Use of Copper(II)/Ethylene Diamine-Cotton Complex for the Adsorption of Residual Dyes

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ABSTRACT: The chemical modification of cotton is performed by successive reactions with thionyl chloride followed by ethylene diamine (ED) to prepare aminoalkyl amino cotton namely ED-cotton. Evidence of attaching ethylene diamine groups onto cotton is provided by nitrogen determination and thermogravimetry analysis. Because of complexation, the ethylene diamine-grafted groups immobilizes Cu(II) ions from buffered solution at pH 6. The formation of a 1/1 complex is assessed by the adsorption limit values. The binary system [Cu(II)/ED-cotton] is then tested for the adsorption of two acid dyes (Acid Blue 25 and Calmagite) as ligands in the metal-coordinating process. The adsorption of Cu(II) onto ED-cotton and of the dyes onto Cu(II)/ED-cotton is followed spectrometrically. The observed stoichiometries of the ternary-formed complex [Dye/Cu(II)/ED-cotton] are 1/1/1 with Acid Blue 25 and 0.75/1/1 with Calmagite at 20°C. The Langmuir and Freundlich isotherms constants for the adsorption of the tested dyes onto Cu(II)/ED-cotton are evaluated from the experimental data, but better agreement is obtained by using the composite isotherm of Jossens. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1389–1396, 2007

Key words: adsorption; dyes; heavy metals; grafted cotton

INTRODUCTION

A number of heavy metal ions and dyes plays a significant role in contaminating sea, streams, and rivers. Although these chemicals are largely used at an industrial scale, they are known as toxic and/or cancerigen. The need for an effective and economical removal of these pollutants resulted in a search of unconventional methods and systems that might be used in this field. Cellulose is a very promising raw material for the preparation of various functional polymers. Many of our investigations into the chemical modifications and applications of cellulose have demonstrated that cationized cellulose, wood, maize-cob flour, and cotton can be used as adsorbent for acid dyes and chromium oxy-anions.[1–3] In another work, the adsorption of metal ions such as Cu(II), Cr(III), Cd(II), Ni(II) and dyes such as Acid Blue 25, Calmagite, and Eriochrome Blue Black B is performed onto amidoximated cellulose (Am-Cell).[4] Different ways are possible for the adsorption of these pollutants onto Am-Cell: adsorption of each pollutant alone on the support, or cumulative adsorption of both metal ions and dyes on the same support. In the last case, the pollutants may be adsorbed simultaneously from a unique solution, or successively from two different solutions. Recently, the adsorptive ability of the quaternary composite complexes system Cu(II)/EDTA/Chitin/Cellulose was studied,[5] and it was demonstrated that for some salts of acid dyes, the composite complexes show improved adsorption power compared to the non Cu(II) preadsorbed one.

The use of aminoalkyl amino cellulose (AmAC) with different lengths in the alkyl chain was investigated as heavy metal ions adsorbent.[6] The authors conclude that metal ions are adsorbed rapidly on AmAC from aqueous solutions, particularly in the case of Cu(II). The effectiveness of AmAC as adsorbents decreased with increasing length of the methylene moiety, and AmAC from ethylene diamine (ED) was the most effective.

The aim of the present work is to investigate the possibilities of ternary complex formation between two acid dyes [Acid Blue 25 (AB25) and Calmagite (Calma)], Cu(II) ions, and ED-cotton using a batch process under several experimental conditions.

EXPERIMENTAL

Materials

Syrian Cotton was supplied by SITEX (Société Internationale de Textile, Monastir, Tunisia). All reagents

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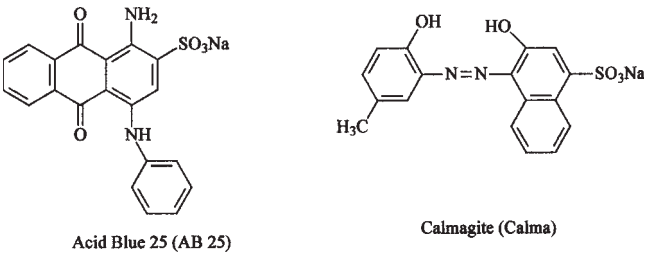

Figure 1 Chemical structures of the selected dyes.

[dimethylformamide (DMF), thionyl chloride, ethylene diamine (ED, 85% aqueous solution), ammonium hydroxide, potassium hydrogen phthalate (for the Clark-Lub's buffer solutions),[7] and the salt ($CuCl_2 \cdot 2H_2O$)] were supplied by Aldrich (Sigma–Aldrich Chimie Sarl, Saint-Quentin Fallavier, France) and used without further purification. The dyes used in the adsorption experiments, namely Acid Blue 25 and Calmagite (referred to as AB25 and Calma, respectively), were supplied by Hoechst (Frankfort, Germany) and known for their capacity of metal complexation due to the presence of donor atoms in their structures. Their chemical structures and characteristics are given in Figure 1 and Table I, respectively.

Preparation of ED-cotton

Syrian cotton is purified as previously described.[1] Ethylene diamine grafted cotton (ED-cotton) is prepared in two steps, which can be represented as in Figure 2. The first step is the preparation of 6-chlorodeoxycellulose (6-CDC) according to the method reported previously.[6] The second step is carried out as follows. In a round bottomed flask are placed 1 g of 6-CDC, 30 mL of distilled water, and 10 mL of 85% ED aqueous solution. The mixture is stirred for more than 3 h at reflux. At the end of the reaction, the mixture is filtered, washed thoroughly with a mixture of methanol and acetone (50/50 v/v), and then dried. The nitrogen content of the final product is 3.8%. At this nitrogen content corresponds a number of coordinating sites per gram of support, C_a = 1.357 mmol/g obtained from the following relation:

$$C_a = \frac{(\%\mathrm{N})}{2.M_\mathrm{N}} \frac{1}{100} \times 10^3 \,\mathrm{mmol/g} \qquad (1)$$

where, %N is the nitrogen content of ED-cotton and M_N is the molecular weight of nitrogen. The percentage of nitrogen content was determined by the Cole and Parks modification of the semimicro Kjeldahl method.[8]

Characterization of ED-cotton

At the beginning, we noted that the solubility of cellulose was modified by the chemical treatment: the original cotton was insoluble in 85% ED aqueous solution, but ED-cotton became soluble. In addition, when the nitrogen content of ED-cotton reached 4.5%, this highly modified cotton became soluble in the methanol/acetone washing mixture.

The differential thermal analysis (DTA), thermogravimetry (TG), and derivative thermogravimetry (DTG) thermograms of cotton and ED-cotton were obtained with a SETARAM® derivatograph (Faculté des Sciences de Monastir-Tunisie). 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. The results of thermal decomposition of cotton and ED-cotton are presented in Figure 3(a,b), respectively. The DTA curve of cotton shows an exothermic reaction beginning at 300°C and ending at 405°C. This exotherm is interrupted by an endotherm with a peak temperature at 329°C. The endotherm can be attributed to dehydration and depolymerization leading to the formation and evaporation of flammable volatile products; the large exotherm peak at 350°C may be due to oxidation of these products. The last large exotherm maximum at 460°C represents oxidation of the charred residues. The high-molecular-weight charred residues[9,10] start burning in air at about 405°C and glowing is complete at 500°C with char yield of 30% as shown in TG [Fig. 3(a)].

The typical DTA thermogram [Fig. 3(b)] of preferentially primary substituted cellulose of the ED-cotton[11] shows a small endotherm with a peak at 255°C. This may be visualized as resulting from the scission of amino groups from ED-cotton. The TG curve shows only a mass loss of 3% in this temperature range. The large exotherm in the range 300–429°C due to the oxidative decomposition of substituted and unsubstituted portions of cellulose is interrupted by a small endotherm peak at 344°C corresponding to the scission of the grafted ethylene moieties from the compound. The TG curve also shows that the rapid loss of mass of the analyzed compound takes place in this temperature range and about 60% mass disappears during this process. The next large exotherm begin-

TABLE I
Characteristics of Dyes

Dye					
Name	Referred to as[a]	Supplier	λ_{max} (nm)	Purity[c] (%)	Molar weight (g/mol)
Acid Blue 25	AB25	Hoechst[b]	600	100	416.39
Calmagite	Calma	Hoechst[b]	526	100	358.37

[a] See Figure 1.
[b] Frankfurt, Germany.
[c] As indicated by the supplier.

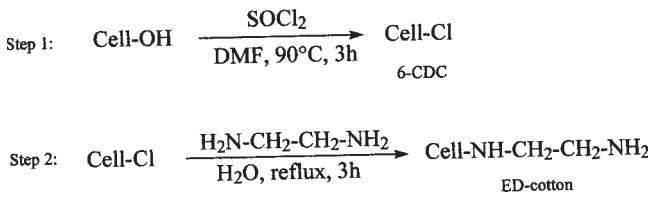

Figure 2 Preparation of ED-cotton.

ning at 435°C and ending at 600°C is associated with the oxidation of charred residues.[11]

The endothermic peak corresponding to moisture desorption at around 98–100°C was retained for cotton and ED-cotton.[11] On the TG curves, the loss of mass in this temperature range is more important for ED-cotton than for cotton indicating a significant change in the moisture regain.

Loading of ED-cotton with Cu(II) ions

The loading of ED-cotton with Cu(II) ions is carried out as described in the literature.[6] ED-cotton (0.1 g) with 10 mL of $5 \times 10^{-2}M$ aqueous solution of Cu(II) ion is stirred for 24 h at room temperature in a closed vessel to load the ED-cotton up to saturation. The pH is adjusted at 6 with a Clark-Lubs' buffer solution.[7] The [Cu(II)/ED-cotton] complex is filtered off, washed with distilled water, and dried under reduced pressure at 25°C for 24 h. The remaining Cu(II) ions in the filtrate are determined by spectrometric titration.[7] The initially white color of ED-cotton becomes blue turquoise after adsorption of Cu(II) ions.

Dye adsorption onto Cu(II)/ED-cotton

For the determination of the affinity of [Cu(II)/ED-cotton] complex for the two tested dyes, the equilibrium isotherms were realized in batch procedure by simple contact under stirring between the solid support (0.1 g) and 100 mL of the aqueous solution of the dye of initial concentration C_0 in an Ahiba Nuance® laboratory machine for a period of 4 h at the desired temperature. The concentration of the dye remaining in the solution C_e was measured with an UVIKON 941

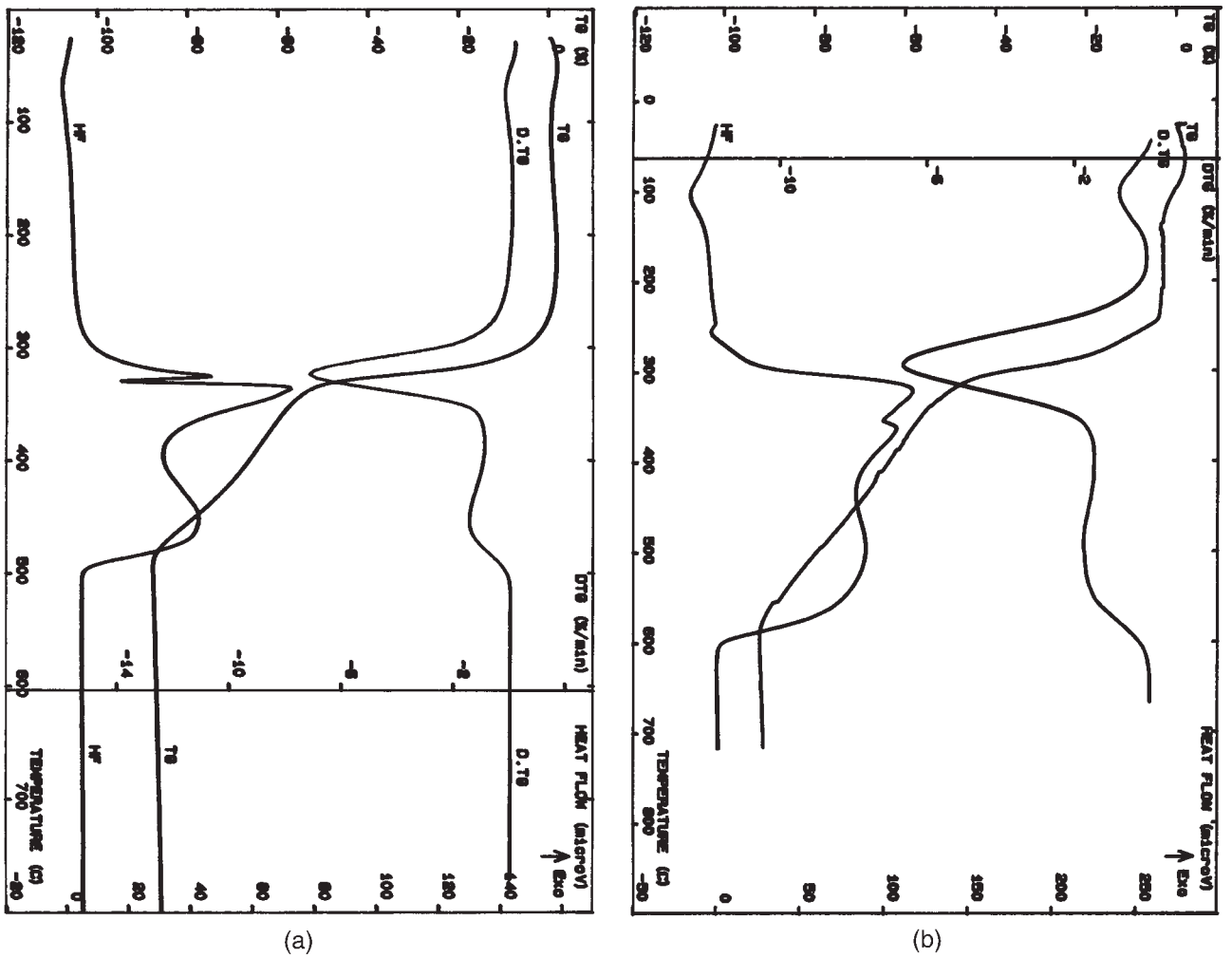

Figure 3 Thermal analysis of (a) cotton in air and (b) ED-cotton in air.

Plus® spectrophotometer at the wavelength corresponding to its maximum of adsorption, and the amount of adsorbed dye Y_e was then deduced from the difference with C_0. The adsorption isotherms were studied at four different temperatures between 20 and 80°C.

RESULTS AND DISCUSSION

Effect of pH on the adsorption of dyes and Cu(II) onto ED-cotton

First, it can be noticed that at pH 6, ED-cotton does not present any affinity for the studied acid dyes as shown in Figure 4. Although a remarkable quantity of dyes was adsorbed onto the ED-cotton fibers at pH 3 for AB25 and pH 3.5 for Calma, the adsorption of both dyes decreased dramatically in the pH range 4–7. This is because the protonated amino groups on ED-cotton, responsible for the adsorption process in this case, decreased when the pH values increased. At very low pH values (1–2), protonation of anionic sulfonate groups of dyes prevents their adsorption on the solid support. For the adsorption of Cu(II) onto ED-cotton, it was observed that the increase of the pH of aqueous Cu(II) ions solution from 3 to 6 caused a significant increase in the amount of adsorption and reached the maximum value at a pH value of 6 where a 1/1 metal/ED-cotton stoichiometry is observed. At low pH values (range of 1–3), the high hydrogen ion concentration at the interface repels the positively charged metal ions electrostatically and prevents their approach to the fiber surface. Therefore, the lower adsorption values were observed at lower pH values, as seen in Figure 4. The same results were previously observed for the adsorption of Cu(II) ions onto amidoximated cellulose.[7]

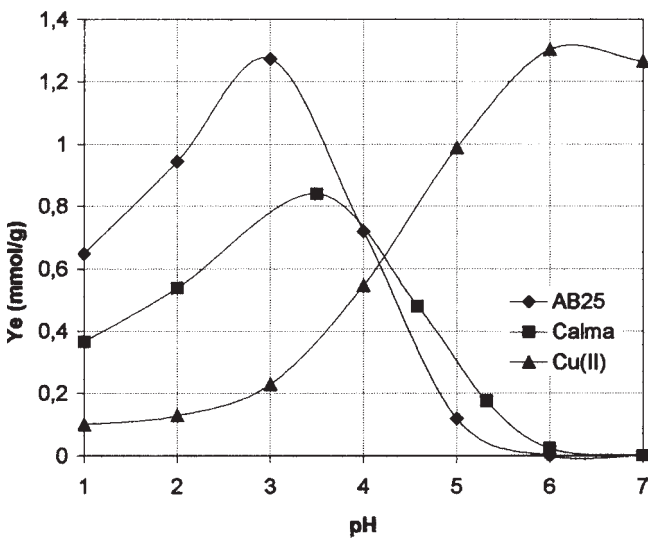

Figure 4 Effect of pH on the adsorbed amount of dyes and Cu(II) ions on ED-cotton.

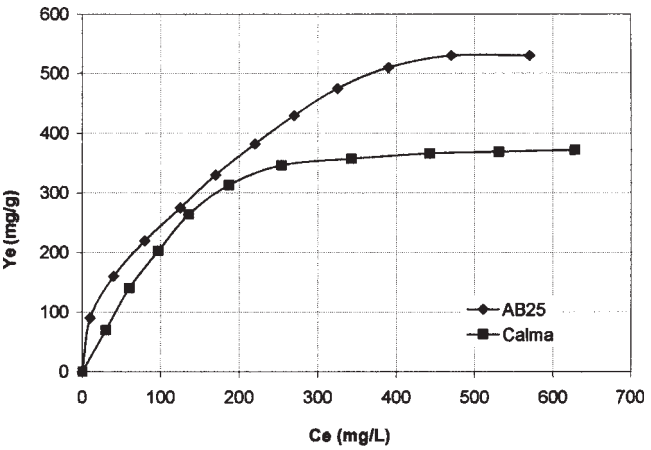

Figure 5 Adsorption isotherms of the dyes on Cu(II)/ED-cotton complex; temperature = 20°C.

Adsorption of dyes onto ED-cotton loaded with Cu(II) ions

Such experiments need first to saturate the ED-cotton support with Cu(II) ions at a 1/1 ratio. Secondly, the loaded support is introduced into the dye solution and maintained until equilibrium is reached. All the experiments were carried out at pH 6, where the highest adsorption of Cu(II) ions onto ED-cotton was obtained. Figure 5 represents the adsorption isotherms Y_e versus C_e for the two studied dyes onto [Cu(II)/ED-cotton] with $C_a = 1.357$ mmol/g and shows that at saturation, high capacities of binding are registered for each dye. At 20°C, the adsorbed quantities per gram of support reach 530 mg or 1.27 mmol for AB25 and 372 mg or 1.03 mmol for Calma. The saturation limit corresponds to molar quantities of dyes slightly lower than the C_a value of the support. This observation is attributed to the steric hindrance of the voluminous dye molecule, which cannot reach all the [Cu(II)/ED-cotton] sites created in the mass of the cotton. Furthermore, these results indicate that the dyes can act as efficient ligands for coordinating metal already involved in ED-cotton complex. Indeed, at pH 6, ED-cotton support, having initially no affinity with the dyes, becomes a strong adsorbent for these molecules when it is loaded with Cu(II) ions. The absence of metal ions in the filtrate confirms the strong complexation power of dyes toward [Cu(II)/ED-cotton] complex. Table II presents the adsorption of dyes onto [Cu(II)/ED-cotton] support, showing the formation of ternary complexes [Dye/Cu(II)/ED-cotton] with 1/1/1 stoichiometry for AB25 and 0.75/1/1 stoichiometry for Calma at 20°C. The phthalate ions used for pH control also act as ligand,[6] in place of water molecules. The stoichiometry of the adsorption of dyes onto metals indicates that the dyes exchange coordination sites with phthalate ions. It has been verified that the maximum quantities of complexed Cu(II) ions (q_{ref}) given in Table II are identi-

TABLE II
Comparison between C_a and the Maximum Quantity of Adsorbed Cu(II) ions at pH = 6 q_{ref} and C_a and the Maximum Solid-Phase Dye Concentration Y_{ref}

	Maximum quantity of adsorbed Cu(II) at pH 6			Quantity of adsorbed dyes at equilibrium					
				AB25			Calma		
Sample	T (°C)	q_{ref} (mmol/g)	q_{ref}/C_a	Y_{ref} (mmol/g)	Y_{ref}/q_{ref}	Y_{ref}/C_a	Y_{ref} (mmol/g)	Y_{ref}/q_{ref}	Y_{ref}/C_a
Cu(II)ED-cotton,	20	13	0.95	1.27	0.97	1.04	1.04	0.8	0.76
C_a = 1.36 mmol/g	40	1.25	0.92	1.16	0.93	0.93	0.93	0.74	0.68
	60	1.15	0.85	0.62	0.54	0.45	0.45	0.4	0.33
	80	1.05	0.77	0.07	0.06	0.22	0.22	0.21	0.16

cal in the presence or absence of phthalate ions. Table II also establishes a comparison between the efficiency of the used support in the present work and the other already described[4] and having comparable C_a values. It appears that at 20°C, [Cu(II)/Am-Cell] binary complex is slightly more efficient than the [Cu(II)/ED-cotton] one only in the case of Calma dye. Finally, the ability for metal complexation follows the series: H_2O < phthalate < dye < ED-cotton. Possible complex structures of [AB25/Cu(II)/ED-cotton] and [Calma/Cu(II)/ED-cotton] are presented in Figure 6.

Effect of the temperature on the adsorption of dyes onto Cu(II)-ED-cotton

The effect of the temperature on the adsorption of AB25 onto [Cu(II)/ED-cotton] complex is shown in Figure 7. As generally observed, the adsorption of dyes from aqueous solution is affected by the temperature with the adsorption capacity being decreased remarkably as the temperature increased. This is possibly due to the exothermic effect from the surroundings during the adsorption process. At 80°C, the adsorption capacity is practically null indicating that the [Cu(II)/ED-cotton] complex is no efficient as adsorbent of dyes at high temperatures. On the other hand, the heating has no great influence on the adsorbed Cu(II) ions, which remain close to C_a. On cooling, dye molecules are again adsorbed on the [Cu(II)/ED-cotton] support, indicating a reversible phenomenon. Heating the ternary complex [Dye/Cu(II)/ED-cotton] in aqueous medium can be used as an efficient method to regenerate the binary system [Cu(II)/ED-cotton]. Finally, the ED-cotton can be valorized in terms of dyes and Cu(II) ions depollution by a ternary complex [Dye/Cu(II)/ED-cotton] at low temperatures or only Cu(II) ions depollution by a binary system [Cu(II)/ED-cotton] at both low and high temperatures.

Adsorption isotherms

A number of equations exist enabling the distribution of dye between the adsorbent and the dye solution, at equilibrium, to be correlated. Three widely used forms, namely those of Langmuir, Freundlisch, and Jossens, were used to evaluate the sorption behavior of the modified cotton.

Analysis of the adsorption of dyes onto Cu(II)/ED-cotton through the Langmuir isotherm

The Langmuir equation in its linear form is given as:[12]

$$\frac{C_e}{Y_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (2)$$

where Q represents the adsorbate concentration in the solid phase for a complete monolayer coverage

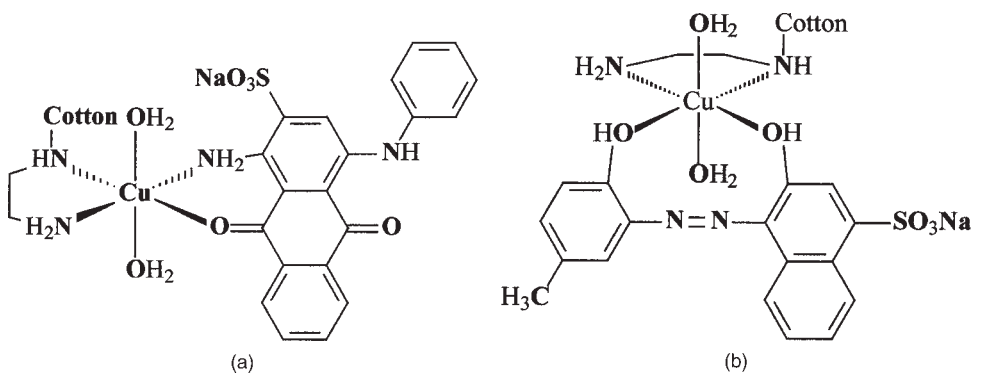

Figure 6 Proposal of associative structures between (a) AB25 and Cu(II)/ED-cotton complex and (b) Calma and Cu(II)/ED-cotton complex.

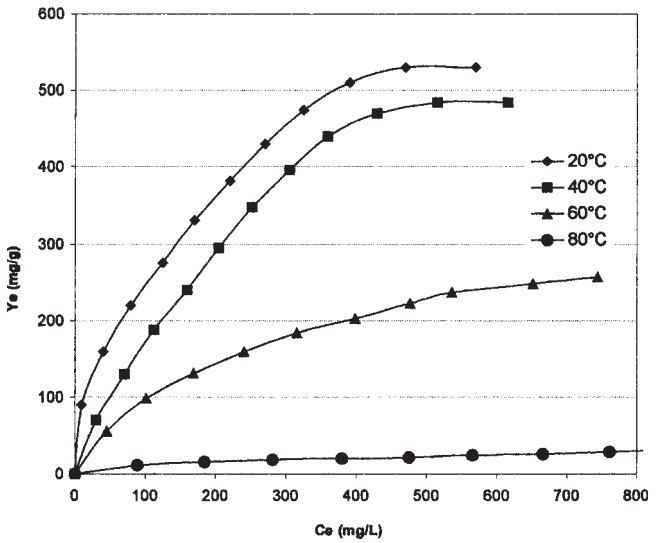

Figure 7 Influence of the temperature on the adsorption of AB25 on Cu(II)/ED-cotton complex.

or, if not possible, for the limit adsorption capacity (mg/g) on sites and b is the Langmuir constant related to adsorption energy (L/mol). The product $Q{\cdot}b = K_L$ is the Langmuir equilibrium constant. Plotting the ratio of concentrations in the solution (C_e) and in the solid (Y_e) versus the solution concentration gave straight lines (e.g., Fig. 8) from which the Langmuir constants for all the studied systems were estimated and presented in Table III. For the two tested dyes, the three values of C_a, the maximum solid-phase dye concentration at the equilibrium Y_{ref} and Q were always very close to each other, whatever the temperature considered. These results confirm a strong coordinating interaction between dyes and [Cu(II)/ED-cotton] system and confirm that the formed ternary complexes [dye/Cu(II)/ED-cotton] possess the stoichiometry 1/1/1 for AB25 and 0.75/1/1 for Calma.

This modeling involved $K_L = Q{\cdot}b$ (L/g). K_L represented the equilibrium constant and can be used to determine the enthalpy of adsorption, ΔH, using the Clausius–Clapeyron equation:[13]

$$K_L = A \exp(-\Delta H/RT) \tag{3}$$

$$\log K_L = \frac{-\Delta H1}{2.303RT} + \log A \tag{4}$$

Figure 9 shows a plot of log K_L versus $1/T$ for the adsorption of the two tested dyes onto [Cu(II)/ED-cotton] binary system. The associated enthalpies when a solvated dye molecule is adsorbed onto the [Cu(II)/ED-cotton] support for AB25 and Calma are −49.23 and −63.81 kJ/mol, respectively. As it is reflected from the negative heat of adsorption values, adsorption is an exothermic process and is responsible for the reduction in adsorption as the temperature is increased. Heat of adsorption values show that the physical adsorption take place in the adsorption of AB25 and Calma on [Cu(II)/ED-cotton] support.

The essential characters of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L, which is defined as follow:[14–16]

$$R_L = \frac{1}{1 + b\,C_{\text{ref}}} \tag{5}$$

where C_{ref} is the highest fluid-phase concentration. The R_L values between 0 and 1 indicate favorable adsorption of dyes onto [Cu(II)/ED-cotton] binary system. The values of R_L for each adsorbent/adsorbate system are given in Table III. The two tested dyes systems show favorable adsorption, namely, $0 < R_L < 1$.

Analysis of the adsorption of dyes onto Cu(II)/ED-cotton through the Freundlich isotherm

The Freundlich equation has the general form:[17]

$$Y_e = P(C_e)^{1/n} \tag{6}$$

where P and $1/n$ are characteristic constants. Equation (6) linearizes in logarithmic form

$$\log Y_e = \log P + \frac{1}{n} \log C_e \tag{7}$$

for the convenience of data fitting and parameter evaluation. P was taken as a relative indicator of adsorption capacity, while $1/n$ is indicative of the energy or intensity of the reaction. Figure 10 shows typical

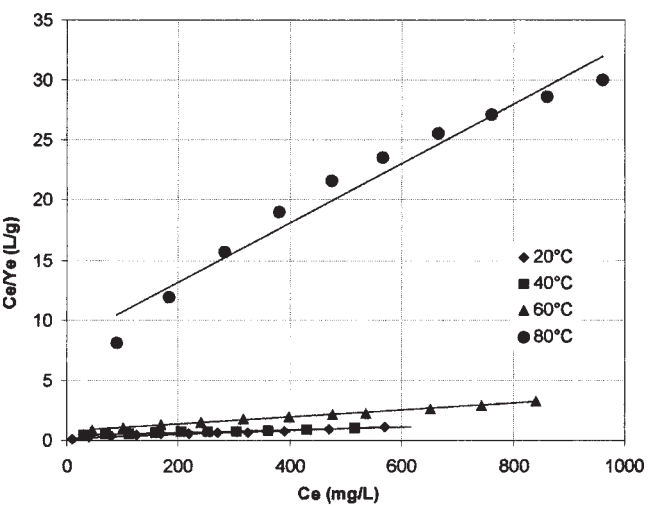

Figure 8 Influence of the temperature on Langmuir isotherms for the adsorption of AB25 on Cu(II)/ED-cotton complex.

TABLE III
Langmuir Constants and Enthalpy of Adsorption of the Dyes on Cu(II)/ED-Cotton

			Langmuir constants				
Dyes	T (°C)	Y_{ref} (mg/g)	Q (mg/g)	K_L (L/g)	b (L/mg)	R_L	ΔH (kJ/mol)
AB25	20	530	533	4.8	0.009	0.2	−49.23
	40	485	480	2.4	0.005	0.3	
	60	260	260	1.3	0.005	0.2	
	80	32	30	0.12	0.004	0.2	
Calma	20	372	374	4.87	0.013	0.1	−63.81
	40	333	315	1.9	0.006	0.2	
	60	160	160	0.32	0.002	0.3	
	80	21	20	0.06	0.003	0.3	

Freundlich plots for the two tested dyes and Table IV lists the Freundlich constants P and n using various temperatures. 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 the theories.[18] In all cases, the exponents are $n > 1$, showing that the adsorption is favorable.

Analysis of the adsorption of dyes onto Cu(II)/ED-cotton through the Jossens isotherm

The modeling with Jossens equation[19]

$$Y_e = \frac{iC_e}{1 + j(C_e)^m} \tag{8}$$

represents a combination between the two previous models, of Langmuir and Freundlich, as it was previously demonstrated[20] and it represents three constants i, j, and m. These constants, obtained from adsorption data by an iterative procedure, are given in Table IV. Figure 11 shows that this last model better fits the experimental data, as compared to Langmuir and Freundlich models, for AB25.

CONCLUSIONS

A specific sorbent namely ED-cotton is prepared by the reaction of ED with 6-chlorodeoxycellulose in aqueous medium. This sorbent exhibits a high capacity for Cu(II) ions complexation at pH 6. When the amino groups of ED-cotton are already involved in a Cu(II) ions complex, high adsorptive capacities were observed for AB25 and Calma dyes as ligand in the metal-coordinating process, namely, 530 mg or 1.27 mmol and 372 mg or 1.03 mmol, respectively. The optimal processing conditions for the adsorption of dyes onto Cu(II)/ED-cotton system were determined to be a pH of 6 and a temperature of 20°C. A 1/1/1 dye/metal/ED-cotton stoichiometry is observed for AB25 and 0.75/1/1 for Calma. The isotherms of Langmuir, Freundlich and Jossens were used to evaluate the sorption behavior of AB25 and Calma. The Jossens model was more suitable for this sorption process. The influence of the temperature was studied and enthalpies of adsorption were determined. With regards to its main use (purification and recycling of industrial wastewater), this complex has the possibility of being an effective adsorbent in terms of Cu(II)

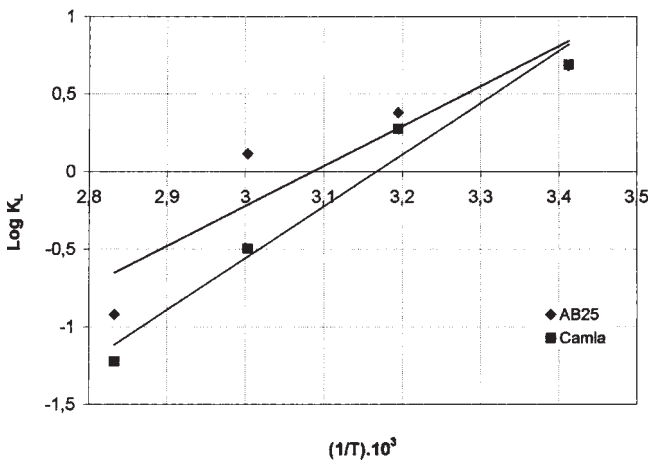

Figure 9 Log K_L versus reciprocal of temperature.

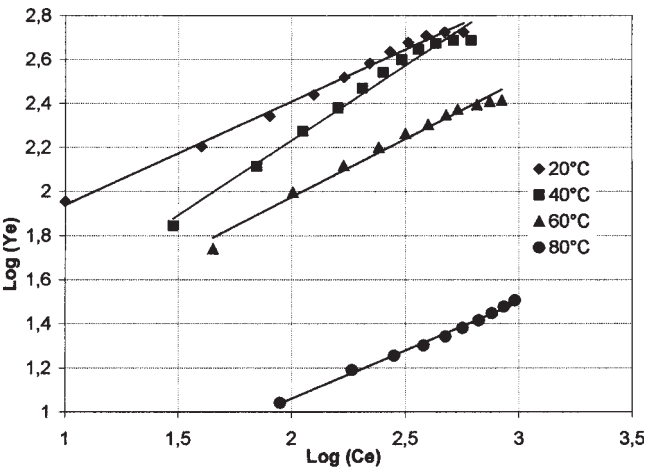

Figure 10 Freundlich analysis for the adsorption of AB25 on Cu(II)/ED-cotton complex at different temperatures.

TABLE IV
Freundlich and Jossens Constants for the Adsorption of the Dyes onto Cu(II)/ED-Cotton

		Freundlich constants		Jossens constants			Correlation
Dye	T (°C)	P	n	i (L/g)	j (L/mg)	m	coefficient
AB25	20	29.41	2.12	11.04	0.14	0.66	0.997
	40	7.50	1.47	1.70	6.73	1.87	0.975
	60	8.14	1.89	1.45	0.01	0.91	0.990
	80	1.52	2.27	1.37	0.83	0.56	0.998
Calma	20	19.53	2.07	2.72	0.05	1.38	0.995
	40	6.77	1.61	1.40	0.02	1.76	0.966
	60	0.10	1.33	0.54	0.08	0.46	0.974
	80	0.30	1.57	0.04	0.06	1.42	0.972

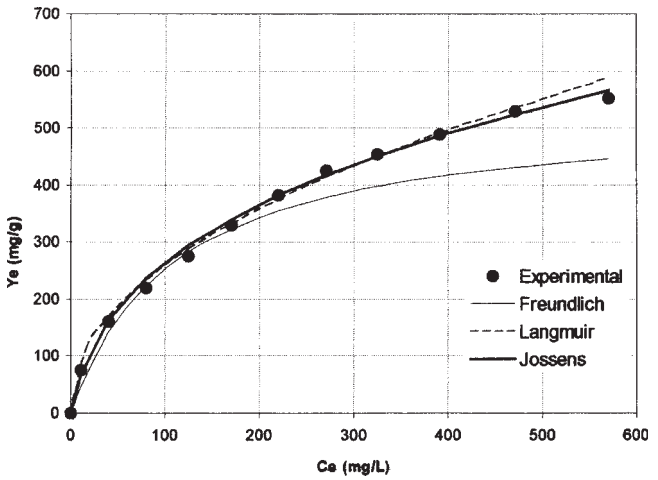

Figure 11 Comparison of theoretical isotherms with experimental data for the adsorption of AB25 on Cu(II)/ED-cotton complex; temperature = 20°C.

ions depollution by a binary system [Cu(II)/ED-cotton] or dye and Cu(II) ions depollution by a ternary complex [Dye/Cu(II)/ED-cotton].

NOMENCLATURE

A pre-exponential factor in Clausius–Clapeyron equation
b constant related to the energy of adsorption (L/g)
C_e dye concentration in solution at equilibrium (mg/L)
C_0 initial dye concentration in solution (mg/L)
C_{ref} highest fluid-phase concentration (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)
m constant in Jossens isotherm
n adsorption intensity
P measure of adsorption capacity [mg(mg/L)$^{1/n}$/g]
Q dye concentration at monolayer coverage (mg/g)
q_{ref} the maximum quantity of adsorbed Cu(II) ions at pH = 6 (mmol/g)
R universal gas constant (kJ mol^{-1} K^{-1})
R_L dimensionless constant separation factor
Y_e dye concentration at equilibrium (mg/g)
Y_{ref} maximum solid-phase dye concentration (mg/g)

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