Synthesis and Characterization of Graphene Oxide/Hydrogel Composites and Their Applications to Adsorptive Removal Congo Red from Aqueous Solution

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Abstract. Graphene oxide / (polyvinylpyrrolidone / acrylic acid) composite GO/ (PVP-AAc) was studied as adsorbent for the Congo red dye. The synthesized composites hydrogels were characterized by Fourier transform infrared spectroscopy (FTIR). The process of adsorption of the Congo red (CR) dye on the surface of the GO/ (PVP-AAc) composite has reached equilibrium state within 60 minutes. The rate of adsorption of the dye on the surface was good due to the high surface area characteristic of the surface of the composite. The adsorption kinetics of the dye on the surface of the composite GO/ (PVP-AAc) were studied using of pseudo-first order model and pseudo-second order model. The results indicated that the adsorption process follows the pseudo-second order model. The effects of temperature, ionic strength and pH were also studied. In order to determine the maximum adsorption, the linear forms of isotherm of adsorption were studied, Langmuir, Freundlich, and Temkin equations. Also were studied the thermodynamic functions of the process of adsorption of, Gibbs free energy (G), Entropy (S), and Enthalpy (H).

1. Introduction
Many dyes are used in many different industries such as textiles, plastics, paper, printing, food, dyeing, and cosmetics to color the products that have been manufactured [1-3]. Colors are important features of many liquid wastes where they are easy to detect and access to their sources [4].

It is therefore necessary to remove these pollutants from the wastewater before dumping it in the water bodies [5,6]. Dyes also contain many organic substances, carcinogens, mutants and toxic substances that make water unsuitable for human consumption, agriculture and harmful to fish and living organisms [7,8]. Colored water affects the nature of water through the inability of sunlight to penetrate water, which reduces the activity of photosynthesis of aquatic plants. Dyes are stable and unaffected by biodegradation and are stable against both oxidizing and light factors. Traditional methods used to remove dyes from water have become inefficient, difficult and time-consuming [9,10]. It is therefore necessary to use more convenient methods and less time, and adsorption is a good and economic means to remove pollutants from water [11].

2. Method
2.1 Materials
Natural graphite powders, acrylic acid (AAc), polyvinylpyrrolidone (PVP), N, N’-methylene bisacrylamide (MBA), potassium persulfate (KPS), Congo red (CR), supplied from (BDH, Chemicals, England). Sodium hydroxide, Sodium chloride, Potassium chloride, Calcium carbonate, were supplied from (Fluka, Germany). Potassium permanganate, sodium nitrate, concentrated sulfuric acid, hydrochloric acid, hydrogen peroxide (30%) were purchased from Kemiu Chemical Reagent Co, Ltd, China. All the reagents used were analytical grade pure with no further purification, and all the solutions were prepared with deionized water.
2.2 Preparation of graphene oxide
Prepared of the graphene oxide by using the Hummer Method by adding 46 mL of concentrated sulfuric acid in a 1L flask in an ice bath at 0 °C with continuous stirring. Then add 1g of 5 m of graphite powder, and 1g of sodium nitrate to the beaker with continuous stirring for 4 hours, then add 6 g potassium permanganate gradually so that the addition (20 minutes) continues stirring for 5 minutes, then remove the ice bath and leave at 35 °C with constant stirring for three hours, then add 92 mL distilled water very slowly so that the extension takes 20 minutes 10 min. Add 10 mL of hydrogen peroxide (30%) with stirring for 30 min to remove excess potassium permanganate. This was confirmed by changing the color of the solution from the dark to the yellow color, indicating the oxidation of all the graphite to the graphene oxide after separation and wash with 10% solution of the HCl several times until the disposal of sulfates and this was confirmed by the solution of barium chloride, Wash with distilled water several times until you reach a neutral acidic function for filtration, and then place in an vacuum oven at 45 °C for one day.

2.3 Preparation of (PVP-AAc) and GO/ (PVP-AAc) composite
The GO / (PVP – AAc) composite is prepared by 0.2-0.0 % w/v solution of GO is prepared by dissolving it in distilled water using the ultrasonic bath for 60 minutes and mixing with the PVP and AAc hydrogel components by mixing (10: 1), where 1mL of GO is added to 10mL of PVP and AAc hydrogel by 20% and 80% respectively, and 1mL is added to the crosslinking agent (MBA), as well as 1mL of the KSP initiator. The mixture is placed in polyethylene test tubes, stirred mix well, and pass on nitrogen gas for 20-15 minutes. The tubes are then placed in a water bath to gradually raise the temperature from 45 °C to 65 °C. This increase in temperature is as follows: 45 °C for one hour, 55 °C for two hours and 65 °C for two hours. The aggregate is then cooled and removed from the tubes, and then cut into small pieces (approximately 6mm). Then wash them with ethanol and distilled water for a week to remove all unreacted monomers. Then dry at room temperature and then dry by an electric oven at 50 °C to 60 °C until a constant weight. For prepared of (PVP-AAc) hydrogel only by same above method without added graphene oxide.

2.4 Adsorption studies
In order to study the adsorption of the dye (CR) on the adsorbent surface GO/(PVP-AAc) composite , a number of different dye concentrations were used, which were used in a series of different experiments to determine the effect of the time of the contact, the amount of adsorbate, the best the pH of the solution for dye adsorption, The appropriate temperature (5,15,25,35), ionic strength, adsorption kinetics, isotherms which apply to the process of adsorption of dye on the adsorbent surface GO/(PVP-AAc) composite . Where 10 ml of the dye solution was used with 0.05 grams of surface and placed in the shak ng device to obtain the largest amount adsorbate of dye. The dye concentrations were determined by visible ultraviolet radiation. To calculate the amount of material absorbed on the adsorbent surface, the following mathematical relationship was used:

\[ Q_e = \frac{V_{ot}(C_0 - C_e)}{m} \]

Where: \( Q_e \) the amount of the absorbate material (mg/g), \( V_{ot} \) the total volume of the solution of the absorbed substance (L), \( C_0 \) the primary focus of the adsorbate substance (mg/l), \( C_e \) Concentration at equilibrium of absorbent material (mg/L), \( m \) the weight of the absorbed material (g) [12].

2.5 Fourier transform infrared spectroscopy (FT-IR)
The FTIR spectroscopy was used to characterize the chemical structure of GO / (PVP – AAc) composite. The spectra of solid-state materials were recorded using the KBr within a range of (400 – 4000) cm\(^{-1}\).

3. Results and discussion
3.1 Characterization of GO, P (PVP-AAc) and GO/P (PVP-AAc)
Figure 1 shows the infrared spectra of the graphite and the graphene oxide within a range from 400-4000 cm\(^{-1}\), where the graphite spectrum showed a wide peak at 3440 cm\(^{-1}\), due to OH stretching, which belong to the water molecules absorbed by the graphite, and absorbance at 3010 cm\(^{-1}\) is due to the vibration stretching of C-H backbone in the structure of the graphite, whereas the peaks that appeared at (1605,1580) cm\(^{-1}\) are due to the
vibration of the C = C groups within the ring in the carbon structure, at 1100 cm\(^{-1}\), its due to the bending vibration of the C-H groups.

The infrared spectra of the graphene oxide showed a wide peak at 3400 cm\(^{-1}\) due to O-H stretching vibrations of the carboxyl group as well as adsorption of water molecules on the surface of the graphene oxide also having a peak at 2950 cm\(^{-1}\) is due to the stretching vibration of C-H, the peak at 1720 cm\(^{-1}\) to the stretching vibration of the (C = O). The peak that appeared at 1620 cm\(^{-1}\) is due to the stretching vibration of the unoxidized C = C groups in the carbon structure. There is also a stretching vibration at 1220 cm\(^{-1}\) due to C-O (carboxyl, C-OH). The spectrum also showed a peak at 1060 cm\(^{-1}\) stretching vibration due to the C-O-C groups [13].

Figure 1. FTIR spectra of Graphite and Graphene Oxide

The FTIR spectra of the P (PVP-AAc) hydrogel and its composite shows in figure 2, for hydrogel, the range (3500-3200) cm\(^{-1}\), wide absorption which indicate overlapping between the N-H and O-H peaks, as for the C-H bonds found in the aliphatic compounds in the hydrogel synthesis, absorption bands were shown within the range (2600-2940) cm\(^{-1}\), which represents the symmetrical and asymmetric stretching vibrations of the alkyl groups (-CH\(_2\)) in the hydrogel. The C = O, found in acrylic acid, PVP, and MBA, has shown absorption peaks within the range (1620-1740) cm\(^{-1}\) and the range (460-1000) cm\(^{-1}\), the absorption peaks showed that the bonds C=C, C-N and C-O. but the FTIR for GO/P(PVP-AAc) composite showed the shift of the groups bands reveals the interactions between the carboxylic groups on P (PVP-AAc) and GO platelets[13] given in figure 2.

Figure 2. FTIR spectra of P (PVP-AAc) and GO/P (PVP-AAc)

3.2 Effect of Contact Time

The time of the adsorption of the Congo red (CR) dye of this shown on the surface of the composite adsorbent GO/ (PVP-AAc). As in figure 3, there was an increase in the amount of the adsorbent material with increasing time of contact of the adsorbent surface with the solution.
3.3 Adsorption of the dye

The results indicated that the amount of dye absorbed on the surface was good and as shown in figure 4. The dye concentration was drawn against the amount of the adsorbed material to show the process of adsorption of the dye to the surface at 25 °C. This is due to the presence of active groups available for adsorption of pigment on the surface, which carries positive charges such as amide groups and amine groups, as well as the negatively charged oxygen aggregates present in the Congo red dye. This difference in charge between functional groups of the dye and surface adsorbent increases adsorption [13-15].

3.4 Adsorption Isotherm

The results show that the process of adsorption corresponds to (S) class according to the Giles classification as shown in figure 5. This type is characterized by the particles of the adsorbate material being vertically or slanted on the surface of the adsorbent. The surface is not homogeneous. The Langmuir, Freundlich, and Timken equations were used, as shown in figures 5, 6 and 7 respectively, to interpret the resulting data from the adsorption process obtained at 25 °C. The results show that the process of adsorption of the dye on the surface of the adsorbent is identical to the isotherm Freundlich. Table 1 shows the correlation coefficients and constants of isotherm of Langmuir, Freundlies, and Timken [16-17].
Table 1. The correlation coefficients and constants of isotherm of Langmuir, Freundlich and Timken of adsorption (CR) dye on surface GO/ (PVP-AAC)

| Langmuir equation | Freundlich equation | Timken equation |
|-------------------|--------------------|-----------------|
| $K_L$ | $q_{m}$ | $R^2$ | $K_F$ | $N$ | $R^2$ | $K_T$ | $b$ | $R^2$ |
| 0.0675 | 77.5193 | 0.860 | 9.9357 | 2.3020 | 0.946 | 0.5792 | 16.797 | 0.835 |

Figure 5. Isotherm of Langmuir to adsorb the (CR) dye on the surface GO/ (PVP-AAC)

$y = 0.0129x + 0.191$
$R^2 = 0.8602$

Figure 6. Isotherm of Freundlich to adsorb the (CR) dye on the surface GO/ (PVP-AAC)

$logQ_e$ vs $logC_e$

$y = 0.4344x + 0.9972$
$R^2 = 0.9463$
Figure 7. Isotherm of Timken to adsorb the (CR) dye on the surface GO/ (PVP-AAC)

3.5 Effect of temperature
Table 2 and figure 8 show that the amount of material adsorbate on the adsorbent surface is increased by increasing the temperature. This leads to that adsorption process is endothermic, which is updated caused by that increasing the temperature reduces the viscosity of the solution, thus increasing the spread of the material that is adsorbate on the surface. The kinetic energy of the molecules increases by increasing the temperature and thus increases the chance of their interaction with the active sites as well as increasing the penetration into the pores of the adsorbent material [18-20].

| Temperature (°C) | C_e (mg/L) | Q_e (mg/g) | C_e (mg/L) | Q_e (mg/g) | C_e (mg/L) | Q_e (mg/g) | C_e (mg/L) | Q_e (mg/g) |
|-----------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 5°C             | 0.07931    | 9.603448   | 0.155172   | 18.84483   | 0.506897   | 20.3069    | 3.258621   | 1.348276   |
| 15°C            | 0.231034   | 3.810345   | 0.326517   | 18.84483   | 0.734483   | 20.7069    | 4.231034   | 1.348276   |
| 25°C            | 4.775862   | 25.12069   | 4.975862   | 20.56897   | 5.886207   | 20.7069    | 5.858621   |            |
| 35°C            | 9.603448   | 27.46552   | 14.5069    | 27.15517   | 4.145069   | 27.7586    | 6.05172    |            |

Table 2. Amount of dye (CR) absorbed at surface GO/ (PVP-AAC) at different temperatures
The thermodynamic functions, the change in the enthalpy, the change in free energy, the change in the entropy, were calculated as shown in the table 3. Where the results show that, the value of the change in the enthalpy is positive value and this indicates that the reaction is endothermic. The negative value of free energy indicates that the adsorption process is spontaneous. The positive charge for the change in entropy indicates a random increase of the molecules adsorbate as a result of increase kinetic energy [21].
3.6 Effect of ionic strength
The results shown in Table 5 and figure 10 show that the amount of the adsorbate on the surface increases with increasing salt concentration in the solution. This is due to the decrease in solubility of the dye in the solution, due to the overlap between the salt ions used and the solvent molecules. There is a competition between salt ions and dye ions to interact with the solvent [22]. The double layer is also formed by salt ions, which increases the adsorption of the adsorbate molecules on the surface [23].

| Concentration (mol/L) | $Q_e$ (mg/g) | Concentration (mol/L) | $Q_e$ (mg/g) | Concentration (mol/L) | $Q_e$ (mg/g) | Concentration (mol/L) | $Q_e$ (mg/g) |
|-----------------------|--------------|-----------------------|--------------|-----------------------|--------------|-----------------------|--------------|
| 100                   | 16.78276     | 0                     | 16.78276     | 0                     | 16.78276     | 0                     | 16.78276     |
| 100                   | 16.85172     | 0.005                 | 16.78276     | 0.005                 | 16.79655     | 0.005                 | 16.78276     |
| 100                   | 17.12069     | 0.01                  | 17.05862     | 0.01                  | 16.8562      | 0.01                  | 16.78276     |
| 100                   | 17.21034     | 0.03                  | 17.20345     | 0.03                  | 17.26552     | 0.03                  | 17.26552     |
| 100                   | 17.39655     | 0.05                  | 17.33448     | 0.05                  | 17.3517      | 0.05                  | 17.3517      |
| 100                   | 17.61034     | 0.1                   | 17.52069     | 0.1                   | 17.26552     | 0.1                   | 17.26552     |
| 100                   | 18.56897     | 0.15                  | 17.83793     | 0.15                  | 17.47241     | 0.15                  | 17.47241     |
| 100                   | 18.92069     | 0.2                   | 18.23103     | 0.2                   | 18.0931      | 0.2                   | 18.0931      |
| 100                   | 19.26552     | 0.25                  | 18.85172     | 0.25                  | 18.43793     | 0.25                  | 18.43793     |

3.7 Adsorption kinetic
The kinetics of the process of adsorption for the congo red dye have been studied on the surface of the adsorbent, using the two kinetics equation, pseudo-first order and pseudo-second order. As shown in table 6 and figure 11 a and b. The results showed that the kinetic equation of the pseudo-second order is more compatible with the adsorption kinetic of the dye on the surface. This was done based on correlation coefficients ($R^2$) as shown in the table below [24, 25].

| $H$ (kJ mol$^{-1}$) | $G$ (kJ mol$^{-1}$) | $S$ (J mol$^{-1}$ K$^{-1}$) | Equilibrium Constant(K) |
|---------------------|---------------------|-----------------------------|--------------------------|
| 10756.650           | -7718.320           | 61.996                      | 5.6349                   |
Table 6. Correlation coefficients and kinetic constants of the pseudo- first order and pseudo- second order of adsorption of dye (CR) on the surface GO/ (PVP-AAC)

|               | pseudo- first order | pseudo- second order |
|---------------|---------------------|----------------------|
| $K_1$         | 0.0407              |                      |
| $q_e$         | 3.1386              |                      |
| $R^2$         | 0.8162              |                      |
| $K_2$         | 0.0339              |                      |
| $q_e$         | 17.0068             |                      |
| $R^2$         | 0.9995              |                      |
| $H$           | 9.8135              |                      |

Figure 11. (a) Model of pseudo- first order (b) Model of pseudo- second order of adsorption of dye (CR) on the surface GO/(PVP-AAc)

3.8 Effect of pH
The results of the study of the effect of the acidic function of the solution on the amount of the adsorbate on the surface of the adsorbent, figure 12. Where it was observed that the highest value of adsorption was at the value of the acid function ($pH = 7$). The extent of the acidic function within the study was ($pH = 1-7$). It is necessary to study the effect of the acidic function because the $pH$ directly affects the adsorbent surface charge as well as the adsorbate species and the ionization of these species [26].

The increase in the amount of the absorbate material with the increase in the value of the acidic function is due to the electrostatic attraction between the negative ions of the dye in the solution and the positive ions on the surface. It is also possible to obtain the ion exchange between the species in the solution and the surface of the adsorbent, which depends heavily on the value of the acid function. It is also possible to affect the acidic function on the surface of the adsorbent through the increase of pore capacity and distribution on the surface and thus increase the surface area prone to adsorption and this helps to increase the amount of adsorbate on the surface adsorbent [27].

Figure 12. Effect of pH on adsorption (CR) dye
4. Conclusions
GO/ (PVP-AAc) composite was studied as adsorbent for the Congo red dye. The synthesized composites hydrogels were characterized by Fourier transform infrared spectroscopy (FTIR). The process of adsorption of the Congo red (CR) dye on the surface of the GO/ (PVP-AAc) composite has reached equilibrium state within 60 minutes. The results indicated that the adsorption process follows the Pseudo- Second Order Model. The effects of temperature, ionic strength and pH were also studied. In order to determine the maximum adsorption, the linear forms of isotherm of adsorption were studied, Langmuir, Freundlich, and Temkin equations. Also were studied the thermodynamic functions of the process of adsorption of, Gibbs free energy (G), Entropy (S), and Enthalpy (H).

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