Adsorption of Acid Dyes from Aqueous Solution on a Chitosan-cotton Composite Material Prepared by a New Pad-dry Process

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ABSTRACT

In this paper, we developed a method that may be considered as an easy and economical way to prepare chitosan-cotton composite (CH-cotton) materials using an electrolytes-free pad-dry process in which the cure step was performed in an oven microwave to provide a cotton fabric with greatly enhanced affinity for acid dyes. Evidence of successful interaction between cotton and CH through formation of hydrogen bonding and/or ion dipole interactions was analysed by FTIR spectroscopy. Influence of cure time onto the weight per surface unit of samples has been studied and five CH-cotton composite materials with different %CH content (I-V) were prepared. Crosslinking of cellulosic chain molecules of cotton fiber through CH segments was confirmed by Wrinkle Recovery Angle (WRA) and Tensile properties measurements. CH-cotton samples were then tested as adsorbent of four acid dyes from no-electrolytes aqueous solution [Indigo Carmine (AB74), Acid Red 183 (AR183), Acid Blue 161 (AB161) and Acid Yellow 17 (AY17)]. Results were monitored using, reflectance spectro-colorimeter and spectrophotometer analyses. Data obtained with treated cotton showed better dye exhaustion than obtained with untreated one. The modelling of the adsorption isotherms was performed by Langmuir equation and the thermodynamic parameters were evaluated. Globally, the lack of affinity of cotton for acid dyes is widely overcome by the use of low %CH content ranging from 0.079 to 0.515

INTRODUCTION

Acid dyes are typically only applied to fibres with positive charges such as polyamide in an acidic bath. They are not used for cotton coloration owing to their low affinity for the fiber and small molecular size that makes it easy for the dye molecules to move out in water. However, the fact that cationic cotton can also be effectively dyed with acid dyes is demonstrated in the literature [1, 2].

A number of studies on cotton dyeing have been carried out to improve the dye uptake and fastness properties [3-5]. Rastogi et al. [6] created affinity in cotton for acid dyes by introducing cationic sites in the fibre. Cotton fabrics were treated with a cationic agent, Discofix DBA, and then dyed. It was found that the dyed cationized cotton exhibited a good colour yield and wet fastness properties even without mordanting. In addition, poly(ethyleneimine) (PEI) has been used as a cationic agent in cotton dyeing with acid dyes [7]. It was found that PEI increased the dye adsorbed on cotton and also decreased the dye desorption from the fibre. Rattanaphani et al. [8] have investigated the adsorption and thermodynamics of acid dyeing of cotton pretreated with CH compared with untreated cotton. The effect of sodium chloride (NaCl) on the dyeing process with, and without, pH control was studied. Results were compared with those from the acid dyeing of pretreated and untreated cotton with CH.

We have previously developed cationic cellulosic materials for several applications [9-12]. Now, in this experiment, we propose to describe the elaboration of CH-cotton composite material with differing %CH content using an easy and economical technique. Then, prepared materials were characterized and the adsorption capacity of four acid dyes from aqueous solutions, under several experimental conditions was reported without applying electrolytes in the dye bath. Comparison of dye exhaustion onto CH-cotton materials with that of untreated cotton fabric was carried out using different analyses. The effect of temperature on the exhaustion rate of dyes for

each adsorbent/adsorbate system has been also investigated. The modelling of the adsorption isotherms was also performed by Langmuir equation and the thermodynamic parameters were evaluated.

EXPERIMENTAL METHODS

Dyestuffs

Four different commercial available textile dyestuffs were used in this study. All dyestuffs were purchased from Sigma Aldrich (Chemi Sarl, Saint Quentin Fallavier, France) and used without further purification. The characteristics and chemical structures of the selected dyestuffs are listed in *Table I* and *Figure 1*, respectively.

TABLE I. The Physical and Chemical Characteristics of the Selected Dyes

Dye (C.I. Name)	Supplier	λ_{max} (nm)[a]	Purity[b] (%)	Molecular Weight (g/mol)	Chemical Structure[c]
Indigo Carmine	Aldrich	614	90	537.38	AB74
Acid Red 183	Aldrich	498	60	584.87	AR183
Acid Blue 161	Aldrich	609	40	416.39	AB161
Acid Yellow 17	Aldrich	412	60	551.3	AY17

[a]Measured experimentally, [b]Given by the Supplier, [c]See *Figure 1*

.

Cotton Fabric Preparation

The cotton fabric used was supplied by SITEX (Société Internationale de Textile, Sousse, Tunisia). To remove the wax and impurities, the cotton fabric was put in boiling water (liquor ratio of 1:40 w/v) to which 1.5 mL/L of sodium hydroxide (10M), 4 g/L of non-ionic detergent and 3 g/L of sodium carbonate were added. The mixture was boiled for 90 min. The cotton was then removed, washed with hot water and cold water in order to avoid break down of the emulsion and precipitation of the impurities on the cotton, squeezed to remove excess liquor and then air dried. Finally, it was washed with distilled water. The purified but unbleached cotton was then dried at room temperature.

Then, subjected to a bleach process: cotton fabric was treated with a solution containing 87.5 mL/L NaOCl (12°) and 2 g/L of sodium carbonate in a bath with a liquor ratio of 1:40 (w/v) (the pH of the solution was adjusted to 9 – 10 using 0,1M NaOH and was maintained throughout the experiment) for 60 min at room temperature, after it was thoroughly rinsed with cold water. Cotton fabric was then removed and applied to a solution containing 5 mL/L of sodium bisulfite, $NaHSO_3$ (5M), and 0.5 mL of H_2SO_4 (density =1.84) at 30°C for 15 min at room temperature, rinsed with distilled water and air-dried. Auxiliaries were all laboratory grade chemicals and purchased from Sigma Aldrich.

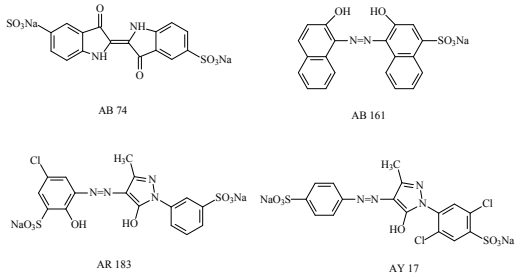

FIGURE 1. Chemical structure of the selected dyes

Preparation of CH-Cotton Composite Material by Pad Dry Cure Process

Chitosan (2-Amino-2-deoxy-(1→4)-β-D-glucopyranan, total impurities <1%, viscosity > 400 m Pa.s) was purchased from the Sigma Aldrich Chemical Company. CH solution was prepared by stirring 1g of CH powder in 1% (v/v) aqueous acetic acid solution (85%) until complete dissolution at 90°C. Approximately 7.5 cm^2 textured bleached cotton fabric samples, prepared as previously noted, were immersed directly in 100 mL aqueous solutions of CH squeezed to a wet pick up of 100%. Then, pinned to the original dimensions, dried at 90°C for 5 minutes and finally placed in an oven microwave at 800 Watt for different cure times. After being returned to room temperature, samples were thoroughly rinsed with distilled water to remove the non-reacted amount of CH and washed using 2 g/L non-ionic wetting agent at 100°C for 10 minutes, rinsed with hot and cold water and finally oven-dried at 40°C for 24 h. Five samples of CH-cotton (I-V) with different weight per surface unit [M (g/m^2)] were prepared and listed in *Table II.*

TABLE II. Colour Coordinates of the Untreated Cotton and CH-cotton Materials.

Samples	Time (s)	M (g/m^2)	% CH	Colour coordinates				
				*L**	*a**	*b**	*c**	*h*
Cotton	0	238.568	0	92.89	0.08	2.22	2.22	87.99
I-CH-cotton	20	238.757	0.079	92.65	-0.3	2.11	2.13	98.14
II-CH-cotton	40	238.947	0.158	92.32	-0.35	2.3	2.37	98.45
III-CH-cotton	60	239.136	0.238	91.53	-0.38	2.49	2.52	98.72
IV-CH-cotton	80	239.609	0.436	91.65	-0.28	2.95	2.89	95.65
V-CH-cotton	100	239.799	0.515	91.87	-0.24	3.39	3.4	94.05

The weight per surface unit of the control sample and prepared composite material was measured, according to a standard method prescribed by [NF G 07-104]. It was calculated using the following equation:

$$M = m \times \frac{10000}{s} \quad (1)$$

Where *m* is the mass of the sample (g) and *s* is the surface of the same sample (cm^2). %CH add-on was defined according to equation:

$$\%\ CH = \frac{M_f - M_0}{M_0}.100 \quad (2)$$

Where M_f and M_0 are the weight per surface unit of the treated and untreated material respectively.

Figure 2 shows that the weight per surface unit obtained by CH application to cotton fabric is slightly higher and increase with the increment in the cure time. After 100s, the weight per surface unit amplified only 0.5%. This could be related to the viscosity and solubility properties of CH. More weight add-on can be obtained but thermal degradation of CH-cotton has been observed during the cure process.

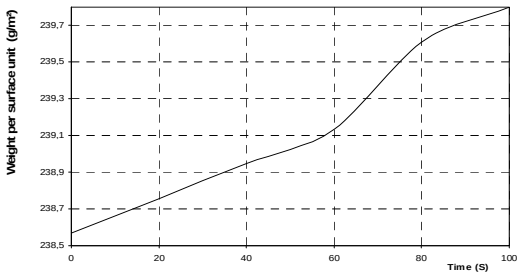

FIGURE 2. Variation of the Weight per surface unit (g/m^2) versus time.

Characterization of CH-Cotton Composite Material by FT-IR Spectroscopy

The nature of the interaction between the two polymers CH and cotton is of interest to our present study. FTIR has often been used as a useful tool in determining specific functional groups or chemical bonds that exist in a material. The presence of a peak at a specific wavenumber would indicate the presence of a specific chemical band. For CH and CH-cotton composite material, if specific interactions took place between the two polymers, the most obvious and significant difference would be the appearance of new peaks or shift of existing peaks. *Figure 3* shows the FTIR spectra of bleached cotton (a), CH powder (b), I-CH-cotton (c) and V-CH-cotton (d) composite material and were obtained with a Perkin-Elmer 1760-X Infrared Fourier (FTIR) spectrometer. The FTIR spectrum of CH in *Figure 3b* shows peaks assigned to the saccharide structure at 899 and 1153 cm^{-1}, the amine group peak at around 1601 cm^{-1} and the OH and NH peaks centred at 3428 cm^{-1}. Additionally, examination of the FTIR spectra of I-CH-cotton and V-CH-cotton composite materials in *Figure 3c* and *d* revealed an obvious difference in the intensity of amine group peak as mentioned above. The intensity of this band is related to the amount of CH incorporated in the composite material. Compared to FTIR spectrum of bleached cotton in *Figure 3a*, its appearance not only confirms the presence of CH, but allows an easy monitoring of the chemical interactions of the amino groups. The FTIR spectrum of bleached cotton in *Figure 3(a)* shows peak for the OH functional groups at 3413 cm^{-1}, the most obvious difference in the spectra for cotton, I-CH-cotton and V-CH-cotton is observed to be the shift of the broad peak for OH and NH groups from 3413 to 3434 and to 3469 cm^{-1} with the increase of CH content in CH-cotton composite material, indicating that an increased amount of amine groups were incorporated into the cotton matrix and interacted with the OH groups of cotton [13].

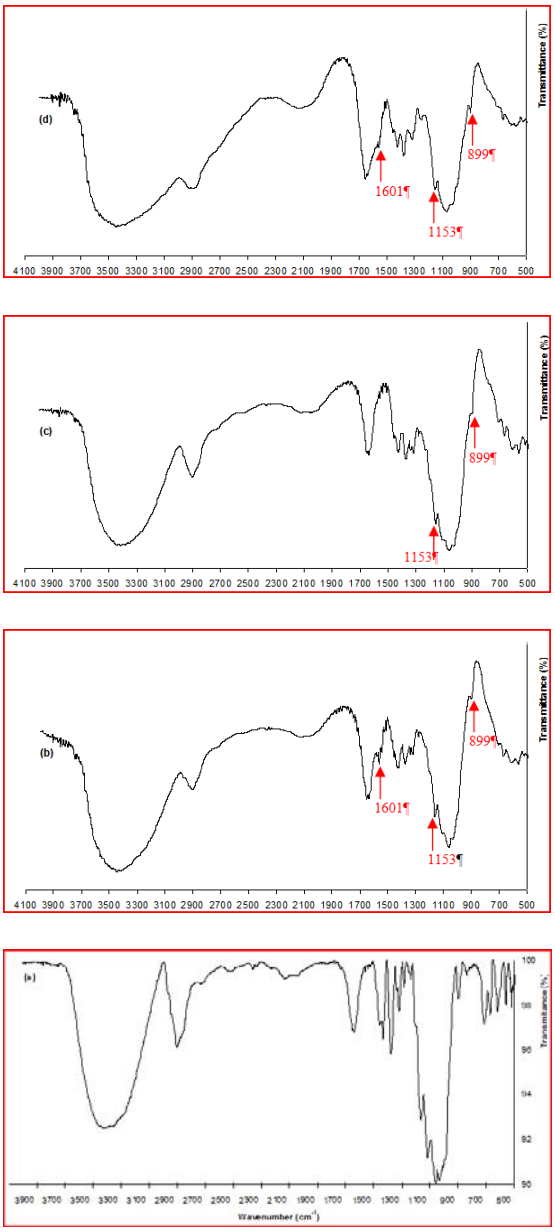

FIGURE 3. Infrared spectrums of bleached cotton (a), CH powder (b), I-CH-cotton (c) and (d) – V-CH-cotton.

Figure 4 proposes a sort of interaction of CH with cotton under acidic conditions. In fact, the CH contains amine groups, -NH2, which would be in the protonated cationic form (-NH3+) in acidic solution, in contact with the nucleophilic surface of bleached cotton, it could be interacted via hydrogen bonding and/or ion-dipole interactions forming crosslinked biopolymers composites.

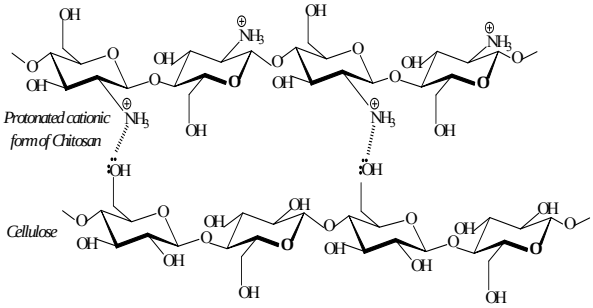

FIGURE 4. Chemical structure of CH-cotton composite material.

Adsorption of Dyestuff onto CH-cotton Composite Material

The lack of affinity of cotton for anionic dyes is currently overcome by the use of high concentrations of electrolytes in the dye bath (such as sodium chloride and sodium sulfate). The high concentrations of electrolytes serve a dual role; overcoming the negative charge built-up on the cotton fibre and reducing the solubility of the dye. Present work has introduced a process designed to provide a cotton fabric with greatly enhanced affinity for acid dyes, without use of electrolytes. The prepared CH-cotton composite materials (I-V), untreated samples and 100 ml dye solution of the initial concentration C_0 are just stirred mechanically in an Ahiba Nuance® laboratory machine for a period of 2 h at different temperatures. The pH of dye bath is maintained at 6 using buffer solution. 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 (λ_{max}) and the solute concentration in the solid phase, Y_e, is then deduced by the difference (C_0-C_e). Adsorption isotherms are studied under modification of the two parameters: %CH and dye-solution temperature.

RESULTS AND DISCUSSION

Wrinkle Recovery Angle

Since CH is a high molecular weight polymer, its application to cotton can affect its feel and other physical properties [3]. Physical properties of CH-cotton composite material were compared to control cotton fabric by measuring the Wrinkle Recovery Angle (WRA) [Crease Recovery Angle Tester AATCC 66-1989] in dry state. It can be seen from *Figure 5* that CH-cotton composite material showed much higher wrinkle resistance as compared to control sample. In fact, the WRA increased by increasing the %CH. The enhancement in the WRA is reasonable, since increasing the %CH will increase the availability of cross-linking molecules and consequently increase its accessibility to crosslink the cellulosic hydroxyls. WRA reached 90 units when %CH achieved 0.5, indicating a high improvement as

compared to the initial value (65) for lower %CH add-on.

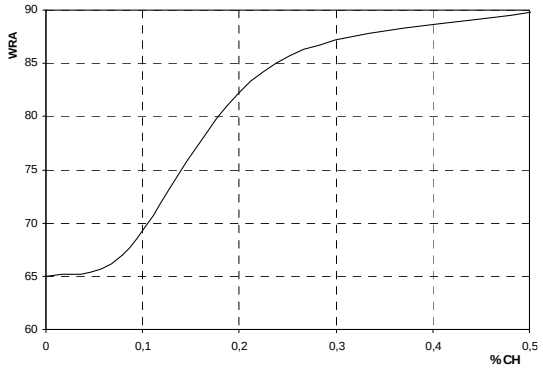

FIGURE 5. Variation of WRA versus %CH.

Tensile Properties of CH-cotton Composite Material

Tenacity of some selected fabric samples were measured, according to a standard method prescribed by [NF G 07-001] using a Cantilever Test Method LLOYD®. The results obtained were based on an average of 10 tests in the warp direction of each sample. The test strip specimens were ravelled to a size of 50 mm × 20 mm between the jaws of the machine and the tests were performed with a traverse speed of 100 mm/min at a pretension of 0.5 N. Elongation test (mm) at break was given in *Figure 6*. It can be seen from experimental data that increasing the %CH leads to an increment in the values of tensile strength. This increment may be due to the crosslinking action and amount of CH linked to cellulose through the formation hydrogen bonding and/or ion dipole interaction. Elongation in dry state became constant from 0.2%CH indicating that II-CH-cotton is already more resistant to breaking than cotton.

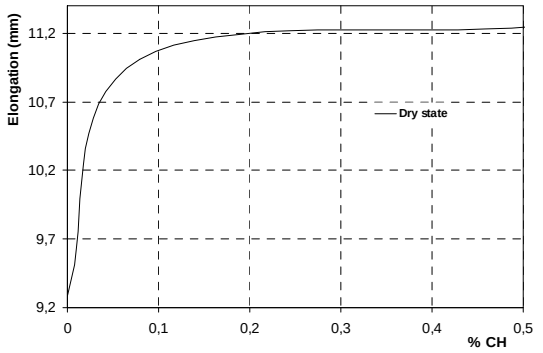

FIGURE 6. Variation of the elongation versus % CH.

Colorimetric Measurements

Non dyed CH-cotton Composite Material

The colour changes of CH-cotton composite material against %CH were measured using the L^*, a^*, b^* coordinates of the CIE [Commission International d'Eclairage, 1976] colour space. Five parameters were, therefore, recorded; chromaticity parameters [a^* (red-green) and b^* (yellow-blue)], lightness (L^*), the parameter (h) which represents what we call «colour» in the current language (it distinguishes the objects of the qualifiers red, green, blue, etc independently of the brightness of these objects) and finally the notion of coloration degree, that means the "saturation", can be approached by the parameter (c^*). In fact, the saturation tries to express the degree with which a colour, pure in the beginning (saturated), can be «washed» of white. It can be seen from the experimental data obtained by reflectance spectrocolorimeter that treating bleached cotton fabrics in the presence of different %CH can provide CH-cotton composite material other colour properties. Variation of the five colour coordinates parameters reported in *Table II* confirm that the discoloration is much more important in CH-cotton composite material than in bleached cotton, and is more significant in CH-cotton samples with higher %CH.

In addition, *Figure 7* showed that the reflectance (R%) decreased on increasing %CH, in particular, for wavelength value higher than 550 nm indicating that the CH-cotton composite material had a yellow appearance.

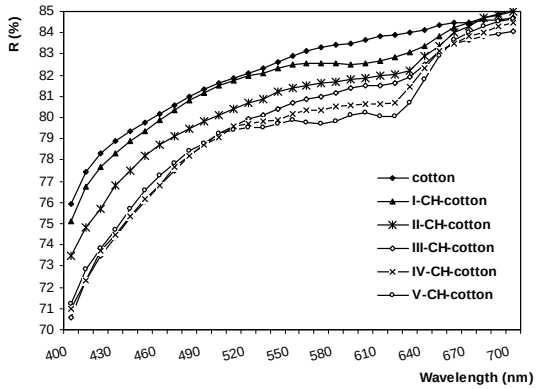

FIGURE 7. Variation of the reflectance [R (%)] of non dyed CH-cotton material versus %CH

Dyed CH-Cotton Composite Material

Figure 8 represented the variation of reflectance versus %CH for AB74 (a), AR183 (b), AB161 (c) and AY17 (d). It is clear that reflectance values of

dyed CH-cotton, as compared to the non dyed cotton, are a function of %CH for the four selected dyes. In fact, increasing the %CH leads to lower values. This behaviour could be attributed to the amount of dye attached to CH-cotton composite material through the interaction between the protonated amine group and the anionic group of the dye molecule. The explanation for this is that, in aqueous solutions, the acid dye was dissolved and the sulfonate group was dissociated and converted to anionic ions. The dye fixation process then proceeded due to the electrostatic interaction between cationic form (-NH_3^+) of CH-cotton and anionic dye ions. When the cationic sites increase, the maximum solid-phase dye concentration increase again. The registered minimum reflectance were observed at the wavelength 614 nm, 500 nm, 610 nm and 420 nm for AB74, AR183, AB161 and AY17, respectively and are in good agreement with those listed in *Table I.*

Additionally, the colour strength, expressed as K/S, was measured using the Kubelka-Munk equation [14]. The relationship between reflectance R(%), previously described, and colour strength was thus shown in equation (3).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{3}$$

Where K is the absorption coefficient and S is the scattering coefficient

Table III showed that the colour strength values for the four studied dyes increase with %CH in CH-cotton composite material and reached the highest values for V-CH-cotton.

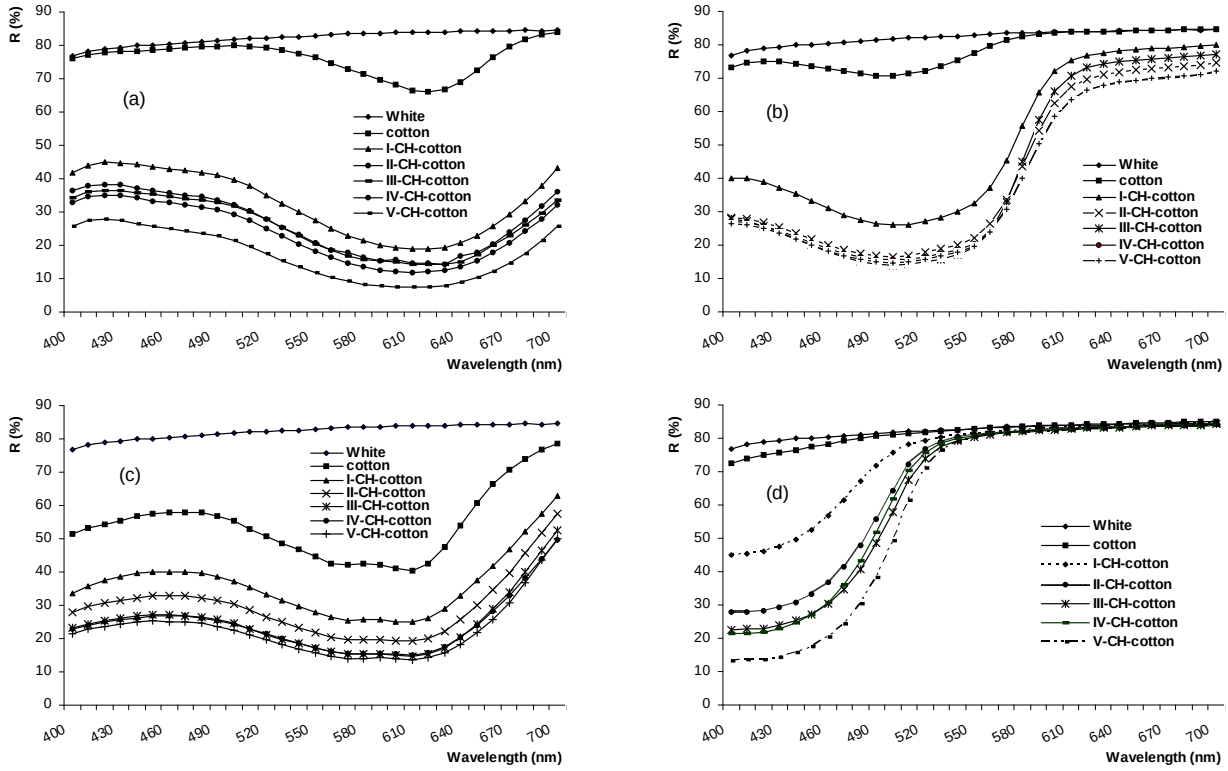

FIGURE 8. Reflectance for AB 74 (a), AR 183 (b), AB 161 (c) and (d) AY 17 versus %CH.

Additionally, it has been seen that the highest K/S was noted for AB74 compared with the selected ones, indicating that this dye has more affinity to CH-cotton than the others.

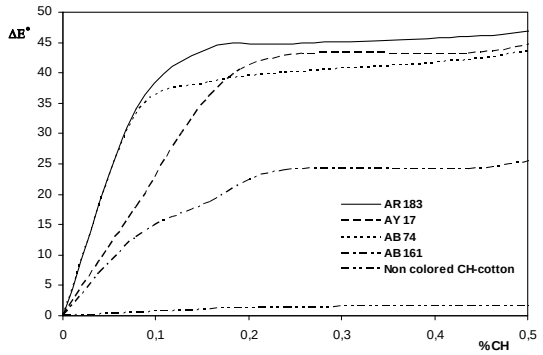

FIGURE 9. Total Colour Difference for AB 74 (a), AR 183 (b), AB 161 (c) and AY 17 (d).

Figure 9 showed the results accorded to the total colour difference (ΔE*) calculated according to the following equation, using the corresponding untreated material (bleached cotton) as reference [15]:

$$\Delta E^{*} = \left[(\Delta L^{*})^{2} + (\Delta a^{*})^{2} + (\Delta b^{*})^{2} \right]^{1/2} \quad (4)$$

Where: $\Delta L^{*} = L^{*} - L_0{}^{*}$; $\Delta a^{*} = a^{*} - a_0{}^{*}$; $\Delta b^{*} = b^{*} - b_0{}^{*}$ and ($L_0{}^{*}$, $a_0{}^{*}$, $b_0{}^{*}$) were defined as the colour coordinates values of the control samples of the four selected dyes. It can be easily concluded that increasing the amount of CH crosslinked to cotton leads to higher total colour difference values. In fact, the increment in %CH is accompanied by the increase in ($-NH_3^{+}$) sites responsible of the adsorption process of dyes. Each colour difference reported in this paper is the average of three measurements. From 0.238 %CH, ΔE* reached approximately constant values for the four selected dyes, revealing that II-CH-cotton may be considered efficient for the adsorption of acid dyes. In fact, no additional total colour difference was observed above.

Evaluation of Dye Uptake onto Composite Material

The percentage dye exhaustion (*Ex*.[%]) for selected dyes was determined by comparing concentration C_0 and C_e of dye in dye bath before and after adsorption, respectively. It was calculated according to the following expression [16]:

$$Ex.[\%] = \frac{C_0 - C_e}{C_0} \quad (5)$$

As seen from *Table III*, high sorption capacities were noted, CH-cotton composite material showed a higher dye uptake than the untreated cotton. The highest values were observed for AB74 dye onto V-CH-cotton. This behaviour was also in agreement with colour strength data discussed earlier.

Effect of Temperature on the Adsorption of Dyes

As mentioned and discussed above, the application of CH to cotton fabric could provide a significant enhancement of dye uptake from aqueous solution. However, the adsorption phenomenon is usually affected by many parameters, particularly temperature. In fact, the temperature affects two major aspects of adsorption: the equilibrium position in relation with the exothermicity of the process and the swelling capacity of the adsorbent. Thus, adjustment of temperature may be required in the adsorption process. The effect of temperature on the adsorption of dyes such as AB74 is shown in *Figure 10*. As generally observed, the uptake capacity of CH-cotton composite material decreases with increasing temperature, due to the enhanced magnitude of the reverse (desorption) step in the mechanism. The interactions established between CH-cotton and dyes are therefore reversible in this case. This is possibly due to the exothermic effect of the surroundings during the adsorption process [8].

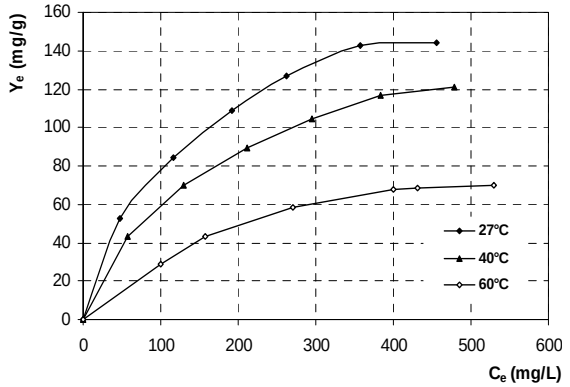

FIGURE 10. Effect of Temperature on the Adsorption of AB74 onto I-CH–cotton.

Adsorption Isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and so are critical in optimising the use of adsorbents. Therefore, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption system to remove dye from effluent. It is so important to establish the most appropriate correlation for the equilibrium curves. The distribution of dye between the adsorbent and the solution, at equilibrium, has been expressed using various equations. In most previous adsorption works, we have adopted either the Langmuir, Freundlich or Jossens isotherms for adsorption data correlation [9-11]. The Langmuir isotherm is valid for dynamic equilibrium adsorption–desorption processes on completely homogeneous surfaces with negligible interaction between adsorbed molecules [17]. The expression of the model data then allowed us to get physical interpretations of the adsorption process and to deduce the thermodynamic parameters from the equilibrium constants.

Langmuir Isotherm

The experimental equilibrium data for the uptake of the four dyes by CH-Cotton material have been correlated with the rearranged Langmuir's model of adsorption [17]. In the Langmuir model it is assumed that the thickness of the adsorbed layer is monomolecular in nature. The model assumes uniform energies of adsorption on a surface containing a finite number of identical sites. The linear form of the isotherm has been used to analyse the experimental data. It was given by the following equation [18]:

$$\frac{C_e}{Y_e} = \frac{1}{K_L} + \frac{C_e}{Q_L} \qquad (6)$$

Where C_e and Y_e are the equilibrium dye concentrations in the aqueous (mg. L^{-1}) and solid (mg.g^{-1}) phases, respectively; Q_L and K_L are Langmuir constants related to the capacity of adsorption and energy of adsorption, respectively. A plot of C_e/Y_e versus C_e [*Figure 11*] yield the Langmuir equilibrium constant K_L. *Table III* summarized the values of K_L for the different studied adsorbate/adsorbent systems.

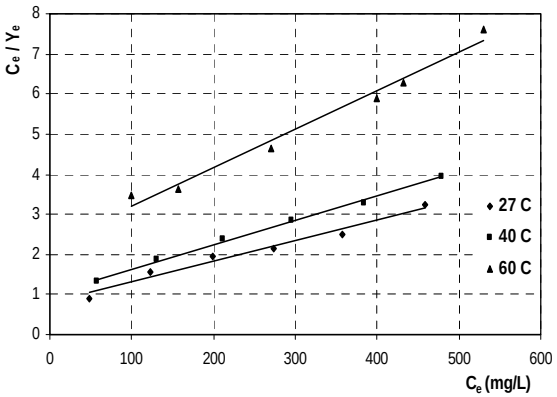

FIGURE 11. Langmuir plots for I-CH–cotton, MLR = 1:100, contact time = 2 h.

Thermodynamic Study

The equilibrium constant K_L may be used to determine the enthalpy of adsorption, $\Delta H°$, using the Clausius-Clapeyron equation [19].

TABLE III. Colour Strength, Dye Exhaustion, Thermodynamic Parameters values and Effect of the Temperature on the Adsorption of Dyes onto CH-cotton Composite Material

Dyes	Samples	Temperature (°C)	K/S	*Ex.*[%]	Y_e (mg/g)	K_L (mL/mg)	ΔG° (KJ)	ΔH° (KJ)	ΔS° (J/K)
AB74	Cotton	27	0.79	19.815					
	I-CH-cotton	27	1.713	62.185	66	11.3	-6.05		
		40			60	10	-5.99	-12.96	-21.66
		60			55	6.6	-5.22		
	II-CH-cotton	27	2.419	83.193	85	10.6	-5.89		
		40			80	9	-5.72	-12.79	-21.27
		60			71	6.3	-5.1		
	III-CH-cotton	27	2.71	88.403	89	8.8	-5.42		
		40			82	7.1	-5.1	-12.35	-20.04
		60			71	5.4	-4.67		
	IV-CH-cotton	27	3.227	90.924	92	8.6	-5.37		
		40			83	7.3	-5.17	-12.84	-21.43
		60			75	5.1	-4.51		
	V-CH-cotton	27	5.803	91.429	92	8	-5.19		
		40			85	6.1	-4.71	-12.24	-19.89
		60			78	5	-4.46		
AR183	Cotton	27	0.06	2.526					
	I-CH-cotton	27	1.052	25.553	40	10	-5.74		
		40			33	7.2	-5.48	-5.27	-7.78
		60			28	8.6	-5.69		
	II-CH-cotton	27	1.798	32.132	50	9.2	-5.54		
		40			42	9	-5.72	-6.36	-2.2
		60			38	7.3	-5.39		
	III-CH-cotton	27	2.295	35.421	56	8	-5.19		
		40			48	7.8	-5.35	-6.71	-5.49
		60			41	6.3	-4.96		
	IV-CH-cotton	27	2.533	57.789	63	9	-5.48		
		40			55	8.7	-5.63	-6.59	-4.44
		60			50	7	-5.31		
	V-CH-cotton	27	2.672	76.211	70	9.2	-5.54		
		40			64	7.8	-5.41	-6.38	-3.44
		60			58	7.4	-5.47		
	Cotton	27	0.043	2.222					
AB161	I-CH-cotton	27	1.137	31.852	33	10	-5.74		
		40			27	8.8	-5.66	-7.28	-3.94
		60			20	7.5	-5.58		
	II-CH-cotton	27	1.711	38.519	40	10	-5.74		
		40			30	8	-5.41	-7.21	-4.02
		60			25	7.7	-5.65		
	III-CH-cotton	27	2.397	45.926	47	7.9	-5.16		
		40			33	7	-5.06	-7.73	-5.32
		60			27	5.8	-4.87		
	IV-CH-cotton	27	2.452	56.296	63	8	-5.19		
		40			58	7.3	-5.17	-7.08	-3.19
		60			50	6	-4.96		
	V-CH-cotton	27	2.723	63.963	75	7.4	-4.99		
		40			70	6	-4.66	-7.53	-4.98
		60			65	5.6	-4.77		
	Cotton	27	0.045	3.265					
AY17	I-CH-cotton	27	0.33	4.807	13	6.2	-4.55		
		40			7	5.4	-4.39	-10.78	-14.89
		60			7	4	-3.84		
	II-CH-cotton	27	0.936	5.344	14	5.5	-4.25		
		40			9	4	-3.61	-10.22	-13.72
		60			8	3.8	-3.7		
	III-CH-cotton	27	1.318	15.695	17	6.3	-4.59		
		40			22	5	-4.19	-10.55	-14.47
		60			21	4.2	-3.97		
	IV-CH-cotton	27	1.437	29.259	41	6.8	-4.78		
		40			33	5	-4.19	-10.64	-15
		60			30	4.6	-4.22		
	V-CH-cotton	27	2.782	53.75	60	4.8	-3.91		
		40			53	4	-3.61	-10.27	-13.46
		60			50	3.2	-3.22		

$$K_L = A\exp(\frac{-\Delta H^\circ}{RT}) \quad (7)$$

The associated enthalpies, calculated through Plotting LnK_L versus $1/T$, when a solvated dye molecule is adsorbed onto the solid support are listed in *Table III*. The negative values indicate that heat is liberated during the adsorption process. The small negative values of ΔH° suggested the adsorption to be physical one. ΔG° and ΔS° thermodynamic parameters related to the adsorption process were also evaluated using the following equations [20, 21]:

$$\Delta G^\circ = -R \cdot T \cdot Ln(K_L) \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (9)$$

The free energy (ΔG°) change was evaluated using equation (8), while entropy (ΔS°) changes of the adsorption were calculated from equation (9). The results are reported in *Table III*. The negative value of the free energy indicated the spontaneous nature of the four studied dyes adsorption onto the different adsorbate CH-cotton materials. Also, the negative value of the entropy change was consistent with the decreased randomness after the adsorption of dyes.

CONCLUSION

To sum up, the present method may be considered as an easy and economical way to prepare CH-cotton composite material. IR spectroscopy analysis confirmed the evidence of interaction between cotton and CH. Changes or improvements in appearance, including WRA and tensile properties, are the direct consequences of cross-linking of cellulosic chain molecules of cotton fibre through CH segments formed during the pad-dry-cure process.

To test their capacities for the adsorption of four acid dyes, spectrocolorimeter and spectrophotometer analyses illustrated that high sorption capacities are thus found for AB74, AR183, AB161 and AY17, respectively. Moreover, it can be elucidated that the lack of affinity for acid dyes is widely overcome by the use of low %CH content ranging from 0.079 to 0.515. The effect of temperature on the exhaustion rate of dyes for each adsorbent/adsorbate system was reported, varying from 27°C to 60°C. As a result, the uptake capacity of CH-cotton composite material decreases with the increment in temperature values and hence indicating the exothermic effect of the surroundings during the adsorption process. The modelling of the adsorption isotherms by Langmuir equation has been studied and the thermodynamic parameters were evaluated. The enthalpy, the free energy (ΔG°) and the entropy (ΔS°) changes of the adsorption were calculated at various temperatures. These parameters then allowed us to deduce some results related to the exothermic and spontaneous nature of the adsorption phenomenon and the evolution of the disorder during the adsorption process. The negative value of the free energy indicated the spontaneous nature of the four studied dyes adsorption onto the different adsorbate CH-cotton materials. Also, the negative value of the entropy change was consistent with the decreased randomness after the adsorption of dyes. Application of CH onto cotton is thus an alternative way to create cationic sites on cotton. We have observed that some of the special characteristics and uses of CH-cotton composite materials, such as its use in adsorption, are clearly worthy of exploration in the context of the synthesis of composites. This method is also useful in preparing cellulosic materials containing immobilized amino groups. Such materials should have both the strength of cellulose and the functionality of CH. This work can be further extended to study wash durability and crocking tests that could significantly impact the potential utility of the technology adopted for the preparation of the studied composite material.

NOMENCLATURE

a^*: dimensionless chromaticity parameter

a_0^* : dimensionless chromaticity parameter related to the control sample

Δa^* dimensionless chromaticity colour difference

A: preexponential factor in Clausius–Clapeyron equation

b^*: dimensionless chromaticity parameter

b_0^* : dimensionless chromaticity parameter related to the control sample

Δb^* : dimensionless chromaticity colour difference

c^*: dimensionless parameter related to coloration degree

C_0: initial dye concentration in solution (mg/L)

C_e: dye concentration in solution at equilibrium (mg/L)

ΔE^* : dimensionless total colour difference

h: dimensionless parameter related to colour

K: absorption coefficient in kubelka-Munk equation

K_L: Langmuir energies constant

L^*: dimensionless lightness parameter

L_0^* : dimensionless lightness parameter related to the control sample

ΔL^* : dimensionless lightness colour difference

M: weight of the sample per surface unit (g/m^2)
m: mass of the sample (g)
Q_L: dye concentration at monolayer coverage (mg/g) related to Langmuir equation
R: reflectance (%)
R: universal gas constant (kJ mol^{-1} K^{-1})
s: surface of the sample (cm^2)
S: scattering coefficient in kubelka-Munk equation.
Y_e : the solute concentration in the solid phase (mg/g)
$\Delta H°$: enthalpy of adsorption (kJ/mol)
$\Delta G°$: free energy change (kJ/mol)
$\Delta S°$: entropy change (J/K)

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