

Stipa Tenacissima L Cationized Fibers as Adsorbent of Anionic Dyes

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ABSTRACT: The extraction of *Stipa tenacissima* L Alfa fibers was performed using alkaline procedure to remove noncellulosic substances such as pectin, lignin, and hemicellulose. The degree of polymerization of extracted and purified Alfa fibers was determined using viscosimetric method and extracted fibers were used as a cationic ion-exchange material by treating alkali-cellulose of Alfa with EpoxyPropylTriMethylAmmonium Chloride (EPTMAC). Evidence of grafting was monitored using IR spectroscopy and thermogravimetry analysis. Two EPTMAC-Alfa fibers with different %N were prepared and tested as adsorbent of four acid dyes: Acid Blue 25 (AB 25), Acid Yellow 99 (AY 99), Reactive Yellow 23 (RY 23), and Acid

Blue 74 (AB 74). The modeling of the adsorption isotherms using Langmuir, Freundlich, and Jossens allowed the determination of isotherm constants leading to characterize the different adsorbent/adsorbate systems prepared. Thermodynamic parameters such as change in free energy (ΔG), the enthalpy (ΔH), and the entropy (ΔS) were also evaluated. Additionally, regeneration of adsorbent solid supports by desorption process in fixed bed column was reported. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3148–3161, 2010

Key words: adsorption; biopolymers; dyes/pigments; ion exchangers; modeling

INTRODUCTION

Large textile industries have developed in several countries. This can lead to significant problems in discharging aqueous wastes. Decolorization of waste water took into consideration unconventional methods and systems that have been extensively investigated and a number of studies were reported.^{1–12} Much of our research into the chemical modifications and applications of natural and synthetic polymers have demonstrated that cationized cotton, wood, maize-cob flour, and nylon fibers can be used as efficient adsorbents for acid dyes and developed adsorption process produce high-quality treated effluents.^{4–7} Our focus bears on the testing of various low-cost supports for the uptake of pollutants from textile waste water. Alfa is a plant belonging to the genus *Stipa tenacissima* L family. It is a Mediterranean plant which grows in arid and semiarid regions. It is usually used for the production of paper and biodegradable composites as reinforcement.¹³ Alfa like all plants has three principal chemical constituents, namely cellulose, hemicellulose, and lignin. The extraction of fibers from Alfa involves re-

moval of noncellulosic substances which can be assured by chemical procedures including acid or alkaline processes.¹⁴ The fibers extracted could be used as an effective ion-exchange material for application in waste water treatment through simple chemical modification. The main objectives of this work are as follows: (i) to extract Alfa fibers from *Stipa tenacissima* L plant and its modification with EPTMAC (ii) to examine its capacity for the uptake of acid dyes (iii) to fit the adsorption isotherms of the four selected dyes onto cationized Alfa fibers using Langmuir, Freundlich, and Jossens models (iiii) to evaluate the thermodynamic parameters influencing the adsorption of dyes onto cationized Alfa fibers. The regeneration of the adsorbent was also investigated.

EXPERIMENTAL

Materials

All reagents [dimethylformamide (DMF), tri-*n*-ethylamine (TEA), and EPTMAC] were supplied by Aldrich (Sigma-Aldrich Chimie Sarl, Saint-Quentin Fallavier, France) and used without further purification for the cationization of Alfa fibers. The acid dyes listed in the adsorption experiments were Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74 (referred to as AB 25, AY 99, RY 23,

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and AB 74, respectively). They were used in the form of commercial salts. Their characteristics and molecular structures are given in Table I and Figure 1, respectively.

Extraction of cellulose fibers from *Stipa tenacissima* L

Cellulosic fibers were extracted from Alfa plant using a chemical process carried out by the method developed in our laboratory in two steps as was described previously.¹⁵ The first step was the peroxide bleaching: in a round-bottomed flask, were placed 5 g of fresh Alfa, which were harvested from Tunisian Middle West fields, 200 mL of distilled water, and 10 mL of H₂O₂ [30% (W/W)]. The mixture is stirred for more than 6 h at 90°C. At the end of the reaction, the bleached Alfa was filtered using a 0.45 μm membrane filter, washed thoroughly with hot and cold water, and then dried at room temperature.

The second step involved the extraction of cellulosic Alfa fibers. Different experiments were investigated for this aim and only alkaline boiling process using sodium hydroxide was reported. Indeed, sodium hydroxide has an important role in removing lignin due to the alkaline cleavage of ether linkages in the lignin, which may be accompanied by a condensation reaction.¹⁶ Klemm et al.¹⁷ have shown that for low concentrations of sodium hydroxide, a so-called monomolecular water is formed in the solution system. This water paves the way for the penetration of the ion dipole of sodium hydroxide, which increases with alkaline concentration. The depth of this penetration expands at high-sodium hydroxide concentrations. Meanwhile, high temperature can provide the ions with high-penetration energy. In this way, sodium hydroxide can attack both pectin and lignin due to the contact between them. As a result, pectin is completely attacked without any residue after alkaline boiling. Residual lignin and other impurities decrease with increasing sodium hydroxide concentration and treatment time.¹⁴

For the alkaline boiling process, the temperature of extraction and the concentration of NaOH solution were fixed, respectively, at 50°C and 0.25M for a period of 4 h. Afterward, the extracted fibers were washed until neutral pH of washing water and were subjected to soxhlet extraction with acetone for 24 h

to remove the organic products that were not eliminated during the alkaline treatment. Finally, Alfa fibers were dried at room temperature until reaching a constant weight.

Yield of extraction

The efficiency of extraction represents the variation of the sample weight before and after extraction:

$$\%R = 100 \times \frac{m_f}{m_a} \quad (1)$$

where m_a and m_f are the weights of dried Alfa before and after extraction, respectively.

For the experimental conditions adopted in this study, the value of R was 32.5% which can be considered acceptable compared with other studied extraction methods.¹⁸

Degree of polymerization \overline{DP}_V

The degree of polymerization was determined using a viscosimetric method after dissolving the cellulose Alfa fibers in a dilute solution of cupriethylenediamine hydroxide according to the French standard [NF T12-005].¹⁹ The viscosity was determined with an Ubbelohde viscosimeter® (AVS 410). The method involved the measuring of the specific viscosity (η_{spec}). If η_0 represents the absolute viscosity of a solvent and η the viscosity of a polymer solution, the specific viscosity is calculated as follows:

$$\eta_{\text{spec}} = \frac{\eta}{\eta_0} - 1 \quad (2)$$

$$\text{or } \eta_{\text{spec}} = \frac{t - t_0}{t_0} \quad (3)$$

where t_0 is the efflux time of pure cupriethylenediamine solution and t is the efflux time of Alfa solution.

The intrinsic viscosity of a polymer is related to the molecular mass by the Mark-Houwink-Sakurada equation:

$$\eta = K \overline{DP}_V^a \quad (4)$$

where K is a constant depending on the solvent at a given temperature and a is the value that describes

TABLE I
Characteristics of Dyes

Dyes	Number of anionic groups	Supplier	λ_{max} (nm)	Purity (%)	Molecular weight (g/mol)
Acid Blue 25 (AB 25)	1	Aldrich	600	45	416.39
Acid Yellow 99 (AY 99)	1	Aldrich	445	45	496.35
Acid Blue 74 (AB 74)	2	Aldrich	608	98	466.36
Reactive Yellow 23 (RY 23)	3	Hoechst	430	90	665.00



Figure 1 Chemical structures of the selected dyes.

the flexibility of the molecules.²⁰ In this study, the Polymer/Solvent system corresponds to Cellulose/Cupriethylenediamine and according to the French standard [NF T12-005],¹⁴ the value of \overline{DP}_V is calculated according to the following eq. (5):

$$\overline{DP}_V = \frac{\eta}{7.5 \times 10^{-3}} \quad (5)$$

The specific viscosity (η_{spec}), the intrinsic viscosity (η), and the viscosity average (\overline{DP}_V) of Alfa and cotton fibers (taken as a reference) are given in Table II. As can be shown, the degree of polymerization of Alfa fibers can be considered low when compared with the cotton one. In fact, extraction and purification procedures used to obtain cellulose from Alfa degraded the biopolymer and decreased the \overline{DP}_V value.²¹

Cationization of Alfa fibers and characterization

The EPTMAC-Alfa is prepared in two steps as shown in Figure 2. The first step was the preparation of sodium-treated Alfa (NaOH-Alfa). Purified Alfa is treated with an aqueous solution of sodium hydroxide (5N) at room temperature for 12 h, followed by washing, neutralization with 1% acetic acid, washing again, and drying in air at room temperature for 2 days. The second step is carried out as follows: In a 500-mL three-necked flask fitted with a dropping funnel, a mechanical stirrer unit, and reflux condenser are placed 200 mL of DMF, 3 mL of TEA, and 10 g of NaOH-Alfa. The mixture is heated in an oil bath at 90°C for 1 h, and then 10 mL of EPTMAC is added dropwise, while stirring and maintaining the temperature at 90°C. When the addition was complete (after about 30 min), the temperature is increased to 120°C. After the desired reaction time, the sample is removed and washed thoroughly with a mixture of ethanol and methanol (50/50 v/v), then with acidified water (1% v/v HCl), and, finally, rinsed with distilled water and dried. The sample was then subjected to a repeated Soxhlet extraction with ethanol to remove the unreacted EPTMAC and dried at 40°C under vacuum for about 72 h until a constant weight is

TABLE II
The Specific Viscosity (η_{spec}), Intrinsic Viscosity (η), and Degree of Polymerization (\overline{DP}_V) of Cotton and Fibers Extracted from *Stipa Tenacissima* L

Sample	η_{spec}	η	\overline{DP}_V
Alfa fibers	0.66	5.6	746
Cotton fibers	2.31	16.31	2174

obtained. Two samples of EPTMAC-Alfa (I-II) are prepared, with differing %N content depending on the reaction time. For this nitrogen content correspond a number of adsorption sites per gram of support named capacity of adsorption and noted C_a (mmol/g) obtained from the following relation:

$$C_a = \frac{(\%N)}{M_N} \frac{1}{100} \times 10^3 \text{ mmol/g} \quad (6)$$

where, %N is the nitrogen content in the cationized sample and M_N is the molecular weight of nitrogen. The percentage of nitrogen content was determined according to Cole and Parks modification of the semimicro Kjeldahl method.²² The degree of grafting (%G) is calculated from the weight uptake percentage as previously defined.⁴

The FTIR spectra of the tested fibers were evaluated in this study and were recorded using Nicolet® 510M Infrared Fourier Spectrophotometer in the wave number of 500–4000 cm^{-1} .

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were also investigated. All analyses reported were run under a dynamic air (dried) atmosphere flowing at 100 mL/min and at a scanning rate of 10°C/min. The samples were cut to 1–2 mm length and 4 ± 0.5 mg was taken for each analysis. Each sample was heated from 25 to 600°C using a SETARAM® derivatograph.

Dye adsorption

For the adsorption isotherms determination 0.1 g of EPTMAC-Alfa fibers and 100 mL dye solution of the initial concentration C_0 are stirred mechanically in an Ahiba Nuance® laboratory machine for 2 h at the desired temperature. It was verified that this time is sufficient for the equilibration of the different heterogeneous systems. The effect of pH was studied and it was found that the maximum adsorption

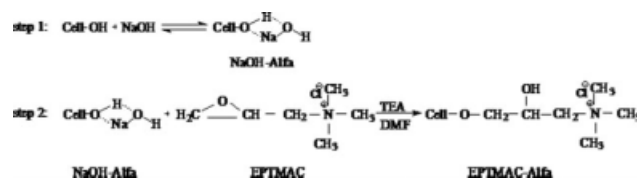


Figure 2 Preparation of EPTMAC-Alfa.

capacities of the selected dyes were obtained at pH 7. Indeed, at lower pH values, the high hydrogen ion concentration neutralizes the anionic sulfonate groups of the tested dyes and prevents their approach to cationized sites grafted onto Alfa fibers. Therefore, lower adsorption capacities were observed at lower pH values. On the other hand, at higher pH values, the abundance of OH⁻ ions diminish the electrostatic interaction between negatively charged dye anions and positively charged adsorption sites causing a significant reduce of the amount of dye removal.

The mixture was then filtered through a 0.45 μm membrane filter at the fixed temperature of adsorption process. After return to the room temperature, the concentration of the dye remaining in the solution is measured using a JANWAY[®] 6100 spectrophotometer at the maximum wavelength (λ_{\max}) of the absorbance. The amount of adsorbed dye, Y_e (mg/g), was calculated as follows:

$$Y_e = \frac{(C_0 - C_e) \times V}{W} \quad (7)$$

$$\text{Desorption (\%)} = \frac{\text{Amount of dye desorbed to the desorbed medium}}{\text{Amount of dye adsorbed on the adsorbent} \times \text{Purity of the dye}} \times 100 \quad (8)$$

It is particularly important to consider the degree of purity given by the supplier. Indeed, the electrolyte initially present in dyes, which allows the adjustment of their shade, is not adsorbed by the support.

RESULTS AND DISCUSSIONS

Characterization of the modified Alfa fibers

The nitrogen content was found to increase with increasing reaction time and reached 0.6% value after 6 h as shown in Table III. The original aspect of the grafted Alfa fibers remained unchanged during chemical modification with the exception of the color which became slightly yellowish. The solubility of Alfa fibers is also modified by this chemical treatment: the LiCl-dimethylacetamide system²³ dissolves the nontreated Alfa fibers in a 2-day period at room temperature, where II-EPTMAC-Alfa needs only 1 day. In another test, the nitrogen content reached 0.8%, but unfortunately this highly grafted Alfa fiber becomes soluble in water at room temperature and was thus unsuitable for its application as adsorbent of dyes in aqueous solutions.

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

Desorption studies

The loaded support was prepared as follows: a sample of 1 g of I-EPTMAC-Alfa was immersed in 1 L of aqueous dye solution at a concentration corresponding to the limit value Y_{ref} . When the solution became uncolored, the half of the loaded sample was crammed into a Perspex column of 6 cm height surrounded by a layer of glass wool ensuring a thermal insulation from the outside area. Desorption was monitored by a peristaltic pump at a flow rate of 10 mL/min and was performed in 100 mL of eluent solution. The concentration of recovered dye is then measured using a JANWAY[®] 6100 spectrophotometer at maximum absorption of each dye (Fig. 3). The influence of the temperature on the desorption process was also studied and conducted in the (30–90)°C range. The efficiencies of the desorption was calculated using the following equation:

FTIR spectroscopy studies were carried out to observe the chemical changes occurring on the Alfa surface fibers induced by chemical modification. Figure 4 shows the IR spectra of raw Alfa fibers and II-EPTMAC-Alfa (%N = 0.6). The FTIR traces for II-EPTMAC-Alfa shows the appearance of new peaks. The absorption bands obtained at 1380 and 2810 cm⁻¹ indicate the C–H bending and stretching of methyl groups.²⁴ The signal at 1160 cm⁻¹ is assigned to C–N stretching.²⁴ These peaks confirm the introduction of ammonium groups in the Alfa fibers structure. With these additional peaks, FTIR spectra of treated fibers shows a disappearance of a peak in the range 3650 and 3500 cm⁻¹ and this could be due to the use of OH groups during the first step of modification.²⁴

TABLE III
Nitrogen Content (%N) and Degree of Grafting (%G) of the Different EPTMAC-Alfa Compounds

Samples	Reaction time (min)	%N	%G	
			Found	Calculated ^a
I-EPTMAC-Alfa	120	0.30	3.5	3.27
II-EPTMAC-Alfa	360	0.60	7	6.54

^a Calculation based on %N.

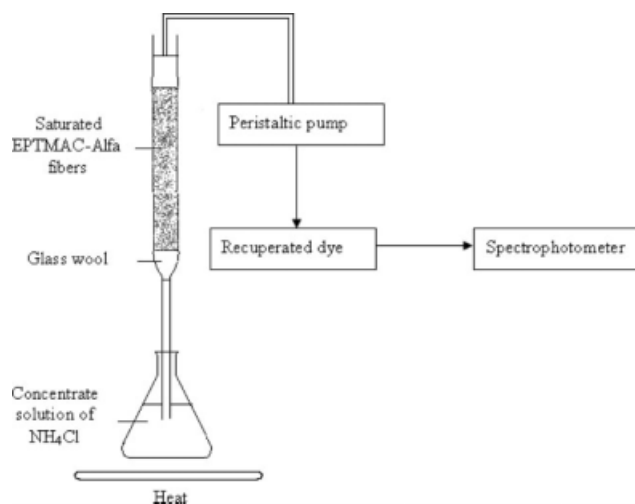


Figure 3 Different steps for the regeneration of EPTMAC-Alfa.

Additional evidence of incorporation of quaternary ammonium groups onto the Alfa fibers structure was obtained from the decomposition behavior in thermogravimetry. Figure 5(a,b) illustrate the dynamic TGA and TA curves of untreated Alfa fibers and II-EPTMAC-Alfa, respectively. They display an endothermic dip with a minimum at 98°C due to moisture evaporation. The loss of mass in this temperature range is practically identical for the two samples indicating an insignificant change in moisture regain. The DTA curve of Alfa, shows an exothermic reaction beginning at about 300°C and ending at 400°C with a maximum at 338°C, and associated with the main pyrolytic reaction of the cellulose. The second large exotherm maximum at 490°C represents oxidation of the charred residues.²⁵ The high-molecular-weight charred residues start burning in air at about 400°C and glowing is complete at 550°C with char yield of 40% as shown in TG [Fig. 5(a)]. The typically DTA thermogram [Fig. 5(b)] of preferential primary substituted cellulose of EPTMC-Alfa shows a small exotherm at 207°C corresponding to the burning of the grafted ammonium groups leading to the formation and evaporation of flammable volatile products.²⁶ The TG curve shows a very small mass loss in this temperature range. The other exotherm in the range 300–400°C due to dehydration, depolymerization, and oxidative decomposition of substituted and unsubstituted portions of the cellulose is interrupted by an endotherm peak at 340°C corresponding to the scission of the grafted propyl moieties from the compound. The TG curve also shows that the rapid loss of mass of the thermal analyzed compound takes place in this temperature range and about 50% mass disappears during this process. The other exotherm beginning at 400°C and ending at 500°C with a peak at 437°C,

associated with the final stage of decomposition and oxidation of the char.^{27,28}

Adsorption of dyes onto EPTMAC-Alfa fibers

As with cotton⁴ and sawdust,⁵ initially untreated Alfa fiber does not adsorb any of the four tested dyes. Indeed, when a cellulosic polymer is immersed in water, it develops a substantial negative charge which consequently gives rise to electrostatic repulsion of anionic dyes.²⁹ The enhancement in dye adsorption can be overcome by modification performed on Alfa fibers. Figure 6 shows curves of Y_e vs. C_e for the adsorption of each four tested dyes onto I-EPTMAC-Alfa (%N = 0.3) at 20°C. A limit value Y_{ref} (mg/g) is observed for each dye and high-adsorption capacities are found: AB 25, AY 99, and RY 23 being adsorbed to a monolayer capacity of 541, 513, and 395 mg (dye)/g (EPTMAC-Alfa fibers), respectively. AB 74 has lower saturation capacities, namely 223 mg/g. Experimental data confirms that EPTMAC-Alfa is an excellent adsorbent for anionic dyes due to the presence of cationic sites grafted in polymer chains. Table IV establishes a comparison between the efficiency of the new cationized support, cationized cotton, and cationized sawdust as dye adsorbents for low %N at 20°C. It appears that I-EPTMAC-Alfa is really more effective than the other supports in this range of %N. The result can be attributed to various factors, including that (i) Alfa fibers have a more complex chemical structure than cotton, and (ii) all hydroxyl groups (alcoholic functions in cellulose and alcoholic-phenolic function in lignin) can undergo the chemical modification in the conditions of treatment.

Many factors which affect the degree of adsorption are as follows: the fraction of colored ions in the

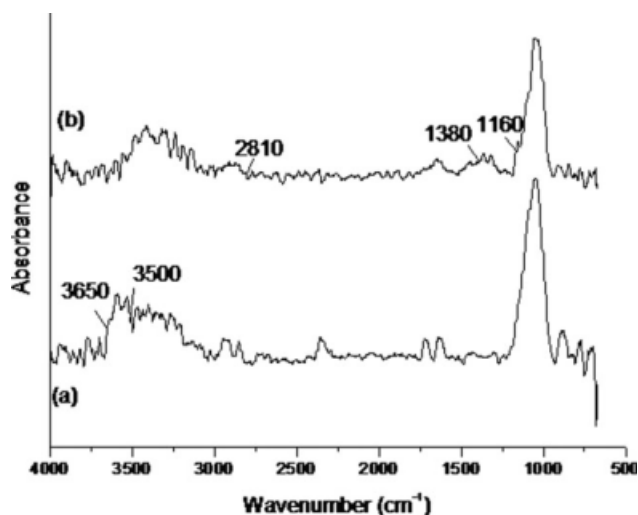


Figure 4 FTIR spectrums of (a) untreated Alfa and (b) II-EPTMAC-Alfa fibers.

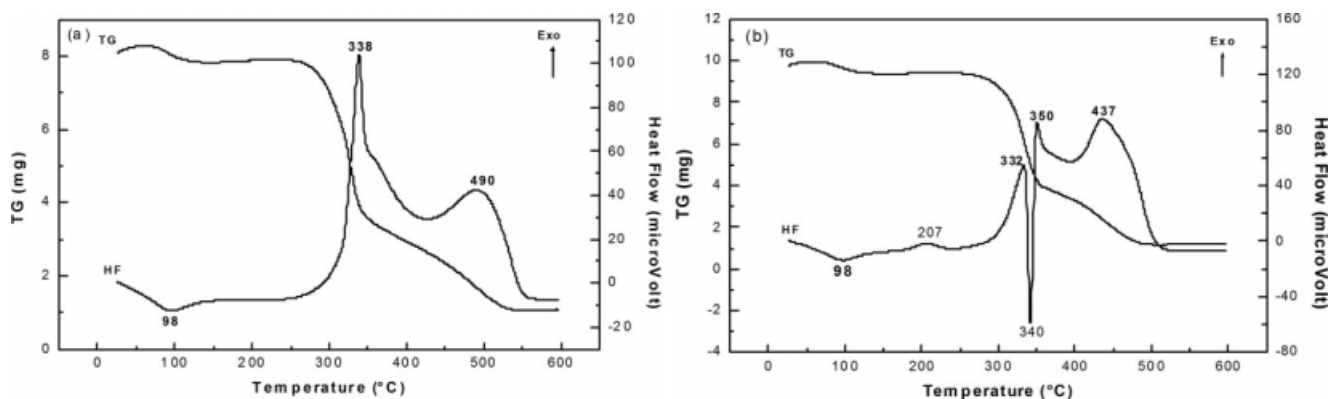


Figure 5 Thermal analyses of (a) untreated Alfa in air and (b) II-EPTMAC-Alfa fibers in air.

commercial salts, the molecular volume of dye and its planarity, the chelating ability of the adsorbent/adsorbate system, and the aggregation ability of the dye. Figure 7 summarizes the interaction modes between the selected dyes and adsorbent. In the case of AB 25 [Fig. 7(a)] because of the strongly aromatic character, these molecules have a great tendency to aggregate by superposition of molecules being placed in parallel. This does not induce an electrostatic repulsion between the two molecules since sulfonate groups ($-\text{SO}_3^-$) are moving away the ones from the others. This phenomenon has been previously observed for the adsorption of AB 25 onto cationized nylon.⁷

For AY 99 [Fig. 7(b)], it appears that the positive charge of the chromium ion incorporated in the molecular structure of the dye exerts an electrostatic repulsion between the adsorbed molecules at the surface of the solid support that reduced the number of occupied functional sites. In the case of RY 23 [Fig. 7(c)], it seems that the presence of anionic groups that does not participate in adsorption process (such as carboxylate groups) induce an electrostatic repulsion between molecules of dyes and diminishes the diffusion of dyes onto cationized EPTMAC-Alfa fibers. In addition to that, the large structure of dye molecule provokes a steric hindrance which makes the approach of a dye molecule to an adsorption site effectively difficult. Finally, for AB 74 [Fig. 7(d)], it seems that the presence of two sulphonate groups diametrically opposed in their chemical structures makes the aggregation increasingly difficult and/or one dye molecule can interact with two grafted cationic sites.⁴

Effect of nitrogen content

Nitrogen content can be considered among the most determinant parameters of adsorption capacity. It is known that the increase in the nitrogen content of the support increases the number of cationic sites present in the EPTMAC-Alfa fibers, which in turn

increases the amount of dye attached to the support at the equilibrium. In this study, it seems that the increase in %N is accompanied by a decrease in the maximum solid-phase dye concentration fixed onto the support at the equilibrium (Y_{ref}). Indeed, it can be shown from Figure 8, which represents adsorption isotherm of AB25 onto I and II-EPTMAC-Alfa at 20°C, that the increment of %N from 0.3 to 0.6% is accompanied by a decrease in the maximum adsorption capacity from 541 mg/g to 519 mg/g. An alternative presentation of these results is given in Table V which establishes a comparison of the effectively maximum solid-phase dye concentrations at the equilibrium (Y) calculated in (mmol/g) and the capacities of the adsorbents C_a . It will be noted that:

First, for I-EPTMAC-Alfa, the ratio Y/C_a for the four tested dyes is higher than 2, indicating that the adsorption phenomenon is not only attributed to the interaction of anionic dyes with grafted cationic sites but also to the diffusion of dye molecules onto the amorphous zones due to the presence of lignin in Alfa fibers as observed for EPTMAC-sawdust 5 and/or to the complex chemical structure of Alfa as it is explained in the previous section.

Second, for II-EPTMAC-Alfa, the ratio Y/C_a is slightly higher than the unity for all the tested dyes,

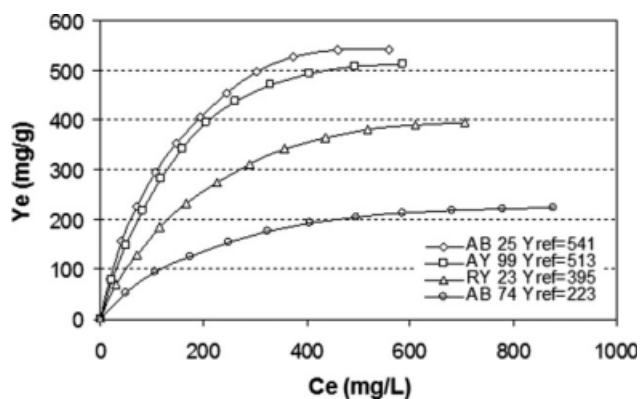


Figure 6 Adsorption of dyes on I-EPTMAC-Alfa (%N = 0.3); temperature = 20°C.

TABLE IV
Comparison Between Cationized Cotton, Cationized Sawdust, and Cationized Alfa as Dye Adsorbents at 20°C

Dye	EPTMAC-cotton (%N = 0.5)		EPTMAC-sawdust (%N = 0.5)		EPTMAC-Alfa (%N = 0.3)	
	Y_{ref} (mg/g)	Q (mg/g)	Y_{ref} (mg/g)	Q (mg/g)	Y_{ref} (mg/g)	Q (mg/g)
AB 25	288	294	412	416	541	714
AY 99	326	333	260	270	513	666
RY 23	174	175	249	256	395	526
AB 74	126	127	103	104	223	277
Reference	4		5		This work	

indicating that adsorption is almost occurred by cationized sites and quantities of diffused dyes onto amorphous zones decreased. This can be attributed to the swelling of cellulosic fibers when %N increases. Diffusion of dyes onto amorphous zones becomes difficult and adsorption is assured by electrostatic interactions. Under these circumstances, I-EPTMAC-Alfa will be considered more efficient than II-EPTMAC-Alfa one.

Effect of temperature

Temperature controls two major aspects of adsorption: the swelling behavior of the adsorbent and the solubility of the adsorbate molecules which affects the rate of its diffusion through the solution to the adsorbent. Figure 9 shows the effect of temperature, ranging from 20 to 80°C, on the extent of the adsorption of AB 25 onto I-EPTMAC-Alfa fibers. As

can be observed, the adsorption capacity decreases with increasing temperature. This is due to the ionic force established between the modified Alfa fibers and the dye, which is destabilized with the increase in temperature. This phenomenon may be due to the exothermic effect of the surrounding during the adsorption process.⁸ Moreover, the increment of the temperature increases the solubility of the acid dyes allowing the formation of stronger interaction forces between the dye molecules and the aqueous solution against those between the dye molecules and the adsorbent which decreases the amount of adsorbed dye onto the EPTMAC-Alfa fibers. Temperature influences in this case the desorption step and consequently the reversibility of the adsorption equilibrium since an elevation of this parameter increases the escaping tendency of selected dyes from the interface of the adsorbent (Fig. 10).

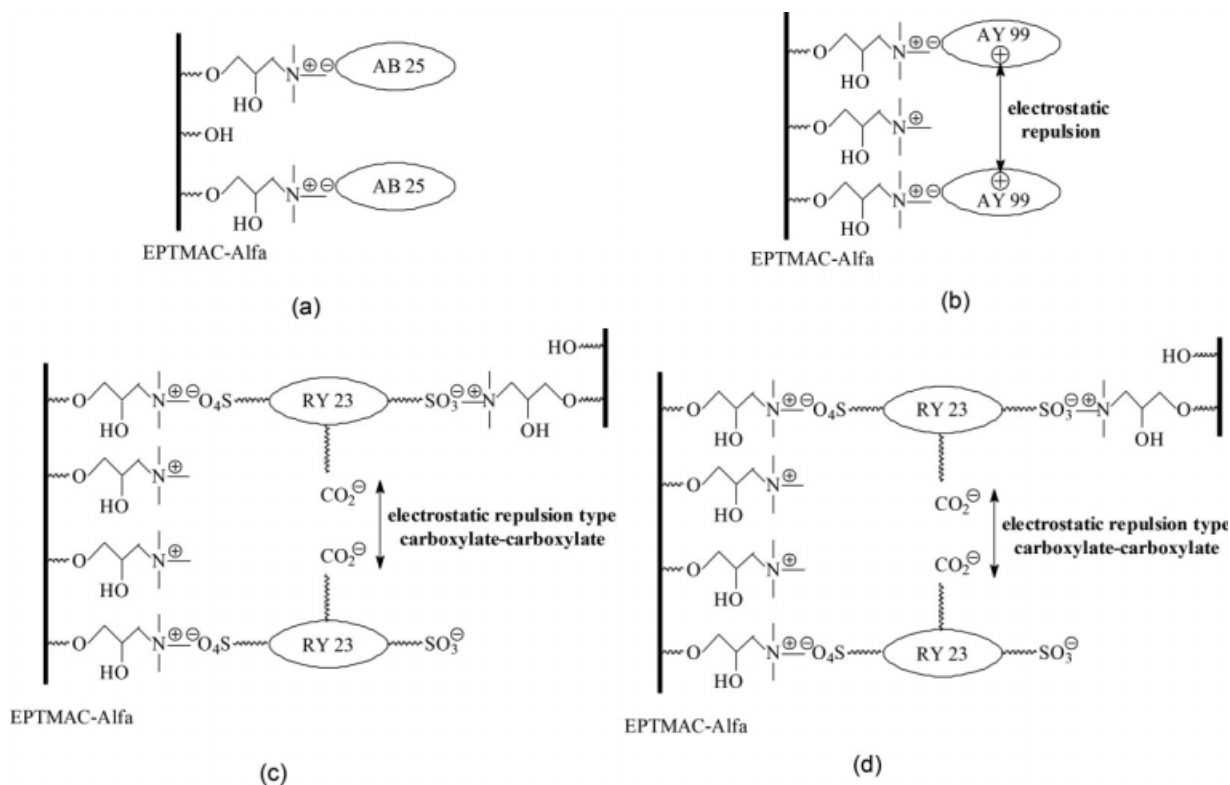


Figure 7 Proposal interaction modes between: (a) AB 25, (b) AY 99, (c) RY 23, (d) AB 74, and the adsorbent.

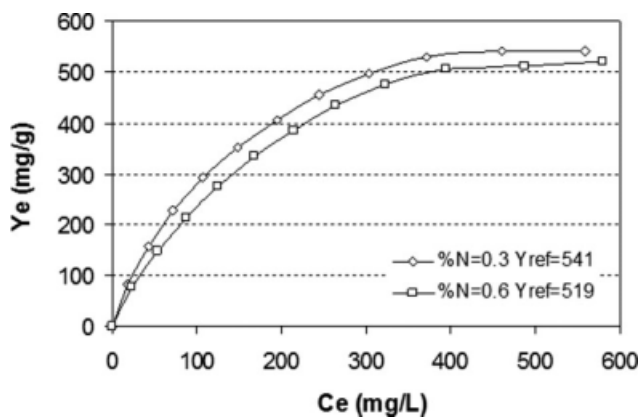


Figure 8 Effect of nitrogen content for the adsorption of AB 25; temperature = 20°C.

Modeling

To examine the mechanism of retention between molecule dye and the support at equilibrium, three theoretical models of adsorption were adopted in this: Langmuir, Freundlich, and Jossens isotherms.

Langmuir model

The Langmuir isotherm model is valid for mono-layer adsorption on specific homogenous sites containing a finite number of identical sites and assumes that all the sorption sites are energetically uniform. The Langmuir equation is represented as follows:

$$Y_e = \frac{QbC_e}{1 + bC_e} \tag{9}$$

where C_e is the liquid-phase concentration of the adsorbate at equilibrium (mg L^{-1}), Y_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), Q is the concentration of adsorbate in the adsorbent corresponding to complete coverage of the available site or the limiting adsorption capacity, and b is the adsorption coefficient. Equation (9) can be written in a linear form to facilitate the fitting of the experimental data for parameters calculation:

$$\frac{C_e}{Y_e} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{10}$$

Values of Q and b were evaluated from slope and intercept of linear plots of C_e/Y_e versus C_e , respectively (Fig. 11). Langmuir isotherms are found to be linear for all adsorbent/adsorbate systems studied, and the correlation coefficients, R^2_{1r} , were all above 0.953 (Table VI). However, as can be seen from Table VI, there is no agreement between the experimental values Y_{ref} and the theoretical values Q . In all cases, $Q > Y_{ref}$ indicating that functional sites are

TABLE V Comparison Between the Adsorption Capacity, C_a , the Maximum Solid-Phase Dye Concentration, Y_{ref} , and the Quantity of Pure Dye Adsorbed, Y^a , at 20°C

Sample	Quantity of adsorbed dyes at equilibrium											
	AB 25			AY 99			RY 23			AB74		
	%N	C_a (mmol/g)	Y_{ref} (mg/g)	Y_{ref} (mg/g)	Y^a (mmol/g)	Y/C_a	Y_{ref} (mg/g)	Y^a (mmol/g)	Y/C_a	Y_{ref} (mg/g)	Y^a (mmol/g)	Y/C_a
I-EPTMAC-Alfa	0.30	0.214	541	513	0.465	2.172	395	0.534	2.495	223	0.468	2.186
II-EPTMAC-Alfa	0.60	0.4285	518	479	0.435	1.015	368	0.499	1.164	211	0.443	1.033

^a Y (mmol/g) = $\frac{Y_{ref}(\text{mg/g})}{\text{Molecular Weight}} \times (\text{purity})$.

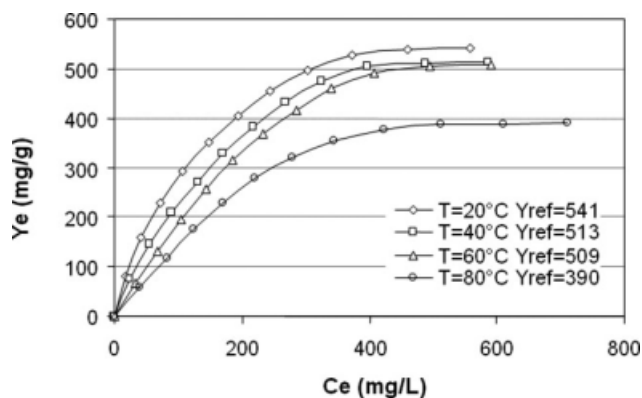


Figure 9 Effect of temperature on the adsorption of AB 25 onto I-EPTMAC-Alfa (%N = 0.30).

completely used in adsorption process. Table IV summarizes some literature results of the comparison of Q for the adsorption of selected dyes into various quaternized supports.

The higher b values at 20°C for all the tested dyes indicated strong binding force toward the reactive sites. Thus, the interaction forces weakened at higher temperature and enhanced magnitude of the desorption step in the mechanism.

Using the following equations, the thermodynamic parameters of the adsorption process, namely Gibbs free energy (ΔG), the change in enthalpy (ΔH), and entropy (ΔS), were determined from the Langmuir model:

$$\Delta G = -RT \ln K_L \quad (11)$$

$$K_L^{4,8,30} = Qb \quad (12)$$

$$\ln K_L = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (13)$$

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

The plot of $\ln(K_L)$ as a function of $1/T$ allows the determination of ΔH and ΔS from the slope and the intercept, respectively (Fig. 12). Thermodynamic parameters were listed in Table VI. The negative values of ΔG indicated the spontaneous nature of adsorption for AB 25, AY 99, and RY 23 at different temperatures.³¹ Whereas values of free energy changes ΔG for the uptake of AB 74 were positive at higher temperatures. This result showed that the adsorption was unspontaneous, indicating less driving force and hence resulting in lesser adsorption

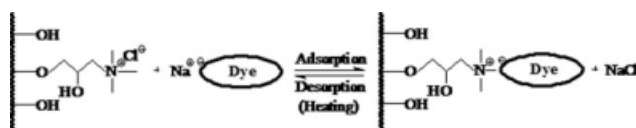


Figure 10 Reversibility of adsorption reaction.

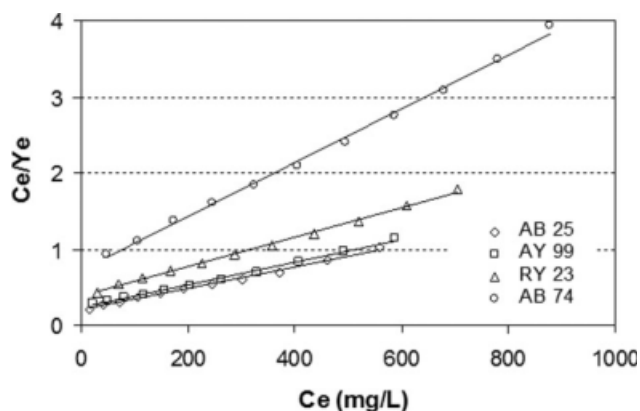


Figure 11 Langmuir plots for the four dyes on I-EPTMAC-Alfa (%N = 0.3); temperature = 20°C.

capacities.³² This was also confirmed by the adsorption isotherm studies. It should be noted that the standard free energy change increases with increasing temperature confirming that a better adsorption is obtained at lower temperatures.³³ The negative values of ΔH suggested the exothermic behavior of the adsorption process and showed that a smaller amount of heat is consumed to transfer the dye molecules from aqueous solution into adsorbent. This result is supported by the decreasing adsorption of selected dyes with the increase in temperature as was showed earlier. Similar results were observed for adsorption of the same dyes onto cationized sawdust.⁵ The negative values of ΔS indicated greater order of reaction at the solid/solution interface during the adsorption process.³⁴

Freundlich model

The Freundlich model, which suggests the presence of different types of adsorption sites, is used for heterogeneous surface energies. The amount of adsorbed dye is a function of the concentration in bath to the power of $(1/n)$ until the complete formation of the monolayer.

The general form of the equation relative to this model is as follows:

$$Y_e = p(C_e)^{1/n} \quad (14)$$

The linear form of eq. (14), which allows the determination of P and n measuring, respectively, the adsorption capacity and the adsorption energy, is represented as follows:

$$\log Y_e = \log P + \frac{1}{n} \log C_e \quad (15)$$

The obtained results showed the poorest fit of experimental data by Freundlich model. Indeed,

TABLE VI
Langmuir Constants and Thermodynamic Parameters of Adsorption of the Dyes on I-EPTMAC-Alfa Fibers

Dyes	% N	T (°C)	Y _{ref} (mg/g)	Langmuir constants				Thermodynamic parameters		
				Q (mg/g)	b (L/mg)	r	R ² ₁	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
AB 25	0.30	20	541	714	0.0070	0.203	0.995	-3.921	-12.556	-29.624
	0.30	40	513	714	0.0048	0.258	0.985	-3.252		
	0.30	60	509	833	0.0031	0.356	0.963	-2.584		
	0.30	80	390	588	0.0035	0.281	0.954	-2.191		
AY 99	0.30	20	513	666	0.0063	0.210	0.994	-3.527	-14.099	-36.736
	0.30	40	420	625	0.0037	0.279	0.986	-2.240		
	0.30	60	411	625	0.0032	0.310	0.975	-1.940		
	0.30	80	400	714	0.0021	0.402	0.953	-1.229		
RY 23	0.30	20	395	526	0.0049	0.221	0.997	-2.353	-10.685	-28.571
	0.30	40	340	476	0.0038	0.256	0.988	-1.556		
	0.30	60	290	384	0.0043	0.220	0.985	-1.441		
	0.30	80	235	322	0.0036	0.240	0.980	-0.476		
AB 74	0.30	20	223	277	0.0050	0.184	0.997	-0.814	-14.099	-45.516
	0.30	40	182	256	0.0032	0.250	0.974	0.464		
	0.30	60	179	270	0.0024	0.306	0.980	1.140		
	0.30	80	171	285	0.0017	0.374	0.986	1.954		

Figure 13 shows deviation from linearity on the Freundlich plot and the correlation coefficients, R^2_2 , (Table VII) are slightly lower than that obtained from the other studied models. In all cases, values of n are superior to 1 ($1.362 < n < 2.033$). According to Treybal,³⁴ this result means that the adsorption is favorable or beneficial and the support can be used in the purification of waste water.

Jossens model

Weber and Matthews,³⁶ stipulate that there is a superposition of adsorption: the saturation of sites having homogeneous energies (adsorption in ammonium sites) according to the Langmuir model and adsorption with heterogeneous energies (adsorption in amorphous zone) according to the Freundlich model.

The general form of Jossens equation is as follows:

$$Y_e = \frac{iC_e}{1 + j(C_e)^m} \quad (16)$$

The three parameters i , j , and m of different systems of adsorption, determined by iteration using a

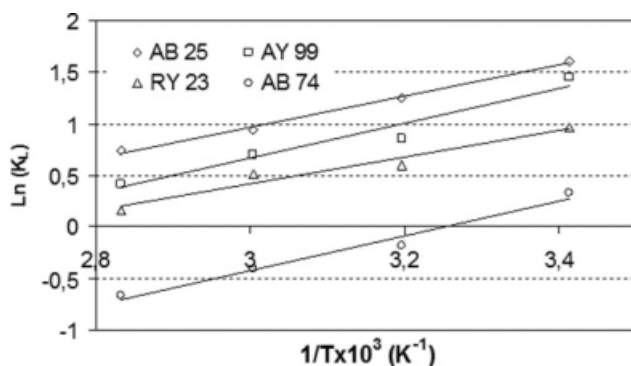


Figure 12 Log K_L versus $1/T$ plots (%N = 0.3).

computer program (MicrocalORigin6®), and correlation coefficients are reported in Table VII. When $j = 0$, the adsorption is named linear; the quantity of adsorbed dye depends only on the concentration of dye introduced in bath. As can be seen from Table VII, the correlation coefficients R^2_3 were extremely high. This showed that the Jossens model represents a better fit to adsorption data than the other two isotherm equations. This was also confirmed in Figure 14 which depicts a comparison between theoretical models and experimental isotherm.

Isotherm shape

The isotherm shape was defined by Weber and Chakravorti.³⁷ Considering a Langmuir-type adsorption process, the isotherm shape can be classified by a term “ r ” which is a dimensionless constant separator factor. In fact, it indicates the type of isotherm to be irreversible ($r = 0$), favorable ($0 < r < 1$), linear ($r = 1$), or unfavorable ($r > 1$).

A relationship between r and the Langmuir’s equation is given by eq. (16)⁴:

$$r = \frac{1}{1 + bC_{ref}} \quad (17)$$

Separator factor values for each adsorbent/adsorbate system are given in Table V and Figure 15 which is a plot of the dimensionless solid-phase concentration, q , against the dimensionless liquid-phase concentration, X .

The relation between q , X , and the Langmuir isotherm is given as follows:

$$q = \frac{X}{r(1 - X) + X} \quad (18)$$

TABLE VII
Freundlich and Jossens Constants for the Adsorption of the Dyes on I-EPTMAC-Alfa Fibers

Dyes	%N	T (°C)	Freundlich constants			Jossens constants			
			P	n	R ² ₂	i (L/g)	j (L/mg)	m	R ² ₃
AB 25	0.30	20	19.656	1.795	0.965	4.080	0.00202	1.160	0.998
	0.30	40	11.887	1.598	0.964	2.564	0.00014	1.496	0.998
	0.30	60	06.789	1.404	0.966	1.969	0.00001	1.821	0.999
	0.30	80	06.885	1.529	0.929	1.534	0.00001	1.809	0.999
AY 99	0.30	20	16.243	1.739	0.951	3.350	0.00085	1.271	0.999
	0.30	40	08.623	1.592	0.954	1.872	0.00021	1.401	0.999
	0.30	60	06.590	1.503	0.950	1.631	0.00010	1.487	0.999
	0.30	80	04.033	1.362	0.966	1.206	0	1.922	0.999
RY 23	0.30	20	12.625	1.817	0.966	2.208	0.00155	1.148	0.999
	0.30	40	07.608	1.660	0.949	1.427	0.00024	1.373	0.999
	0.30	60	07.887	1.759	0.935	1.207	0.00013	1.464	0.999
	0.30	80	05.421	1.704	0.928	0.840	0.00005	1.567	0.999
AB 74	0.30	20	09.246	2.033	0.951	1.145	0.00145	1.146	0.998
	0.30	40	03.974	1.696	0.956	0.597	0.00004	1.598	0.999
	0.30	60	02.882	1.587	0.956	0.497	0.00003	1.600	0.999
	0.30	80	01.944	1.477	0.972	0.419	0.00004	1.510	0.999

where

$$X = \frac{C_e}{C_{\text{ref}}} \quad \text{and} \quad q = \frac{Y_e}{Y_{\text{ref}}}$$

For a single solute adsorption system, C_{ref} is usually the highest fluid-phase concentration and Y_{ref} is the equilibrium solid-phase concentration coexisting with C_{ref} .

In all cases, $0 < r < 1$. This proves that the adsorption of different dyes on modified Alfa fibers is favorable and the process is reversible. The results from this study should help to underpin future improved practical applications of the reuse of modified Alfa fibers in adsorption process. Regeneration is thus possible; this is in agreement with data obtained in temperature effect study.

Desorption of the dyes

This study is monitored as described in the Ref. 38. Recovery of the adsorbed dyes from EPTMAC-Alfa

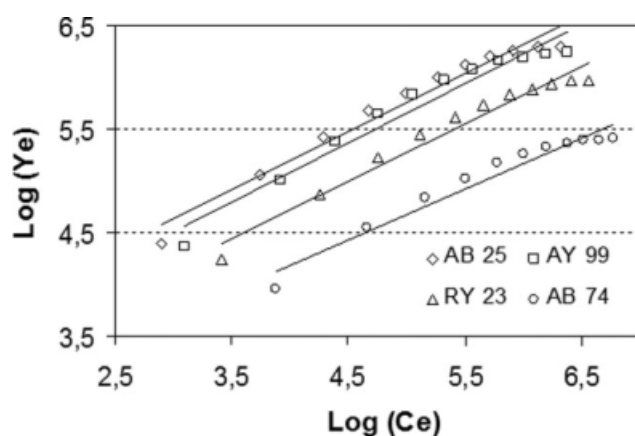


Figure 13 Freundlich plots for the dyes on I-EPTMAC-Alfa (%N = 0.3); temperature = 20°C.

fibers was studied in fixed bed column. The desorption of tested dyes was checked with various eluents namely HCl (1 mol/L), KCl (2 g/L), and NH₄Cl (2 g/L). Results showed that: (i) the use of concentrated solution of HCl caused the damage of the adsorbent that limit its use as anionic exchanger support, (ii) the use of KCl decreased the amount of desorbed dye due to the possible precipitation that might take place within the saturated support between the potassium ions and the anionic molecules of the dyes that prevented the circulation of eluent solution through the column, and (iii) NH₄Cl (2g/L) was found to be the better eluent for conducting desorption studies. The same eluent was used in desorption of the same tested dyes from cationized sawdust and good efficiencies of desorption were obtained.³⁹

The effect of temperature on the desorption of dyes such as AB 25 is depicted in Figure 16. The results show that the increment of the eluent

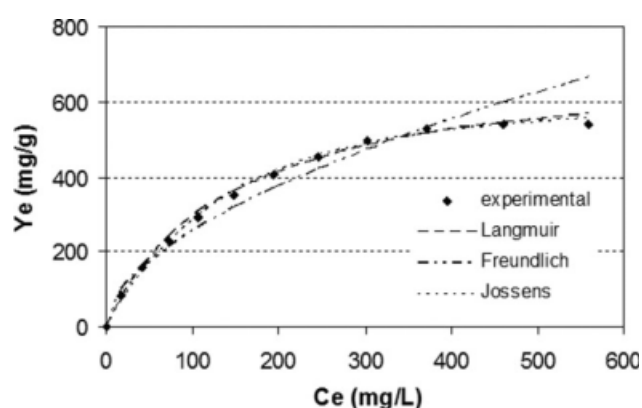


Figure 14 Comparison between theoretical isotherms and experimental results for adsorption of AB 25 on I-EPTMAC-Alfa; temperature = 20°C.

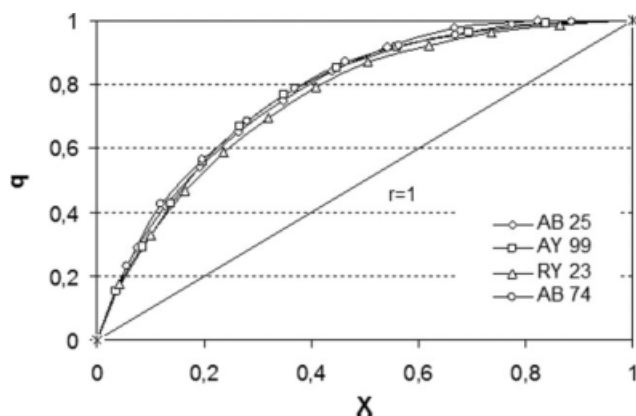


Figure 15 Variation of q as function of X for the four dyes (% $N = 0.3$); temperature = 20°C.

temperature is accompanied with an increase in the amount of recovered dye. This confirms the results concerning the effect of temperature on adsorption as discussed before. According to this, the temperature turned to be favorable for the desorption process. In addition, the majority of desorbed dye was achieved by first 10 mL of the eluent and the rest is desorbed in three 10 mL increments. Results of desorption are summarized in Table VIII and revealed that for the four tested dyes, the highest recovered dye percentage are observed at 90°C using 10 mL of eluent and varied between 52% for AB 74, 70% for RY 23, 76% for AY 99, and 78% for AB 25. We note that the recovery of AB 25 is more important than for AB 74. These results were consistent with adsorption enthalpy values. In fact, when the energy is important, the molecule of the dye is less stable and thus it is easier to be desorbed.

CONCLUSIONS

This study used extracted Alfa fibers by alkaline boiling process as a raw material for preparing a

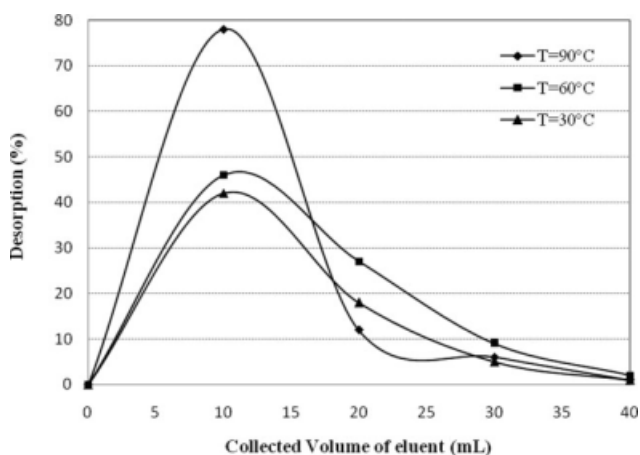


Figure 16 Effect of eluent temperature on desorption of AB 25 from I-EPTMAC-Alfa.

TABLE VIII Percentage of Recuperated Dye at Different Temperatures of NH_4Cl Aqueous Solution

Dye	Eluent temperature (°C)	Eluent volume (mL)	Desorption (%) ^a
AB 25	30	10	42
		20	18
		30	05
		40	01
	60	10	46
		20	27
		30	09
		40	02
	90	10	78
		20	12
		30	06
		40	01
AY 99	30	10	30
		20	21
		30	05
		40	01
	60	10	45
		20	25
		30	07
		40	03
	90	10	76
		20	09
		30	04
		40	02
RY 23	30	10	28
		20	17
		30	03
		40	02
	60	10	40
		20	21
		30	06
		40	03
	90	10	70
		20	07
		30	03
		40	02
AB 74	30	10	26
		20	13
		30	02
		40	02
	60	10	32
		20	19
		30	09
		40	02
	90	10	52
		20	13
		30	08
		40	02

^a Calculated from eq. (8). ^a **Bold values** represent the highest percentages of each recuperated dye using a minimum of eluent volume (10 mL) and at the optimum temperature of recuperation (90°C).

new ion-exchange support. Cationization of Alkali-cellulose of Alfa fibers is monitored with EPTMAC in nonaqueous medium and prepared EPTMAC-Alfa shows its efficiency to bind acid dyes. High sorption capacities are obtained as follows: 541, 513, 395, and 223 mg dye g^{-1} I-EPTMAC-Alfa,

respectively, for Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74. The experimental data was analyzed using Langmuir, Freundlich, and Jossens isotherms. Results of batch experiments indicated that the Jossens model fits the acid dyes adsorption process well. Thermodynamic constants were also calculated and the overall adsorption process was exothermic and spontaneous for the uptake of AB 25, AY 99, and RY 23 by EPTMAC-Alfa fibers at different temperatures. The partial regeneration of the support was possible and the percentage of desorbed dye varied between 52% for Acid Blue 74, 70% for Reactive Yellow 23, 76% for Acid Yellow 99, and 78% for Acid Blue 25.

NOMENCLATURE

a	value that describes the flexibility of the molecules	Y	effectively maximum solid-phase dye concentration (mmol/g)
b	Langmuir constant related to the energy of adsorption (g/L)	Y_{ref}	maximum solid-phase dye concentration (mg/g)
C_a	Capacity of adsorption of cationized Alfa (mmol/g)	η_0	absolute viscosity of a solvent
C_e	dye concentration in solution at equilibrium (mg/L)	η	viscosity of a polymer solution
C_0	initial dye concentration in solution (mg/L)	η_{spec}	specific viscosity
C_{ref}	maximum fluid-phase dye concentration (mg/L)		
\overline{DP}_V	degree of polymerization		
ΔG	Gibbs free energy (kJ mol ⁻¹)		
ΔH	enthalpy of adsorption (kJ/mol)		
i	constant in Jossens isotherm (L/g)		
j	constant in Jossens isotherm (L/mg)		
K	constant depending on the solvent at a given temperature		
K_L	Langmuir equilibrium constant		
m	constant in Jossens isotherm		
m_a	weight of Alfa before extraction (g)		
m_f	weight of dried Alfa after extraction (g)		
n	adsorption energy		
P	measure of adsorption capacity [mg(mg/L) ^{1/n} /g]		
q	dimensionless solid-phase concentration at equilibrium		
Q	dye concentration at monolayer coverage (mg/g)		
r	dimensionless constant separator factor		
R	universal gas constant (kJ mol ⁻¹ K ⁻¹)		
%R	efficiency of extraction		
ΔS	entropy of adsorption (J K ⁻¹ mol ⁻¹)		
t	efflux time of cellulose solution		
t_0	efflux time of pure cupriethylenediamine solution		
X	dimensionless liquid-phase concentration at equilibrium		
Y_e	dye concentration at equilibrium (mg/g)		

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