

# Immobilization of Residual Dyes onto Ion-Exchanger Cellulosic Materials

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**ABSTRACT:** This article reports on the preparation of cationized cotton fiber by treating alkali cellulose cotton fibers with epoxy propyltrimethylammonium chloride (EPTMAC) in a nonaqueous medium and its use as support for the immobilization of pollutant dyes. Evidence of attaching quaternary ammonium groups onto cellulose is provided by IR analysis, nitrogen determination, and weight uptake. Four EPTMAC–Cotton fiber samples with different nitrogen content (0.5–1.85) are tested for the adsorption of four acid dyes (Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74). Adsorption is followed spectrometrically, the capacity of adsorption depending on the nitrogen content and on the number of anionic groups in the dye. The Langmuir and Freundlich isotherms constants are evaluated from the experimental data, but better agreement is obtained by using a composite isotherm of the general form  $Y_e = iC_e/(1 + jC_e^m)$ , where  $i$ ,  $j$ , and  $m$  are constants. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 171–183, 2000

**Key words:** cationized cotton; acid dyes; adsorption isotherm; exchange capacity

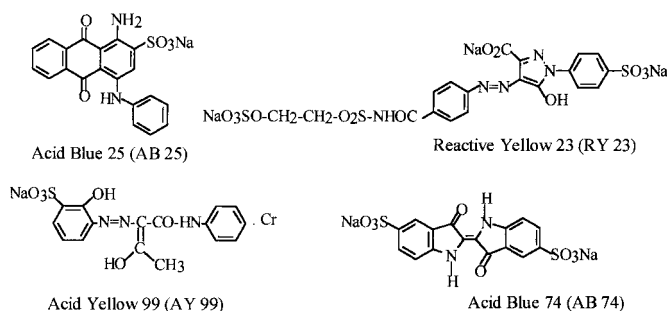
## INTRODUCTION

The removal of dyes from industrial effluents is an ever-increasing problem as governmental legislation becomes more stringent. Adsorption onto a solid support has attracted considerable interest as a suggested method for the removal of color from textile waste waters. A number of studies have been reported with regard to the adsorption equilibrium and kinetics of dye-removal processes using various adsorbents.<sup>1–9</sup> Available dye adsorbents are wood,<sup>10–14</sup> peat,<sup>9,10,15,16</sup> chitin,<sup>17–22</sup> chitosan,<sup>23,24</sup> pith,<sup>25</sup> and several low-cost materials

(teakwood bark, etc.).<sup>26</sup> Among the various groups of dyes, acid dyes are the most frequently used in dyeing substrates such as wool, silk, nylon, and leather.<sup>27</sup> Due to the anionic character of these dyes, cationized cellulose has been used for improving the dyeability of cotton fibers<sup>28–30</sup> and the adsorption of the wasted dyes.<sup>31–33</sup> Such cationized cellulose is prepared by the reaction of epoxy propyltrimethylammonium chloride (EPTMAC) which links quaternary ammonium sites to the cellulose. The low nitrogen content (0.1–0.7%), the low capacity of exchange (0.6 meq/g), and the high swelling in aqueous media (50%) leading to a hydrogel limit its performance in use as a solid support for removing color from effluents. In some difficult cases, the elimination of dyes may be achieved by using activated carbon,<sup>34–39</sup> but the cost of regeneration of the carbon usually limits its use to the “polish-

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**Figure 1** Chemical structures of the selected dyes.

ing stage” of the treatment. However, certain synthetic polymeric adsorbents may offer distinct advantages in specifically defined cases.<sup>40</sup> This article describes the preparation of EPTMAC–Cotton with a high content of ammonium sites and its capacity to adsorb at different temperatures four acid dyes from aqueous solutions, under several experimental conditions.

## EXPERIMENTAL

### Materials

Syrian cotton fibers were supplied by SITEX (Société Internationale de Textile, Monastir, Tunisia). All reagents [dimethylformamide (DMF), tri-*n*-propylamine (TPA), and EPTMAC] were supplied by Aldrich (Sigma-Aldrich Chimie Sarl, Saint-Quentin Fallavier, France) and used without further purification. The dyes used in the adsorption experiments are shown in Figure 1 and are used in their commercially available form, blended with mineral salts to adjust their dyeing power. Their characteristics are given in Table I.

### Techniques

#### Preparation of EPTMAC–Cotton

Syrian cotton is purified by a mild alkaline scouring (2% NaOH and 0.2% owf of a wetting agent) for 5 h at 110°C in an Ahiba Nuance laboratory machine using a liquor ratio of 10 : 1, followed by washing with distilled water and drying in air at room temperature. The EPTMAC–Cotton is prepared in two steps, which can be represented as in Figure 2. The first step is the preparation of sodium hydroxide-treated cotton (NaOH–Cotton). Purified cotton is treated with aqueous sodium hydroxide (12 *N*) at room temperature for 2 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 100 mL of DMF, 3 mL of TPA, and 10 g of NaOH–Cotton. 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 is complete

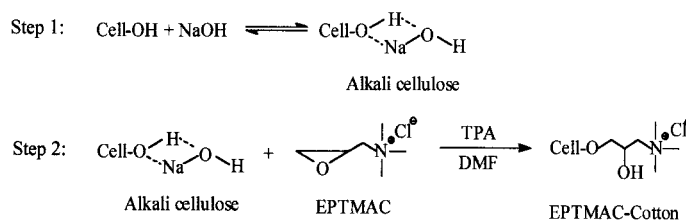
**Table I** Characteristics of the Selected Dyes

Dyes (C.I. Name)	Supplier	$\lambda_{\max}$ (nm)	Purity <sup>a</sup> (%)	Molecular Weight (g/mol)	Chemical Structure <sup>b</sup>
Acid Blue 25	Aldrich	600	45	416.39	AB 25
Reactive Yellow 23	Hoechst <sup>c</sup>	430	90	665	RY 23
Acid Yellow 99	Aldrich	445	45	496.35	AY 99
Acid Blue 74	Aldrich	608	98	466.36	AB 74

<sup>a</sup> Given by the supplier.

<sup>b</sup> See Figure 1.

<sup>c</sup> Frankfurt, Germany.



**Figure 2** Preparation of EPTMAC-Cotton.

(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 is then subjected to a repeated Soxhlet extraction with ethanol to remove the unreacted EPTMAC and dried at 80°C for about 72 h until a constant weight is obtained. Four samples of EPTMAC-Cotton (I-IV) are prepared, with differing ammonium group content depending on the reaction time. The chemical modification of cellulose, when operated in swelling medium such as DMF, occurs essentially in the amorphous region and at the surface of the crystallites of cellulose.<sup>41</sup>

#### Characterization of the EPTMAC-Cotton

The degree of grafting is calculated from the weight-uptake percentage:

$$\% G = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

$m_0$  and  $m_1$  being the weight of dry cellulosic material before and after treatment, respectively. The modification of cotton is also monitored by the nitrogen content, which gives rise to a theo-

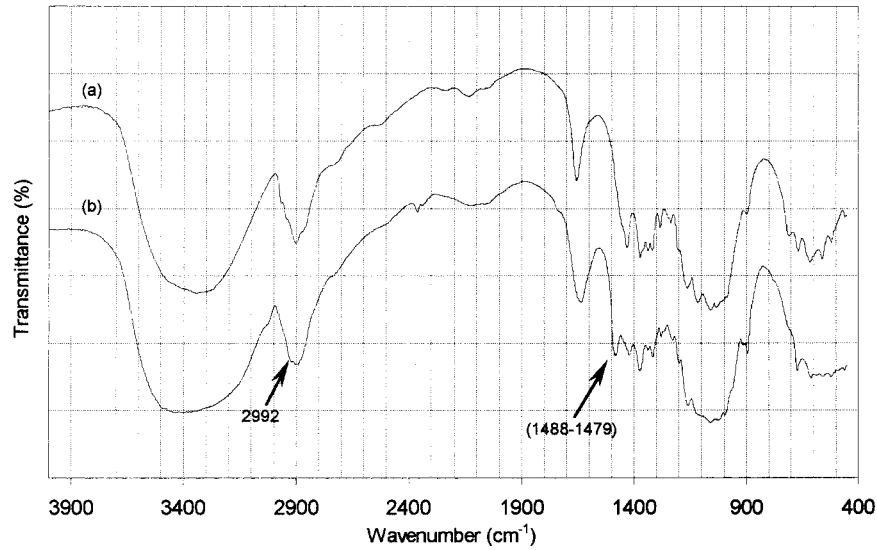
retical weight uptake, generally in agreement with the measured value. The nitrogen content of the EPTMAC-Cotton in a given series is found to increase with increasing reaction time; a nitrogen content of 1.85 is obtained after 2 h of reaction. The degree of grafting and the nitrogen content analysis of the final products are shown in Table II. The original aspect of cotton fibers is unchanged during the chemical modification, except the color, which becomes slightly brownish. The solubility of cellulose is also modified by this chemical treatment: The original cotton is soluble in cadoxene, but about 40% of IV-EPTMAC-Cotton (with a nitrogen content of 1.85%) has become insoluble. In a similar way, the LiCl-dimethylacetamide system<sup>42</sup> dissolves the nontreated cellulose in a 3-day period at room temperature, when IV-EPTMAC-Cotton needs only 1 day. In one experiment, the nitrogen content reached 3.8%, but this highly modified cotton becomes soluble in water at room temperature and was thus unsuitable for its intended application.

IR spectra of cotton and IV-EPTMAC-Cotton are obtained with a Perkin-Elmer 1760-X infrared Fourier (FTIR) spectrometer. Figure 3 shows the IR spectra of the control and modified fibers. It can be seen from the graph (b) that for the IV-EPTMAC-Cotton sample additional peaks are

**Table II** Degree of Grafting and Nitrogen Content of EPTMAC-Cotton Compounds

Samples	Reaction Time (min)	% N	% G	
			Found	Calculated <sup>a</sup>
I-EPTMAC-Cotton	30	0.5	7	5.45
II-EPTMAC-Cotton	60	1	14	10.90
III-EPTMAC-Cotton	90	1.5	18	16.35
IV-EPTMAC-Cotton	120	1.85	23	20.17

<sup>a</sup> Calculation based on % N.



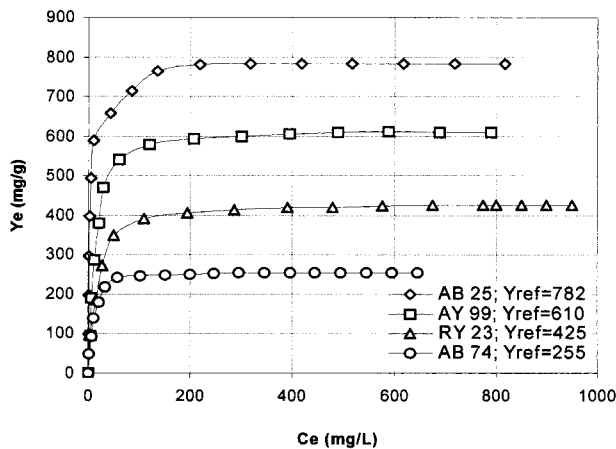
**Figure 3** Infrared spectrum of (a) control cotton and (b) EPTMAC-Cotton.

obtained at 1488–1479 and 2992  $\text{cm}^{-1}$ . They are due to C–H bending and stretching of methyl groups, confirming the introduction of quaternary ammonium groups in the cotton cellulose structure.

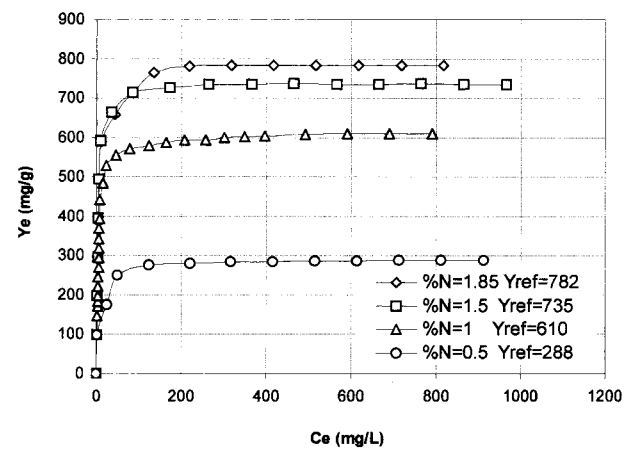
**Adsorption**

In two-phase systems maintained at a specific temperature, a single curve (adsorption isotherm) can be drawn for the solute concentration in the solid phase,  $Y_e$ , as a function of the solute concentration in the fluid phase,  $C_e$ . The adsorption isotherms are determined by immersing a given mass of EPT-

MAC-Cotton (I–IV) in a series of different dye solutions of varying concentration. The modified cotton and 100 mL dye solution of the initial concentration  $C_0$  are stirred mechanically in an Ahiba Nuance laboratory machine for a period of 2 h at different temperatures. The concentration of dye remaining in solution ( $C_e$ ) is measured using an Uvikon 941 Plus spectrophotometer at the wavelength corresponding to the maximum of absorbance ( $\lambda_{\text{max}}$ ) and  $Y_e$  is then deduced by difference with  $C_e$ . Adsorption isotherms are studied under modification of the two parameters: nitrogen content and dye-solution temperature.



**Figure 4** Adsorption of dyes on IV-EPTMAC-Cotton (% N = 1.85); temperature = 20°C.



**Figure 5** Effect of nitrogen content for the adsorption of Acid Blue 25; temperature = 20°C.

**Table III Comparison Between No. Sites and Quantity of Adsorbed Dyes at 20°C**

Sample	% N	No. Sites (mmol/g)	Quantity of Adsorbed Dyes (mmol/g)			
			AB 25	AY 99	RY 23	AB 74
I-EPTMAC-Cotton	0.5	0.36	0.32	0.29	0.23	0.26
II-EPTMAC-Cotton	1	0.72	0.66	0.5	0.51	0.42
III-EPTMAC-Cotton	1.5	1.07	0.80	0.55	0.54	0.48
IV-EPTMAC-Cotton	1.85	1.32	0.84	0.53	0.57	0.53

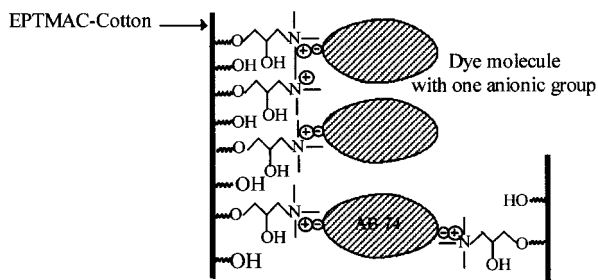
## RESULTS AND DISCUSSION

### Treatment of Colored Waters by Modified Cotton

First, it can be noticed that the untreated cotton fiber does not adsorb any of the four dyes as previously described.<sup>43</sup> The treated fibers show considerable adsorption due to the presence of ammonium sites capable of interacting by an ionic mechanism with the sulfonate groups of the dyes (and/or sulfate and carboxylate groups in the case of AY 23). Figure 4 shows curves of  $Y_e$  versus  $C_e$  for the adsorption of each of the four dyes on IV-EPTMAC-Cotton (nitrogen content 1.85%) at a temperature of 20°C. A limit value  $Y_{ref}$  is obtained for each dye; high adsorption capacities are observed for AB 25 (782 mg/g) and AY 99 (610 mg/g) and less adsorption is exhibited by RY 23 (425 mg/g) and AB 74 (255 mg/g). The values indicated here concern the weight of the commercial dye, including the added salts.

### Effect of Nitrogen Content

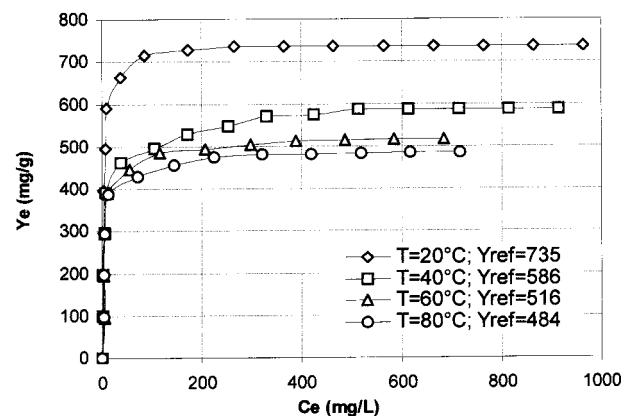
The number of sites present in the EPTMAC-Cotton fibers is the principal factor controlling the adsorption capacity. Therefore, a wide range in nitrogen content EPTMAC-Cotton was investigated. The influence of the nitrogen content is



**Figure 6** Disposition of molecules of dyes on the surface of the adsorbent.

shown in Figure 5 for AB 25. The quantity of dye attached to the support increases with the nitrogen content of the support, but not linearly: At a low nitrogen content, a factor 2 in the capacity of adsorption is observed when the nitrogen content is twice that of the reference (0.5–1%). At higher nitrogen content, it appears to be impossible to utilize all ammonium sites for adsorption. This is probably due to steric hindrance, particularly with large dye molecules, and also to the presence of more than one anionic group per dye molecule. For this reason, an alternative presentation of these results is given in Table III with a comparison of the concentration in ammonium sites in the support (mmol/g) and the concentration of adsorbed dye (mmol/g) calculated on pure dye:

- For AB 25 with one sulfonate group per mol, the amount of adsorbed dye corresponds approximately to the same number of available sites for 0.5–1% nitrogen content. Thereafter, for higher nitrogen content, a decrease in the adsorption capacity is observed as previously stated.



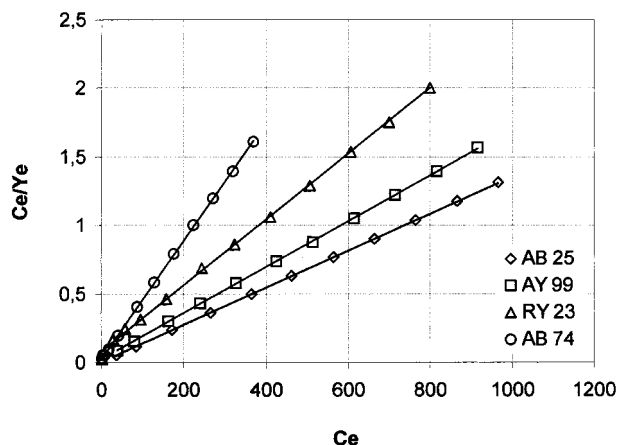
**Figure 7** Effect of temperature on the adsorption of AB 25 on III-EPTMAC-Cotton (% N = 1.5).

- For AY 99 (one sulfonate group per mol), steric hindrance occurs as soon as the nitrogen content reaches 1% (the value of the adsorbed dye is  $\frac{2}{3}$  the number of sites).
- For the two remaining dyes RY 23 and AB 74 (with two or three anionic sites per dye molecule), almost no supplementary adsorption is observed when the nitrogen content increases from 1 to 1.85. In the case of AB 74, the adsorbed dye corresponds to approximately half the number of sites; this may be due to the interaction between the two sulfonate groups of one dye molecule with two sites.

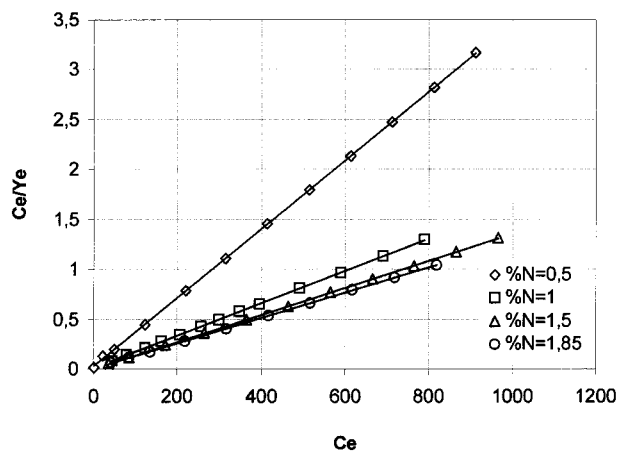
According to the Giles distribution,<sup>44,45,46</sup> adsorption is more effective at low concentrations. Thus, it becomes increasingly difficult for the dye molecules to approach a site when their concentration increases. The shape of the curve indicates that under these conditions the adsorption takes place by an ionic mechanism and that the dye molecules have a perpendicular disposition to the surface of the adsorbent as shown in Figure 6. For all the dyes, ionic interactions are initially established between sulfonate groups of the dye and quaternary ammonium groups of the modified cotton.

**Effect of Temperature**

The effect of temperature on the adsorption of dyes such as AB 25 is shown in Figure 7. As generally observed, the adsorption capacity of modified cotton decreases with increasing tem-



**Figure 8** Langmuir plots for the four dyes on III-EPTMAC-Cotton; temperature = 20°C.

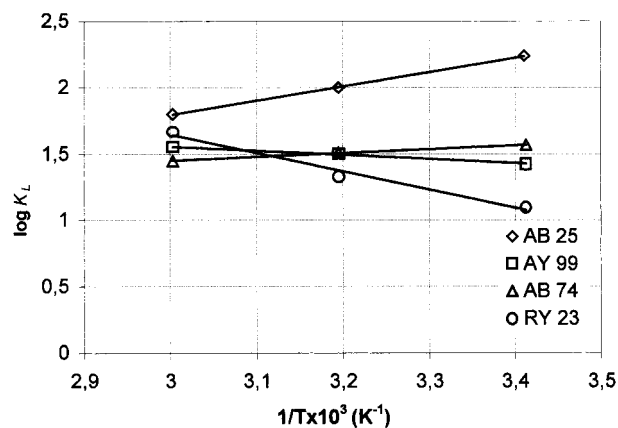


**Figure 9** Effect of nitrogen contents on Langmuir isotherms for adsorption of Acid Blue 25 on EPTMAC-Cotton; temperature = 20°C.

perature, due to the enhanced magnitude of the reverse (desorption) step in the mechanism. The interactions established between the modified cotton and dye are therefore reversible in this case. This is possibly due to the exothermic effect of the surroundings during the adsorption process.<sup>17</sup>

**Adsorption Isotherms**

The distribution of dye between the adsorbent and the solution, at equilibrium, has been expressed using various equations. Three widely used forms are the Langmuir, Freundlich, and General isotherms.



**Figure 10**  $\log K_L$  versus reciprocal of temperature (% N = 1.5).

**Table IV** Langmuir Constants from Eqs. (2) and (4)

Dye	% N	Temperature (°C)	$Y_{\text{ref}}$ (mg/g)	Langmuir Constants		
				$Q$ (mg/g)	$K_L$ (L/g)	$b$ (L/mg)
AB 25	0.5	20	288	294	35.28	0.12
	1	20	610	625	100.00	0.16
	1.85	20	782	769	146.11	0.19
	1.5	20	735	714	171.36	0.24
	1.5	40	586	588	58.80	0.10
	1.5	60	516	526	52.60	0.10
	1.5	80	484	500	70.00	0.14
AY 99	0.5	20	326	333	23.31	0.07
	1	20	550	556	33.36	0.06
	1.85	20	610	625	43.75	0.07
	1.5	20	585	588	23.52	0.04
	1.5	40	459	479	38.32	0.08
	1.5	60	456	456	36.48	0.08
	1.5	80	446	455	50.05	0.11
RY 23	0.5	20	174	175	8.75	0.05
	1	20	378	385	26.95	0.07
	1.85	20	425	435	30.45	0.07
	1.5	20	400	417	12.51	0.03
	1.5	40	420	435	21.75	0.05
	1.5	60	381	385	46.20	0.12
	1.5	80	346	357	14.28	0.04
AB 74	0.5	20	126	127	26.67	0.21
	1	20	200	200	120.00	0.60
	1.85	20	255	263	31.56	0.12
	1.5	20	230	233	37.28	0.16
	1.5	40	195	200	40.00	0.20
	1.5	60	166	169	27.04	0.16
	1.5	80	162	164	39.36	0.24

**Analysis Through Langmuir Isotherms**

The experimental equilibrium data for the uptake of the four dyes by EPTMAC–Cotton have been correlated with the rearranged Langmuir's model of adsorption.<sup>47</sup> The Langmuir isotherms are valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir expression is represented by the following equation:

$$Y_e = \frac{QbC_e}{1 + bC_e} \quad (2)$$

where  $Q$  is the concentration of adsorbate in the solid phase (mg dye/g EPTMAC–Cotton) corre-

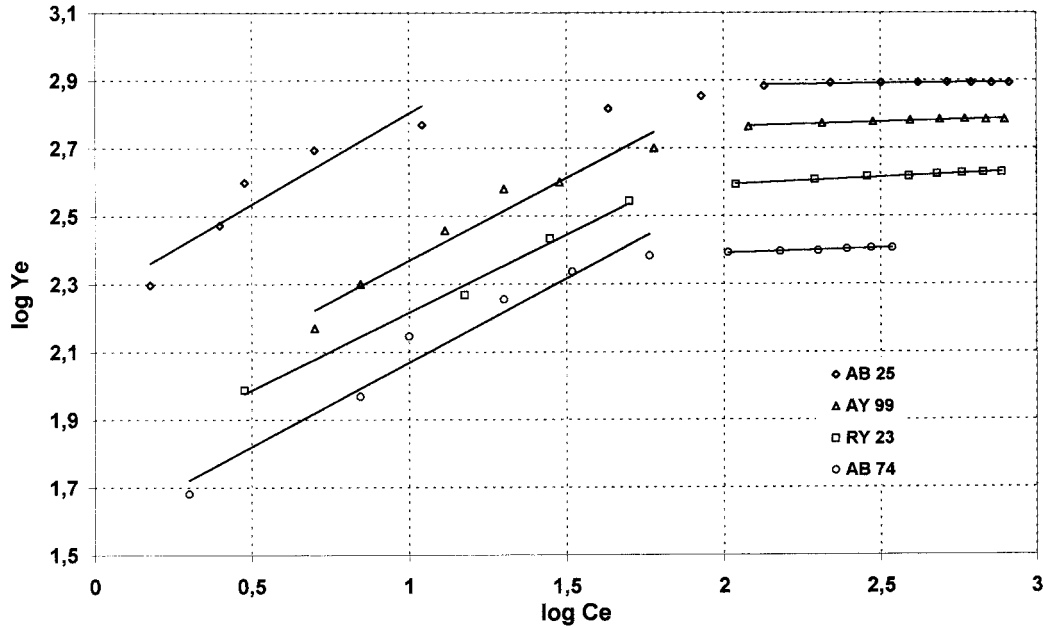
sponding to a complete coverage of the available sites or to the limiting adsorption capacity, and  $b$  is the adsorption coefficient. Equation (2) can be written in a linear form (3) to facilitate the fitting of the experimental data for parameter calculation:

$$\frac{C_e}{Y_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

A plot of  $C_e/Y_e$  versus  $C_e$  yields  $Q$  and  $b$  (Figs. 8 and 9) and, finally, the Langmuir equilibrium constant,  $K_L$ , is obtained from eq. (4):

$$K_L = Qb \quad (4)$$

The equilibrium constant  $K_L$  may be used to determine the enthalpy of adsorption,  $\Delta H$ , using the Clausius–Clapeyron equation:



**Figure 11** Freundlich analysis for the adsorption of four dyes on IV-EPTMAC-Cotton (% N = 1.85); temperature = 20°C.

$$K_L = A \exp(-\Delta H/RT) \quad (5)$$

$$\log K_L = \frac{-\Delta H}{2.303R} \frac{1}{T} + \log A \quad (6)$$

Figure 10 shows a plot of  $\log K_L$  versus  $1/T$  for a nitrogen content of 1.5%. The associated enthalpies when a solvated dye molecule is adsorbed onto the solid support for AB 25, AY 99, RY 23 and AB 74 are  $-20.5$ ,  $+6.0$ ,  $+26.3$ , and  $-5.5$  kJ/mol, respectively. A positive value of  $\Delta H$  means that desolvation of the aqueous dye requires more energy than that liberated by adsorption onto the support. The negative values indicate that heat is liberated during the adsorption process. Table IV summarizes the Langmuir constants and shows that there is good agreement between the experimental value  $Y_{\text{ref}}$  and the calculated value  $Q$ .

#### Analysis Through Freundlich Isotherm

The Freundlich equation<sup>48</sup> is used for heterogeneous surface energies in which the energy term,  $Q$ , of the Langmuir equation varies as a function of the surface coverage,  $Y_e$ , strictly due to variation in the heat of adsorption. The Freundlich equation has the general form

$$Y_e = PC_e^{1/n} \quad (7)$$

where  $P$  and  $1/n$  are characteristic constants. The linear form of eq. (7) is

$$\log Y_e = \log P + \frac{1}{n} \log C_e \quad (8)$$

For convenience of data fitting and parameter evaluation,  $P$  is taken as a relative indicator of adsorption capacity, while  $1/n$  is indicative of the energy or intensity of the reaction. The magnitude of the exponent  $n$  gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values of  $n > 1$  represent favorable adsorption conditions according to Treybal.<sup>49</sup> Figure 11 shows typical Freundlich plots ( $\log Y_e$  versus  $\log C_e$ ) which can be assimilated according to Fritz and Schlunder<sup>50</sup> to two straight lines. Table V summarizes the Freundlich constants obtained from the plots shown in Figure 11. In all cases, the exponent is in the range  $3.5 < n < 9.3$ , showing beneficial adsorption.

#### Analysis Through General Isotherm

Figures 8 and 11 show that the Langmuir equation agrees very well with the adsorption data,



**Table V** Freundlich Constants from Eq. (8)

Dye	% N	Temperature (°C)	Freundlich Constants	
			<i>P</i>	<i>n</i>
AB 25	0.5	20	104.61	6.05
	1	20	185.18	5.86
	1.85	20	300.00	6.08
	1.5	20	231.20	5.11
	1.5	40	165.65	4.57
	1.5	60	152.00	5.11
	1.5	80	158.12	5.21
AY 99	0.5	20	94.70	4.73
	1	20	270.4	9.22
	1.85	20	151.73	4.32
	1.5	20	106.02	3.55
	1.5	40	155.13	5.47
	1.5	60	142.90	5.11
	1.5	80	150.74	5.45
RY 23	0.5	20	80.42	8.41
	1	20	121.11	5.42
	1.85	20	102.10	4.18
	1.5	20	81.02	3.90
	1.5	40	106.43	4.44
	1.5	60	125.22	5.40
	1.5	80	86.65	4.48
AB 74	0.5	20	107	3.74
	1	20	127.52	6.60
	1.85	20	59.71	3.52
	1.5	20	67.90	4.27
	1.5	40	87.40	7.33
	1.5	60	62.36	5.56
	1.5	80	67.11	6.11

but it is not the case with the Freundlich equation. A general isotherm taking into account both the Langmuir and Freundlich expressions was postulated by Weber and Matthews<sup>51</sup> and is represented by the following equation:

$$Y_e = iC_e/[1 + j(C_e)^m] \quad (9)$$

For practical design purposes in a system operating over a wide range of concentration, this “intermediate” isotherm is often a more realistic representation of the system. The general isotherm has three unknowns, namely, *i*, *j*, and *m*; consequently, these data were determined by iteration using a computer program. The results are presented in Table VI. To assess the different isotherms and how they compare to experimental

results, the theoretical plots for each isotherm are presented with the experimental data for the adsorption of AB 25 on EPTMAC–Cotton in Figure 12. The weaknesses of the Langmuir isotherm are highlighted in the region of monolayer coverage; the Freundlich isotherm does not appear to be able to characterize the adsorbent/adsorbate system in all the range of concentrations, but the general isotherm is in good agreement with experimental data at high concentration.

### Effect of Isotherm Shape

Weber and Chakravorti<sup>52</sup> considered the influence of the form of the isotherm on whether adsorption is “favorable” or “unfavorable.” For a Langmuir-type adsorption process, the isotherm shape can be classified by a term, “*r*,” a dimensionless constant separation factor, which is defined by the following relationship given by Hall et al.:<sup>53</sup>

$$r = \frac{1}{1 + bC_0} \quad (10)$$

The parameter indicates the isotherm shape according to Table VII. The values of “*r*” are shown for the four dyes in Figure 13, which is a plot of the dimensionless solid-phase concentration, *q*, against the dimensionless liquid-phase concentration, *X*. The relation between these terms and the Langmuir isotherm is considered to be

$$q = \frac{X}{r(1 - X) + X} \quad (11)$$

where

$$X = \frac{C_e}{C_{\text{ref}}} \quad (12)$$

and

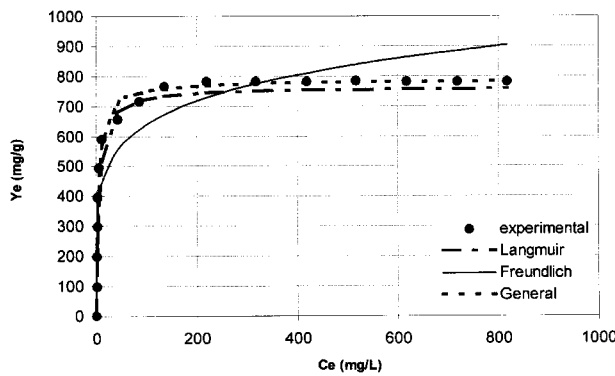
$$q = \frac{Y_e}{Y_{\text{ref}}} \quad (13)$$

For a single solute adsorption system,  $C_{\text{ref}}$  is usually the highest fluid-phase concentration and  $Y_{\text{ref}}$  is the equilibrium solid-phase concentration coexisting with  $C_{\text{ref}}$ . Substitution of eqs. (12) and (13) into (11) yields

**Table VI General Isotherm Constants for the Various Adsorption Systems**

Dye	% N	Temperature (°C)	General Isotherm Constants			Correlation Coefficient
			<i>i</i> (L/g)	<i>j</i> (L/mg)	<i>m</i>	
AB 25	0.5	20	73.25	0.63	0.94	0.998
	1	20	98.10	0.13	1.03	0.988
	1.85	20	190.54	0.25	0.99	0.983
	1.5	20	152.57	0.17	1.03	0.986
	1.5	40	147.10	0.32	0.96	0.991
	1.5	60	71.80	0.13	1.00	0.973
	1.5	80	97.34	0.19	1.00	0.982
AY 99	0.5	20	43.22	0.17	0.96	0.998
	1	20	54.16	0.12	0.97	0.971
	1.85	20	44.72	0.04	1.08	0.987
	1.5	20	21.73	0.02	1.07	0.990
	1.5	40	36.65	0.07	1.00	0.972
	1.5	60	29.50	0.05	1.03	0.992
	1.5	80	49.31	0.10	1.01	0.998
RY 23	0.5	20	12.88	0.07	0.99	0.999
	1	20	69.16	0.24	0.95	0.982
	1.85	20	24.92	0.05	1.02	0.996
	1.5	20	38.30	0.23	0.86	0.988
	1.5	40	26.40	0.09	0.94	0.983
	1.5	60	81.75	0.27	0.96	0.987
	1.5	80	28.14	0.11	0.94	0.996
AB 74	0.5	20	244.22	2.90	0.93	0.994
	1	20	162.28	0.95	0.97	0.991
	1.85	20	22.36	0.06	1.06	0.997
	1.5	20	38.74	0.16	1.00	0.998
	1.5	40	346.84	2.59	0.93	0.980
	1.5	60	157.84	1.57	0.91	0.982
	1.5	80	124.17	1.04	0.94	0.988

$$r = \frac{C_e[Y_{ref} - Y_e]}{Y_e[C_{ref} - C_e]} \tag{14}$$



**Figure 12** Comparison of theoretical isotherms with experimental results for adsorption of AB 25 on IV-EPTMAC-Cotton (% N = 1.85); temperature 20°C.

By substituting for  $Y_e$  from eq. (2),

$$r = \left[ \frac{C_e}{Y_e} \right] \left[ \frac{Y_{ref} - QbC_e/(1 + bC_e)}{C_{ref} - C_e} \right] \tag{15}$$

$$r = [1 + bC_e] \left[ \frac{C_{ref}/(1 + bC_{ref}) - C_e/(1 + bC_e)}{C_{ref} - C_e} \right] \tag{16}$$

$$r = \left[ \frac{1}{1 + bC_{ref}} \right] \left[ \frac{C_{ref}(1 + bC_e) - C_e(1 + bC_{ref})}{C_{ref} - C_e} \right] \tag{17}$$

**Table VII Effect of Separation Factor on Isotherm Shape**

Separation Factor " $r$ "	Type of Isotherm
$r > 1$	Unfavorable
$r = 1$	Linear
$0 < r < 1$	Favorable
$r = 0$	Irreversible

$$r = \left[ \frac{1}{1 + bC_{\text{ref}}} \right] \quad (18)$$

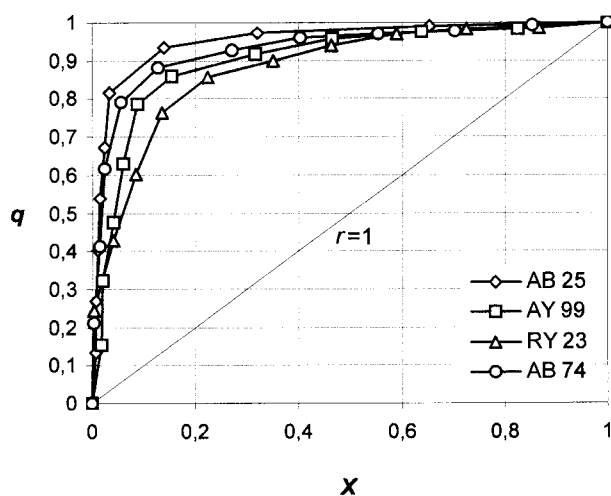
Since  $C_{\text{ref}}$  is the highest fluid-phase concentration encountered (i.e.,  $C_{\text{ref}} \cong C_0$ ), eqs. (10) and (18) are equivalent. The values of " $r$ " for each adsorbent/adsorbate system are given in Table VIII. All four dye systems show favorable adsorption, namely,  $0 < r < 1$ .

## CONCLUSIONS

A strong basic ion-exchange cotton was obtained by reacting alkali-treated cotton with EPTMAC in DMF at 120°C for 2 h. The factors affecting acidic dye removal from aqueous solution were studied on EPTMAC–Cotton. EPTMAC–Cotton is an excellent adsorbent. High adsorptive capacities were observed for the adsorption of acid dyes, namely, 782, 610, 425, and 255 mg dye g<sup>-1</sup> EPTMAC–

**Table VIII Separation Factors for the Various Adsorption Systems**

Dye	% N	Temperature (°C)	$b$ (L/mg)	$r$
AB 25	0.5	20	0.12	0.010
	1	20	0.16	0.010
	1.85	20	0.19	0.008
	1.5	20	0.24	0.007
	1.5	40	0.10	0.020
	1.5	60	0.10	0.017
AY 99	0.5	20	0.07	0.021
	1	20	0.06	0.022
	1.85	20	0.07	0.020
	1.5	20	0.04	0.033
	1.5	40	0.08	0.020
	1.5	60	0.08	0.020
RY 23	0.5	20	0.05	0.024
	1	20	0.07	0.020
	1.85	20	0.07	0.021
	1.5	20	0.03	0.045
	1.5	40	0.05	0.028
	1.5	60	0.12	0.013
AB 74	0.5	20	0.21	0.011
	1	20	0.60	0.005
	1.85	20	0.12	0.027
	1.5	20	0.16	0.020
	1.5	40	0.20	0.016
	1.5	60	0.16	0.016
	1.5	80	0.24	0.014



**Figure 13** Dimensionless concentration isotherms as functions of the separation factor for the four dyes (% N = 1.5); temperature = 20°C.

cotton for Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74, respectively. Theoretical Langmuir and general isotherms were compared with experimental data and good agreement was obtained. All isotherms were shown to be favorable and the effect of the EPTMAC–Cotton nitrogen content was significant. The influence of temperature was studied and enthalpies of adsorption were determined. Freundlich's isotherm was found to be unable to characterize the adsorbent/adsorbate system in this case. With regards to its main use (purification and recycling of industrial water), this process is a finishing treatment which allows

- Discoloration of dyeing effluents by adsorption of the dissolved dyes.
- Recycling of the purified waters.

## NOMENCLATURE

$A$	preexponential factor in Clausius–Clapeyron equation
$b$	constant related to the energy of adsorption (g/L)
$C_e$	dye concentration in solution at equilibrium (mg/L)
$C_0$	initial dye concentration in solution (mg/L)
$C_{\text{ref}}$	maximum fluid-phase dye concentration (mg/L)
$\Delta H$	enthalpy of adsorption (kJ/mol)
$i$	constant in general isotherm (L/g)
$j$	constant in general isotherm (L/mg)
$m$	constant in general isotherm
$n$	adsorption intensity
$P$	measure of adsorption capacity [mg(mg/L) <sup>1/n</sup> /g]
$q$	dimensionless solid-phase concentration at equilibrium
$Q$	dye concentration at monolayer coverage (mg/g)
$R$	universal gas constant (kJ mol <sup>-1</sup> K <sup>-1</sup> )
$r$	dimension constant separation factor
$X$	dimensionless liquid-phase concentration at equilibrium
$Y_e$	dye concentration at equilibrium (mg/g)
$Y_{\text{ref}}$	maximum solid-phase dye concentration

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