Dye Adsorption and Desorption Properties of *Mentha pulegium* in Single and Binary Systems

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ABSTRACT: This article deals with the dye adsorption and desorption properties of *Mentha pulegium* (*MP*) from single and binary (mixture of dyes) systems. Direct Red 80 (DR80) and Acid Black 26 (AB26) were used as model dyes. The Fourier transform infrared (FTIR) was used to investigate the biosorbent characteristics. The effects of biosorbent dosage, contact time, dye concentration, salt, and pH on dye removal were studied. The biosorption isotherms, kinetics, and thermodynamic were studied. In addition, dye desorption was carried out to study adsorbent recovery. The results showed that the isotherm data of single and binary systems of dyes followed the Langmuir isotherm. The adsorption kinetic of the dyes was found to conform to a pseudosecond order kinetic model. Desorption tests showed maximum dye releasing of 97% for DR80 and 95% for AB26 in single system and 92% for DR80 and 94% for AB26 in binary system of dyes at pH 12. The thermodynamic data showed that the biosorption process is spontaneous, endothermic, and a physisorption reaction. It can be concluded that *MP* is an ecofriendly biosorbent to remove dyes from single and binary systems. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1489–1499, 2011

Key words: adsorption; dyes/pigments; FTIR; UV–Vis spectroscopy

INTRODUCTION

Dyes are used as colorants in different industries such as textile, paper, pharmaceutical, food, cosmetic, etc.[1,2] Large quantities of colored wastewater are discharged from the dyeing process with strong persistent color that is esthetically and environmentally unacceptable.[3] Some of the dyes are toxic and even carcinogenic to aquatic organisms.[4–7] Thus, several governments have established environmental restrictions with regard to the quality of colored wastewater and forced dye-using industries to remove of dyes from their effluents before discharging.

Several treatment methods for pollutant removal such as biological, chemical, and physical processes have been investigated.[3,8–14] 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 using several biosorbents has been studied.[15–29]

A literature review showed that *Mentha pulegium* (*MP*) was not used as a biosorbent. *MP*, more commonly known as pennyroyal, is an herbaceous perennial plant in the mint genus. The composition of *MP* has been investigated and three chemotypes have been established: pulegone-type, piperitenone/piperitone-type, and isomenthone/neoisomenthol-type.[30–32]

In this study, *MP* was used as a biosorbent to remove Direct Red 80 (DR80) and Acid Black 26 (AB26) from single and binary systems. The effects of biosorbent dosage, contact time, dye concentration, salt, and pH have been studied at 25°C. The adsorption isotherms (Longmuir, Freundlich, and Dubinin-Radushkevich models), adsorption kinetics (pseudofirst order, pseudosecond order, and intraparticle diffusion), adsorption thermodynamics, and dye desorption were studied in single and binary systems of dyes. Desorption studies were conducted to elucidate the mechanism and recovery of the adsorbate and biosorbent.

EXPERIMENTAL

Chemicals

MP was obtained from Iran. Direct Red 80 (DR80) and Acid Black 26 (AB26) were used as model dyes and purchased from Ciba (Iran). Other chemicals were Analar grade from Merck (Germany).

Surface characteristics

To investigate the surface characteristics of *MP*, Fourier transform infrared (FTIR, Perkin–Elmer

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TABLE I
Initial Dye Concentration (mg/L) Used in Single and Binary Systems

Single system		Binary system	
$C_{0,DR80}$	$C_{0,AB26}$	$C_{0,DR80}$	$C_{0,AB26}$
25	25	25	25
50	50	50	50
75	75	75	75
100	100	100	100

Spectrophotometer Spectrum One) in the range 450 to 4000 cm^{-1} was studied.

Biosorption procedure

The biosorption measurements were conducted by mixing various amounts of *MP* in jars containing 200 mL of a dye solution (50 mg/L) at various pHs (2–10). The pH of the solutions was adjusted by adding a small amount of H_2SO_4 or NaOH. Experiments were conducted at different dye concentrations using 2 g/L *MP* for DR80 and AB26 in single and binary systems at pH 2 and 25°C for 120 min (Table I).

Dye concentration was calculated using eqs. (1) and (2). For a binary system of components *A* and *B* that were measured at wavelengths of λ_1 and λ_2, respectively, to give optical densities of d_1 and d_2[33]:

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

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

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

The changes of absorbance were determined at certain time intervals during the biosorption process. After experiments, the samples were centrifuged by Hettich EBA20 and then the dye concentration was determined. A CECIL 2021 UV–VIS spectrophotometer was used to determine the dye concentration. The maximum wavelength (λ_{max}) of DR80 and AB26 to determine residual dye concentration in solution was 540 and 550 nm, respectively. To investigate the salt effect on dye removal efficiency, 1 mmol of Na_2SO_4, $NaHCO_3$, K_2CO_3, and NaCl were added to 200 mL of dye solution (50 mg/L), 2 g/L *MP* for DR80 and AB26 in single and binary systems (pH 2 and 25°C for 120 min).

Desorption studies

The used *MP* for the biosorption of 50 mg/L of dye solution was separated and dried. Then the biosorbent was agitated with 200 mL of distilled water at different pH values (2–12) for the predetermined equilibrium time of the desorption process. The desorbed dye was measured.

RESULTS AND DISCUSSION

Surface characteristics

FTIR study

The FTIR of *MP* showed that the peak positions were at 3383.78 cm^{-1}, 2923.4 cm^{-1}, 2845.41 cm^{-1}, 1690.81 cm^{-1}, 1444.32 cm^{-1}, and 1048.65 cm^{-1} (Fig. 1). The band at 3383.78 cm^{-1} was due to O—H and *N*—H stretching. The bands at 2923.40 cm^{-1} and 2845.41 cm^{-1} represented the CH_2 asymmetric and symmetric stretching vibrations, respectively. The bands at 1690.81 cm^{-1} and 1523.51 cm^{-1} reflected the carbonyl group stretching (amide) and N H bending, respectively. Bands at 1305.59 and 1168.67 corresponded to C—H bending and C—O stretching, respectively.[34,35]

Surface coverage

To account for the biosorption behavior of the dyes on *MP*, the Langmuir type equation related to surface coverage (θ) was used. The equation is expressed as follows[36]:

$$bC_0 = \theta/1 - \theta \quad (3)$$

where C_0 and b are initial dye concentration and a constant, respectively.

The fraction of biosorbent surface covered by dyes was studied by plotting the surface coverage values against dye concentration at different temperatures. The plots are presented in Figure 2. It is seen from the figure that the surface coverage on *MP* 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

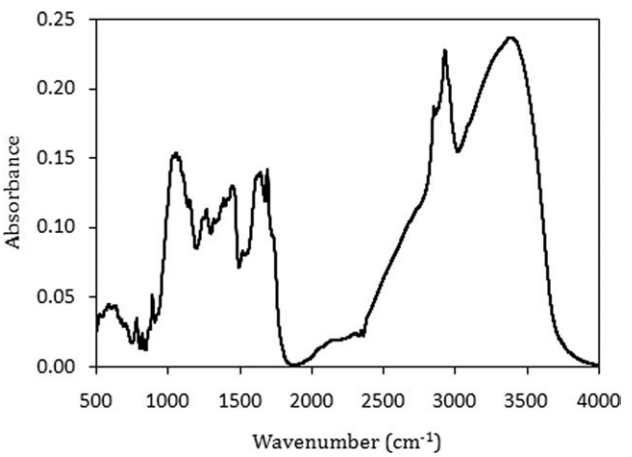

Figure 1 FTIR spectrum of *MP*.

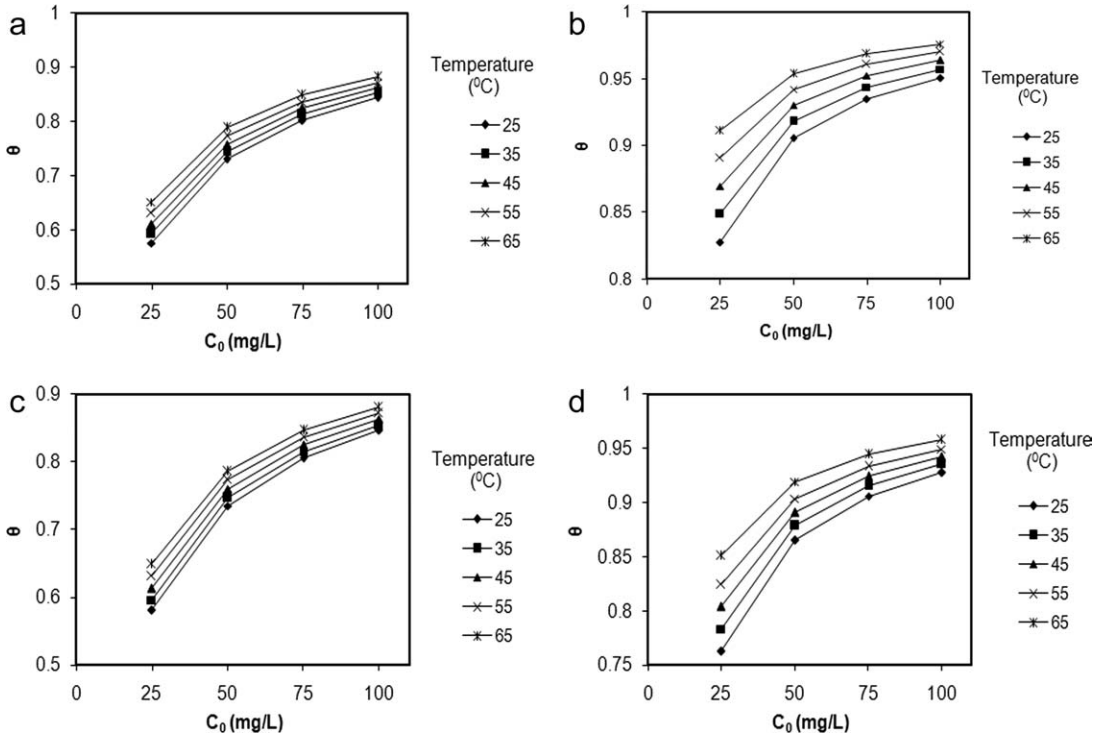

Figure 2 Plots of surface coverage (θ) against initial concentration of dyes at different temperatures (a) DR80 (sin), (b) AB26 (sin), (c) DR80 (bin), and (d) AB26 (bin) (pH: 2 and adsorbent: 2 g/L for DR80 and AB26 in single and binary systems).

increasing temperatures in the condition of same dye concentration. These results show that higher dye concentrations and biosorption temperatures will be benefit for dye coverage onto *MP* with a monomolecular layer. The result of surface coverage indicates that *MP* will be very effective in removing dyes from aqueous solutions.

Effect of operational parameters on dye removal

Biosorbent dosage

Biosorbent dosage is used to determine the capacity of a biosorbent for initial adsorbate concentration. The effect of *MP* dosage on dye removal in single and binary systems is shown in Figure 3. The percentage of dye removal increased with the *MP* dosage up to a certain limit and then it reached a constant value. Optimum *MP* dosage, 2 g/L for DR80 and AB26 for both single and binary systems was selected for 200 mL of 50 mg/L dye solution. The increase in biosorption of dyes with increasing *MP* dosage was due to the availability of more active surface sites of *MP* for biosorption.

A given mass of *MP* can adsorb only a fixed amount of adsorbate. Therefore, the initial concentration of biosorbent is very important. The reason for increase in the biosorption efficiency with increase in biosorbent dosage is the increase of unoccupied biosorption sites through biosorption process.[37]

Contact time

Contact time is used to assess of practical application of biosorption process. Figure 3 showed the uptake of dye as a function of contact time at different dosages of biosorbent. It is observed from the graphs that dye biosorption on *MP* is a slow process and equilibrium is attained within 80 min. Then biosorption is found to be nearly constant. At the initial stage of biosorption, vacant surface sites are available, once equilibrium is attained; the remaining vacant sites are difficult to be occupied. It can be attributed to the repulsive forces between the molecules on the biosorbent and in the bulk phase.[38,39]

Dye concentration

The effect of initial dye concentration of DR80 and AB26 in single and binary systems on dye removal was studied (Fig. 4). The results show that dye removal percentage decreases when the dye concentration increases. It can be attributed that the active sites on biosorbent for dye removal decreases when dye concentration increases.

Salt

Wastewater of textile industries contains various types of suspended and dissolved compounds such as dyes, acids, alkalis, salts, surfactants, metal ions,

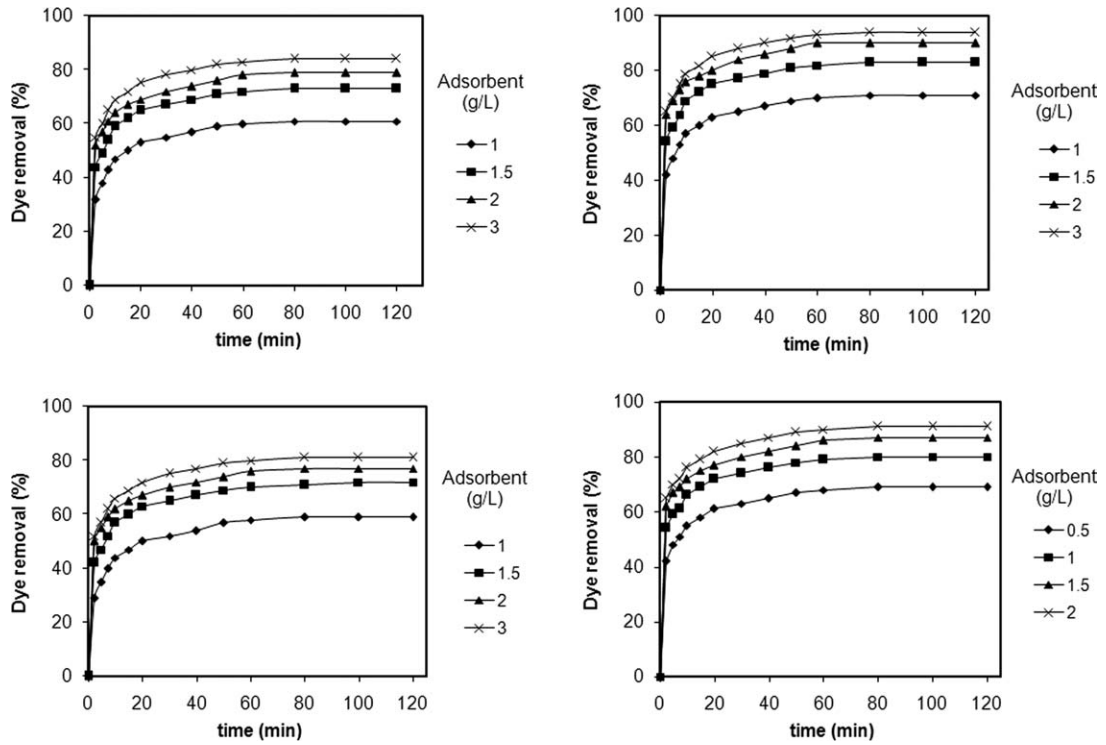

Figure 3 Effect of adsorbent dosage and time on dye removal onto *MP* (a) DR80 (sin), (b) AB26 (sin), (c) DR80 (bin), and (d) AB26 (bin) (pH: 2, T: 25°C and dye: 50 mg/L).

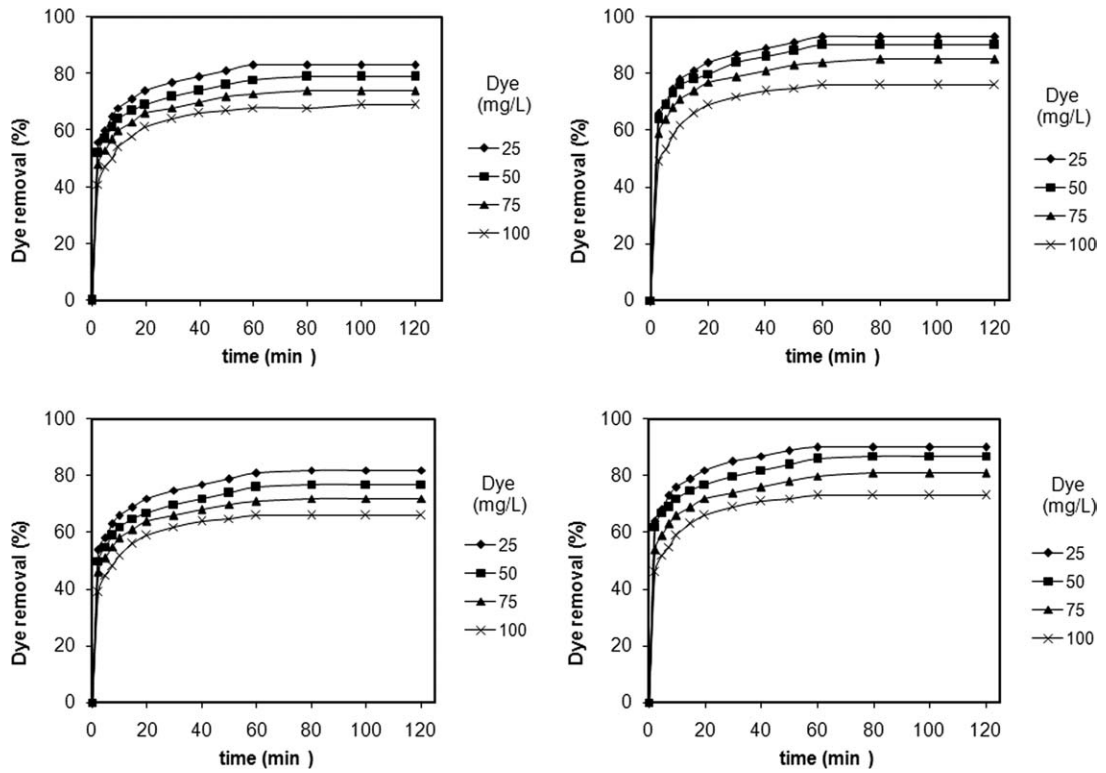

Figure 4 Effect of dye concentration on dye adsorption onto *MP* (a) DR80 (sin), (b) AB26 (sin), (c) DR80 (bin), and (d) AB26 (bin) (pH: 2, T: 25°C and adsorbent: 2 g/L for DR80 and AB26 in single and binary systems).

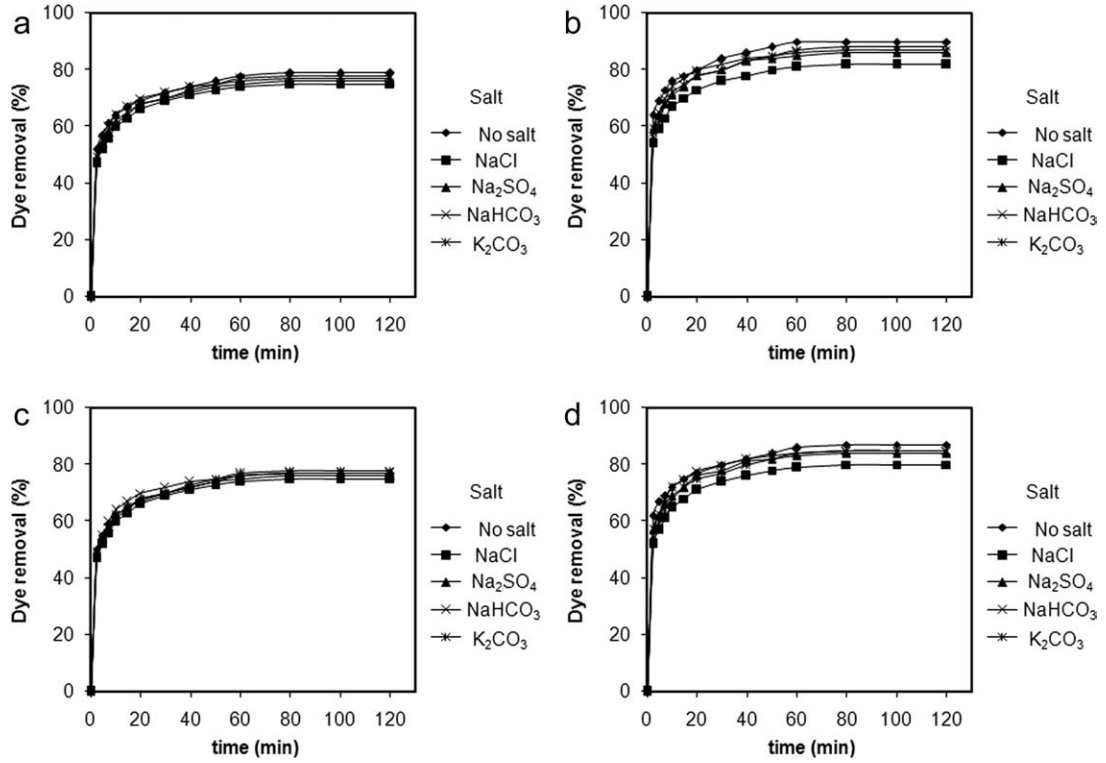

Figure 5 Effect of salt on dye adsorption onto *MP* (a) DR80 (sin), (b) AB26 (sin), (c) DR80 (bin), and (d) AB26 (bin) (pH: 2, dye: 50 mg/L, T: 25°C and adsorbent: 2 g/L for DR80 and AB26 in single and binary systems).

etc. Anions such as nitrate, carbonate, sulfate, and chloride are the most common ions present in textile wastewater.[40] To investigate the effect salt on dye removal efficiency, Na_2SO_4, $NaHCO_3$, K_2CO_3, and NaCl were added to dye solution. Figure 5 illustrates that dye removal capacity of dyes by *MP* in single and binary system is decreased in the presence of inorganic anions because they compete with dyes for biosorption on *MP*.

Solution pH

The final dye concentration after biosorption varied significantly with the initial pH of the dye solution. The studies in this report were carried out over a broad pH range of 2 to 10. The effect of pH on the biosorption of DR80 and AB26 in single and binary systems by *MP* is shown in Figure 6.

MP has groups such as amino, which could also be affected by the pH of solution. Therefore, the electrostatic attraction, as well as the organic properties and structure of dye molecules and *MP*, could play a very important role in dye biosorption on *MP*. At pH 2, a high electrostatic attraction exists between the positively charged surface of the biosorbent and the anionic dye. As the pH of the system increases, the number of negatively charged sites increases. Negatively of charged surface site on the *MP* does not favor the biosorption of dye anions due to electrostatic repulsion. In addition, lower biosorption of DR80 and AB26 at alkaline pH is due to the presence of negative sites adsorbing of the dye for the biosorption sites. The effective pH was 2 and used in further studies.

Biosorption isotherms

Single system

Biosorption isotherm indicates the relation between the mass of dye adsorbed at constant temperature

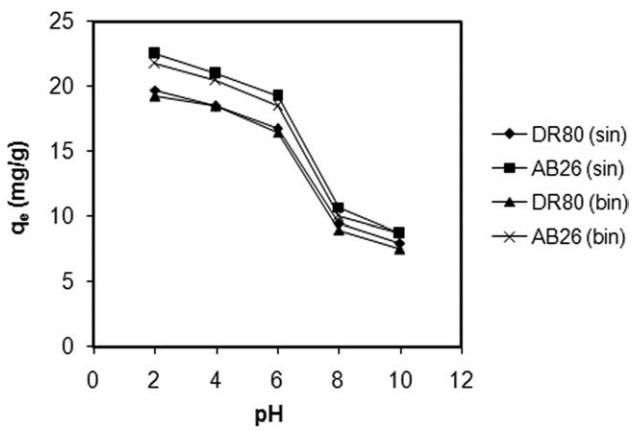

Figure 6 Effect of pH on dye adsorption onto *MP* (dye: 50 mg/L, T: 25°C and adsorbent: 2 g/L for DR80 and AB26 in single and binary systems).

TABLE II
Isotherm Constant for Dye Adsorption at 25, 50, 75, and 100 mg/L Dye Concentrations onto *MP* (200 mL Solution, pH 2.5, T 25°C, and Adsorbent: 2 g/L for DR80 and AB26 in Single and Binary Systems)

	Langmuir				Freundlich			Dubinin-Radushkevich			
System	Q_0	K_L	R_L	R_1^2	K_F	n	R_2^2	q_m	β	R_3^2	E_a
Single						DR80					
	52.356	0.058	0.256	1	4.591	1.684	0.987	69.673	0.012	0.999	6.454
						AB26					
	46.296	0.192	0.094	0.999	9.766	2.187	0.962	70.237	0.008	0.988	7.856
Binary						DR80					
	50.251	0.055	0.245	0.999	4.396	1.709	0.991	65.229	0.012	0.999	6.455
						AB26					
	46.948	0.129	0.134	0.999	7.732	2.016	0.967	69.382	0.009	0.989	7.332

per unit mass of biosorbent and liquid phase dye concentration at equilibrium. In addition, it presents how dye can be distributed between the liquid and solid phases at various equilibrium concentrations and how efficiently a given biosorbent interacts with adsorbate. 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 biosorption sites determine the shape of isotherm.[41]

Several models such as Langmuir, Freundlich, and Dubinin-Radushkevich isotherms have been used to describe the experimental data of biosorption isotherms to optimize the design of a biosorption system to remove dyes from solutions.

The Langmuir equation often describes by monolayer biosorption. This model assumes a uniform energy of biosorption and a single layer of adsorbed solute at a constant temperature. The Langmuir model is the most frequently employed model and given by as follows[42]:

$$q_e = Q_0 K_L C_e / (1 + K_L C_e) \quad (4)$$

where q_e, C_e, Q_0, and K_L are the amount of solute adsorbed at equilibrium (mg/g), the concentration of adsorbate at equilibrium (mg/L), maximum biosorption capacity (mg/g), and Langmuir constant (L/mg), respectively.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L, which is defined by the following equation[43]:

$$R_L = 1/(1 + K_L C_0) \quad (5)$$

The nature of the biosorption process 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 were indicated that the biosorption processes were favorable (Table II).

To study the applicability of the Langmuir isotherm for the dye biosorption onto *MP*, linear plot of C_e/q_e against C_e was plotted and the values of Q_0, K_L, R_L, and R_1^2 (correlation coefficient) are shown in Table II.

The Freundlich equation is another well-known model for biosorption. 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 biosorbent and surface biosorption is not rate limiting step.[44]

The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of biosorption over the surface. Freundlich isotherm can be expressed by as follows[45–48]:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where K_F is biosorption capacity at unit concentration and $1/n$ is biosorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$).[37] Equation (6) can be rearranged to a linear form as follows:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (7)$$

To investigate the applicability of the Freundlich isotherm for the dye biosorption onto *MP*, linear plot of log q_e versus log C_e was plotted and the values of K_F, n, and R_2^2 (correlation coefficient) are shown in Table II.

To deepen the understanding of biosorption mechanism, Dubinin-Radushkevich (D-R) isotherm model was chosen to apply on biosorption study. The D-R isotherm can be used to describe biosorption on both homogenous and heterogeneous surfaces.[49] A linear form of D-R isotherm is as follows:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

where β, q_m, and ε are a constant related to the mean free energy of biosorption (mol^2/kJ^2), the theoretical saturation capacity, and the Polanyi potential, respectively. Polanyi potential is equal to $RT \ln(1 + (1/C_e))$, where R (8.314 J/mol K) is the gas constant and T (K) is the absolute temperature (K).

To investigate the applicability of the Dubinin-Radushkevich isotherm for the dye biosorption onto *MP*, linear plots of ln q_e versus ε^2 was plotted and the values of β, q_m, and R_3^2 (correlation coefficient) are shown in Table II.

The plots of specific sorption, ln q_e against ε^2 for D-R isotherm equation, from the β values the mean energy of biosorption (E_a) can be calculated using eq. (9).[50]

$$E_a = (2\beta)^{-1/2} \tag{9}$$

Based on eqs. (8) and (9), the isotherm constants, E_a and correlation coefficients (R_3^3) are calculated and presented in Table II. From Table II, the value of E_a is 7.856 kJ/mol for AB26 and 6.455 kJ/mol for DR80 in single systems and 7.332 kJ/mol for AB26 and 6.455 kJ/mol for DR80 in binary systems. The mean energy of biosorption is the free energy change when one mole of the ions is transferred from infinity in the solution to the surface of the solid. The value of this parameter can give information about biosorption mechanism. When one mole of ions is transferred, its value in the range of 1 to 8 kJ/mol indicates physical biosorption,[51] the value of E_a is between 8 and 16 kJ/mol, which indicates the biosorption process, followed by ion-exchange,[52] whereas its value in the range of 20 to 40 kJ/mol is indicative of chemical biosorption.[53] So, it seems that physical mechanism is dominating in the biosorption process.

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

Binary system

In this work, an extended Langmuir model, Freundlich, and (D-R) isotherm (single system equation) were employed to fit the experimental data for binary systems.[54]

The extended Langmuir model is as follows:

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

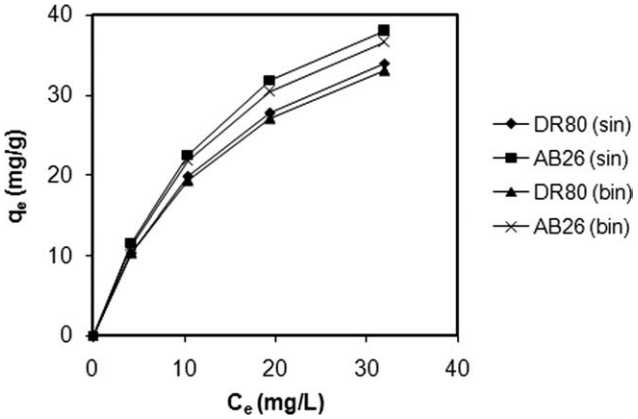

Figure 7 Isotherms of dye adsorption onto *MP* (pH: 2, T: 25°C and adsorbent: 2 g/L for DR80 and AB26 in single and binary systems).

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

In biosorption from binary dye solutions, the amounts of dye adsorbed were expressed as follows:

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

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

According to eqs. (11-1) and (11-2) we have the following:

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

After rearrangement, a linear form of the extended Langmuir model in 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 $C_{e,1}/q_{e,1}$ had linear correlation with $C_{e,1}$ and $C_{e,1}q_{e,2}/q_{e,1}Q_{0,2}$ if the biosorption 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 listed in Table II. It can be seen that the isotherm of an individual dye in the binary dye systems followed the extended Langmuir model. Figure 7 shows the biosorption isotherms of dyes (q_e vs. C_e) using *MP* in single and binary systems.

Biosorption kinetics

Kinetic data provide information regarding the mechanism of biosorption that is important for the efficiency of the process. It is important to know the rate of biosorption during removing contaminants from wastewater to optimize the design parameters because kinetic of system controls the adsorbate

TABLE III
Kinetic Constant for Dye Adsorption at 25, 50, 75, and 100 mg/L Dye Concentrations onto *MP* (200 mL Solution, pH 2.5, T 25°C, and Adsorbent: 2 g/L for DR80 and AB26 in Single and Binary Systems)

			Pseudofirst order			Pseudosecond order			Intraparticle diffusion		
System	Dye (mg/L)	$(q_e)_{Exp}$	$(q_e)_{Cal.}$	k_1	R_4^2	$(q_e)_{Cal.}$	k_2	R_5^2	k_P	I	R_6^2
Single						DB78					
	25	10.4	4.6	0.056	0.921	10.5	0.047	0.999	0.622	5.284	0.575
	50	19.7	8.6	0.055	0.915	20.1	0.021	0.999	1.194	9.837	0.591
	75	27.7	12.1	0.058	0.933	28.2	0.016	0.999	1.689	13.821	0.591
	100	34	17.7	0.073	0.960	35.1	0.011	0.999	2.213	16.137	0.632
						AB26					
	25	11.6	4.5	0.060	0.885	11.8	0.049	0.999	0.669	6.196	0.536
	50	22.5	8.7	0.058	0.875	22.8	0.024	0.999	1.285	12.045	0.532
	75	31.9	12.5	0.058	0.876	32.4	0.016	0.999	1.843	16.831	0.543
	100	38.0	18.4	0.075	0.953	38.7	0.014	0.999	2.348	18.990	0.587
Binary						DB78					
	25	10.2	4.6	0.056	0.923	10.4	0.042	0.999	0.625	5.063	0.598
	50	19.2	8.6	0.055	0.918	19.6	0.022	0.999	1.175	9.472	0.601
	75	27.0	12.1	0.057	0.936	27.5	0.016	0.999	1.661	13.274	0.601
	100	33.0	17.6	0.073	0.963	33.8	0.013	0.999	2.140	15.528	0.630
						AB26					
	25	11.2	3.5	0.046	0.629	11.4	0.055	0.999	0.645	6.054	0.529
	50	21.7	8.5	0.055	0.899	22.1	0.023	0.999	1.244	11.495	0.542
	75	30.4	12.9	0.055	0.910	30.9	0.014	0.999	1.816	15.341	0.580
	100	36.5	15.2	0.060	0.881	37.2	0.014	0.999	2.271	18.082	0.594

residence time and reactor dimension. As a result, predicting the rate at which biosorption takes place for a given system is probably the most important factor in biosorption system design.[54]

Several kinetics models (Pseudofirst order, pseudosecond order, and intraparticle diffusion) are used to test the experimental data such as the examination of the controlling mechanisms of biosorption process, (chemical reaction, diffusion control, and mass transfer).[55,56]

Pseudofirst order equation is generally represented as follows[57,58]:

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

where k_1 is the equilibrium rate constant of pseudofirst order kinetics (1/min).

After integration and 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 biosorption of DR80 and AB26 in single and binary systems onto *MP* at different dye concentrations (25, 50, 75, and 100 mg/L) have been tested to obtain the rate parameters. The k_1, the experimental q_e ($(q_e)_{Exp}$), and correlation coefficients (R_4^2) under different dye concentrations values were calculated and given in Table III.

Data were applied to the pseudosecond order kinetic rate equation which is expressed as follows[57,59]:

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

where k_2 is the equilibrium rate constant of pseudosecond order (g/mg min). On integrating the eq. (16), eq. (17) is obtained.

$$t/q_t = 1/k_2q_e^2 + (1/q_e)t \tag{17}$$

To understand the applicability of the model, linear plots of t/q_t versus t at different dye concentrations (25, 50, 75, and 100 mg/L) for the biosorption of dyes in single and binary systems onto *MP* were drown. The k_2, the experimental q_e ($(q_e)_{Exp}$) and correlation coefficients (R_5^2) were calculated from these plots and given in Table III.

The possibility of intraparticle diffusion resistance affecting biosorption was explored by using the intraparticle diffusion model as follows:

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

where k_p and I are the intraparticle diffusion rate constant and intercept, respectively.

The k_p, I, and correlation coefficients (R_6^2) under different dye concentrations values were calculated plots and given in Table III. Values of I (Table III)

TABLE IV
Thermodynamic Parameters of Dye Adsorption onto *MP* (200 mL Solution, pH 2, T 25°C, and Adsorbent: 2 g/L for DR80 and AB26 in Single and Binary Systems)

				ΔG (kJ/mol)				
	Dye (mg/L)	ΔH (kJ/mol)	ΔS (J/mol K)	298 K	308 K	318 K	328 K	338 K
Single				DR80				
	25	6.583	29.438	−2.189	−2.483	−2.778	−3.072	−3.367
	50	5.446	23.474	−1.549	−1.784	−2.019	−2.253	−2.488
	75	4.592	18.302	−0.862	−1.045	−1.228	−1.411	−1.594
	100	4.066	14.502	−0.255	−0.400	−0.545	−0.690	−0.835
				AB26				
	25	18.373	76.964	−4.562	−5.332	−6.102	−6.871	−7.641
	50	11.531	51.010	−3.670	−4.180	−4.670	−5.200	−5.710
	75	7.431	33.506	−2.553	−2.888	−3.223	−3.559	−3.894
	100	4.882	20.158	−1.125	−1.327	−1.528	−1.730	−1.932
Binary				DR80				
	25	6.242	27.725	−2.019	−2.297	−2.574	−2.851	−3.128
	50	5.050	21.183	−1.262	−1.474	−1.686	−1.898	−2.110
	75	4.352	16.658	−0.612	−0.778	−0.945	−1.111	−1.278
	100	3.847	12.632	0.083	−0.043	−0.170	−0.296	−0.422
				AB26				
	25	11.531	51.010	−3.670	−4.180	−4.690	−5.200	−5.710
	50	8.604	38.800	−2.959	−3.346	−3.734	−4.122	−4.510
	75	5.944	26.176	−1.857	−2.118	−2.380	−2.642	−2.903
	100	4.466	17.456	−0.735	−0.910	−1.085	−1.259	−1.434

give an idea about the thickness of the boundary layer, i.e., the larger intercept the greater is the boundary layer effect. According to this model, the plot of uptake should be linear if intraparticle diffusion is involved in the biosorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step.[60–62] 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 other kinetic models may control the rate of biosorption, all of which may be operating simultaneously.

The linear fit between the t/q_t versus contact time (t) and calculated correlation coefficients (R^2) for pseudosecond order kinetics model show that the dye removal kinetic using *MP* can be approximated as pseudosecond order kinetic (Table III). In addition, the experimental q_e ($(q_e)_{Exp}$) values agree with the calculated ones ($(q_e)_{Cal}$), obtained from the linear plots of pseudosecond order kinetics (Table III).

In addition, an increase in initial dye concentration leads to an increase in the biosorption capacity of dye on *Mentha pulegium*. This indicates that the initial dye concentration plays an important role in the biosorption capacity of dyes on *Mentha pulegium*.

Thermodynamic studies

Thermodynamic parameters including the Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are the actual indicators for practical application of a biosorption process. According to the values of these parameters, what process will occur spontaneously can be determined. The thermodynamic parameters were determined using the following equations[63]:

$$\Delta G = \Delta H - T\,\Delta S \tag{19}$$

$$K_c = C_A/C_S \tag{20}$$

$$\ln K_c = (\Delta S/R) - (\Delta H/RT) \tag{21}$$

where K_c, C_A, C_S, R, and T are the equilibrium constant, the amount of dye adsorbed on the adsorbent of the solution at equilibrium (mol/L), the equilibrium concentration of dye in the solution (mol/L), the gas constant (8.314 J/mol K), and the absolute temperature (K), respectively.

By plotting a graph of $\ln K_c$ versus $1/T$, the values ΔH and ΔS can be estimated from the slopes and intercepts. The obtained thermodynamic parameters were given in Table IV. Positive ΔH suggests endothermic reaction. The positive value of ΔS suggests the increased randomness at the solid/solution interface during the biosorption of dyes onto *MP*. The negative values of ΔG imply the spontaneous nature of the biosorption process. Furthermore, the decrease in the values of ΔG with the increasing temperature indicates the biosorption 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 a range of −80 to −400 kJ/mol.[64] The values of ΔG obtained in this study are within the ranges of the physisorption mechanism.

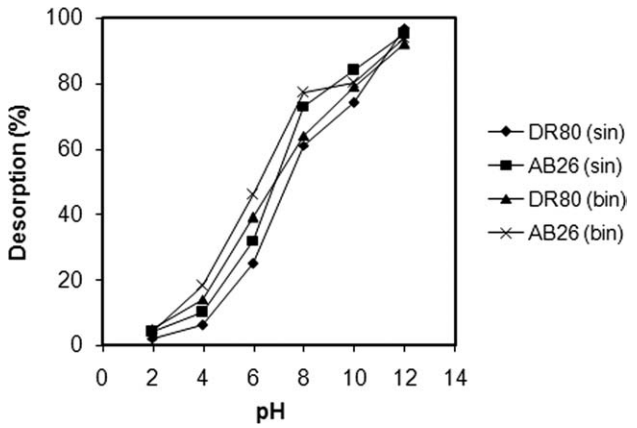

Figure 8 Effect of pH on desorption of dyes from *MP* (pH: 2, dye: 50 mg/L, T: 25°C and adsorbent: 2 g/L for DR80 and AB26 in single and binary systems).

Desorption studies

The regeneration of the biosorbent may make the treatment process economical. Desorption studies help to elucidate the mechanism and recovery of the adsorbate and biosorbent. Desorption tests (Fig. 8) showed that maximum dye releasing of 93% for DR80, 86% for AB26, and 83% for binary system was achieved in aqueous solution at pH 12. As the pH of the system increases, the number of positively charged sites decreased which favors desorption of dyes.

CONCLUSIONS

The results of this investigation showed that *Mentha pulegium* had effective biosorption capacity for the removal of DR80 and AB26 in single and binary systems from aqueous solutions. The experimental results were analyzed using the Langmuir, Freundlich, and Dubinin-Radushkevich models and the correlation coefficients for Langmuir equation fitted better than Freundlich and Dubinin-Radushkevich equation. Biosorption kinetic of dyes in single and binary dyes systems was found to conform to pseudosecond order. At alkaline pH, the number of positively charged sites decreased which favored desorption of dyes. Positive ΔH showed endothermic reaction. The positive value of ΔS suggested the increased randomness at the solid/solution interface during the biosorption of dyes onto *MP*. The negative values of ΔG implied the spontaneous nature of the biosorption process. On the basis of the data of this study, one could conclude that the *Mentha pulegium* being an ecofriendly biosorbent for dye removal from colored textile wastewater.

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