

Cationized Nylon as Adsorbent for Anionic Residual Dyes

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ABSTRACT: For use as an ion exchanger, a cationized nylon (EPTMAC–nylon) was prepared by reacting nylon-6,6 with epoxy propyl trimethyl ammonium chloride (EPTMAC), using anhydrous tin chloride (SnCl₂) as catalyst in a nonaqueous medium. Evidence of grafting was provided by atomic force microscopy and the exchange capacity of EPTMAC–nylon was evaluated by potentiometric titration. The adsorption of four dyes (Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74) from aqueous solutions using a batch process was studied according to the

adsorption capacity of the cationized support. The effect of experimental parameters such as dye concentration and adsorption temperature were analyzed. The adsorption isotherms were determined at different temperatures and modeled using Langmuir, Freundlich, and Jossens equations. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2513–2522, 2004

Key words: nylon; dyes/pigments; isotherms; adsorption; ion exchangers

INTRODUCTION

Lignocellulosic materials, such as wood or cotton fibers, appeared very effective, after a functionalization by quaternary ammonium groups, in the depollution of dyeing wastewater by catching acid dyes.^{1–3} The cationization of cellulose, carried out by the action of epoxy propyl trimethyl ammonium chloride (EPTMAC), establishes on this support positively charged sites, the number of which governs its adsorption capacity. Playing the role of exchangers, they can release under certain conditions the accumulated pollutants that allow them to be recycled. However, these vegetal supports are subject to partial degradation in an aqueous medium and exhibit a modest mechanical behavior. Because they are not very compatible with a high number of adsorption/desorption cycles, their lifetime and economic development are limited.

Nylon-6,6 in the form of a textile fiber is a synthetic material of great diffusion used in particular for the manufacture of carpets and moquettes. This material, possibly modified, was used to carry out specific adsorptions, in particular during chromatographic separation.^{4–7} In addition, the antistain processing of textiles requires products that must also present ionic interactions to be adsorbed on the surface of fibers and

to effectively prevent the adsorption of stain.⁸ Finally, a nylon fiber, processed first with epichlorhydrine and then with a tertiary amine, was tested for the fixing of an acid dye, methanil yellow.⁹

In this work, nylon-6,6 was used as exchanger material because its mechanical resistance is considerably higher than that of natural fibers.¹⁰ The adsorption capacity of cationized nylon was tested toward the same dyes as in the cases of cotton and sawdust.^{1,2}

EXPERIMENTAL

Dyes

The chemical formulas of dyes tested in this study, Acid Blue 25 (AB25), Acid Yellow 99 (AY99), Reactive Yellow 23 (RY23), and Acid Blue 74 (AB74), are given in Figure 1.

Nylon preparation

The textile support used was a nylon-6,6 fabric, supplied by SITEX (5000 Monastir, Tunisia) under the reference 102F34. The fabric was first extracted with a mixture of petroleum ether and dichloromethane (50/50 v/v) in a Soxhlet apparatus. The extraction lasted 18 h, and was followed in all cases by drying in a vacuum desiccator to allow a fast evaporation at ambient temperature. Thereafter the fabric underwent a second extraction in the Soxhlet with acetone for 12 h

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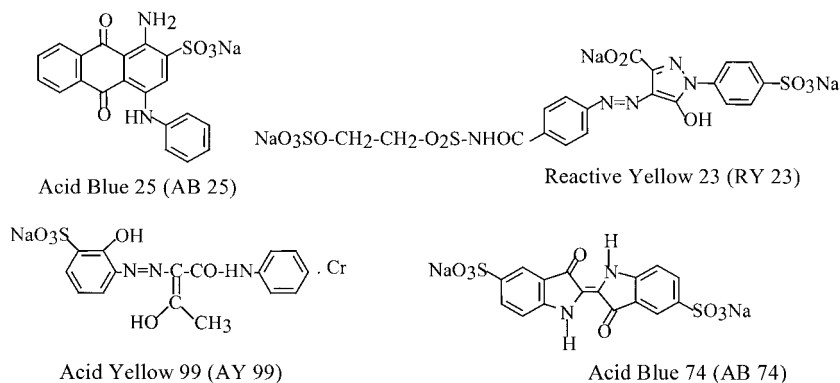


Figure 1 Chemical structures of the tested dyes.

to remove the remaining sizing products. Drying was completed in the same manner for 24 h.

Nylon cationization

All reagents [dimethylformamide (DMF), anhydrous tin chloride (SnCl₂), and EPTMAC] were supplied by Aldrich (Sigma-Aldrich Chimie Sarl, Saint-Quentin Fallavier, France) and used without further purification. The grafting reaction (**Scheme 1**) consisted in soaking 10 g of nylon-6,6 in 100 mL of DMF containing 0.05 g of SnCl₂ at a temperature of 110°C. After 1 h, the temperature was lowered to 90°C, and to the mixture 10 mL of EPTMAC was added dropwise over a period of 1 h. The temperature was then maintained at 110°C for 2 h. After cooling to ambient temperature, the fabric was washed first with acidified water (1% v/v HCl) and then with distilled water. The sample was then subjected to a repeated Soxhlet extraction with ethanol for 24 h to remove the unreacted EPTMAC and dried at 25°C for 72 h until a constant weight was obtained. Contrary to the white color of unprocessed nylon-6,6, the EPTMAC-nylon fabric exhibits a yellowish color. The percentage of grafting *G* was calcu-

lated from the mass uptake attributed to the grafting reaction. By increasing the reaction time and EPTMAC concentration higher values of *G* were obtained. Unfortunately, when this material was brought into contact with aqueous medium, the EPTMAC-nylon was transformed into a gel that was unusable as pollutant adsorbent. For this reason, only one modified fiber with a *G* value of 5.6 wt % was tested in the present work.

Characterization of modified nylon

Viscosimetric molecular mass *M_v*

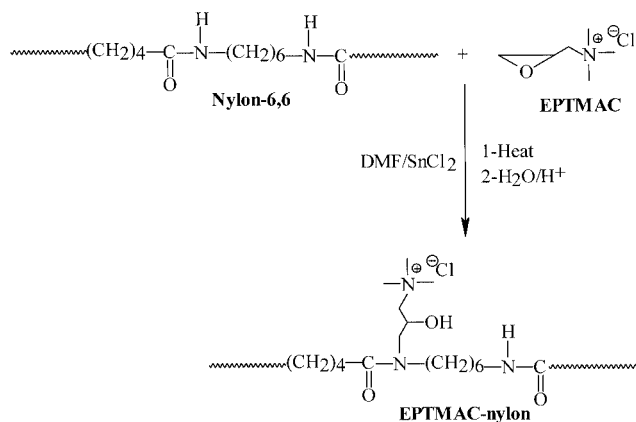
As a result of lateral grafting onto the nylon polymeric chain, an increase in the viscosity of a solution of this grafted material was expected. The viscosimetric molecular mass *M_v* was obtained on a semiautomatic capillary viscosimeter Viscologic TI1 (Sematech, Nice, France) using a Ubbelohde-type capillary (internal diameter 0.5 mm) and a formic acid/water (90/10 v/v) mixture as solvent. The *K* and *a* coefficients of the Mark-Houwink eq. (1) for the present polymer/solvent system are 3.53 × 10⁻² (mL/g) and 0.786, respectively.¹¹

$$[\eta] = K(M_v)^a \quad (1)$$

These same values were also applied to EPTMAC-nylon because the structure was modified only in a limited way. Measurements led to values of 30,800 and 33,900 g/mol for nylon and EPTMAC-nylon, respectively. Although this increase by 10% is not a very significant variation, it nonetheless indicates that no chain degradation occurred during the reactions carried out for the cationization.

Determination of the exchange capacity *C_a*

To evaluate the exchange capacity *C_a*, a sample of 1 g of EPTMAC-nylon was first treated with 50 mL of 1M



Scheme 1 Cationization of nylon-6,6 with EPTMAC.

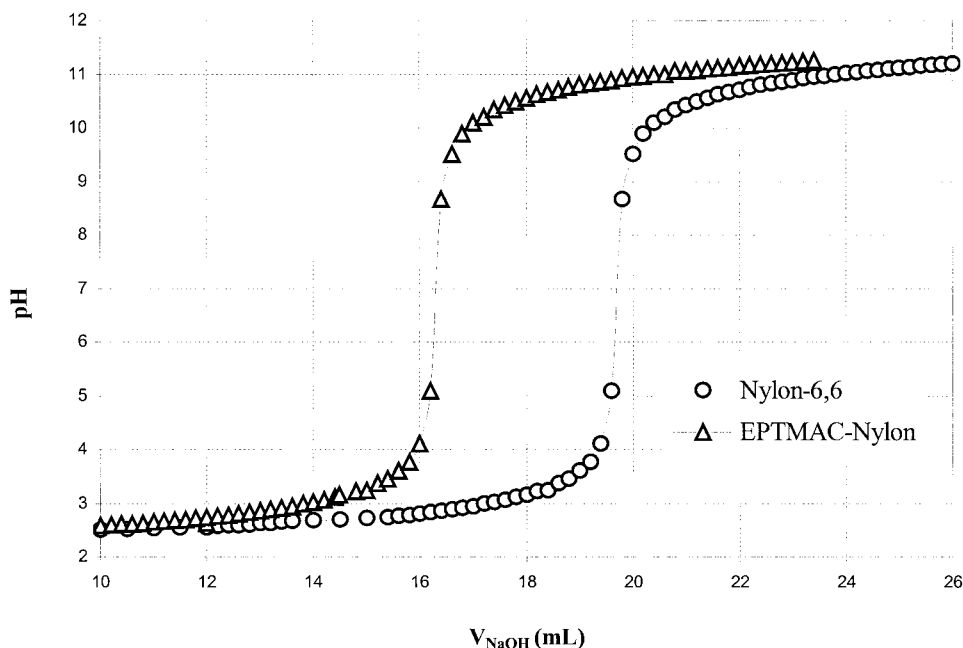


Figure 2 Acid–base titration of untreated and cationized nylon.

NaOH solution to exchange the chloride counter-ion with hydroxyl anions. After washing with deionized water until neutral pH, EPTMAC–nylon was equilibrated with 10 mL of 0.2M HCl solution and 40 mL of 1M NaCl solution. The excess of acid was then titrated with a 0.1M NaOH solution. The adsorption capacity C_a (expressed in milliequivalents per gram of support) was obtained from the following relation:

$$C_a = \frac{(V_0 - V_g)(M)}{m} \quad (\text{mequ/g}) \quad (2)$$

where V_0 and V_g are the volumes (mL) of sodium hydroxide solution necessary for the neutralization of the remaining acid after exchange with nylon-6,6 (blank) and EPTMAC–nylon, respectively; M is the molarity of the sodium hydroxide solution; and m (g) is the mass of the sample. Titration curves are shown in Figure 2 and an exchange capacity C_a of 0.37 mequ/g was obtained, in accordance with the calculation made from the G value.

Atomic force microscopy (AFM)

The microscope used was the Nanoscope III multi-mode-AFM (Digital Instruments, Santa Barbara, CA). The stereotypes were carried out in tapping mode, which consists in sweeping the surface of the sample using a tip oscillating at a frequency close to that of the cantilever resonance (300 kHz). The contact with the surface is done when the tip reaches the maximum amplitude of oscillation. Contrary to the contact mode,

the siliceous tip, which is in intermittent contact with the surface, does not modify the state of this surface.

Figure 3(a) shows that untreated nylon fiber has a smooth surface and a cross section not constantly circular, exhibiting flattening distributed randomly all along the fiber, probably attributable to the extrusion and texturation operations. A fiber treated in the same conditions without EPTMAC (solvent only) presents the same aspect as that of untreated fiber. On AFM imaging of EPTMAC–nylon [Fig. 3(b)], a very significant increase in the roughness of the surface of the grafted fiber was observed, which was attributed to the grafted cationic sites.

Batch adsorption of dyes

For the adsorption in batch procedure, the EPTMAC–nylon (1 g) and the dye solution (100 mL) of known initial concentration C_0 , were stirred mechanically in an Ahiba Nuance laboratory machine (Salvis AG, Reussbühl, Switzerland) at the desired temperature over a period of 3 h, sufficient to reach equilibrium [pH = 6.5 (that of deionized water)]. The quantity of adsorbed dye Y_e was calculated from the dye remaining in the solution C_e . This latter was obtained using an Uvikon 941 Plus spectrophotometer (Kontron Instruments, Milan, Italy) at the wavelength corresponding to the maximum of absorbance of the studied dye. Each experimental point of the adsorption isotherm represents the use of a load of adsorbent and is thus independent of the others. Several tests carried out under identical conditions revealed a good reproducibility with a variation within 1%.

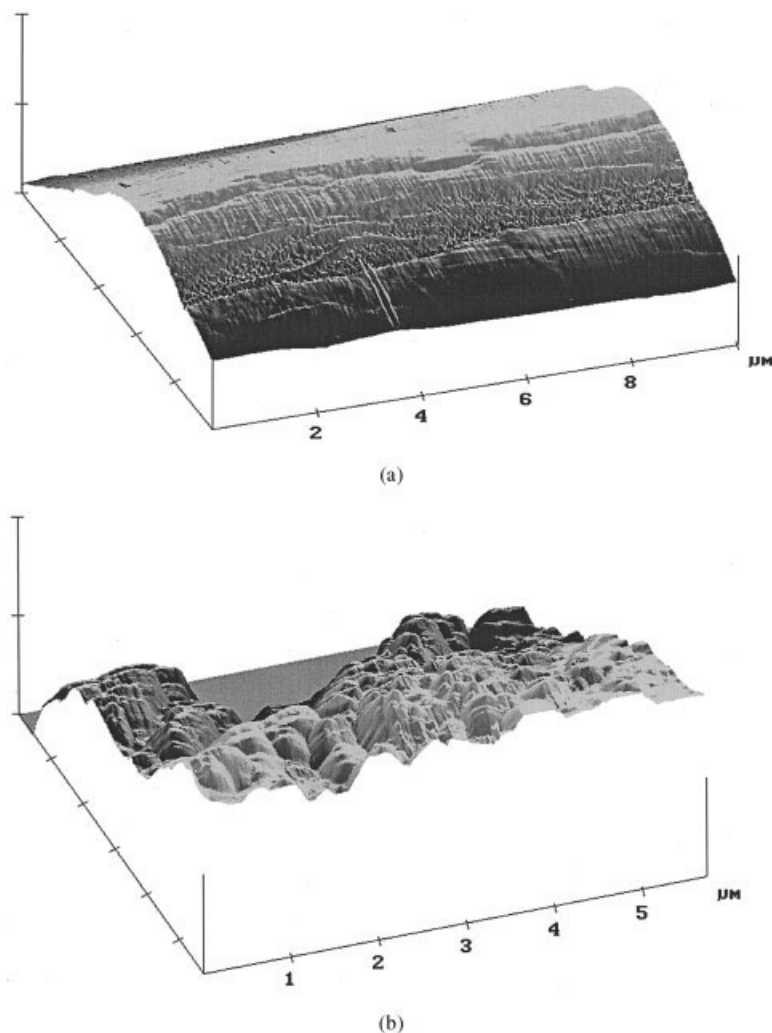


Figure 3 AFM view of (a) untreated nylon-6,6 fiber and (b) EPTMAC-nylon fiber.

RESULTS AND DISCUSSION

It is worth noting that, under the chosen operating conditions, untreated nylon-6,6 does not present any affinity with respect to the studied dyes as indicated in the literature for acid dyes.¹²

Dye diffusion

The process of dye interaction with the treated nylon fiber must be controlled by Fick's law, which implies that the quantity of dye penetrating in a cylindrical fiber is proportional to the square root of time \sqrt{t} .¹³ Figure 4 shows the plots of Y_e versus \sqrt{t} for the different studied dyes. All the curves present a linear increase until an equilibrium is reached within 1 to 3 h. Generally, diffusion in nylon fiber presents a first step with a slow diffusion rate, attributed to the external crystalline structure of the fiber, which constitutes a barrier for the diffusion of solutes.¹⁴ This phenomenon is not visible in the present study because of

the cationization treatment involving a possible surface disorganization.

Adsorption isotherms

Figure 5 shows the adsorption isotherms of the four dyes at 20°C and indicates adsorption capacities of 97, 93, and 105 mg/g for AY99, RY23, and AB74, respectively. These three acid dyes exhibit a similar behavior toward EPTMAC-nylon, whereas AB25 has a much greater affinity for this fiber with an adsorption capacity of 206 mg/g. All curves reach a plateau level and according to Giles et al.,^{15,16} this plateau corresponds to the formation of a monolayer of dyes on the accessible surface of the fibers. For the three dyes AY99, RY23, and AB74, Table I indicates that the ratio between the maximum concentration of adsorbed dye and the adsorption capacity Y_{ref}/C_a is always lower than unity (i.e., all cationic sites are not occupied by one dye molecule), probably because of steric hin-

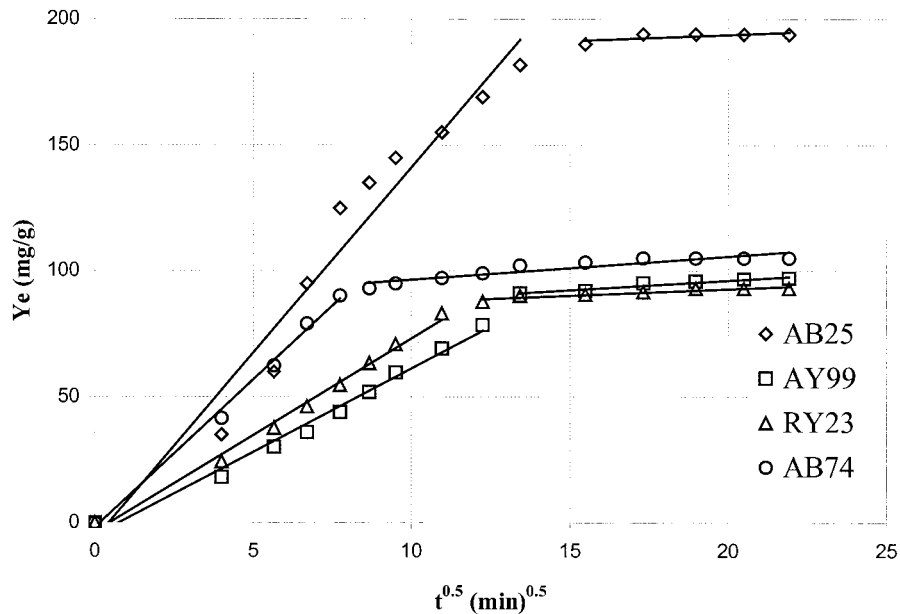


Figure 4 Fick's law Y_e versus \sqrt{t} for dye diffusion in EPTMAC-nylon.

drance and/or the presence of more than one anionic charge in the dye structure.

The particularly higher adsorption capacity in the case of AB25, with a value higher than unity for this ratio, can be attributed to two different adsorption steps:

1. The most efficient is a strong adsorption on cationic sites as for the former dyes.
2. A second one probably involves a partial dye aggregation such as dimerization well known in

solution. Here, the phenomenon is more likely analogous to stacking, a weak aggregation of dye molecules sometimes observed in dyeing of cellulose and nylon.¹⁷ Indeed, the AB25 molecule is relatively compact, with a planar skeleton and presents only one anionic group. When this negative charge is engaged in the adsorption process, there is no difficulty for a second dye molecule to be adsorbed on the first one by aromatic ring overlapping. This is not the case for AY99, RY23, and AB74, which are larger

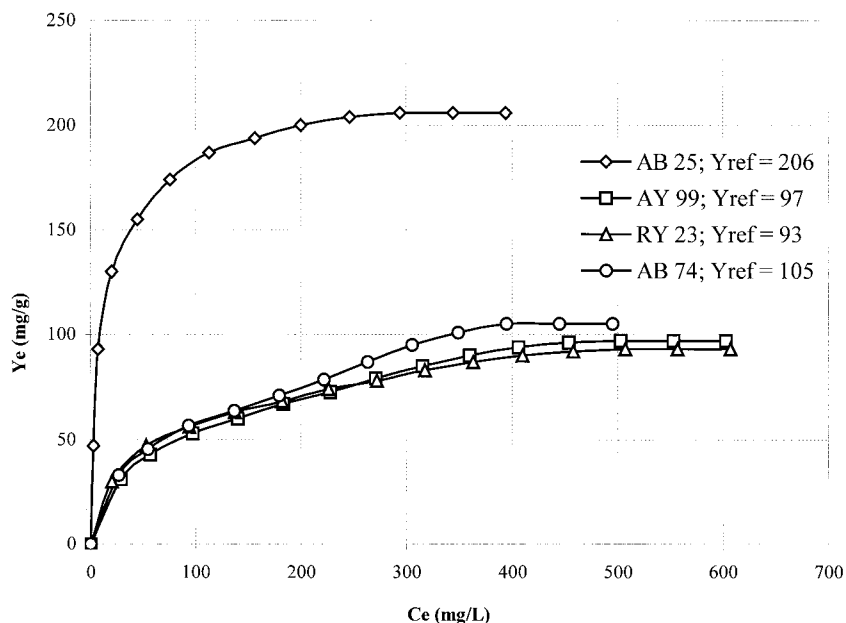


Figure 5 Adsorption isotherms of dyes on EPTMAC-nylon (temperature = 20°C).

TABLE I
EPTMAC–Nylon as Dye Adsorbents

C_a (megu/g)		EPTMAC–cotton		EPTMAC–sawdust		EPATMAC	
Dye	Molecular weight	0.36		0.36		0.37	
		Y_{ref} (mmol/g)	Y_{ref} C_a	Y_{ref} (mmol/g)	Y_{ref} C_a	Y_{ref} (mmol/g)	Y_{ref} C_a
AB 25	416.39	0.32	0.88	0.46	1.27	0.49	1.33
AY 99	496.35	0.29	0.80	0.23	0.64	0.19	0.51
RY 23	665	0.23	0.64	0.33	0.91	0.14	0.37
AB 74	466.36	0.26	0.72	0.21	0.58	0.22	0.60
Reference		Ref. 1		Ref. 2		This work	

molecules bearing more than one negative charge.

Table I also establishes a comparison between the efficiency of this new support and the others already described^{1,2} and having the same C_a value. It appears that EPTMAC–nylon is really more effective than the other supports only in the case of AB25.

Effect of temperature

In the case of AB25, Figure 6 shows that increasing the temperature from 20 to 80°C decreases the adsorbed quantity by 34%. This is not the case with the three other dyes where this reduction is limited to less than 10%. Literature results³ also indicate variations of dye adsorption that may increase or decrease when the temperature is raised. This influence of the temperature in the case of AB25 is mainly ascribed to an unhooking of the second layer of molecules interact-

ing with those adsorbed on cationic sites. In addition, when the temperature increases from 20 to 60°C, the dye/site proportion passes from 1.33 to 1. This confirms that the interaction responsible for the aggregation is weaker than the ionic interaction between EPTMAC–nylon and dye. However, this effect of the temperature is definitely lower compared to the adsorption of these same four dyes on EPTMAC–cotton¹ and EPTMAC–sawdust² where reductions of 20 to 50% of the adsorbed quantities have been observed when increasing the temperature from 20 to 80°C. The EPTMAC–nylon support appears then to preserve its efficiency on a broader range of temperature than the other supports previously studied.

Isotherms modelization

A number of equations were proposed to correlate the distribution of dye, at equilibrium, between the adsorbent and the dye solution. The three most widely used

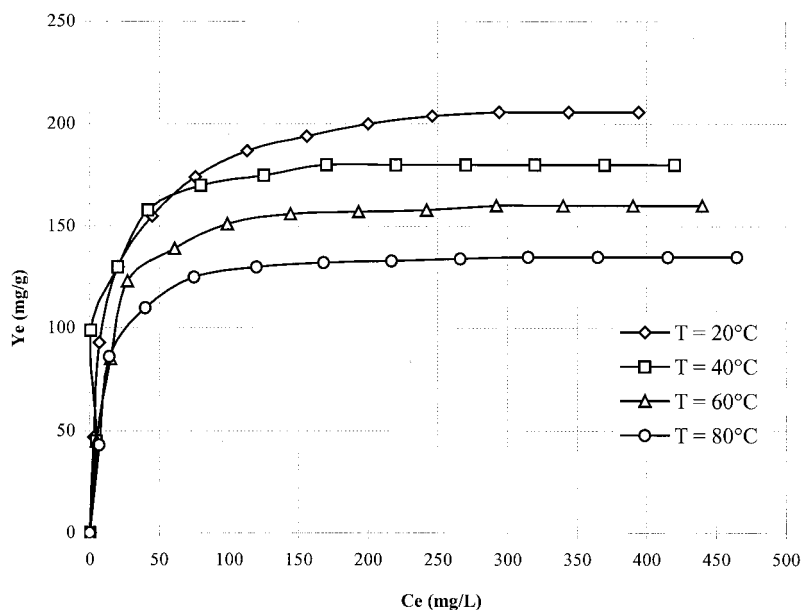


Figure 6 Effect of temperature on the adsorption of AB25 on EPTMAC–nylon.

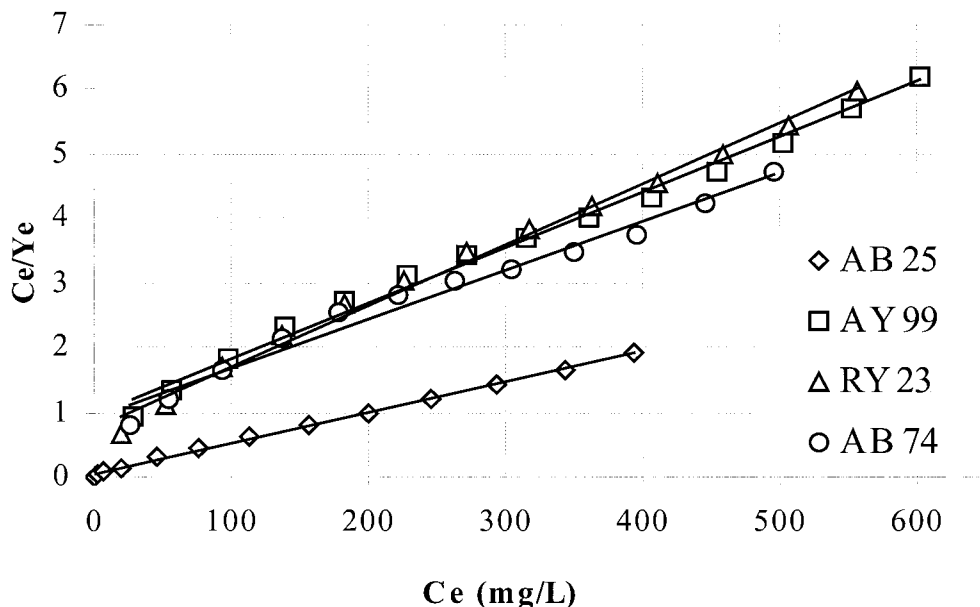


Figure 7 Langmuir isotherms for the four dyes on EPTMAC-nylon (temperature = 20°C).

are the Langmuir,¹⁸ Freundlich,¹⁹ and Jossens^{20,21} models. (All parameters are defined in the Nomenclature section.)

Analysis by langmuir isotherm

The Langmuir equation may be plotted in a linear form shown by eq. (3):

$$\frac{C_e}{Y_e} = \frac{1}{K_L} + \frac{C_e}{Q} \tag{3}$$

A plot of C_e/Y_e versus C_e is shown in Figure 7 for the adsorption of the studied dyes on EPTMAC-nylon. The Langmuir constants were determined and are listed in Table II. The values of constant Q are important because they represent the maximum or monolayer adsorption capacity of EPTMAC-nylon for a particular dye.

The Langmuir constant $K_L = Qb$, determined at various temperatures, furnishes the adsorption enthalpy ΔH using the Clausius-Clapeyron equation:

$$K_L = A \exp\left(\frac{-\Delta H}{RT}\right) \tag{4}$$

The enthalpies associated with the adsorption of an initially solvated dye onto the solid support are -4.32, -6.15, -6.20, and -3.62 kJ/mol for AB25, AY99, RY23, and AB74, respectively. Adsorption is in all cases exothermic, indicating that the links formed between the dyes and the support are stable.

Analysis by the freundlich isotherm

The Freundlich equation for a linear plot is represented by eq. (5):

$$\log Y_e = \log P + \frac{1}{n} \log C_e \tag{5}$$

Data arising from the Freundlich analysis show that a plot of $\log Y_e$ versus $\log C_e$ presents some curvature

TABLE II
Langmuir Constants for Dyes Adsorbed onto EPTMAC-Nylon ($C_a = 0.37$ mequ/g)

Dye	Temperature (°C)	Y_{ref} (mg/g)	Langmuir constants		
			Q (mg/g)	b (L/mg)	K_L (L/g)
AB 25	20	206	202	0.089	17.970
	40	180	185	0.086	15.910
	60	160	164	0.092	15.080
	80	135	139	0.100	13.900
AY 99	20	97	116	0.009	1.044
	40	95	114	0.008	0.912
	60	92	112	0.008	0.896
	80	87	107	0.008	0.856
RY 23	20	93	131	0.008	1.048
	40	91	128	0.008	1.024
	60	88	126	0.007	0.882
	80	85	133	0.005	0.665
AB 74	20	105	106	0.012	1.272
	40	102	104	0.012	1.248
	60	100	101	0.011	1.111
	80	98	99	0.010	0.990

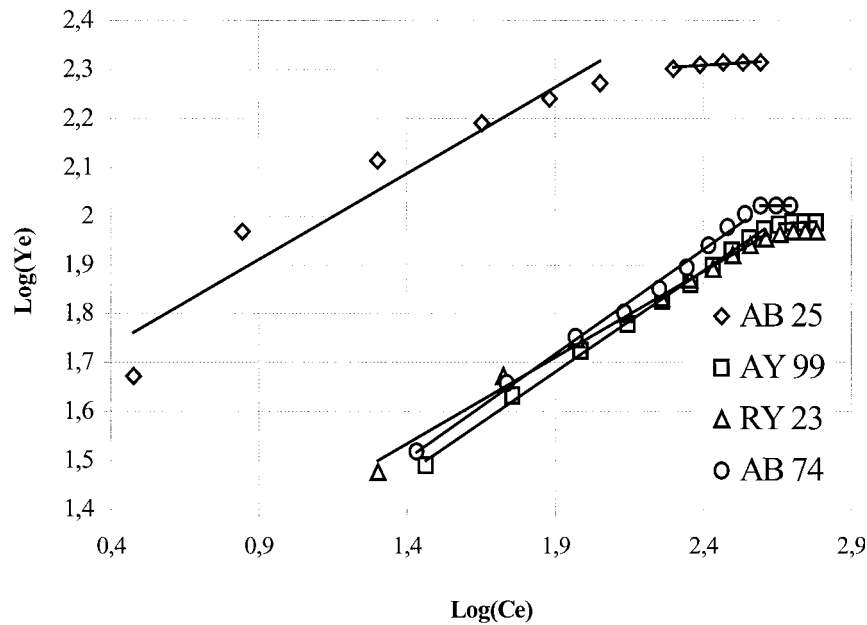


Figure 8 Freundlich isotherms for the four dyes on EPTMAC–nylon (temperature = 20°C).

(Fig. 8). According to Fritz and Schlunder,²² these results can be better represented by more than one straight line. The Freundlich constants for the four dyes in the different systems are obtained from the linear portion having the highest slope and are reported in Table III. For all experiments, the exponent n is in the range $1.74 < n < 3.47$, showing that adsorption is favorable.

TABLE III
Freundlich Constants for Dyes Adsorbed onto
EPTMAC–Nylon ($C_a = 0.37$ mequ/g)

Dye	Temperature (°C)	Freundlich constants	
		P	n
AB 25	20	43.09	3.20
	40	31.17	2.55
	60	32.68	3.04
	80	32.44	3.47
AY 99	20	8.01	2.44
	40	6.58	2.26
	60	6.26	2.28
	80	5.25	2.17
RY 23	20	11.18	2.87
	40	10.88	2.87
	60	9.77	2.76
	80	8.48	2.65
AB 74	20	8.01	2.33
	40	6.77	2.22
	60	4.66	1.97
	80	3.09	1.74

Analysis by the Jossens isotherm

The Jossens equation,^{20,21} expressed as

$$Y_e = \frac{iC_e}{1 + j(C_e)^m} \quad (6)$$

generally gives a better correspondence with experimental data²³ for dye adsorption. The three unknowns in this equation, that is, i , j , and m , are determined by iteration using a computer program. The results are presented in Table IV.

To assess the different isotherms and their ability to correlate with the experimental results, the theoretical plots for each isotherm and the experimental data are shown in Figure 9 in the case of AB25 at 60°C. It obviously appears that the Freundlich model is not appropriate, probably because of the two-step adsorption previously mentioned. The Langmuir model is acceptable for the low-concentration range. Nevertheless, the Jossens model fits perfectly the experimental data in the total range of concentration as previously observed for EPTMAC–cotton¹ and EPTMAC–sawdust.²

Effect of isotherm shape

The adsorption process is efficient only because the isotherm Y_e versus C_e is composed of two lines, a first one quasi-vertical followed by a second at a plateau value. The shape of the isotherm can be characterized in a normalized representation of $q = Y_e/Y_{\text{ref}}$ versus X

TABLE IV
Jossens Constants for Dyes Adsorbed onto
EPTMAC–Nylon ($C_a = 0.37$ mequ/g)

Dye	Temperature (°C)	Jossens Constants			Correlation coefficient
		i (L/g)	j (L/mg)	m	
AB 25	20	25.92	0.18	0.93	0.998
	40	7.71	9.60	0.85	0.984
	60	11.60	0.06	1.04	0.993
	80	10.72	0.06	1.04	0.995
AY 99	20	2.62	0.12	0.74	0.989
	40	2.42	0.11	0.75	0.987
	60	2.32	0.14	0.72	0.993
	80	1.42	0.06	0.77	0.997
RY 23	20	3.78	0.15	0.79	0.999
	40	3.35	0.13	0.78	0.993
	60	3.40	0.15	0.77	0.993
	80	2.82	0.14	0.76	0.995
AB 74	20	6.91	0.59	0.63	0.996
	40	2.17	0.10	0.72	0.997
	60	1.25	0.03	0.81	0.995
	80	1.05	0.03	0.80	0.993

= C_e/C_{ref} by a dimensionless constant separation factor “ r ” proposed by Hall et al.²⁴ as in eq. (7):

$$r = \frac{1}{1 + bC_0} \tag{7}$$

For a Langmuir-type adsorption process, Weber and Chakravorti²⁵ consider a sorbent to be “favorable” when $0 < r < 1$ with a value as small as possible,

corresponding in Figure 10 to the dashed lines. The values of “ r ” for the four dyes are given in Table V and all four systems show favorable adsorption, that is $r > 0$, with r near zero (Fig. 10), particularly for AB25.

CONCLUSIONS

A novel ion-exchange polyamide was obtained by reacting nylon-6,6 with EPTMAC in DMF at 110°C for 2 h. For the adsorption of acid dyes, only moderately short times are required to reach equilibrium and high adsorptive capacities were observed: 206, 97, 93, and 105 mg dye/g EPTMAC–nylon for AB25, AY99, RY23, and AB74, respectively. Theoretical isotherms were compared with experimental data. The influence of temperature was studied and enthalpies of adsorption were determined. Good agreement with previous results on cotton and wood sawdust was obtained.

NOMENCLATURE

- A preexponential factor in Clausius–Clapeyron equation
- b constant related to the energy of adsorption (L/g)
- C_a adsorption capacity of the support (mequ/g)
- C_e dye concentration in solution at equilibrium (mg/L)
- C_0 initial dye concentration in solution (mg/L)
- ΔH enthalpy of adsorption (kJ/mol)
- i constant in Jossens isotherm (L/g)
- j constant in Jossens isotherm (L/mg)
- K_L Langmuir equilibrium constant (L/g)

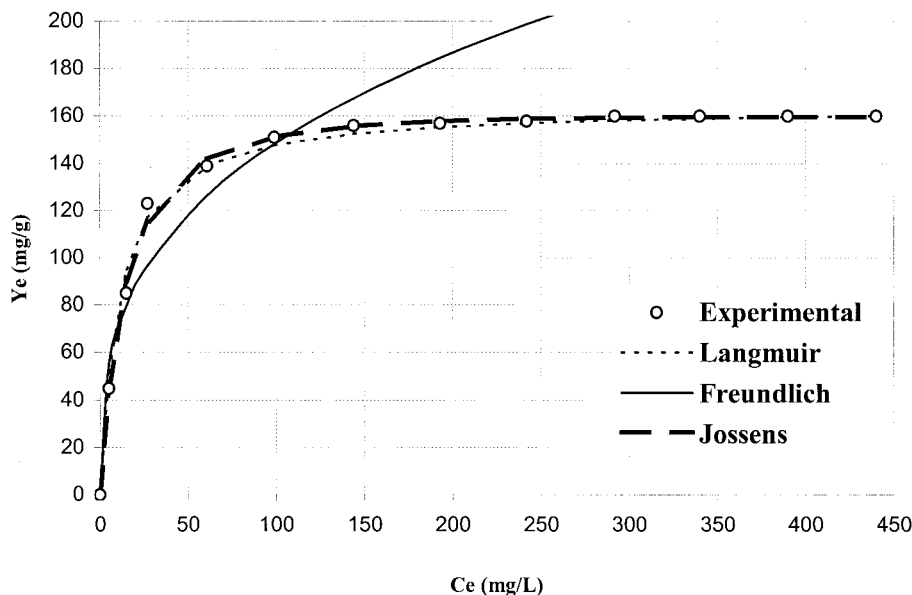


Figure 9 Comparison of theoretical isotherms with experimental data for AB25 on EPTMAC–nylon (temperature = 60°C).

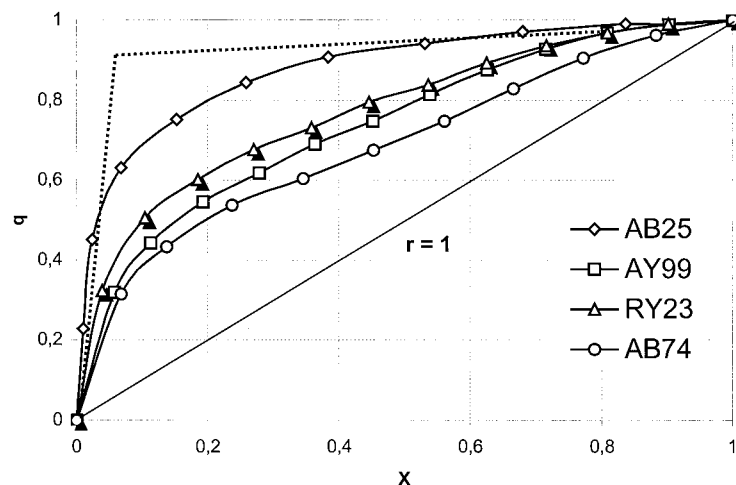


Figure 10 Dimensionless concentration isotherms as a function of the separation factor for the four dyes (temperature = 20°C).

m	constant in Jossens isotherm
n	adsorption intensity
P	measure of adsorption capacity $[\text{mg}(\text{mg}/\text{L})^{1/n} / \text{su.} / \text{pi} / \text{g}]$
q	dimensionless solid-phase concentration at equilibrium
Q	dye concentration at monolayer coverage (mg/g)
r	dimensionless constant separation factor
R	universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$)
X	dimensionless liquid-phase concentration at equilibrium
Y_e	dye concentration at equilibrium (mg/g)
Y_{ref}	maximum solid-phase dye concentration (mg/g)

TABLE V
Separation Factors for the Various Adsorption Systems

Dye	Temperature (°C)	b (L/mg)	r
AB 25	20	0.089	0.04
	40	0.086	0.07
	60	0.092	0.04
	80	0.100	0.03
AY 99	20	0.009	0.18
	40	0.008	0.19
	60	0.008	0.18
	80	0.008	0.19
RY 23	20	0.008	0.19
	40	0.008	0.19
	60	0.007	0.22
	80	0.005	0.28
AB 74	20	0.012	0.17
	40	0.012	0.15
	60	0.011	0.14
	80	0.010	0.15

References

- Baouab, M. H. V.; Gauthier, R.; Gauthier, H.; Chabert, B.; Rammah, M. B. *J Appl Polym Sci* 2000, 77, 171.
- Baouab, M. H. V.; Gauthier, R.; Gauthier, H.; Rammah, M. B. *J Appl Polym Sci* 2001, 82, 31.
- Hashem, A.; El-Shishtawy, R. M. *Adv Sci Technol* 2001, 19, 197.
- Gan, H.-Y.; Shang, Z.-H.; Wang, J.-D. *J Chromatogr* 2000, 867, 161.
- Gan, H.-Y.; Shang, Z.-H.; Wang, J.-D.; Liu, X.-L. *Chromatographia* 2001, 53, 450.
- Beeskow, T.; Kroner, K. H.; Anspach, F. B. *J Colloid Interface Sci* 1997, 196, 278.
- Weissenborn, M.; Hutter, B.; Singht, M.; Beeskow, T. C.; Birger Anspach, F. *Biotechnol Appl Biochem* 1997, 25, 159.
- Burkinshaw, S. M.; Gotsopoulos, A. *J Appl Polym Sci* 2000, 77, 3062.
- Jan, D. E.; Raghavan, S. *Colloids Surf A Phys Chem Eng* 1994, 92, 1.
- Morton, W. E.; Hearle, J. W. S. *Physical Properties of Textile Fibres*, 2nd ed.; Heinemann: London, 1975; p 283.
- Burke, J. J.; Orofino, T. A. *J Polym Sci* 1969, 7, 1.
- Peters, R. H. *Textile Chemistry, Vol. III: The Physical Chemistry of Dyeing*; Elsevier: New York, 1975; p 295.
- Krank, J.; Park, G. S. *Diffusion in Polymers*; Academic Press: London, 1968.
- Peters, R. H. *Textile Chemistry, Vol. III: The Physical Chemistry of Dyeing*; Elsevier: New York, 1975; p 347.
- Giles, C. H.; Smith, D.; Huitson, A. *J Colloid Interface Sci* 1974, 47, 755.
- Giles, C. H.; D'Silva, A. P.; Easton, I. A. *J Colloid Interface Sci* 1974, 47, 766.
- Hihara, T.; Okada, Y.; Morita, Z. *Dyes Pigments* 2000, 45, 131.
- Langmuir, I. *J Am Chem Soc* 1918, 40, 1361.
- Freundlich, H. *Colloid and Capillary Chemistry*; Matheun: London, 1926.
- Jossens, L.; Prausnitz, J. M.; Fritz, W.; Schlunder, E. U.; Myers, A. L. *Chem Eng Sci* 1978, 33, 1097.
- Weber, W. J.; Mathews, A. P. *AIChE Symp Ser* 1976, 166; *AIChE J* 1976, 73, 91.
- Fritz, W.; Schlunder, E. U. *Chem Eng Sci* 1981, 36, 721.
- MacKay, G.; Porter, J. F.; Prasad, G. R. *Water Air Soil Pollut* 1999, 114, 423.
- Hall, K. R.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T. *Ind Eng Chem Fundam* 1966, 5, 212.
- Weber, T. W.; Chakravorti, R. K. *AIChE J* 1974, 20, 228.