Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
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Journal of Applied Sciences 5 (3): 527-531, 2005
ISSN 1812-5654

Preparation and Characterization of Cotton Textile Graft Copolymers as Cation Exchanger

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Abstract: Acrylic Acid (AA) was graft copolymerized with cotton cellulose in fabric form to prepare poly (AA)-cotton graft copolymer cation exchanger using Fe^{2+}/BrO_3^- redox system in aqueous medium under a nitrogen atmosphere. The effect of Fe^{2+}, BrO_3^- and monomer concentrations, pH as well as time and temperature of polymerization were studied by determining the grafting parameters gravimetrically, like Graft Yield (GY %) and Graft Reaction Efficiency (GRE %). On the other hand, the newly prepared poly (AA)-cotton graft copolymers were characterized for different heavy metals ions removal to determined their suitability as cation exchanger. On the basis of a detailed investigation of the above factors, the appropriate conditions for grafting were as follows: Fe^{2+}, 0.005 mol L^{-1}; BrO_3^-, 0.001 mol L^{-1}; pH, 2; monomer, (50% based on weight of substrate); time, 90 min and temperature, 35°C. On the other hand, the potential value of the newly prepared poly (AA)-cotton graft copolymer to serve as cation exchanger was assessed through measurements of critical properties such as removal of different heavy metal ions from their solutions as well as durability.

Key words: Cotton, acrylic acid, grafting, initiator, heavy metals

INTRODUCTION

Grafting of synthetic polymeric chains is one of the most recurrent used methods to increase the compatibility between cellulose and different synthetic polymers[1]. A wide variety of monomers either hydrophilic or hydrophobic have been grafted onto cellulose[2-5], but in general acrylic monomers are the most commonly used. Redox initiators have been the most widely used for this task, where system based on ceric are commonly reported[6-8]. On the other hand, a novel series of ion exchange cellulose and starch have been prepared and evaluated[9-17]. Finally, this study is undertaken with a view to establish the optimum conditions of grafting acrylic acid onto cotton fabric in presence of Fe^{2+}/BrO_3^- redox pair as well as its characterization as cation exchanger.

MATERIALS AND METHODS

Cotton fabric (400 g m^{-2}, 21 Picks x 61 ends/cm) kindly supplied by Misr Spinning and Weaving Co., El-Mehalla El-Kubra. It was used after purification by scouring for 2 h at the boil using aqueous solution containing 1% sodium hydroxide. It was then thoroughly washed and air-dried at room temperature. Acrylic acid stabilized with 0.01% hydroquinone was freshly distilled at 75°C and pressure of 100 mm Hg; it was stored at 10°C until used. Ferrous sulphate (AR, BDH), potassium bromate (E. Merck) hydrochloric acid, sodium hydroxide, mercuric chloride, copper sulphate, zinc acetate, nickel chloride and lead acetate were reagent grade chemicals.

Grafting procedure: The graft polymerization reaction was carried out in 100 mL flasks containing an aqueous solution of acrylic acid. The flasks were stoppered and placed in a thermostatic water-bath until the required temperature was reached. The cotton fabric and calculated amount of ferrous sulphate and sulphuric acid were then added to the reaction mixture. A known amount of bromate solution was added to initiate the reaction and the reaction was performed under continuous flow of nitrogen gas to remove the dissolved oxygen. The contents were shaken occasionally during polymerization. After the desired reaction time, the flask contents were drained and the sample was thoroughly washed with distilled water and repeatedly extracted with hot water until constant weight i.e. complete poly acrylic acid (homopolymer) removal.

The grafting parameters were calculated gravimetrically as follows:

$$\text{Graft Yield (GY \%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Where, W_2 is the dry weight of grafted sample after extraction of homopolymer and W_1 is the dry weight of the original sample.

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$$\text{Graft Reaction Efficiency (GRE \%)} = \frac{W_2 - W_1}{W - W_1} \times 100$$

Where, W is the dry weight of polymerized sample before extraction of homopolymer.

Heavy metal ions removal: Solutions (50 mL) containing metal ions (2.5 g L^{-1}) were treated with the (1 g) poly (AA)-cotton graft copolymer as cation exchanger. After 24 h contact time, the adsorption value was calculated by estimating the metal ion concentration before and after treatment with poly (AA)-cotton graft copolymers having different graft yields by titration against standard EDTA.

RESULTS AND DISCUSSION

Effect of ferrous ion concentration on the grafting parameters: Increasing the ferrous ion concentrations from 0.001 to 0.005 mol L^{-1} led to an increase in the grafting parameter, while increasing the ferrous ion concentration above 0.005 mol L^{-1} led to a decrease in the grafting parameter (Fig. 1). Increasing the grafting parameters by increasing the ferrous ion concentration up to 0.005 mol L^{-1} may be duo to an increase in the free radicals produced by Fe^{2+}/BrO^{-}_{3} redox pair resulting in the faster rate of production of cotton cellulose macro radicals. While decreasing the grafting parameters after 0.005 mol L^{-1} may be duo to the inhibiting effect of ferric ions produced by the oxidation of ferrous ions. On the other hand, the termination of the growing grafted chains was also observed during the graft co polymerization reaction initiated by H_2O_2/Fe^{2+} redox system after certain concentration of ferrous ions[18].

Effect of bromate ion concentration on grafting parameters: The increase in bromate ion concentration led to a decrease in grafting parameters. This can be attributed to higher formation of homopolymer (Fig. 2).

Effect of pH on the grafting parameters: It was found that, the grafting parameters were decreased with increasing the pH within the range studied (Fig. 3). This can be explained with respect to, it is well known that, grafting could be favored in acidic medium; while in neutral or alkaline medium the grafting could not be effected duo to the immediate precipitation of ferrous hydroxide.

Effect of acrylic acid concentration on the grafting parameters: It is evident that the graft yield is directly related to the acrylic acid concentration within the range

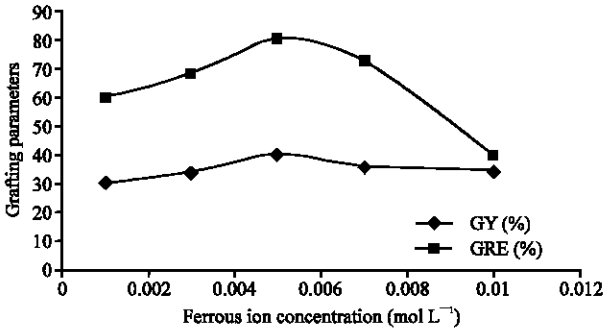

Fig. 1: Effect of ferrous ion concentrations on the grafting parameters
Reaction conditions: Cotton fabric, 2 g; [BrO_3^-], 0.002 mol L^{-1}; pH, 2; [AA], (50% based on weight of substrate); Time, 90 min, temperature, 35°C, material to liquor ratio, 1:50

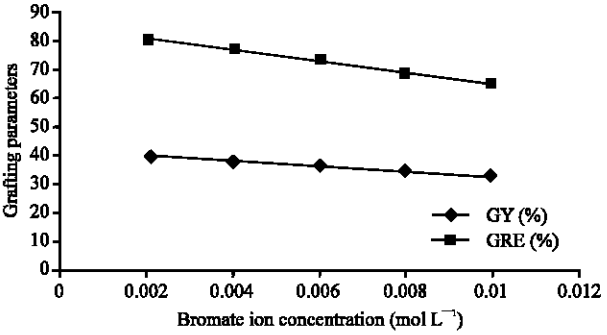

Fig. 2: Effect of bromate ion concentration on the grafting parameters
Reaction conditions: Cotton fabric, 2 g; [Fe^{+2}], 0.005 mol L^{-1}; pH, 2; [AA], (50% based on weight of substrate); Time, 90 min, temperature, 35°C, material to liquor ratio, 1:50

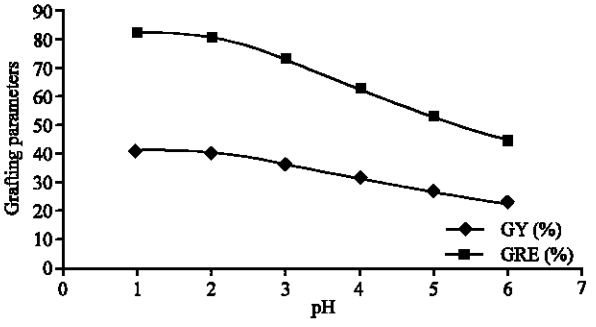

Fig. 3: Effect of changing pH on the grafting parameters
Reaction conditions: Cotton fabric, 2 g; [Fe^{+2}], 0.005 mol L^{-1}; [BrO_3^-], 0.002 mol L^{-1}; [AA], (50% based on weight of substrate); Time, 90 min, temperature, 35°C, material to liquor ratio, 1:50

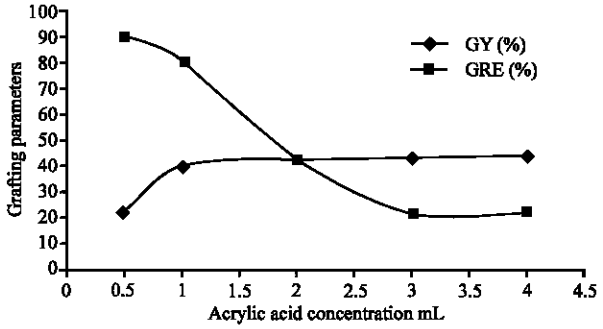

Fig. 4: Effect of acrylic acid concentration on the grafting parameters
Reaction conditions: Cotton fabric, 2 g; [Fe^{+2}], 0.005 mol L^{-1}; [BrO_3^-], 0.002 mol L^{-1}; pH, 2; Time, 90 min, temperature, 35°C, material to liquor ratio, 1:50

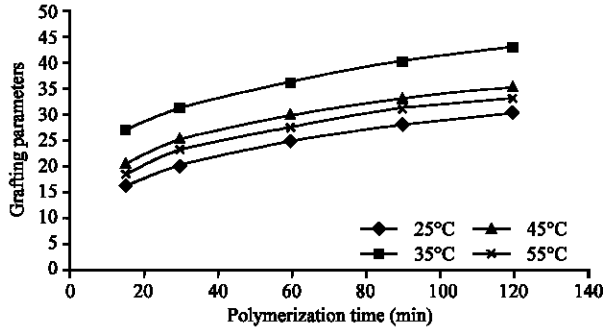

Fig. 5: Effect of reaction time and temperature on the grafting parameters
Reaction conditions: Cotton fabric, 2 g; [Fe^{+2}], 0.005 mol L^{-1}; [BrO_3^-], 0.002 mol L^{-1}; pH, 2; [AA], (50% based on weight of substrate); material to liquor ratio, 1:50

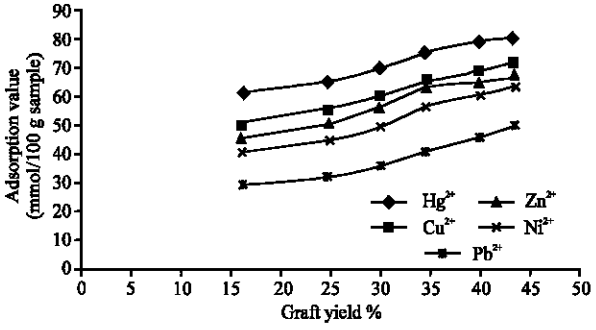

Fig. 6: Adsorption value (mmol/100 g sample) of different grafted cotton fabrics for different heavy metal ions removal

studied (Fig. 4). This is merely duo to greater availability of the monomer molecules at higher acrylic acid concentration in the proximity of cotton cellulose fabric.

While on the other hand, with respect to graft reaction efficiency %, the results imply that it decreases as the acrylic acid concentration increases, unlike the graft yield. This suggests that, beside its favorable effect on grafting reaction, the concentration of acrylic acid seems to have an outstanding effect on the homopolymerization reaction. Since the grafting reaction competes with the homopolymerization and since the concentration of acrylic acid acts more in favor of the latter and the observed decrement in GRE by increasing acrylic acid concentration can be explained.

Effect of reaction time and temperature: There was an increase in the grafting parameters with increasing reaction time within the range studied (Fig. 5). This may be duo to an addition of greater number of acrylic acid molecules to the growing grafting chain. This is seen irrespective of the polymerization temperature used. However, the extent of grafting is determined by temperature; the extent of grafting increases by raising the polymerization temperature from 25 to 35°C then decreases by raising the polymerization temperature thereafter. Results of grafting reaction efficiency are in accordance with those of grafting reaction.

This behaviour can be attributed to the increased rate of polymerization up to 35°C. A further increase in polymerization temperature could result in the enhanced mobility of cotton cellulose macroradicals that may lead to termination of the grafting chain, so, a decrease in the grafting parameters above 35°C was observed.

Tentative mechanism of grafting: The interaction between Fe^{2+} and BrO^-_3 ions in the grafting medium led to generation of hydroxyl and halogen free radicals as follows:

$$Fe^{2+} + BrO^-_3 + H_2O \rightarrow Fe^{3+} + BrO^-_2 + OH^{\bullet} + OH^-$$
$$Fe^{2+} + BrO^-_2 + H_2O \rightarrow Fe^{3+} + BrO^- + OH^{\bullet} + OH^-$$
$$Fe^{2+} + BrO^- + H_2O \rightarrow Fe^{3+} + Br^- + OH^{\bullet} + OH^-$$
$$Fe^{2+} + BrO^- + H_2O \rightarrow Fe^{3+} + Br^{\bullet} + 2OH^-$$

The hydroxyl and halogen free radicals abstract hydrogen atoms from the cotton cellulose molecules producing cellulose free radical (Cell-O$^{\bullet}$).The monomer molecules, which are in close vicinity to the sites of reaction, become acceptors of the cotton radicals resulting in chain initiation and thereafter themselves become free radical donors to the neighboring molecules, causing the grafted chain to grow. These grafted chains were determined by disproportionnation, coupling or chain transfer to give graft copolymer.

The following steps represent the reaction mechanism:

$$Cell\text{-}OH + R^{\bullet} \rightarrow CellO^{\bullet} + RH$$

Where, $R^{\bullet}$ stands for $OH^{\bullet}$ and $Br^{\bullet}$ free radicals.

Initiation

$$CellO^{\bullet} + M \rightarrow CellOM^{\bullet}$$
$$R^{\bullet} + M \rightarrow RM^{\bullet}$$

Propagation

$$CellO^{\bullet} + M \rightarrow CellOM^{\bullet}_{1}$$
$$CellOM^{\bullet}_{1} + M \rightarrow CellOM^{\bullet}_{2}$$
$$CellOM^{\bullet}_{n-1} + M \rightarrow CellOM^{\bullet}_{n}$$
$$RM^{\bullet} + M \rightarrow RM^{\bullet}_{1}$$
$$RM^{\bullet}_{1} + M \rightarrow RM^{\bullet}_{2}$$
$$RM^{\bullet}_{n-1} + M \rightarrow RM^{\bullet}_{n}$$

Termination

$$CellOM^{\bullet}_{n} + CellOM^{\bullet}_{n} \rightarrow \text{graft copolymer}$$
$$CellOM^{\bullet}_{n} + RM^{\bullet}_{n} \rightarrow \text{graft copolymer}$$
$$RM^{\bullet}_{n} + RM^{\bullet}_{n} \rightarrow \text{graft copolymer}$$

Characterization of the prepared copolymer as cation-exchanger

Removal of heavy metal ions: Poly (acrylic acid)-cotton graft copolymers having different graft yields ranged from (16.1-43.5%) were used for removing different heavy metal ions from their solutions. The different heavy metal ions used were Hg^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2} and Pb^{+2}.The obtained results are set out in Fig. 6.

It is seen from Fig. 6 that, the amount of heavy metal ions removed (expressed as adsorption value mmol/100 g sample) is governed by the extent of grafting expressed as graft yield % and nature of metal ion. As the capacity of the exchanger (graft yield %) increases from 16.1 to 43.5%, the magnitude of removal of heavy metal increases irrespective of the nature of metal ion used. It is also seen that, the synthesized poly (acrylic acid)-cotton graft copolymers, as cation exchanger is more effective in removing Hg^{+2} than all other metal ions in question and follow the order:

$$Hg^{+2} > Cu^{+2} > Zn^{+2} > Ni^{+2} > Pb^{+2}$$

This is in accordance with lrving-William's series[19] for the stability of various ligands with nitrogen or oxygen as coordinating atoms for divalent transition metal ions.

Table 1: Durability of poly (AA)-cotton graft copolymer cation exchanger

Durability of poly (AA)-cotton graft copolymer cation exchanger having different graft yields after;

Zero cycle	5 cycles	10 cycles	20 cycles
16.1	15.8	15.8	15.8
24.9	24.0	24.0	24.0
30.2	29.7	29.7	29.7
34.7	33.8	33.8	33.8
40.2	39.9	39.9	39.9
43.5	42.9	42.9	42.9

Durability: Table 1 represents the durability after 20 cycles of the aforementioned synthesized cation exchanger. The exchanger acquires excellent durability and therefore stability within the range studied.

ACKNOWLEDGMENT

I wish to express my deepest thanks and appreciation to Prof. Dr. H. Al-Bar Professor of Organic Chemistry, Faculty of Science, Chemistry Department, King Abdul Aziz University for providing all basic laboratory facilities as well as his interest and cooperation throughout this work.

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