RESEARCH ARTICLE

Synthesis and Swelling Behavior of Hydrogel Graphene oxide-poly (AA-co-AM) Composite for Removal of Toxic Rhodamine-B dye

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ABSTRACT

This study aims to identify the most important properties of adsorption using a cheap, inexpensive (GO/P(AA-co-MA) hydrogel surface that can be prepared with ease and have high efficiency in removing dyes from water. The important physical and chemical properties of hydrogel surface were studied, including field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM). Also, several crucial factors in adsorption were studied, including the equilibrium time, effect of the pH, effect of the surface weight of the hydrogel, effect of salt concentration, and temperature. The results showed that the best adsorption efficiency for Rhodamine B dye removal was (36.8 mg/g), the best adsorption time was about one hour, and the best weight for dye removal was 0.05 g. The free Gibbs energy, enthalpy, and entropy were found the reaction is spontaneous.

Keyword: Adsorption, B dye, Hydrogel, Pollution, Removal, Rhodamine Thermodynamic.

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INTRODUCTION

The polluted water resulting from the upcoming textile industries contains many hazardous pollutants, including dyes, and also includes a high percentage of organic pollutants. Annually about 900,000 dyes are produced, with a 15% loss of textile dyes during the treatment process, and they are taken out to the water as liquid waste.[1-4] This liquid waste is very harmful to the environment and is not capable of decomposition and is highly toxic, and causes many diseases.[5,6] Rhodamine B dye is one of the most important and most widely used dyes for industries such as printing and dyeing fabrics, leather, paper, paint and other industries, so the organic dyes are considered the most dangerous and cause many problems when used cause itching in the skin and eye irritation as well as problems in the aquatic environment and affect living organisms, so it must be disposed of Among these dyes from west water, the use of easy and cheap chemical and physical methods, and these traditional methods are ozone, liquid membrane, photocatalysis, adsorption and other methods.[7-9] The adsorption process is one of the most important techniques used to remove dyes in water using very high-efficiency surfaces.[10] It can be prepared from cheap and available materials, such as activated carbon, CNT, carbon oxide, clay, and hydrogel.[11-14] It was based in this study on the use of a surface with good efficiency to remove (GO / P(AA-co-MA)) hydrogel. Several important adsorption factors were studied, such as the effect of surface weight and pH solution.

EXPERIMENTAL PART

Preparation of (GO/P(AA-co-MA) Hydrogel Composite

For the preparation of (AA-co-MA) hydrogel, several steps begin with preparing the solutions of the substances that are intervention in the installation of the hydrogel. (4% w/v) of maleic acid (MA), and (8% w/v) of acrylic acid (AA) were prepared in distilled water, then 20% of MA and 80% of AA, and with the addition (0.8% w/v) of GO by the ratio (1:10) of the mixture were mixed, respectively. The mixture is stirred well, and is then added the cross-linker agent, MBA (0.20 mol/L), while still stirring, is then added to the initiator KSP (0.0361 mol/L). he mixture is then placed in polyethylene test tubes, and nitrogen gas is passed on for 10 to 15 minutes. The tubes are then placed in a hot water bath where the temperature is gradually increased from 45 to 65°C. The temperature increase is as follows: 45°C for 1-hour, 55°C for 2 hours, 65°C for 2 hours.

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The prepared hydrogel is then cooled and removed from the tubes, and then cut into small pieces about 6 mm long. Then wash them with ethanol and distilled water for a week to remove all non-reactive monomers. Then dry at room temperature and then dry by an electric oven from 50°C to 60°C until get a constant weight.

Rhodamine B Dye

The dye Rh-B is one of the most important aromatic compounds containing triphenylmethane with xanthine rings (Figure 1). It has a molecular weight of 479.02 g/mol. The chemical structure of the dye is $C_{28}H_{31}ClN_2O_3$, and the solubility of the dye in water is 8 to 15 g/L (20°C). It is red to violet powder.

Calibration Curves

The process of preparing a calibration curve for (Rhodamine B dye) was based on taking a weight of 0.1 gm of the dye. It was dissolved in 100 mL to get a concentration (100 mg/L) where a series of solutions were prepared (1–83 mg/L) The absorbance was measured at λ_{max} of the dye and plotted against the values of Rhodamine B dye concentration as shown (Figure 2).

Adsorption Studies

Dye concentration (10–500 mg/L), the concentration used in the experiment whose pH solution was studied at a concentration of 200 mg/L, was the adsorption of dye on the surface of GO/P(AA-co-MA). The pH was titrated with hydroxide sodium and hydrochloric acid at solution 0.1 N. Also, at a concentration of 200 mg/L, the surface weight of GO/P(AA-co-MA) hydrogel (0.01, 0.02, 0.003, 0.04, 0.05, and 0.06 g) was studied, at room temperature. A clear effect on the adsorption process where three salts were taken NaCl, KCl, and CaCO3 at deferent weight rang (0.001–0.1 g). Using shaker water-bath adsorption, experiments were conducted. 10 mL was taken at a concentration of 200 mg/L of dye at a weight of 0.05 g of the hydrogel at room temperature, where the dye's pH was equal 6.6, where the equilibrium time was an hour. The solution was separated using a centrifuge for 10 minutes, and the concentration was measured using a UV-vis spectrophotometer at 553 nm. The adsorption efficiency of the dye was calculated using the hydrogel based on Equation (1).

$$Qe = \frac{Co-Ce}{w} * V \quad (1)$$

RESULT AND DISCUSSION

FESEM

To know the nature and porosity of the prepared surface, as well as to know the size and shape of the particles and the nature of their distribution, before the adsorption process uses the technique FESEM for each of (P(AA-co-MA)) and after the graphene loading process (GO/P(AA-co-MA)). It was noted that the surface of the hydrogel is rough and heterogeneous. After loading graphene oxide, the surface became less rough and contained many cavities and after the adsorption process.[6,15,16] It was observed that all the active sites of the (GO/P(AA-co-MA-) surface were filled, indicating that the adsorption process had successfully occurred as appear in Figure 3.

TEM

A technique TEM was studied for the hydrogel surface before and after the graphite oxide loading process. After the loading process, it was noticed that the surface contained many aliases due to loading (GO) on the surface.[17,18] After the adsorption process and loading dye on the surface, we notice some dark spots, evidence of the adsorption process as appear in Figure 4.

Effect of pH Solution

One of the most important factors affecting the adsorption process is the effect of pH when using optimum conditions, weight of hydrogel (0.05 g) temperature (25°C) and dye concentration (200 mg/L), where by the increase in pH (2-10) increases the adsorption efficiency from (33.56–35.88 mg/g).[19,20] The best adsorption capacity in basic medium at pH 10 as a result of the process of attraction between positive ions of the dye and ions negative surface as shown in Figure 5.

Effect of Ionic Strength

The effect of ionic strength on adsorption of Rhodamine B dye onto hydrogel was studied via a chain of investigational studies constructed via different concentrations of NaCl, KCl, CaCO3 from 0.001 to 0.1 $g.L^{-1}$. As shown in Figure 6, when the concentration of salt increased, the adsorption capacity increases because of the effect of electrostatic repulsion and found the best salt CaCO3 gives higher adsorption capacity compared.

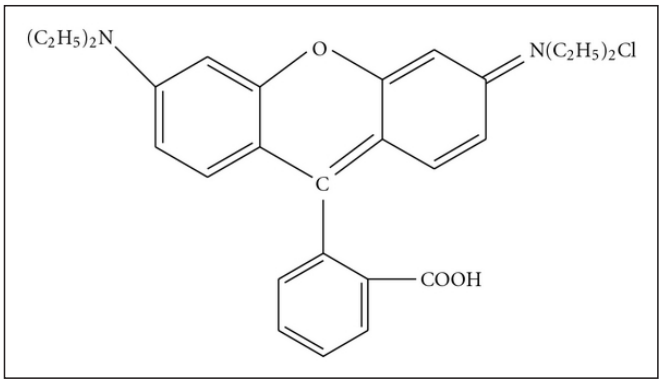

Figure 1: Chemical structure of Rhodamine B dye

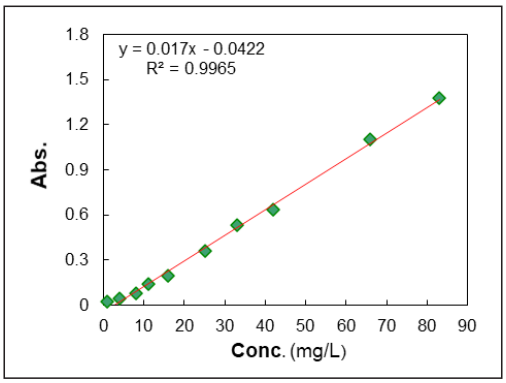

Figure 2: Calibration curve Rhodamine B dye

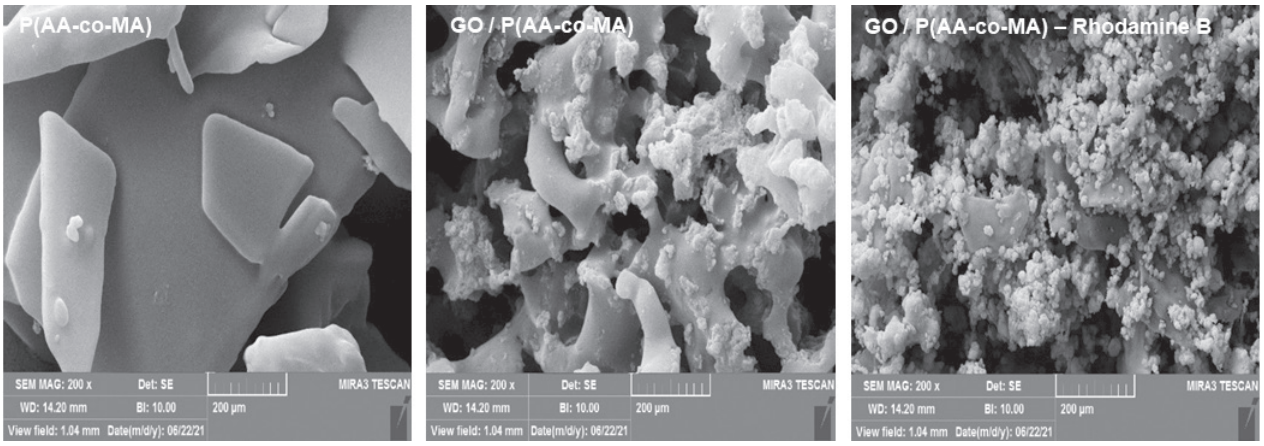

Figure 3: FESEM image a) p(AA-co-MA), b) GO/p(AA-co-MA), c) GO/p(AA-co-MA)-Rhodamine B dye

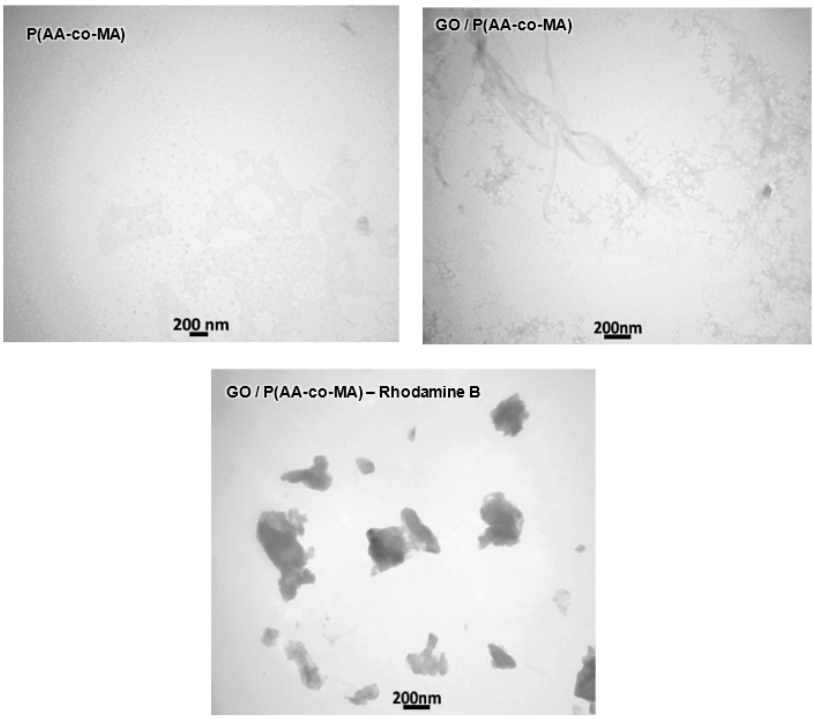

Figure 4: TEM image a) p(AA-co-MA), b) GO/p(AA-co-MA), c) GO/p(AA-co-MA)-Rhodamine B

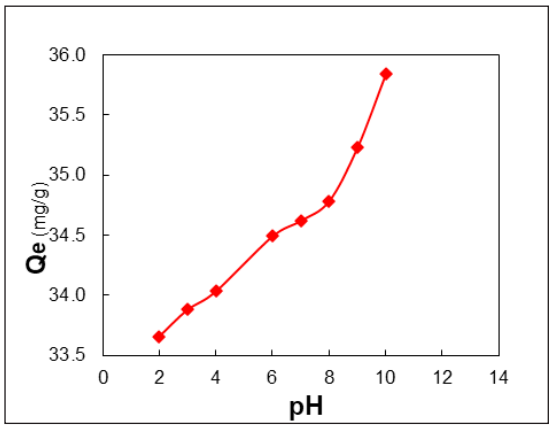

Figure 5: Effects of pH on the Rhodamine B dye adsorption onto hydrogel

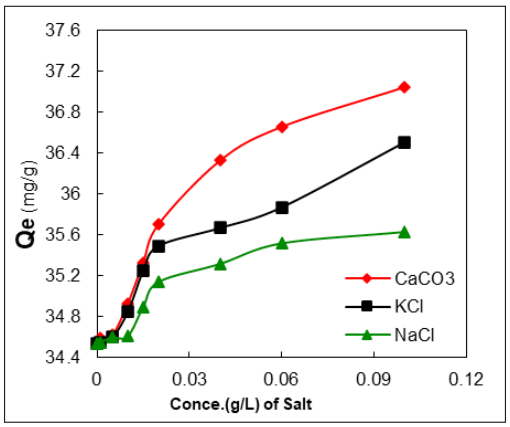

Figure 6: Effect of concentration ionic strength on adsorption Rhodamine B dye onto hydrogel

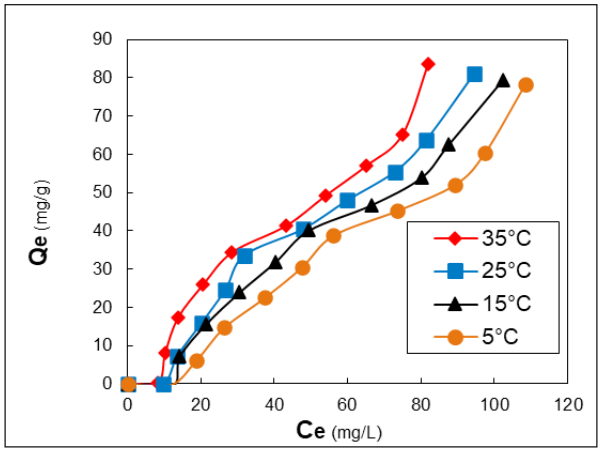

Figure 7: Adsorption isotherms of Rhodamine B dye onto hydrogel at different temperatures

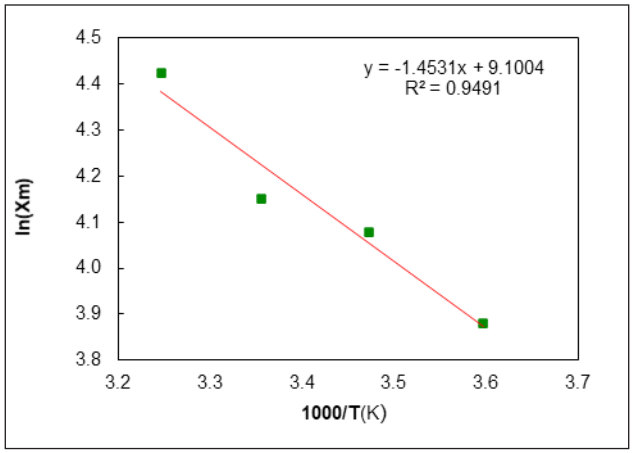

Figure 8: Plot ln Xm against the absolute temperature of the adsorption Rhodamine B dye) ono hydrogels.

Table 1: Effect of temperature on maximum adsorption of Rhodamine B dye onto hydrogels

			Ce = 81	
T (°C)	*Tk*	*1000/T(K^{-1})*	*Xm*	*lnXm*
5	278	3.5971	48.5	3.8815
15	288	3.4722	59	4.0775
25	298	3.3557	63.5	4.1511
35	308	3.2467	83.5	4.4248

Table 2: Parameter of thermodynamic of adsorption for Rhodamine B dye onto hydrogel

ΔH (KJ mol^{-1})	*ΔG (kJ mol^{-1})*	*ΔS (J $mol^{-1}K^{-1}$)*	*Equilibrium constant*
12.081	-3.384	11.356	3.902

Effect of Solution Temperature and Thermodynamic Parameter

Figure 7 shows the effect of temperature on the adsorption of Rhodamine B dye on the surface hydrogel at optimal conditions, from equilibrium time of one hour, dye concentration 200 mg/L and hydrogel weight 0.05 gm. Whereas, through the results, it was noticed that with increasing temperature (5–35°C), the adsorption efficiency increased from (78.33 to 83.59 mg /g).[21-23]

Parameters of thermodynamic of Rhodamine B dye like enthalpy, free Gibbs energy, and entropy assess from the difference equilibrium constant (K) of the thermodynamic by temp. As appear in Table 1.

The heat of adsorption (ΔH) can be estimation in equation:[24]

$$Ln\ X_m = -\frac{\Delta H}{RT} + constant\ (2)$$

$$\Delta G = -RT\ LnK\ (3)$$

ΔS can be found from the ΔG equation

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

$$Ln\ K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}\ (5)$$

If ln K plot vs 1/T, we would find a straight line having a slope of - ΔH/ R and an intercept ΔS/R.

Figure 8 and Table 1 demonstrate these factors, whereas Table 2 shows the thermodynamic values of estimating dye adsorption onto hydrogel. Table 2 found that the enthalpy value is positive for an endothermic reaction, and the value of free Gibbs energy is negative, which is a spontaneous reaction.

CONCLUSION

In this study, a polymer formed (p(AA-co-MA)) was prepared. Graphene oxide was loaded (GO/ p(AA-co-MA)) on it to increase the surface area and surface efficiency in removing the dye, where the adsorption efficiency reached (83.58 mg/g). The pH was studied, and it was better (pH 10) in the alkaline medium, and the thermodynamic functions were analyzed. It was found that the reaction was spontaneous.

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