Quaternized triethanolamine-sebacoyl moieties in highly branched polymer architecture as a host for the entrapment of acid dyes in aqueous solutions

Meriem Bendjelloul, El Hadj Elandaloussi, Louis-Charles de Ménorval and Abdelhadi Bentouami

ABSTRACT

This paper reports the synthesis of a hyperbranched polymer by a cost-effective one-step copolymerization of A3 and B2 monomers, namely, triethanolamine and sebacoyl chloride, respectively, followed by methylation of tertiary amine groups. The structure of the hyperbranched polymer QTEAS as an efficient material for the removal of acid dyes was demonstrated by Fourier transform infrared spectroscopy (FTIR), cross polarization magic angle spinning (CPMAS) 13C NMR, thermogravimetric analysis (TGA), powder X-ray diffraction (DRX) and scanning electron microscopy (SEM). The removal of indigo carmine (IC) and Evans blue (EB) was expected to be driven by the electrostatic attraction between positively charged quaternary ammonium groups within the hyperbranched polymer and the negatively charged dyes. The removal process was found to be closely connected to the total number of sulfonate groups on the surface of the dyes. Nonetheless, the ionic strength does not affect the dyes' removal efficiency by the hyperbranched polymer. The sorption capacities at saturation of the monolayer \( q_{\text{max}} \) were determined to be 213.22 mg g\(^{-1}\) and 214.13 mg g\(^{-1}\), for IC and EB, respectively, thus showing the greater affinity of QTEAS sorbent for both dyes. Despite its extended molecular structure, EB is removed with the same effectiveness as IC. Finally, the great efficiency of the highly branched polymer for dye removal from colored wastewater was clearly demonstrated.

Key words | Evans blue, hyperbranched polymer, indigo carmine, ion exchange, regeneration, removal of dyes

INTRODUCTION

Wastewaters originating from the textile industry are polluted, as they contain residual color and other chemical substances (O’Neill et al. 1999). The non-biodegradable nature of the residual dye in the wastewaters may also obstruct light penetration, thus inhibiting aquatic life in the ecosystem (Walsh et al. 1980; Kuo 1992; Forgacs et al. 2004; Rai et al. 2005). In addition, many dyes are toxic and even carcinogenic and pose a serious threat to various microbiological or animal species (Willcock et al. 1992).

Apart from adsorption using low-cost adsorbents deriving from renewable resources or less expensive natural materials (Bouzaïda & Rammah 2002; Aygun et al. 2003; Nakamura et al. 2003; Prado et al. 2004; Ozacar & Sengil 2005; Ferrero 2007; Amin 2009), numerous methods such as biological (Abadulla et al. 2000), electrochemical (Fernandez-Sanchez & Costa-Garcia 2000), photochemical (Hachem et al. 2001; Barka et al. 2008; Tahiri Alaoui et al. 2009; Benalioua et al. 2015), and membrane filtration (Ma et al. 2012) technologies have been successfully employed for the removal of dyes.
from wastewaters. Recently, several studies have shown the effectiveness of dendritic nanomaterials for water treatment due to their outstanding removal capacity, higher surface area and large number of active sites for interaction with pollutants (Qu et al. 2006; Saeed et al. 2008; Zhou et al. 2005).

Dendrimers are a class of highly branched three-dimensional polymers characterized by a compact shape that have numerous reactive functional end groups and room between branches for taking up guest molecules (Tomalia & Fréchet 2001). Dendrimers have been shown to be effective for dyeing fibers. For instance, Burkinshaw et al. (2000) used a dendrimer containing primary amino groups for the pretreatment of cotton in order to enhance the color strength of the fiber with reactive dyes. Polyamidoamine dendrimers have also been reported as promising candidates for different applications including water purification (Diablo et al. 1999; Xu & Zhao 2005). Extraction and encapsulation of dyes by dendrimers have been reported by several authors. At sufficiently low pH, dendrimers containing tertiary amine groups are able to give an acid–base interaction with acid dyes. The process is totally reversible since at alkaline pH, the number of positively charged sites on the surface of the dendrimer decreases, thus favoring the dyes’ release. In this regard, Baars et al. (1997) investigated poly(propylene imine) dendrimers for the extraction of an acid dye from water by amine groups in an apolar solvent. The same principle of dye encapsulation has been applied by Cooper et al. (1997) for the extraction of an acid dye by a modified dendrimer in liquid CO2.

One of the major factors that influences the performance of polymeric sorbents is the nature of the functional groups available on their surface for interactions with contaminants. These functional groups determine the removal capacity, stability, and reusability of the sorbent material. According to the literature (Wawrzakiewicz & Hubicki 2009a, 2009b, 2009c), the use of commercially available anion-exchanger resins to remove acid dyes from water has been thoroughly investigated. These resins showed high potential for adsorption of anionic dyes and excellent adsorption capacity due to their high content of positively charged functional groups. Moreover, complete regeneration without loss of their sorption capacity can be achieved in alkaline media (Karcher et al. 2001, 2002).

The current study was set to prepare a hyperbranched polymer as an efficient material for solid-liquid extraction of acid dyes. The hyperbranched polymer QTEAS was synthesized by a cost-effective one-step copolymerization of multifunctional A3 and B2 monomers, namely, triethanolamine and sebacoyl chloride, followed by methylation of amine groups. Quaternization of tertiary amine groups was necessary to lead to a material with plenty of positively charged sites on its surface, and this was also intended for rightly avoiding pH adjustment in our sorption studies. Sebacoyl monomer was chosen for its chain length (8 sp3 carbons) in order to get ample room between the branches in the QTEAS hyperbranched material, thus facilitating the encapsulation of guest molecules. Although its structure is not as perfect as that of dendrimers, QTEAS will still have many similar characteristics and properties of dendrimers, such as the three-dimensional globular architecture and abundant quaternary amine groups required for the removal of targeted dyes by electrostatic interactions. Two negatively charged dyes were chosen for the study: indigo carmine (IC), a divalent anion that is a real concern in textile wastewaters and a diazo dye with extended molecular structure; Evans blue (EB), a tetravalent anion (see Table 1). Furthermore, the structure of the prepared macromolecule is demonstrated by Fourier transform infrared spectroscopy (FTIR), cross polarization magic angle spinning (CPMAS) 13C NMR, thermogravimetric analysis (TGA), powder X-ray diffraction (DRX), and scanning electron microscopy (SEM). Sorption kinetics, isotherms, effect of pH, ionic strength, and effect of temperature have been investigated to identify a sorption mechanism of the dyes. Moreover, the data were analyzed using different well-known adsorption isotherms and kinetics models. The high performance of the QTEAS material after regeneration cycles has been carefully examined to ascertain its stability and reusability. Finally, the great efficiency of the hyperbranched polymer for dye removal from colored wastewater was clearly demonstrated.

**EXPERIMENTAL**

**Preparation of QTEAS material**

All chemicals were analytical reagent grade and were used without further purification. The procedure for the preparation of hyperbranched QTEAS from A3 and B2 monomers (2:3 molar ratio) is depicted in Figure 1. Triethanolamine (5.60 g, 37.50 mmol) in a 500 mL solution of toluene/pyridine (V/V) was placed into a 1 L three-neck
flask equipped with a condenser and a mechanical stirrer. This solution was kept at 0 °C, and neat sebacoyl chloride (12 mL, 56.25 mmol) was slowly added. During the whole addition (30 min), the reaction temperature was kept at 0 °C and was then allowed to gradually rise to 10 °C. After stirring at 10 °C for 2 h, a dark brown chunk was formed and stuck to the stirring rod, allowing no further efficient stirring. Then, excess iodomethane (20 mL) was added and

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Molecular structure</th>
<th>MW (g mol⁻¹)</th>
<th>λ_{max} (nm)</th>
<th>Charges on surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indigo carmine (IC)</td>
<td><img src="image" alt="Indigo carmine" /></td>
<td>466.35</td>
<td>610</td>
<td>2</td>
</tr>
<tr>
<td>Evans blue (EB)</td>
<td><img src="image" alt="Evans blue" /></td>
<td>960.81</td>
<td>610</td>
<td>4</td>
</tr>
</tbody>
</table>

**Figure 1** Synthesis of ideal QTEAS hyperbranched polymer from A3 and B2 monomers.
the reaction mixture was heated to 40°C for 2 h. The solid was collected by suction filtration and abundantly washed with hot water then with acetone. The product was further Soxhlet extracted with acetone for 2 days and finally dried in an electric drying oven at 100°C for 24 h. The material was sieved to a particle size of 250 μm to produce 12.76 g of QTEAS as a dark brown solid.

**Characterization**

An infrared spectrum was obtained on a (2.5 wt %) sample in a KBr disk from 400 to 4,000 cm⁻¹ using a Nicolet Avatar 330 Fourier transform IR spectrometer. The CPMAS ¹³C NMR spectrum of QTEAS was recorded on a Bruker 300 (Digital NMR Avance) spectrometer. X-ray diffraction (XRD) patterns were recorded from 20 = 3.5 to 70° on a Phillips X’Pert MPD diffractometer using monochromatic CuKa radiation (λ = 1.5418 Å) at 40 kV and 30 mA. The thermal stability of the sample was performed using TGA on a NETZSCH STA 409 PC/PG simultaneous thermal analyzer at a heating rate of 10°C/min under nitrogen atmosphere. The morphology of the QTEAS hyperbranched polymer was examined at high magnification using a HITACHI S-4800 SEM.

**Sorption experiments**

Stock solutions (500 mg L⁻¹) of the dyes were prepared by dissolving IC and EB in distilled water, and test solutions of desired concentrations were obtained by further dilution with distilled water. Dye solutions of desired pH values were adjusted using HCl (0.1 N) and NaOH (0.1 N). The concentrations of the dyes were measured with a HACH DR4000 U UV-visible spectrophotometer at 610 nm for both dyes. The sorbed amounts of the dyes were determined from the difference between the initial and final concentrations by the following mass balance equation, $q_e = (C_i - C_e)V/w$, where $q_e$ is the amount (mg g⁻¹) of dye sorbed, $C_i$ and $C_e$ are the initial and equilibrium dye concentrations (mg L⁻¹) in solution, respectively, $V$ is the adsorbate volume (L) and $w$ is the sorbent weight (g). All experiments described below were undertaken in either duplicate or triplicate.

The removal of IC and EB by QTEAS was investigated in batch experiments by stirring 50 mg of material with 50 mL of dye solution in 200 mL stoppered glass bottles at 25°C for 3 and 6 h for IC and EB, respectively. Each isotherm consisted of 10 dye concentrations varying from 50 to 500 mg L⁻¹. The equilibrium concentrations of different combinations were measured by the spectrophotometer and referenced with the calibration curves. The kinetic measurements were carried out using similar equipment and conditions. The sample mass was 50 mg, and the volume of the dye solution was 50 mL (50 mg L⁻¹) in this series of tests. The mixtures were stirred at predetermined intervals of time, and were drawn for dye concentration analysis. Experiments with each dye were performed to determine the effect of pH on dye removal. The pH range studied was from 2 to 10. The sample mass was 50 mg, and the dye concentration was 50 mg L⁻¹ (50 mL) in this series of tests. The influence of temperature on the removal process was studied at three different temperatures (25, 35, and 45°C) with QTEAS suspensions in IC and EB solutions (50 mg L⁻¹). The suspensions were stirred during 3 h and 6 h for IC and EB, respectively, and then the dye concentration was analyzed.

**Desorption and reusability**

To assess the feasibility for consecutive reuse of QTEAS, sorption–desorption studies of IC and EB on the hyperbranched polymer were carried out at room temperature using 50 mg of material and 50 mL of dye solution at a concentration of 50 mg L⁻¹. Initially, the sorbent material was loaded with the dye following the general sorption procedure described above. The recovered material was washed with distilled water, air dried, and then suspended in 50 mL of aqueous NaOH solution (0.1 M) for desorption of the dye. The obtained suspensions were stirred for 15 min, then centrifuged and the regenerated material was thoroughly washed with distilled water and subsequently suspended in dye solutions under the same conditions as above. The sorption–desorption cycles were repeated three times.

**RESULTS AND DISCUSSION**

**Characterization of QTEAS**

The prepared hyperbranched polymer is absolutely insoluble in a wide range of solvents including high boiling polar...
Aprotic solvents such as DMF and DMAc. Owing to experimental difficulty, we were not able to characterize the material by using established methods such as MALDI-TOF mass spectrometry for the determination of the degree of branching, purity, and structural integrity of the polymer. Nevertheless, the morphology of QTEAS was determined by SEM, and Figure 2(a) shows an overview image indicating a globular topology of the prepared material typical of hyperbranched macromolecules with three-dimensional architecture. The average thickness diameter of QTEAS was estimated to be in the range of 300–350 μm. Figure 2(b) and 2(c) show the detailed view of the hyperbranched polymer and reveal that mesoporous spongelike scaffolds could be produced upon efficient polymerization. The detailed image (Figure 2(c)) shows a highly smooth surface with irregularly distributed pores of different sizes and shapes bound together in a three-dimensional network. The random orientation of the pores within the polymer network suggests that growth defects occur due to steric crowding within the branches. The XRD pattern of QTEAS is shown in Figure 3(a). A wide and blunt peak between 15° and 32° and centered at 20.7° in the XRD pattern is an indication of the amorphous nature of QTEAS.

The high degree of polymerization is evidenced by common features present in the FTIR spectrum. As shown in Figure 3(b), the spectrum of the QTEAS hyperbranched polymer features a strong carbonyl–carboxylic absorption band at 1,745 cm⁻¹, stemming from the large number of carbonyl bonds of both esters and carboxylic acid termini groups. The two absorption bands appearing at 2,932 and 2,847 cm⁻¹ are mainly due to the stretching vibration of sp³ carbons of alkyl groups. In addition, the band centered at 3,444 cm⁻¹ is characteristic of the OH stretching band of both the carboxylic acid and alcohol termini groups. The appearance of the absorption bands at 1,160 cm⁻¹ and 1,094 cm⁻¹, assigned for C–O antisymmetric stretching and C–O–C bond stretching, respectively, is an indication of an efficient esterification. Moreover, Figure 3(b) shows two distinguished absorption bands, one appearing at 1,462 cm⁻¹ assigned to the sp³ C–H of methylene substituent of quaternary amine groups and a shoulder around 1,523 cm⁻¹, belonging to the C–N⁺ groups (Colthup et al. 1990). Finally, the band centered at 1,642 cm⁻¹ in the spectrum could be assigned to a symmetric deformation of quaternary ammonium, which proves the successful quaternization of tertiary amine groups of the hyperbranched polymer (Jin et al. 2010).

To obtain more structural information, the QTEAS hyperbranched polymer was subjected to solid state CP-MAS ¹³C NMR. The spectrum (Figure 4(a)) is well resolved and shows a sharp intense signal at 173.7 ppm which is consistent with carbon atoms of carbonyl C=O (ester and carboxylic acid) groups. The efficiency of the polymerization reaction is also confirmed by the appearance of two broad signals of low intensities assigned around 59.9 ppm and 50.4 ppm, characteristic of ethylene groups of triethanolamine and methyl groups of quaternary ammonium salt moieties, respectively. Lastly, the strong overlapped signal centered at 30.7 ppm is attributable to the 8 sp³ carbons of sebacoyl branches. Nevertheless, residual molecules of the solvents entrapped inside the hyperbranched polymer, most likely placed between the inner branches which makes drying unattainable, give rise to a broad signal around 127 ppm in the spectrum.

The thermal stability of the synthesized QTEAS was studied by TGA (Figure 4(b)). The first derivative of the
TG curve is proportional to the rate of decomposition, and represents the temperature corresponding to the maximum rate of weight loss \(T_{\text{max}}\). As shown in Figure 4(b), the mass loss occurs in multiple steps within the temperature range of 78–426 °C. The initial decomposition temperature \(T_{\text{D1}}\) is approximately 158 °C. Upon initial heating, the gradual loss of mass (1.71%) proceeded with a \(T_{\text{D}}\) of 78 °C, which is probably due to the loss of physically adsorbed water and/or residual solvent entrapped in the polymer network from the reaction workup. This was followed by two major mass losses at 178.5 °C and 310.5 °C corresponding to the degradation of the alcohol/carboxylic acids termini, which are subject to rapid thermal degradation and ester bond breaking in the branches of QTEAS, respectively. Further heating above 300 °C resulted in extensive chain scission and QTEAS decomposition, with a mass loss of about 73% at 455 °C. The TGA data indicate that 13% of the total weight of the sample remains after heating to the highest temperature (800 °C).

**Effect of contact time**

Figure 5(a) shows the effect of contact time on the removal of dyes by QTEAS. For an initial dye concentration of 50 mg L\(^{-1}\), the results revealed that the removal process is rather faster for IC than for EB. Thus, a quite fast sorption of IC occurs during the first hour of the process so that the maximum dye, up to 83%, is sequestered from the solution vs. 59% for EB, for which the process is marked by a slower stage as the sorbed amount of dye reaches equilibrium. Then, the sorption rate continues to increase at a relatively slow speed with contact time until total removal of the dyes was reached. This was accomplished approximately after 3 h and 6 h for IC and EB, respectively. Similar behavior has been observed for the sorption of C.I.
Direct Blue 86 and C.I. Direct Red 23 onto multiwalled carbon nanotubes modified by a poly(propylene imine) dendrimer (Eskandarian et al. 2014). The authors have found that the removal of direct dyes by the dendritic material is rapid during the initial period of time, followed by a slowdown, then becomes stagnant as contact time increases. The dye molecules are encapsulated by the dendritic material via surface exchange reactions (encapsulation mechanism) until the surface functional sites are fully occupied (Froehling 2000; Yiyun & Jiepin 2005; Mahmoodi et al. 2010). Accordingly, the presence of abundant readily accessible sorption sites at each branching point of the hyperbranched material suggests that the removal process is very likely driven by strong ionic interactions between the positively charged quaternary amine groups on the surface of the QTEAS material and anionic dyes in solution.

In order to examine the controlling mechanism of the sorption process, pseudo-first order model and pseudo-second order kinetic models were used to analyze the experimental data.

The pseudo-first order model can be expressed in its linear form by Equation (1):

$$\log (q_e - q_t) = \log q_e - k_1 t$$

(1)

The pseudo-second order model can be expressed in its linear form by Equation (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(2)

where $k_1$ (min$^{-1}$), $k_2$ (g mg$^{-1}$ min$^{-1}$) are the rate constants of the pseudo-first order and the pseudo-second order for the sorption process, respectively, $q_e$ and $q_t$ (mg g$^{-1}$) are the amounts of dye sorbed at equilibrium and at time $t$ (min), respectively.

Figure 5(b) and Figure 5(b) inset show the linear fit plots of the pseudo-first order and pseudo-second order models, respectively. The equilibrium sorption capacity ($q_e$), the rate constants ($k_1$, $k_2$), and the coefficient ($R^2$) values were calculated from the linear plots. The parameters obtained for the two models are presented in Table 2. Perfect correlation is however observed between experimental data and the pseudo-second order kinetic model with excellent correlation coefficients. Additionally, the calculated $q_e$ values from the model were totally in agreement with experimental sorption capacities, emphasizing therefore the efficiency of the model. In the literature, many studies have shown that

<table>
<thead>
<tr>
<th>Dye</th>
<th>$q_e, exp$ (mg g$^{-1}$)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$q_{e,cal}$ (mg g$^{-1}$)</th>
<th>$k_2$ (g mg$^{-1}$ min$^{-1}$)</th>
<th>$q_{e,cal}$ (mg g$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC</td>
<td>49.92</td>
<td>0.025</td>
<td>30.48</td>
<td>0.884</td>
<td>4.03</td>
<td>50.15</td>
</tr>
<tr>
<td>EB</td>
<td>49.67</td>
<td>0.011</td>
<td>32.77</td>
<td>0.941</td>
<td>8.93</td>
<td>50.65</td>
</tr>
</tbody>
</table>

Table 2 | Kinetics constants for IC and EB dyes’ sorption onto QTEAS.
adsorption kinetics of numerous dyes onto various polymer-based adsorbents are well fitted by the pseudo-second order model. For example, Renault et al. (2008) have found that the pseudo-second order was the best model for describing the adsorption kinetics of AB 25 dye on cross-linked starch ion-exchanger.

**Effect of pH**

The pH of the solution is a key factor when evaluating the removal efficiency of dyes on pH variation. The influence of pH was examined at target pH values set between 2 and 10 for preventing alteration of the ionic character and aggregation state of the anionic dyes and alkaline hydrolysis of the QTEAS polyester. Figure 6(a) shows the effect of solution pH on IC and EB removal by the QTEAS hyperbranched material at room temperature. First of all, it is noteworthy to point out that the pH of the solution has practically no effect on the amount of dyes sorbed onto QTEAS. Indeed, within the wide pH range (from pH 2 to 10) of dye solutions, sorption efficiencies of IC and EB onto QTEAS are actually steady and removal percentages are higher than 98% within the whole pH range. Similar results have been already reported by Greluk & Hubicki (2011) for the sorption of Acid Orange 7 by strongly basic quaternary ammonium resins. QTEAS adsorbent with a high number of charge sites at any pH showed high performance in IC and EB uptake in the whole pH range suggesting the ion-exchange mechanism. However, analysis of the literature data show that the predominant adsorption mechanism during adsorption of the organic anions by strongly basic quaternary ammonium resins is not only ion-exchange, but other cooperative adsorption mechanisms occur besides the predominant ion-exchange which take place through hydrogen bonding and hydrophobic interactions (Wawrzkiewicz & Hubicki 2009a, 2009b, 2009c).

Although the surface of the QTEAS adsorbent is tidy, with positively charged quaternary ammonium groups which make it a powerful reactant toward anionic dyes, the presence of alcohol/carboxylic acid termini groups within the polymer could however participate in the removal process via covalent, coulombic, hydrogen bonding or weak van der Waals forces with the dyes’ functional groups (−OH, −NH₂, −SO₂Na, −N=). To shed light on the adsorption mechanism of the anionic dyes on the QTEAS material, a selective adsorption experiment was carried out using a mixture of cationic and anionic dyes in aqueous solutions. Figure 6(b) (photo in the left corner) shows that preliminary tests revealed that QTEAS was not able to remove the cationic dye Rhodamine B (RhB) at a concentration of 50 mg L⁻¹ from aqueous solutions after 16 h of contact time. Figure 6(b) shows also the UV-vis spectra of aqueous solutions of RhB/IC (3/2) (cationic dye RhB (100 mg L⁻¹); anionic dye IC (100 mg L⁻¹)) mixture before and after the adsorption process. As shown in Figure 6(b), after 16 h of contact time, IC was almost completely removed from the mixture solution by the QTEAS adsorbent, whereas RhB remained intact in the solution. These results suggest that the removal process of anionic dyes by QTEAS could be an ion-exchange mechanism and also
confirm that the QTEAS adsorbent has a selective adsorption property for anionic dyes and could have potential for application in purification of cationic dyes from anionic dyes.

Sorption isotherms

The sorption isotherms of anionic dyes IC and EB onto QTEAS are reported in Figure 7(a). The isotherms are superimposed and characterized by a regular shape with a steep initial slope, and are concave to the concentration axis. The great affinity of QTEAS material for the dyes is suggested by the quantitative removal at low dye concentrations. The adsorption of IC and EB onto QTEAS increases with increasing initial dye concentration to reach equilibrium.

The experimental data were analyzed by using Langmuir and Freundlich isotherm models.

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}}b}
\]

(3)

The Freundlich isotherm equation can be written in the linear form as given below:

\[
\log q_e = \frac{1}{n} \log C_e + \log K_F
\]

(4)

where \(q_e\) (mg g\(^{-1}\)) is the amount of dye adsorbed per gram of sorbent, \(q_{\text{max}}\) (mg g\(^{-1}\)) is the maximum sorption capacity per gram of adsorbent, \(C_e\) (mg L\(^{-1}\)) is the equilibrium concentration of dye in solution, and \(b\) (L mg\(^{-1}\)) is the Langmuir constant related to the energy of adsorption, \(K_F\) (L g\(^{-1}\)) is the relative adsorption capacity constant of the adsorbent and \(1/n\) is the intensity of the adsorption constant.

As shown in Figure 7(b), the analysis of the equilibrium experimental data of IC and EB sorption onto QTEAS by utilizing the Freundlich and Langmuir isotherm equations gave linear plots. The linearized forms of both Freundlich and Langmuir isotherms were found to be linear over a broad concentration range with good to excellent correlation coefficient values (see Table 3). These results clearly indicate that both models adequately fitted the experimental data of the dyes’ removal by QTEAS material.

As shown in Table 3, both dyes are removed with the same order of magnitude by the hyperbranched polymer. The greater affinity of QTEAS sorbent for both dyes IC and EB is confirmed by the sorption capacities at saturation of the monolayer. Despite its extended molecular structure, EB is sorbed onto QTEAS with quite similar effectiveness (0.891 meq g\(^{-1}\) for EB vs. 0.914 meq g\(^{-1}\) for IC). These results suggest that EB has greater access to the surface of QTEAS without inducing a

<table>
<thead>
<tr>
<th>Dye</th>
<th>(q_{\text{max}}) (mg g(^{-1}))</th>
<th>(b) (L mg(^{-1}))</th>
<th>(R^2)</th>
<th>(K_F) (L g(^{-1}))</th>
<th>(1/n)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC</td>
<td>213.22</td>
<td>0.42</td>
<td>0.999</td>
<td>146.05</td>
<td>0.07</td>
<td>0.911</td>
</tr>
<tr>
<td>EB</td>
<td>214.13</td>
<td>0.32</td>
<td>0.999</td>
<td>121.88</td>
<td>0.11</td>
<td>0.947</td>
</tr>
</tbody>
</table>

Table 3 | Langmuir and Freundlich isotherm constants for the sorption of IC and EB dyes onto QTEAS dendritic polymer

Figure 7 | Sorption isotherm for IC and EB dyes onto QTEAS (a) and Freundlich and Langmuir (inset) plots for IC and EB dyes’ removal by QTEAS (b).
quick saturation of sorption sites because of steric hindrance and clearly show that the dyes’ removal is closely linked to the total charge on the surface of the dyes’ molecules. Nonetheless, the highest $b$ value found for IC dye (0.42 vs. 0.32 for EB) indicates that QTEAS shows a little preference on binding divalent anion IC than the tetravalent anion EB. Finally, these results also confirm the presence of readily accessible sorption sites and strongly suggest the homogeneous distribution of active quaternary ammonium groups on the surface of the hyperbranched polymer. The QTEAS hyperbranched polymer showed better sorption capacities for IC and EB dyes compared to those of other adsorbents reported in the literature for the removal of these dyes (see Table 4).

**Thermodynamic parameters**

The removal of IC and EB by the QTEAS sorbent was studied at three temperatures to determine the thermodynamic parameters, and the results are summarized in Table 5. The dyes’ uptake decreased with an increase in temperature, indicating an exothermic process.

The thermodynamic parameters $\Delta G$, $\Delta H$, and $\Delta S$ were calculated by using the following equation (Zhu et al. 2010):

$$\log K_L = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} = \frac{\Delta H}{RT}$$  \hspace{1cm} (5)

where $T$ is the temperature (K), $R$ is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and $K_L$ is the Langmuir equilibrium constant (L mg$^{-1}$).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>$q_{\text{max}}$ (mg g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion-exchanger (Lewatit MonoPlus M-600)</td>
<td>IC</td>
<td>43.6</td>
<td>Wawrzkiewicz &amp; Hubicki (2009d)</td>
</tr>
<tr>
<td>Carbonaceous material</td>
<td>IC</td>
<td>92.83</td>
<td>Gutiérrez-Segura et al. (2009)</td>
</tr>
<tr>
<td>Pyrolyzed sewage sludge</td>
<td>IC</td>
<td>30.82</td>
<td>Otero et al. (2003)</td>
</tr>
<tr>
<td>QTEAS</td>
<td>IC</td>
<td>213.22</td>
<td>This study</td>
</tr>
<tr>
<td>QTEAS</td>
<td>EB</td>
<td>214.13</td>
<td>This study</td>
</tr>
<tr>
<td>Commercial activated carbon (PAC)</td>
<td>EB</td>
<td>135.2</td>
<td>Prola et al. (2013)</td>
</tr>
<tr>
<td>Natural bentonite</td>
<td>EB</td>
<td>160.45</td>
<td>Chandra et al. (2013)</td>
</tr>
<tr>
<td>Mg-Al-CO3 LDH</td>
<td>EB</td>
<td>107.5</td>
<td>Bouraada et al. (2014)</td>
</tr>
</tbody>
</table>

**Table 5 | Thermodynamic parameters for IC and EB removal by QTEAS**

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
</table>

The vant’Hoff plot of $\log K_L$ versus $1/T$ gave straight lines. The calculated slope and intercept from the plot were used to determine $\Delta H$ and $\Delta S$, respectively (Table 5). The negative value of $\Delta G$ ($-51.75$ to $-26.11$ kJ mol$^{-1}$) at each temperature implies a favorable and spontaneous adsorption process and confirms the affinity of the QTEAS material for IC and EB dyes. In general, the change in free energy for physisorption is between $-20$ and $0$ kJ mol$^{-1}$, whereas chemisorption is in the range of $-80$ to $400$ kJ mol$^{-1}$ (Renault et al. 2008; Abdel Salam et al. 2012; Eskandarian et al. 2014). These values are in the intervals between physisorption and chemisorption, thus suggesting that the process is a physical adsorption enhanced by a chemical effect (Renault et al. 2008). The negative value of $\Delta H$ indicates that the adsorption is exothermic and also suggests that the sorption process is a physical adsorption enhanced by chemical interactions between the anionic dyes and the quaternary amine groups through ion-exchange.

**Influence of ionic strength on IC and EB adsorption process on QTEAS**

Textile wastewaters usually contain inorganic salts to improve the dying process and to promote the transfer of dye to fabrics (Arslan et al. 2000). The use of salts can alter the properties of the adsorbent surface charge and adsorbate such as its solubility, ionic nature, which ultimately affects the adsorption process by either increasing or decreasing the adsorption capacity (Arafat et al. 1999; Bautista-Toledo et al. 2008). Figure 8 shows the influence of NaCl concentration varying from 0.1 to 1 mol L$^{-1}$ on the removal efficiency of IC and EB dye solutions of 50 mg L$^{-1}$ using the hyperbranched QTEAS polymer. As shown in Figure 8, both dyes are quantitatively removed from solutions (R > 95%) even when the NaCl concentration is up to 1 mol L$^{-1}$. The results showed that IC and
EB adsorption on the hyperbranched QTEAS polymer were not affected by the presence of NaCl in the whole range of the salt concentration. Similar results have been reported by Karcher et al. (2001, 2002) on the effect of the presence of inorganic salts on the adsorption of the reactive dyes on anion-exchanger resins.

Desorption and reusability

The desorption studies contribute to elucidating the nature of the adsorption process and allow the recovery of the dyes as well as the regeneration of the adsorbent to make the treatment process economical. The QTEAS hyperbranched material can be readily regenerated with a 0.1M NaOH aqueous solution. Therefore, quantitative desorption rates were achieved for both dyes over three repeated sorption–desorption cycles. IC and EB dyes were instantly released as soon as the dye-loaded sorbent made contact with the alkaline solution. This was illustrated by instantaneous coloration of the solution. Nonetheless, the sorbent material was left in contact with the alkaline solution for 15 min of contact time, a period considered as sufficient for the dyes' desorption to be achieved, and on the other hand to prevent alkaline hydrolysis of the hyperbranched polymer. As shown in Figure 9, the third repeated use of QTEAS material for the removal of IC and EB dyes showed neither signs of deterioration nor any decrease in its capacity for the dyes' sorption. Finally, the high performance of the QTEAS ion-exchanger indicates that its reusability is quite feasible.

CONCLUSIONS

In the present study, the sorption of two acid dyes onto QTEAS hyperbranched polymer was investigated. The results demonstrated that the hyperbranched polymer performs efficiently in a wide pH range of dye solutions. From the kinetic studies, it was found that the sorption process followed the pseudo-second order model. The sorption isotherms were adequately fitted by the Langmuir isotherm model and the removal process was found to take place by the electrostatic attraction between the positively charged hyperbranched polymer and the negatively charged dyes. Nevertheless, the ionic strength does not affect the dyes' removal efficiency by the hyperbranched polymer. Moreover, the removal capacity is closely connected to the total sulfonate groups on the surface of the dyes. The calculated thermodynamic parameters indicated the exothermic and spontaneous nature of the removal process. Finally, the third repeated use of QTEAS material for the dyes' removal showed no decrease of its capacity for the dyes' sorption.
The overall results illustrated that QTEAS can be effectively used as an ion-exchanger for the removal of acid dyes from colored wastewaters.

REFERENCES


