Radiation-induced grafting of glycidyl methacrylate onto cotton fabric waste and its modification for anchoring hazardous wastes from their solutions

Hesham H. Sokker[a], Sayed M. Badawy[b], Ehab M. Zayed[c], Faten A. Nour Eldien[c], Ahmad M. Farag[c,*]

[a] National Center for Radiation Research & Technology, Cairo, Egypt
[b] National Center for Clinical and Environmental Toxicology, Faculty of Medicine, Cairo University, Egypt
[c] Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt

ABSTRACT

Ion exchange adsorbents based on cellulosic fabric wastes carrying sulfonic acid and amine functional groups were synthesized by radiation-induced graft polymerization of glycidyl methacrylate (GMA) with subsequent chemical modification of the epoxy groups of poly-GMA graft chains with sodium sulfite/H_2SO_4 and triethylamine, respectively. The conversion of epoxy groups into the functional groups was investigated. Factors affecting on grafting process such as radiation dose, monomer concentration and solvent were studied. The synthesized adsorbent and its applications in the removal of different types of hazardous pollutants e.g. acidic dye, cobalt, dichromate and phenols from aqueous solution were also studied.

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1. Introduction

Sorption-active natural and synthetic fibers and textile materials have been widely used in various industrial fields. Their electrochemical properties, such as transport number and electrical resistance, have been vastly improved. At the same time, ion-exchange membrane is a typical functional polymer and can be used not only as a separation membrane, but also as a new functional material [1].

Among different innovative techniques used for production of sorption-active materials, the application of economical and ecologically clean radiation technologies is now under attention of researches [2–4]. In particular, the utilization of radiation-induced graft polymerization technique allows to introduce inert polymeric matrix, the chains of a monomer with a desirable functional groups, or to graft the chains of a precursor-monomer, which can be subsequently modified. Owing to the limited number of vinyl monomers with functional groups, the second approach may be considered as the most perspective one. At present, an epoxy group containing monomer glycidyl methacrylate, is successfully used as a precursor-monomer for production of polymeric adsorbents of variety of applications on the base of membranes, films, fibers and fabrics. There are numerous publications on glycidyl methacrylate (GMA)

radiation-induced graft polymerization and subsequent ring opening of the epoxy groups with various reagents, such as amines and hydroxyl-amine [5,6], sulfuric acid [7] and others. This work aims at the synthesis of adsorbed materials with strong sulfonic acid and triethylamine functional groups by radiation-induced graft polymerization of GMA onto cotton fabric and subsequent ring opening of the epoxy groups of the poly-GMA graft chains with sodium sulfite/H_2SO_4 and triethylamine and application of the modified adsorbent materials for recovery of acidic dye, cobalt, dichromate and phenols.

2. Experimental

2.1. Materials

Cobalt Co (II) was used as cobalt chloride hexahydrate $CoCl_2 \cdot 6H_2O$; it is red crystals and easily soluble in water. Isopropyl alcohol was supplied by El Nasser Chemical Co., Egypt. Phenol, potassium dichromate, GMA, sodium sulfate, triethylamine were supplied by Merck Chemicals Co. (Germany). Acid Red 37 (Sandolane Rubinole E-3GSL) with molecular formula ($C_{18}H_{14}N_4Na_2O_8S_2$) was purchased from Hoechst AG (Germany) and was used without further purification.

Sample of cellulosic fabrics was supplied by Miser Company for Spinning and Weaving, El-Mahala, Egypt. The cotton fabrics used in this study are considered waste fabric pieces from different tailoring process, being mill-scoured and bleached plain weave cotton fabric.

* Corresponding author. Tel.: +20 12377 3794; fax: +20 23572 7556.
E-mail address: afarag49@yahoo.com (A.M. Farag).

2.2. Graft polymerization

To a known weight of cotton fabric waste, placed in a round-bottomed flask, an appropriate amount of GMA, dissolved in methanol/water mixture (60:40, v/v), was added. The polymerization reaction was allowed to proceed using a ^{60}Co gamma source with different radiation dose. The resulting grafted cotton fabric waste was washed thoroughly with distilled water and then refluxed with hot water for 5 h in order to dissolve any homopolymer that may be attached to the surface of cotton fabric. The grafted sample was then dried in an electric oven at 60 °C to constant weight. The percentage grafted was determined by the percentage increase in weight according to the following relationship:

$$\% \text{ Grafting} = \frac{W_g - W_o}{W_o} \times 100$$

where W_o and W_g represent the initial weight and the grafted weight of fabric waste, respectively.

2.3. Conversion of epoxy group to sulfonic acid group

The epoxy group of poly-GMA chain was allowed to react with sodium sulfite (Na_2SO_3), dissolved in isopropyl alcohol (IPA) and water, the composition was Na_2SO_3:(IPA):water equal to 10:15:75 wt%. The grafted cellulosic fabric with GMA was immersed in Na_2SO_3 solution at 80 °C for a period ranging from 0.5 to 5 h. The fiber was taken out and repeatedly washed with water. The remaining epoxy groups were converted to diol groups by reaction with 0.5 M H_2SO_4 for 2 h at 80 °C.

2.4. Conversion of epoxy group to triethylamine

Poly-GMA was chemically modified using excess of triethylamine as follows: triethylamine (3.5 g, 0.1 mol) was dissolved in dimethylformamide (100 mL) and added to poly-GMA cotton fabric (5 g, 0.021 mol epoxide). The mixture was heated at 100 °C for 72 h. The chemically modified cotton fabric was then collected by filtration and washed with ethanol, water and finally with acetone. After exhaustive extraction with acetone, the chemically modified cotton fabric was vacuum dried at 60 °C overnight.

2.5. Adsorption experiments

To determine the adsorption isotherm, a known mass (0.2 g) of the adsorbent i.e., chemically modified cellulose–poly-GMA, was immersed in a series of acid red dye, Co (II) and potassium dichromate, prepared in buffer solutions at different pH values (pH = 3, 7 and 9 in case of dye and dichromate and pH = 3, 4 and 5 in case of cobalt), whereas phenol was prepared without pH adjustment. The adsorbent and the pollutant's solution (100 mL) were placed in 125 mL glass-stoppered flask and then left for 3 days at room temperature (25 °C). The concentration of the resultant solution was then determined by spectrophotometer in case of dye and dichromate and atomic absorption in case of Co (II). The concentration of phenol was determined by gas chromatography (GC) technique.

3. Instruments and techniques

3.1. Gamma irradiation source

Irradiations were carried out using a ^{60}Co gamma irradiator (Gamma Chamber 4000 A, India) with a cylindrical irradiation chamber. All irradiations were carried out at ambient temperature (about 45 °C in the chamber) and at a dose rate of about 0.8 kGy/h and the gamma absorption dose was determined by Frick Dosimeter.

3.2. UV spectrophotometer

The concentrations of dye and dichromate solutions were determined by measuring the absorbance at different wave length; λ512 and 540 nm, respectively. Optical density measurements were carried out against blanks of individual solvents at room temperature (25 °C) using a Perkin-Elmer 601 single beam UV–VIS spectrophotometer and quartz cell of 1 cm optical length.

3.3. Atomic absorption

A Perkin-Elmer-2380 atomic absorption instrument was used in the determination of heavy metal ion concentration. The relationship between the absorbed intensity from a line and the concentrations of associated element was calculated and this determined the line's calibration curve.

3.4. Gas chromatographic analysis

Hewlett Packard 5890 gas chromatograph with an HP 30-m capillary column (injector temperature program 200 °C; ovens, 60 °C isotherm; FID 200 °C and nitrogen as carrier gas with flow rate of 20 mL min^{-1}) was used for analysis of the sample. The investigated samples were introduced in a micro-quantity (1.2×10^{-3} cm^3) by the aid of microsyringe in the form of pulse into the instrument. The sample was transferred directly by inert gas (nitrogen) to the gas chromatograph.

3.5. Scanning electron microscope (SEM)

JEOL ISM-400 Scanning Microscope (JEOL, Japan) was used for scanning electron microscopy measurements.

3.6. FT-IR spectroscopy

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

3.7. Thermal gravimetric analysis (TGA)

Thermal gravimetric analyses of cotton fabric, grafted cotton fabric, chemically modified poly-GMA with sulfonic acid group and chemically modified poly-GMA with triethylamine were carried by a Shimadzu TGA-50H instrument.

4. Results and discussion

A mutual irradiation technique was used for irradiating the cotton fabric samples in the monomer solution with γ-radiation. This results in radical formation on the cellulosic chain; the sites of radical formation become the points of initiation for the side chains. At the same time, radiation-induced polymerization of the monomer and thus a mixture of graft copolymer and homopolymer were obtained [8,9]. The grafted cotton fabric was then extensively washed with boiling water to remove the homopolymer and the unreacted monomer. Irradiation by ionizing radiation is able to initiate radical polymerization at ambient temperature in the absence of chemical radical initiators. In the radiation-induced polymerization, the rate of initiation is temperature-independent and the polymerization process takes place at the radiation cell temperature. The overall activation energies are much smaller than in the chemically initiated process [10].

The produced polymer itself induce radiolysis and the radicals formed on adjacent polymer chains can react together to give a covalent bond, thereby linking the polymer molecules together
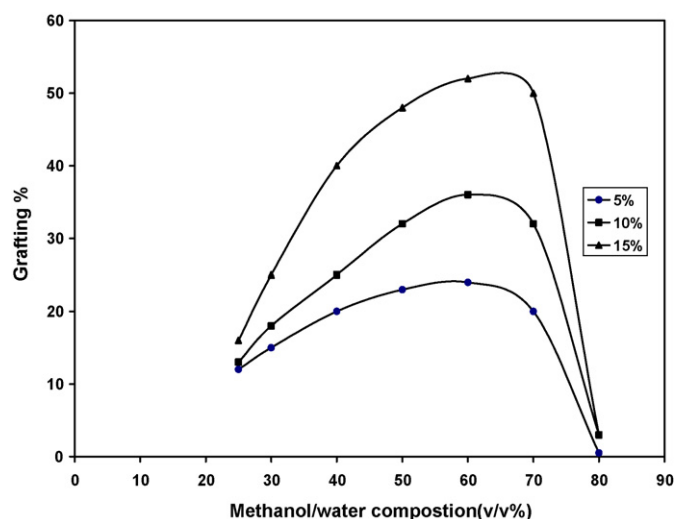
Fig. 1. Effect of solvent ratio (methanol/water ratio) on the grafting percent at different monomer concentrations.

and a three-dimensional network structure is formed giving a crosslinked polymer [11]. The presence of additives, such as solvent, affects the initiation step due to its radiolysis to initiate free radicals. The predominant variables which influence the grafting yield include absorbed dose and dose rate, concentration of monomer, and type and composition of solvents.

4.1. Effect of solvent

The solvent plays an important role in the graft polymerization. The indirect effects of solvents with both monomer and the activated cellulose lead to an increase in the accessibility of activated sites to monomers. The importance of the solvent is attributed to its radiolysis, the enhancing swelling of cellulose and the compatibility of monomer with cellulose [12]. Radiolysis of solvent leads to the formation of radicals capable of abstracting hydrogen atom from cellulose and giving additional grafting sites. The uniformity of the grafting and the diffusion of monomer are also enhanced in the presence of solvent [13].

Solvent composition has a great effect on the grafting yield. Methanol is a very useful solvent to obtain GMA grafting by the pre-irradiation method [14]. However, no grafting was obtained by the mutual method using pure methanol solvent. Fig. 1 shows the effect of methanol/water ratio on the grafting yield at a constant radiation dose of 1 kGy. Three monomer concentrations were studied: 5, 10, and 15%. It is obvious that, for all monomer concentrations, no grafting were obtained at high methanol ratio (8:2 methanol/water); i.e., increasing of monomer concentration did not increase the degree of grafting at pure methanol. The maximum grafting yield was obtained at a solvent ratio of 6:4 methanol/water. At this solvent concentration, increasing monomer concentration enhanced the graft polymerization.

4.2. Effect of radiation dose

The effect of increasing the radiation dose and dose rate of the graft polymerization system usually leads to a significant enhancement in the degree of grafting. The number of branches formed and their lengths are influenced by the dose and the dose rate [15].

The variation of grafting with radiation dose in graft polymerization of GMA onto fabric waste and different monomer concentrations is shown in Fig. 2. The degree of grafting increases with radiation dose in the range from 0 to 1.5 kGy and then tends
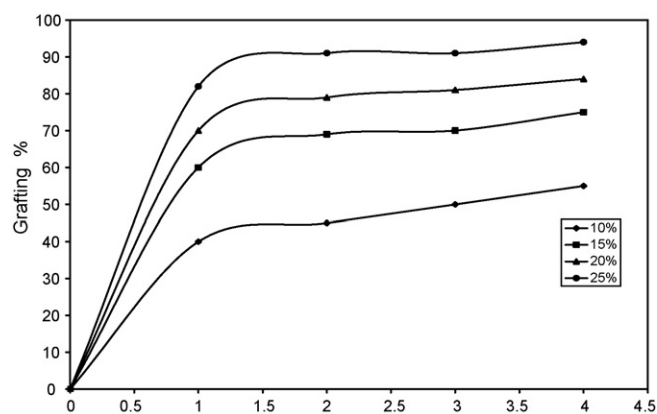

Fig. 2. Effect of radiation dose on the grafting percent at different monomer concentrations.

to level off, i.e., the number of radicals formed by radiation initiation increases linearly with radiation dose and then reaches a certain limiting value at a higher dose. At higher irradiation doses the grafting tends to level off due to the recombination of some of the free radicals without initiating graft polymerization [16]. The leveling off could be traced back to the fact that, at higher levels of grafting, the reaction becomes a diffusion controlled process [10].

4.3. Effect of monomer concentration

The effect of monomer concentration on graft polymerization of GMA onto cotton fabric waste samples is shown in Fig. 3. Four concentrations of monomer, from 10 to 25 vol% in methanol:water (6:4) was used at a dose rate of 0.8 kGy/h. It can be seen that increasing monomer concentration is accompanied by a significant increase in the degree of grafting.

Fig. 4 shows the degree of grafting versus time curves obtained at various monomer concentrations (vol%) in methanol/water (6:4 ratio). It is observed that, for all monomer concentrations; 10–25%, the degree of grafting increases with grafting time. At the lower monomer concentration (10%), the initial rate of grafting is relatively fast followed by a slower rate. At higher monomer concentration (25%), the initial rate of grafting is fast and then level off due to the consumption of the monomer, as well as to the reduction in the number of active sites on the cellulose backbone accessible for the grafting as the reaction proceeds [17]. The higher the monomer concentration, the higher the degree of grafting (up to 25% monomer concentration). The rate of graft polymerization, or the rate of monomer consumption in the grafting process, is
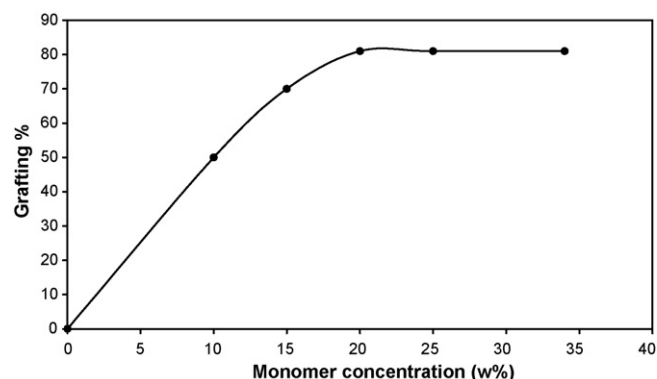

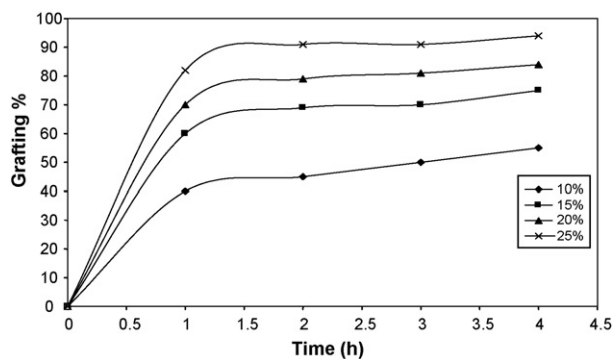Fig. 3. Effect of monomer concentration on the grafting % at radiation dose (2 kGy).

Fig. 4. The degree of grafting versus time curves obtained at various monomer concentrations.

related to the monomer concentration by the following equation [18].

$$R_p = \frac{-dM}{dt} = K_p \left(\frac{R_i}{2K_t} \right)^{1/2} [M]$$

where K_p and K_t are the propagation and bimolecular termination rate constants, respectively. R_i is the number of moles of free radicals produced on cellulose polymer per second, i.e., the rate of initiation.

### 4.4. Synthesis of adsorbent cellulosic fabric

Ion exchange adsorbents based on cellulosic fabric waste carrying sulfonic acid and amine functional groups were synthesized by radiation-induced graft polymerization of GMA with subsequent chemical modification of the epoxy groups of poly-GMA graft chains with sodium sulfite/H_2SO_4 and triethylamine, respectively. The conversions of epoxy groups into sulfonic acid and amine functional groups were investigated. The synthesized adsorbent and its application in the removal of different types of pollutants from aqueous solution were also studied.

The introduction of the sulfonate and amine groups onto cellulosic fabric waste by radiation-induced graft polymerization of the GMA chain and subsequent ring opening of the epoxy groups by sulfonation and amination are shown in Schemes 1 and 2, respectively.

4.5. Characterization

4.5.1. Infrared spectroscopy

Fig. 5 illustrates the FT-IR spectra of the cotton fabric, the grafted cotton fabric and the modified cotton fabric with sulfonic acid and amine functional groups.
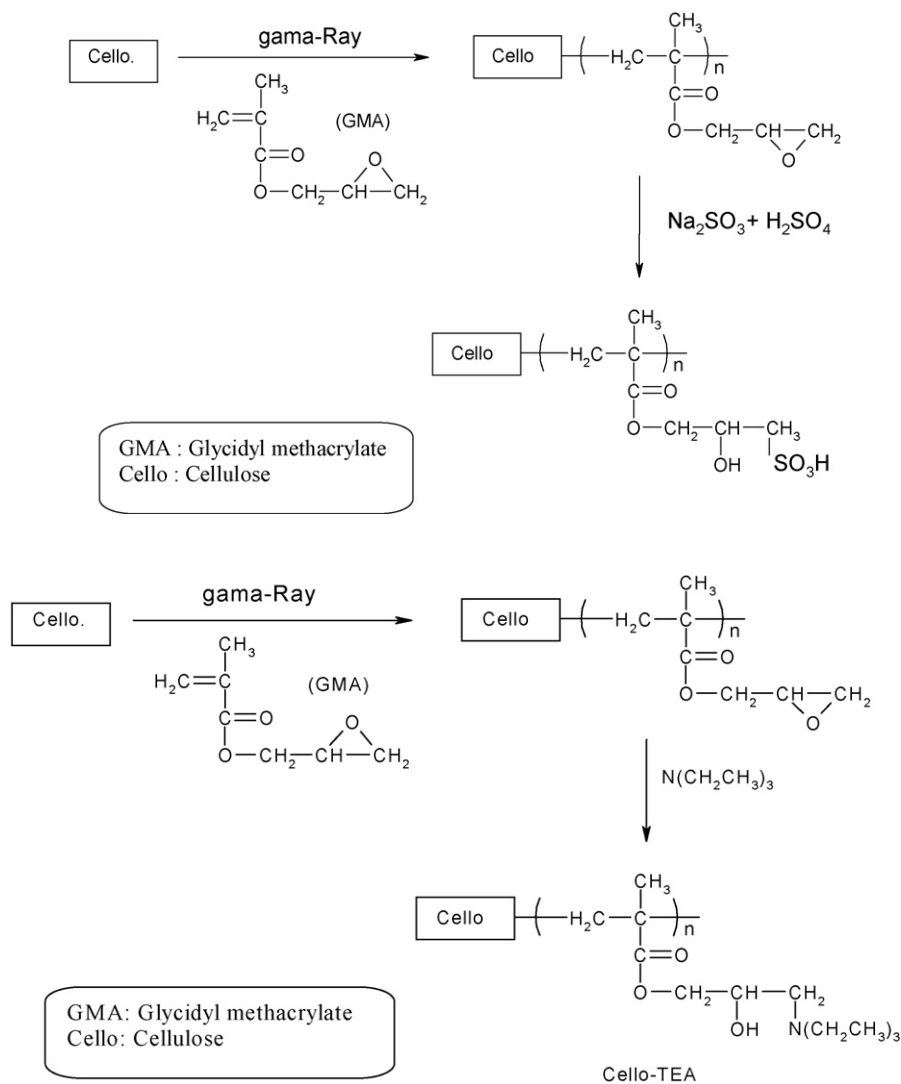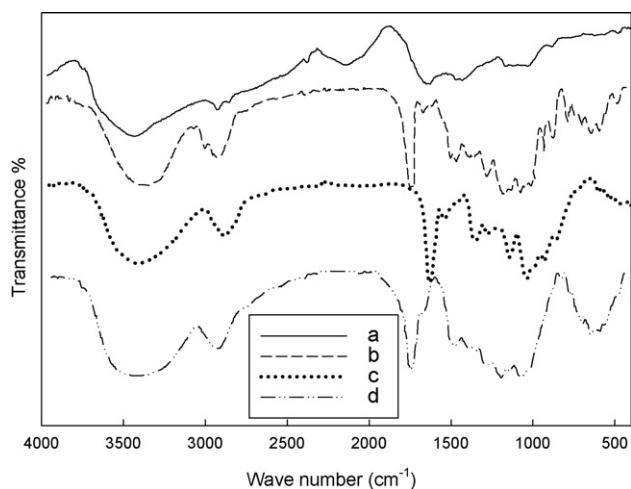
Fig. 5. FTIR of (a) cotton fabric blank, (b) grafted cotton fabric with GMA, (c) chemically modified poly-GMA with sulfonic acid group, (d) chemically modified poly-GMA with triethylamine.

Fig. 5a shows the FT-IR spectrum of the original cotton fabric. The IR spectrum of the GMA-grafted fabric (Fig. 5b) shows the absorption bands at 1732, 1307 and 1115 cm^{-1}, arising from C=O and C–O–C stretching vibration as well as three bands at 1264, 950–815 and 755 cm^{-1} attributed to epoxy ring. After sulfonation, the absorption bands of epoxy rings at 1264, 950–815 and 755 cm^{-1} disappeared. In addition, there is a new absorption band at 3418 cm^{-1} due to –OH stretching vibration and characteristic absorption bands of the sulfonate group at 1249, 1034 and 665 cm^{-1}, respectively, on the IR spectrum (Fig. 5c). After 7 h of amination with triethylamine a new absorption bands at 3423 cm^{-1} characteristic for N–H stretching vibration of amino groups was observed. The presence of these characteristic bands confirms the grafting cotton with GMA and chemical modification of the grafted cotton fabric–poly-GMA with sulfonic acid and triethylamine, respectively.

4.5.2. Thermal stability

The thermal stability and degree of hydrophilicity of cellulosic fabric were investigated by thermogravimetric analysis (TGA) and compared with the starting materials. Fig. 6 shows the TGA of cotton fabric (Fig. 6a), grafted cotton fabric with GMA Fig. 6b, chemically modified poly-GMA with sulfonic acid group (Fig. 6c) and chemically modified poly-GMA with triethylamine (Fig. 6d).
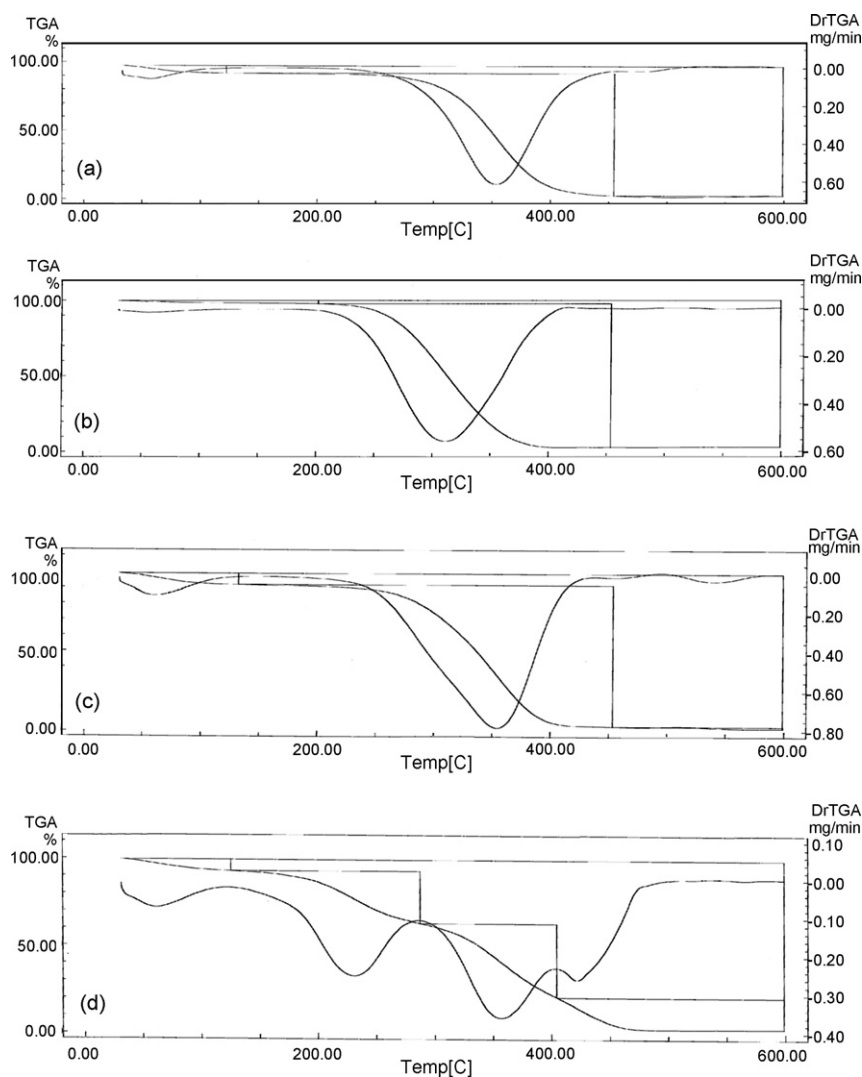

Fig. 6. Thermal analysis of (a) cotton fabric blank, (b) grafted cotton fabric with GMA, chemically modified poly-GMA with sulfonic acid group (c) and chemically modified poly-GMA with triethylamine (d).

Fig. 7. Scanning electron microscope (SEM) of (a) cotton fabric blank, (b) grafted cotton fabric with GMA, chemically modified poly-GMA with sulfonic acid group (c) and chemically modified poly-GMA with triethylamine (d).
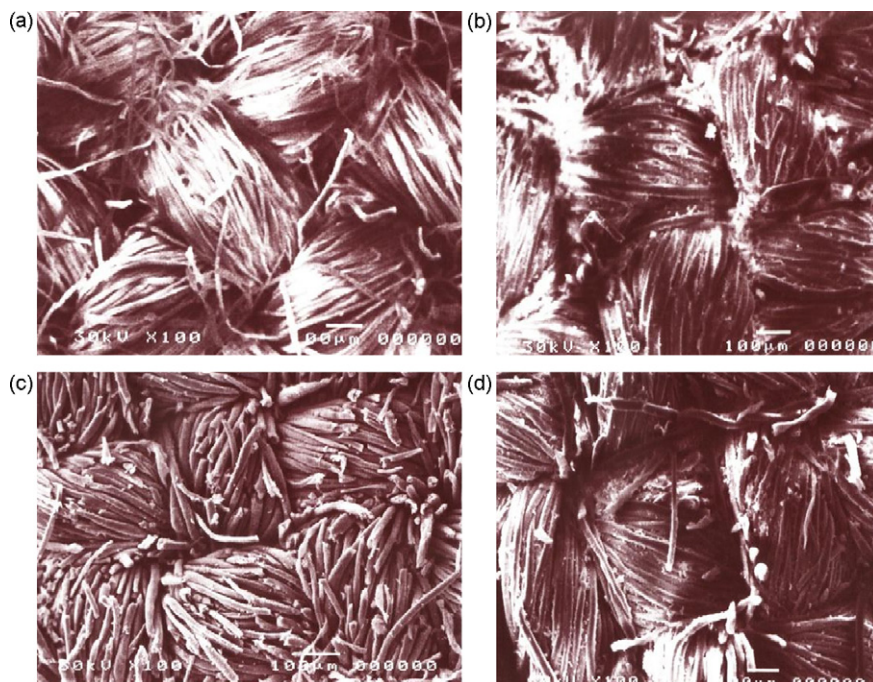
The first step of weight loss indicated that the degree of hydrophilicity decreases with grafting due to hydrophobic nature of GMA, whereas the degree of hydrophilicity increases (Fig. 6c) due to the introduction of hydrophilic sulfonic acid group. The same behavior was observed in Fig. 6d due to incorporation of amino group. The ratio of water content in cotton fabric was 5% which increases to 7.1 and 6.4% with chemical modification of poly-GMA by sulfonic acid and triethylamine, respectively.

The thermal stability was studied from the decomposition in the second step of the thermograms as shown in Fig. 6. The cotton fabric is thermally stable up to 290 °C and the grafted cotton fabric is thermally stable up to 250 °C. The decomposition of modified poly-GMA with sulfonic acid started at 260 °C and distributed over a wide range due to multi-degradation process, whereas the decomposition of chemically modified cotton fabric with triethylamine started at lower temperature (100 °C). The multi-degradation could be backed to three steps of weight loss: (1) removal of sulfonic acid groups, (2) decomposition of the backbone graft chain, and (3) decomposition of cellulose chain at a higher temperature range. Fig. 6d shows four steps of weight loss including removal of amino groups.

4.5.3. Scanning electron microscopy

Fig. 7 depicts the morphology as obtained by scanning electron microscopy of (a) the ungrafted cellulose fabric, (b) grafted cellulose fabric with GMA, (c) chemically treated cotton fabric poly-GMA with sulfonic acid and (d) chemically treated cotton fabric poly-GMA with triethylamine. The micrograph of the grafted materials showed that the diameter of each individual fiber apparently greater than that of the fiber in ungrafted materials. For the chemically treated cotton fabric-poly-GMA with sulfonic acid (c) the fiber became thicker and covered with smooth layer of deposits caused by the hydrophilic nature of sulfonic acid. The entire fiber also appeared to be coated with deposits as a result of penetration and diffusion of sulfonic acid groups through the fiber. For the chemically treated cotton fabric–poly-GMA with triethylamine, there is a pronounced swelling of the fibers; polymer

bridges were formed in some areas leading to bond individual fibers together.

4.6. Adsorption of metal and organic pollutants

The cotton fabric treated with sulfonic acid groups was tested for the removal of dye, cobalt from aqueous solution and phenol in methanol, whereas the chemically treated cotton fabric with triethylamine was tested for the removal of dichromate from aqueous solution.

4.7. Removal of acid dye by cotton fabric treated with sulfonic acid

Fig. 8 shows the equilibrium concentration (mg/L) versus the amount adsorbed X/M (mg/g) of Acid Red at different pH values, where:
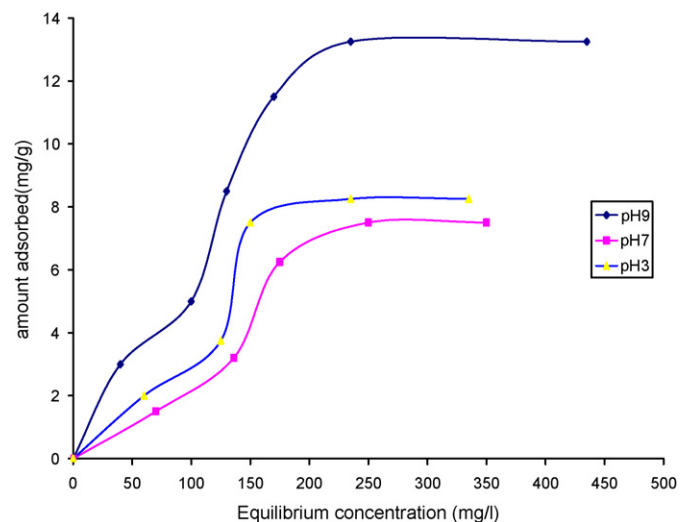

Fig. 8. Equilibrium concentration (mg/L) versus the amount of dyes adsorbed X/M (mg/g) at different pH values.
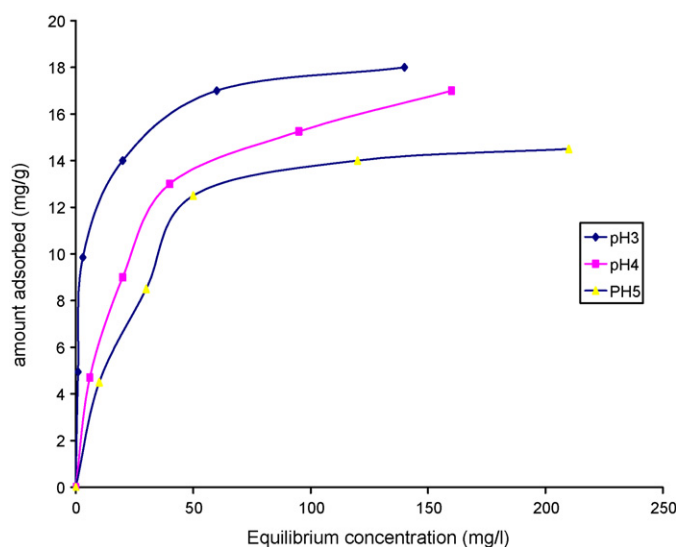
Fig. 9. Equilibrium concentration (mg/L) versus the amount adsorbed of cobalt X/M (mg/g) at different pH values.

X: mass of solute adsorbed.
M: mass of adsorbate.

In general, the uptake of anionic dyes (acid and direct dyes) is much higher in acidic solutions than those in neutral and alkaline conditions. For acid dye, the uptake decreases with increasing pH. The equilibrium adsorption capacity of dyes at different pH values was found to be 52, 31 and 41% at pH = 3, 7 and 9, respectively.

At lower pH, more protons will be available to HSO_3 to form $H_2SO_3^+$; thereby increasing electrostatic attraction between the negatively charged dye anions and the positively charged adsorption sites and causing an increase in dye adsorption. This explanation of pH effect agrees with previous work [19].

4.8. Removal of cobalt ions by cotton fabric treated with sulfonic acid

In order to determine the adsorption properties of the cation-exchange of the fabric, asset of batch experiments towards Co (II) ions binding from water solution at different pH values: 3, 4 and 5 was performed. Fig. 9 shows the equilibrium concentration (mg/L) versus the amount adsorbed X/M (mg/g) at different pH values. Owing to the formation of metal hydroxide, the pH of the solution could not be increased above 5. From Fig. 9, it is observed that the equilibrium adsorption capacity of Co (II) ions at pH = 3, 4 and 5 are 78, 83 and 91%, respectively, i.e., the availability of the fabric treated with sulfonic acid for metal ion removal is dependent on pH and the amount of metal ion uptake slightly increases as the pH increases. The result suggests that the metal ion uptake under high acidic condition was slightly decreased for cation exchanger due to formidable competition from H^+ [20].

4.9. Removal of phenol by cotton fabric treated with sulfonic acid

Removal of organic pollutants from contaminated waste water and ground water is critical for ensuring the safety of water supplies world wide. Because these contaminants are often flammable, toxic and carcinogenic, their presence in drinking water sources is a major environmental concern. The major water contaminants from oil, in the order of importance, are sulfides, dissolved phenol, and nitrogen compounds [21].
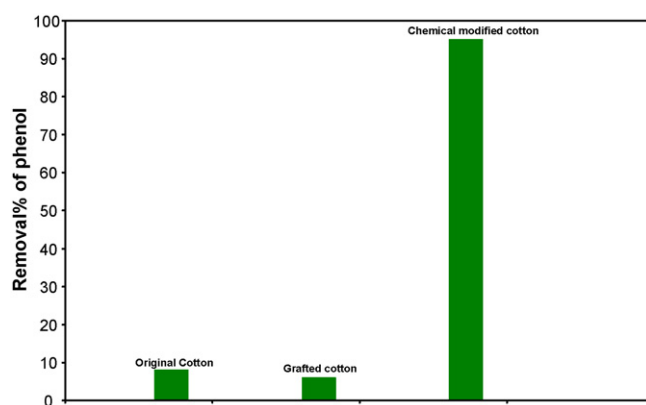

Fig. 10. Removal percent of phenol at initial concentration of 500 ppm, after sorption by using original, grafted and chemically modified grafted cotton fabric with sulfonic acid.

The present study is focused on developing an effective and modified adsorbent available for the removal of non-ionic organic contaminant (NOC) such as phenol, which is the major component of the waste water from petroleum refiners [22].

Fig. 10 shows the removal (%) of phenol at initial concentration of 500 ppm, after sorption by using original, grafted and chemically modified grafted cotton fabric with sulfonic acid. It can be seen that, for original cotton fabric, the equilibrium adsorption capacity of phenol is 8%, whereas for the grafted cotton with GMA, the removal percent is 6%, and for the chemically modified grafted cotton fabric with sulfonic acid, the equilibrium adsorption capacity reaches 95%.

The lower removal percent of original cotton fabric is due to the inert nature of polymeric matrix with desirable function groups, whereas the hydrophobic nature of GMA with limited number of vinyl monomers with function groups may be the reason for its low removal efficiency.

Modification of the grafted cotton fabric with sulfonic acid resulted in introduction of sulfonic acid function which has excellent hydrophilicity and they also give higher recovery than their unmodified analogues [23–26]. The higher tendency of chemically modified cotton fabric for adsorption of phenol than their unmodified analogues may be attributed to hydrogen bonds [27], which are expected to occur between hydrogen and hydroxyl groups of phenol molecules and the sulfonic acid group on the monomer units of the chemically modified grafted cotton fabric.

4.10. Removal of dichromate ions by chemically modified grafted cotton fabric with triethylamine

The CrO_4^{2-} anions sorption onto chemically modified grafted cotton fabric with triethylamine was tested in a batch system. The influence of pH and initial metal ion concentration on removal percent are reported.

Fig. 11 shows the equilibrium concentration (mg/L) versus adsorption capacity (mg/g) of chemically modified grafted cotton fabric with triethylamine at different pH values: 3, 7 and 9. The equilibrium adsorption capacity of CrO_4^{2-} reaches to 87%.

It is well known that the metal ion adsorption on both non-specific and specific adsorption is pH dependent [28]. The pH influences the metal chemistry in solution or the protonation or deprotonation of the adsorbent [29]. The pH dependence of equilibrium adsorption data of Cr (VI) anions is shown in Fig. 11. As seen from the figure, the adsorption of Cr (VI) anion onto the (poly-GMA) TEA was pH dependent and adsorption of Cr (VI) anion increased
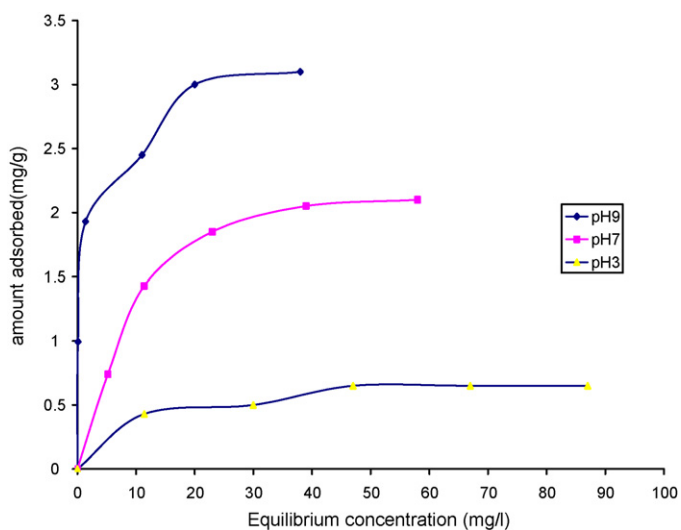
Fig. 11. Equilibrium concentration (mg/L) and the amount adsorbed of potassium dichromate X/M (mg/g) at different pH values.

when the medium pH decreased. The maximum adsorption pH was obtained at pH = 3. The metal adsorption depends on the protonation or unprotonation of functional groups on the surface of the chemically modified grafted cotton fabric. Cr (VI) exists in anionic form (i.e., $Cr_2O_7^{2-}$, $HCrO_4^{-1}$, CrO_4^{2-} and $HCr_2O_7^{-1}$) in aqueous solution, and the fraction of any particular species is dependent on chromium ion concentration and pH [30].

At acidic pH, the amino groups of (poly-GMA) TEA are positively charged, which leads to an electrostatic attraction of the negatively charged chromium species. In other words, lower pH, due to protonation of binding sites of the sorbent resulting from high concentration of proton, causes an increase in the binding of chromium species [31].

As seen in Fig. 11, the experimentally observed steep increase in chromium ion removal as the medium pH decrease can be explained by rapid increase in concentration of the protonated form of the amino group of triethylamine [30].

It is clear from these results that triethylamine incorporated poly-GMA showed more affinity to CrO_4^{2-} anion. In this adsorption system, the binding of CrO_4^{2-} anion is achieved by ion-chelating property of (poly-GMA) TEA.

5. Conclusion

Synthesis of sorption-active cotton fabric has been achieved by radiation-induced graft polymerization of GMA onto cotton fabric with subsequent modification. Varying experimental parameters such as absorbed dose, reaction time and solvent composition on the GMA grafted cotton fabrics with a wide range of GMA-chain density have been investigated. Subsequent modification was carried out via incorporation of sulfonic acid and amine groups by reacting of the epoxy groups of the poly-GMA graft chains with sodium sulfite and triethylamine. The values of the adsorption capacity of the synthesized adsorbent materials towards cobalt, acidic dye, dichromate and phenol have been evaluated. The results showed that the prepared adsorbent fabric can be applied for the removal of both cation and anion hazardous wastes.

References

[1] K. Lee, S. Choi, H. Kang, Preparation and characterization of polyalkene membranes, J. Chromatogr. A 948 (2002) 129–138.
[2] V.S. Ivanov, Radiation Chemistry of Polymer, Utrecht, The Netherlands, 1992.
[3] R. Mehnert, Electron beams in research and technology, Nucl. Instrum. Methods Phys. Res. B 105 (1995) 348–358.
[4] S. Machi, Prospects for the application of radiation processing and the activities of the IAEA, Radiat. Phys. Chem. 52 (1998) 591–597.
[5] S.H. Choi, Y.C. Nho, G.T. Kim, Adsorption of Pb and Pd on polyethylene membrane with amino group modified by radiation-induced graft copolymerization, J. Appl. Polym. Sci. 71 (1999) 643–650.
[6] K. Lee, H. Kang, D. Joo, S. Choi, Adsorption behavior of urokinase by the polypropylene film with amine, hydroxylamine and polyol groups, Radiat. Phys. Chem. 60 (2001) 473–482.
[7] M. Kim, K. Saito, S. Furusaki, T. Sugo, Comparison of BSA adsorption and Fe sorption to the diol group and tannin immobilized onto a microfiltration membrane, J. Membr. Sci. 85 (1993) 21–28.
[8] A.M. Dessouki, M. El-Tahawy, H. El-Boohy, S.A. El-Mongy, S.M. Badawy, Chemical reactive filter paper prepared by radiation-induced graft polymerization, Radiat. Phys. Chem. 54 (1999) 627–635.
[9] S.M. Badawy, H.H. Sokker, S.H. Othman, A. Hashem, Cloth filter for recovery of uranium from radioactive waste, Radiat. Phys. Chem. 73 (2005) 125–130.
[10] H.M.M. NizamEL-Din, S.M. Badawy, A.M. Dessouki, Chelating polymer granules prepared by radiation-induced homopolymerization, J. Appl. Polym. Sci. 77 (2000) 1405–1412.
[11] S.M. Badawy, A.M. Dessouki, Cross-linked polyacrylonitrile prepared by radiation-induced polymerization technique, J. Phys. Chem. B 107 (2003) 11273–11279.
[12] A. Hebeish, J. Guthrie, The Chemistry and Technology of Cellulosic Copolymers, Springer, Berlin, 1981.
[13] V.T. Stannett, Co-polymerization of grafting, Radiat. Phys. Chem. 35 (1990) 82–87.
[14] H. Yamagishi, K. Saito, S. Furusaki, T. Sugo, I. Ishigaki, Introduction of a high-density chelating group into a porous membrane without lowering the flux, Ind. Eng. Chem. Res. 30 (1991) 2234–2237.
[15] J.E. Wlison, Radiation Chemistry of Monomers, Polymers and Plastic, Dekker, New York, 1947.
[16] J.L. Garnett, Grafting, Radiat. Phys. Chem. 14 (1979) 79–99.
[17] A. Hebeish, A. Kantouch, Khalil, M.G. El-Rafie, Graft copolymization of vinyl monomers on modified cotton, J. Appl. Polym. Sci. 17 (1973) 2547–2556.
[18] G. Odian, M. Sobel, A. Rossi, R. Klein, T. Acker, Radiation-induced graft polymerization of styrene to nylon, J. Polym. Sci. A 1 (1963) 639–645.
[19] S. Abdel-Aal, Y. Gad, A. Dessouky, Use of rice straw and radiation-modified maize starch/acrylonitrile in the treatment of wastewater, J. Hazard. Mater. B129 (2006) 204–215.
[20] H. Abd El-Rehim, E. Hegazy, A. Ali, Selective removal of some heavy metal ions from aqueous solution using treated polyethylene-g-styrene/maleic anhydride membranes, React. Funct. Polym. 43 (2000) 105–116.
[21] H.M. Mofidi, Environmental conservation in the petroleum industry with particular references to refining, petroleum industry and environment, in: UNDP Semin. Pap. Doc. 1, 1974, pp. 309–385.
[22] S. Koh, J. Dixon, Preparation and application of organo-minerals as adsorbents of phenol, benzene and toluene, Appl. Clay Sci. 18 (2001) 111–112.
[23] L. Schmidt, J. Sun, J. Fitz, D. Hagen, C. Markell, E. Wisted, Solid-phase extraction of phenols using membranes loaded with modified polymeric resins, J. Chromatogr. A 641 (1993) 57–61.
[24] N. Masque, M. Galia, R. Marce, F. Borrull, Chemically modified polymeric resin used as sorbent in a solid-phase extraction process to determine phenolic compounds in water, J. Chromatogr. A 771 (1997) 55–61.
[25] J. Sun, J. Fritz, Chemically modified resins for solid-phase extraction, J. Chromatogr. A 590 (1992) 197–202.
[26] J. Fritz, P. Dumont, L. Schmidt, Methods and materials for solid-phase extraction, J. Chromatogr. A 691 (1995) 133–140.
[27] K. Issa, R. Elena, Absorption of metal ions and swelling properties of poly (acrylic acid-co-itaconic acid) hydrogels, J. Macromol.: Pure Appl. Chem. 38 (2001) 543–558.
[28] E. Valdman, L. Erijman, F. Pessoa, S. Leite, Continuous biosorption of Cu and Zn by immobilized waste biomass *Sargassum* sp., Proc. Biochem. 36 (2001) 869–873.
[29] G. Bayramoglu, A. Deniliz, S. Bektas, M. Arica, Entrapment of *Lentinus sajor-caju* into Ca-alginate gel beads for removal of Cd (II) ions from aqueous solution: preparation and biosorption kinetics analysis, Microchem. J. 72 (2002) 63–76.
[30] Y. Sag, T. Kutsal, Determination of the biosorption activation energies of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*, Proc. Biochem. 35 (2000) 801–807.
[31] O. Genc, L. Soysal, G. Bayramoglu, M.Y. Arica, S. Bektas, Procion Green H-4G immobilized poly (hydroxyethylmethacrylate/chitosan) composite membranes for heavy metal removal, J. Hazard. Mater. 97 (2003) 111–125.