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Poly(methyl methacrylate-ethylene glycol dimethacrylate) copolymer for adsorptive removal of erythrosine dye from aqueous solution

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ABSTRACT

The preparation and characterization of poly(methyl methacrylate-ethylene glycol dimethacrylate), (poly(MMA-EGDMA)) polymer for erythrosine adsorption has been investigated. Erythrosine is a synthetic red dye used to color food. Water-soluble acid dyes have caused serious water pollution. Poly(MMA-EGDMA) polymer showed better adsorption performance for erythrosine at acidic region and at 30°C. The adsorption process had also been verified by Langmuir and Freundlich adsorption isotherms at 30, 40, and 50°C. Free energy of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were calculated to predict the nature of adsorption. The estimated value for ΔG° was calculated as −125.6 kJ/mol at 303 K (30°C). The estimated value for ΔH° was found as −60.69 kJ/mol at 303 K. The negative value for ΔH° indicated that the adsorption of erythrosine on poly(MMA-EGDMA) polymer was an exothermic process.

Keywords: Erythrosine; Poly(MMA-EGDMA); Dye removal; Adsorption isotherm; Thermodynamic parameters

1. Introduction

Water-soluble acid dyes are used widespread as coloring agents in a variety of products such as foodstuff, paper, textiles, and leather [1–3]. For example, 1,000 tones/year or more of dyes are discharged into waste streams by textile industries alone worldwide [4]. Some of water-soluble acid dyes are permitted in foodstuff too. Acceptable daily intake values of water-soluble acid dyes are strictly controlled by laws and regulations in various countries [1]. Acceptable daily intake values for erythrosine are 0–0.1 mg/kg [5]. Unfortunately, these dyes are still illegally used as additives in foodstuffs to enhance the appearance of products. These dyes are carcinogenic [6,7], causes reproductive and neurological disorders [8,9], hyperactivity [10], severe allergies [11], sensitivity to light, including rashes, swelling, and trouble in breathing in human beings [12]. Furthermore, water-soluble acid dyes have caused serious environmental pollution [13]. Erythrosine is highly water soluble and belongs to the xanthene class of dyes. It consists essentially of disodium 2-(2,4,5,7-tetraiodo-3-oxidooxoxanthen-9-y1) benzoate monohydrate. Erythrosine is widely used in dyeing a variety of materials such as wool, silk, and nylon. It is also used as a colorant in drugs, cosmetics, plastics, cocktails, tinned cherries and fruits, biscuits, chocolates, garlic sausages, salmon spreads, scotch eggs, stuffed olives, sweets, bakery items, snack foods, chewing gums, jellies, wines, drugs, ice creams, coloring food, in printing inks, lipstick and pharmaceutical industries, etc [14–16]. This dye is highly toxic, causes

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various types of allergies, thyroid activities, carcinogenicity, DNA damage behavior, neurotoxicity, and xenoestrogen nature in the humans and animals [14,17]. Water-soluble acid dyes have caused serious water pollution [1]. A secondary pollution problem in these processes will arise because of excessive chemical use. Industry wastewater removal methods involve physical and/or chemical processes [18–21]. Several methods have been developed for water-soluble acid dyes to be removed from wastewater. However, several commercially available methods are expensive and therefore researchers are investigating cheaper ways [22].

In this study, the preparation and characterization of poly(methyl methacrylate-ethylene glycol dimethacrylate) (poly(MMA-EGDMA)) polymer for Erythrosine adsorption has been investigated. The experiments were carried out in a batch system to optimize operation variables: contact time, adsorbent dosage, erythrosine concentration, temperature, and pH. Adsorption isotherms were analyzed by Langmuir and Freundlich adsorption isotherms for different temperatures. Thermodynamic parameters were also calculated.

2. Experimental

2.1. Reagents

Erythrosine (KRK Gıda, İstanbul, Turkey) is a commercial product and its structure is shown in Fig. 1. 1´1´Azobis(cyclohexanecarbonitrile), ethanol, methanol, dimethyl sulfoxide (DMSO), methyl methacrylate (MMA), and ethylene glycol dimethylacrylate (EGDMA) were obtained from Sigma–Aldrich (USA). Doubly distilled water was used throughout this study. Other chemicals were of laboratory reagent grade and used without further purification.

2.2. Preparation of poly(MMA-EGDMA)

Polymer was prepared by MMA as the functional monomer, EGDMA as a crosslinker and the polymerization was initiated by adding 1´1´Azobis(cyclohexanecarbonitrile). MMA (4 mmol) and EGDMA (20 mmol) were dissolved in 4 mL porogenic solvent DMSO. After the pre-polymerization process at room temperature, 50 mg 1´1´Azobis(cyclohexanecarbonitrile) was added to the mixture to start the polymerization process. The mixture was sonicated for 10 min. and then the solution was deoxygenated with nitrogen gas for 5 min, because the presence of dissolved oxygen in the solution prevents the free radical polymerization. After that, the flask was sealed carefully and then polymerization was carried out in a water bath at 60°C for 24 h. The consisting polymer was crushed and powdered.

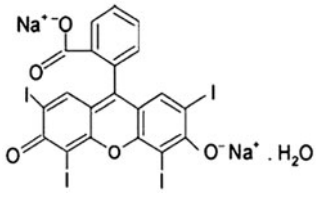

Fig. 1. The chemical structures of erythrosine.

2.3. Spectrophotometric analysis

A series of standard solutions (0.001–0.008 mM) were prepared from the stock solution of erythrosine (0.015 mM) in distilled water. The changes in absorbance were determined with a Perkin–Elmer Lambda 35 Spectrophotometer, using distilled water as reference. The measurements were taken at λ_{max} 525 nm.

2.4. Adsorption studies

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms [23]. The adsorption experiments were carried out in a batch process by using aqueous solution of erythrosine with poly(MMA-EGDMA) and experiments were conducted to observe the effect of various parameters such as contact time, amount of adsorbent, pH, temperature, and dye concentration. The adsorption characteristics of erythrosine were studied at a varying pH range from 3.5 to 8.5. The adsorption of erythrosine was also recorded in the concentration range from 1×10^{-5} to 1×10^{-4} M at a fixed pH of 3.5 and temperatures 30, 40, and 50°C.

2.5. Characterization

The synthesized poly(MMA-EGDMA) has been characterized using different analytical techniques such as FTIR (FT-IR Perkin Elmer Spectrum BX), scanning electron microscope (SEM) (XL30-SFEG, FEI/Philips), and by TGA/DSC (TGA analyzer, Perkin Elmer SII 7300) in nitrogen atmosphere. The polymer was heated from 25 to 800°C at a constant heating rate of 10°C min^{-1}.

3. Results and discussion

3.1. FTIR analysis

The surface chemistry FTIR spectra of poly(MMA-EGDMA) is presented in Fig. 2. FTIR transmission spectra were acquired in the range of 4,000–400 cm^{-1}

using a Fourier Transform Infrared spectrometer (FT-IR) (FT-IR Perkin–Elmer Spectrum BX). All samples were previously dried for 24 h at 60°C to avoid water-related bands interference. It can be seen from Fig. 2(a) that poly(MMA-EGDMA) exhibited a stretching vibration band of –CH at a wavelength of 2,955 cm^{-1}. The peak at 1,733 cm^{-1} was assigned to stretching vibration band of C–O, while the peaks at 1,456 and 1,164 cm^{-1} were assigned to the stretching vibration bands of $–CH_3$ and $–O–CH_3$, respectively. After the adsorption of dye into polymers, new peaks were observed at 1,637–1,616 and 3,483–3,412 cm^{-1} (Fig. 2(b)).

3.2. TGA analysis

Thermal stability of the hydrogels has been determined by thermogravimetric studies. This technique reveals the loss of mass of a given substance during the heating process [24]. The TG and DTG curves recorded for poly(MMA-EGDMA) is given in Fig. 3. The thermal degradation of poly(MMA-EGDMA) occurred over a wide temperature range in nitrogen atmosphere (330–470°C) and two stages of weight loss were observed. poly(MMA-EGDMA) (2.96 mg) exhibited a major DTG peak near 383°C and the effect corresponded to a 54% loss. The second step was around at 435°C and 73% weight loss was observed. Kashiwagi et al. showed that for poly(methyl methacrylate) complete degradation is observed at 450°C [25].

3.3. SEM analysis

The morphology of the prepared polymer was investigated using SEM imaging. As represented in Fig. 4 at two different resolutions, the polymer showed a typical morphology of crushed materials, presenting random shapes and sizes due to the necessary grinding of the material. There are many micropores on the surface of poly(MMA-EGDMA), facilitating the fast binding of dye molecules.

3.4. Effect of contact time

Effect of contact time on the adsorption capacity of erythrosine by poly(MMA-EGDMA) was studied. The contact time between the polymer and the dye solution is one of the most important parameters that affect the performance of an adsorption process. The initial concentration of dye solution was 0.015 mM and 5 ml of the dye solution was added on to a specific amount of polymer. Fig. 5 shows the removal efficiency of erythrosine as a function of incubation

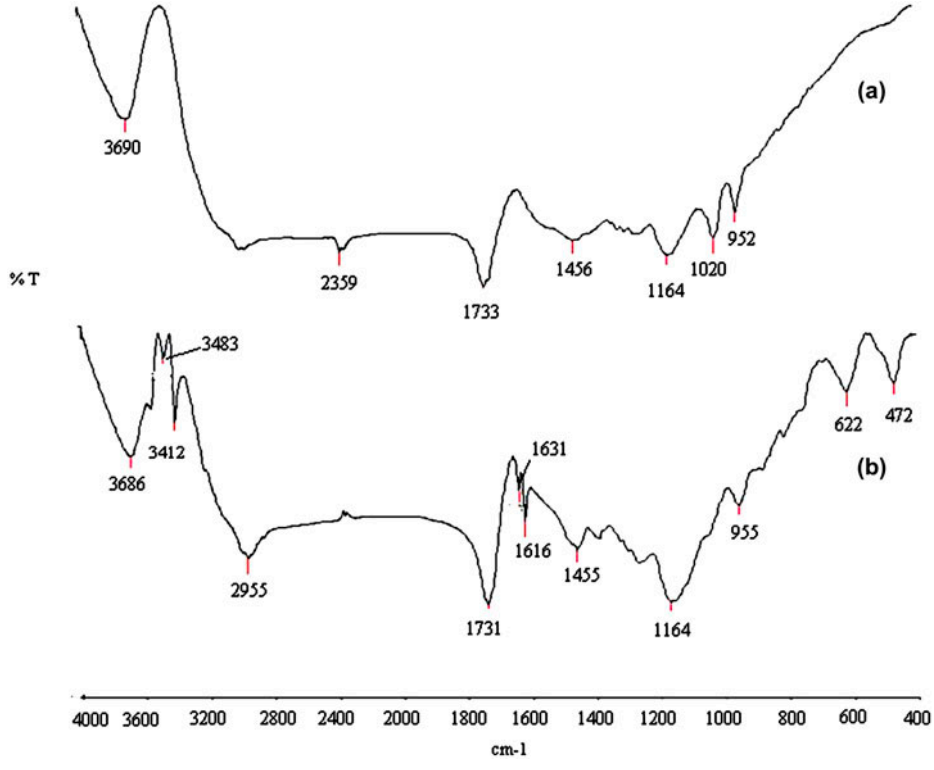

Fig. 2. FTIR spectra of (a) untreated poly(MMA-EGDMA), (b) dye-adsorbed poly(MMA-EGDMA).

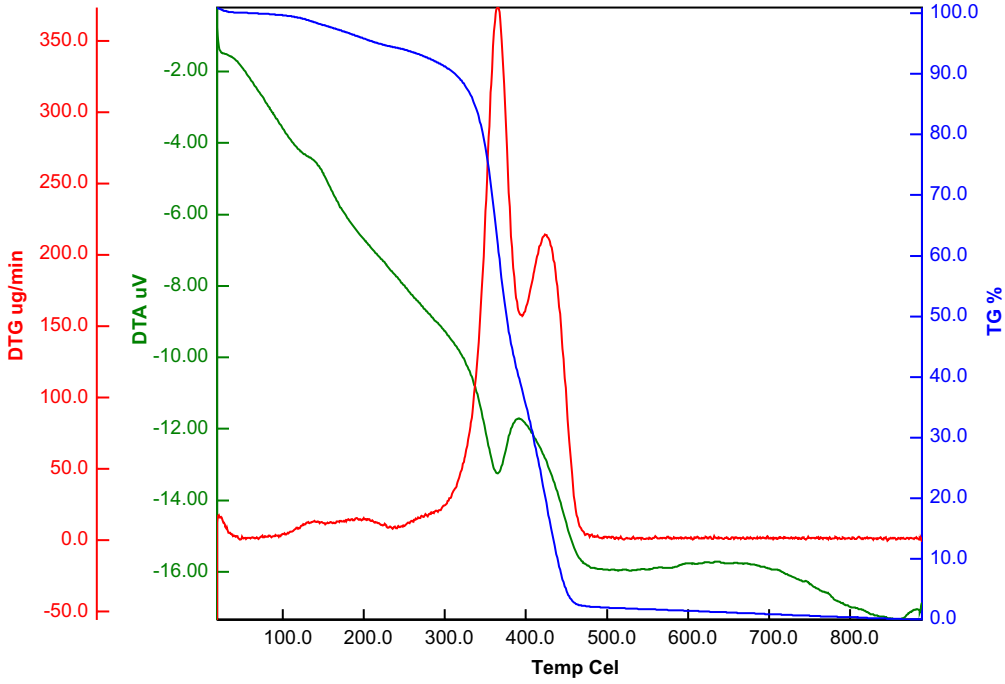

Fig. 3. TG thermograms and DTG curves of poly(MMA-EGDMA).

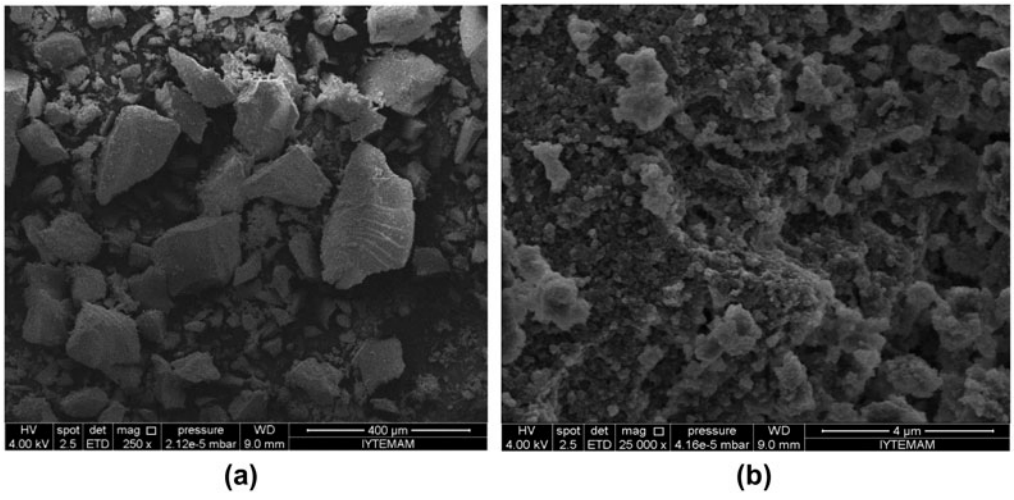

Fig. 4. SEM micrographs of poly(MMA-EGDMA).

times ranging between 5 and 240 min. The results show that the adsorption is very rapid. The adsorption efficiency of erythrosine increased to 30% in five minutes of contact time and the time required to attain equilibrium was determined as 75 min.

Kaur and Datta studied erythrosine B adsorption onto montmorillonite, and they reported that the adsorption process was found to be extremely rapid with 99% of the dye having the initial concentration of 50 mg/dm^3 being adsorbed in the first minute of the contact time. Dye adsorption reached the equilibrium within 5 min of the contact time showing 99.7% uptake [26].

3.5. Effect of adsorbent dose

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for

a given initial concentration of the adsorbate [27]. To investigate the adsorption capacity of the copolymer, different amounts of polymers ranging from 5 to 50 mg were incubated with the dye solution (0.015 mM) for 75 min. As the polymer dosage increases, the amount of adsorbed erythrosine is increased and better adsorption is observed. In this study, the results were calculated as the adsorption capacity (μg/g) for the determination of an appropriate amount of polymer. Maximum adsorption was observed when 20 mg polymer dose was used and this polymer amount was chosen for further studies (Fig. 6).

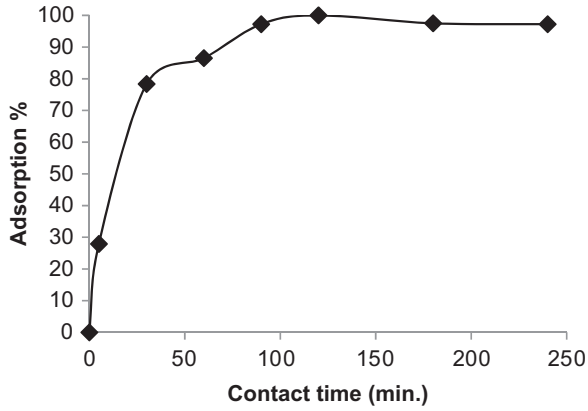

Fig. 5. Effect of contact time on the adsorption capacity of poly(MMA-EGDMA). Experiment conditions: initial dye concentration 0.015 mM; adsorbent dosage 50 mg; temperature 30˚C; stirring rate 100 rpm.

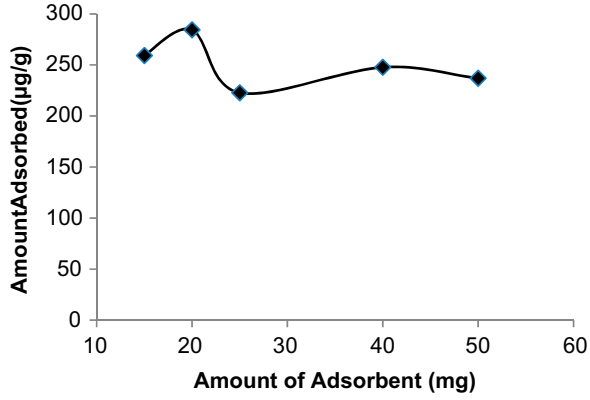

Fig. 6. Effect of adsorbent dosage on the adsorption capacity of poly(MMA-EGDMA). Experiment conditions: initial dye concentration 0.015 mM; adsorbent dosage range 5–50 mg; temperature 30˚C; stirring rate 100 rpm.

3.6. Effect of pH

The pH of an aqueous solution is an important controlling parameter in the process of adsorption. The effect of pH can be also explained by considering the surface charge on the adsorbent material. Effect of pH on the adsorption of erythrosine was performed using 20 mg of polymer. The dye solutions were prepared in various buffers such as 0.1 M sodium acetate, sodium citrate, potassium phosphate, and tris–HCl, between pH 3.5 and 8.5. As seen from Fig. 5, maximum adsorption was found at pH 3.5.

Jain and Sikarwar reported that the strong force of interaction between the dye and both the adsorbents that, either H^+ or OH^- ions could influence the adsorption capacity. They studied adsorptive removal of erythrosine dye onto activated low-cost de-oiled mustard and the maximum uptake of dye takes place at pH 2.0–4.6 (99%) colour removal in case of activated carbon and for activated de-oiled mustard at pH 3.5 (95%) colour removal [4]. Kaur and Datta reported that the pH of the aqueous dye solution did not have a pronounced effect on the adsorption capacity of montmorillonite as the % dye uptake was found to be nearly the same at all the pH values investigated [26]. Copello et al. studied the adsorption of various dyes including erythrosine on chitosan hydrogel/SiO_2 and chitin hydrogel/SiO_2 hybrid materials. Erythrosine as an acid dye, its maximum adsorption was observed at a low pH [15].

3.7. Effect of temperature

The degree of adsorption depends on the temperature. The rate of adsorption was also studied in the temperature range of 30–50˚C for different concentrations of dye solutions (0.01–0.1 mM) at a specific time (Fig. 7). The adsorption uptake was decreased by increasing the temperature from 30 to 50˚C, indicating that the adsorption process was exothermic in nature. Gupta et al. studied the measurement of kinetics at different temperatures (30, 40, and 50˚C) and reported that erythrosine adsorption was increased with the increasing of the temperature. They also calculated the half-life of each process and it was found to decrease with increase in temperature. Their results showed that adsorption of erythrosine on hen feathers was endothermic in nature [14]. Jain and Sikarwar showed that adsorption of erythrosine was concluded to be endothermic and spontaneous. The adsorption followed the order 30 < 40 < 50˚C [4].

3.8. Effect of Erythrosine concentration

Twenty milligram of polymer was suspended in 5 ml dye solution (0.01–0.4 mM) which was prepared in 0.1 M pH 3.5 acetate buffer. An increase in concentration of dye solution, the extent of adsorption onto

polymer increased almost linearly in the range of 0.01–0.3 mM. Above 0.3 mM, the adsorption reached the saturation point and the capacity of the polymer for erythrosine was calculated to be as 104.5 mg/g experimentally (Fig. 5). Gupta et al. studied the effect of concentration for the uptake of erythrosine on hen feathers at different temperatures and they observed that the initial removal of dye was fast and at higher concentrations the percentage uptake gradually decreased [14]. Jain and Sikarwar reported that the optimum adsorption capacity of the activated carbon and de-oiled mustard for erythrosine was 5.0×10^{-5} M [4]. The uptake of erythrosine, separately over bottom ash and de-oiled soya was investigated at initial concentration ranges from 1×10^{-5} to 6×10^{-5} M at a fixed pH and at different temperatures 30, 40, and 50°C by Mittal et al. They observed that increase in the efficiency of adsorbents with the increase in concentration of the dye in the solution was evident. Also for the bottom ash and de-oiled soya, the uptake was almost 100% at low concentrations and about 90 and 39%, respectively, at higher concentrations of the dye at 50°C [28].

4. Adsorption isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms [23,28]. In the present study, two adsorption isotherms: Langmuir and Freundlich, were applied to describe the equilibrium data of adsorption onto poly (MMA-EGDMA) at different temperatures. The adsorption data were analyzed with the help of the following linear forms of Freundlich and Langmuir isotherms [4,29–31].

The logarithmic form of Freundlich model is given by the equation:

$$\log\ q_e = \log\ K_f + \log\ C_e/n \tag{1}$$

where q_e is the amount adsorbed (mol g^{-1}), C_e is the equilibrium concentration of the adsorbate (M), and K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively [4,32]. When log q_e was plotted against log C_e, slope was obtained $1/n$ (Fig. 8). Freundlich constants K_f and n are calculated and the values at different temperatures are given in Table 1. The more heterogeneous surface will bring the $1/n$ value closer to zero. The magnitude of the exponent "n" gives indication of the favorability and K_f the capacity of the adsorbent or adsorbate system [33].

Adsorption isotherm data have been described by the Langmuir adsorption isotherm [4,34].

$$1/q_e = 1/b \cdot Q_0 \cdot C_e + 1/Q_0 \tag{2}$$

where q_e is the amount adsorbed (mol/g) and C_e is the equilibrium concentration of the adsorbate (mol/l). Q_0 and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ was plotted against $1/C_e$, slope was obtained $1/bQ_0$ (Fig. 9). The Langmuir constants Q_0 and b are calculated and the values of these constants are tabulated for the highest R^2 value in the Table 1.

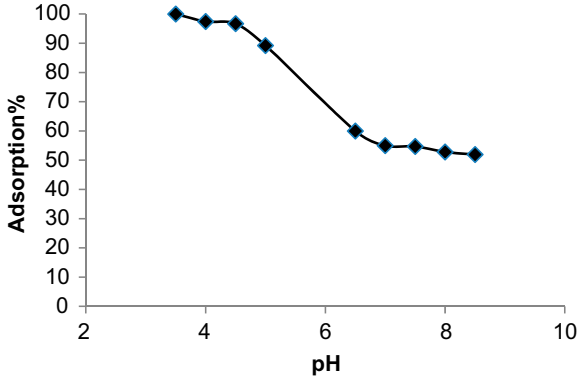

Fig. 7. Effect of pH on the adsorption capacity of poly (MMA-EGDMA). Experiment conditions: initial dye concentration 0.015 mM; adsorbent dosage 20 mg; pH range 3.5–8.5; temperature 30°C; stirring rate 100 rpm.

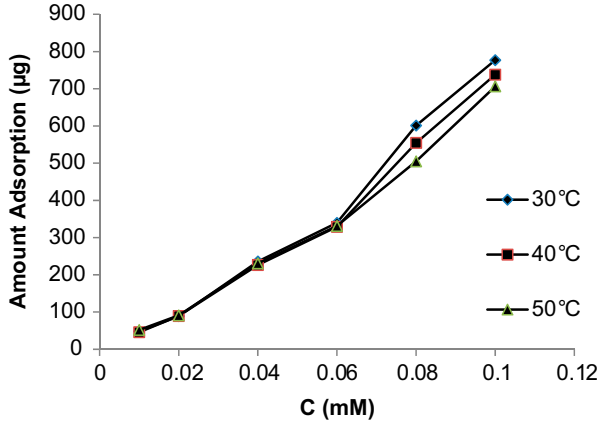

Fig. 8. Effect of temperature on the adsorption capacity of poly(MMA-EGDMA). Experiment conditions: initial dye concentration range 0.01–0.1 mM; adsorbent 20 mg; initial solution pH 3.5; temperature range 30–50°C; stirring rate 100 rpm.

Table 1
Adsorption isotherm of erythrosine by MMA-EGDMA at different temperatures

Temperature (℃)	Freundlich isotherm			Langmuir isotherm			
	K_f	n	R^2	Q_o (mol g^{-1})	b (L mol^{-1})	R_L	R^2
30	24.7	0.689	0.8398	1.2×10^{-4}	64.8×10^{3}	0.072	0.8945
40	21.1	0.868	0.8781	1.31×10^{-4}	21.7×10^{3}	0.187	0.9935
50	16.8	1.51	0.8685	1.85×10^{-4}	21.4×10^{3}	0.19	0.9758

The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter, R_L, which is usually defined by:

$$R_L = 1/1 + b \cdot C_0 \quad (3)$$

where b values were derived from Langmuir isotherm and C_0 is the initial concentration.

This parameter indicates that isotherm will be shaped according to the following adsorption characteristics: $R_L > 1$ unfavorable; $R_L = 1$ corresponds to linear; $0 < R_L < 1$ is favorable; and $R_L = 0$ is irreversible [35]. The values of R_L obtained were found between 0 and 1 for 30, 40, and 50℃ temperatures, and confirms that the ongoing adsorption process is favorable. The same method has already been adopted [4] to confirm the favorability of a Langmuir type of adsorption (Figs. 10 and 11).

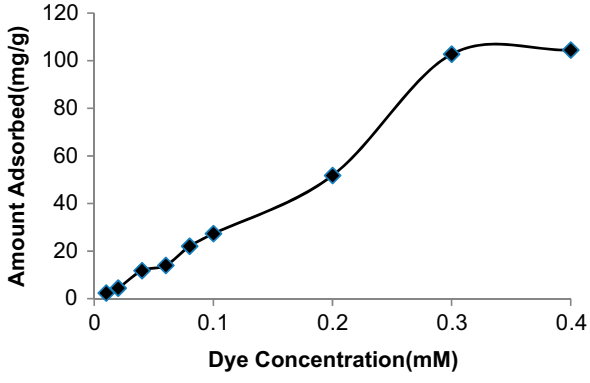

Fig. 9. Effect of erythrosine concentration on the adsorption capacity of poly(MMA-EGDMA). Experiment conditions: initial dye concentration range 0.01–0.4 mM; adsorbent dosage range 20 mg; initial solution pH 3.5; temperature 30℃; stirring rate 100 rpm.

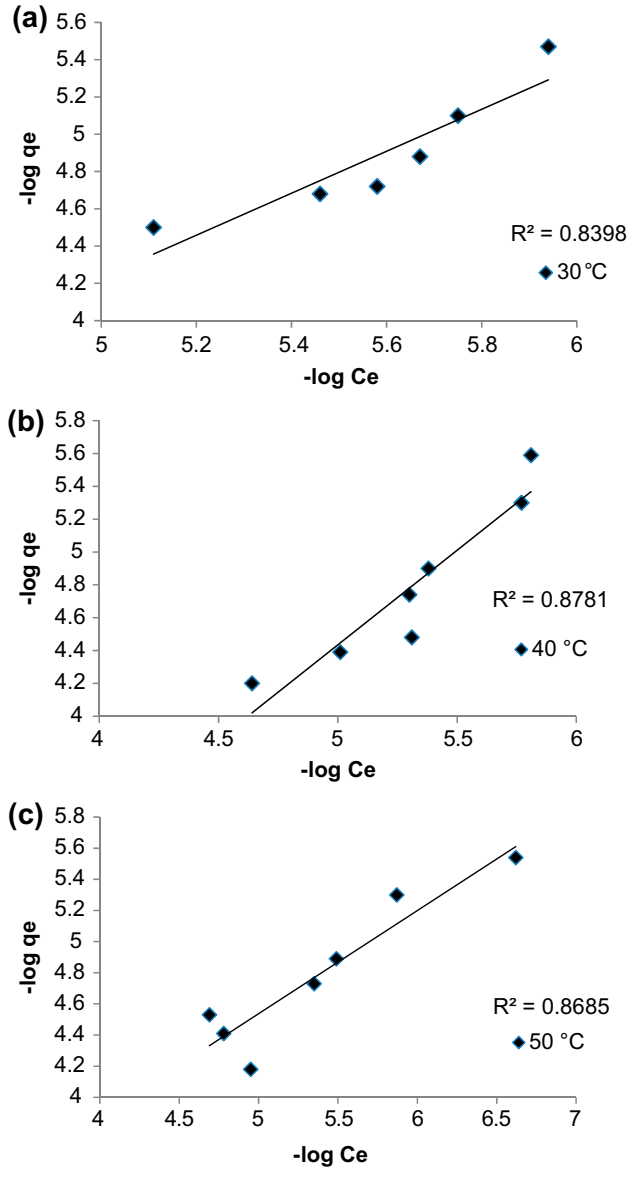

Fig. 10. Freundlich adsorption isotherm of Erythrosine onto poly(MMA-EGDMA). Experiment conditions: dye concentration range 0.01–0.2 mM; adsorbent dosage 20 mg; pH 3.5; temperature (a) 30℃, (b) 40℃, (c) 50℃; stirring rate 100 rpm.

4.1. Thermodynamic parameters

In environmental processes, both energy and entropy factors must be considered in order to determine which process will occur spontaneously [36]. Thermodynamic study is important for an adsorption process because it depicts the uptake of an adsorbate [27]. The adsorption study was assessed at 30, 40, and 50°C and the adsorption uptake was found to decrease with increasing temperature from 30 to 50°C for all initial concentrations, indicating the nature of the adsorption process was exothermic. Similar observations were also reported by other researchers [37,38]. The value of ΔH° determines whether a process is endothermic or exothermic. Here the value of ΔH° was found to be negative and it verified the reaction involved was exothermic. Also the negative value of ΔG° indicated the spontaneous nature of adsorption of erythrosine onto the polymer. The positive value of ΔS° showed the good affinity of erythrosine towards poly(MMA-EGDMA).

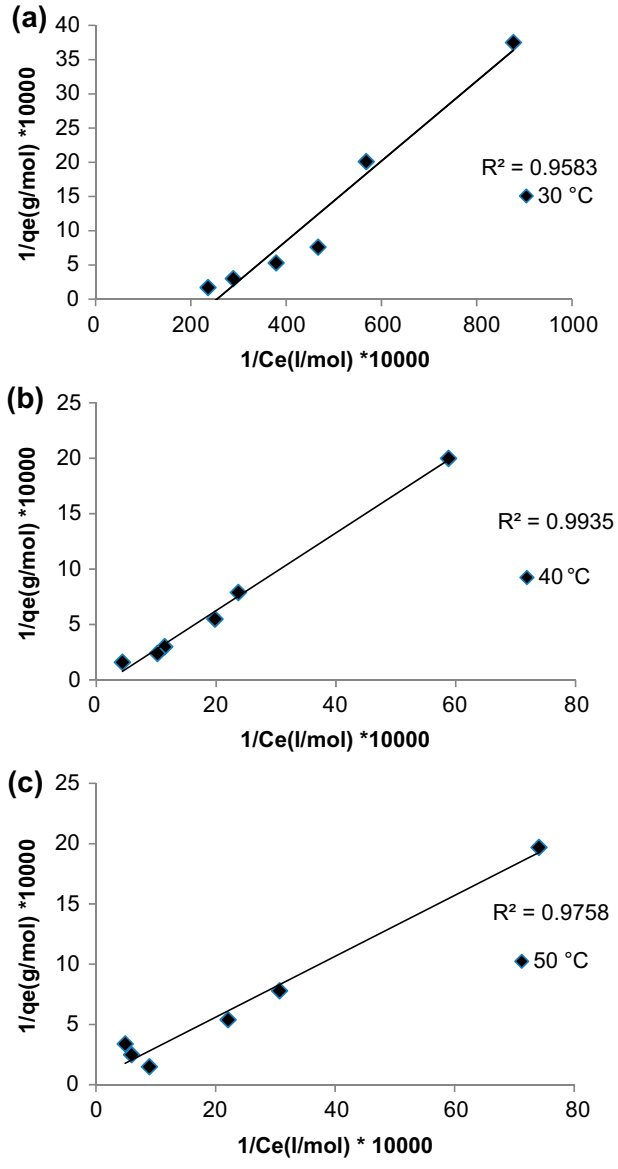

Fig. 11. Langmuir adsorption isotherm of erythrosine onto poly(MMA-EGDMA). Experiment conditions: dye concentration range 0.01–0.2 mM; adsorbent dosage 20 mg; pH 3.5; temperature (a) 30°C, (b) 40°C, (c) 50°C; stirring rate 100 rpm.

Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated using the following equations:

$$(\Delta G^{\circ}) = -2.303\,RT\,\log K_c \tag{4}$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{5}$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \tag{6}$$

Thermodynamic parameters ΔG°, ΔH° and ΔS° were calculated and the values are shown in Table 2.

where K_c is the adsorption isotherm constant, R is the gas constant (8.314 $JK^{-1}\,mol^{-1}$), and T is the absolute temperature, respectively. ΔH° and ΔS° can be calculated from the slope and intercept of log K vs. (1/T) from Eq. [28,39].

5. Conclusion

The adsorption of erythrosine from an aqueous solution using poly(MMA-EGDMA) had been investigated, under different reaction conditions, such as pH, temperature, contact time, adsorbent dose, and dye concentration in batch system. Optimal pH for poly (MMA-EGDMA) was found to be 3.5. Under optimized conditions, the capacity of the polymer was found as 104.5 mg/g. The results obtained for different temperatures fitted well with the linear form of Lang-

Table 2
Parameters of the thermodynamics for the adsorption of erythrosine by poly(MMA-EGDMA) at 30°C, 40°C and 50°C

$-\Delta G^{\circ}$ (kJ mol^{-1})	Erythrosine
30°C	125.6
40°C	127.8
50°C	129.9
ΔH (kJ mol^{-1})	−60.69
ΔS (kJ $mol^{-1}\,K^{-1}$)	214.25

muir adsorption isotherm. The calculated thermodynamic parameters showed that the adsorption process was spontaneous and exothermic in nature.

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