

# Radiation-Induced Graft Copolymerization of Cellulosic Fabric Waste and Its Application in the Removal of Cyanide and Dichromate from Aqueous Solution

N. A. El-Kelesh,<sup>1</sup> S. E. Abd Elaal,<sup>1</sup> A. Hashem,<sup>2</sup> H. H. Sokker<sup>1</sup>

<sup>1</sup>Department of Polymer Chemistry National Center for Radiation Research and Technology, P. O. Box 29, Nasr City, Cairo, Egypt

<sup>2</sup>National Research Center, Dokki, P.C. 12622, Cairo, Egypt

Received 24 December 2005; accepted 18 December 2006

DOI 10.1002/app.26183

Published online 23 April 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Graft polymerization and crosslinking in radiation processing are attractive techniques for modification of the chemical and physical properties of the conventional polymer. The graft polymerization and subsequent chemical treatment can introduce a chelate agent function into a conventional polymer such as cellulosic fabric. Cellulosic graft copolymers were prepared by the reaction of the fiber with acrylonitrile (AN) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) in DMF initiated by  $\gamma$ -radiation <sup>60</sup>Co. The grafted fabric was chemically treated with hydroxyl amine to obtain amidoxime

from. Factors affecting the grafting such as radiation dose, monomer concentration and solvent concentration as well as monomer composition was investigated. The chemically modified graft fabric was applied for recovery of cyanide and dichromate from aqueous solution. CN<sup>-</sup> shows 89% removal, whereas dichromate has 65% removal. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1336–1343, 2007

**Key words:** radiation; grafting; adsorption; cyanide; dichromate

## INTRODUCTION

The presence of free and metal-complex cyanides and dichromates in industrial wastewater is an important environmental problem considering the acute toxicity of these species to living organisms. Cyanide emissions are increasing at a high rate and this is a cause for concern since they act as a poison for living organisms even at very low concentrations.<sup>1–3</sup>

The treatment of cyanide wastes from mining operations, electroplating process, coal gasification and from other industries is attracting public and regulatory attention.<sup>4,5</sup> A number of studies have shown that cellulosic materials can adsorb metallic ions from aqueous and nonaqueous solutions.<sup>6–9</sup> Through the introduction of functional groups into cellulosic substrates, the adsorptive capacity for metallic ions may be enhanced<sup>10–12</sup> or retarded<sup>7</sup> depending on the nature of the ions and the functional groups. Common ionic function groups are strong acid, strong base and weak base, amphoteric ion exchangers, containing both acid and base functional groups.<sup>13</sup> The affinity of K towards AMPS is relatively low according to Eromosele et al.<sup>14</sup> The Cellulose-PAN has a moderate adsorption for Cr (III) in comparison with other heavy metal ions such as Zn and

Cu.<sup>15</sup> On the other hand it was found that, although poly (amidoxime) possesses low selectivity for alkaline earth metal ions, especially K, which has a very low affinity towards PAO, it has a relatively high affinity towards Cr(III).<sup>16</sup> Furthermore, Bicakt et al. show that the amount of anions adsorbed is stoichiometrically related to the amount of metals that has been sequestered. Taking the case of Cu<sup>2+</sup>-Cl<sup>-</sup> and Zn<sup>2+</sup>-Cl<sup>-</sup> systems, the amount of Cl<sup>-</sup> anions adsorbed is almost twice that of the amount of metals. For a Cu<sup>2+</sup>-So<sub>4</sub><sup>2-</sup> system, amount of So<sub>4</sub><sup>2-</sup> anion adsorbed is equal to the amount of Cu<sup>2+</sup> sequestered. Clearly, the anion/metal ratios are almost the same as that of their free salts.<sup>17,18</sup>

Graft copolymers derived from cellulosic substrates and synthetic polymers have been shown to adsorb metallic ions from solutions.<sup>19</sup> Specifically, amidoxime-group-containing grafted cellulose formed by the reaction of nitrile group with hydroxylamine showed an enhanced ability to adsorb heavy metal ions.<sup>17</sup> The present communication describes the adsorption of cyanide and dichromate from aqueous solution by graft copolymerization of cellulose fabric with AN and AMPS followed by amidoximation, which produce fabric have both anionic and cationic character.

## EXPERIMENTAL

### Materials

AN (acrylonitrile) with purity 99.9% was supplied by Merck (Germany); AMPS of purity 99.9% was

Correspondence to: S. E. Abd Elaal (abdelaal\_samia@hotmail.com).

supplied by Merck (Germany); potassium dichromate and potassium cyanide was supplied by El-Nasr Company (Egypt); cellulose fabric was supplied from El-Nasr El-Beda C. (El-Mahala, Egypt).

### Experimental techniques

#### Graft copolymerization procedure

A definite weight of the fabric was placed in a round bottomed flask, an appropriate amount of AN and AMPS (dissolved in DMF) was added and the polymerization reaction was allowed to proceed using  $^{60}\text{Co}$  gamma source at different radiation doses. The grafted fabrics was washed thoroughly with DMF, then washed with hot water for 5 h in order to extract any homopolymer that may have attached to the surface of the fabrics. The grafted sample was then allowed to dry in an air oven at  $60^\circ\text{C}$  until constant weight was reached. The grafted percentage was determined by the percent increase in weight as follows:

$$\% \text{ Graft} = \frac{(w_g - w_0)}{w_0} 100$$

where  $w_0$  and  $w_g$  represent the weights of initial and grafted fabric, respectively.

#### Modification with hydroxylamine

The chemical modification of fabric waste based on AN and AMPS copolymer was carried out as follow:

A thirty percent hydroxylamine solution (methanol/water = 1/1) at pH 7 and 10 g of grafted cellulose fabric were added to a reactor equipped with magnetic stirrer and reflux condensator. The reaction was performed for 20 h at  $70^\circ\text{C}$  under stirring. The modified cellulose fabric was rinsed with methanol and dried at  $40^\circ\text{C}$  under reduced pressure.

#### UV Spectrophotometer

The concentration of Cr (VI) was determined by measuring the absorbance at wavelength 540 nm. Optical density measurements were carried out against blanks of the individual solvents at room temperature ( $25^\circ\text{C}$ ). The instrument with a single beam UV visible spectrometer, Milton Roy spectronic 1201 (USA), was used.

#### Measurements of dichromate and cyanide

##### Determination of dichromate

The sample (1 mL) containing lesser than 100 ppm of Cr (VI) was mixed with 3.3 mL of 0.2M  $\text{H}_2\text{SO}_4$  and 1 mL of 1, 5 diphenylcarbazide prepared by dissolving 250 mg in 50 mL acetone stored in brown bottle and discarded when solution became discol-

ored; after 10 min the pink violet color solution was analyzed for  $\text{Cr}^{6+}$  ions at 540 nm.

##### Determination of cyanide

Two to three drops of diphenylcarbazide indicator was added to 10 mL of potassium cyanide, then titrated with standard 0.1M-silver nitrate solution until violet color was just produced. The diphenylcarbazide indicator was prepared by dissolving 0.1 g of the solid in  $100 \text{ cm}^3$  of ethanol.

#### Characterization of grafted and chemically modified cellulosic fabrics

##### Infrared spectroscopy

Analysis by infrared spectroscopy was carried out using Mattson 1000, Unicam, England in the range from  $400\text{--}4000 \text{ cm}^{-1}$ .

##### Thermal gravimetric analysis

Shimadzu TGA system of type TGA-50 in nitrogen atmosphere 20 mL/min was used in this investigation with heating rate of  $10^\circ\text{C}/\text{min}$ .

##### Scanning electron microscope

The surface topography of the original and grafted and chemically modified cellulosic fabric was studied using HEOL SEM-25 (Japan).

#### Adsorption experiments

A given mass of adsorbent, chemically treated grafted fabric (0.29) was immersed in potassium cyanide and potassium dichromate solutions without pH adjustment. The adsorbent and KCN,  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (100 mL) was placed in a 125-mL glass-stopped flask and stirred for 8 h using a shaking water bath with 299 rpm at  $30^\circ\text{C}$ .

## RESULTS AND DISCUSSION

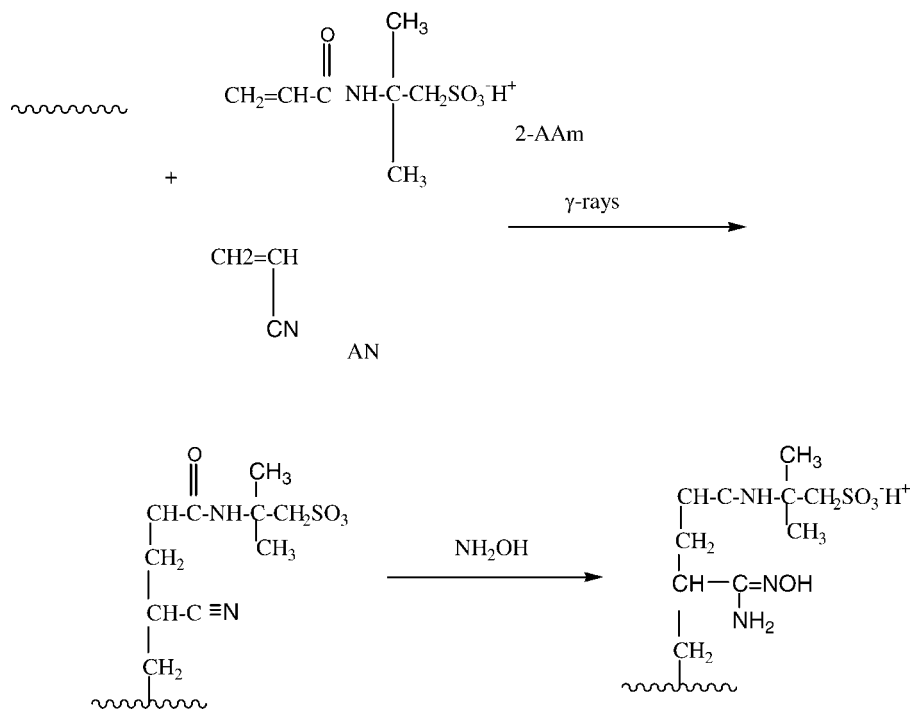
It is now generally recognized that initiation of radicals on cellulose involves oxidation of glycol linkages leading to C—C bond scission,<sup>20</sup> oxidation of cellulose chain-ends containing hemiacetal linkage.<sup>21</sup> Gaylord and Anoud<sup>22</sup> proposed a nonradical mechanism in which the formation of graft copolymer on cellulose is the result of a donor acceptor type of interaction between complex formed by the monomer, cellulose, and the uncomplexed monomer. In the presence of vinyl monomer, the cellulose macroradical is added to the double bond of AN, resulting in covalent bond formation between the monomer and the cellulose with the creation of free radical on the monomer, that is, a chain is initiated. Subsequent

addition of a monomer molecule to the initiated chain propagates grafting onto the cellulose.<sup>23</sup> The experimental results show that the reactivity ratio of AN and AMPS was 1.2 and 0.7 respectively. According to the results, it is very clear that:

1. The present poly(AN-co-AMPS) can be depicted as a random copolymer.

2. The present poly(AN-co-AMPS) can be depicted as diblock copolymer, which probably composed of PAN mixed with some AMPS units, or of AMPS sequence formed after consumption of AN.<sup>24</sup>

The proposed mechanism of graft copolymerization can be represented as shown below:



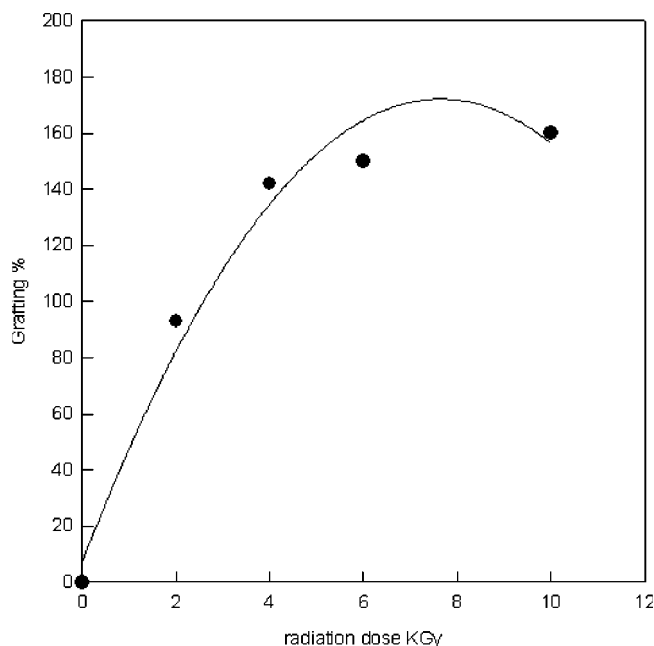
### Effect of radiation dose

The graft copolymerization is initiated by the  $^{60}\text{Co}$  gamma irradiation in which the process is mainly a free radical mechanism. Therefore, the grafting is governed by the concentration of free radicals formed in both the polymer substrate and comonomer solution. The influence of dose (2–10 kGy) on the grafting yield of AMPS/AN in DMF as a solvent onto cellulosic fabric waste is investigated and shown in Figure 1. It is obvious that the grafting yield increases with increasing dose for each comonomer composition (20 : 80, 30 : 70, 40 : 50, 60 : 40 AMPS : AN binary mixture), a possible explanation is that the increase in the irradiation dose resulted in increasing concentration of free radicals formed in the polymer substrate as well as in the comonomer binary system, which initiates mainly graft copolymerization because of lesser termination of free radicals with the polymer growing radicals and recombination of primary

radicals resulting from a longer chain length of the grafted copolymer and elimination of homopolymerization.<sup>25,26</sup>

### Effect of comonomer composition

The grafting of AMPS/AN binary monomer mixtures of various relative compositions onto cellulosic fabric is investigated at different radiation doses (3–10 kGy) in DMF as a solvent. Figure 2 shows that the grafting yield increase with increasing the content of AMPS in comonomer feed solution to reach a maximum value at (20 : 80 wt % AMPS/AN) comonomer composition. Thereafter, at higher contents of AMPS, the degree of grafting falls down to reach a lower value at (60 : 40 wt %) (AMPS/AN) comonomer composition. At content of AMPS higher than 50 wt % a dense yield homopolymer is formed which retards the grafting process because of restriction in its diffusivity in such



**Figure 1** Effect of radiation dose on the degree of grafting of AMPS/AN comonomer composition (20/80 wt %) at 40% solvent concentration.

viscous medium and no monomer solution can diffuse into the interior regions of the cellulose to initiate new grafting sites.<sup>27</sup>

#### Effect of solvent concentration

The effect of dilution of (AMPS/NA) binary monomer mixture with DMF (20–50%) at different comonomer composition on the grafting process onto cellulosic fabric is investigated and shown in Figure 2. It can be seen that the degree of grafting increases with increasing the degree of dilution for comonomer compositions up (20/80 wt %) (AMPS/AN) and all radiation doses carried out in this study, that is, with increasing the solvent content in the reaction medium the degree of grafting increases.

This can be explained by the fact that: In the ordered region of cellulose. The monomer must first diffuse to the free radical sites before graft copolymerization can be initiated. The fraction of the free radical sites which actually initiate polymerization has been found to be low. The free radical sites located within highly ordered or crystalline regions of the fabrics have less tendency to be terminated when treatment with solvents that cause considerable change in the dimension of the fabrics.<sup>28</sup> In addition, with increasing the dilution the free radicals becomes much more freely in its mobility in the medium. On the other side; the cellulosic in the network structure of cellulose are relaxed and

energetically stable that allowed the monomer radicals to penetrate and diffuse through the matrix to link the active sites participated in the cellulosic chains.

#### Characterization

##### IR Spectroscopy

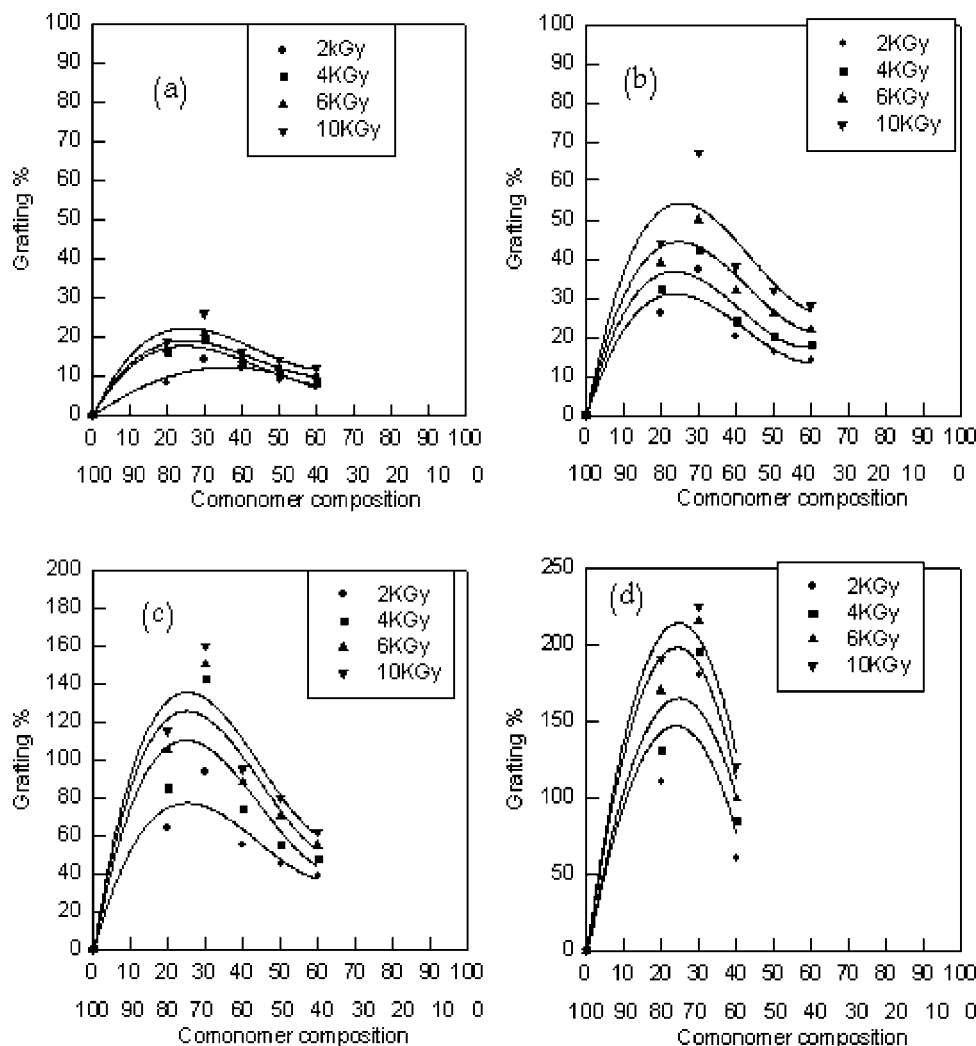
Cellulose grafted with a comonomer AMPS/AN was characterized using IR. IR. Analysis was performed for the dried fabric before grafting and after grafting amidoximation [Fig. 3(a–c)] to confirm grafting and amidoximation process. The IR spectra of the grafted fabric [Fig. 3(b)] indicate the appearance of a new bond at  $2194\text{ cm}^{-1}$  characteristic of C–N nitrile which is shifted due to grafting of the comonomer, a bond at  $1693\text{ cm}^{-1}$  characteristic of C=C of amide, bond at  $1515\text{ cm}^{-1}$  characteristic of N–H bending of amide, bond at  $1050\text{ cm}^{-1}$ , and band at  $663\text{ cm}^{-1}$  stretch for S–O. Figure 3(c) shows the disappearance of the band at  $1693\text{ cm}^{-1}$  characteristic for nitrile group and was replaced by the bands of  $2985\text{--}3502\text{ cm}^{-1}$  (broad, N–H and O–H stretching vibration) and a band at  $1639\text{ cm}^{-1}$  (C=N stretch vibration).

##### Surface morphology studies

The morphology of the ungrafted cellulose (a), grafted cellulose with AN and AMPS (b) and chemically modified grafted cellulose fabric with hydroxylamine (c) was confirmed by SEM, as shown in Figure 4. SEM of grafted cellulose show a pronounced swelling effect on the fiber and the diameter of the individual fiber seems to become thicker than that of ungrafted fabric, also surface is almost covered with branches of poly AN and poly AMPS, which is completely absent from the ungrafted fabric, whereas (c) shows no more barnacles on the surface due to amidoximation and cleavage of  $\text{CN}^-$  N group.

##### Thermal stability

The thermal stability and degree of hydrophilicity of the fabric waste were investigated by thermogravimetric analysis (TGA) and compared with the start materials. Figure 5 shows the TGA of cotton fabric (a), grafted cotton fabric with AMPS/AN (20/80 wt %) and amidoximated grafted cotton fabric. The first step of weight loss indicated that the degree of hydrophilicity increase with grafting due to the presence of hydrophilic sulfonic acid groups, but the degree of hydrophilicity is not so high due to the presence of hydrophobic nitrile groups. The ratio of water content in cotton fabric was 2%



**Figure 2** Effect of comonomer composition and radiation dose on grafting % at 20% (a), 30% (b), 40% (c), and 50% (d) solvent concentration.

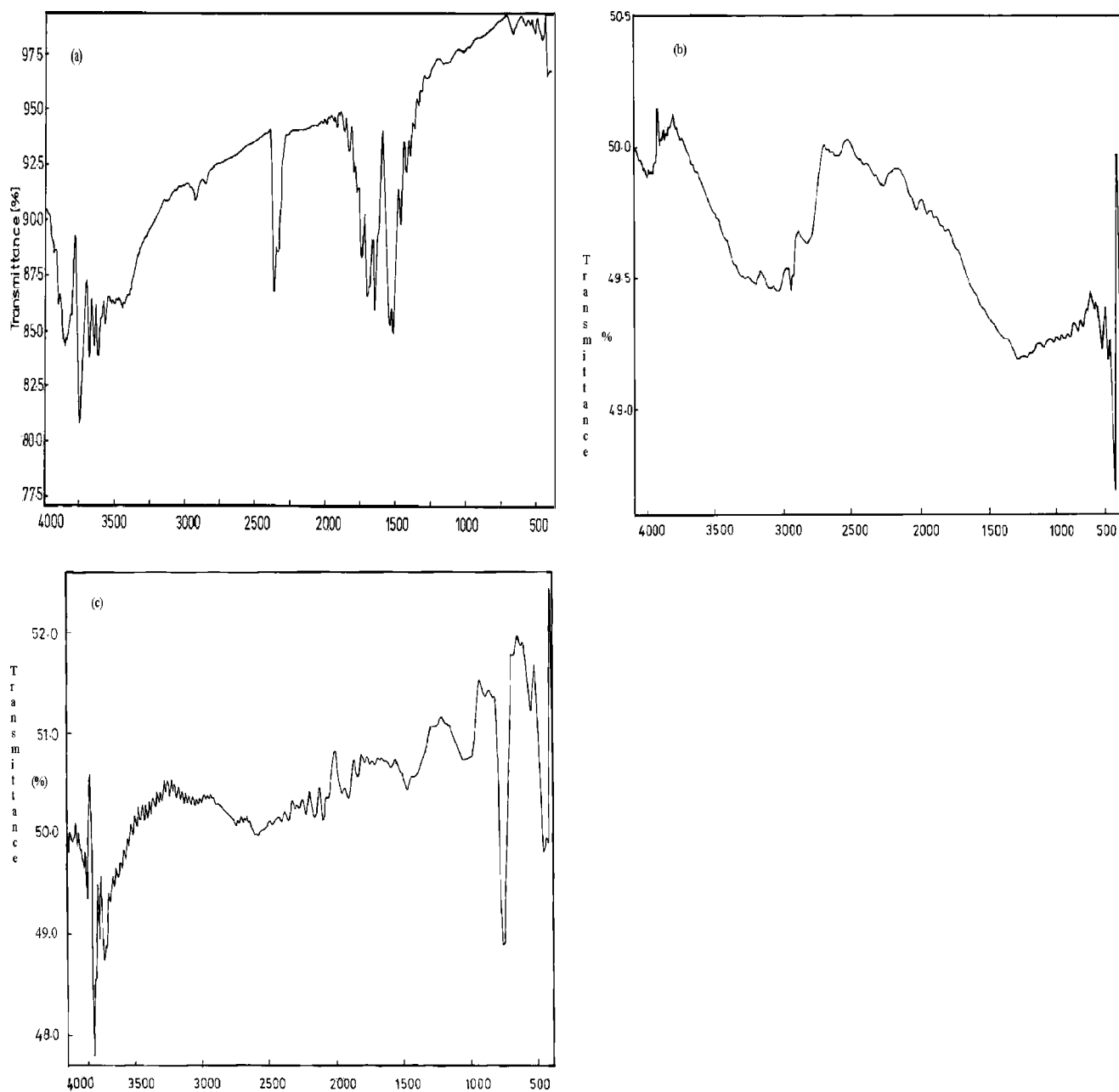
which increase to 3.4% with grafting and then increased to 7.6% with subsequent amidoximation reaction.

The thermal stability was studied from the decomposition in the second step of the thermograms as shown in Figure 5. The cotton fabric was thermally stable up to 290°C and gives 2.0% residue over 600°C. The grafted cotton fabric was thermally stable up to 250°C and gives 45% residue over 600. The amidoximated grafted cotton fabric was thermally stable up to 200°C and gives 10% residue over 600°C. The decomposition of the amidoximated grafted cotton fabric started at a lower temperature 200°C and was distributed over a wide range due to multidegradation process. The multidegradation process of cotton fabric could be backed to four steps of weight loss: (1) removal of amidoxime groups, (2) carboxylic groups at a lower temperature range, (3) The decomposition of the

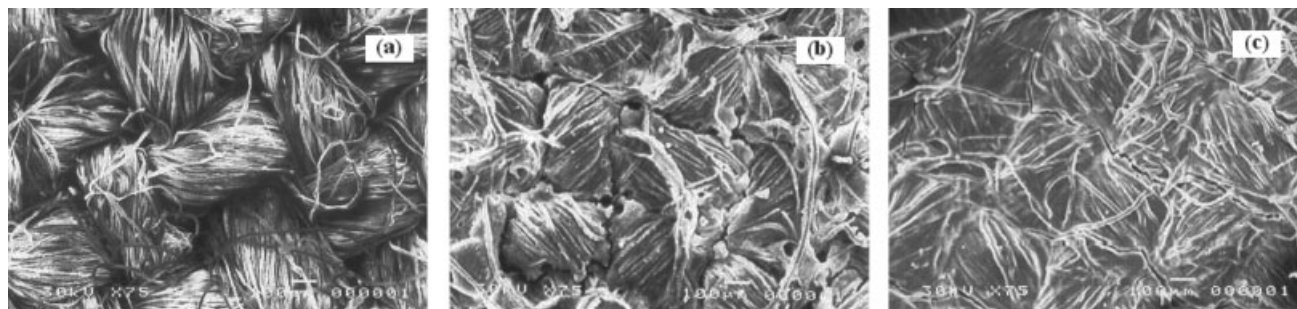
backbone graft chain, and (4) cellulose chain at a higher temperature range.<sup>29</sup>

#### Adsorption of cyanide and dichromate

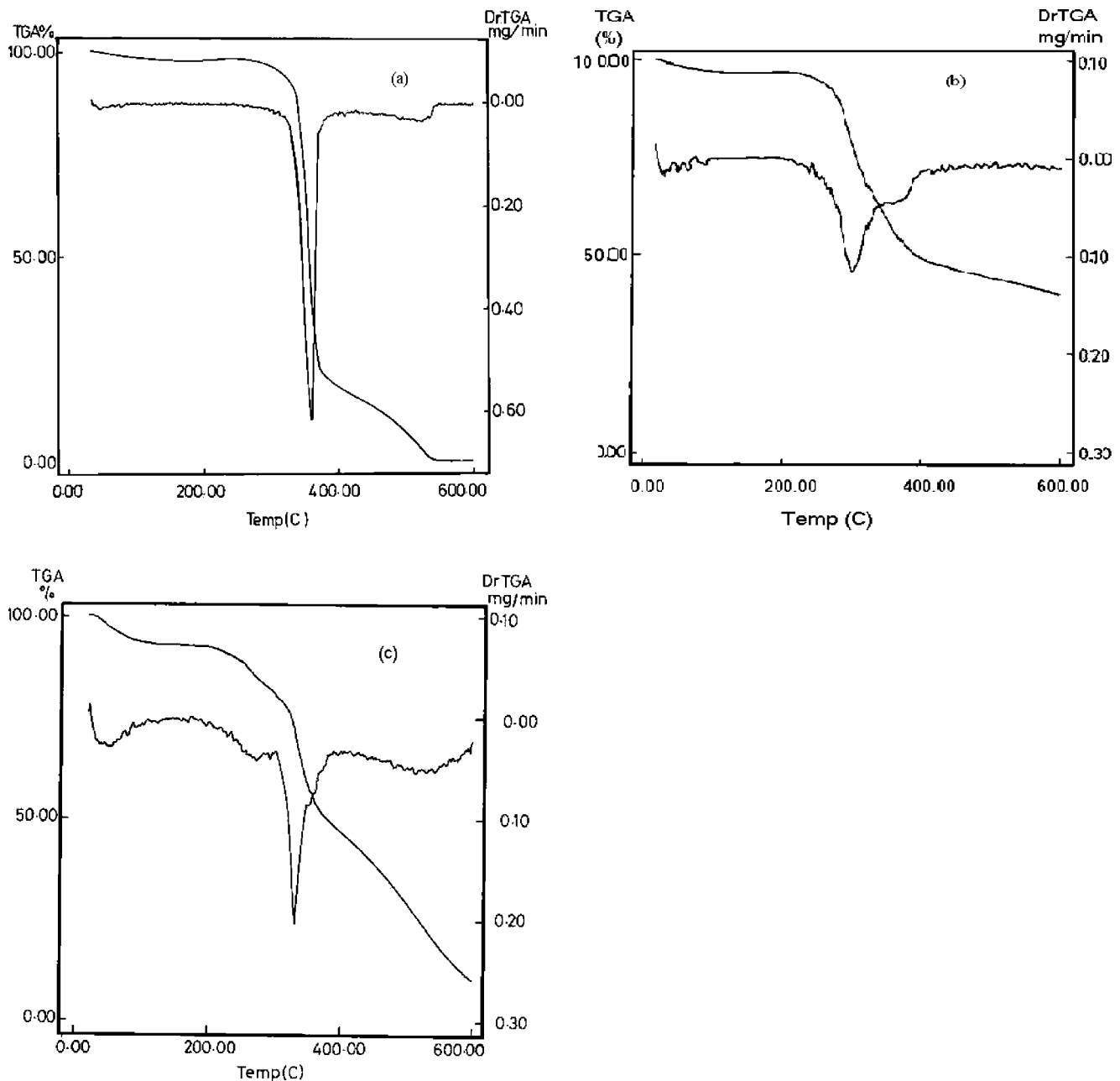
The grafted unmodified and modified fabric with hydroxylamine were evaluated on fixing amino ( $\text{CN}^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ) from aqueous solution. The results are shown in Figure 6 (unmodified) and Figure 7 (modified cellulose fabric with hydroxylamine). The results have shown that for unmodified cellulose fabric the removal percentage of CN,  $\text{Cr}_2\text{O}_7$  is 35, 24%, respectively. It is well known that AMPS have both cationic and anionic function groups ( $\text{SO}_3$  and  $\text{CONH}$ ), which are available for removal of CN,  $\text{Cr}_2\text{O}_7$ . The modification of the grafted cellulose with hydroxylamine and consequently, introducing a complexing group on the surface of cellulosic



**Figure 3** IR spectra of cellulose (a), Cellulose grafted with AN and AMPS (b), and modified grafted cellulose (c).



**Figure 4** SEM of cellulose blank (a), cellulose grafted with AN and 2-AMPS (b), and amidoximated grafted cellulose (c).

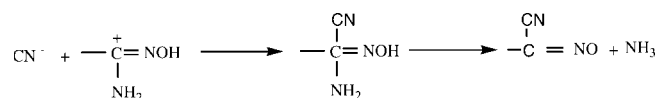


**Figure 5** TGA of cellulose (a), Cellulose grafted with AN and AMPS (b), and modified grafted cellulose (c).

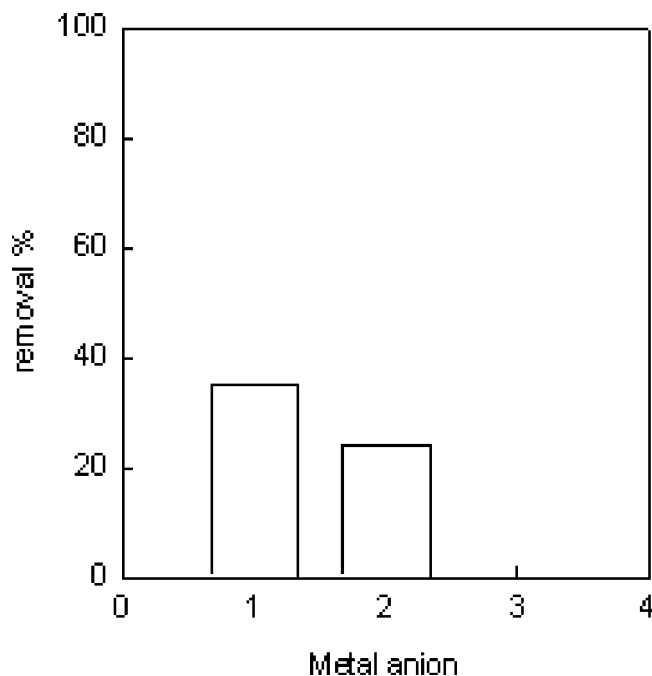
fabric based on acrylonitrile enhance the adsorption capacity of metallic ion.<sup>30</sup>

The high removal of the amidoximated grafted cotton fabric can be attributed to the fact that the hydroxylamine treatment of PAN produces amidoxime and carboxylic groups.<sup>31</sup> The formed carboxylic group plays an important role in the interaction with metallic ions, as well as increase the hydrophilicity of the cotton fabric which enhance the diffusion of dichromate and cyanide ions within the cotton fabric. Also the amidoxime group interact through the carbonyl group with  $\text{CN}^-$  radical. The active touto-

merism of amidoxime group represented its high affinity to adsorb the negative anion  $\text{CN}^-$  group to become as follows:



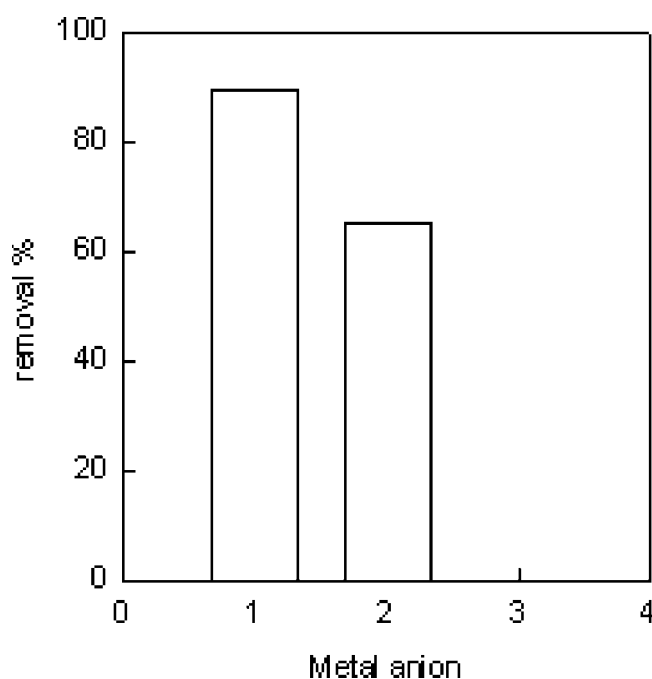
Furthermore, the affinity of AMPS and amidoxime towards K and Cr ions<sup>13-15</sup> indicate the cationic and anionic behavior of the grafted fabric.



**Figure 6** Removal % of cyanide (1) and dichromate (2) by grafted cellulosic fabric (20/80 wt%) AMPS/AN monomer composition and at solvent concentration 40%.

### CONCLUSION

Graft copolymers by AN, AMPS cellulosic substrate have been shown to adsorb anions such as CN, Cr<sub>2</sub>O<sub>7</sub> from aqueous solution. Specifically, amidoxime



**Figure 7** Removal % of cyanide (1) and dichromate (2) of chemically modified grafted cellulosic fabric (20/80 wt %) AMPS/AN monomer composition and at 40% solvent concentration.

group-containing grafted cellulose formed by the reaction of nitrile group with hydroxylamine showed an enhanced ability to adsorb the anion (CN, Cr<sub>2</sub>O<sub>7</sub>) from aqueous solution.

### References

- Bozzi, A.; Guasaquillo, I.; Kiwi, J. *Appl Catal B: Environ* 2004, 55, 203.
- Gijzen, H. J.; Bernal, E.; Ferrer, H. *Water Res* 2000, 34, 2447.
- Pablo, F.; Stauber, J. L.; Bucjney, R. T. *Water Res* 1997, 31, 2435.
- Hassan, S. Q.; Kupfeleand, M. P.; Grosse, D. W. *J Air Waste Manage Assoc* 1991, 41, 710.
- Grosse, D. W. *J Air Pollut Control Assoc* 1986, 36, 603.
- Eromosele, I. C.; Otitolaye, O. O. *Bull Environ Contam Toxicol* 1994, 52, 5301.
- Eromosele, I. C.; Eromosele, C. O.; Orisakiya, J. O.; Okufi, S. *Bioresource Technol* 1996, 58, 25.
- Eromosele, I. C.; Abare, L. D. *Bioresource Technol* 1998, 66, 129.
- Okieimen, E. F.; Ebhoaye, J. E. *J Appl Polym Sci* 1986, 32, 4971.
- Okieimen, F. E.; Mays, A. O.; Oriakhi, C. O. *J Environ Anal Chem* 1988, 32, 23.
- Okieimen, F. E.; Ogbeifun, D. E.; Nwala, G. N.; Kumsah, C. A. *Bull Contam Toxicol* 1985, 34, 866.
- Okieimen, F. E.; Orhorhoro, F. I. *J Environ Anal Chem* 1986, 24, 319.
- Drang, E. S.; Avram, E.; Dinu, M. V. *Polym Adv Technol*, to appear.
- Eromosele, I. C.; Bayero, S. S. *Bioresource Technol* 2000, 71, 279.
- Sakai, Y.; Matsuguchi, M.; Yonesato, N. *Electrochim Acta* 2001, 46, 1509.
- Badawy, S. M.; Sokker, H. H.; Dessouki, A. M. *J Appl Polym Sci* 2006, 99, 1180.
- Bicak, N.; Atay, T.; Koza, G. *J Appl Polym Sci* 1998, 68, 103.
- Mitani, T.; Fukumuro, N.; Yoshimoto, C.; Ishii, H. *Agric Biol Chem* 1991, 55, 2419.
- Ighodalo, C. S.; Bayero, S. *Bioresource Technol* 2000, 71, 279.
- Mino, C.; Kaizerma, S.; Rasmussen, E. *J Am Chem Soc* 1959, 81, 1494.
- Cumberbirch, R. J. E.; Holker, J. R. *J Soc Dyers Colourists* 1966, 82, 59.
- Gylord, N. G.; Anond, L. C. *J Polym Sci* 1972, 10, 285.
- Deo, H.; Gotmare, V. D. *J Appl Polym Sci* 1990, 72, 887.
- Pang, X. A.; Sun, H. M.; Shen, Q. *Polymer* 2004, 45, 4029.
- Hegazy, E.-S. A.; Abd El-Rehim, H. A.; Shawky, H. A. *Radiat Phys Chem* 2000, 57, 85.
- Kiatkamgornwong, S.; Chvajarenpun, J.; Nakason, C. *Radiat Phys Chem* 1993, 42, 50.
- Hegazy, E. A.; Ishigaki, I.; Okamoto, I. *J Appl Polym Sci* 1981, 26, 3117.
- Baugh, P. J.; Hinojosa, O.; Arthur, J. C. *J Appl Polym Sci* 1967, 11, 1139.
- Roberts, E. J.; Rowland, S. P. *Environ Sci Technol* 1973, 7, 552.
- Fisher, H. J.; Lieser, K. H. *J Anal Chem* 1993, 346, 934.
- Egawa, H.; Kabany, N.; Shuto, T.; Jyo, A. *J Appl Polym Sci* 1992, 46, 129.
- Kubota, H.; Suzuki, S. *Eur Polym J* 1995, 31, 701.