8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT

Radiation induced graft copolymerization of cellulosic fabric waste and its application in the removal of cyanide and dichromate from aqueous solution

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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 γ-radiation ^{60}Co. The grafted fabric was chemically treated with hydroxyl amine to obtain amidoxime form. 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 removal of cyanide and dichromate anions from aqueous solution. The CN^- shows removal percent of 89%, whereas dichromate has 65% removal percent only .

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 for living organisms. Cyanides emission are increasing at a fast rate and this is a cause of concern since they are a poison for living organisms even at very low concentrations [1-3].

The treatment of cyanide wastes from mining operations, electroplating process, coal gasification and from other industries is attracting public and regulatory attention [4, 5]. A number of studies have shown that cellulosic materials can adsorb metallic ions from aqueous and non-aqueous solutions [6-9]. Through the introduction of functional groups into cellulosic substrates, the adsorptive capacity for metallic ions may be enhanced [10-12] or retarded [7] depending on the nature of the ions and the functional groups.

Graft copolymers derived from cellulosic substrates and synthetic polymers

have been shown to adsorb metallic ions from solutions [13]. Specifically, amidoxime group-containing grafted cellulose formed by the reaction of nitrile group with hydroxylamine showed an enhanced ability to adsorb heavy metal ions [14]. The present communication is to study the adsorption of cyanide and dichromate from aqueous solution by graft copolymerization of cellulose fabric with AN and AMPS followed by amidoxination which produce fabrics have both anionic and cationic character.

Experimental

1-Materials:

AN (acrylonitrile) with purity 99.9% was supplied by Merck (Germany), AMPS of purity 99.9% was supplied by Merk-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.

2- Experimental techniques

2.1. 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}Co gamma source at different radiation doses. The grafted fabrics was washed throughly with DMF, then extracted with hot water for 5 hrs in order to extract any homopolymer which may have attached to the surface of the fabrics. The grafted samples were then allowed to dry in an air oven at 60°C untill constant weight. The grafted percentage was determined by the percent increase in weight as follows:

$$\%\,\text{Graft} = \frac{(w_g - w_o)}{w_o} X100$$

where: w_o and w_g represent the weights of initial and grafted fabric, respectively.

2.2- Modification with hydroxylamine:

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

30% hydroxylamine solution (methanol / water = 1/1) at pH 7 and 10 g of grafted cellulose fabric were added to a reactor equiped with magnetic stirrer and reflux condensator. The reaction was performed for 20 h at 70°C under stirring. The

modified cellulose fabric was rinsed with methanol and dried at 40 ^{o}C under a reduced pressure.

2.3- 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, $K_2Cr_2O_7$ solution (100 ml of concentration 100ppm) was placed in a 125 ml glass-stopped flask and stirred for 8 h using a shaking water bath with 300 rpm at 30^{o}C. The concentration of potassium cyanide and dichromate remaining in solution was measured as follow:

a)- Determination of dichromate:

The sample (1 ml) containing lower than 100 ppm of Cr (VI) was mixed with 3.3 ml of 0.2 M H_2SO_4 and 1 ml of 1, 5 diphenylcarbazide prepared by dissolving 250 mg in 50 ml acetone stored in brown bottle and descared when solution become descolored after 10 min the pink violet color solution was analyzed for Cr^{6+} ions at 540 nm.

b)- Determination of cyanide:

2-3 drops of diphenylcarbazide indicator is added to 10 ml of potassium cyanide, then titrate with standard 0.1M-silver nitrate solution until violet colour is just produced.The diphenylcarbazide indicator is prepared by dissolving 0.1g of the solid in 100 ml of ethanol. 1 mole $AgNO_3$ = 2 moles CN^{-}.

3. Characterization of grafted and chemically modified cellulosic fabrics:

3.1- Infrared spectroscopy:

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

3.2- 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^{o}C / min.

3.3- Scanning Electron Microscope:

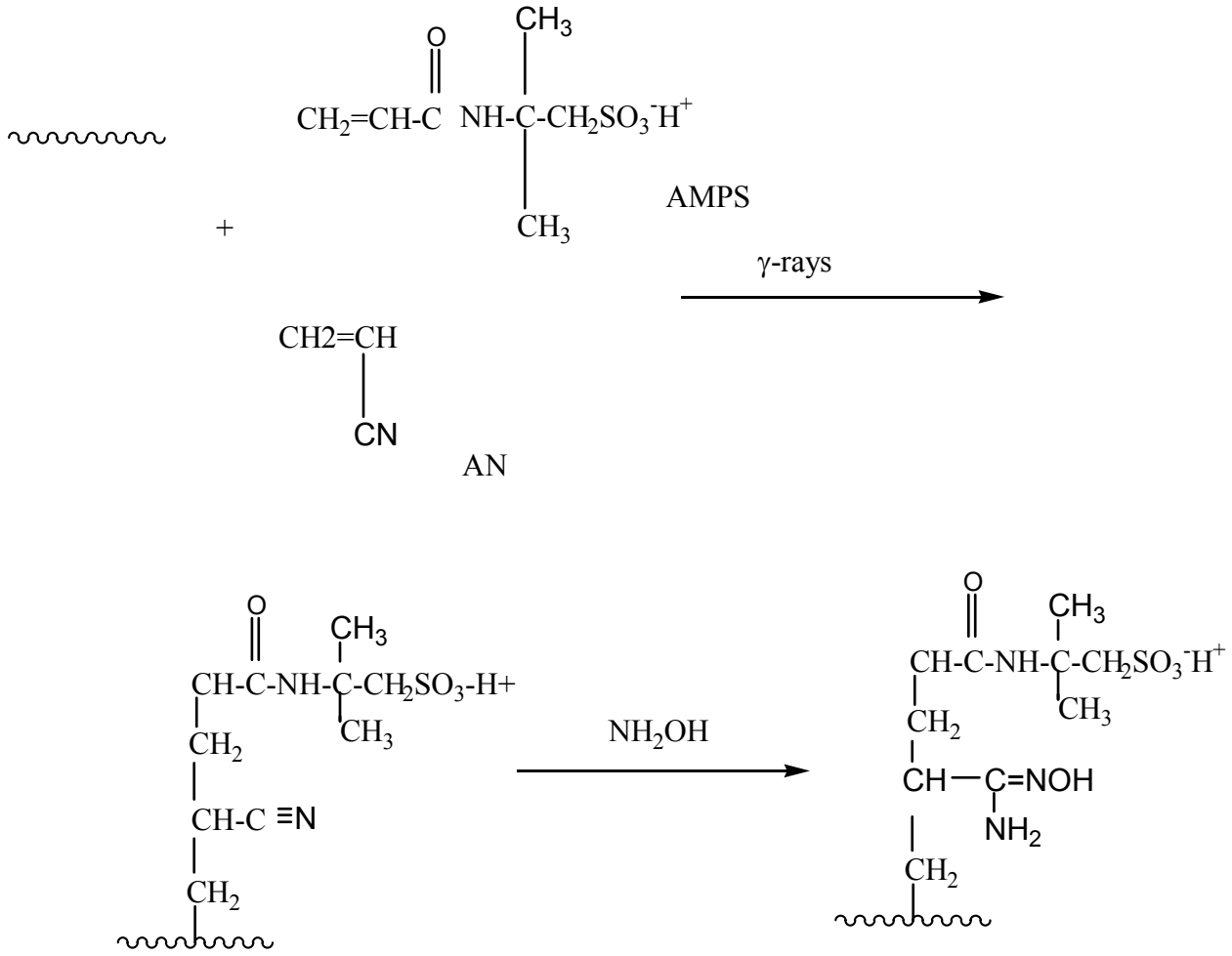
The surface topography of the original and grafted and chemically modified cellulosic fabric was studied using model HEOL SEM-25 (Japan).

3.4- U.V 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^{o}C).A single beam U. V. visible spectrometer.Milton Roy spectronic 1201, U.S.A was used.

Result and Discussion

It is now generally recognized that initiation of radicals on cellulose involves oxidation of glycol linkages leading to C-C bond scission [15], oxidation of cellulose chain-ends containing hemiacetal linkage [16]. Gaylord and Anoud [17] proposed a non radical 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 monomers. 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 [18]. The propose mechanism of graft copolymerization can be represented as follow:.



1-Effect of radiation dose:

As this graft copolymerization is initiated by the ^{60}Co gamma irradiation in which the process is mainly a free radical mechanism. Therefor, the grafting is governed by the concentration of free radicals formed on both the polymer substrate and co-monomer 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 Fig (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 on the polymer substrate as well as in

the comonomer binary system which initiates mainly graft copolymerization due to 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 elemination of homopolymerization [19, 20].

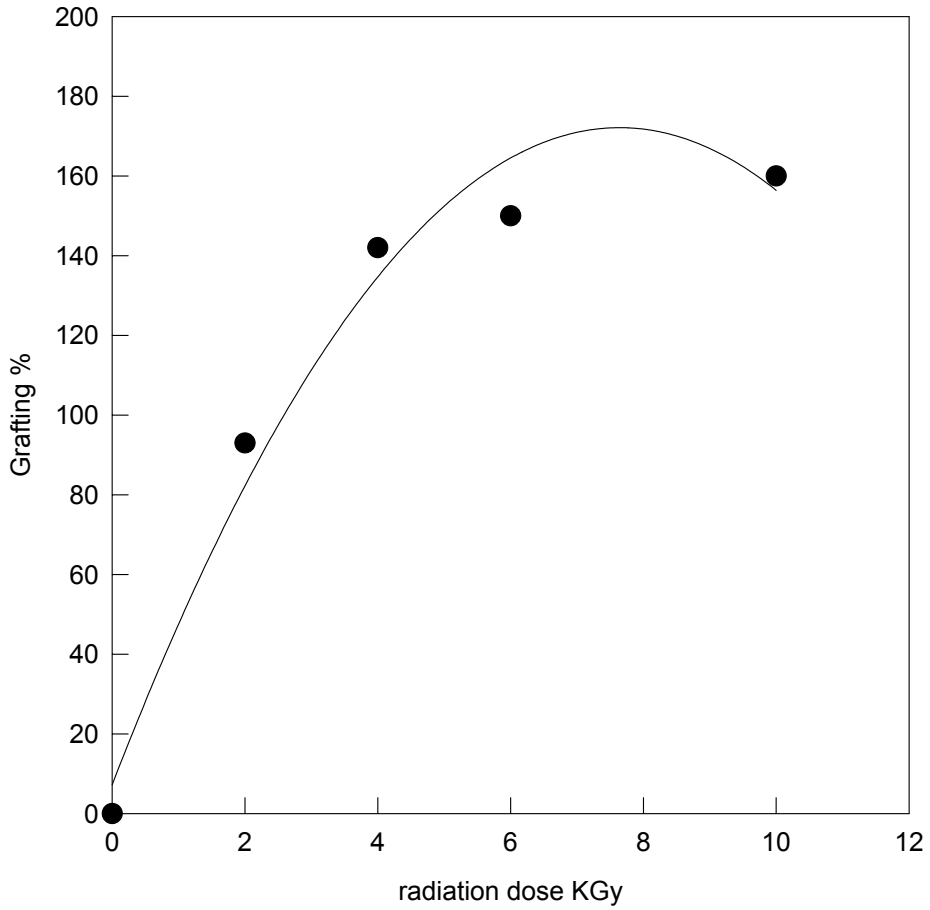
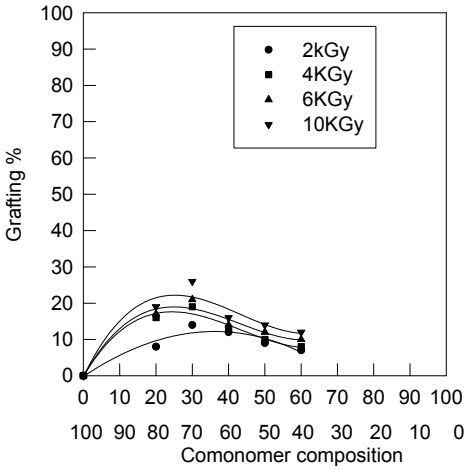


Fig (1) : Effect of radiation dose on the degree of grafting of 2-AAm/AN comonomer composition (30/70 wt %) at 40 % solvent concentration.

2- 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. Figs.(2-5) show that the grafting yield increase with increasing the content of AMPS in comonomer feed solution to reach a maximum value at (30:70 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 contents of AMPS higher that 50% wt % a dense yeiled homopolymer is formed which retards the grafting process because of restriction in its diffusivity in such viscous medium and no monomer solution can diffuse into the initiated regions of the polymer to initiate new grafting[21].



Fig(2) : Effect of comonomer composition and radiation dose on grafting % at 20 % solvent concentration.

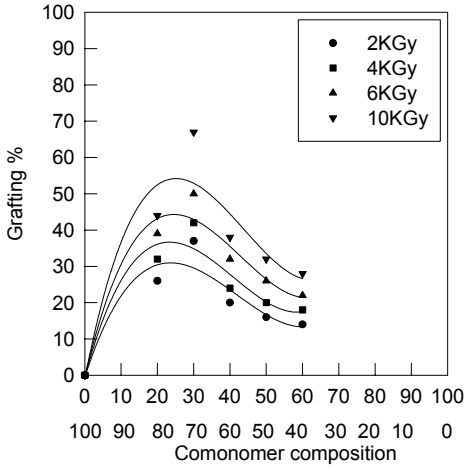


Fig (3) : Effect of comonomer composition and radiation dose on grafting % at 30 % solvent concentration.

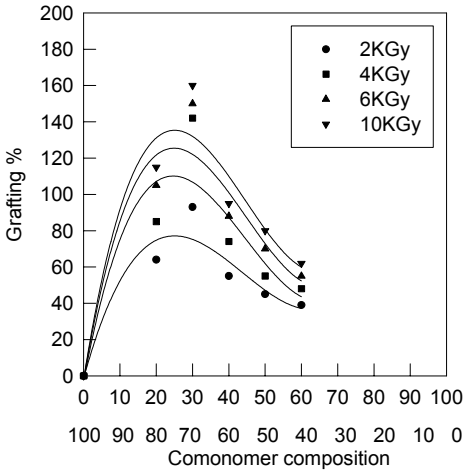


Fig (4) : Effect o comonomer composition and radiation dose on grafting % at 40 % solvent concentration.

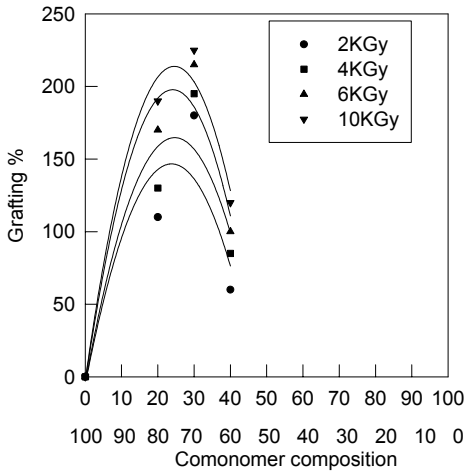


Fig (5) : Effect of comonomer composition and radiation dose on grafting % at 50 % solvent concentration.

3. 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 Figs (2-5). It can be seen that the degree of grafting increases with increasing the degree of dilution for comonomer compositions up to (30/70 wt %) (AMPS/AN) and all radiation doses carried out in this study i.e. 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 reigon of cellulose, the monomer must first diffuses 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 the ordered or crystalline reigons of the fabrics have less tendency to be terminated when treated with solvents that cause considerable change in the dimensions of the fabrics[22].

Characterization

IR. Spectroscopy:

Cellulose grafted with a comonomer AMPS/AN was characterized by using IR-spectra.The Analysis was performed for the dried fabric before grafting, after grafting and amidoxination (Fig 6- a, b, c) to confirm grafting and amidoximation process. The IR spectra of the grafted fabric (Fig. 6-b) indicate the appearance of a new band at 2194 Cm^{-1} characterize the C-N nitrile which is shifted due to grafting of the comonomer, a bond at 1693 Cm^{-1} characterize the C=C of amide, band at 1515 Cm^{-1} characterize to the N-H bending of amide, band at 1050 Cm^{-1}, symmetric stretch for C=C Characteristic of sulfonic acid and band at 663 Cm^{-1} stretch for S-O. Fig (6-c) shows the disappearance of the band at 1693 Cm^{-1} characterize the nitrile group and was replaced by the bands of 2985 – 3502 Cm^{-1} (broad, N-H and O-H streching vibration) and a band at 1639 Cm^{-1} (C=N stretch vibration).

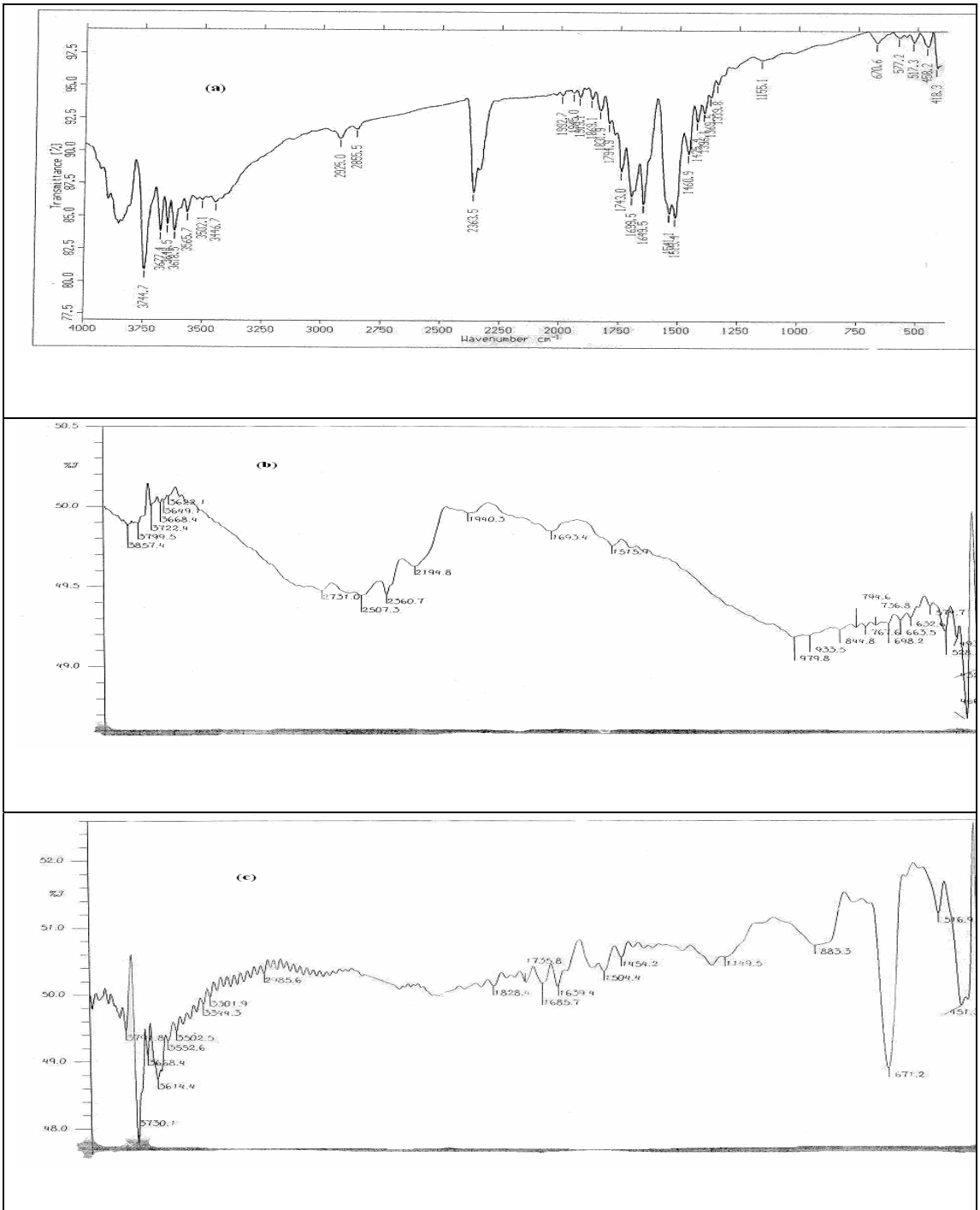


Fig.(6):- IR spectra of cellulose blank (a), cellulose grafted with AN and 2-AMPS (b) and amidoximated grafted cellulose (c).

Surface morphology of the cellulosic fabric.

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 Fig (7). 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 in case of the ungrafted fabric, whereas Fig (c) shows no more branches on the surface due to amidoximation .

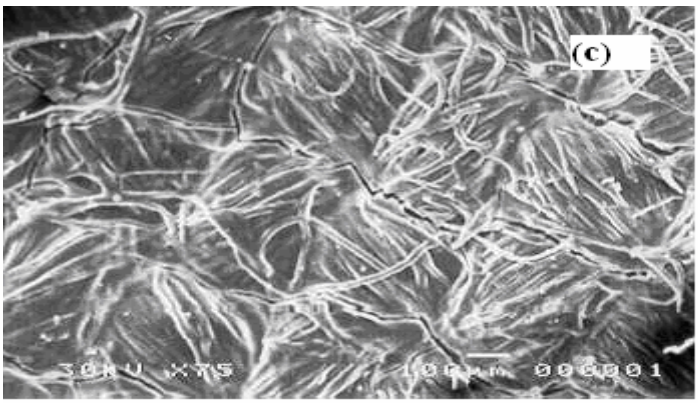


Fig.(7):- SEM of cellulose blank (a), cellulose grafted with AN and 2-AMPS (b) and amidoximated grafted cellulose (c).

Thermal Stability:

The thermal stability and degree of hydrophilicity of the cloth fibers were were investigated by thermogravimetric analysis (TGA) and compared with the start materials. Fig.(8) 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 hydroplilicity increase with grafting due to the presence of hydroplilic sulfonic acid groups, but the degree of hydrophilicity is not so high due to the presence of hydropholic nitrile groups. The ratio of water content in cotton fabric was 2% which increases 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 Fig.(8). The cotton fabric was thermally stable up to 290^{o}C and gives 2.0 % residue over 600 ^{o}C. The grafted cotton fabric was thermally stable up to 250 ^{o}C and gives 45% residue over 600 ^{o}C. The amidoximated grafted cotton fabric was thermally stable up to 200 ^{o}C and gives 10% residue over 600 ^{o}C. The decomposition of the amidoximated grafted cotton fabric started at a lower temperature 200 ^{o}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[23].

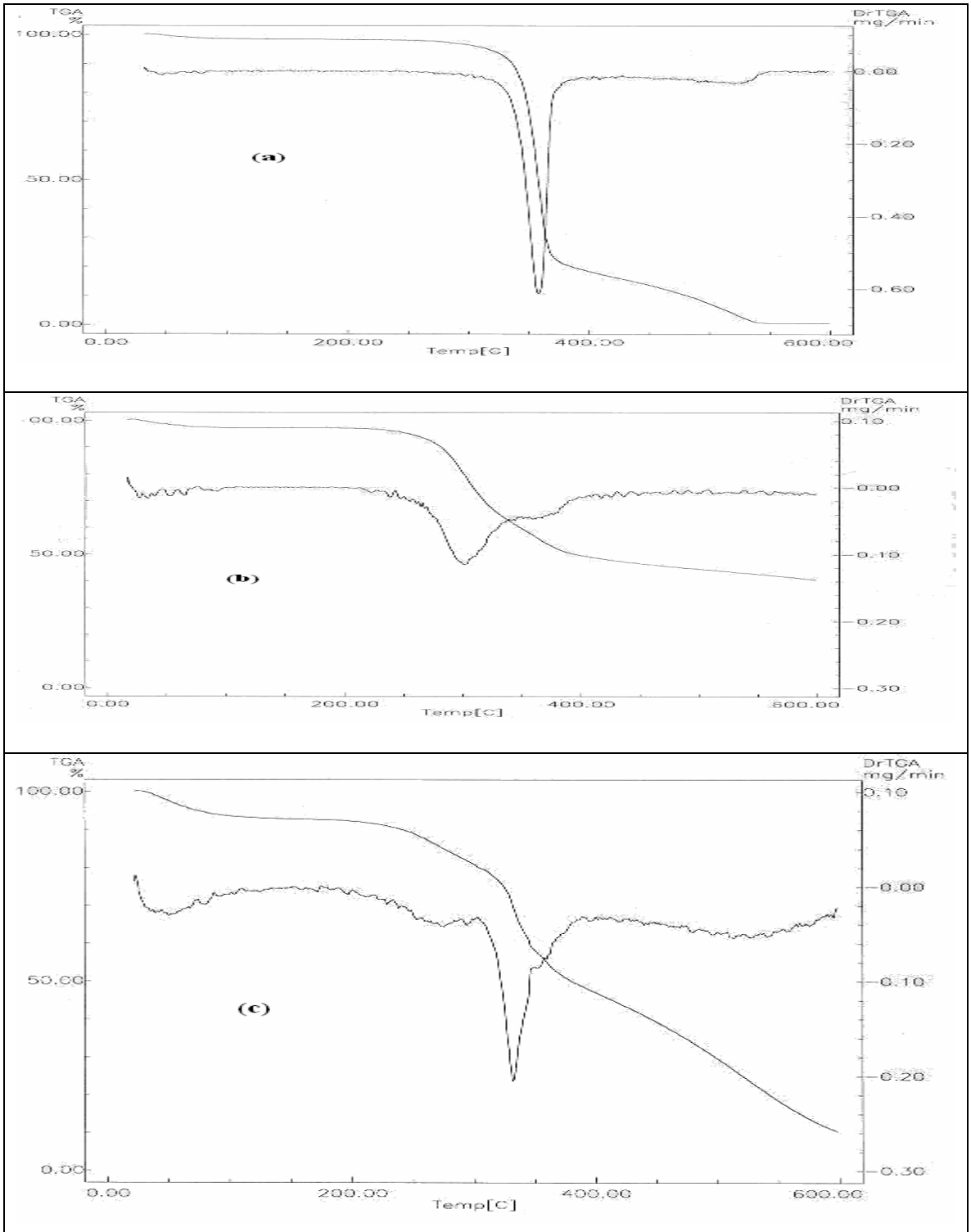


Fig.(8):- TGA of cellulose blank (a), cellulose grafted with AN and 2-AMPS (b) and amidoximated grafted cellulose (c).

Adsorption of cyanide and dichromate:

The grafted unmodified and modified fabric with hydroxylamine were evaluated on fixing (CN^-, $Cr_2O_7^{2-}$) from aqueous solution. The results are shown in Fig (9) unmodified) and Fig (10) (modified cellulose fabric with hydroxylamine). The results show that for unmodified cellulose fabric the removal % of CN and Cr_2O_7 is 35 and 24 %, respectively. It is well known that AMPS have both cationic and anionic function groups (SO_3 and CONH). Which are available for the removal of CN, Cr_2O_7. The modification of the grafted cellulose with hydroxylamine and consequently, introducing a complexing group on the surface of cellulosic fabric based on acrylonitrile enhances the adsorption capacity of metallic ion [(24)].

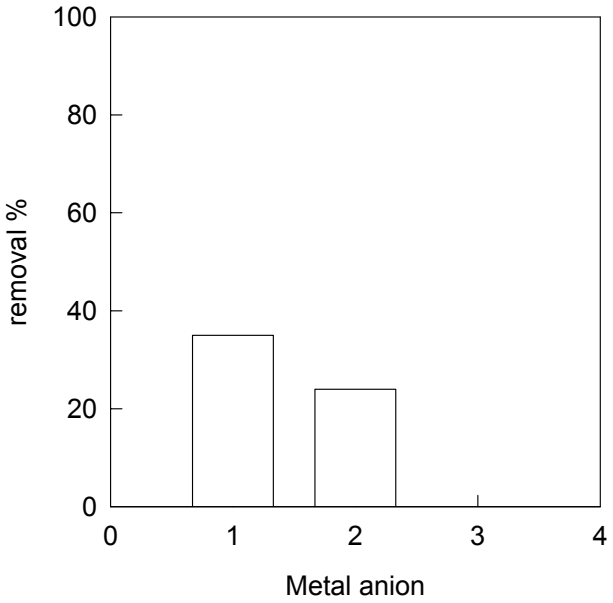
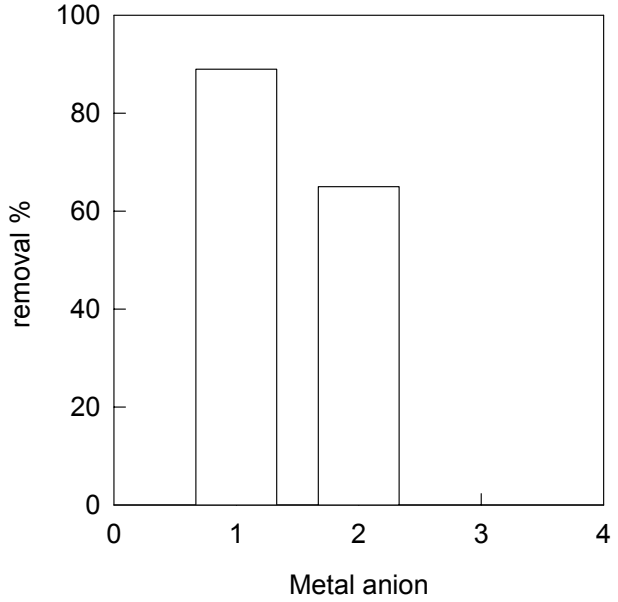


Fig (9): Removal % of cyanide(1) and dichromate (2) by grafted cellulosic fabric (20/80 wt%) AMPS/AN monomer composition and at solvent concentration 40%.



Fif (10): Removal % of cyanide (1) and dichromate (2) of chemicallymodified grafted cellulosic fabric (20/80 wt %) AMPS/AN monomer composition and at 40 % solvent concentration.

The mechanism of adsorption are generally believed to include coordinate chelation of the metallic ions with -N H2 and HO- [25] or by –coordination with four HO- group [26]. Such chelation enables the anionic group (CN^-, $Cr_2O_7^{-2}$) to be much free from the metallic ion and its ability for interaction with sulfonic acid group becomes increasingly high, which explain the high removal percent of cyanide and dichromate for the chemically modified grafted cellulosic fabric 89, 65%, respectively as shown in Fig.(10).

The high removal of the amidoximated grafted cotton fabric can be attributed to the fact that the methanolic hydroxylamine treatment of PAV produces amidoxime and carboxylic groups [26]. The formed carboxylic group plays an important role in the interaction with metallic ions, as well as increases the hydrophilicity of the cotton fabric which enhance the diffusion of dichromate and cyanide anions within the cotton fabric.

Conclusion:

Graft copolymers of cellulose grafted with AN, AMPS cellulosic substrate have been shown to adsorb anions such as CN^-, $Cr_2O_7^{-2}$ from aqueous solutions. Specifically, amidoxime group-containing grafted cellulose formed by the reaction of nitrile group with hydroxylamine showed an enhanced ability to adsorb the anions (CN^-, $Cr_2O_7^{-2}$) from aqueous solution.

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