

Removal of Basic Blue 41 from Aqueous Solution by Carboxymethylated *Posidonia oceanica*

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ABSTRACT: The aim of this work is to improve the retention capacity already noticed for the raw *Posidonia* towards basic dyes and notably for basic blue 41 (BB41). To improve the fixation rate of these cationic entities, we have undertaken the introduction of carboxymethylate groups on the raw *Posidonia*. Thus, we have obtained materials with various carboxymethylate groups contents (from 10 to 30%). We have then studied the fixation capacities of BB41 on the different materials. We have noticed that the retention capacity of modified *Posidonia* was improved compared to the raw one. We have studied the effect of different pa-

rameters influencing the fixation capacities such as initial dye concentration, support dose, contact time, pH, carboxymethylate groups content, and temperature. This phenomenon of retention is compared to classic models of Langmuir and Freundlich. Some thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes have been studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1215–1225, 2007

Key words: *Posidonia*; chemical modification; carboxymethylate groups; basic dye; retention; carboxymethylcellulose

INTRODUCTION

In wastewater treatment technology, various biological^{1,2} and physicochemical methods^{3–5} have been applied for dye removal. Retention on solid materials is one of these methods which is comparatively more useful for dye removal^{6,7} since it has been found to be an efficient and economically cheap process. Different materials were used in this aim such as waste orange peel,⁸ banana pith,⁹ cotton waste, rice husk, teakwood bark,¹⁰ bagasse pith, maize cob, natural clay,¹¹ bentonite clay,¹² and aquatic plants.^{13,14} However, the amounts of adsorbed dyes on the above-mentioned materials are not very high. Some retention capacities, for the most preferment materials,¹⁵ are between 200 and 600 g/kg and for the other¹⁶ they can be even lower than 50 g/kg. To improve the efficiency of the sorption processes, it is essential to develop more effective retention materials with higher retention capacities. The studies using aquatic plants as a biosorbent for dyes are relatively few. The aquatic plant *Posidonia oceanica* is widely distributed, fast-growing, and available in large quantity on Mediterranean coasts¹⁷ and its carboxymethylated derivatives have been used as adsorbents in the present work. *Posidonia oceanica* is collected from the Tunisian coasts. Indeed, huge quantities of this plant are accumulated every year and every summer the beaches must be cleaned.

Many investigations have been undertaken to study the retention process of dyes on solid surfaces through ion-exchange mechanism^{18,19} to increase their capacity. These have allowed an understanding of some sorption processes and improved the fixation capacity for the ionic dye molecules, thereby the extent of textile dyeing or the depollution of wastewater emanating from such processes. Since the dyeing process frequently occurs in an aqueous phase, notably an increase in the quantity of fixed basic dye may be obtained by incorporating some negatively charged groups on the surface of the material being dyed.

The goal of the present study is to evaluate the potential of the *Posidonia* and improve its performance before and after grafting of carboxymethylate groups to remove basic dyes from aqueous solution. We chose Basic Blue 41 (BB41) for our experiment. Four different values of the carboxymethylate content ranging from 10 to 30% of the support mass have been obtained using different reaction conditions to yield four different materials referred to below as modified *Posidonia* P1–4. The untreated biomass, P0, was also tested.

Retention isotherms have been studied. The effects of initial dye concentration, support dose, contact time, pH, carboxymethylate groups content of the retention material, and temperature have also been studied.

EXPERIMENTAL PROCEDURES

Preparation of modified *Posidonia oceanica*

Posidonia oceanica (Fig. 1) was collected from Tunisian coasts (Mediterranean coast). It was cleaned using

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Figure 1 *Posidonia oceanica* plant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water and dried at 80°C in a hot air oven for 24 h. The crushed biomass was suspended in ethyl alcohol under mechanic stirring at room temperature. Then, the desired amount of NaOH was added from a 40% aqueous solution to this suspension. The flask was heated at 45°C and left overnight under stirring. Monochloroacetic acid MAC (34.5 g) was then added to the mixture. The reaction was stopped by addition of acetic acid. Modified *Posidonia* was recovered by filtration and washed several times with a large amount of ethanol/water (80/20 v/v) and oven dried at 50°C.

Determination of degree of grafting and exchange capacity

There are various methods to determine the degree of substitution, such as the classical methods of volumetric titration of the carboxyl groups,^{20–22} ¹H-NMR, ¹³C-NMR spectroscopy,^{23,24} and HPLC²⁵ methods.

In the present work, we have used a back titration method to determine the exchange capacity (EC). This technique was described in literature for cationized cotton.²⁶ 0.1 g of MPO was treated with 10 mL of HCl solution (0.2M). After reactions with the carboxylate —COO[−]Na⁺ groups, the remaining acid is evaluated by using a titrated solution of NaOH (0.1M). The exchange capacity EC, expressed in mole of carboxylate groups per gram of support, was calculated from the following expression:

$$EC = \frac{(V_0 - V_n)M}{m} \quad (1)$$

where V_0 and V_n are the volume (L) of NaOH solution necessary to neutralize the remaining acid of untreated *Posidonia* P0 and MPO respectively; M is the molarity of the sodium hydroxide solution and m is the mass (g) of the sample, respectively.

The degree of grafting (DG) is calculated from the weight uptake:

$$DG (\%) = \frac{m_f - m_i}{m_i} \times 100 \quad (2)$$

where m_f and m_i are the weights of the modified and untreated *Posidonia* samples, respectively.

Fourier transform infrared analysis

The measurements were performed using a Bio-rad spectrometer. A total of 50 scans were taken for each sample with a resolution of 4 cm^{−1} and the scanning range was from 500 to 4000 cm^{−1}. A mixture of 5 mg of dried samples and 200 mg of KBr was pressed into a disk for FTIR measurement.

Preparation of basic dye solution

Basic Blue 41 (BB41) (Maxilon Blue GRL; CI 11,105) manufactured by Bayer was used in this study without any purification. Its structure is illustrated in Figure 2. The stock solution was prepared by dissolving 3 g of BB41 in 1 L of distilled water, mixed for 4 h. An experimental solution was prepared by diluting the stock solution with distilled water when necessary.

Retention procedure

Retention experiments were conducted by contacting the supports (P0, P1, P2, P3, P4) (50 mg) with a volume (100 mL) of Basic Blue 41 solution in a series of flasks. The pH solution was adjusted by adding a small amount of HCl or NaOH. These flasks were reciprocated in AHIBA NUANCE (SALVIS SA, Zollhausstrasse 2, CH-6015 Reussbühl) shaker at 45 rpm at desired temperature (30, 40, 60, or 80°C). At the end of contact time, the supports were removed by centrifugation (Bioblock Scientific Centrifugeuse 55,701) during 15 min at 5300 rpm.

To measure the dye concentration, the solutions were analyzed by an UV/visible spectrophotometer (CECIL, CE 2021, 2000 series) at wavelength corresponding to the maximum absorbance of the dye solution ($\lambda_{\max} = 609$ nm). The adsorbed quantity at

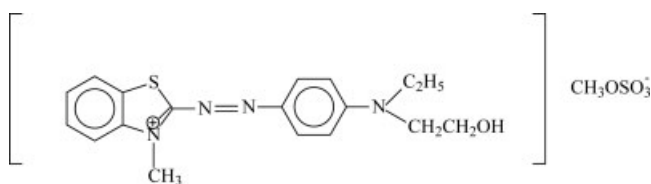


Figure 2 Schematic representation of BB41.

TABLE I
DG, EC, and the Experimental Conditions for Modified *Posidonia*

Sample	Time (h)	DG		
		(%) ^a	10 ⁻³ mole of carboxylate group per gram of support ^b	EC (10 ⁻³ mol of carboxylate group per gram of support) ^c
P1	1	10	1.23	1.21
P2	4	15	1.85	1.90
P3	6	18.75	2.3	2.90
P4	12	30	3.70	3.65

^a Calculation based on eq. (2).

^b Calculation based on weight uptake.

^c Calculation based on acid-base titration [eq. (1)].

equilibrium, Q_e (mg/g), was calculated according to the following equation:

$$Q_e = (C_0 - C_e) \frac{V}{W} \quad (3)$$

where C_0 and C_e are respectively, the initial and equilibrium solution concentration (mg/L), V is the volume of the solution (100 mL), and W is the weight of adsorbent (50 mg) used.

RESULTS AND DISCUSSION

Characterization of prepared MPO

Four MPO supports with different grafted carboxymethylate content have been prepared by modifying only the time (Table I). The four different samples namely P1, P2, P3, and P4 were stored in a dessicator before

use. The reaction occurring between *Posidonia* component and monochloroacetic acid are schematically shown in Figure 3. As the hydroxyl groups are disposed towards reaction, lignin and hemicellulose, in addition to cellulose, may participate in the carboxymethylation of *Posidonia*.

The values of DG and EC and the experimental conditions for each grafted sample are illustrated in Table I. For each samples, the values from the two methods are in agreement.

The obtained MPO supports are also characterized by FTIR spectroscopy. Figure 4(a) shows the FTIR spectra of starting cellulose extracted from *Posidonia oceanica*. Figure 4(b) illustrates the FTIR spectra of the four carboxymethylated *Posidonia*. In the last spectra, OH absorption band occurs in the region of 3450 cm⁻¹ and the carboxylate anion —COO⁻ absorption band appears at 1610 cm⁻¹ confirms the fixation of carboxylic acid salt on *Posidonia*.

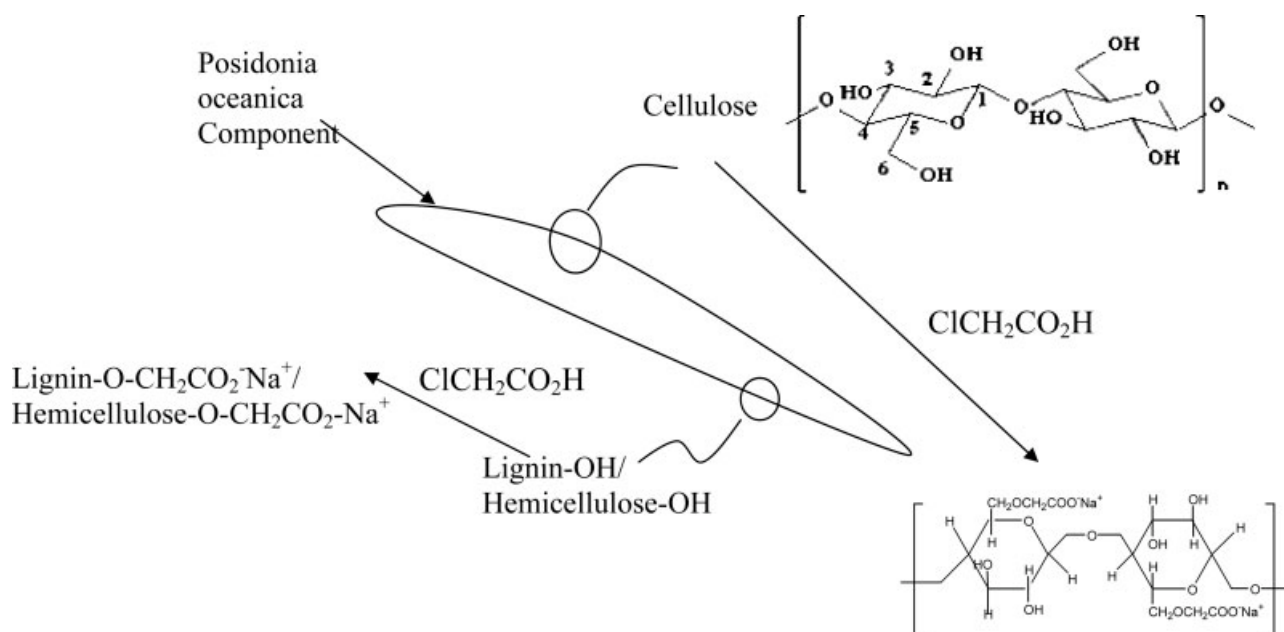


Figure 3 Possible reactions occurring when carboxymethylating *Posidonia*.

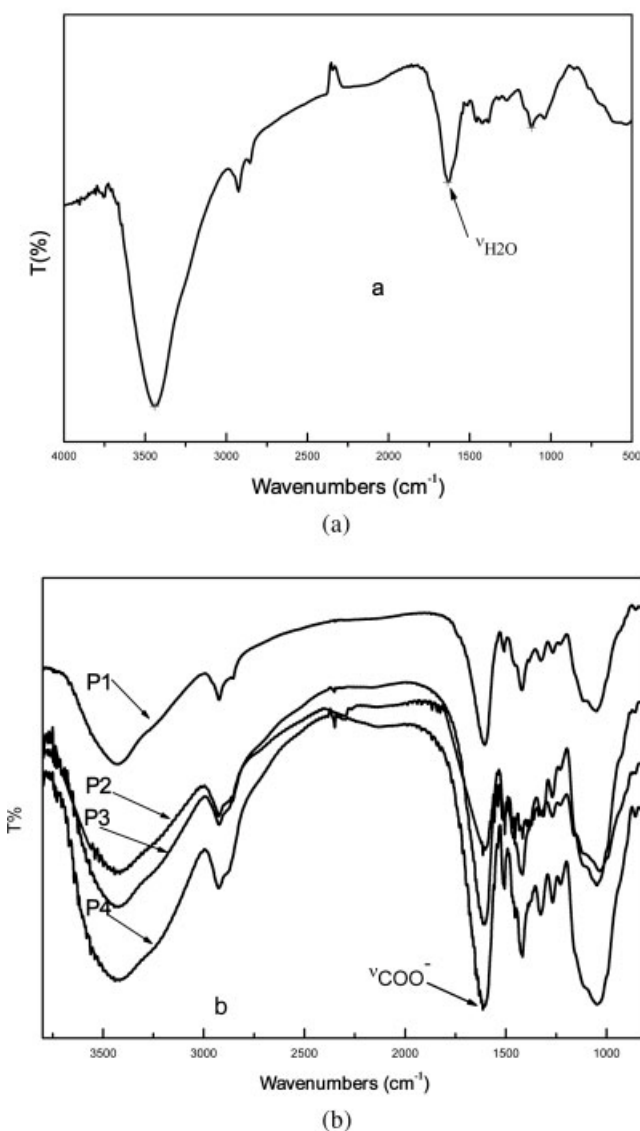


Figure 4 IR spectra of cellulose extracted from *Posidonia* (a) and modified (P1, P2, P3, and P4) *Posidonia oceanica* (b).

Effect of initial concentration of dye on retention kinetics

To study the retention isotherms of dye (BB41) onto the four prepared supports, one of the most important parameter to be determined is the contact time necessary to reach equilibrium. This parameter is influenced by the initial dye concentration. The contact time for different supports has been determined. The results are presented in Figure 5. It can be seen that, for all the samples studied, the fixed amount of dye rises quite quickly and reaches rapidly, after about 60 min, the equilibrium. So, 300 min was chosen as contact time for the rest of the study to ensure an equilibrium condition for any initial dye concentration.

We have studied the variation of contact time for different initial dye concentrations (100, 200, and 300 mg/L). For this, we have chosen, among the pre-

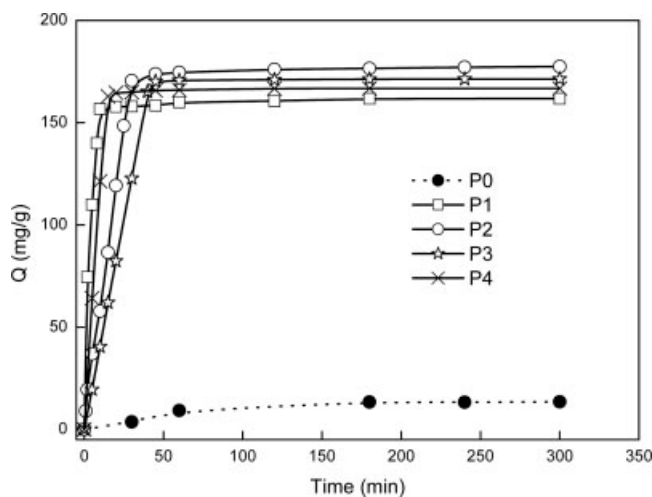


Figure 5 Retention kinetics of BB41 onto various supports prepared. Conditions, initial concentration 100 mg/L, support dose 50 mg in 100 mL of dye solution, temperature 30°C, pH 7.

pared supports, the sample P2 that gives the maximum of retention (Fig. 6). The uptake of BB41 increased with increasing the initial dye concentration. Indeed, the uptake of BB41 onto P2, for example, increased from 178.08 to 460 mg/g when initial dye concentration increases from 100 to 300 mg/L (Fig. 6). We can conclude that the initial dye concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases. We also notice in Figure 6 that the equilibrium contact time is about 60 min for all the used initial dye concentrations.

Effect of pH

Basic Blue 41 when dissolved in water releases cations in solution. Thus, retention of this dye is influ-

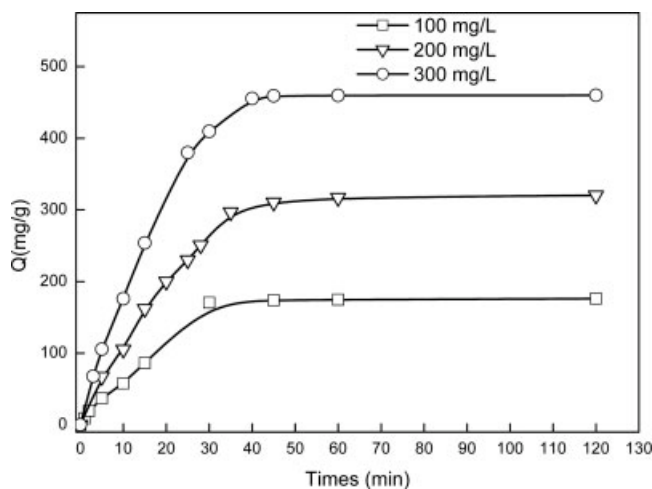


Figure 6 Effect of initial dye concentration on the retention of BB41 onto P2. Conditions: support dose 50 mg in 100 mL of dye solution, temperature 30°C, pH 7.

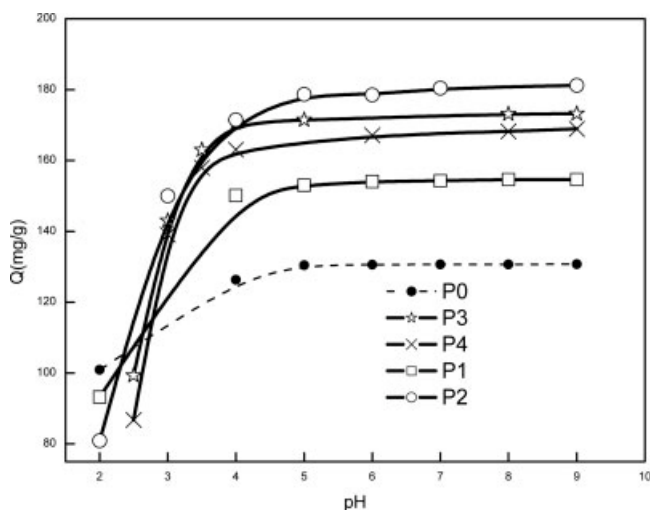


Figure 7 Effect of pH on retention of BB41 onto P1, P2, P3, P4, and P0. Conditions: support dose 50 mg in 100 mL of dye solution; agitation time 5 h, initial dye concentration 100 mg/L, temperature 30°C.

enced by the modified *Posidonia* surface charge, which in turn depends on the pH solution. Consequently, the pH value of the solution is an important controlling parameter in the retention process. The effect of pH on BB41 adsorption (100 mg/mL) onto *Posidonia* (50 mg) is illustrated in Figure 7. The different curves $Q = f(\text{pH})$ (Fig. 7) show that the quantity uptakes of dye fixed by the MPO increase when pH increases until reaching a maximum for pH about 6. Similar results of pH effect were also reported for the retention of basic dye onto orange peel,¹⁶ onto *Spirodela polyrrhiza*,²⁷ and by various activated carbons.²⁸ No significant increase in uptake quantities was observed beyond pH 7, and the highest amounts of retention are 154.62, 178.52, 173.2, 168.69, and 130 mg/g for

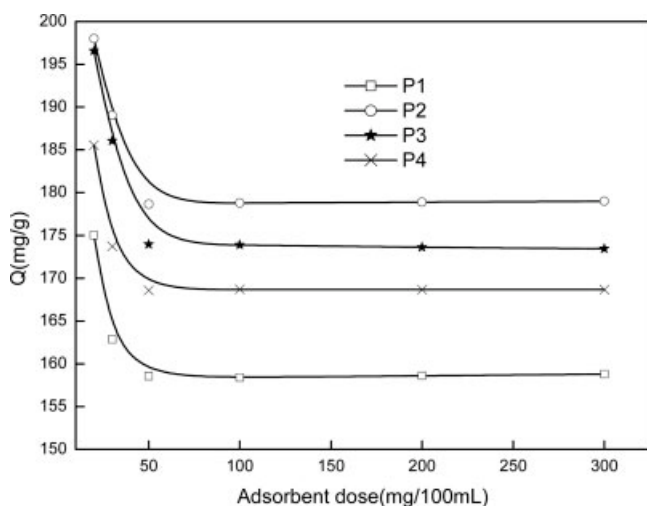


Figure 8 Effect of support dose on the retention of BB41 onto P1, P2, P3, and P4. Conditions: agitation time 5 h, initial dye concentration 100 mg/L, temperature 30°C, pH 7.

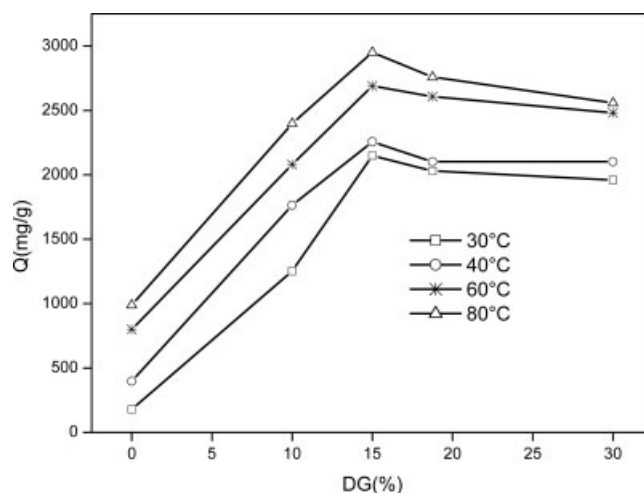


Figure 9 Effect of DG on the retention of BB41 at different temperatures. Conditions, support dose 50 mg in 100 mL of dye solution, agitation time 5 h, pH 7.

P1, P2, P3, P4, and P0, respectively. The low uptake of BB41 at pH acid values may be explained on the basis of surface binding sites of the MPO. Indeed, at low pH values more protons will be available to protonate carboxylic groups. According to Banatt et al.,²⁹ at low pH values, H^+ may compete with dye ions for the retention sites of MPO. At high pH values, deprotonation of carboxylic groups takes place, thereby increasing electrostatic attractions between positively charged dye and negatively charged MPO. Consequently, the surface charge of the material surface becomes negative above pH 7. This explains the maximum retention of basic dye onto the negative surface of the MPO in the pH range of 7–9. We can also note that the retention capacity increases with DG from P0 to P2 and decreases from P2 to P4 and this is for any pH value.

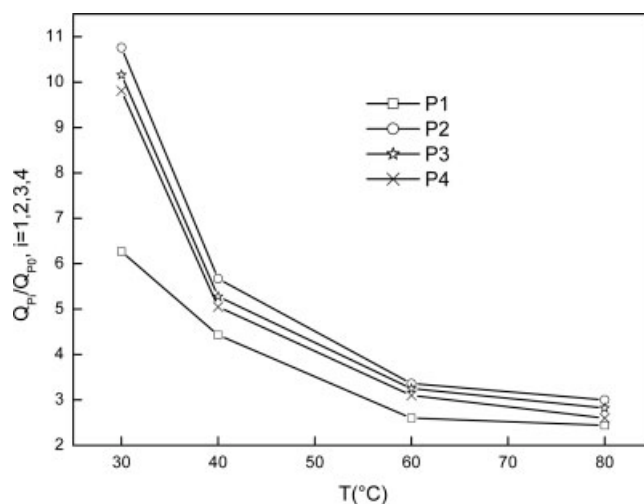


Figure 10 Q_{Pi}/Q_{P0} ratio as a function of temperature for the modified supports.

TABLE II
Comparison Between the First- and Second-Order Sorption Rate Constants and Between Calculated and Experimental Q_e Values for Different Supports

Sample	$Q_{e,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (1/min)	$Q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg/min)	$Q_{e,cal}$ (mg/g)	R^2
P0	13.50	0.013	13.94	0.97058	0.00092	16.06	0.93257
P1	161.83	0.24746	162.2257	0.92972	0.00191	170.6452	0.88683
P2	177.44	0.21555	174.7062	0.98853	0.00143	185.6785	0.97807
P3	172.4	0.04747	176.48064	0.96451	0.00034	191.2660	0.9098
P4	166.76	0.36939	169.46346	0.95588	0.00268	178.7025	0.90144

This observation is the same for the following studied parameters.

Effect of support dose

Figure 8 shows the effect of support dose on the removal of BB41 from aqueous solutions (100 mg/L) by modified *Posidonia* (P1, P2, P3, and P4). The retention efficiency increases with the decrease of the support dose. Further, at a low support dose, the smaller amount of adsorbent implies the higher amount of the dye contact with per weight unit of the adsorbent. The similar phenomenon was also observed by the adsorption of methylene blue onto raw date pits.²⁹

Effect of carboxymethylate groups grafted on *Posidonia* materials

Figure 9 shows that the adsorbed capacity increases with the carboxymethylate groups content until 15%. After this percentage, the retention capacity does not increase but decreases slightly with carboxymethylate groups content. This decrease could probably be attributed to the increase of steric hindrance when the receptor site density increases and one molecule of dye may hide some receptor sites to not be occupied.^{30,31}

Figure 10 showed clearly that at different temperatures the modified *Posidonia* (P1, P2, P3, and P4) are more effective than the untreated *Posidonia* and a ratio (Q_{Pi}/Q_{P0} , $i = 1,2,3,4$; Q_{Pi} represents the retention capacity of the support Pi) between 3 and 11 was noticed.

Effect of temperature

The study of the temperature effect shows that in all the studied materials the retention capacity increases with increasing temperature (Fig. 9). Indeed, by increasing the temperature of the retention from 30 to 80°C, the uptake quantity of the dye increased from 1252.2 to 2398 mg/g for P1, from 2149 to 2950.88 mg/g for P2, from 2030.12 to 2758.98 mg/g for P3, and from 1960 to 2558.21 mg/g for P4. Consequently, it is clear that adsorption equilibrium is temperature-dependant. This effect could be explained by the material polymer expanding and therefore the number of accessible acti-

vated receptor sites increases that could increase the adsorbed quantity.

Kinetic and equilibrium models

Kinetic models

The kinetics of dye retention onto modified and pure *Posidonia* have been studied using the Lagergren models, pseudofirst- and pseudosecond-order kinetics. The expressions of these two models are respectively:

$$Q = Q_e(1 - \exp(-k_1t)) \quad (4)$$

$$Q = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (5)$$

where k_1 (1/min) and k_2 (g/mg/min) are the Lagergren rate constant of pseudofirst- and second-order respectively. Q_e (mg/g) and Q (mg/g) represent the amount of the dye adsorbed at equilibrium and at time t (min) respectively.

We have calculated the values of k_1 , k_2 , and Q_e using both models by fitting procedure without any linearization to have the maximum information

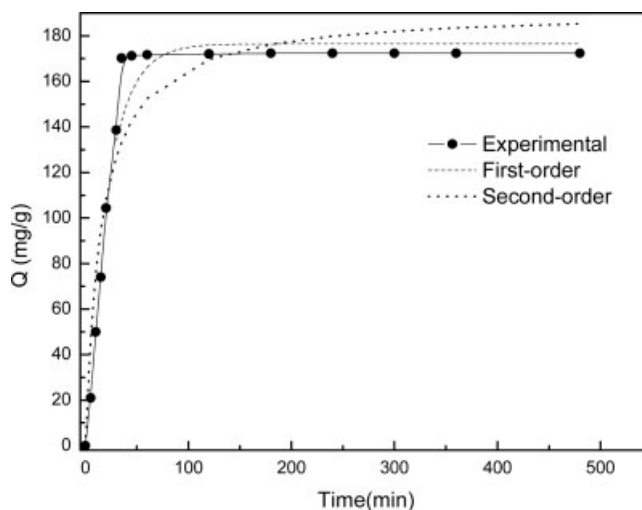


Figure 11 Comparison between the measured and modeled time profiles for retention of BB41 onto P3. Conditions: initial dye concentration 100 mg/L, support dose 50 mg in 100 mL of dye solution, temperature 30°C, pH 7.

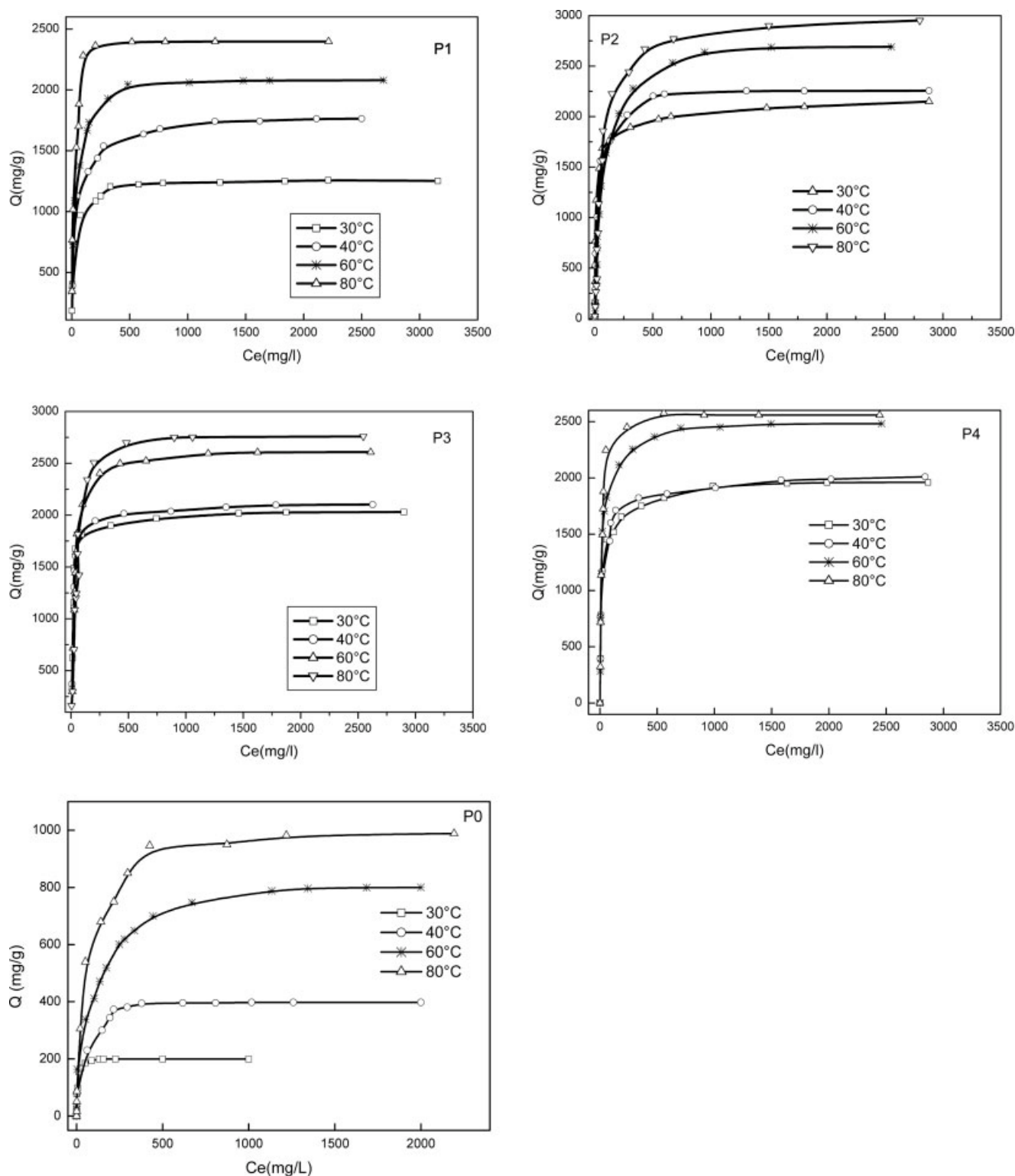


Figure 12 Retention isotherms of BB41 onto P1, P2, P3, P4, and P0. Conditions: agitation time 5 h, support dose 50 mg in 100 mL of dye solution, pH 7.

directly from the experimental measurements. It was shown (Table II) that the values of Q_e calculated with the help of the pseudosecond-order model agrees with to the experimental values. However, the values calculated using the pseudofirst-order model are very

close to the experimental ones. This shows that the retention of BB41 onto *Posidonia* follows pseudofirst-order kinetics. A similar phenomenon has been observed in the Kinetic experiment of methylene blue onto dried *Spirodela polyrrhiza*²⁸ and in the kinetic

TABLE III
Langmuir Parameters for Various Samples
at Different Temperatures

Sample	T(°C)	b(L/mg)	K _L (L/g)	Q _{max} (mg/g)	R ²	R _L
P0	30	0.182	37.342	205	0.994	0.016
	40	0.026	11.020	412	0.962	0.0183
	60	0.012	10.02	818	0.975	0.0391
	80	0.024	22.783	929	0.992	0.0182
P1	30	0.077	95.680	1231	0.994	0.0040
	40	0.049	83.522	1696	0.982	0.0080
	60	0.046	96.190	2049	0.983	0.0078
	80	0.072	173.700	2384	0.978	0.0061
P2	30	0.051	108.152	2107	0.956	0.0089
	40	0.032	75.201	2302	0.979	0.0133
	60	0.012	35.673	2849	0.985	0.0288
	80	0.010	35.321	3214	0.975	0.0308
P3	30	0.037	79.679	2125	0.892	0.0129
	40	0.041	89.699	2185	0.923	0.0114
	60	0.022	61.642	2782	0.952	0.0170
	80	0.013	43.079	3081	0.964	0.0252
P4	30	0.069	130.619	1884	0.975	0.0073
	40	0.072	139.200	1911	0.960	0.0066
	60	0.064	158.403	2451	0.978	0.0061
	80	0.062	167.251	2655	0.986	0.0062

experiment of basic dyes using sludge biomass as an adsorbent.³² For example, Figure 11 typically illustrates a comparison between the calculated and measured results for retention of BB41 onto support P3. From Figure 11, we noticed that the first-order model fitted better the experimental data than the pseudosecond-order model. The measured results (Fig. 11) indicate that the retention rate was very fast at the beginning stage of retention. We can notice also (Table II) that there is no proportionality between the values of k_1 and the grafted degree DG of carboxymethylate groups notably at high values. This behavior could be explained by the fact that the retention phenomenon is occurred in het-

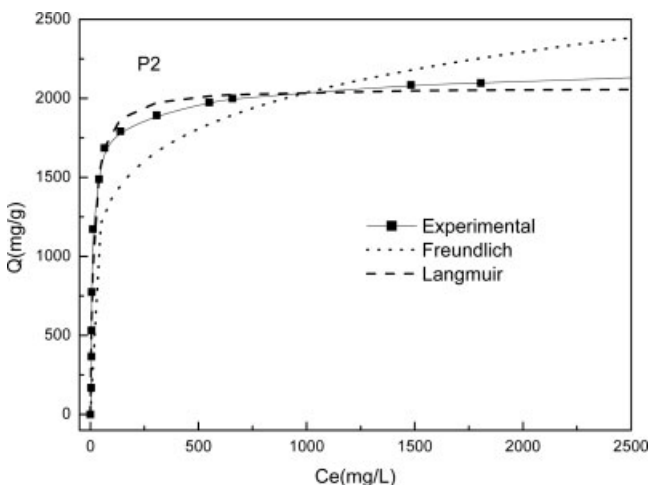


Figure 13 Comparison between theoretical isotherms and experimental data for the retention of BB41 onto P2. Conditions: agitation time 5 h, support dose 50 mg in 100 mL of dye solution, temperature 30°C, pH 7.

erogeneous media. Consequently, the kinetic in such media and therefore the rate constant depends on various parameters often difficult to evaluate such as diffusion, accessibility of receptor sites, and so on.

Retention isotherms

The equilibrium retention of BB41 onto MPO was expressed in term of sorption isotherms. Experimental retention isotherms were determined for a nonmodified and modified *Posidonia* with four carboxymethylate percentages and the contact time for each experiment was 5 h at pH 7. All retention isotherms exhibited negative concavities before attaining a saturation level. As illustration of these experimental data we plotted in Figure 12 the adsorption isotherms for the all samples in temperature range 30–80°C. All experimental isotherms were commonly fitted to Langmuir model:

$$Q_e = \frac{K_L C_e}{1 + b C_e} \quad (6)$$

where Q_e is the equilibrium adsorbed quantity (mg/g), C_e is the concentration of BB41 at equilibrium (mg/L), b and K_L are Langmuir constants.

The values of all Langmuir parameters related to the studied adsorption isotherms are illustrated in Table III.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor defined as follows:

$$R_L = \frac{1}{1 + b C_{ref}} \quad (7)$$

where C_{ref} is the initial concentration of BB41.

TABLE IV
Parameters Obtained from the Freundlich Equation

Sample	Temperature (°C)	P	n	R ²
P0	30	38.93952	2.92337	0.88915
	40	75.75993	4.00946	0.94421
	60	86.70831	3.14917	0.9443
	80	65.04593	2.54137	0.87604
P1	30	292.97694	4.89542	0.87065
	40	442.35099	5.19846	0.89185
	60	494.4017	4.88482	0.87716
	80	605.82306	4.81794	0.82442
P2	30	619.90092	5.80833	0.84394
	40	523.6612	4.87375	0.86543
	60	155.56133	2.49472	0.83507
	80	126.77582	2.27078	0.78645
P3	30	468.01457	4.89325	0.67441
	40	572.09871	5.40956	0.67891
	60	430.92302	3.88961	0.74209
	80	265.50714	2.9498	0.76498
P4	30	537.3156	5.52531	0.8426
	40	551.4462	5.55016	0.83972
	60	544.43379	4.52134	0.81079
	80	608.31116	4.73311	0.75592

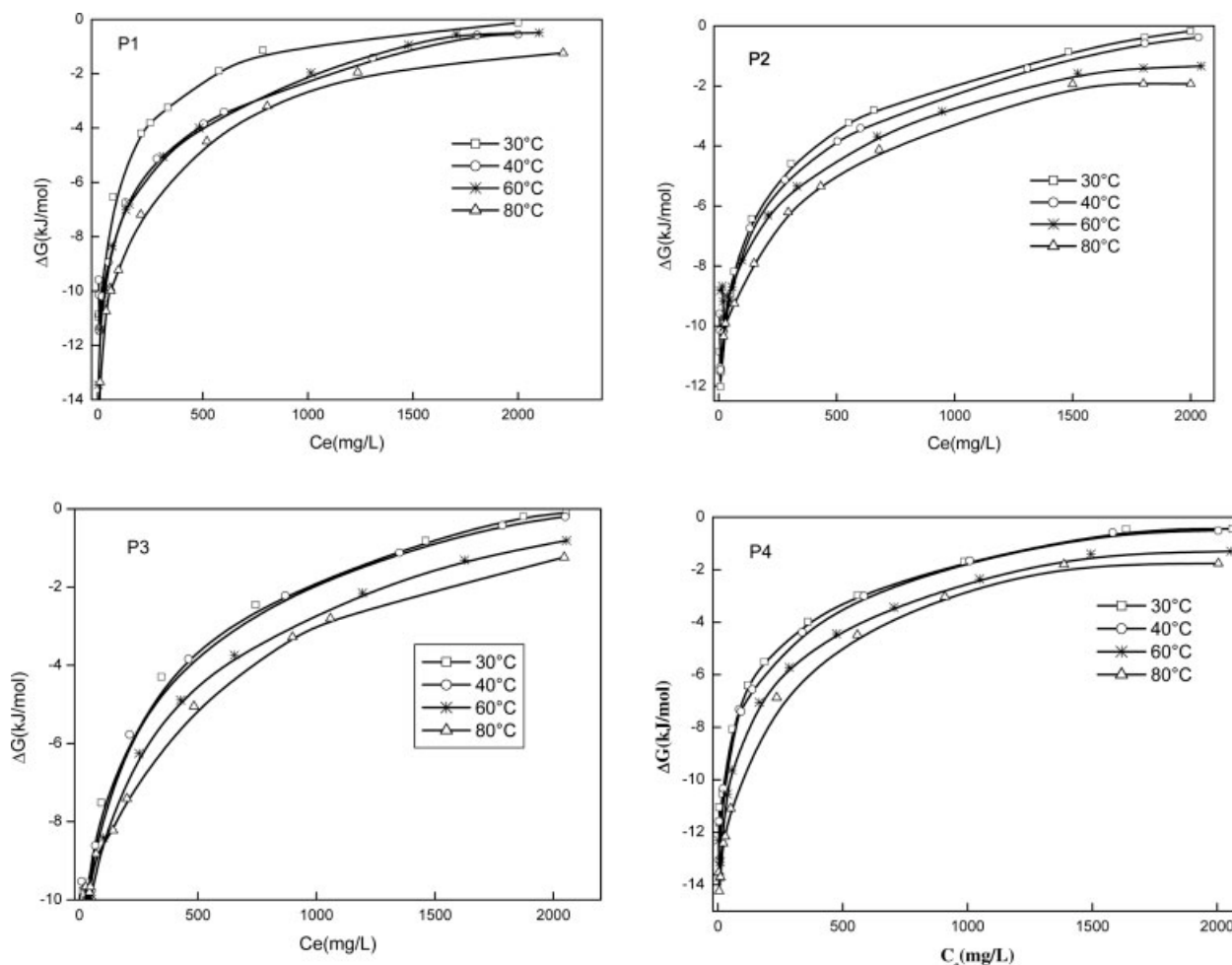


Figure 14 Change in free energy with respect to different equilibrium concentration for the retention of BB41 on MP.

R_L values for all adsorption isotherms are found to be less than 1 and greater than 0. These results indicate that the retention of BB41 onto *Posidonia* is favorable.³²

We have also fitted the retention isotherms using the Freundlich equation, which is often used for heterogeneous surface energy systems.

$$Q_e = PC_e^{1/n} \quad (8)$$

where Q_e is the equilibrium adsorbed quantity (mg/g), C_e is the concentration of BB41 at equilibrium (mg/L), n and P are Freundlich constants.

Figure 13 shows an example of comparison of the theoretical models of Langmuir and Freundlich to the experimental data for the sample P2 at 30°C. The Langmuir model shows a better fit to experimental data than the Freundlich one. Further, based on the correlation coefficient (R^2) shown in Table III and IV, the retention isotherms can be better described by the Langmuir equation.

Estimation of some thermodynamic parameters

The thermodynamic parameters such as free energy ΔG^0 (kJ/mol), enthalpy ΔH^0 (kJ/mol), and entropy

ΔS^0 (kJ/mol/K) changes for the process were estimated using the following equation:^{33,34}

$$\Delta G^0 = -RT \ln K_c \quad (9)$$

$$K_c = \frac{C}{C_e} \quad (10)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (11)$$

where T is the absolute temperature (K); R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); K_c is the equilibrium constant; C represents the amount of dye (mg) fixed by the support per cubic meter of solution at equilibrium; and C_e represents the equilibrium concentration (mg/m^3) of the dye in the solution.

The isotherms data in Figure 12 were applied to calculate the equilibrium constant using eq. (9) and then the change of free energy [eq. (10)]. Figure 14 shows the plots of ΔG^0 versus C_e for retention of BB41. The negative values of ΔG^0 indicate that overall retention processes are spontaneous. We noticed in Figure 14 that at low equilibrium concentration C_e of

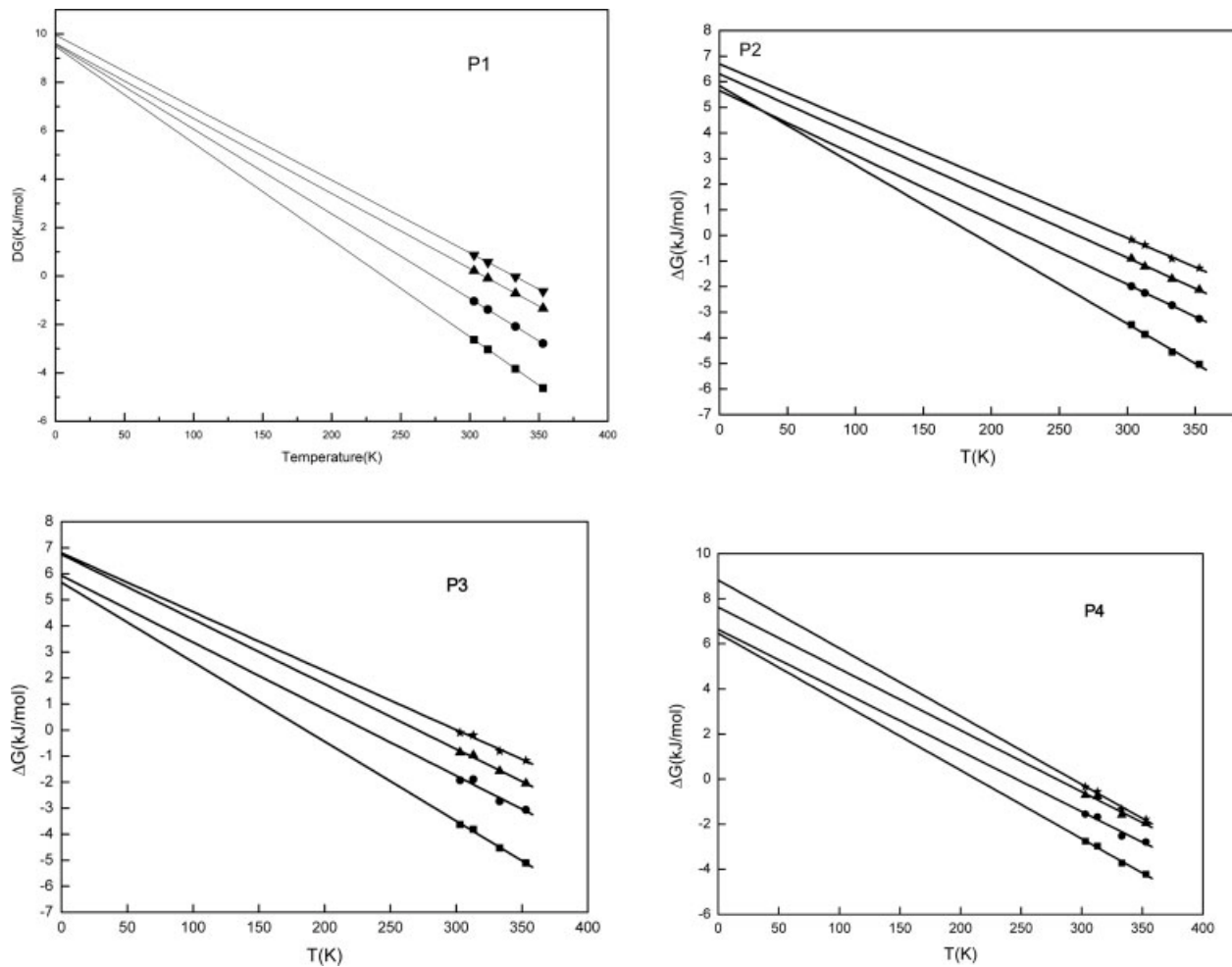


Figure 15 Behavior of ΔG^0 as a function of temperature for the modified supports at four different residual concentrations: ■ 500 mg/L, ● 1000 mg/L, ▲ 1500 mg/L, and ★ 2000 mg/L.

the dye solution, the driving force of the retention process is more important than the one at high equilibrium concentration since the value of ΔG^0 are more negative. Furthermore, the negative ΔG^0 value decreased with an increase in temperature, indicating that the spontaneous nature of retention is proportional to the temperature.

The graph of ΔG^0 versus T would yield a straight line (Fig. 15). Values of ΔS^0 and ΔH^0 were estimated from the slope and intercept of that line. When the value of ΔH^0 is positive, this corresponds to the dye molecule BB41 taking energy from the solvent during the sorption process, which will then be endothermic. From Figure 16, it is shown that the higher the equilibrium concentration, the higher the ΔH^0 . Indeed when the equilibrium concentration increases, the interaction between dye molecules themselves increases and hence the sorption process requires more energy to take place.

The positive values of ΔS^0 (Fig. 15) suggest randomness at the solid/solution interface during the retention of BB41 on MPO. Figure 17 depicts plots of the

variation of equilibrium concentration versus the equilibrium concentration for each MPO studied. All data indicate that ΔS^0 decreases when equilibrium concen-

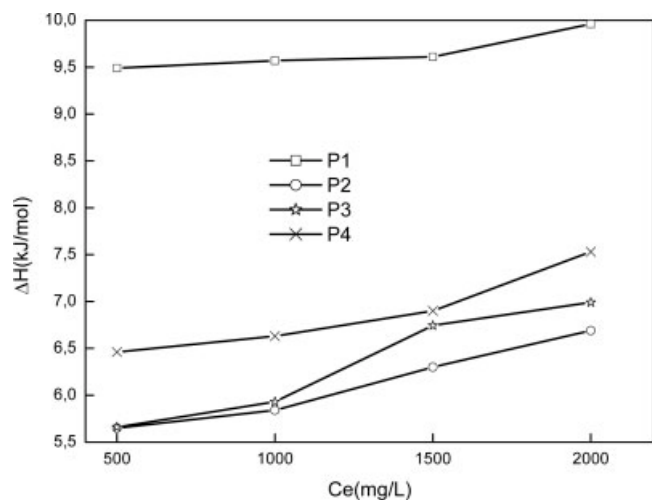


Figure 16 Change in enthalpy ΔH^0 for the retention of BB41 on MPO.

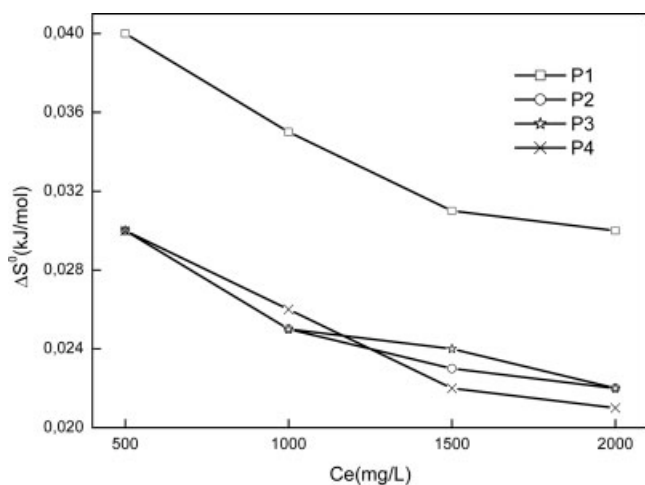


Figure 17 Change in entropy ΔS^0 for the retention of BB41 on MPO.

tration increases. This behavior can be explained by the order and disorder. Hence, at low equilibrium concentration, the greater the disorder of the dye molecule, the more important is the variation of entropy. Indeed, at low concentration, the probability to find an empty site is important and the molecule moves at the surface with more freedom. However, at high concentration, the reverse applies. When the saturation is reached, there is no empty site that corresponding to an ordered surface and so ΔS^0 goes toward zero.

CONCLUSIONS

This study investigates the equilibrium and the kinetic retention of BB41 on the different prepared supports (P1, P2, P3, and P4). The modified *Posidonia* has very high retention capacities to remove basic dye BB41, whose maximum uptake ranges from 1252 to 2149 mg/g at 30°C, from 1764 to 2256.4 mg/g at 40°C, from 2080 to 2690 mg/g at 60°C, and from 2398 to 2950.88 mg/g at 80°C. To compare with untreated *Posidonia*, the modified *Posidonia* exhibits excellent retention performance of BB41. The retention capacities of the carboxymethylate *Posidonia* are much higher than those of untreated *Posidonia* for basic dye BB41. It is shown that the major retention sites of MPO is a carboxylate group, the strong electrostatic interaction between $-\text{CO}_2^-$ of MPO and dye cations can be used to explain the high retention capacity of cationic dye onto carboxymethylated *Posidonia*. The retention capacities are affected significantly by the initial dye concentration, pH, and support dose. The uptake increases with increasing initial dye concentration and pH, but with decreasing adsorbent dose. The analysis of the kinetic data showed the uptake of basic blue 41 on the prepared supports to be pseudofirst-order reaction. The

Langmuir equation describes well the experimental equilibrium isotherms. The thermodynamic parameters indicate that the dye retention was spontaneous and endothermic in nature.

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