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Single and Binary System Dye Removal from Colored Textile Wastewater by a Dendrimer as a Polymeric Nanoarchitecture: Equilibrium and Kinetics

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This paper deals with the removal of textile dyes from aqueous solutions by a poly(propylene imine) dendrimer (PPI) as a polymeric nanoarchitecture in single and binary (mixture of dyes) systems. Direct Blue 78 (DB78) and Acid Black 26 (AB26) were used as model dyes. The effects of operational parameters such as dendrimer concentration, contact time, dye concentration, inorganic anions (salts), and pH have been studied on dye removal. Adsorption isotherms (Langmuir, Freundlich, and Tempkin models), adsorption kinetics (pseudofirst order, pseudosecond order, and intraparticle diffusion), and dye desorption were studied in single and binary dye systems. It was found that the isotherm data of DB78 and AB26 in single and binary systems of dyes followed the Langmuir isotherm. Adsorption kinetics of dyes in single and binary dye systems were found to conform to a pseudosecond order model. Desorption tests showed that the maximum dye releases of 93 % for DB78 and 86 % for AB26 in a single system and 90 % for DB78 and 84 % for AB26 in a binary system of dyes were achieved in aqueous solution at pH 12. On the basis of the data of the present study, it can be concluded that the dendrimer as a polymeric nanoarchitecture is an eco-friendly adsorbent with a relatively large adsorption capacity and may be a suitable alternative for elimination of dyes from aqueous media.

Introduction

Synthetic dyes are present in our everyday life, and their usage is continuously growing. Dyes have been widely used as colorants in different industries such as textile, paper, pharmaceutical, food, cosmetic, etc.[1] The annual dye production is in excess of $7 \cdot 10^5$ tons. Approximately $7 \cdot 10^4$ tons of dyes are annually discharged into wastewater by the textile industry. Producers and users of dyes are interested in stability, and consequently, are producing dyes which are more difficult to degrade after application.[2]

Large quantities of colored wastewater are discharged from the dyeing process with strong persistent color that is aesthetically and environmentally unacceptable.[3] Some of the dyes are toxic and even carcinogenic to aquatic 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.

Several treatment methods for dye removal 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. The adsorption of dyes and other pollutants using several adsorbents has been studied.[18−32]

Dendrimers are a class of organic compounds characterized by a compact shape, a highly branched structure of great regularity, a large number of end groups, and room between the branches for taking up guest molecules. Two general strategies used in dendrimer synthesis are divergent and convergent routes. Dendrimers are built up from a central polyfunctional core in the divergent route.[33] The building blocks are added layer by layer in a repeated reaction cycle. Each next cycle leads to a higher generation of dendrimer. In the convergent route, first complete wedges (dendrons) are prepared, which are subsequently coupled to a central core.[34] Dendrimers are polymeric nanoarchitectures.[35] Dendrimers are used as carriers for cytostatic agents, culture of organs and tissue, gene therapy, wound healing, etc.[36,37] In addition, dendrimers have been applied to extract dyes either in liquid−liquid systems or liquid−solid systems.[38−41]

A literature review showed that dye removal using a poly(propylene imine) dendrimer as a polymeric nanoarchitecture has not been studied in a binary dye system. In this study, a poly(propylene imine) dendrimer (PPI dendrimer) was used to remove Direct Blue 78 (DB78) and Acid Black 26 (AB26) dyes from single and binary systems. The effects of operational parameters such as dendrimer concentration, contact time, dye concentration, inorganic anions (salts), and pH on dye removal have been studied at 25 °C. The adsorption isotherms (Langmuir, Freundlich, and Tempkin models), adsorption kinetics (pseudofirst order, pseudosecond order, and intraparticle diffusion) and dye desorption were investigated in single and binary dye systems.

Experimental Section

Chemicals and Materials. Dendrimer was obtained from the SYMO-Chem BV Co. The chemical structure of dendrimer is shown in Figure 1. The Direct Blue 78 (DB78) and Acid Black 26 (AB26) dyes were used as model dyes and purchased from Ciba. The chemical structures of the dyes are shown in Figure 2. Other chemicals were Analar grade from Merck. The pH of

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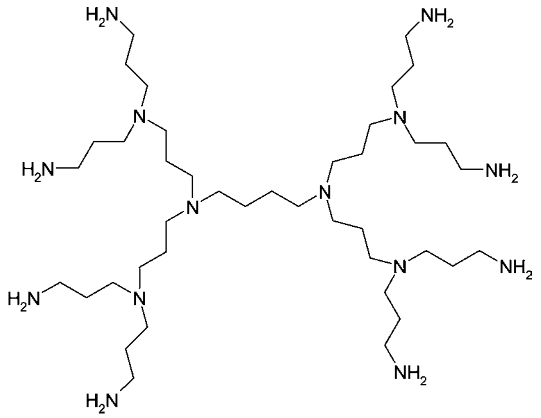
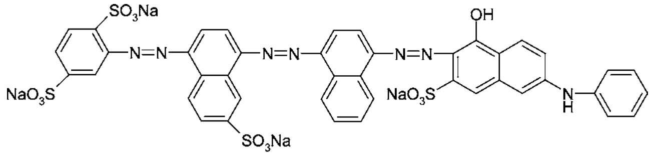
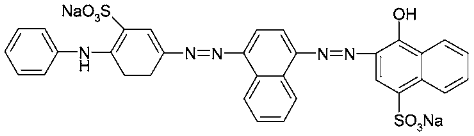


Figure 1. Chemical structure of the PPI dendrimer.



DB78



AB26

Figure 2. Chemical structure of dyes.

Table 1. Initial Dye Concentration Used in Single and Binary Systems

single system		binary system	
$C_{0,\mathrm{DB78}}$	$C_{0,\mathrm{AB26}}$	$C_{0,\mathrm{DB78}}$	$C_{0,\mathrm{AB26}}$
25	25	25	25
50	50	50	50
75	75	75	75
100	100	100	100

the solutions was adjusted by adding a small amount of H_2SO_4 or NaOH. A CECIL 2021 UV−vis spectrophotometer was used to determine the dye concentration.

Adsorption Procedure. The adsorption measurements were conducted by mixing various amounts of dendrimer in jars containing 200 mL of a dye solution (50 $mg \cdot L^{-1}$) at various pHs (2 to 10). pH studies were conducted to determine the optimum pH at which maximum color removal could be achieved with dendrimer for each of the two dyes. Experiments were performed at different dye concentrations using 1.8 $mg \cdot L^{-1}$ dendrimer for DB78 and AB26 in single and binary systems at pH 2 and 25 °C for 30 min (Table 1).

Dye concentrations were calculated as follows: for a binary system of components, A and B were measured at λ_1 and λ_2, respectively, to give optical densities of d_1 and d_2[42]

$$C_A = (k_{B2}d_1 - k_{B1}d_2)/(k_{A1}k_{B2} - k_{A2}k_{B1}) \qquad (1)$$

$$C_B = (k_{A1}d_2 - k_{A2}d_1)/(k_{A1}k_{B2} - k_{A2}k_{B1}) \qquad (2)$$

where k_{A1}, k_{B1}, k_{A2}, and k_{B2} are the calibration constants for components A and B at two wavelengths λ_1 and λ_2, respectively.

The changes of absorbance were determined at certain time intervals [(2.5, 5, 7.5, 10, 15, 20, 25, and 30) min] during the adsorption process. After the experiments, the samples were centrifuged by a Hettich EBA20, and then the dye concentration was determined. To investigate the inorganic anion (salt) effect on dye removal efficiency, 1 mmol Na_2SO_4, $NaHCO_3$, K_2CO_3, and NaCl were added to 200 mL of dye solution (dye, 50 $mg \cdot L^{-1}$; dendrimer for DB78 and AB26 in single and binary systems, 1.8 $mg \cdot L^{-1}$; pH 2 and 25 °C for 30 min).

Desorption Studies. The PPI dendrimer used for the adsorption of 50 $mg \cdot L^{-1}$ dye solution was separated from the solution by centrifugation and dried. Then the adsorbent was agitated with 200 mL of distilled water at different pH values (2 to 12) for the predetermined equilibrium time of the desorption process. The desorbed dye was determined.

Results and Discussion

Effect of Operational Parameters on Dye Removal. Dendrimer Concentration. The effect of dendrimer concentration on dye removal in single (sin.) and binary (bin.) systems is shown in Figure 3. The percentage removal increased with increasing dendrimer concentration up to a certain limit, and then it reached a constant value. The optimum dendrimer concentration, 1.8 $mg \cdot L^{-1}$ dendrimer for DB78 and AB26 in single and binary systems, was selected for 200 mL of 50 $mg \cdot L^{-1}$ dye solution. The increase in adsorption of dyes with increasing dendrimer concentration was due to the availability of more active surface sites of dendrimer for adsorption.

A given mass of dendrimer can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbent is very important. The reason for the increase in the adsorption efficiency with an increase in adsorbent dosage is unsaturation of adsorption sites through the adsorption process.[43]

Contact Time. Contact time is used to assess the practical application of the adsorption process. Figure 3 shows the uptake of dye as a function of contact time at different dosages of adsorbent. It is observed from the graphs that dye adsorption on dendrimer is a very fast process, where > 90 % of the adsorption takes place within the first 2.5 min and equilibrium is attained within 5 min. Beyond the equilibrium time, adsorption is found to be nearly constant. It can be attributed that at the initial stage of adsorption vacant surface sites are available, and once equilibrium is attained, the remaining vacant sites are difficult to be occupied, probably caused by the repulsive forces between the molecules on the adsorbent.[44,45]

Dye Concentration. The effect of initial dye concentration of DB78 and AB26 in single and binary systems on dye removal was studied (Figure 4). The results show that dye removal decreases when the dye concentration increases. It can be attributed to that the active sites on adsorbent for dye removal decrease when the dye concentration increases.

Inorganic Anions. Textile wastewater contains various types of suspended and dissolved compounds such as dyes, acids, alkalis, salts, surfactants, metal ions, etc. Anions such as nitrate, carbonate, sulfate, and chloride are the most common ions present in textile wastewater. To investigate the inorganic anion effect on dye removal efficiency, 1 mmol Na_2SO_4, $NaHCO_3$, K_2CO_3, and NaCl were added to dye solution. Figure 5 illustrates the dye removal capacity of the PPI dendrimer in single and binary systems. Dye removal efficiency decreases in the presence of inorganic anions because they compete with dyes in adsorption onto the dendrimer. The interactions of the anions with protonated amino groups contributed to reduce the polymer solubility (dehydrating effect), decreasing the availability of protonated amino groups.[46]

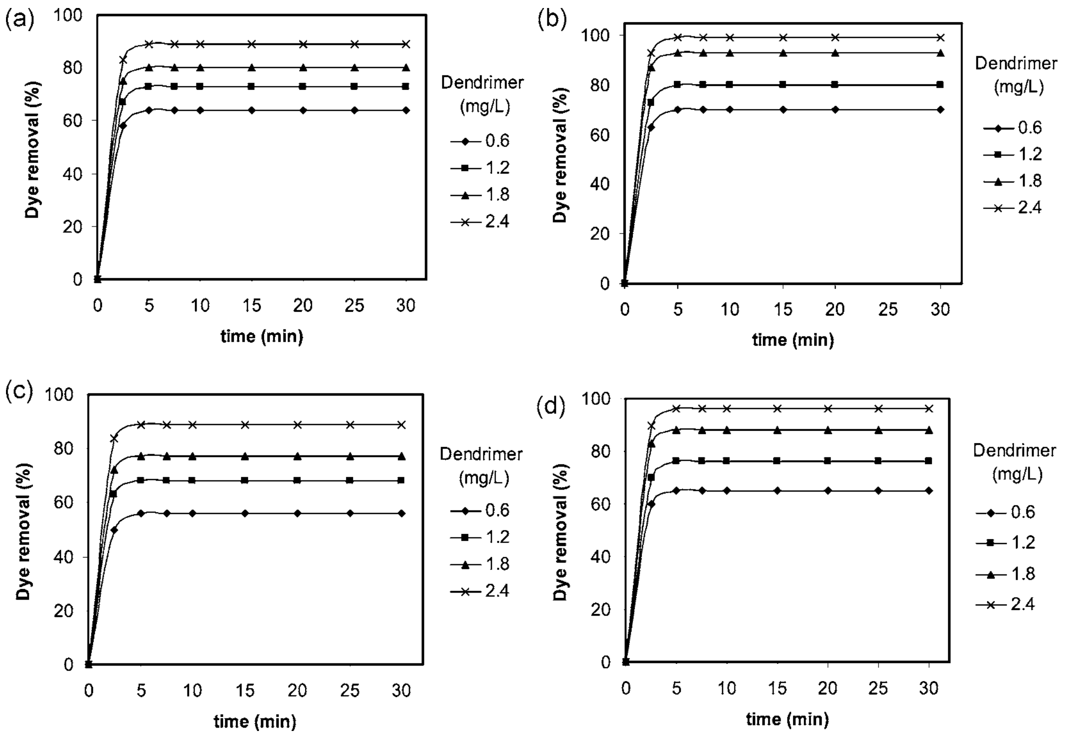


Figure 3. Effect of dendrimer concentration and time on dye removal by dendrimer (a) DB78 (sin.), (b) AB26 (sin.), (c) DB78 (bin.), and (d) AB26 (bin.) (pH 2, 25 °C, and $C_0 = 50\ \mathrm{mg \cdot L^{-1}}$).

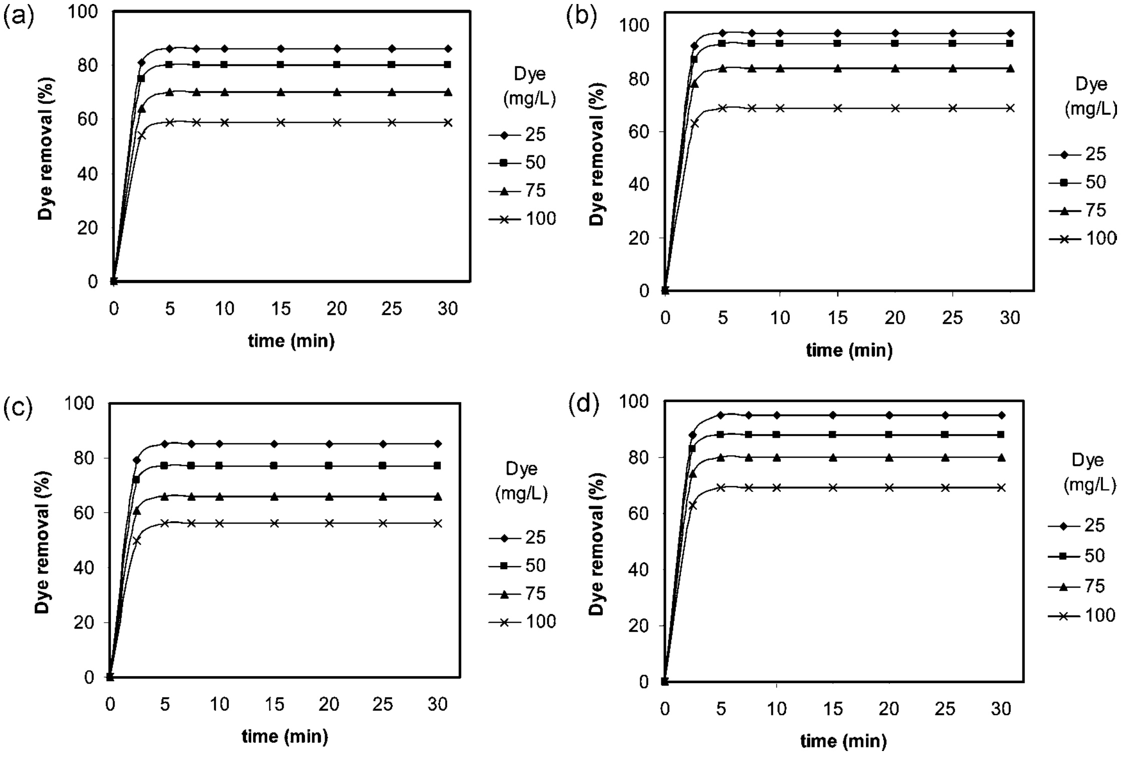


Figure 4. Effect of dye concentration on dye removal by dendrimer (a) DB78 (sin.), (b) AB26 (sin.), (c) DB78 (bin.), and (d) AB26 (bin.) (pH 2, 25 °C, and $C_{\mathrm{dendr}} = 1.8\ \mathrm{mg \cdot L^{-1}}$ for DB78 and AB26 in single and binary systems).

Solution pH. The final dye concentration after adsorption varied significantly with the initial pH of the dye solution. Experiments were carried out over a broad pH range of 2 to 10. The effect of pH on the adsorption of DB78 and AB26 in single and binary systems by the PPI dendrimer is shown in Figure 6.

At pH 2, a high electrostatic attraction exists between the positively charged surface of the dendrimer and the anionic dye molecules. As the pH of the system increases, the number of positively charged sites decreases. Reduction of positively charged sites on the dendrimer does not favor the adsorption of anionic dye molecules due to the decreasing of electrostatic attraction.[47] The effective pH was 2 and was used in further studies.

Adsorption Isotherms. Single System. Adsorption isotherms indicate the relation between the mass of dye adsorbed at

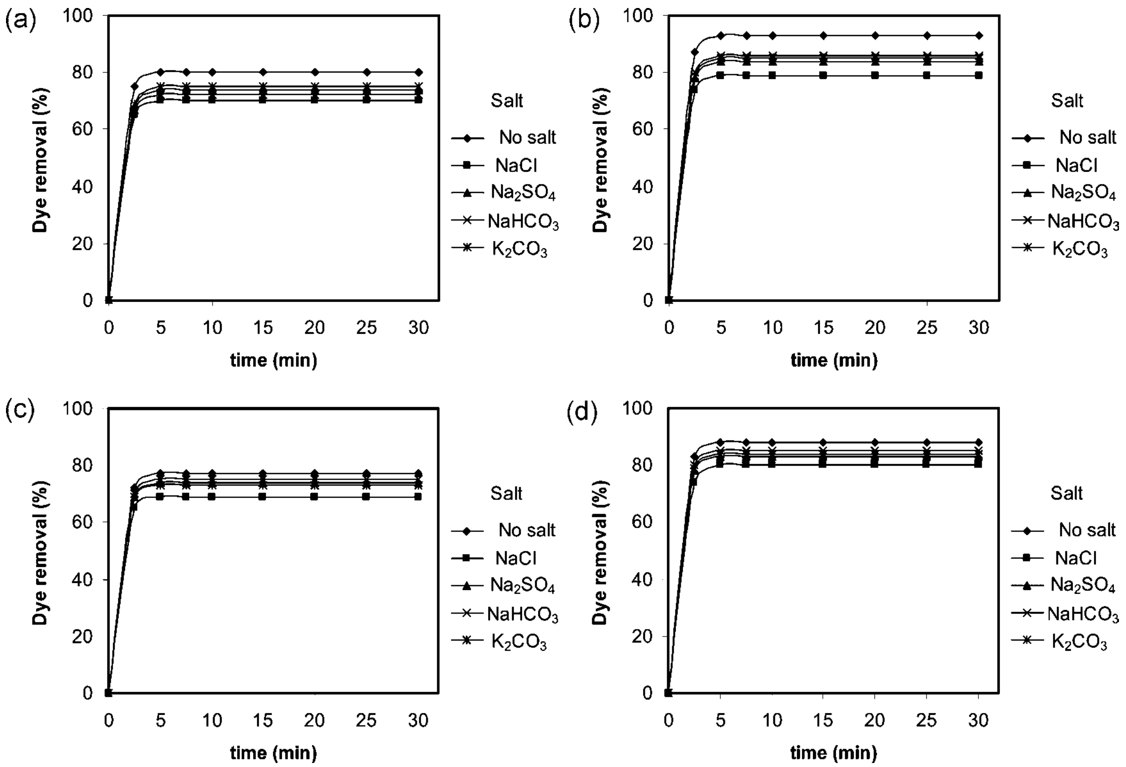


Figure 5. Effect of inorganic anions on dye removal by dendrimer (a) DB78 (sin.), (b) AB26 (sin.), (c) DB78 (bin.), and (d) AB26 (bin.) (pH 2, $C_0 = 50$ mg·L^{-1}, 25 °C, and $C_{\mathrm{dendr}} = 1.8$ mg·L^{-1} for DB78 and AB26 in single and binary systems).

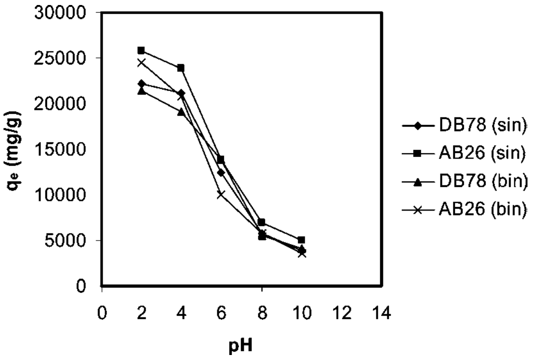


Figure 6. Effect of pH on dye removal by dendrimer ($C_0 = 50$ mg·L^{-1}, 25 °C, and $C_{\mathrm{dendr}} = 1.8$ mg·L^{-1} for DB78 and AB26 in single and binary systems).

constant temperature per unit mass of adsorbent and liquid phase dye concentration at equilibrium. They present how dyes can be distributed between the liquid and solid phases at various equilibrium concentrations. The shape of the isotherm depends on 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. Adsorption isotherms provide information on how the adsorption system proceeds and indicate how efficiently a given adsorbent interacts with adsorbate.[48]

Many isotherm models such as the Langmuir, Freundlich, and Tempkin isotherms have been used in the literature to describe the experimental data of adsorption to optimize the design of an adsorption system to remove pollutants from solutions because it is important to establish the most appropriate correlation for the equilibrium curve.

The Langmuir isotherm often describes monolayer adsorption. This model assumes a uniform energy of adsorption and a single layer of adsorbed solute at a constant temperature. The Langmuir model is the most frequently employed model and is given by[49]

$$q_e = Q_0 K_L C_e/(1 + K_L C_e) \tag{3}$$

where q_e, C_e, Q_0, and K_L are the amount of solute adsorbed at equilibrium (mg·g^{-1}), the concentration of adsorbate at equilibrium (mg·L^{-1}), maximum adsorption capacity (mg·g^{-1}), and Langmuir constant (L·mg^{-1}), respectively.

As illustrated in Table 2, the coefficients of determination, R_1^2, for the Langmuir isotherm model were greater than 0.999 for the single and binary dye systems. The results revealed that the number of adsorption sites on the PPI dendrimer was limited, and dye molecules formed a monomolecular layer on the adsorbent at saturation. The plots of the total amount of dyes adsorbed against the total equilibrium dye concentration were well fitted by the Langmuir equation (Table 2).

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter, R_L, which is defined by the following equation[50]

$$R_L = 1/(1 + K_L C_0) \tag{4}$$

where C_0 is the initial dye concentration. The nature of the adsorption process is defined to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Values of R_L indicated that the adsorption processes were favorable (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

Table 2. Isotherm Constants for Dye Adsorption at Different Dye Concentrations [(25, 50, 75, and 100) mg·L^{-1}] onto Dendrimer[a]

	Langmuir				Freundlich			Tempkin		
system	Q_0	K_L	R_L	R_1^2	K_F	n	R_2^2	K_T	B_1	R_3^2
					DB78					
Single	33333	0.150	0.118	0.999	7672	2.418	0.955	1.230	8570	0.992
					AB26					
	50 000	0.500	0.038	0.999	16003	3.507	0.941	10.826	6851	0.982
					DB78					
Binary	33 333	0.150	0.118	0.999	7399	2.521	0.970	1.237	7886	0.997
					AB26					
	50 000	0.222	0.083	0.997	12671	2.943	0.986	4.024	7953	0.996

[a] 200 mL of solution, pH 2, 25 °C, and $C_{\mathrm{dendr}} = 1.8$ mg·L^{-1} for DB78 and AB26 in single and binary systems.

energies of adsorbent, and also surface adsorption is not a rate-limiting step.[51] The strength of the linear relationship can be expressed by the coefficient of determination (R_2^2). Its value is used to evaluate how the Freundlich model represents the experimental data.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. The Freundlich isotherm can be expressed by[52−55]

$$q_e = K_F C_e^{1/n} \tag{5}$$

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

$$\log q_e = \log K_F + (1/n) \log C_e \tag{6}$$

The n, K_F, and R_2^2 values for the Freundlich adsorption isotherm are shown in Table 2.

The Tempkin isotherm contains a factor that explicitly takes into account the adsorbing species adsorbent interactions. The Tempkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent−adsorbate interactions. In addition, the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.[56,57]

The Tempkin isotherm is given as

$$q_e = RT/b \ln(K_T C_e) \tag{7}$$

This can be linearized as

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{8}$$

$$B_1 = RT/b \tag{9}$$

where B_1 and K_T are the Tempkin constants and can be determined by a plot of q_e versus $\ln C_e$. Also, T is the absolute temperature (K), and R is the universal gas constant (8.314 J·mol^{-1} K^{-1}). The constant b is related to the heat of adsorption.

The values of K_T, B_1, and R_3^2 (coefficient of determination values of Tempkin isotherm) are shown in Table 2.

Binary System. In this work, the extended Langmuir (eq 10), Freundlich, and Tempkin (single system equation) models were employed to fit the experimental data.[58]

$$q_{e,i} = (Q_0 K_{L,i} C_{e,I})/(1 + \sum K_{L,i} C_{e,i}) \tag{10}$$

where $K_{L,i}$ is the adsorption equilibrium constant of dye i in the mixed dye system.

In adsorption from binary dye solutions, the amounts of dye adsorbed were expressed as

$$q_{e,1} = (K_{L,1} Q_{0,1} C_{e,1})/(1 + K_{L,1} C_{e,1} + K_{L,2} C_{e,2}) \tag{11-1}$$

$$q_{e,2} = (K_{L,2} Q_{0,2} C_{e,2})/(1 + K_{L,1} C_{e,1} + K_{L,2} C_{e,2}) \tag{11-2}$$

According to Eqs. (11-1) and (11-2), we have

$$(K_{L,2} C_{e,2})/(K_{L,1} C_{e,1}) = (Q_{0,1} q_{e,2})/(q_{e,1} Q_{0,2}) \tag{12}$$

After rearrangement, a linear form of the extended Langmuir model in a binary dye system was obtained.

$$(C_{e,1}/q_{e,1}) = (1/K_{L,1} Q_{0,1}) + (C_{e,1}/Q_{0,1}) + (q_{e,2} C_{e,1}/q_{e,1} Q_{0,2}) \tag{13}$$

According to eq 13, the values of $C_{e,1}/q_{e,1}$ have a linear correlation with $C_{e,1}$ and $C_{e,1}q_{e,2}/q_{e,1}Q_{0,2}$ if the adsorption obeyed the extended Langmuir model. By using eq 13 as the fitting model, the isotherm parameters of an individual dye in the binary dye solutions were estimated and are listed in Table 2. It can be seen that the isotherms of an individual dye in the binary dye systems followed the extended Langmuir model. Figure 7 shows the adsorption isotherms of dyes (q_e versus C_e) using a dendrimer in single and binary systems.

Adsorption Kinetics. Adsorption kinetics provides information regarding the mechanisms of adsorption that are important for the efficiency of the process. It is important to know the rate of adsorption during removing contaminants from wastewater to optimize the design parameters because the kinetics of the system controls the adsorbate residence time and reactor 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.[58]

To design an effective model, investigations were made on adsorption rate. Several kinetics models (pseudofirst order,

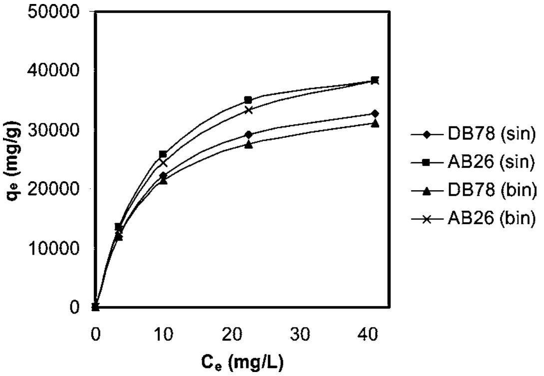


Figure 7. Adsorption isotherms of dye removal by dendrimer (pH 2, 25 °C, and $C_{\mathrm{dendr}} = 1.8\ \mathrm{mg \cdot L^{-1}}$ for DB78 and AB26 in single and binary systems).

pseudosecond order, and intraparticle diffusion) were used to test the experimental data such as the examination of the controlling mechanisms of the adsorption process.[59,60]

The pseudofirst order equation is generally represented as follows[61,62]

$$dq_t/dt = k_1(q_e - q_t) \tag{14}$$

where q_t and k_1 are the amount of dye adsorbed at time t ($\mathrm{mg \cdot g^{-1}}$) and the equilibrium rate constant of pseudofirst order kinetics ($\mathrm{L \cdot min^{-1}}$), respectively.

After integration by applying conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then eq 14 becomes

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t \tag{15}$$

The straight-line plots of $\log(q_e - q_t)$ versus t for the adsorption of DB78 and AB26 in single and binary systems onto dendrimer at different dye concentrations [(25, 50, 75 and 100) $\mathrm{mg \cdot L^{-1}}$] have been tested to obtain the rate parameters. The k_1, q_e, and coefficients of determination (R_4^2) under different dye concentrations were calculated and are given in Table 3.

Data were applied to the pseudosecond order kinetic rate equation which is expressed as[61,63]

$$dq_t/dt = k_2(q_e - q_t) \tag{16}$$

where k_2 is the equilibrium rate constant of the pseudosecond order kinetic model ($\mathrm{g \cdot mg^{-1} \cdot min^{-1}}$). On integrating eq 16

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \tag{17}$$

To understand the applicability of the model, linear plots of t/q_t versus t at different dye concentrations [(25, 50, 75, and 100) $\mathrm{mg \cdot L^{-1}}$] for the adsorption of dyes in single and binary systems onto dendrimer are shown in Figure 8. The k_2, q_e, and coefficients of determination (R_5^2) were calculated from these plots and are given in Table 3.

The possibility of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion model as

$$q_t = k_p t^{1/2} + I \tag{18}$$

where k_p is the intraparticle diffusion rate constant.

To understand the applicability of the intraparticle diffusion, linear plots of q_t against $t^{1/2}$ at different dye concentrations [(25, 50, 75, and 100) $\mathrm{mg \cdot L^{-1}}$] for the adsorption of dyes in single and binary systems onto dendrimer are plotted, and the values of k_p, I, and coefficients of determination (R_6^2) are shown in Table 3.

Values of I (Table 3) give an idea about the thickness of the boundary layer; i.e., the larger the intercept, the greater the boundary layer effect. According to this model, a plot of uptake should be linear if intraparticle diffusion is involved in the adsorption process, and if these lines pass through the origin, then intraparticle diffusion is the rate-controlling step.[64−66] When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and shows that the intraparticle diffusion is not the only rate-limiting step but also

Table 3. Kinetics Constants for Dye Adsorption at Different Dye Concentrations [(25, 50, 75, and 100) $\mathrm{mg \cdot L^{-1}}$] onto Dendrimer[a]

	dye	pseudofirst order			pseudosecond order			intraparticle diffusion		
system	($\mathrm{mg \cdot L^{-1}}$)	q_e	k_1	R_4^2	q_e	k_2	R_5^2	k_P	I	R_6^2
					DB78					
single	25	32471	2.338	0.919	12500	$1.6 \cdot 10^{-3}$	0.999	1594	5487	0.495
	50	68628	2.463	0.908	25000	$8 \cdot 10^{-4}$	0.999	2972	10187	0.498
	75	104737	2.517	0.890	33333	$3 \cdot 10^{-4}$	0.999	3945	13143	0.510
	100	119536	2.540	0.889	33333	$4.5 \cdot 10^{-4}$	0.999	4431	14781	0.510
					AB26					
	25	35900	2.363	0.924	14286	$1.6 \cdot 10^{-4}$	1	2652	4607	0.613
	50	82680	2.493	0.905	25000	$8 \cdot 10^{-4}$	0.999	5110	8722	0.621
	75	121899	2.553	0.897	33333	$4.5 \cdot 10^{-4}$	0.999	6941	11736	0.625
	100	146555	2.572	0.886	33333	$4.5 \cdot 10^{-4}$	0.999	7646	12653	0.634
					DB78					
binary	25	34174	2.336	0.910	12500	$1.6 \cdot 10^{-3}$	1	1585	5376	0.502
	50	66481	2.455	0.907	20000	$1.2 \cdot 10^{-3}$	1	2864	9779	0.499
	75	93843	2.505	0.897	25000	$8 \cdot 10^{-4}$	1	3702	12479	0.505
	100	121647	2.530	0.878	33333	$3 \cdot 10^{-4}$	0.999	4251	13808	0.521
					AB26					
	25	39464	2.358	0.906	12500	$1.3 \cdot 10^{-3}$	0.999	2619	4414	0.626
	50	74302	2.482	0.912	25000	$8 \cdot 10^{-3}$	0.999	4821	8316	0.616
	75	117058	2.572	0.895	33333	$4.5 \cdot 10^{-4}$	0.999	6619	1114	0.627
	100	144744	2.544	0.886	33333	$4.5 \cdot 10^{-4}$	0.999	7646	12653	0.634

[a] 200 mL of solution, pH 2, 25 °C, and $C_{\mathrm{dendr}} = 1.8\ \mathrm{mg \cdot L^{-1}}$ for DB78 and AB26 in single and binary systems.

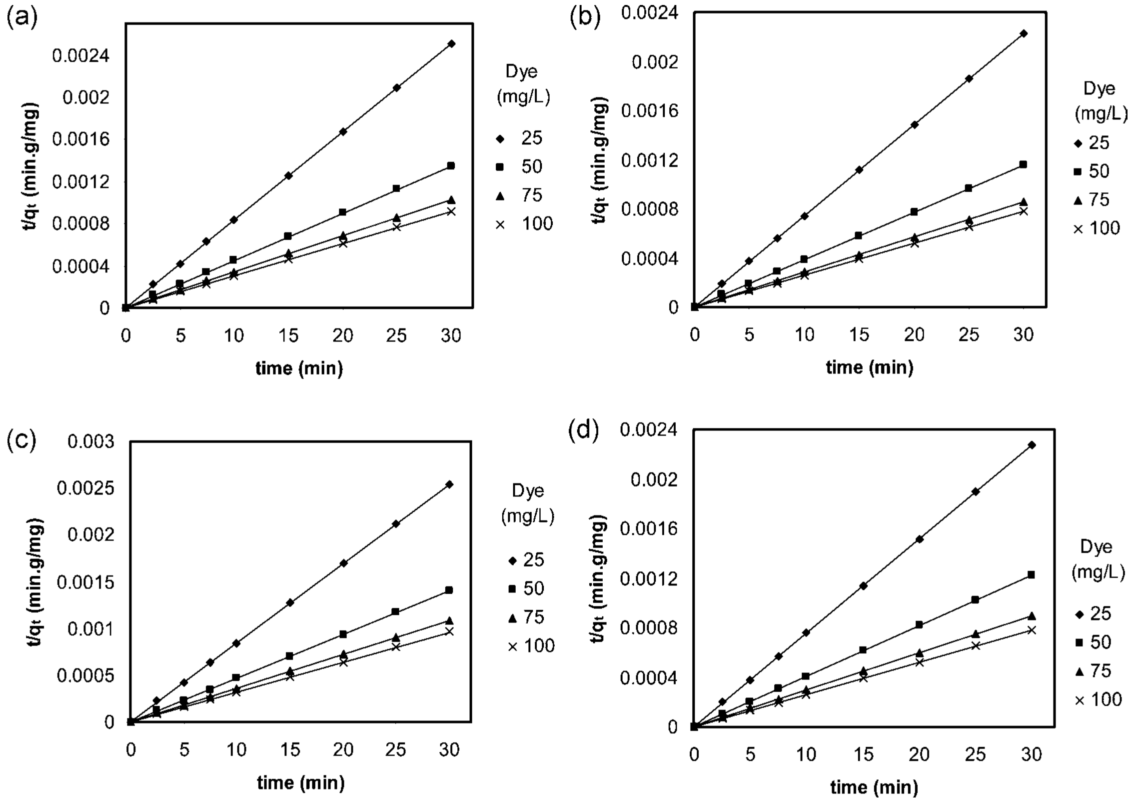


Figure 8. Pseudosecond order adsorption kinetics of dye removal by dendrimer (a) DB78 (sin.), (b) AB26 (sin.), (c) DB78 (bin.), and (d) AB26 (bin.) (pH 2, 25 °C, and $C_{\mathrm{dendr}} = 1.8\ \mathrm{mg \cdot L^{-1}}$ for DB78 and AB26 in single and binary systems).

that other kinetics models may control the rate of adsorption, all of which may be operating simultaneously.

Results showed that the rates of sorption were found to conform to the pseudosecond order kinetic model with good coefficients of determination (Table 3).

Dye Removal Mechanisms by the PPI Dendrimer

The PPI dendrimer has primary amine groups at each branch end and tertiary amine groups at each branching point. DB78 and AB26 dyes are polar molecules ($\mathrm{R{-}SO_3^-}$). Therefore, the electrostatic attraction, as well as the organic properties and structure of dye molecules and dendrimer, could play a very important role in dye adsorption on dendrimer. At acidic pH, an electrostatic attraction exists between the positively charged surface of the dendrimer and the anionic dye molecules (adsorption mechanism). In addition, dye molecules are encapsulated by the PPI dendrimer which causes the dye removal efficiency (encapsulation mechanism).[40,47,67−69]

Desorption Studies. The regeneration of the adsorbent may make the treatment process economical. Desorption studies help to elucidate the mechanism and recovery of the adsorbate and adsorbent. Desorption tests showed that maximum dye releases of 93 % for DB78 and 86 % for AB26 in single systems and 90 % for DB78 and 84 % for AB26 in binary systems were achieved at pH 12. As the pH of the system increases, the number of positively charged sites decreased which favors desorption of dyes (Figure 9).

Conclusion

The results of this investigation show that PPI dendrimer as a polymeric nanoarchitecture has a very effective adsorption capacity for the removal of DB78 and AB26 in single and binary systems of dyes from aqueous solutions. The experimental results were analyzed using the Langmuir, Freundlich, and Tempkin models. The isotherm data of DB78 and AB26 in single and binary systems of dyes followed the Langmuir isotherm. Adsorption kinetics of dyes in single and binary dye systems were found to conform to a pseudosecond order model. Desorption studies were conducted to elucidate the mechanism and recovery of the adsorbate and adsorbent. At alkaline pH, the number of positively charged sites decreased which favors desorption of dyes. On the basis of the data of the present study, one could conclude that the dendrimer is an eco-friendly adsorbent for dye removal from colored textile wastewater.

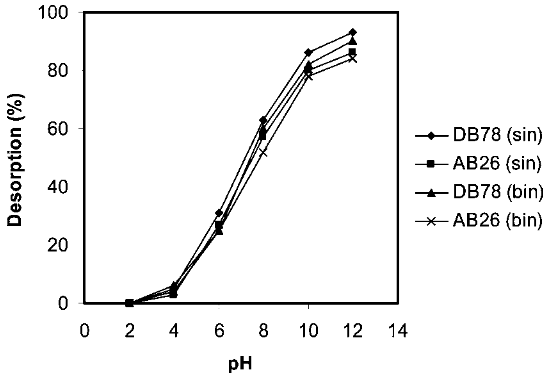


Figure 9. Effect of pH on desorption of dyes from dendrimer (25 °C and $C_{\mathrm{dendr}} = 1.8\ \mathrm{mg \cdot L^{-1}}$ for DB78 and AB26 in single and binary systems).

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