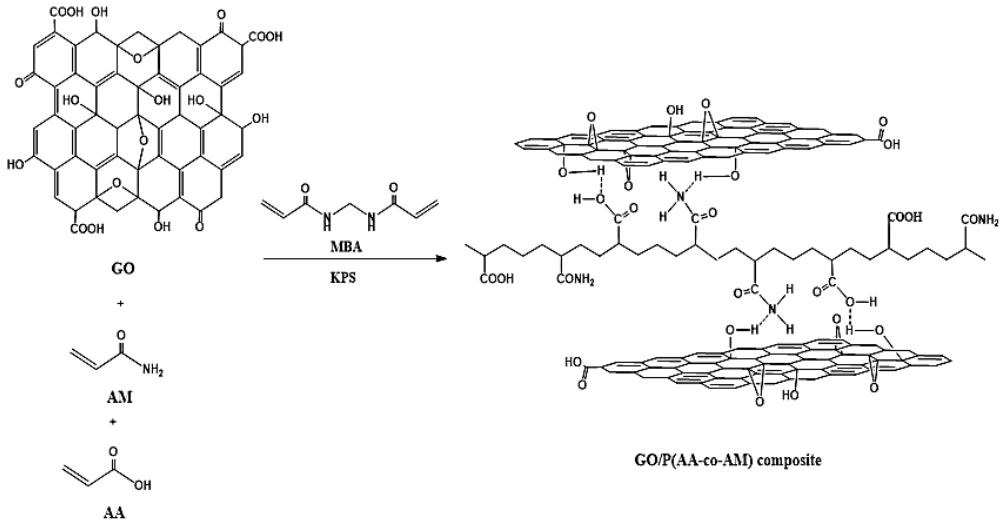

Figure 1 . Preparation of graphene oxide/poly (acrylamide-acrylic acid) hydrogel**.**

Adsorbent

Congo red dye is a compound organic, the salt sodium of 3,3′-([1,1′-bipheinyl]-4,4′-diyl)bis(4amino naphthalene-1sulfonic acid) I.U.P.A.C name sodium 4-amino -3-[4[4(1-amino-4sulfonato-naphthalen2-yl) diazenylphenyl]phenyl]diazanyl-naphthalen1-sulfonate. It is an azo dye. Congo red is soluble in water, gave a red solution colloidal; its solubility is large in the solvents organic. Chemical formula $C_{32}H_{22}N_6Na_2O_6S_2$, molar mass 697. The chemical stretcher is shown in Figure 2.

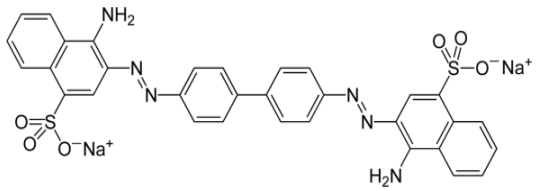

Figure 2. Chemical stretcher of Congo red dye.

Adsorption isotherm

Adsorption experiments was conducted via 10 mL of CR by a have primary conc. in a conical flask of 10 mL. Batch adsorption of CR dye onto adsorbent hydrogel was studied in aqueous solutions via varying experimental conditions, like adsorbent mass (0.001 g – 0.1g), the primary concentration of dye (200 mg L^{-1}), pH (2 – 12), and temperature (10-25°C). Each experiment was repeated three times to find the average. The percentage removal (E%) and the adsorption efficiency q_e (mg g^{-1}) of CR dye were calculated utilizing in equations:

$$q_e = \frac{Vsol.(Co-Ce)}{m} \quad (1)$$

$$\% E = \frac{(Co-Ce)}{Co} x100 \quad (2)$$

Where C_o and C_e are the primary concentrations of equilibrium CR in mg L^{-1} at the same order, V is the solution of CR (L), and m is the quantity of hydrogel (g).

Characterization of composite GO/P (AA-co-Am)

Figure 3 appear the XRD patterns of pure graphite displaying a sharp peak at 2θ ≈ 26.6°, which corresponds to a d-spacing of 3.36. After the oxidation, the formation of GO appearance of a new peak, at 2θ ≈11.9 °, That corresponds to an interlayer d-spacing of 7.60, The formation of OH, epoxy, and groups C=O on both sides of the layers allows water molecules to intercalate, increasing the distance between the layers. The XRD pattern of the composite did not show any crystalline arrangement where it was found that there is a broad peak at the range 2θ = 11°-28°, which is due to the non-crystalline nature. It also indicated that the presence of graphene oxide didn't changes the amorphous structure of the hydrogel, and this confirms that the GO sheets have been exfoliated and dispersed equally in the matrix structure of the hydrogel[10, 11].

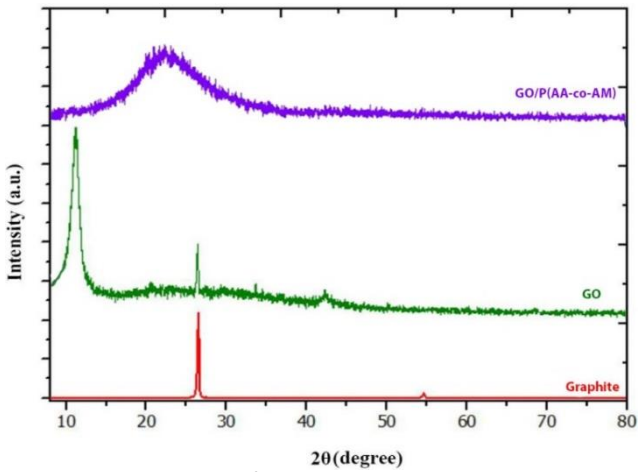

Figure 3. XRD patterns of G, GO and composite GO/P (AA-co- AM)

In Figure 4, the spectrum of FTIR composite before adsorption CR dye shows a broad peak at the range 3200-3660 cm^{-1} due to the overlapping of the vibrations stretching of the OH group in both PAA and PAA GO. The presence of a peak at 2943 cm^{-1} is due to the stretching vib. Of C-H. Also, the peak at 1710cm^{-1} is due to the stretching vib. Of the (CO) group in the P.A.A chain. The absorption peak at 1590cm^{-1} is attributed to bending vibrations of the NH groups in the PAM. Also, the peak at 1673cm^{-1} refers to stretching vibrations of C=C in the GO ring. All enhance the intrusion of GO into the matrix of the hydrogel. The spectrum of FTIR to the adsorption of CR dye on composite appears similar to characteristics as the composite before adsorption except for a few minor changes that intensity of some absorption peaks has changed.[12-14].

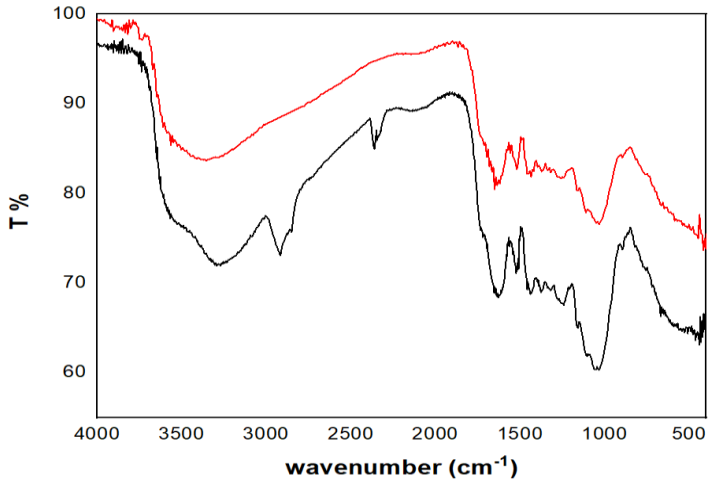

Figure 4. Comparative spectrum of FT-IR of composite before and after adsorption of CR

Figure 5 shows the TGA curve for the composite. It has been observed that four-stage including, the first stage is due to the loss of adsorbed water molecules on the composite. The second stage is due to the loss of functional groups containing oxygen like OH, carboxylate, and epoxy. The three-stage is due to the degradation of the crosslinked polymeric chains, final the four-stage is attributed to the degradation of chains polymer in the composite network [15].

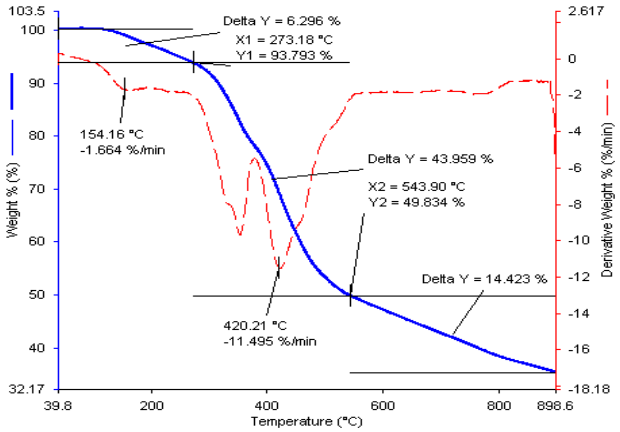

Figure 5. TGA analysis of composite.

Figure 6 (a) The prepared surface Poly (AA-co-AM) is non-porous, smooth, cloud-like, and does not contain cavities, but after loading graphene on the surface GO/Poly(AA-co-AM) it increased the roughness and porosity of the prepared surface, and this is clear through Figure 6(b). Figure 6 (c), after the adsorption process, the surface CR-Poly(AA-co-AM) composite became containing many swellings and clusters irregular, a clear indication of the loading of the dye into the surface pores and the occurrence of the adsorption process[16, 17].

Atomic force microscopy (AFM) was utilized to estimate the surface topography of the composite. Figure 7 appear three-dimensional image D3 of the surface composite, The data appear through the three-dimensional image that the prepared surface has a bumpy nature with clear roughness[18].

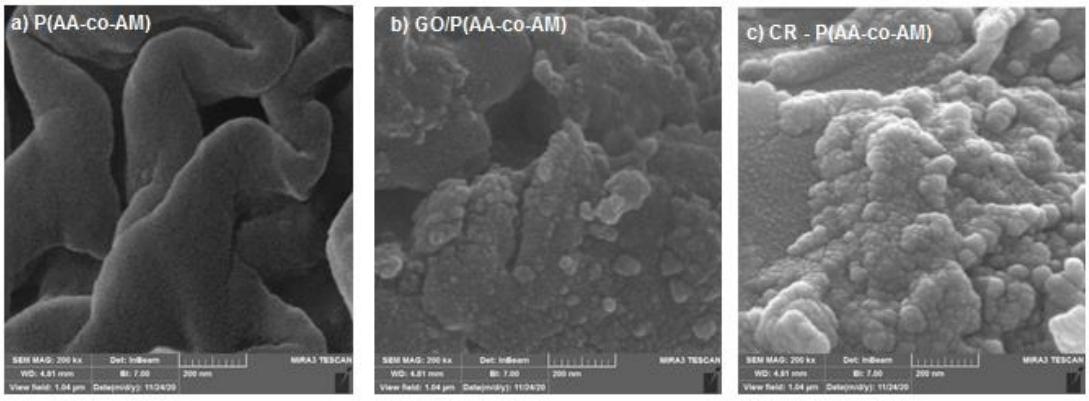

Figure 6. FE-SEM photographs of a) Poly (AA-co-AM), b) GO/Poly (AA-co-AM) composite, c) CR-Poly (AA-co-AM) composite before and after adsorption.

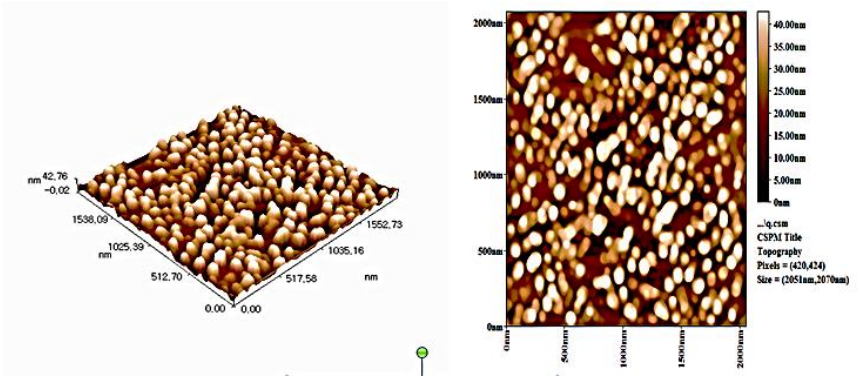

Figure 7. 3D images of AFM for GO/Poly (AA-co-AM).

Effect of pH

The acidity function is one of the utmost significant factors affecting the adsorption process. Therefore, the removal of CR dye was studied, and the pH had a significant role in controlling the charge of the surface, where the effective sites of the surface had a negative charge, and the dye had a relatively positive charge [19, 20]. It was observed that the best the adsorption efficiency of pH 2 and the more pH increased due to lower the adsorption efficiency because hydrostatic repulsion forces between the charge and the surface as shown in Figure 8.

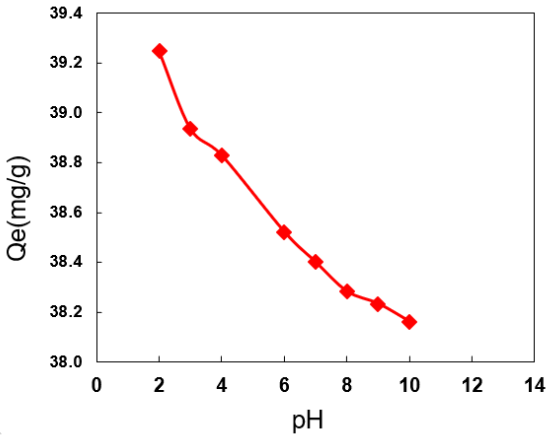

Figure 8. Effects of pH on the CR dye adsorption on composite. (Exp. Condition: primary conc. = 200 mg L^{-1}, Temp. = 20°C, and weight of surface 0.05 gm).

Effect of ionic strength

The influence of ionic strength on adsorption of dye composite was studied by a series of experimental studies constructed via changing NaCl concentration, KCl, from 0.001 to 0.2 mg. L^{-1}. As appear in Figure 9, It can be seen that when increasing the weight of salt the adsorption efficiency decrease because effect of electrostatic repulsion [18, 21].

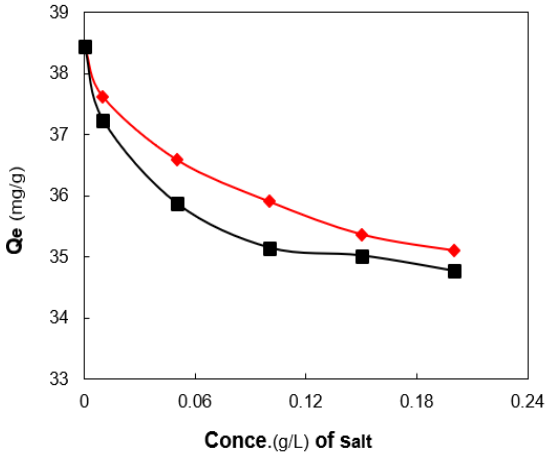

Figure 9. Influence of ionic strength on adsorption CR dye on to composite.

Effect of temperature and thermodynamic study

Temperature is such an important factor regulator the adsorption method. It can modify the adsorption efficiency for composite for a particular CR dye. Thus, the influence of solution temperature on CR dye adsorption via was examined within a temperature series of 10-25°C. Figure 10 shows the rise in percentage removal of CR with the increased temperature. The best percentage removal was happening at 25°C at an equilibrium time of about 2 hr. The increase in percentage removal of CR for identical high in temperature might have resulted from a raise in the rate of diffusion molecules of CR adjoining the surface external and internal pores of the composite [22, 23] .

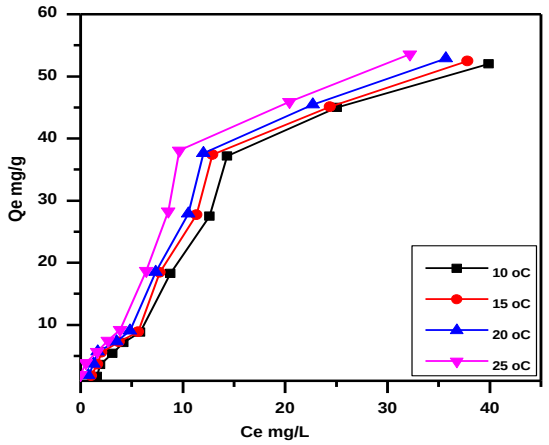

Figure 10. Adsorption isotherms of Congo red (CR) dye on composite at different temperatures.

Thermodynamic factors connecting (ΔG◦), (ΔH◦) and (ΔS◦) are obtained at several temperatures according to the following formulas:

$$\Delta G = -RTlnK \quad (3)$$

$$\Delta G=\Delta H-T\Delta S \quad (4)$$

$$lnk_{eq} = - \Delta G°/RT = - \Delta H°/RT + \Delta S°/R \quad (5)$$

T is the temp. (K), K_{eq} adsorption constant of equilibrium, and R is the gas constant. (ΔH^o) and (ΔS^o) were estimated from the slope and intarcept from the plot of ln X_m vs 1000K/T (Figure 11 and Table 1).

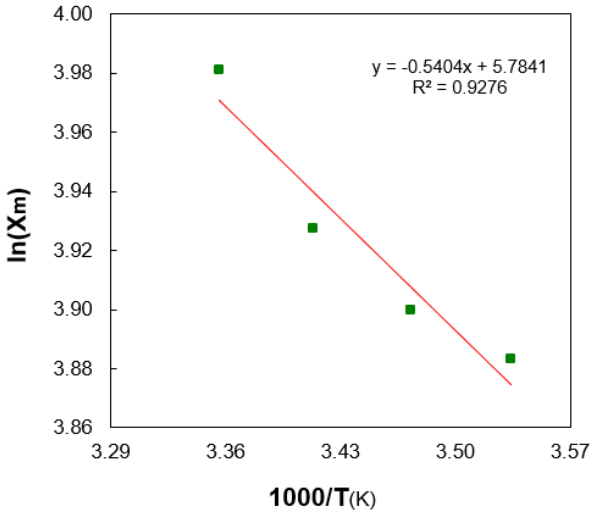

Figure 11. Plot ln X_m against the absolute temp. of the adsorption (CR dye) on to Composite.

Table 1. Effect of temp. for highest adsorption of Congo red on composite

T (°C)	T/k	C_e=32.1	
		X_m	lnX_m
10	283	48.6	3.883624
15	288	49.4	3.89995
20	293	50.8	3.927896
25	298	53.6	3.981549

When the adsorption of dye via hydrogel is exothermic, a rise in the temperature increases the CR adsorption rate but diminishes total adsorption capacity[24]. Temperature raising leads to improvement in the CR diffusivity molecule and consequently in the adsorption rate of diffusion is the rate-limiting step. In addition, temperature affects the desorption step and the reversibility equilibrium adsorption (Table 2).

Table 2. Variations in enthalpy (ΔH), free energy (ΔG), as well as variations in entropy (ΔS) for GR, absorbed on composite

T/K	ΔG^o/KJ mol^{-1}	Keq	ΔH^o/KJ mol^{-1}	ΔS^o/JK^{-1} mol^{-1}
283	-2.6988	7.5700		
288	-2.7386	7.6947	-18.082119	48.089
293	-2.8067	7.9127		
298	-2.9374	8.3489		

Adsorption isotherms

Numerous isotherm models are existing for investigating sorption equilibrium factor, and the most public being is the isotherms Freundlich isotherm and Langmuir model. The model of Langmuir model (Figure 11) is built on the theory that there is a fixed quantity of active sites, which regularly dispersed over the surface of the adsorbent; these sites have identical desirability for adsorbing a monomolecular layer and do not have any interactions

among adsorbed molecules. Moreover, Freundlich isotherm (Figure 12) applicable for heterogeneous surface adsorption. This model supposes a positive relationship among adsorbate concentration adsorbent quantities on the surface. Similarly, the energy sorption proportionally declines at the end of the sorption centers of the adsorbent. Calculation of correlation coefficients done via fitting the experimental equilibrium result for the dye-composite system utilizing Langmuir and Freundlich. Figures 11 and Table 3 appear the highest correlation coefficients (R^2 = 0.9805) related to the model Langmuir [25-28].

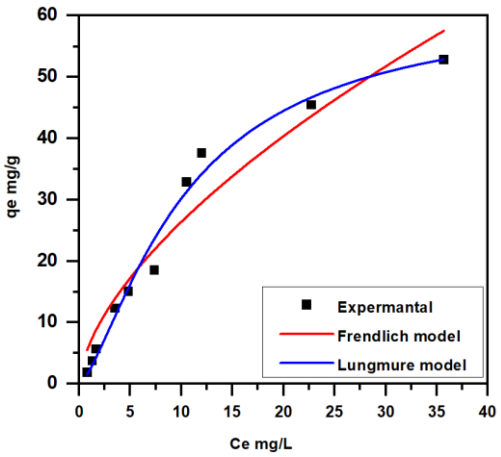

Figure 12. Several adsorption models nonlinear fit of adsorption CR dye onto composite. at different temperatures conc. = 200 mg L^{-1}, Temp. = 20°C.

Table 3. Several factors models for the adsorption study of CR on composite.

Temperature(°C)		20°C
Freundlich	K_F	6.4799 ± 1.3708
	1/n	0.6122 ± 0.0701
	R^2	0.9338
Langmuir	q_m(mg g^{-1})	62.962 ± 6.871
	K_L(L mg^{-1})	0.0363 ± 0.0116
	R^2	0.9805

Adsorption kinetics

First-order equation

The rate constant of adsorption is determined from the following first-order rate expression[29]:

$$\ln(q_e-q_t) = \ln q_e - k_1 t \qquad (6)$$

Kinetics second-model

The kinetics model of the adsorption method might defined in the second-order model [30]. The nonlinear as appear in equation

$$\frac{1}{qt} = \frac{1}{K2qe2} + \frac{1}{qe} t \qquad (7)$$

The kinetic factors for GR adsorption on the composite surface appear in Figures 13 and Table 4. Where note the great applicability of the adsorption method to second-order depending on the value of R^2 = 0.9834. Whereas the applicability to the model first-order decreases due to the little value of the R^2 = 0.9479 [23, 31, 32]. The Elkovich model was utilized for general use to chemisorption. The equation has been useful satisfactorily to some chemi-sorption methods and has been found to cover a wide range of slow adsorption rates. The same equation is often valid of systems in which the adsorbing surface is hetero-generous and is formulated as:

$$qt = \frac{1}{\beta} \beta \ln (\alpha \beta) + \frac{1}{\beta} \ln t \qquad (8)$$

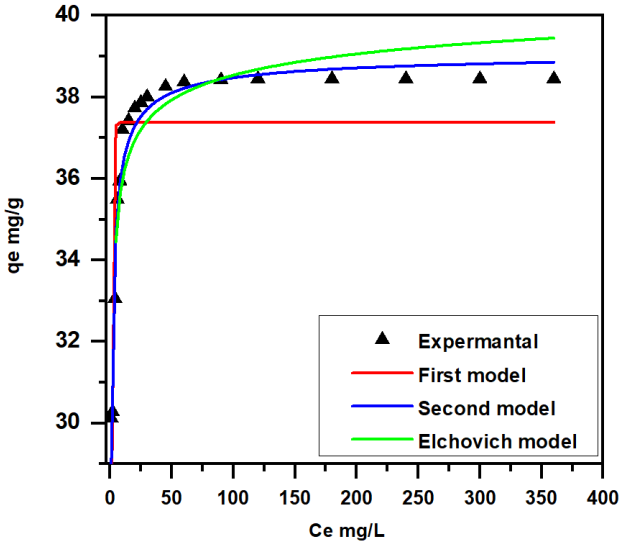

Figure13. Adsorption rate curves dye: exp. cond.: pH 6, GRL conc. 200 mg L ‘, Temp. 20ºC and mass catalyst (0.05 g)

Table 4. Adsorption kinetics factors the adsorption of MG dye.

Model	Equation	Parameters	Value
First-order	$q_t = q_e [1-\exp(k_f t)]$	$K_1(min^{-1})$	1.332 ± 0.1718
		$q_e(calc.)(mg\ g^{-1})$	37.386 ± 0.4799
		R^2	0.5096
Second-order	$q_t = \frac{K2qe2t}{1+K2qet}$	$K_2(g\ mg^{-1}min^{-1})$	2.828 ± 0.434
		$qe(calc.)(mg\ g^{-1})$	39.143 ± 0.233
		R^2	0.9311
Elkovich	$qt=\frac{1}{\beta}l\beta ln(\alpha\beta)+\frac{1}{\beta}lnt$	$\alpha\ (mg\ g^{-1}\ min^{-1})$	0.313± 0.122
		$\beta\ (g\ min^{-1})$	6.413± 0.333
		R^2	0.8773

CONCLUSIONS

1- The prepared GO/P(AA-co-AM) composite surface has very high efficiency in removing textile dyes, as it was prepared from inexpensive and environmentally friendly materials.

2- Three models, first, second and Elkovich, were applied, were found to obey the second model.

3- Two model Freundlich and Langmuir Isotherm were applied, was found to obey the Langmuir Isotherm.

4- best the adsorption efficiency of pH=3

5- Increase removal percentage% of CR with the increased temperature.

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Conflict of interests

There is no conflict of interest.

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