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Thermodynamic properties of dye removal from colored textile wastewater by poly(propylene imine) dendrimer

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ABSTRACT

In this paper, the thermodynamic properties of textile dye removal from aqueous solutions using poly(propylene imine) (PPI) dendrimer were studied. Direct Red 80 (DR80) and Acid Green 25 (AG25) were used as model dyes. The surface coverage of dendrimer was obtained to investigate the adsorbent characteristics. The effect of temperature on dye removal has been studied at different dye concentrations. The adsorption isotherms (Langmuir and Freundlich) and kinetics (pseudo-first-order and pseudo-second-order) were studied in various temperatures. Thermodynamic parameters such as free energy of adsorption (ΔG), enthalpy (ΔH), and entropy (ΔS) changes were calculated to predict the nature of the adsorption. It was found that the isotherm data of DR80 and AG25 followed Langmuir model at different temperatures. Adsorption kinetics of dyes was found to conform to pseudo-second-order with a good correlation coefficient. The estimated values for ΔG showed that the adsorption process was spontaneous. Based on the data of the present study, it can be concluded that PPI dendrimer, as an eco-friendly material, is a suitable adsorbent for the elimination of dyes from colored textile wastewater at different temperatures.

Keywords: PPI Dendrimer; Dye removal; Wastewater; Thermodynamic; Adsorption; Kinetics

1. Introduction

The use of synthetic dyes in our everyday life is continuously growing. Dyes have been widely used as colorants in various industries such as textile, paper, pharmaceutical, food, and cosmetic [1]. The annual dye consumption of different industries is in excess of 700 kilotons and it has been estimated that about 70 kilotons of this amount are annually discharged into wastewaters. Producers and users of dyes are interested in the fastness and stability of dyes on the fabrics, and consequently, they are producing various types of dyes which are more difficult to degrade after their application [2].

Large quantities of colored wastewaters are discharged from the dyeing process with a strong persistent color which is esthetically and environmentally unacceptable [3]. Some dyes are toxic and even carcinogenic for aquatic living organisms [4–10]. Thus, several governments have established environmental restrictions with regard to the quality of colored wastewater and have forced dye-using industries to remove dyes from their effluents before discharging them into water bodies.

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Several dye removal methods such as biological, chemical, and physical processes have been investigated extensively [3,11–17]. Adsorption as a physical process can handle large flow rates, producing a high-quality effluent that does not result in the formation of harmful substances, during the process.

Dendrimers are a class of macromolecules characterized by a highly branched structure of great regularity, compact shape, large number of (reactive) end groups, and space between the branches for taking up guest molecules. Dendrimers have low toxicity and immunogenicity [18]. Some properties of dendrimers have provided them a wide range of biological applications such as carriers for cytostatic agents, gene therapy, prevention against HIV, culture of organs and tissue, and wound healing [19,20]. Modified dendrimers have been applied to extract dyes either in liquid–liquid systems [21] or liquid–solid systems (dyeing of polypropylene fibers) [22]. The removal of triarylmethane dyes by polyamidoamine dendrimer has been demonstrated, and the effective parameters such as pH, dendrimer concentration, and generation effects on dye removal percentage have been studied [23]. Also, the extraction of azo dye molecules from aqueous solution using polyamidoamine dendrimer based polymeric network was reported by Ghosh [24].

In this study, poly(propylene imine) (PPI) dendrimer was used for the removal of Direct Red 80 (DR80) and Acid Green 25 (AG25) dyes from aqueous solution. Direct dyes are widely employed for the dyeing of cotton which is one of the most cellulosic fibers used in various textile productions. On the other hand, acid dyes are a class of dyes containing sulfonic groups, which are commonly used with fibers such as polyamide, wool, and silk. These classes of dyes are from the azo group which is the most important and the largest class of synthetic dyes. The azo bonds existing in the azo dyes can be converted into mutagenic and carcinogenic aromatic amines under chemical reactions in water streams, which demonstrate their immediate removal from water effluents [25–28]. Therefore, AG25 and DR80 that are frequently used in textile products were selected as the model dyes to investigate their removal using PPI dendrimer. The effect of temperature on dye removal has been studied at different dye concentrations. The adsorption isotherms (Langmuir and Freundlich), adsorption kinetics (pseudo-first-order and pseudo-second-order), and thermodynamic parameters were studied. The adsorption isotherm and kinetics were studied to find the correlation between the adsorbent and adsorbate at equilibrium and the mechanism of the removal process. Also, the investigation of thermodynamic parameters in an adsorption process at equilibrium condition is essential to indicate the spontaneous nature of the process [29].

2. Experimental

2.1. Chemicals and materials

PPI dendrimer was obtained from SYMO-Chem BV Co. The properties and chemical structure of dendrimer are shown in Fig. 1. C.I. Direct Red 80 (DR80) and C.I. Direct Green 25 (DG25) were used as model dyes and purchased from Ciba. The chemical structures of dyes are shown in Table 1. Other chemicals were of analytical grade and purchased from Merck. The pH of the solutions was adjusted by the addition of a small amount of H_2SO_4 (1 M) or NaOH (1 M) solution. A CECIL 2021 UV–VIS spectrophotometer was used to measure the dye absorbance.

In order to characterize the self-assembled structure of PPI dendrimer, dynamic light scattering (DLS) was conducted. The histogram analysis of the DLS (Fig. 2) indicates that the mean diameter of PPI dendrimer is 1.436 nm.

2.2. Adsorption procedure

The adsorption measurements were conducted by mixing 1.8 mg/L of dendrimer in jars containing 200 mL of dye solution (50 mg/L and pH 2) at different temperatures. pH studies were conducted to determine the optimum pH at which the maximum color removal could be achieved with dendrimer for each dyes.

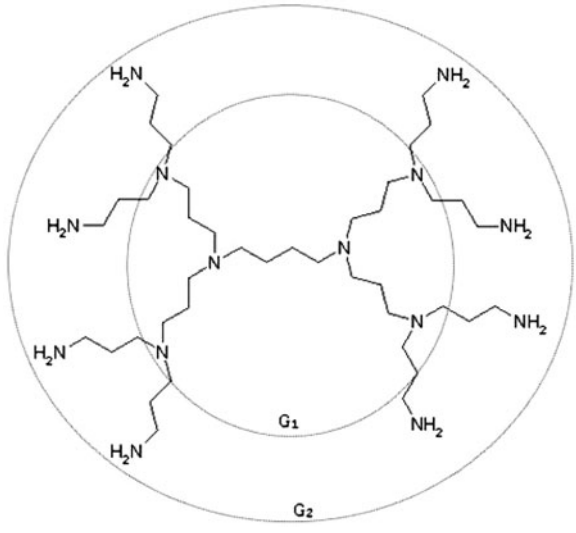

Fig. 1. The chemical structure of PPI dendrimer (G_2, M_W: 773 g/mol and $C_{40}H_{94}N_{14}$).

Table 1
The chemical structures of dye

C.I. generic name	Molecular formula	C.I. constitution no.	λ_{max} (nm)	Molecular weight
C.I. Direct Red 80	$C_{29}H_{19}N_5Na_2O_8S_2$	28160	510	675.6
C.I. Acid Green 25	$C_{28}H_{20}N_2Na_2O_8S_2$	61570	642	622.58

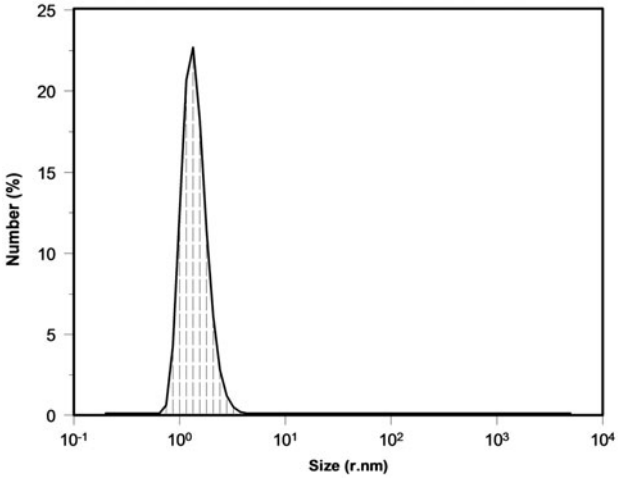

Fig. 2. DLS measurements of the hydrodynamic radius of PPI dendrimer G_2.

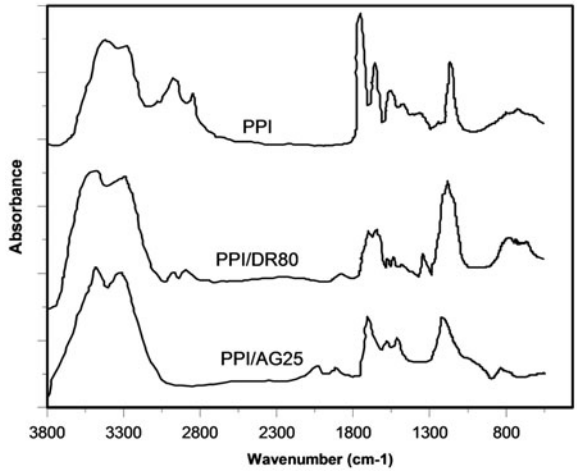

Fig. 3. FTIR spectra of PPI dendrimer before and after the dye adsorption.

3. Results and discussion

3.1. Fourier transform infrared analysis

The Fourier transform infrared (FTIR) spectra of samples were measured by Thermo Nicolet Avatar 360 FTIR Spectrometer within the range of 500–3,800 cm^{-1}. The FTIR spectra of PPI dendrimer before and after the adsorption of dye molecules are illustrated in Fig. 3. The broad peak around 3,400 cm^{-1} observed in all samples can be related to the water adsorption due to the existence of dendrimer amino groups. The peak appearing at 1,200 and 1,600 cm^{-1} in PPI dendrimer can be assigned to the C–N and N–H bending bonds. The peak corresponding to the aromatic C=C is appeared at 1,700 cm^{-1}, and also the peaks at 1,200 and 800 cm^{-1} can be related to the S=O and S–O bonds of dye molecules, which confirms the adsorption of dyes onto the PPI dendrimer [30].

3.2. Effect of pH

The initial pH of the dye solution plays an important role in the adsorption capacity and surface characteristics of the adsorbent, which affects the electrostatic attraction between the adsorbate and adsorbent. According to Fig. 4, the maximum dye removal is achieved at pH 2 and increasing the solution pH will decrease the removal efficiency. At low pH values, the

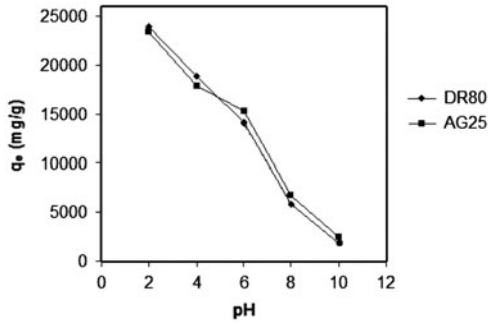

Fig. 4. The effect of pH on DR80 and AG25 removal by PPI dendrimer (dye concentration = 50 mg/L, C_{dendr} = 1.8 mg/L).

terminal amino groups of the PPI dendrimer are protonated and the electrostatic attraction between the positive NH_3^+ groups on the surface of the adsorbent can adsorb the anionic dye molecules and remove them from the aqueous solution. On the other hand, the repulsion forces between the adsorbent at high pH values and negatively charged dye molecules will lead to the lower dye removal efficiencies [30].

3.3. Surface characteristics

To account for the adsorption behavior of dye molecules on dendrimer, the Langmuir type equation related to surface coverage (θ) was used. The equation is expressed as follows:

$$bC_0 = \theta/(1-\theta) \quad (1)$$

The fraction of biomass surface covered by dyes was studied by plotting the surface coverage values against dye concentration at different temperatures. The plots are presented in Fig. 5 which illustrates that the surface coverage on dendrimer increases sharply with the increase of initial dye concentration, and then increases slowly until θ value is close to 1.0. Furthermore, θ value increases with increasing temperatures in the condition of same dye concentration. These results show that higher dye concentrations and adsorption temperatures will benefit the dye molecules coverage onto the dendrimer with a monomolecular layer. The overall result about the surface coverage indicates that dendrimer will be very effective for the removal of dyes from aqueous solutions [31,32].

3.4. Effect of temperature

The adsorption studies were carried out at different temperatures 25, 35, 45, 55, and 65°C, and the

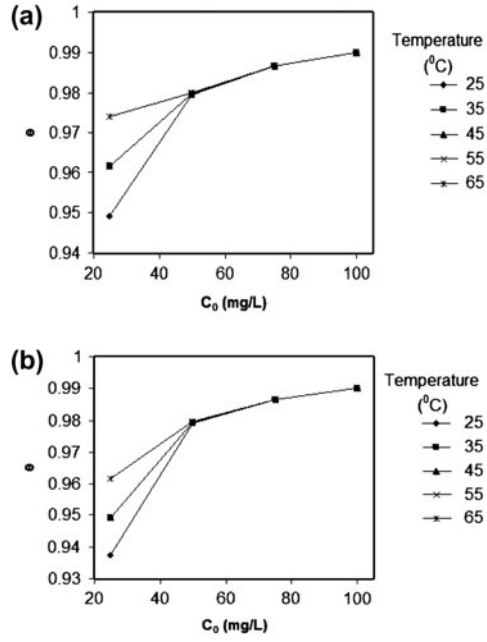

Fig. 5. Plots of surface coverage (θ) against initial dye concentration at different temperatures (a) DR80 and (b) AG25 (pH 2, C_{dendr} = 1.8 mg/L).

results of these experiments are presented in Figs. 6 and 7. The adsorption capacity increases with the increasing temperature, indicating that the adsorption is an endothermic process. This may be a result of increase in the mobility of the dye molecules with the increase of temperature [33]. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface of adsorbent. Furthermore, increasing the temperature may produce a swelling effect within the internal structure of the dendrimer, enabling large amounts of dyes to penetrate further into the adsorbent structure [34].

3.5. Adsorption isotherms

Adsorption isotherm is a graphical representation indicating the relation between the mass of dye adsorbed at constant temperature per unit mass of adsorbent and liquid phase dye concentration at equilibrium. It presents how dye molecules can be distributed between the liquid and solid phases at various equilibrium concentrations. Several factors such as the number of compounds in the solution, their relative adsorbabilities, initial concentration of adsorbate in the solution, and the degree of competition among solutes for adsorption sites determine the shape of isotherm. Adsorption isotherms provide information on

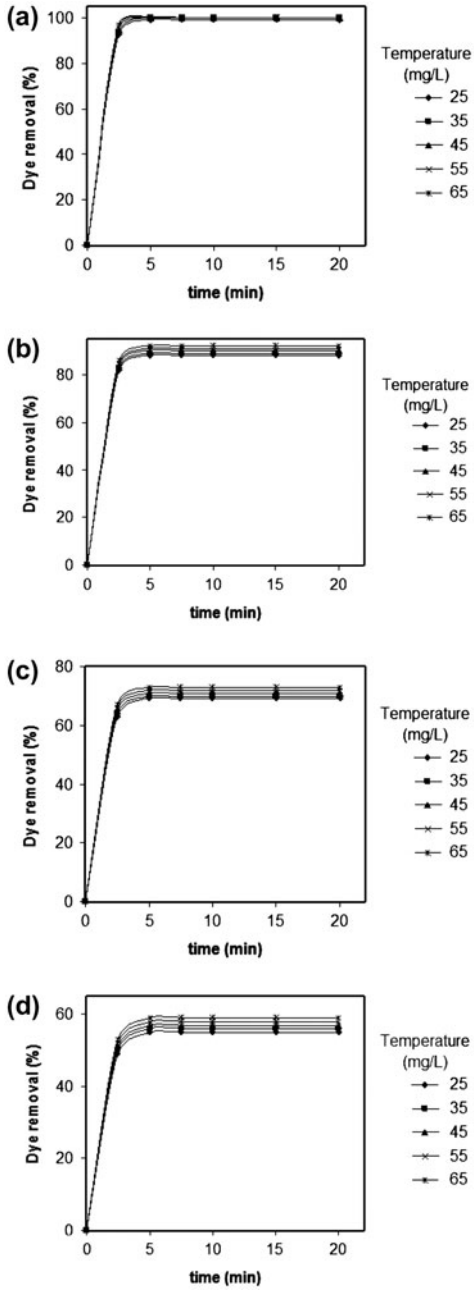

Fig. 6. The effect of time and temperature on DR80 dye removal by dendrimer at different dye concentration. (a) 25, (b) 50, (c) 75, and (d) 100 mg/L (pH 2, C_{dendr} = 1.8 mg/L).

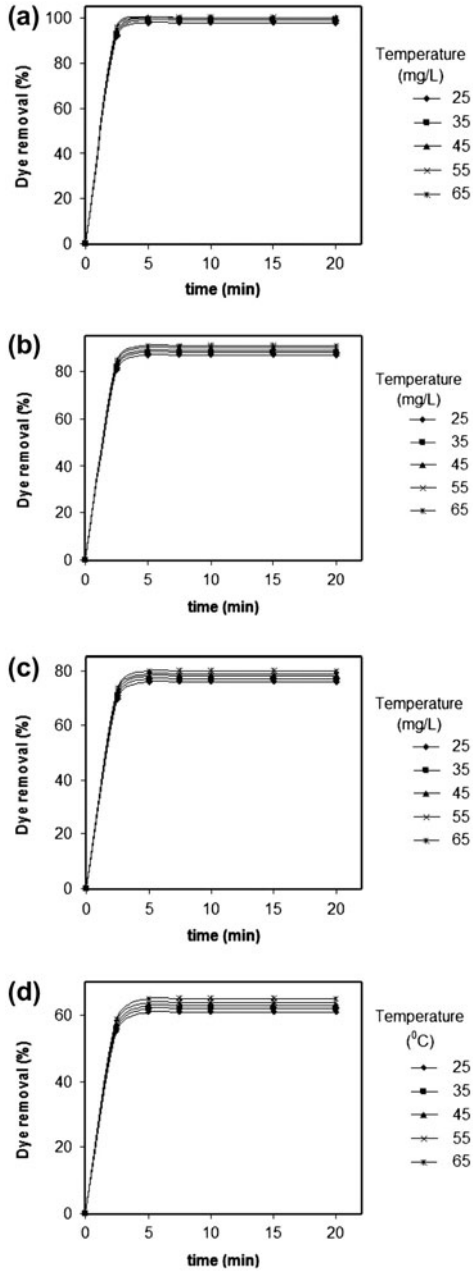

Fig. 7. The effect of time and temperature on AG25 dye removal by dendrimer at different dye concentration. (a) 25, (b) 50, (c) 75, and (d) 100 mg/L (pH 2, C_{dendr} = 1.8 mg/L).

how adsorption system proceeds, and indicate how efficient a given adsorbent interacts with adsorbate [35].

Langmuir equation is often described by monolayer adsorption. This model assumes a uniform energy of adsorption and a single layer of adsorbed solute at a constant temperature. The Langmuir equation can be written as [36]:

$$q_e = Q_0 K_L C_e/(1 + K_L C_e) \quad (2)$$

where q_e is the amount of dye adsorbed on the dendrimer at equilibrium, C_e is the equilibrium concentration of dye solution, K_L is the equilibrium constant, and Q_0 is the maximum adsorption capacity. The linear form of Eq. (2) is:

$$C_e/q_e = (1/K_L Q_0) + (C_e/Q_0) \quad (3)$$

The Q_0 is obtained from the slope of the C_e/q_e vs. C_e plot and K_L is obtained from the intercept. The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter, R_L, defined by:

$$R_L = 1/(1 + K_L C_0) \quad (4)$$

where K_L is the Langmuir constant, C_0 is the initial dye concentration (mg/L), and R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [37]. It has been found that the adsorption of DR80 and AG25 dyes on the dendrimer is favorable and the R_L value is between 0 and 1.

The plots of the total amount of dyes adsorbed against the total equilibrium dye concentration were well fitted by the Langmuir equation (Fig. 8 and Table 2).

The Freundlich equation is one of the well-known models applicable for a single solute system. It is an empirical equation used to describe the distribution of solute between solid and aqueous phases at a point of saturation. The basic assumption of this model is that there is an exponential variation in site energies of adsorbent and also surface adsorption is not the rate limiting step. The strength of linear relationship can be expressed by correlation coefficient. Its value is used to evaluate how the Freundlich model represents the experimental data [38].

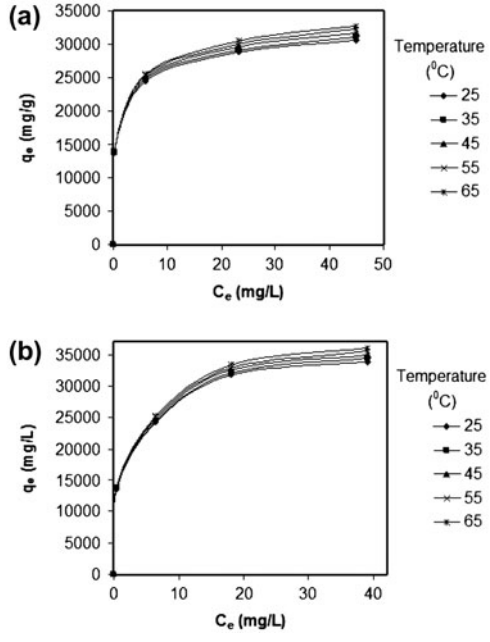

Fig. 8. Adsorption isotherms of dyes using dendrimer (a) DR80 and (b) AG25 $C_0 = 50$ mg/L (pH 2, $C_{dendr} = 1.8$ mg/L).

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Freundlich isotherm can be expressed by [39–42]:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_F is adsorption capacity at unit concentration and $1/n$ is adsorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), and unfavorable ($1/n > 1$) [43]. Eq. (5) can be rearranged to a linear form:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (6)$$

The n values for the Freundlich adsorption isotherm are shown in Table 2.

3.6. Adsorption kinetics

Adsorption kinetics provides information regarding the mechanisms of adsorption that is important for the efficiency of the process. It is important to know the rate of adsorption process during the removal of contaminants from wastewater to optimize the design parameters, because the kinetics of system controls the adsorbate residence time and reactors dimensions. As a result, predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design [44].

In order to design a fast and effective model, investigations were made on adsorption rate. Two kinetics models (pseudo-first-order and pseudo-second-order) have been used to test the experimental data such as the examination of the controlling mechanisms of adsorption process (chemical reaction, diffusion control, and mass transfer) [45,46].

Pseudo-first-order equation is generally represented as follows [47,48]:

$$dq_t/dt = k_1(q_e - q_t) \quad (7)$$

where q_e, q_t, and k_1 are the amount of dye adsorbed at equilibrium (mg/g), the amount of dye adsorbed at time t (mg/g), and the equilibrium rate constant of pseudo-first-order kinetics (1/min), respectively. After integration by applying the conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then Eq. (7) can be written as:

Table 2
Isotherm constants for dye adsorption (200 mL solution, pH 2, $C_0 = 50$ mg/L, and $C_{dendr} = 1.8$ mg/L for DR80 and AG25)

System	Langmuir				Freundlich		
Temperature (°C)	Q_0 (mg/g)	K_L (L/mg)	R_L	R_1^2	K_F	n	R_2^2
DR80							
25	33,333.3	0.75	0.026	0.999	17,470.3	6.377	0.987
35	33,333.3	1	0.020	0.998	19,116.1	7.440	0.997
45	33,333.3	1	0.020	0.998	19,324.1	7.257	0.995
55	33,333.3	1	0.020	0.998	19,543.4	7.087	0.993
65	33,333.3	1.5	0.013	0.998	19,778.8	6.930	0.990
AG25							
25	33,333.3	0.6	0.032	0.997	16,006.6	4.598	0.990
35	33,333.3	0.75	0.026	0.996	17,844.3	5.297	0.993
45	33,333.3	0.75	0.026	0.996	19,449.1	6.020	0.992
55	33,333.3	1	0.020	0.996	20,782.6	6.662	0.990
65	33,333.3	1	0.020	0.997	21,988.7	7.289	0.988

$$\log (q_e - q_t) = \log (q_e) - (k_1/2.303)t \quad (8)$$

The straight-line plots of $\log (q_e - q_t)$ vs. t for the adsorption of DR80 and AG25 by dendrimer at different temperatures (25, 35, 45, 55 and 65°C) have been analyzed to obtain the rate parameters. The k_1, q_e, and correlation coefficients (R^2) under different temperature values were calculated and are given in Table 3.

Data were applied to the Ho and MacKay's pseudo-second-order kinetic rate equation which is expressed as [47,49]:

$$dq_t/dt = k_2(q_e - q_t) \quad (9)$$

where k_2 is the equilibrium rate constant of pseudo-second-order (g/(mg min)). The integrated form of the Eq. (9) is:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (10)$$

To understand the applicability of the model, linear plots of t/q_t vs. t under various dye concentration values at different temperatures by dendrimer are shown in Fig. 9. The k_2, q_e, and correlation coefficients (R^2) were calculated from these plots and are presented in Table 3. From Table 3, adsorption kinetics of dyes was studied and the rates of sorption were found to conform to pseudo-second-order kinetics with good correlation coefficients.

Table 3
Kinetics constants for dye adsorption for DR80 and AG25 (200 mL solution, pH 2, $C_0 = 50$ mg/L, and $C_{dendr} = 1.8$ mg/L)

		Pseudo-first-order				Pseudo-second-order	
Temperature (°C)	$(q_e)_{exp}$ (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
DR80							
25	24,444.4	78,957.8	2.482	0.903	25,000	0.001	0.999
35	24,722.2	79,707.6	2.484	0.904	25,000	0.001	0.999
45	25,000	80,463.7	2.486	0.904	25,000	0.001	0.999
55	25,277.8	81,208.2	2.488	0.905	25,000	0.001	0.999
65	25,555.6	81,940.8	2.488	0.905	25,000	0.001	0.999
AG25							
25	24,166.7	78,216.8	2.479	0.903	25,000	0.001	0.999
35	24,444.4	78,958.7	2.482	0.903	25,000	0.001	0.999
45	24,722.2	79,707.6	2.484	0.904	25,000	0.001	0.999
55	25,000	80,463.7	2.486	0.904	25,000	0.001	0.999
65	25,277.8	81,208.2	2.488	0.904	25,000	0.001	0.999

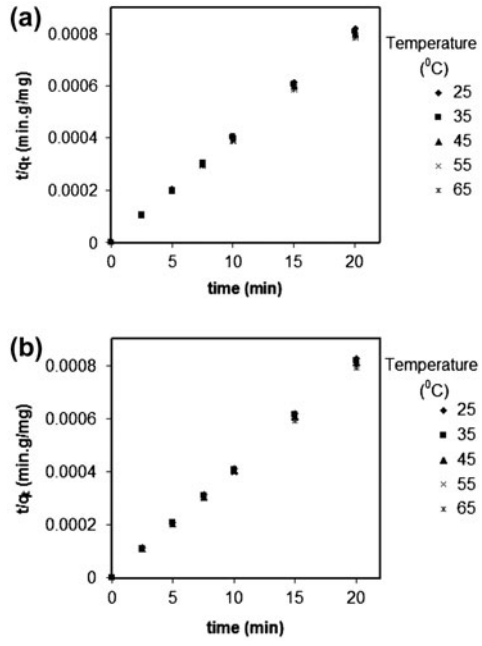

Fig. 9. Pseudo-second-order sorption kinetics of dyes by dendrimer (a) DR80 and (b) AG25 ($C_0 = 50$ mg/L, pH 2, and $C_{dendr} = 1.8$ mg/L).

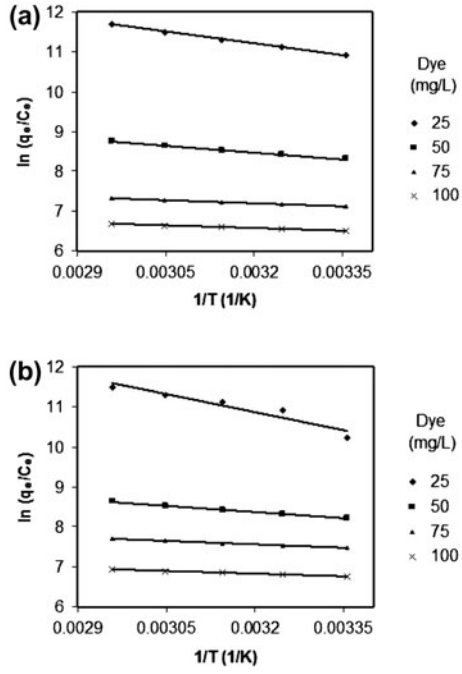

Fig. 10. van't Hoff plots for the adsorption of dyes by dendrimer (a) DR80 and (b) AG25 (pH 2 and $C_{dendr} = 1.8$ mg/L).

3.7. Thermodynamic parameters

Thermodynamic parameters including the changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are the actual indicators for practical application of an adsorption process. According to the values of these parameters, it can be determined what process will occur spontaneously. ΔG can be calculated using Eq. (11). ΔH and ΔS were calculated from the slope and intercept of the linear plot of ln (q_e/C_e) vs. $1/T$ (Fig. 10) according to Eq. (12), i.e. the van't Hoff equation.

$$\Delta G = -RT \ln(q_e/C_e) \tag{11}$$

$$\ln(q_e/C_e) = -\Delta G/RT = -\Delta H/RT + \Delta S/RT \tag{12}$$

The obtained thermodynamic parameters are given in Table 4 and the van't Hoff plots of the adsorption process are shown in Fig. 10. The positive values of ΔH and ΔS suggest endothermic reaction and the increased randomness at the solid/solution interface during the

Table 4
Thermodynamic parameters of dye adsorption for DR80 and AG25 (200 mL solution, pH 2, and $C_{dendr} = 1.8$ mg/L)

			ΔG (kJ/mol) at temperatures				
Dye (mg/L)	ΔH (kJ/mol)	ΔS (J/molK)	298 K	308 K	318 K	328 K	338 K
DR80							
25	16.474	145.886	−26.999	−28.459	−29.917	−31.376	−32.835
50	9.376	100.441	−20.556	−21.560	−22.565	−23.569	−24.573
75	4.066	72.809	−17.631	−18.359	−19.087	−19.815	−20.543
100	3.415	65.651	−16.149	−16.805	−17.462	−18.118	−18.775
AG25							
25	25.045	170.412	−25.738	−27.442	−29.146	−30.850	−32.554
50	8.604	97.107	−20.334	−21.305	−22.276	−23.247	−24.218
75	4.882	78.465	−18.501	−19.285	−20.070	−20.855	−21.639
100	3.585	68.288	−16.765	−17.447	−18.130	−18.813	−19.496

adsorption of dyes by dendrimer, respectively. The negative values of ΔG imply the spontaneous nature of the adsorption process. Further, the decrease in the values of ΔG with the increasing temperature indicates that the adsorption is more spontaneous at higher temperatures. Generally, the change in free energy for physisorption is between –20 and 0 kJ/mol, but chemisorption is in the range of −80 to 400 kJ/mol [50]. The values of ΔG obtained in this study are within the ranges of the physisorption mechanisms.

4. Conclusion

The results of this investigation indicate that dendrimer has effective adsorption capacity for the removal of DR80 and AG25 from aqueous solutions. The experimental results were analyzed by using the Langmuir and Freundlich isotherm models at various temperatures and the correlation coefficients for Langmuir equation fitted better than Freundlich equation. Adsorption kinetics of dyes at different temperatures was found to conform to pseudo-second-order with a high correlation coefficient (R^2). Positive ΔH values showed the endothermic reaction and the positive value of ΔS suggested the increased randomness at the solid/solution interface during the adsorption process. The negative values of ΔG indicated the spontaneous nature of the adsorption process. Based on the data of the present study, it can be concluded that PPI dendrimer is an eco-friendly adsorbent for dye removal from colored textile wastewaters.

Acknowledgments

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