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RESEARCH ARTICLE - CHEMISTRY

Comparative Adsorption of Different Dyes from Aqueous Solutions onto Polymer Prepared by ROP: Kinetic, Equilibrium and Thermodynamic Studies

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Abstract Poly(1,2-epoxy-3-phenoxy)propane was synthesized by ring-opening polymerization using $Sn(Oct)_2$ as a catalyst and benzyl alcohol as an initiator. Homopolymer's epoxy type was acylated with chloroacetyl chloride firstly and then modified with the diethanol amine. The polymers were characterized by FT-IR and ^1H-NMR. Dye adsorption properties of poly(2-phenoxy ethyl [bis(2-hydroxy ethyl)amino]acetate) were investigated by using bromocresol green (BCG), alizarin yellow (AY) and methylene blue (MB). Amounts of dye holding polymers at different times were calculated and plotted as a function of time. According to the removal results, all of the dyes reach its highest efficiency at 90 min. The effect of pH on adsorption of dyes was studied in the pH range of 2–11. Kinetic models known as pseudo-first order and pseudo-second order were used to analyze the mechanism of adsorption, and the results indicated an adsorption kinetic compatible with the pseudo-second order. The Langmuir and Freundlich isotherms were utilized to explain the adsorption equilibrium, and when it was compared with each other, it was revealed that the Langmuir isotherm model was better than Freundlich isotherm. The maximum adsorption capacities of BCG, AY and MB were 52.63, 15.87 and 31.25 mg/g, respectively. Furthermore, thermodynamic properties ($\Delta H°$, $\Delta S°$, $\Delta G°$) of modified polymer were investigated for the three dyes. According to the thermodynamic parameters, the adsorption of the dyes occurred spontaneously and was endothermic. The results of this study support that novel polymer, an inexpensive and effective adsorbent, could be used for dye removal from aqueous solutions.

Keywords Ring-opening polymerization · Modification · Dye adsorption · Kinetic and thermodynamic

1 Introduction

Well-defined linear amphiphilic polymers containing hydroxy segment will be very interesting and are generally polymerized by ring-opening polymerization (ROP) [1–5]. One of the best known polymerization initiators for ROP of aliphatic polyether and polyester is tin(II) bis-(2-ethylhexanoate) commonly known as tin octoate or stannous octoate ($SnOct_2$) because of its solubility, low cost, low toxicity, high efficiency and ease of handling [6–9].

Surface modification has recently become a widely used method because it provides materials different properties and allows them to be used in different areas [10,11]. The chemical modifications of the polymer with amine groups can increase the adsorption capacity due to their ability to produce strong complexes with pollutants [12–15].

Polymers are used as an adsorbent for removal of various organic substances from the water because of their cheap price, stability and reproducible facilities [16–18].

Especially in developing countries, environmental pollution caused by toxic chemicals has increased by increasing world population and industrialization [19]. Dyes are among the most important organic contaminant which caused many environmental and health problems in the world [20–22]. In addition to the negative impact of aquatic plant life, dyes cause the decrease in photosynthesis [23–25]. According to the literature search, various treatment methods such as

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chemical oxidation, adsorption and biological treatments have been used to remove dyes from the aqueous solution [26,27]. Adsorption of dyes with a suitable adsorbent can be an economical and efficient process to remove from water. And also adsorption is an impressive method due to its high efficiency, easy design and not creating a second pollution [28,29].

This study was aimed to evaluate the dye removal performance of amphiphilic polymer which was prepared by ring-opening polymerization method and chemically modified with diethylamine. Three dyes (BCG, AY and MB) were used to investigate the effect of molecular structures of dyes on adsorption capacity. The effect of pH on the adsorption capacity for three dyes was studied. In order to determine the adsorption mechanism, pseudo-first-order and pseudo-second-order kinetic models were used. Langmuir and Freundlich isotherm models were studied, and coefficients were determined. It was seen that the Langmuir model is more acceptable when the calculated isotherm constants are examined. Also, thermodynamic properties (ΔH, ΔS, ΔG) of modified polymer were investigated in all three dyes.

The adsorbent used in this work is a first-time-synthesized and non-commercial polymer. BCG, AY and MB have different properties and have not been studied before together. Modified homopolymer showed higher adsorption capacity for three dyes.

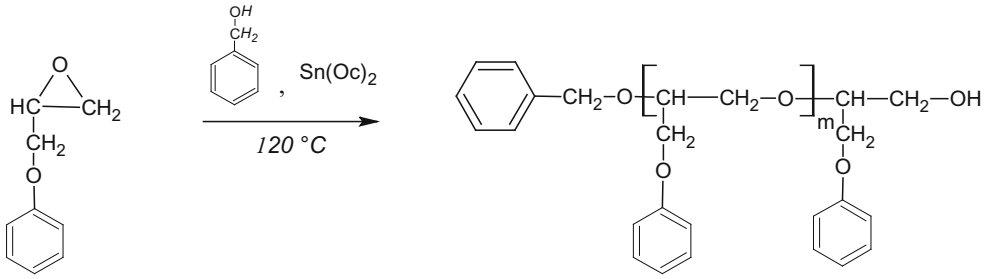
2 Experimental

2.1 Synthesis of Poly(1,2-epoxy-3-phenoxy propane) (PEPP)

1,2-Epoxy-3-phenoxy propane (2 g) was added into a 100-mL well-dried reaction flask under argon atmosphere. Then stannous 2-ethylhexanoate (8.6×10^{-3} g) as catalyst and benzyl alcohol (0.05 g) as initiator were injected into the flask. The reaction mixture was heated at 120 °C for 48 h. After the viscous mixture being diluted by $CHCl_3$ (3 mL), the product was precipitated with petroleum ether and dried for 24 h at 40 °C in the vacuum. Scheme 1 is the ring-opening polymerization reaction of 1,2-epoxy-3-phenoxy propane (EPP).

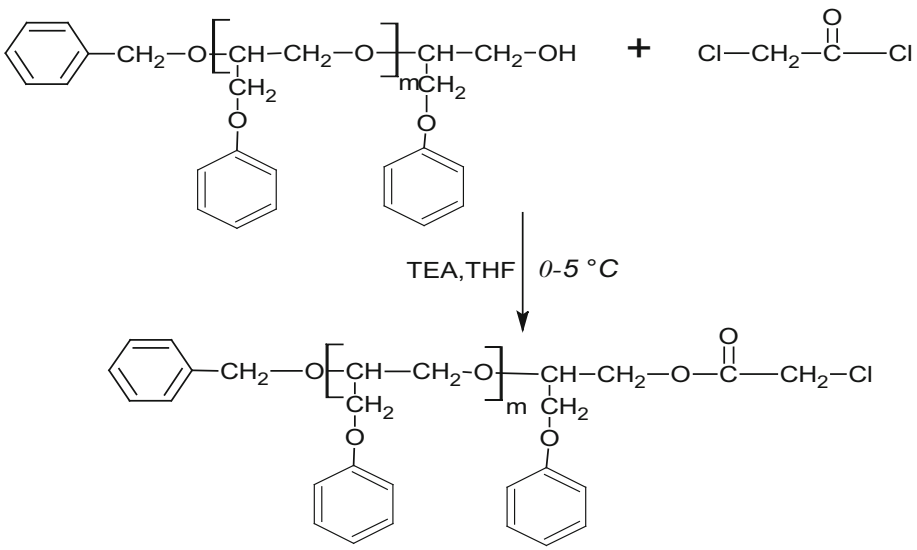
2.2 Synthesis of PEPP-Cl

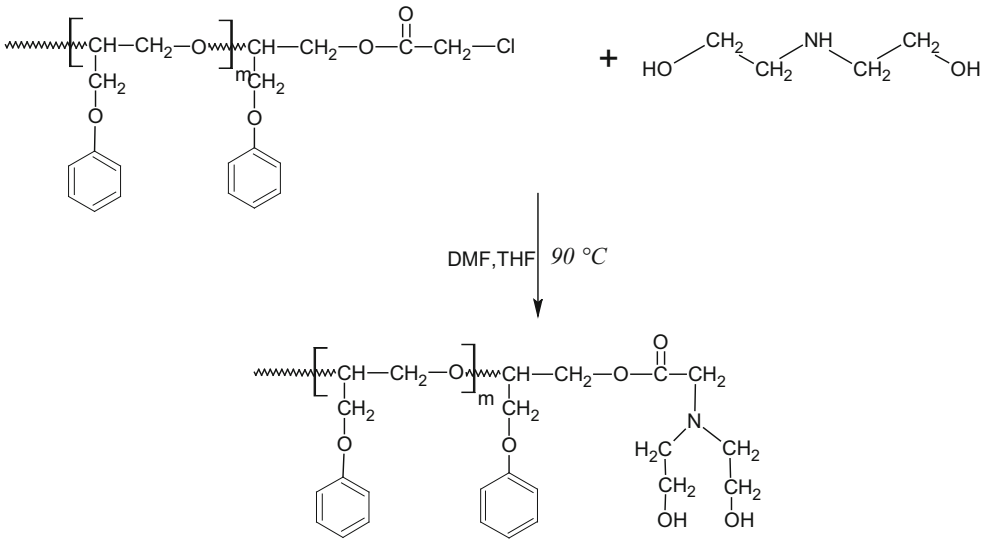
Two grams of PEPP was dissolved in dry tetrahydrofurane (20 mL), and triethylamine (0.63 g) was added. After cooling to 5–6 °C, chloroacetyl chloride (0.72 g) was added gradually



Scheme 1 Ring-opening polymerization of EPP

Scheme 2 Acylation reaction of PEPP





Scheme 3 Modification of PEPP-Cl

for 15 min. The solution which was mixed at room temperature overnight was precipitated within petroleum ether next day and was left in the oven to dry at 40 °C under vacuum.

2.3 Modification of PEPP-Cl with Diethanol Amine

Poly(1,2-epoxy-3-phenoxy) propane (2 g) was dissolved in tetrahydrofurane (10 mL) and dimethylformamide (4 mL) in a three-necked reaction flask. Then diethanolamine (0.7 g) was added and the mixture was stirred under reflux at 90 °C for 24 h. The resulting product was purified by precipitation within ethyl alcohol and dried under vacuum for 24 h at 40 °C.

2.4 Adsorption Properties

The sorption capacity of the modified polymer was determined using bromocresol green (BCG), alizarin yellow (AY) and methylene blue (MB). These dyes were commercial products and used without purification. (Shown in Fig. 1 are the structural formulas of each dye, respectively.) To evaluate the adsorption properties of the modified polymer, 0.1 g of polymer was mixed to 5 mL solution prepared at 1:1 ratio within ethyl alcohol–water solution of dyes at a known concentration in a closed Erlenmeyer flask. Then the solution was stirred by a magnetic stirrer at room temperature. The sorbent was filtrated before measurement. The remaining dyes' concentration in the medium at different times was determined by UV–Vis spectrophotometry. Absorbance values were recorded at λ_{max} for each solution: at 623 nm for BCG, 359 nm for AY and 664 nm for MB.

After certain time intervals, the adsorbed amount (mg/g) of dye at time t, q_t, was calculated using the following equation:

$$q_t = \frac{(c_0 - c_t)V}{m}, \tag{1}$$

where C_0 is the initial concentration and C_t is concentrations of dye solution (mg/L) at time t. V is the volume of solution (L), and m is the mass of used polymer (mg dye/g polymer). Also, adsorbed dye amount at the equilibrium (q_e) was calculated using the equation given by:

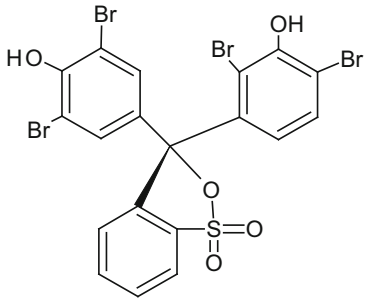
$$q_e = \frac{(c_0 - c_e)\,V}{m}, \tag{2}$$

where C_0 is the initial concentration and C_e is the equilibrium concentrations of dye solution (mg/L) at time t. V is the equilibrium volume of solution (L), and m is the mass of the used polymer (mg dye/g polymer).

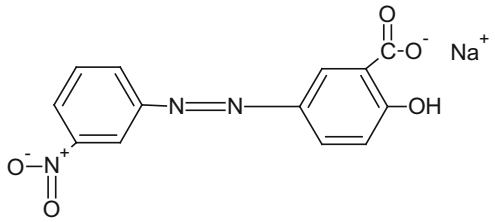
2.5 Measurements

Infrared spectra were recorded on PerkinElmer Spectrum One. The ^{1}H−NMR and 13C-NMR spectra were recorded on an Avence III Bruker (400 MHz) using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal reference. Thermogravimetric analysis (TGA) was performed using a Shimadzu TA-50 instrument at a heating rate of 10 °C/min under the nitrogen atmosphere (10 mL/min). Differential scanning calorimetry (DSC) measurements were taken by DSC-50 at a heating rate of 20 °C/min in a nitrogen flow. Absorbance values were measured using a UV–Vis spectrophotometer (PHARMACIA LKB ULTROSPEC III) at the wavelength.

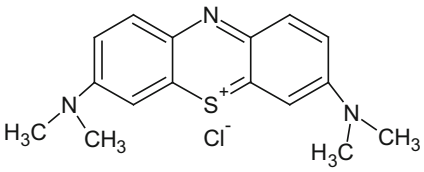
Fig. 1 Chemical structure of dyes



Bromocresol Green(BCG)



Alizarin Yellow (AY)



Methylene Blue(MB)

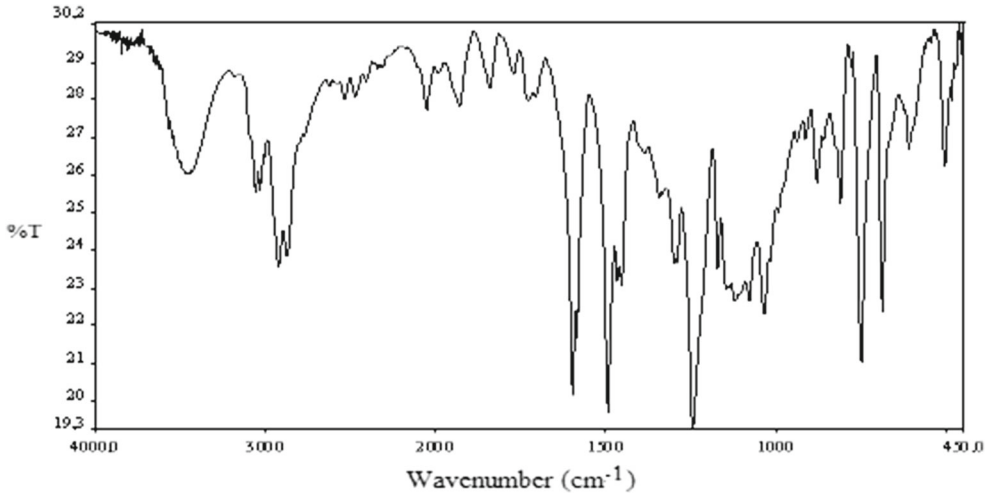


Fig. 2 IR spectrum of PEPP

3 Results

3.1 Characterization of Polymers

The FT-IR spectrum of poly(1,2-epoxy-3-phenoxy)propane (PEPP) synthesized by ring-opening polymerization is shown in Fig. 2. The strong band at 1599 cm^{-1} is the stretching vibration of the aromatic C=C double band and 3465 cm^{-1} confirming –OH group. The $^{1}H-NMR$ spectrum of the polymer is shown in Fig. 3a. The peaks at 6.69–7.34 ppm reveal the aromatic ring protons, 4.15 ppm CH_2 protons attached to the aromatic ring and 3.87 ppm CH_2 protons connected to oxygen in PEPP. In $^{13}C-NMR$ spectrum (Fig. 3b) 120.63 and 69 ppm were characterized by CH carbon in the aromatic ring and CH_2 carbon in the main chain, respectively. PEPP-Cl was prepared by end-capping of living PEPP with excess of chloroacetyl chloride. The FT-IR and $^{1}H-NMR$ spectra of modified PEPP-Cl are shown in Fig. 5a, b. Disappearing of the peak at 1761 cm^{-1} (Fig. 4) carbonyl group, which is adjacent to chlorine methyl group, was used to characterize the structure.

In order to investigate the thermal stability of homopolymer, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were taken using Shimadzu TGA-50 and Shimadzu DSC-50 techniques under nitrogen gas flow (Fig. 6a, b), and the results are shown in

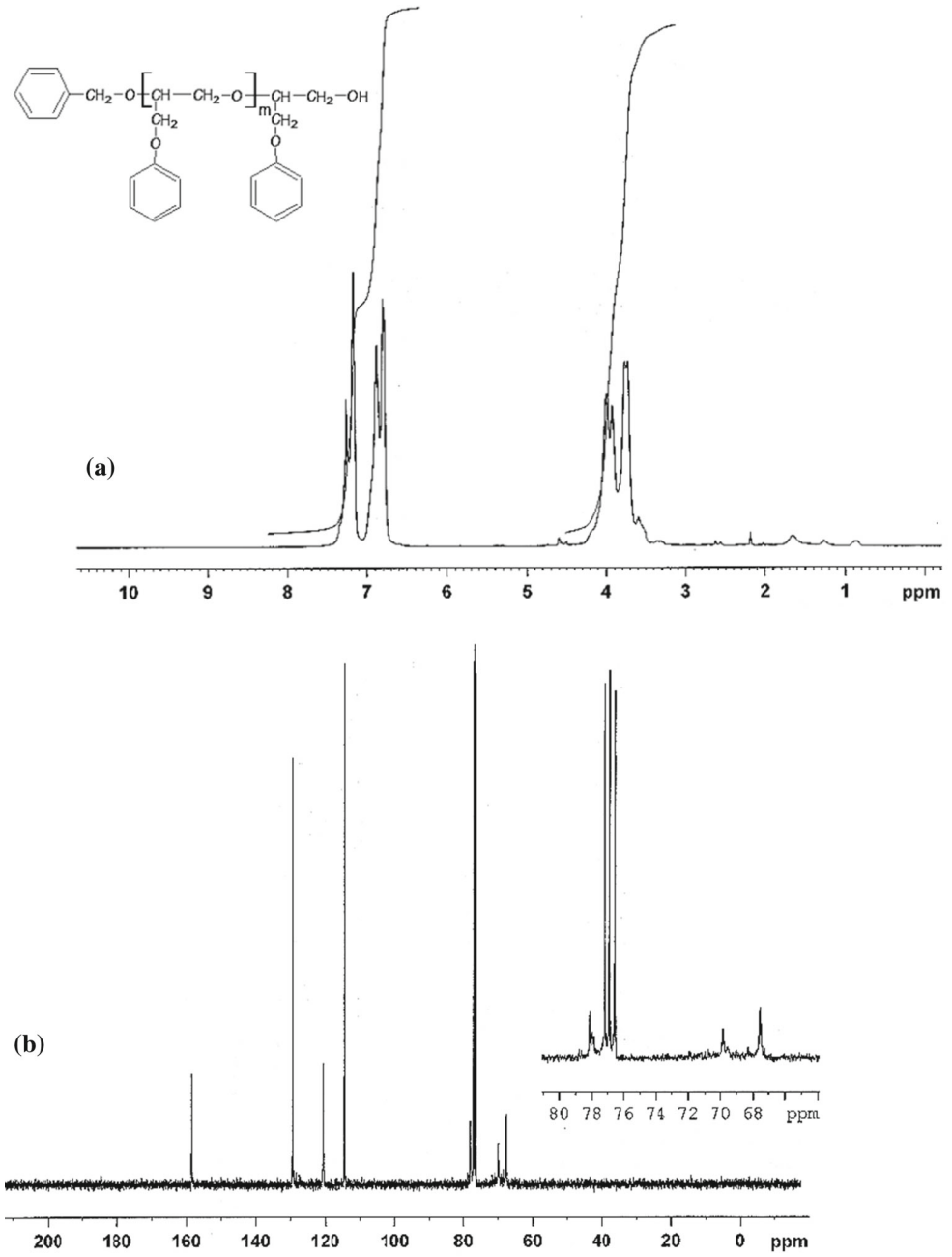


Fig. 3 **a** ^{1}H−NMR and **b** ^{13}C−NMR spectra of PEP

Table 1. The sharp peak in the 197 °C is the melting temperature of the PEPP crystal phase in DSC curve.

3.2 Adsorption Studies

Adsorption of dyes onto modified polymer was measured by UV spectrophotometer according to the method explained in Sect. 2.4. Absorbance values measured at specific time intervals were converted into the amount (mg dye/g polymer) and then graphed as a function of time in Fig. 7 for each dye. It is seen that the adsorption capacities of polymer increased for BCG from 25.41 to 38.12 mg/g, for MB from 18.24 to 28.54 mg/g and for AY from 5.76 to 9.25 mg/g with the increase in adsorption time from 0 to 180 min at room temperature. This indicated a strong interplay between the dye and the polymer. Also, as shown in Fig. 7, more than 90% of the adsorption capacities of modified polymer for three dyes occurred within 90 min. In Figs. 7 and 8 it is clear that the adsorption amount gradually increased with the increased time until equilibrium and then remained stable [30].

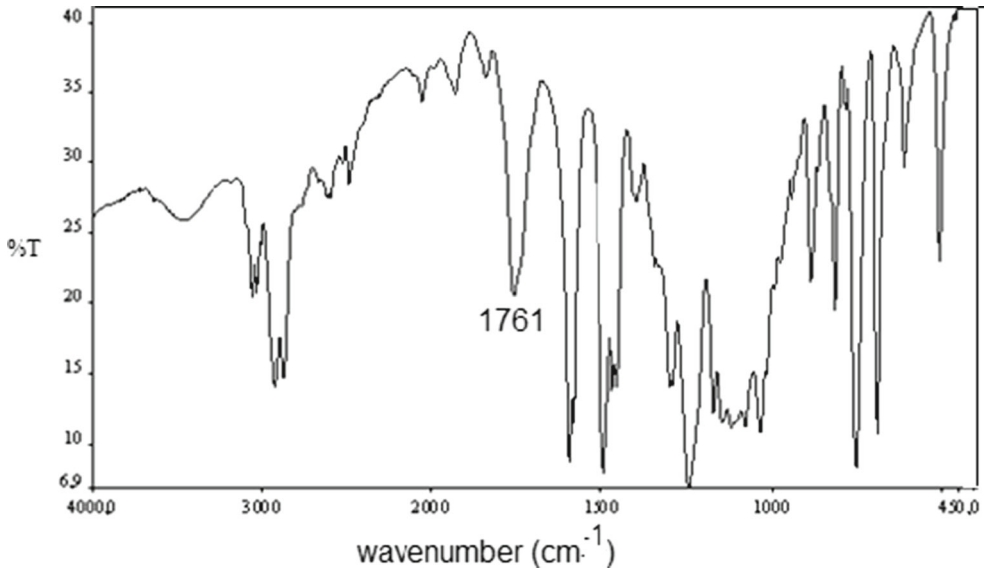


Fig. 4 IR spectrum of PEPP-Cl

In this work, three dyes which differ in chemical structure and property, molecular size and functional groups in their molecule formula were used (see Fig. 1). In Fig. 7, the reason why the amounts of adsorption (mg dye/g polymer) are different from each other can be attributed to the different chemical structures of the dyes. It was clear that BCG displays the best interaction with the polymer. It belongs to triphenylmethane family [31], and in aqueous solution, BCG will ionize to give the monoanionic form. AY is an anionic dye which belongs to the group of anthraquinone dyes [32], and also in this study it shows basic behaviors. MB is a cationic dye [33] that is widely used in adsorption study due to its planar structure with 14 delocalized electrons, and this compound can easily interact with different chemical substances [34].

In order to compare the adsorption behaviors of pure homopolymer and modified homopolymer a graph is shown in Fig. 8. It is seen that the adsorption amount of the modified polymer was found to be 25 times more than homopolymer. This comparison was made for BCG at room temperature.

3.3 Effect of Solution pH

The effect of pH on the adsorption of the dyes was examined in the pH range of 2–11 using an adsorbent of 0.01 g and an initial dye concentration of 100 mg/L at 25 °C. In Fig. 9 it is observed that the adsorption capacity of three dyes increased with increasing pH. The electrostatic attraction between the dye solutions and the adsorbent significantly affects the adsorption capacity of the dyes [35]. Lower adsorption of dyes at acidic pH is due to the fact that dyes adsorb poorly when they are ionized [36]. At higher pH, the polymer that is neutral can be negatively charged and interact with the positive charges of the dyes [37–39]. In this study, optimum pH values were found as 6 for BCG, 11 for AY and 8 for MB.

3.4 Kinetic Study

In this study, two kinetic models were analyzed to investigate the mechanism of adsorption of dyes. These models are the best known and the most used models in adsorption studies. The pseudo-first-order model is given as following linear Eq. (3) [40].

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{3}$$

where q_e is the quantity of dyes adsorbed at equilibrium (mg/g), q_t is the quantity of dyes adsorbed at time t (mg/g), and k_1 is the equilibrium rate constant of pseudo-first order (min). The slope and intercept of the graph of $\ln(q_e - q_t)$ versus t were used to calculated the k_1 and q_e, respectively.

Also, pseudo-second-order model was used to determine the kinetics of adsorption using the following linear Eq. (4) [41].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t, \tag{4}$$

where q_e and q_t (mg/g) are the quantities of adsorbed dye at equilibrium and at time t, and k_2 (g/mg min) is the rate constant of pseudo-second-order equation. The rate parameters q_e and k_2 can be defined from the slope and intercept by the plotting t/q_t versus t.

Values of k_1, k_2, and the correlation coefficient (R^2) are given in Table 2. As shown in the table, the value of q_e calculated from graphics for pseudo-second-order model

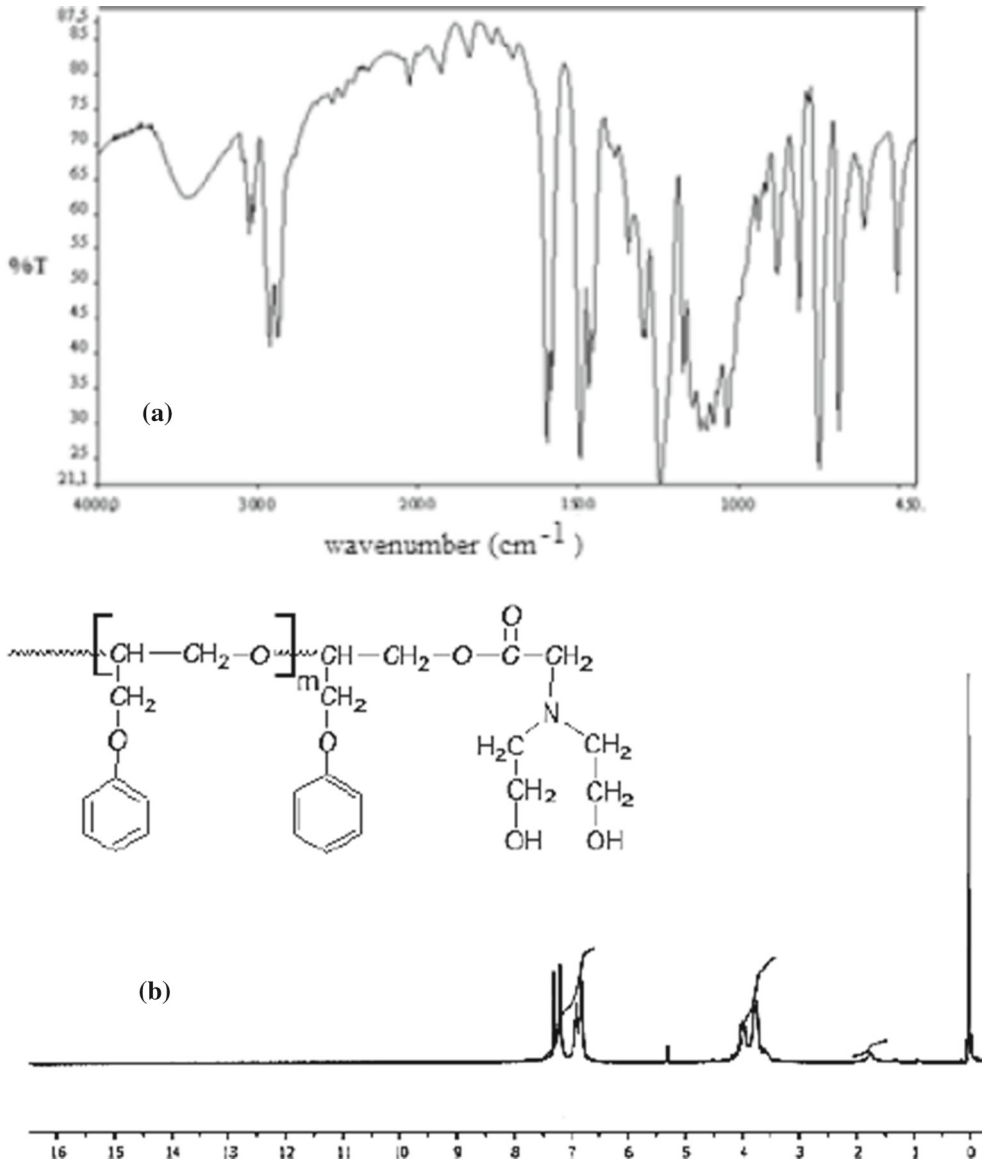


Fig. 5 **a** IR **b** and ^{1}H−NMR spectra of modified PEPP-Cl

is considerably different from the experimental value. For this reason, this model is not a suitable model for describing adsorption kinetics. Also, it can be evidently seen that the calculated q_e value of the pseudo-second-order kinetic model is more convenient with the experimental data than the pseudo-first-order kinetic model does. It is seen that when the correlation coefficients are compared with each other for three dyes the pseudo-second-order model is better. These results demonstrate that the kinetic of adsorption is based on the pseudo-second-order model.

3.5 Adsorption Isotherms

To explain the surface properties of the adsorption process, two classic isotherm models, Langmuir and Freundlich, were used [42]. Langmuir isotherm is originally used to describe the monolayer adsorption. Langmuir is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e, \tag{5}$$

where q_e (mg/g) is the amount of adsorbed dye at equilibrium time, C_e (mg/L) is the concentration of dye solution at equilibrium time, q_{max} is the maximum adsorption capacity (mg/g), and K_L is the adsorption equilibrium constant concerned with the adsorption energy (L/mg).

Freundlich isotherm is the method which carries out on heterogeneous surfaces and describes multilayer adsorption.

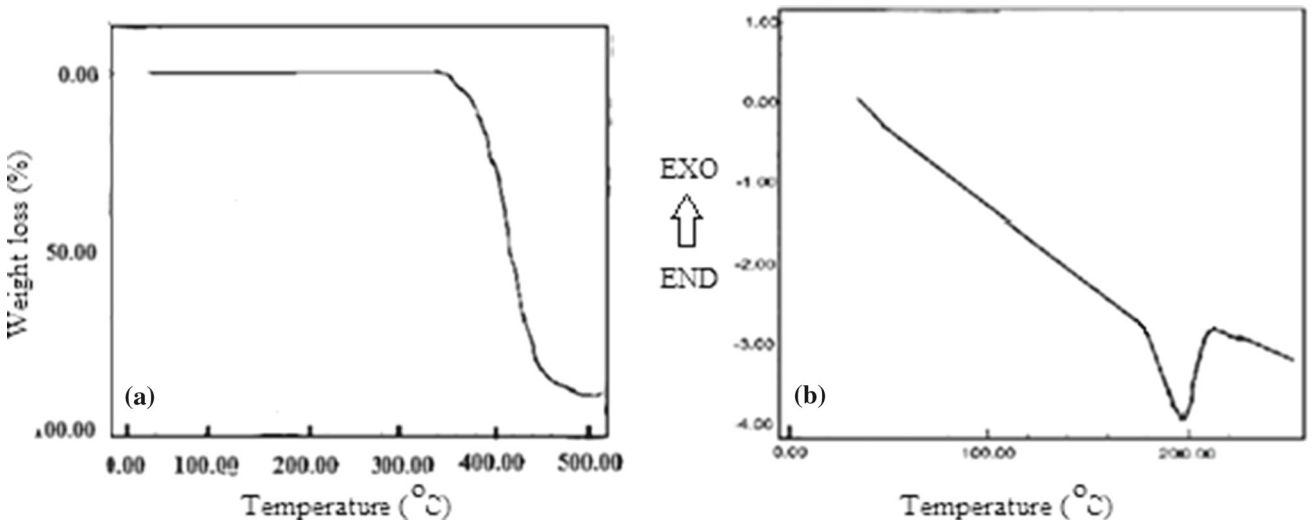


Fig. 6 TGA and DSC curves of PEPP

Table 1 TGA and DSC data of the polymer

Polymer	T_m (°C) [a]	T_i (°C) [b]	T_{2nd} (°C) [c]	T%50 (°C) [d]	%Weight loss at 350 °C	%Residue at 500 °C
PEPP	197	350	480	422	0	10

[a] Glass-transition temperature
[b] Initial decomposition temperature of the first stage
[c] Initial decomposition temperature of the second stage
[d] Decomposition temperature at 50% weight loss

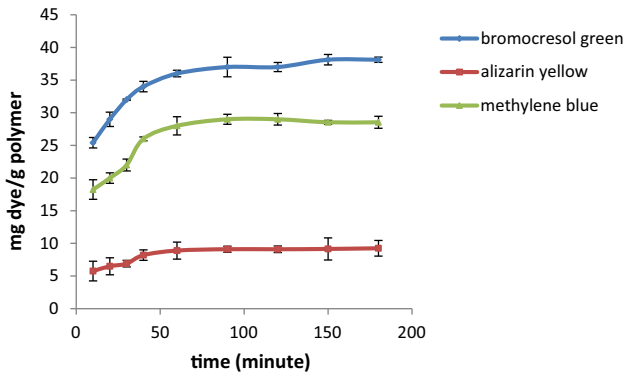


Fig. 7 Effects of contact time on adsorption of dyes (number of replicates $n = 3$; vertical lines in the graph are standard errors)

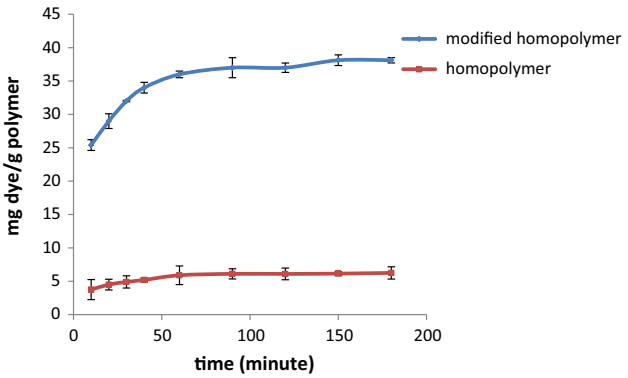


Fig. 8 Effects of contact time on adsorption of BCG for homopolymer and modified homopolymer (number of replicates $n = 3$; vertical lines in the graph are standard errors)

The equation for Freundlich is as follows (6):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \tag{6}$$

where K_F (L/mg) is the Freundlich constant and n is a constant connected to the adsorption degree between solution concentration and adsorption.

Adsorption isotherms give information on the relationship between adsorbed dye and adsorbent and the capacity of adsorption. The adsorption isotherms were analyzed according to linear forms of the Freundlich and Langmuir models in this study. Figures 12 and 13 are linear graphs plotted according to the equations of Langmuir and Freundlich, respectively. Also, the values of the parameters of the two models for three dyes are given in Table 3. These parameters explain the adsorption mechanism and capacity or interest of the sorbent [43].

In Table 3, it is seen that correlation coefficient calculated by Langmuir isotherm model is much better than by Freundlich model for the three dyes. This indicated that the

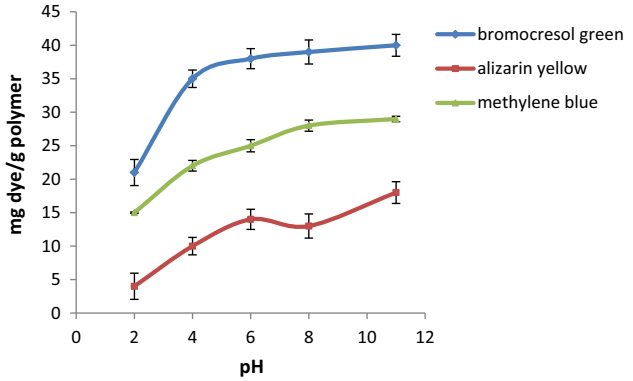


Fig. 9 Effects of pH on adsorption of dyes (number of replicates $n = 3$; vertical lines in the graph are standard errors)

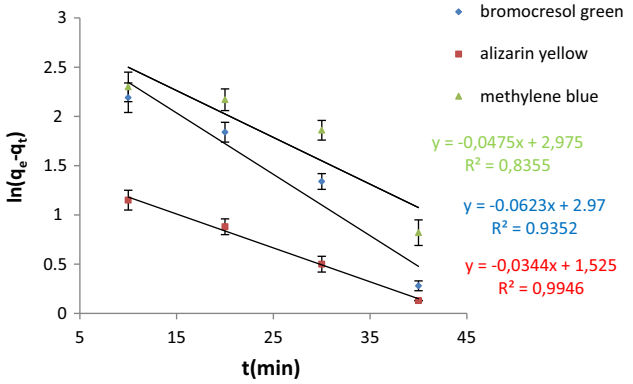


Fig. 10 Pseudo-first-order kinetic plot for dyes (number of replicates $n = 3$; vertical lines in the graph are standard errors)

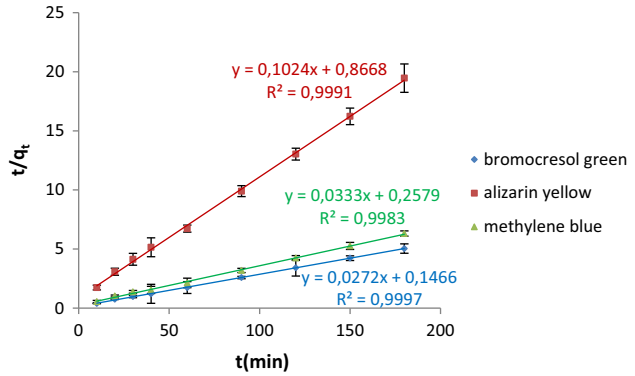


Fig. 11 Pseudo-second-order kinetic plot for dyes (number of replicates $n = 3$; vertical lines in the graph are standard errors)

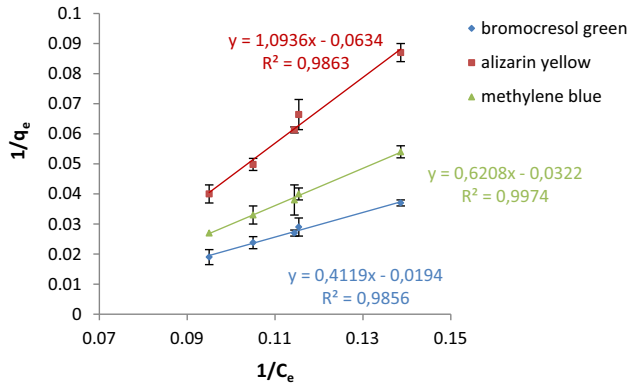


Fig. 12 Langmuir plots for adsorption of dyes onto the polymer (number of replicates $n = 3$; vertical lines in the graph are standard errors)

homogenous adsorption takes place on the polymer for the three dyes. In addition, the calculated value of q_{max} is close to the experimental ones in Langmuir model. In Table 5, q_{max} value found in this study is compared to different adsorbents reported for BCG, AY and MB removal.

3.6 Adsorption Thermodynamics

To study the thermodynamic parameters, for example change in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of adsorption process, the following formulas were used [44]:

$$\Delta G^0 = -RT \ln K_d; \tag{7}$$

$$\Delta G^0 = \Delta H - T\Delta S; \tag{8}$$

$$\ln K_d = \frac{\Delta S}{R} - \Delta H/RT, \tag{9}$$

where K_d is the equilibrium constant (L/mg), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). $\Delta H°$ and $\Delta S°$ were determined from the slope and intercept of the line plotted by ln K_d versus $1/T$, respectively.

The data in Fig. 14 show a linear relation between ln K_d and $1/T$. It is clear that as the temperature increases the value of the equilibrium constant (K_d) and adsorption capacity increases.

Table 2 Kinetic parameters for the adsorption of BCG, AY and MB

Dyes	Pseudo-first-order kinetic				Pseudo-second-order kinetic		
	q_e (exp) (mg/g)	q_e (cal) (mg/g)	k_1 (1/min)	R^2	q_e (cal) (mg/g)	k_2 (g/mg/min)	R^2
BCG	34.32	19.49	0.0623	0.935	36.76	5×10^{-3}	0.999
AY	8.91	4.59	0.0340	0.946	9.79	0.012	0.999
MB	28.18	4.59	0.0475	0.835	30.03	4.3×10^{-3}	0.998

The values of thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) for BCG, AY and MB adsorbed onto modified polymer adsorbent are given in Table 3. The negative values of $\Delta G°$, which were calculated at five different temperatures, showed that the adsorption of dyes was spontaneous and feasible. The positive value of $\Delta H°$ suggests that the dyes' adsorption on the polymer is endothermic, and the positive value of $\Delta S°$ displays the increased randomness during the adsorption of dye on polymer surface [45].

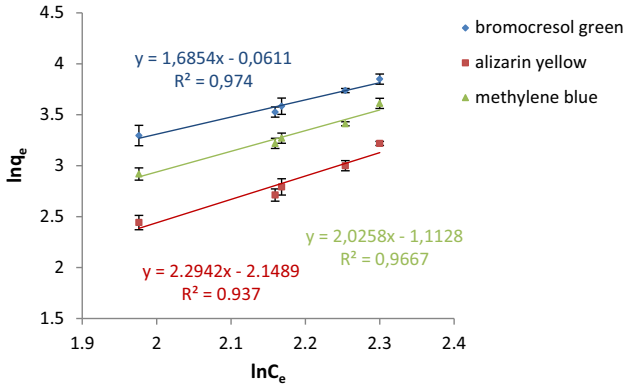


Fig. 13 Freundlich plots for adsorption of dyes onto polymer (number of replicates $n = 3$; vertical lines in the graph are standard errors)

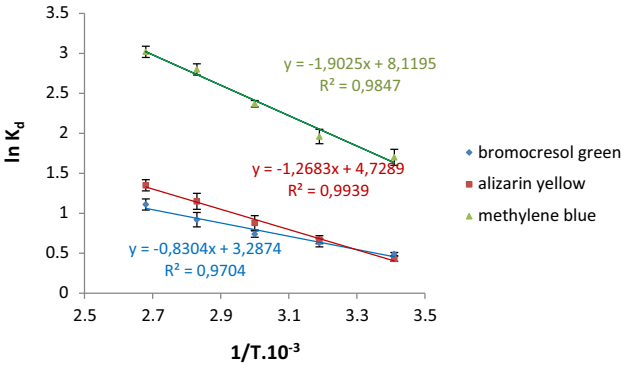


Fig. 14 Plot of $\ln K_d$ versus $1/T \times 10^{-3}$ for adsorption of dyes (number of replicates $n = 3$; vertical lines in the graph are standard errors)

4 Conclusion

In this work, homopolymer produced from 1,2-(epoxy-3-phenoxy)propane was synthesized by ROP using benzyl alcohol as the initiator and $Sn(Oc)_2$ as the catalyst. First,

Table 3 Langmuir and Freundlich isotherm constants and correlation coefficients

Dyes	Langmuir model			Freundlich model		
	q_{max} (mg/g)	K_L (l/mg)	R^2	K_F (mg/g)	n	R^2
BCG	52.63	0.172	0.9856	1.06	0.59	0.974
AY	15.87	0.057	0.9863	8.56	0.43	0.937
MB	31.25	0.052	0.9974	3.04	0.49	0.966

Table 4 Thermodynamic parameters for the adsorption of dyes

Dye	ΔH^0 (J/mol)	ΔS^0 (J/mol K)	ΔG^0 (KJ/mol)				
			293 K	313 K	333 K	353 K	373 K
BCG	6.90	27.26	− 7.98	− 8.52	− 9.07	− 9.61	− 10.16
AY	10.54	39.31	− 11.51	− 12.29	− 13.08	− 13.86	− 14.65
MB	15.81	67.50	− 19.76	− 21.11	− 22.46	− 23.81	− 25.16

Table 5 Maximum adsorption capacities of dyes from aqueous solution using different adsorbents

Sorbent	q_{max} (mg/g)			References
	BCG	AY	MB	
SW-ZnO-PANI	–	–	20.55	[21]
Polypyrrole-coated Fe_3O_4 nanoparticles	–	113.6	–	[32]
ZnO nanorods loaded on activated carbon	57.80	–	–	[46]
Wood charcoal	–	14.9	–	[47]
Anaerobic granular sludge	–	–	86	[48]
Natural zeolite	–	–	4.36	[49]
Nano-γ-alumina	–	39.0	–	[50]
Ziziphus nummularia (ZPN)	19.61	–	–	[51]
Modified PEPP	52.63	15.87	31.25	This study

it was carried out the acylation reaction with chloroacetyl chloride of –OH group in the homopolymer and then was modified with the diethanol amine. The FT-IR and ^{1}H−NMR data confirmed the structures of all homopolymers. Modified homopolymer showed higher adsorption capability for three dyes (BCG, AY and MB). The equilibrium between the dyes and the adsorbent in the solution was ensured within 90 min. The competitive adsorption capacity of the modified polymer for the BCG was higher than that for the other dyes (AY and MB). Also, it was seen that the different structures of dyes cause the different adsorption capacities.

The adsorption kinetic studies showed that pseudo-second-order equation was the best model for this adsorption process. Equilibrium data and constants were observed to follow Langmuir model of dye adsorption on the polymer surface. The thermodynamic analysis showed that the adsorption process was spontaneous and endothermic.

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