Application of Hydrophilic Finished of Synthetic Fabrics Coated with CMC/Acrylic Acid Cured by Electron Beam Irradiation in the Removal of Metal Cations from Aqueous Solutions

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ABSTRACT: Modified textile fabrics were used to remove Cu^{+2} and Cr^{+3} ions from aqueous solutions. For this purpose, modified Nylon-6, polyester woven and knitted fabrics were prepared by coating the surface with a thin layer of aqueous solution of carboxymethyl cellulose (CMC) and acrylic acid (AAc) of thickness 25 μm. Radiation crosslinking of the coated layer was carried out by electron beam irradiation with a constant dose of 30 kGy. Morphology of the coated fabrics was examined by scanning electron microscope (SEM) which indicated the compatibility between the coated layer and fabrics. Properties attributed to the hydrophilicity, especially water uptake and weight loss before and after several washing cycles were followed up. The effect of AAc concentration on the hydrophilic properties of the coated fabrics was studied. A considerable enhancement in water uptake has been attained on increasing AAc content in solution in case of nylon-6 followed by polyester woven followed by polyester knitted fabrics. The performances of the modified textile fabrics were evaluated for the recovery of Cu^{+2} and Cr^{+3} from aqueous solution. The metal ion absorption efficiency of the modified textile fabrics was measured using UV Spectrophotometer analysis and EDX. Parameters affecting the efficiency of these textile fabrics in the removal of metal ions from aqueous solution namely, concentration of AAc and the immersion time were studied. It was found that there was a marked increase in the recovery of metal ions on increasing both immersion time and concentration of AAc. This study evidences that the modified textile fabrics can be used for the purpose of removal of some heavy metals such as Cu and Cr. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3098–3106, 2010

Key words: carboxy methyl cellulose; acrylic acid; hydrophilicity; electron beam

INTRODUCTION

In recent years, particular interest has been devoted to prepare hydrophilic materials exhibiting good water uptake properties. This subject will be the topic of more research. Sorption and permeability of water and water vapor to improve the comfort and wear properties of textiles can be enhanced by increasing the hydrophilic nature of synthetic fabrics.[1] Many workers have prepared hydrophilic substrates by introducing vinyl monomers containing hydrophilic groups such as acrylic acid[2] or acrylamide.[3] Another alternate method in practice to achieve hydrophilicity of natural or synthetic textile is the coating technique. It involves curing of a coated layer which contains hydrophilic groups.[4] Crosslinking of these coated layers can be carried out by chemical initial methods or by electron beam curing.[5] The advantage of electron beam curing over the chemical method is that it does not contain solvent and has no need of temperature.[6] One of the important polymers used in this technique is carboxymethyl cellulose (CMC). CMC is an anionic and water soluble natural polymer derivative. It is widely used in detergents, oil exploration, food applications, paper and textile industries due to its high viscosity.[7] Like many of other natural polymers, CMC is also a degradable polymer under irradiation but can be crosslinked to form hydrogel under suitable irradiating conditions, which has been reported by Liu.[8,9] CMC is a polymer which is largely used in the electron beam finishing. Many types of fabrics are subjected to these techniques. Among those there are synthetic and natural fabrics. Nylon-6, polyester knitted and woven fabrics are considered as a series of hydrophobic polymers which are subjected to electron beam coated technique to modify their hydrophobic properties. Nylon fibers, with their relatively high degree of crystallinity of 65–85%,[10] as well as polyesters with degree of crystallinity of

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20–60%[11] are generally hydrophobic synthetic fabrics. The hydrophilicity of these synthetic fibers can be improved by applying a surface coating technique. In which the coated layer should contain a suitable hydrophilic ingredient. Knitted fabrics are produced by looping the yarn through itself to make a chain of stitches which are then connected together.[12] Whereas the yarns in weaven fabric are crossed over one another. In the present study, Nylon, polyester woven and polyester knitted fabrics were coated with a solution of aqueous CMC containing acrylic acid in presence of cross-linking agent. These coated fabrics were subjected to electron beam irradiation. Hydrophilic properties were determined in terms of water uptake. While the compatibility between the coated layer and the fabric was examined by scanning electron microscope (SEM). The efficiency of coated fabrics for uptaking metal ions such as Cu(II) and Cr(III) was measured using UV- visible Spectrophotometer and EDX.

EXPERIMENTAL

Materials

The polyester woven and polyester knitted fabrics were kindly supplied by the Egyptian Company for Textile (Hosni and Bros.), Cairo, Egypt. Nylon-6 was supplied by El-Nasr Company for Weaving and Net Fabrics (El-Shorbagy), Cairo, Egypt. All these fabrics were scoured and bleached before being used. A laboratory grade acrylic acid monomer with purity 99% procured from Mercke company, Germany was used as received. A sodium salt of CMC (pure polymer) in the form of granules was supplied by El-Nasr Pharmaceutical Chemical-Prolabo (Egypt). *N,N*-Methylene bisacrylamide (MBAM) used, was obtained from Aldrich, WI, was used as a cross-linking agent. Two metal salts copper sulphate pentahydrate and chromium chloride which were purchased from El- Nasr for chemical Industries, Egypt were used throughout this work.

Coating preparation and irradiation

Radiation coating especially by electron beam is one of the most promising techniques.[6] Hence, coating and curing of the coated layer was achieved on different types of textile fabrics such as Nylon-6, Polyester woven and knitted fabrics using the following procedure. A known weight of CMC powder was dissolved in a known volume of distilled water. The coating solution was first prepared by dissolving the required ratios of monomer (acrylic acid) in the aqueous CMC solution with continuous stirring. About 0.2 wt % of crosslinking agent was added to the aqueous solution. The solution was then coated on different fabrics with a floating knife coater with a thickness of 25 μm. The surface coated fabrics were exposed to accelerated electrons using the electron beam accelerator of 1.5 MeV and 25 kW made by High Voltage Engineering, at National Center for Radiation Research and Technology, Cairo, Egypt. The required dose was obtained by adjusting the electron beam energy parameters and conveyor speed. The irradiation dose being used was 30 kGy. The coating percent of coated fabrics was calculated according to eq. (1).

$$\text{Coating percent} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the initial weight of uncoated textile fabric, and W_2 is the final weight of textile fabrics after coating and several washings.

Water uptake measurements

Water uptake measurements were made by using coated and dried samples of known weights. In the process the samples were immersed in distilled water for 24 h at 25°C. The samples were then removed, blotted on absorbent paper and quickly weighed. The percent of water uptake was calculated using the following relation,

$$\text{Water uptake}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

where W_1 is the initial weight of the coated textile fabric, and W_2 the final weight of the coated textile fabric after being immersed in water and blotted.

Washing cycle measurements

Washing cycle measurements were carried out by immersing a known weight of the coated sample (W_1) in water bath at 40°C for 10 min and then dried in a vacuum oven. This process was repeated for 10, 15, and 25 cycles. After each of these washing cycles, the coated textile fabric was weighed (W_2). The weight loss was calculated by the following equation,

$$\text{Weight loss}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (3)$$

Scanning electron microscope (SEM) measurements

The surface morphology of the different fabrics before and after surface coating was examined by scanning electron microscopy (SEM) fixed with EDX unit (JEOL, Tokyo, Japan).

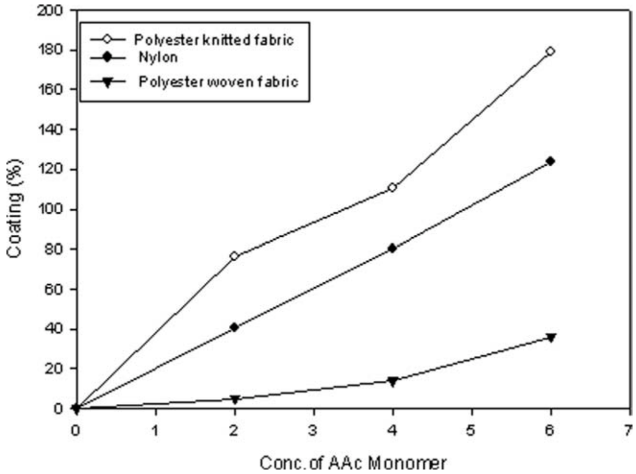

Figure 1 Effect of AAc concentration on % coating for different textile fabrics.

Determination of metal uptake

The metal such as copper sulphate pentahydrate and chromium chloride which are absorbed by the fabrics was estimated by immersing a constant weight (W) of the fabric in the different metal solutions of constant concentration (mg/L) until equilibrium. The residual metal concentration in the solution was measured by UV Spectrophotometer. The metal uptake was carried out in a batch process and determined using 10 mL of the metal ions solution as follows:

$$\text{Metal uptake (mg/g)} = (C_0 - C_1)/100 \times W$$

where C_0, C_1 are the initial and residual concentrations of metal ions in mg/L (ppm), W is the weight of the fabric (g).

RESULTS AND DISCUSSION

Coating percentage measurements

The effect of AAc concentration in the coated layer consisting of CMC and AAc on coating percent has been illustrated in Figure 1. It was found that generally the coating percent of different textile fabrics increases on increasing AAc concentration. This increase may be attributed due to the presence of free radicals obtained during irradiation and available for eventual interaction with coating solution ingredients, namely, the predominantly radiation cross-linkable polyelectrolyte PAA and the predominantly radiation degradable CMC as well as with their radicals and the fabrics. The values of coating percent is arranged according to the following order,

Polyester knitted fabric > Nylon-6 > Polyester woven fabric.

The less value of coating percent for polyester woven fabric when compared to that of knitted one is due to the difference in spinning method which makes the penetration of the coated layer inside the woven fabrics occurs but to a limited extent.[13] There is a similarity between Nylon- 6 and polyester knitted fabric in their nature which explains the high coating percent values obtained for these two fabrics. The high value of coating percent for polyester knitted fabric is due to the direct contact of the coated layer at the interface together with the nature of polyester knitted fabric.[14]

Durability of coated layers towards washing cycle

One of the important properties which must be studied after the treatment of the fabrics is the durability of the coated layer towards washing cycles in case of three acrylic acid concentrations. Hence, the effect of several washing cycles on the durability of the coated fabrics was studied. The results obtained are shown in Table I and from which, it was found that there is a decrease in the value of coating percentage for all fabrics at all AAc concentration under investigation. Also, the durability of % coating for the fabrics is in the following order,

Polyester knitted fabric > Nylon-6 > Polyester woven fabric.

These results again confirm the difference in the stability of the coated layer for the three fabrics under investigation. The weight loss percent of different coated fabrics was calculated and the results obtained are tabulated in Table II. From these results

TABLE I
Durability of Coated Layers Towards Washing Cycle

		% Coating		
Conc. AAc (%)	Washing cycle	Nylon-6	Polyester knitted fabric	Polyester woven fabric
2	Control	152	109	264
	After three washing cycles	42 ± 2.1	78 ± 2.4	5 ± 0.2
4	Control	303	158	219
	After three washing cycles	81 ± 3.6	12 ± 8.4	16 ± 0.3
6	Control	324	259	228
	After three washing cycles	127 ± 5.1	179	39 ± 4.9

TABLE II
Weight Loss (%) of Different Textile Fabrics

	Weight loss (%)		
AAc Conc. (%)	Nylon-6	Polyester knitted fabrics	Polyester woven fabric
2	73	31	98
4	74	30	93
6	62	31	84

it was found that for polyester knitted fabric the increase of AAc concentration in the coated layer does not affect the weight loss (%). This again indicates the stability of the coated layer on this fabric. Where as the weight loss in polyester woven fabric and nylon-6 decreases with increasing AAc concentration in the coated layer. This indicates that the higher stability of the coated layer can be achieved with high AAc concentration (6%). It would be then expected that the durability and stability of the coated layer of the three types of fabrics used in this work are due to the possible chemical linking of side chain of PAAc and eventually CMC with free radicals formed on the fabrics. This process may be facilitated by considering that the solubility parameters of the polyester knitted fabrics (10.73)$(cal/cm^3)^{1/2}$, CMC (11.4)$(cal/cm^3)^{1/2}$, and finally PAA of 12 $(cal/cm^3)^{1/2}$[11] are close enough indicating a possible compatibility between these fabrics and the ingredients of the coated layer. Under these circumstances it may be expected that the chemical linkage through the strong hydrogen bond groups, namely OH groups of PAAc and CMC with the fabrics has taken place.

Water uptake measurements

Sorption and permeability of water are important to the comfort and wear properties of textiles where body contact or extreme humidity levels are encountered. Most of the water sorption and permeation occurs in the amorphous regions of semicrystalline fibers.[15] The dependence of water uptake percent of different unmodified and modified textile fabrics on the conc. of AAc in aqueous solution of CMC is studied. The results obtained are illustrated in Figure 2. The data obtained indicate that initially unmodified polyester knitted fabric, polyester woven and nylon-6 fabric have a low water uptake percent value equal to 25.3, 16.7, and 15.7. On the other hand, there is a marked increase in the water uptake percent in all coated fabrics on increasing AAc concentration but with a different rate. For example, the increase of AAc from 0 to 6% is accompanied by an increase of water uptake from 15.7 to 650.9%, from 16.7 to 278%, and from 25.3 to 230% for Nylon, polyester woven and polyester knitted fabrics respectively. The increase in water uptake is arranged in the following order:

Nylon-6 polyester oven fabric > polyester knitted fabric.

It is noteworthy to observe here that the order of increase in coating percent is contrary to the order of increase in water uptake. That is to say that higher the coating percent, lower will be the water uptake percent and vice versa. This is attributed to the fact that, the higher coating percent results for the complete absorption of the coated layer by the fabric which blocks the opened structure in the fabric and the penetration of water will be restricted. As shown in Figure 2, it can be observed that there is difference in water uptake values for woven and knitted polyester fabrics. In case of knitted fabric, the penetration of water inside the fabric doesn't occur that may be due to the high percent of the coated layer which restrict the water penetration. While in case of woven fabric, the coated layer is

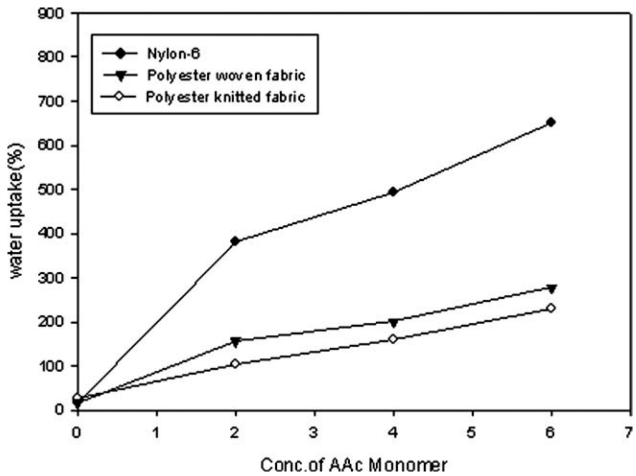

Figure 2 Effect of AAc concentration on water uptake at room temperature for 24 hrs.

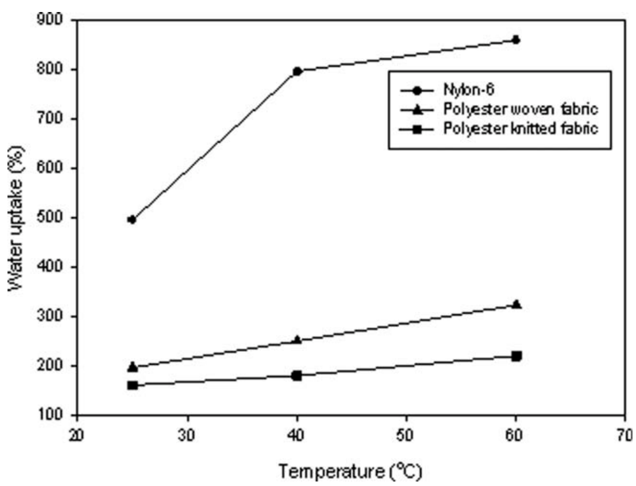

Figure 3 Effect of temperature on water uptake for different textile fabrics at 4% AAc.

TABLE III
Durability of Water Uptake (%) of Coated Textile Fabrics Towards Washing Cycle

		Water uptake (%)		
Conc. AAc (%)	Washing cycle	Nylon-6	Polyester knitted fabric	Polyester woven fabric
2	Control	380	103	156
	After three washing cycles	374 ± 4.3	102	174 ± 2.3
4	Control	493	161	196
	After three washing cycles	471 ± 3.7	155	195 ± 0.2
6	Control	651	230	278
	After three washing cycles	582 ± 17.3	214 ± 1.2	257 ± 2.3

limited so there is a chance for water penetration. The effect of temperature on the water uptake of different coated textile fabrics was studied and the results are shown in Figure 3. It was found that the water uptake (%) increased with increasing temperature for all coated fabrics. This trend was due to the fact that increasing the temperature caused on opening of the coated layer structure on the textile fabrics which facilitated the diffusion and absorption of water.

Durability of water uptake percent of the coated fabrics

It is important to investigate the durability of water uptake properties for the coated fabrics. The percent water uptake was calculated after several washing cycles. The results obtained are shown in Table III. This may be attained by measuring water uptake of coated fabrics after they had been subjected to different washing cycles. Generally, it may be observed that the value of water uptake percent for all fabrics which were subjected to washing cycles is still high and not markedly affected by several times of washing especially at 6% AAc concentration. The water uptake of Nylon-6, polyester woven and polyester knitted fabrics was found to be 570, 256 and 213% after third washing cycle compared to 651, 278 and 230%. This indicates that there is a marked stability of the coated layer towards washing cycle. In other words, increasing the AAc content in the coated layer has increased the electrophilic sites that are chemically linked to the fabric.[1] This behavior may be attributed to the presence of strong chemical bond between components of the coated layer and the fabric. This coating solution which acts as a polymeric binder has a hydrogen bonding functionality or coordinate covalent bond through the two functional groups present on the molecule. Particles attached to the fibers in this manner are firmly adhered and are not easily dislodged.[16]

Surface morphology of modified textile fabrics

SEM technique was used to investigate the surface morphology of different textile fabrics before and after they had been coated and cured by electron beam irradiation. The results obtained are shown in Figures (4–15). The surface of all the uncoated fabrics (Figs. 4, 8, and 12) looks smooth and distinct while the coated fabric seem to be rough (Figs. 5–7, 9–11, and 13–15). The fibers of coated fabrics are no longer smooth and are not distinctly separated from

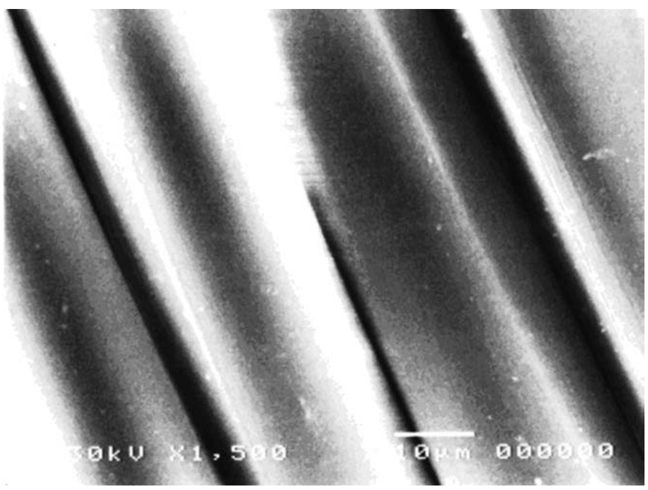

Figure 4 SEM of unmodified nylon-6.

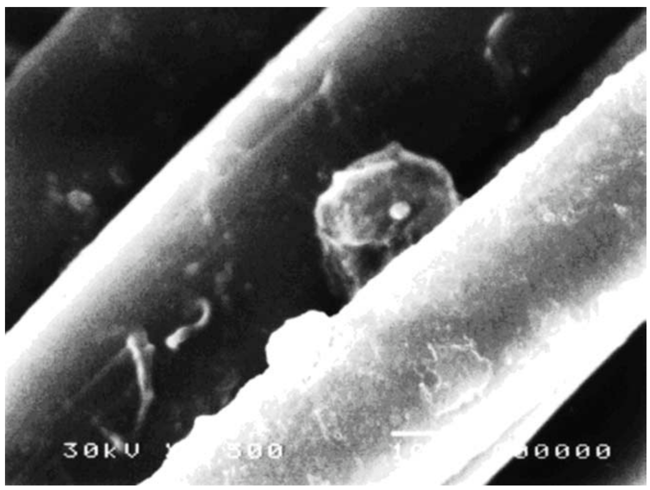

Figure 5 SEM of modified nylon-6 with 2%AAc.

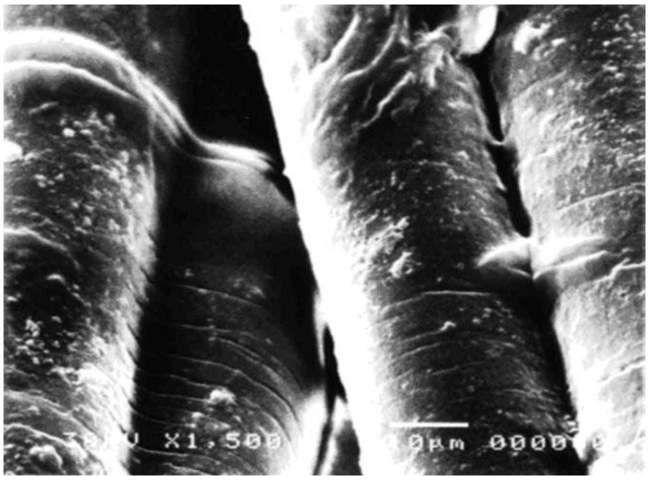

Figure 6 SEM of modified nylon-6 with 4%AAc.

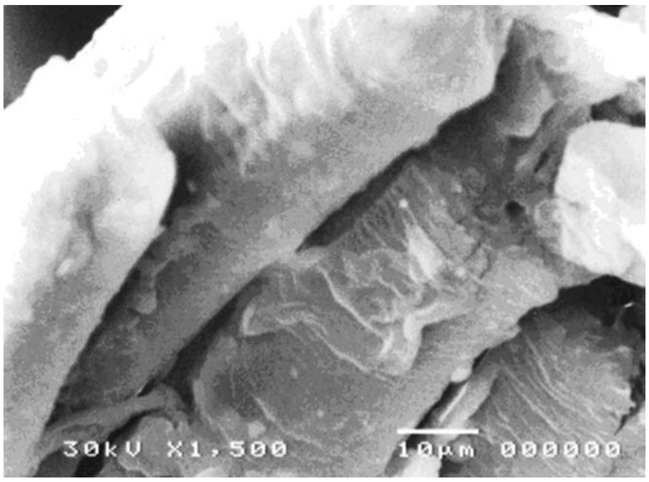

Figure 7 SEM of modified nylon-6 with 6%AAc.

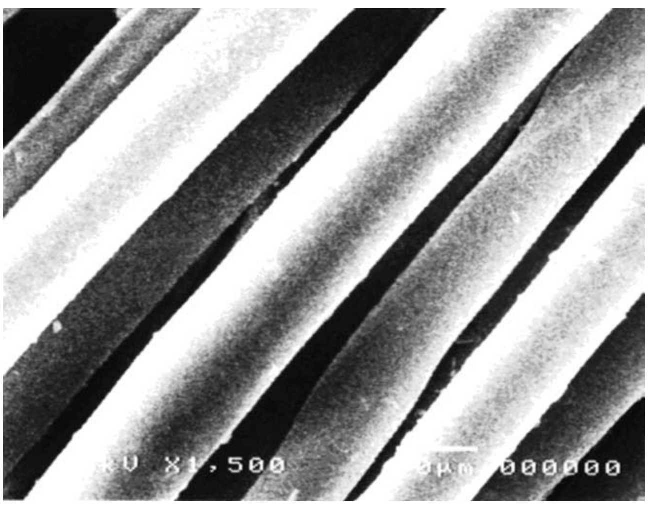

Figure 8 SEM of unmodified polyester woven fabric.

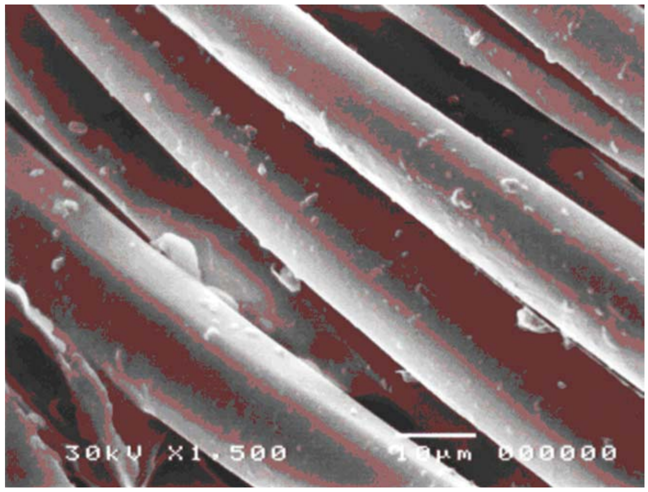

Figure 9 SEM of modified polyester woven fabric with 2% AAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

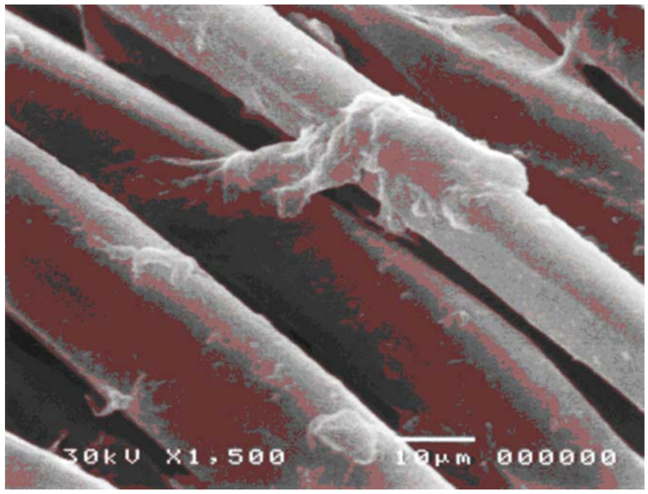

Figure 10 SEM of modified polyester woven fabric with 4% AAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 11 SEM of modified polyester woven fabric with 6% AAc.

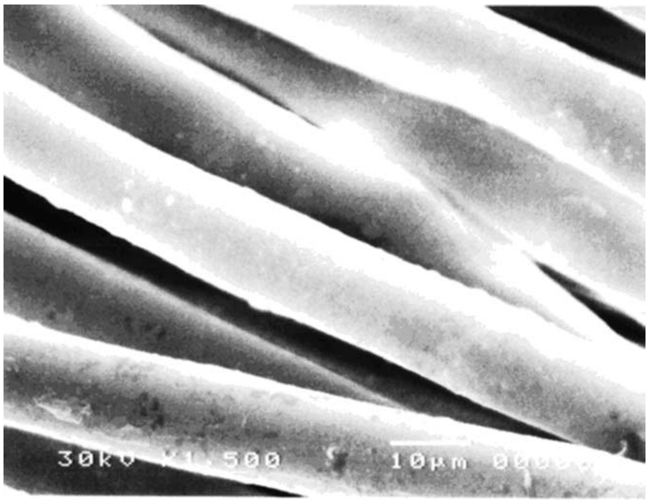

Figure 12 SEM of unmodified polyester knitted fabric.

each other, especially in case of nylon-6 fabric. There is a clear change in dimension of fiber of the fabric after coating, resulting into the closeness, compactness of the weave in the fabric structure as seen in Figure (5–7, 9–11, and 13–15). This behavior may be attributed to the relative covering of fibers with chemically linked PAAc and CMC, which is of larger magnitude in case of polyester knitted and nylon-6 than in polyester woven fabric which again offers confirmation to coating percent results, discussed before. Figures (7, 11, and 15) show clearly the complete covering of fabric with the active ingredient of coating solution containing 6% AAc. This picture provides again further confirmation to previously discussed result of water uptake property.

Sorption of heavy metal ions

In this work, the possibility of using the modified coated fabric for the removal of heavy metal ions

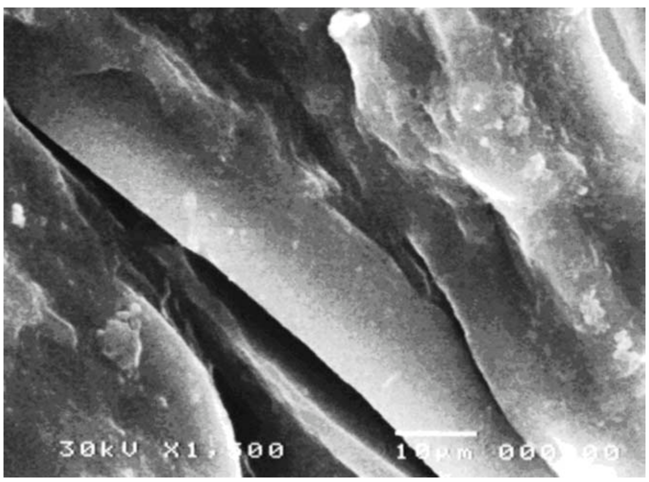

Figure 13 SEM of modified polyester knitted fabric with 2% AAc.

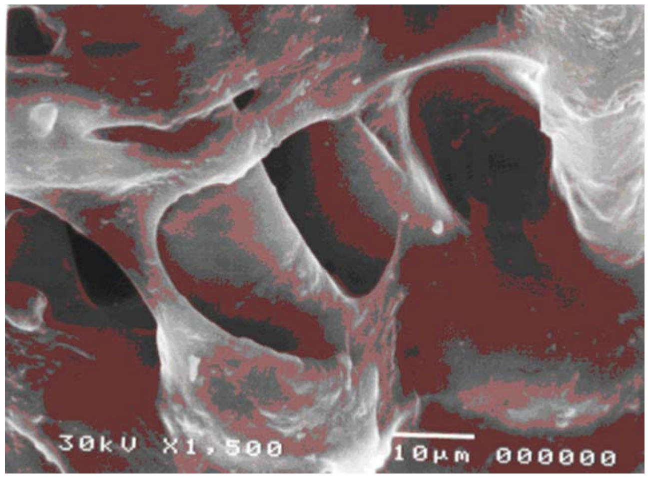

Figure 14 SEM of modified polyester knitted fabric with 4% AAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

such as copper (II) and chromium (III) was investigated. The affinity of the modified fabrics towards these metals ions were studied by using UV-Visible Spectrophotometer and the selectivity of specific metal ions from aqueous solution was measured by EDX.

Determination of % uptake of metal ions using UV-Visible

Spectrophotometer. The metal ions uptake % was measured by UV-Visible Spectrophotometer and the results obtained are shown in Table IV. The results obtained by UV show that the metal uptake % increases on increasing AAc concentration for all textile fabrics under investigation. Moreover, the affinity of metal uptake towards chromium is greater

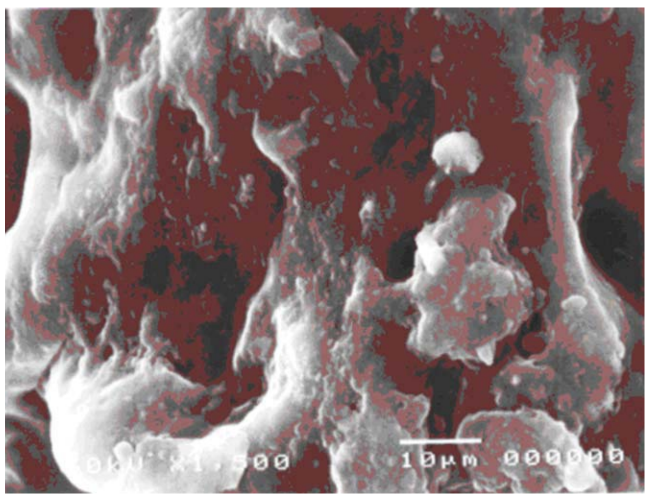

Figure 15 SEM of modified polyester knitted fabric with 6% AAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Sorption of Metals by Different Textile Fabrics

		Amount of metal ion uptake (mg/L)					
		Nylon-6		Polyester woven fabric		Polyester knitted fabric	
Conc. of AAc	Time (h)	Cu(II)	Cr(III)	Cu(II)	Cr(III)	Cu(II)	Cr(III)
2	24	16.4	20.8	10.0	12.0	11.0	13.0
	48	20.1	29.3	17.1	18.2	16.1	17.4
	72	20.1	29.3	17.1	18.2	16.1	17.4
4	24	25.5	28.4	18.1	24.0	15.4	17.8
	48	25.5	37.6	19.5	32.0	17.4	24.5
	72	25.5	37.6	19.5	32.0	17.4	24.5
6	24	29.7	38.4	22.4	25.4	17.4	18.3
	48	42.0	47.5	22.4	27.4	19.3	21.9
	72	50.5	51.6	22.4	27.4	19.3	21.9

than that towards cupper ions. This behavior can be based on the electronegativity, polarizability, size and charge of the ions. Cu^{2+} is defined as acceptor because it is less oxydisable, while Cr^{3+} is defined as donating and is highly oxydisable.[17] This assumption can explain the high efficiency of the Cr^{3+} three

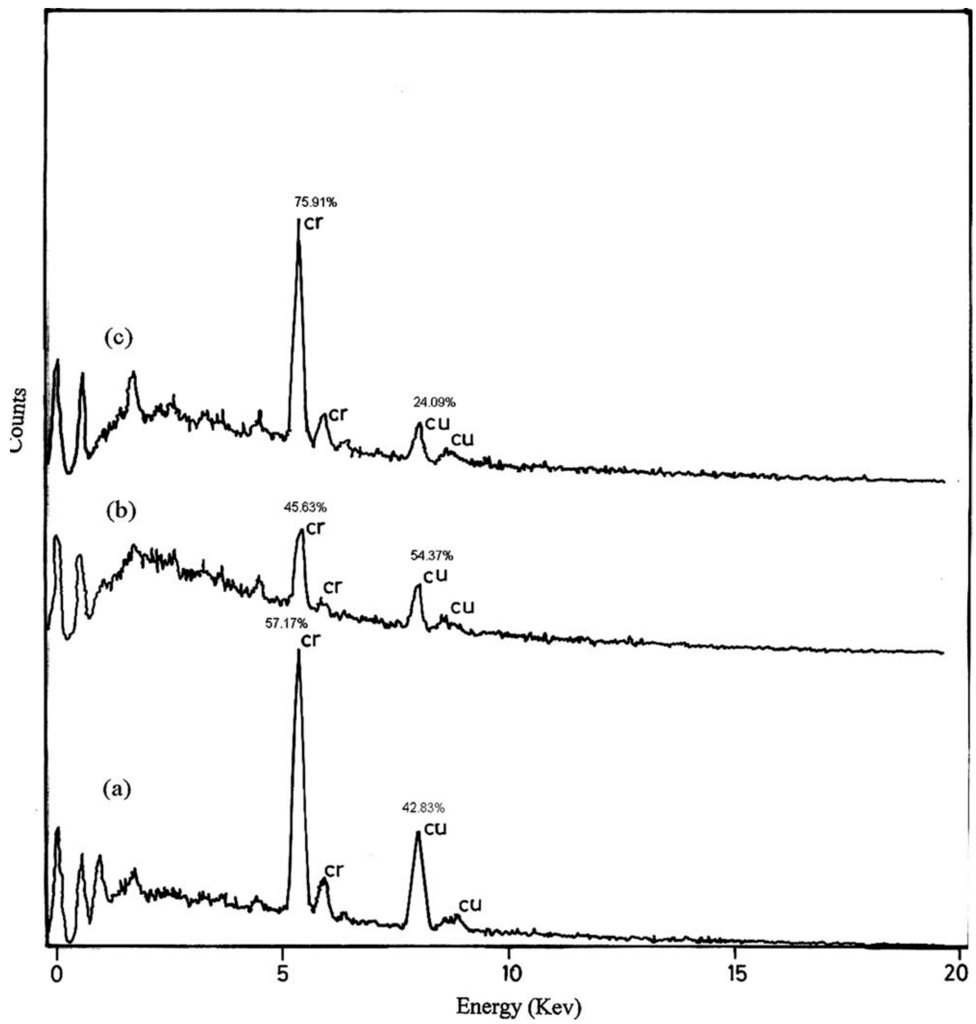

Figure 16 EDX spectra for uptake of different metal ions on (a) Nylon-6 (b) Polyester woven fabric (c) Polyester knitted fabric.

TABLE V
Selectivity of Coated Fabrics Towards Two Metals in a Mixture, Determined by EDX

Types of textile fabrics	Atomic % in coated fabrics	
	Cu(II)	Cr(III)
Nylon-6	42.83	57.17
Polyester woven fabric	45.63	54.37
Polyester knitted fabric	24.09	75.91

complexation with the ingredients of coated layer compared with Cu^{2+}.

Determination of the selectivity of coated fabrics towards metal ions by using EDX

The adsorption selectivity is an indispensable factor for appreciating the capacities of an adsorbent. By this property, the fabrics can be used to adsorb a specific metal ion or separate specific metal ions from a mixed metal ion's solution. Figure 16 and Table V show the results of adsorption of metal ions onto Nylon-6, polyester woven and knitted fabrics from equimolar solution of different metal ions at pH 7. All investigated fabrics have good adsorption capability for Cr(III) than for Cu(II). These results can be explained by considering the valency of metals. The trivalent Cr(III) forms a more stable and strong complex with functional groups of the coated layer. This indicates that the functional groups on the fabrics had a relatively stronger affinity for chromium ions than copper ions. The results obtained by EDX could be used for the separation of Cr(III) in aqueous systems containing Cu(II). In general, it can be concluded that the selectivity of the coated layer in the fabrics towards different metals in a mixture depends mainly on the stability of chelate and ionic valence of the chelated metal.[18]

CONCLUSION

An attempt has been made to prepare different coated textile fabrics to increase their water uptake. Also, this study leads to obtain modified types of textile fabrics of Nylon-6, Polyester woven and knitted fabrics that acquire good hydrophilic properties after being coated with aqueous solution of CMC and AAc. Hydrophilicity of modified fabrics was examined in terms of % water uptake. It was found that there is an improvement in the % water uptake of the coated fabrics. Also, the SEM measurements confirm the occurrence of coating by the complete adhesion between the textile fabrics and the coated layer. The performance of the coated fabrics towards the sorption of metal ions were evaluated by determining the removal of Cu(II) and Cr(III) ions from aqueous solutions. It was found that these coated fabrics show a marked efficiency towards the uptake of these metal ions.

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