



## The Adsorptive Removal of Rhodamine 6G Dye from Aqueous Solution by Using Poly (Fumaric Acid-Co-Acrylic Acid) Hydrogels

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### Abstract

The removal of rhodamine 6G from aqueous solutions was achieved by adsorption using poly (fumaric acid-co-acrylic acid) as adsorbent surface. Several variables that affect the adsorption were studied including adsorbent dosage, contact time, pH, temperature and ionic strength. The results indicate that hydrogel has a strong capability of removing rhodamine 6G dye directly from aqueous solutions. The equilibrium adsorption data is analyzed using three common adsorption models: Langmuir, Freundlich and Temkin. The Thermodynamic parameters  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  are calculated for the adsorption rhodamine 6G onto hydrogel.

**Keywords:** *Hydrogels, Rhodamine6G, Adsorption, Isotherms, Thermodynamic.*

### Introduction

Now a day the growing population has led to the increase contamination of river water, ground water and surface in recent years [1]. Treatment of industrial wastewater is more necessary in the near future due to international regulations which mandate the reduction of different compounds in the cleaned water [2]. In recent years dye contamination has become a serious environmental and social problem due to their environmental toxicity and public health damage [3]. Dyes have long been used in different types of industries such as, dyeing, textiles, paper, plastics, leather, food and cosmetics [4, 5].

The presences of dyes in water are causing problems, such as, reducing oxygen levels in water; interfering with penetration of sunlight into waters; retarding photosynthesis and interfering with gas solubility in water bodies [6]. There are several methods to eliminate this pollutant such as electrochemical treatment [7], coagulation [8], chemical oxidation [9], liquid-liquid extraction [10], membrane filtration [11], flocculation [12], photocatalysis [13] and adsorption [14]. Among these methods, adsorption is the most widely used one because of its ease of operation and comparably low cost [15], simple design [16], high efficiency [17], insensitivity to toxic

substances[18]. Many adsorbents have been tested for the adsorption of dyes from aqueous solutions, such as activated carbon, chitosan, lignin, bentonite, clay, silica gel, and polymeric materials [19, 20]. Hydrogels are three-dimensional polymer networks made up of hydrophilic polymers, crosslinked to form a water-insoluble material that may absorb from 20% up to thousands of times their dry weight in water [21, 22]. Recently hydrogels as novel soft materials have been paid special attention for the efficient adsorption of guest molecules such as heavy metal ions, proteins and water soluble dyes [23].

### Materials and Methods

#### Instruments

- UV-Visible spectrophotometer, Double Beam, Shimadzu. PC 1650, Japan.
- UV-Visible Spectrophotometer, Single Beam, UV -7310, Jenway, UK
- Electronic Balance, Sartorius Lab. L420 B, +0.0001.
- Dunboff metabolic shaking Incubater GCA/precision Scientific.
- Centrifuge tubes, Hettich Universal (D-7200).
- Ph-meter, pH-3110, Intertek, Germany.

- Oven, Memort LOD-080N, Jlabtech, Korea.
- Hotplate-Stirrer, L-81, Jlabtech, Korea.

## Materials

Fumaric acid and acrylic acid were supplied by (Himedia, India). The initiator, potassium persulfate (KPS) was supplied by (Merck, Germany). The multifunctional cross linker is N, N'-methylene bisacrylamide (NMBA) was purchased from (Fluka, Germany). Sodium chloride was obtained from (Fluka, Germany). Rhodamine 6G was purchased from (Merck, Germany) and was used without any further purification. Sodium Hydroxide and Hydrochloric acid were purchased from (Fluka, Germany). All solutions used in experiments were prepared in deionized water.

## Dye Adsorption Experiments

Solutions of dye (10ml) of known concentrations 5-200 ppm were added to stoppered flasks containing 0.1 g of hydrogel powder. The flasks were shaken in a thermostatically controlled water bath at a speed of 150 rpm until equilibrium is attained 90min. This time is sufficient for the adsorption process to reach equilibrium in each case. After the equilibrium time elapsed, the suspensions were centrifuged at 3000 rpm for 10min. A small amount of solution was taken and the concentration of dye was determined by UV-vis spectroscopy using standard calibration curve. Measurements were conducted at  $\lambda_{\max}$  of Rh.6G (530nm). The quantity of dye adsorbed was calculated according to the following equation [24].

$$q_e = \frac{C_0 - C_e \times V_{\text{sol}}}{m} \quad (1)$$

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

## Results and Discussion

### Adsorption Study

#### Effect of adsorbent dosage

The influence of adsorbent dosage on dye adsorption was evaluated by varying the adsorbent dosage which ranged from 0.01 to 0.3 gm by keeping the constant initial dye concentration at 100 mg/L. The results are

shown in (Fig .1). As seen in the (Fig. 1), a rapid increase in amount of adsorbed dye ( $q_e$ ) with increasing the adsorbent dosage was attributed to greater surface area and availability of more adsorption sites. At the same time, however, the amount of adsorbed dye molecule ( $q_e$ ), decreased from 9.697 to 7.847 mg/g when the adsorbent dosage increased from 0.15 to 0.3 gm. The decrease of adsorption capacity was due to the splitting effect of flux or concentration gradient between dye molecules and adsorbent. Hence, by increasing the adsorbent dosage in adsorption medium, the value of  $q_e$  was reduced [25, 26].

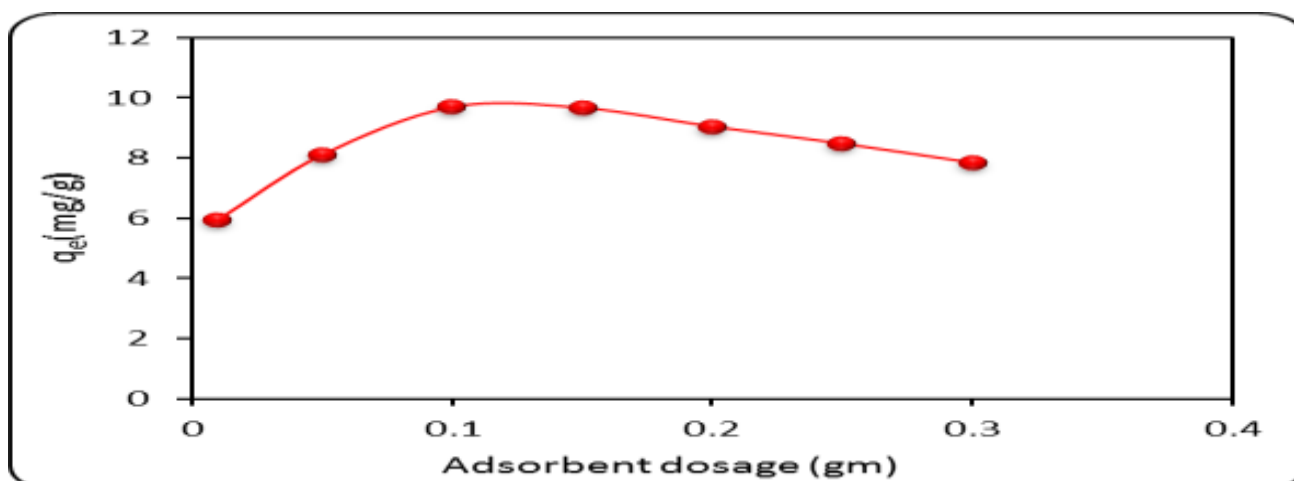


Fig.1: Effect of adsorbent dosage on the adsorption of Rh.6G dye onto hydrogel surface (solution volume = 10mL, dye concentration = 100mg/L, temperature = 15 °C and pH= 7)

### Effect of Contact Time

Fig. 2 shows the effect of contact time on adsorption of Rh.6G on the adsorbent. It can be seen that adsorption capacity increases rapidly at the initial stages of adsorption. Adsorption is very fast in the first 60 minutes

of the experiment and then increases slowly and reaches to equilibrium after 90 min. This is because vacant surface sites of the adsorbents are blocked within the first stages of the adsorption and thus diffusion and adsorption of further dye molecules becomes more difficult [27].

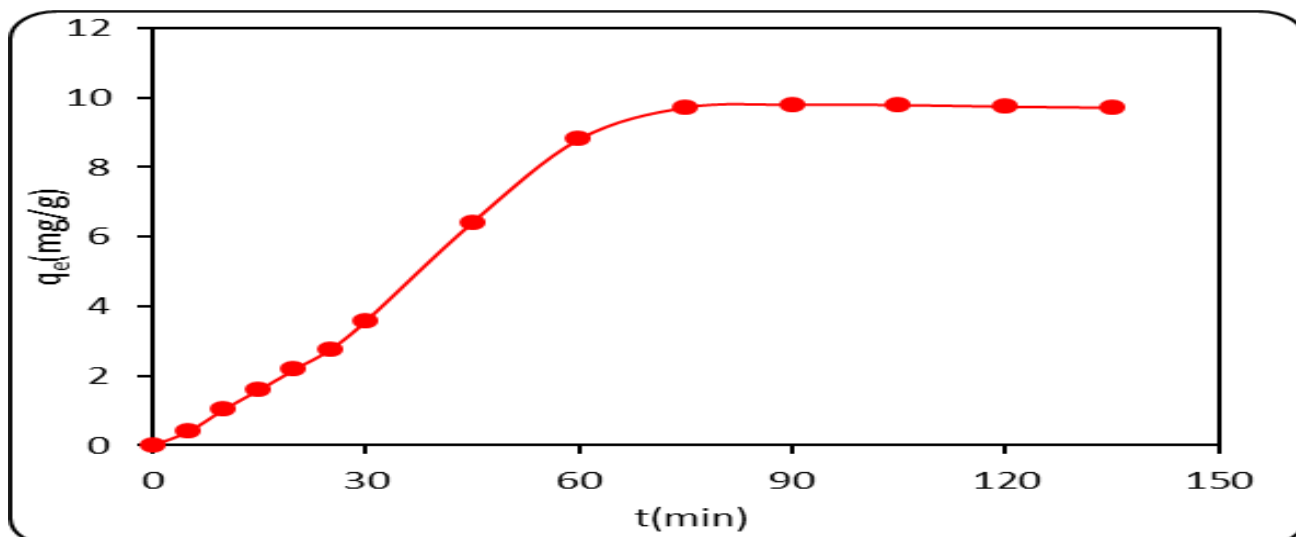


Fig. 2: Effect of contact time on the adsorption of Rh.6G dye onto hydrogel surface (adsorbent dosage = 0.1gm, solution volume = 10mL, dye concentration = 100mg/L, temperature = 15 °C and pH= 7)

### Effect of pH

Since pH of the solution has a strong effect on dye adsorption, experiments were conducted in solutions with different pH adjusted by the addition of HCl or NaOH

solutions (0.01 N). Adsorption of Rh.6G in solutions with pH range from 1 to 12 was investigated and the results are shown in (Fig. 3).

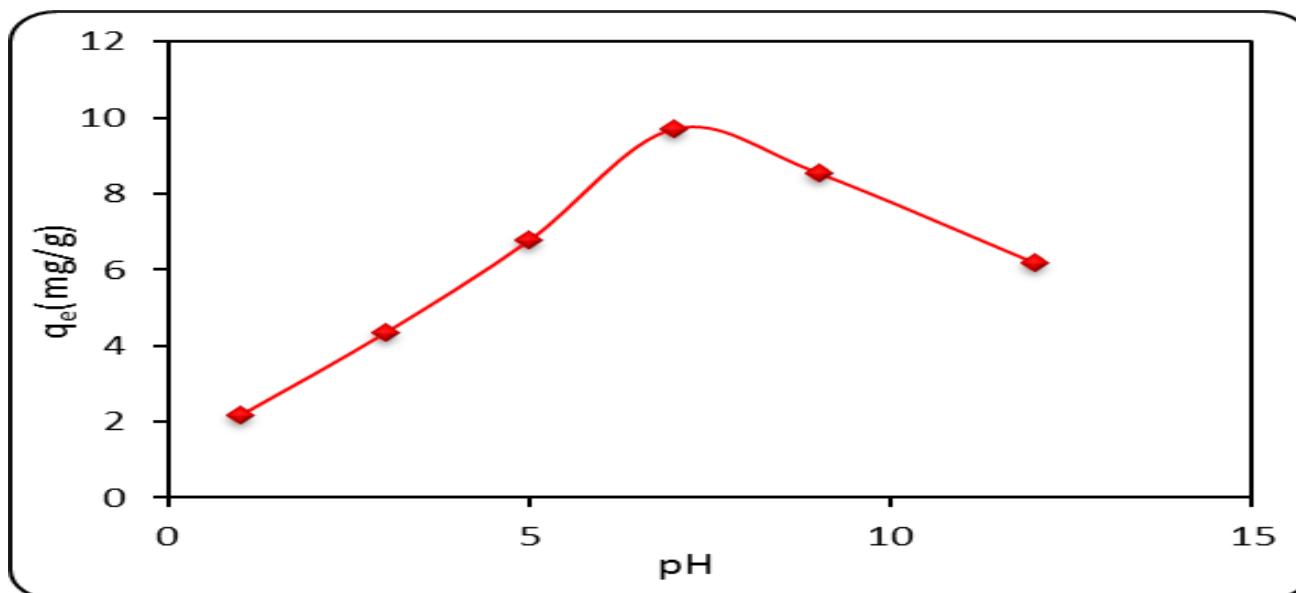


Fig. 3: Effect of pH on the adsorption of Rh.6G dye onto hydrogel surface (adsorbent dosage = 0.1gm, solution volume = 10mL, dye concentration = 100mg/L, temperature = 15 °C)

The solution pH is found to play an important role in the adsorption process because it strongly influenced the binding sites of the adsorbent and the ionization process, Initially, the percentage adsorption was observed to increase with increasing

solution pH, reaching a maximum at pH 7, (Fig. 3).

This increase in the percentage adsorption was due to the availability of more adsorption sites with increasing pH. The

adsorption of dyes on the hydrogel surface generally followed an ionic interaction mechanism in which the surface of the adsorbent determines the type of interactions between the binding sites of the adsorbent and the adsorbate molecules [28]. Therefore, in the solutions of strongly acidic pH, the percentage adsorption was notably low, whereas the percentage adsorption increased with increasing solution pH. The lower percentage adsorption at highly acidic pH can also be attributed to the competitive adsorption of dye molecules with H<sup>+</sup> ions because the concentration of H<sup>+</sup> ions is notably high in strong acidic solutions.

The hydrogel have most anionic binding site; therefore, H<sup>+</sup> ions in an acidic solution compete with cationic dye Rh.6G molecules to interact with anionic binding sites and consequently decrease the adsorption percentage [29]. In contrast, at higher solution pH values from 9 to 12, the excess

Na<sup>+</sup> ions were responsible for the screening effect; the sodium ion basically shields the COO<sup>-</sup> ions in the hydrogel, resulting in a decreased an ionic interaction between cationic dye and hydrogel [30].

### Effect of Temperature and Thermodynamic Study

The effect of temperature on adsorption of Rh.6G on the surface was investigated at different temperatures (15, 20, 30 and 35 °C). The results are shows in (Fig. 4), which shows that the adsorption capacity (q<sub>e</sub>) decreased with an increase in temperature.

The increase in temperature may increase the solubility of the solute, hence decreasing its adsorption affinity towards the surface, in addition, the kinetic energy of dye molecules is enhanced and this weakens the attractive forces between the dye molecules and the binding sites available on the adsorbent surface [31, 32].

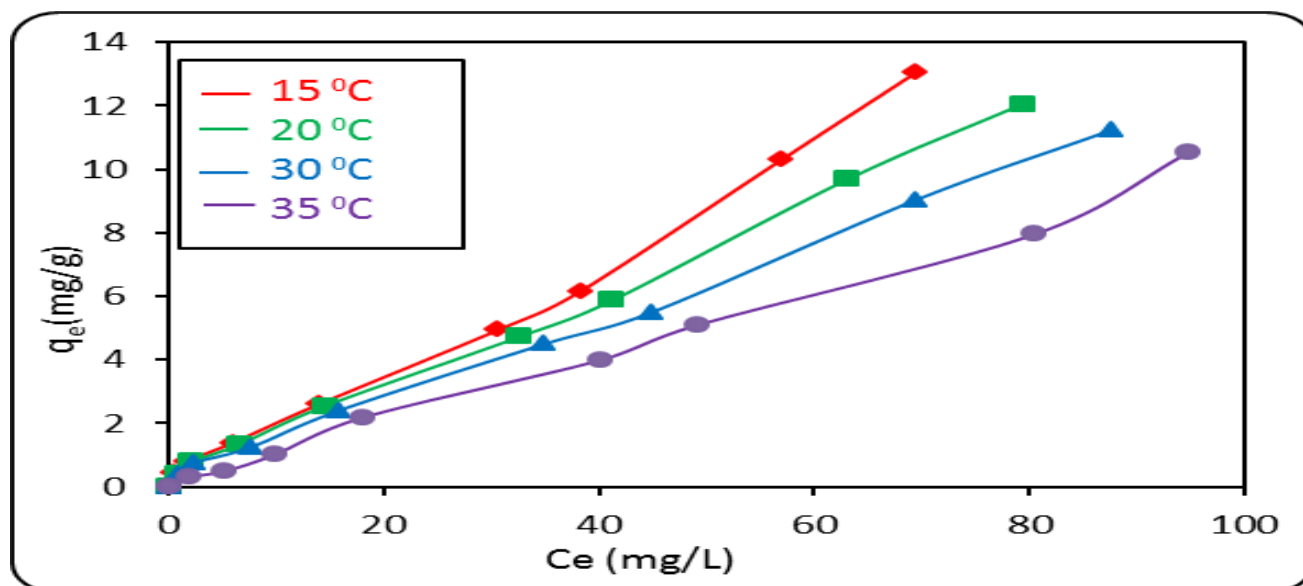


Fig.4: Adsorption isotherms of Rh.6G dye onto hydrogel surface at different temperatures (adsorbent dosage = 0.1gm, solution volume = 10mL dye concentration = 5-200mg/ L and pH= 7)

The thermodynamic behavior of the adsorption of dye onto the hydrogel was investigated through the determination of parameters such as the standard free energy

$$\ln x_m = -\Delta H/RT + \text{constant} \quad (2)$$

$$\Delta G = -RT \ln K_{eq} \quad (3)$$

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

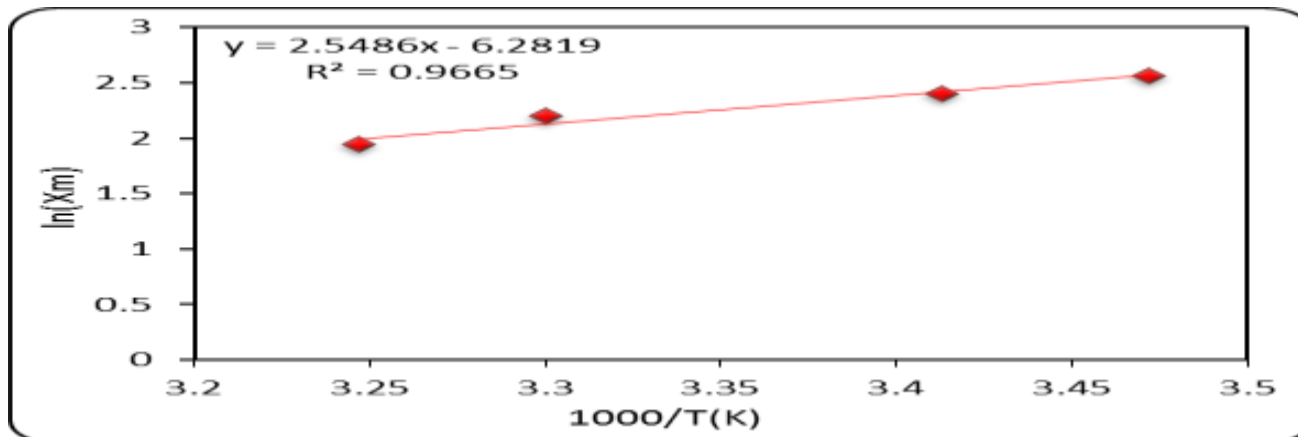
Where, T is absolute temperature in K and R is gas constant (8.314 J K<sup>-1</sup>mol<sup>-1</sup>), K<sub>eq</sub> is equilibrium constant. Value of ΔH was calculated from the intercept and slope of the plot of lnX<sub>m</sub> vs 1/T as show in (Table .1 )

change known as Gibbs free energy (ΔG, kJ.mol<sup>-1</sup>), entropy change (ΔS, J.mol<sup>-1</sup>.k<sup>-1</sup>) and enthalpy change (ΔH, kJ.mol<sup>-1</sup>) were calculated by using following equations:

and (Fig. 5) whereas; ΔG was calculated from Eq. (3) [33, 34]. These values of thermodynamic parameters are shown in (Table .2).

**Table 1: Effect of temperature on the maximum adsorbed quantity for adsorption of Rh.6G dye onto hydrogel surface**

Dye	T °C	T K	1000/T K <sup>-1</sup>	C <sub>e</sub> = 70 mg/L	
				X <sub>m</sub>	ln X <sub>m</sub>
Rh.6G	15	288	3.472	13	2.564
	20	293	3.412	11	2.397
	30	303	3.300	9	2.197
	35	308	3.246	7	1.945



**Fig. 5:** Plot of lnX<sub>m</sub> against reciprocal absolute temperature for the adsorption of Rh.6G dye onto hydrogel surface

**Table 2: Thermodynamic parameters for the adsorption of Rh.6G dye onto hydrogel surface**

Dye	$\Delta H$ (kJ.mol <sup>-1</sup> )	$\Delta G$ (kJ.mol <sup>-1</sup> )	$\Delta S$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )	Equilibrium k <sub>eq</sub> (Constant)
Rh.6G	-17.190	-1.482	-54.543	1.857

The negative value of the  $\Delta H$  for the adsorption of dye on hydrogel indicated that the adsorption was an exothermic process and  $\Delta H$  value were < 20 kJ.mol<sup>-1</sup> so adsorption process is a physical adsorption [ 35] ; while the values of  $\Delta S$  and  $\Delta G$  were both negative . The negative value of  $\Delta S$  suggests a decrease in the degree of freedom of the adsorbed species, The negative value of  $\Delta G$  indicates the spontaneous nature of the adsorption of dye molecules onto hydrogel [36].

**Adsorption Isotherms**

The adsorption isotherm indicates the

distribution of adsorbed molecules between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The analysis of isotherm data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purpose. The adsorption capacity of this system was investigated with the Langmuir, Freundlich and Temkin adsorption isotherms [37].

**Langmuir Isotherm**

Langmuir isotherm is valid for monolayer adsorption. The linearized form of the equation is expressed as [38]:

$$\left(\frac{1}{q_m \cdot K_L} + \left(\frac{1}{q_m}\right) \cdot C_e\right) = \frac{C_e}{q_e} \tag{5}$$

Where C<sub>e</sub> is equilibrium concentration of Rh.6G in solution, q<sub>e</sub> is the amount of Rh.6G adsorbed at equilibrium, q<sub>m</sub> is Langmuir monolayer adsorption capacity, and K<sub>L</sub> is Langmuir constant related to equilibrium

constant of the adsorption dye, the plots of C<sub>e</sub> /q<sub>e</sub> versus C<sub>e</sub> at different temperatures, the slope and the intercept of the linear plots gave the values of q<sub>m</sub> and K<sub>L</sub>, respectively as shown in (Table .3) and (Fig. 6).

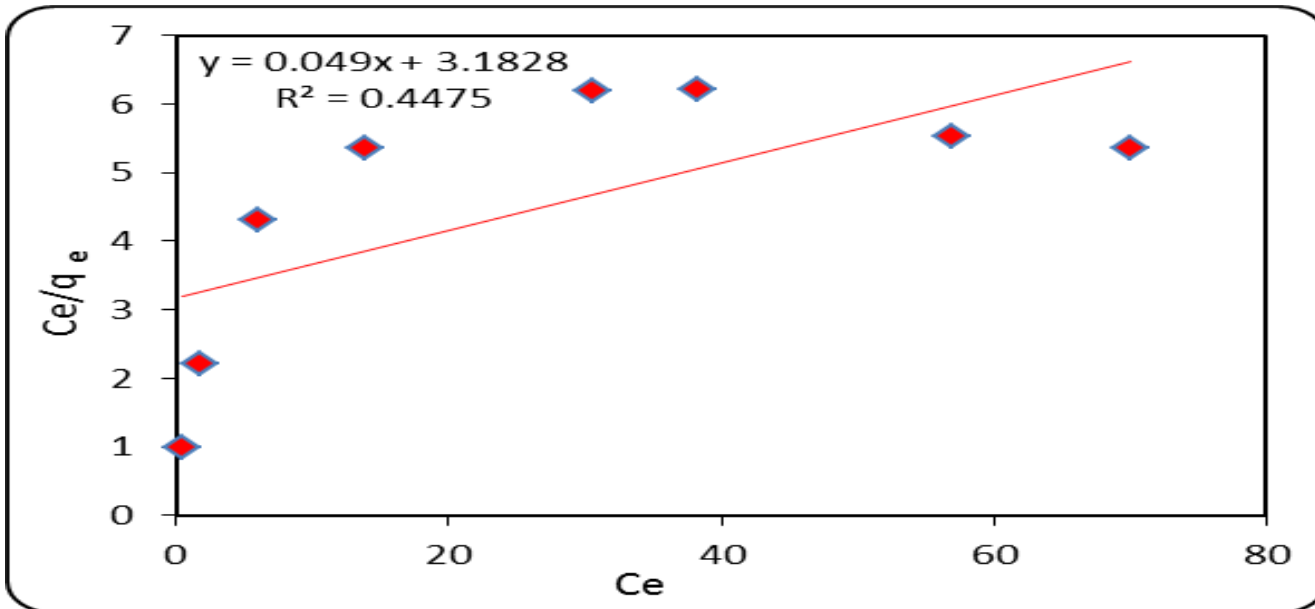


Fig. 6: Langmuir plots for the adsorption of Rh.6G dye onto hydrogel surface at 15°C

**Freundlich Isotherm**

Is a valid multilayer sorption on heterogeneous surface of indefinite number of

binding sites. The linear form of Freundlich equation may be written as [39]:

$$\text{Log } q_e = \text{log } K_f + n \text{ log } C_e \quad (6)$$

Where,  $C_e$  and  $q_e$  are the equilibrium concentration of Rh.6G in solution (mg / L) and the sorption capacity of Rh.6G per unit weight of hydrogel (mg / g), respectively. The Freundlich coefficients  $K_f$  and  $n$ , are related to adsorption capacity and adsorption

intensity of the hydrogel, respectively, were obtained from the slope and the intercept of the linearized Freundlich plots ( $\text{log } q_e$  versus  $\text{log } C_e$ , (Fig. 7) . The values of  $K_f$  and  $n$  along with correlation coefficients ( $R^2$ ) are shown in (Table. 3).

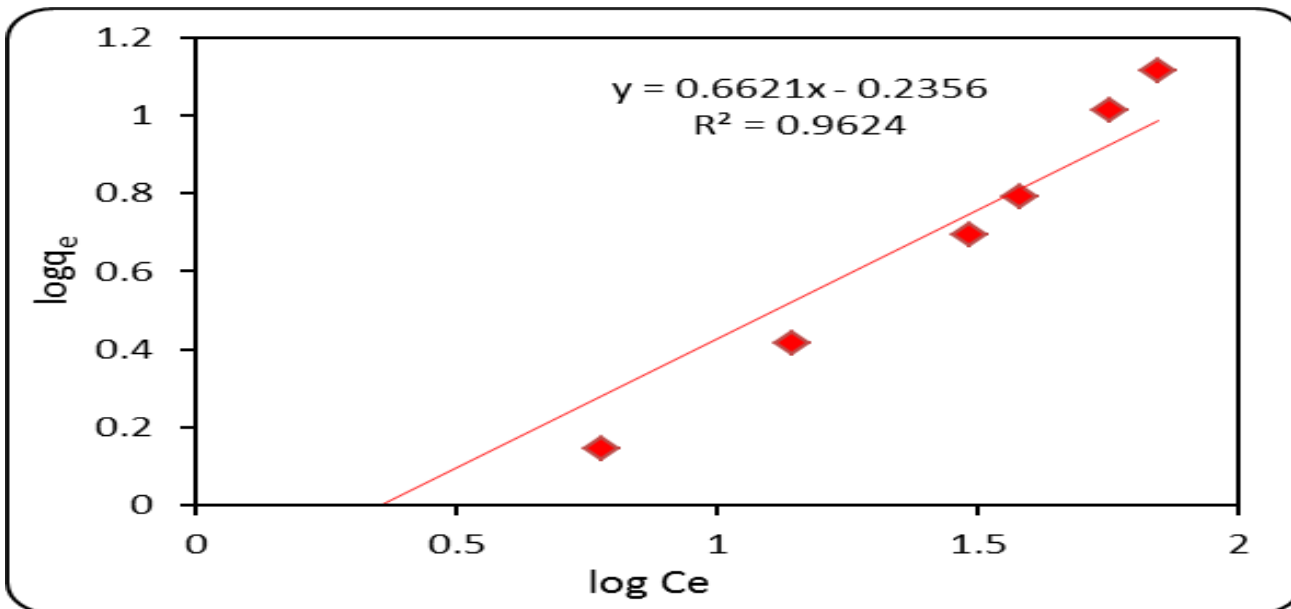


Fig. 7: Freundlich plots for the adsorption of Rh.6G dye onto hydrogel surface at 15°C

**Temkin isotherm**

Temkin isotherm Eq. (7) assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to

adsorbate species–adsorbent interactions, and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [40].

$$q_e = \beta \ln K_T + \beta \ln C_e \quad (7)$$

Where,  $q_e$  is the amount of dye adsorbed per unit weight of adsorbent (mg/g) ,  $k_T$  is Temkin constant ,  $\beta$  is representing the intensity of adsorption.

The linear plot of  $q_e$  versus  $\ln C_e$  (Fig. 8) and the values of  $k_T$  and  $\beta$  are given in (Table. 3).

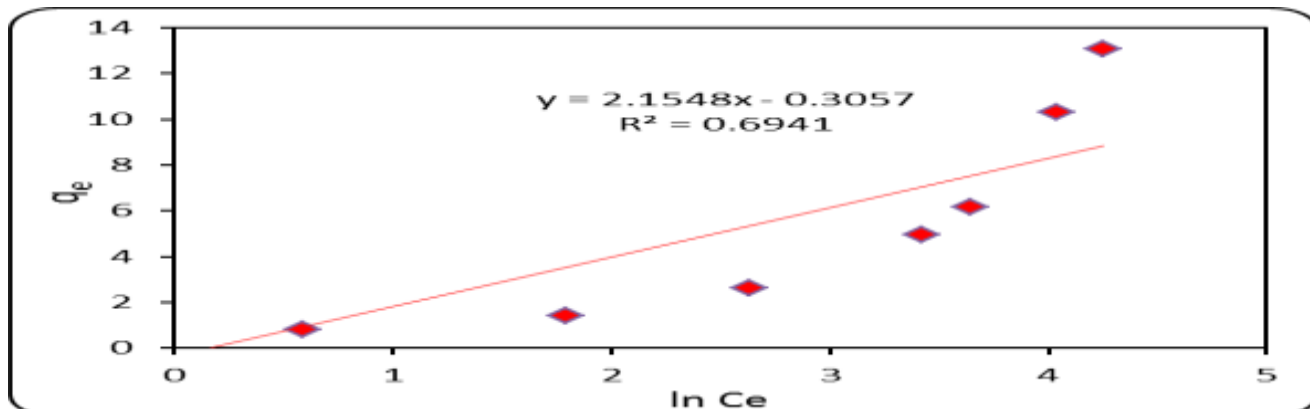


Fig. 8: Temkin plots for the adsorption of Rh.6G dye onto hydrogel surface at 15°C

Table 3: Isotherm parameters for the adsorption of Rh.6G dye onto hydrogel surface

Dye	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	k <sub>L</sub>	q <sub>m</sub>	R <sup>2</sup>	K <sub>f</sub>	n	R <sup>2</sup>	K <sub>T</sub>	β	R <sup>2</sup>
Rh.6G	0.0242	16.181	0.4475	0.636	1.543	0.9624	0.937	2.12	0.6941

In order to determine the best fit isotherm model the correlation factors for all studied isotherm models (Table .3) were compared. The correlation coefficients for Freundlich (R<sup>2</sup> = 0.9624) was highest in comparison to the values obtained for Langmuir isotherm (R<sup>2</sup> = 0.4475) and Temkin isotherm (R<sup>2</sup> = 0.6941). Therefore, Freundlich isotherm found to best fit the equilibrium data for adsorption of Rh.6G onto hydrogel surface [41]. The Freundlich exponents, n, were greater than (n > 1) represents a favorable adsorption condition [42].

**Effect of Ionic Strength**

The influence of ionic strength on adsorption was investigated by introducing variable salt weights (0.01-0.3gm) of sodium chloride into the dye solution.

The results are presented in (Fig. 9), which shows that with the increase of NaCl concentration the adsorption amount of dye decreased constantly. High ionic strength is detrimental to the swelling of the hydrogel, which thereby hinders the full contact of dye molecules with the adsorbent. Besides, salt screens the electrostatic interaction between the adsorbent and dye molecules [43].

The increasing of salt concentration causing a decreasing in q<sub>e</sub> due to a strong competition between the sodium ions and dye ions in the adsorption on active sites the surface including sodium ions characterize by a smaller size compared with dye ions. So the adsorption of sodium ions is faster than the adsorption of dye ions [44].

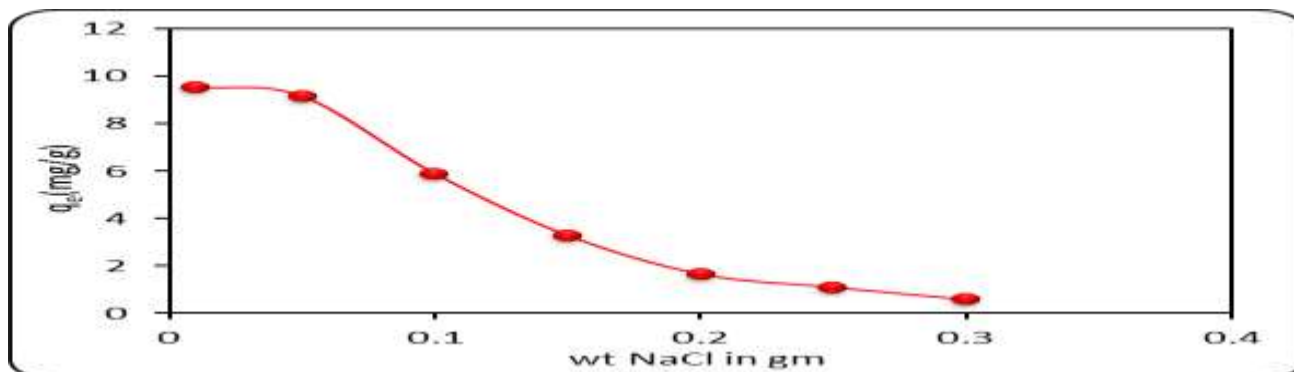


Fig.9: Influence of ionic strength on the adsorption of Rh.6G dye on hydrogel surface (adsorbent dosage = 0.1gm, solution volume = 10mL, dye concentration = 100mg/L, temperature = 15 °C and pH= 7)

## Conclusion

The data show that poly (fumaric acid-co-acrylic acid) hydrogel can be used effectively for the removal of rhodamine 6G dye from an aqueous solution. 0.1g is the optimum dosage of hydrogel to adsorb rhodamine 6G dye. The contact time for the maximum adsorption of the rhodamine 6G on hydrogel surface required is 90 minutes.

The adsorption capacity of the rhodamine 6G dye onto hydrogel increases with an increase the pH and the maximum removal occurred at pH=7. The equilibrium adsorption capacity of rhodamine 6G decreased with increasing the temperature and the maximum removal

occurred at 15°C. The adsorption of rhodamine 6G onto hydrogel is described using the Langmuir, Freundlich and Temkin adsorption isotherm models. The equilibrium data fitted with the Freundlich isotherm. The adsorption of rhodamine 6G is found to be spontaneous and negative value of  $\Delta H$  indicated that the adsorption process is exothermic.

The equilibrium adsorption capacity of rhodamine 6G decreased in the presence of sodium chloride in the solution. Therefore, it can conclude that poly (fumaric acid-co-acrylic acid) hydrogel can be used for the removal of pollutants from aqueous solutions.

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