



RECOVERY OF WATER FROM HEAVY METALS USING CHELATING CHEMICALLY MODIFIED CHITOSAN

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ABSTRACT

Graft copolymerization of diaminomaleonitrile onto chitosan using ceric ammonium nitrate (CAN) as initiator under N₂ atmosphere has been accomplished. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 1.6 M, [CAN] = 5 × 10⁻² mol/L, T = 70°C and t = 3 hr for 0.5 g chitosan. The imparted cyano groups of the grafted chitosan polymer chains (with degree of grafting up to 84%) were converted into amidoxime groups by the reaction with hydroxylamine hydrochloride. The complexation ability of amidoximated DAMN-graft-chitosan copolymer was investigated with respect to the adsorption of Pb²⁺, Cd²⁺, Zn²⁺, Fe³⁺, Cu²⁺, Ni²⁺ and Co²⁺ from aqueous solution. The results show that the recoveries of the metals are ~ 93%.

Key words: Graft copolymerization, Chitosan, Amidoximation, Metal adsorbents.

INTRODUCTION

Chitosan has many interesting biological and chemical properties. The excellent features such as biocompatibility, ecologically safe, biodegradability (degradation products of chitosan are non-toxic, non-immunogenic and non-carcinogenic) and low toxicity with versatile biological activities (chitosan has antimicrobial activity and low immunogenicity) recommends this biopolymer for applications in biomedicine¹⁻⁴. In addition, chitosan is very efficient for interaction with the anionic solutes including dyes in acidic solutions due to the reactive groups, such as -OH and -NH₂. This property has been widely used for the removal of the water-soluble dyes, as an alternative to the conventional sorbents and flocculants⁵. However, due to inter- and intramolecular H-bonding, chitosan is only soluble in few dilute acid solutions (depending on the molecular weight), which limits its applications. As a result, many attempts have been made in chemical modification of chitosan, aiming at improving

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its water solubility. Among these, an ideal way is the graft modification of chitosan⁶⁻⁹. The main advantage in the grafting efforts is the high degree of functionality of chitosan - the molecule backbone contains two hydroxyl groups and one primary amine group per repeat unit. The active primary amino groups on the molecule being reactive provide sites for the attachment of different side groups employing mild reaction conditions. In this way, versatile materials based on chitosan with specific functionality can be obtained. Grafting vinyl monomers onto chitosan is one of the most effective methods to improve the performances of chitosan without sacrificing its properties and also is a challenging field of research with unlimited future prospects. Vinyl graft copolymerization can be described as the modification of a preexisting polymer chain. Graft copolymers are synthesized to improve physicochemical properties of synthetic/natural polymers for applications in agriculture, biomedicine and other fields.

Different studies have been published on the grafting copolymerization of chitosan with various vinyl monomers like methyl acrylate¹⁰, methyl methacrylate¹¹, acrylamide¹², acrylic acid¹³, and acrylonitrile¹⁴ using redox initiators. Many different natural and synthetic materials with chelating properties have been developed for use in chemical processes of industries plants for preventing operational problems or contamination of the environment. Recently, the adsorbents based on natural products and their derivatives deserved particular attentions because of an increasing interest in the removal of heavy metal ions from waste water. For example, synthesis and characterization of amidoximated polyacrylonitrile/organobentonite composite for Cu(II), Zn(II), and Cd(II) adsorption from aqueous solutions and industry wastewaters were evaluated¹⁵.

A new polymer containing double amidoxime groups per repeating unit was synthesized to enhance the metal ion uptake capacity. The adsorption properties of this new polymeric adsorbent, amidoximated poly(N,N'-dipropionitrile acrylamide), for U(VI), V(V), Cu(II), Co(II) and Ni(II) ions were investigated by batch and flow-through processes at very low concentration levels (ppb). The chelating polymer showed high adsorption capacity for uranyl as well as vanadyl ions^{16,17}. As with cellulose and starch, the ceric ion has been a useful initiation method for graft copolymerizing chitin and chitosan with typical vinyl monomers due to the similarities in the chemical structures of these polysaccharides. The obtained materials are convenient for waste water treatment applications, since they are able to absorb various impurities very fast due to their chelation and/or complexation abilities through their reactive groups, such as, amine, amide, nitrile and oxime groups. In addition, these materials can be reused without loss of their sorption characteristics. Water is the most essential part of every aquarium, since it is the media that our fishes and plants live in and

totally rely upon for their feeding and survival. Thus, we need to treat the water and make it as suitable as possible for the aquatic life you keep. Therefore, water treatment can be defined as any procedure or method used to alter the chemical composition or natural behavior of a water supply. In continuation to our work¹⁸⁻²¹, the complexation ability of amidoximated DAMN-graft-chitosan copolymer was investigated in this work with respect to the adsorption of some heavy metals from aqueous solution.

EXPERIMENTAL

Materials and methods

Materials

Chitosan was purchased from India Sea Foods, Kerala, India. Diaminomaleonitrile: (Hebei Furan International Co., Ltd.) [Hebei, China (Mainland)] were used. The initiator, ceric ammonium nitrate (CAN) and other reagents were Merck products. Stock solutions of 1 mg mL^{-1} of Pb^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+} were prepared. They were diluted and mixed to give stock standard solutions of $100 \text{ } \mu\text{g mL}^{-1}$ and the standard solutions were used for all experiments.

Characterization

FTIR spectroscopy of the grafted chitosan was recorded with a Vector 22 Fourier transform infrared spectrometer (Bruker). An ICP/6500 inductively coupled plasma atom emission spectrometer (Perkin-Elmer) was used and the adsorption column is a glass tube (12 x 0.5 cm) containing 0.1 g of resin in high-purity water overnight. It is held in place by cotton-wool. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-2. DSC measurements were performed in temperature range of 20-450°C at the heating rate of 10°C/min in a N_2 atmosphere. Thermal gravimetric analysis (TGA) studies were carried out using Perkin-Elmer TGA-7. Thermo grams were obtained in temperature range of 50-700°C at a constant heating rate of 10°C/min under N_2 atmosphere.

Synthesis of graft copolymers

Diaminomaleonitrile (DAMN) (0.33 g) was added with 1 g of chitosan in water (10 mL) and left overnight. A chitosan aqueous solution of 2 wt. % was prepared by dissolving 20 g of chitosan powder in 1000 mL of acetic acid. After chitosan was dissolved, the solutions were filtered with cheese cloth by vacuum aspiration to remove foam and any undissolved impurities. The ceric ammonium nitrate (0.02-0.06 mol, 0.11-0.33 g) in nitric

acid (0.1-0.4N) was then loaded into the reactor under continuous stirring. The grafting reaction was carried out under nitrogen atmosphere in a 500 mL, four-necked flask equipped with a reflux condenser, a stirrer, dropping funnel, and a gas inlet system immersed in a constant temperature water bath. In all reactions, total volume of the reaction was kept constant. The grafting reaction was carried out for varying time intervals (1-4 hr). After completion of the reaction, the precipitated product was recovered by centrifugation and washed with pure methanol (2×50 mL). The crude copolymer thus obtained was dried till constant weight under vacuum (7.6 mm Hg) for 24 hr at 40°C. The dried product was extracted with dimethylformamide for 48 hr and washed with methanol to remove the homopolymer (polymaleonitrile). The grafted Chitosan (Chitosan-g-DAMN) was dried to a constant weight homopolymer formed in the grafting medium collected and dried in an oven at 70°C.

$$\text{Grafting yield (\%)} = \frac{[(\text{dry wt. of grafted cellulose} - \text{dry wt. of original cellulose}) / \text{dry wt. of original cellulose}] \times 100}{\dots(1)}$$

Grafting efficiency (GE) was calculated as follows:

$$\text{GE (\%)} = \frac{[(\text{wt. of graft}) / (\text{wt. of graft} + \text{wt. of homopolymer})] \times 100}{\dots(2)}$$

Amidoximation of pendant nitrile groups

The obtained graft polymer, DAMN84-g-chitosan (with grafting yield 84%) was reacted with the methanol solution of hydroxylamine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$, at 80°C in the presence of triethylamine. During the amidoximation reaction, samples were taken from the reaction vessel at certain time intervals and the conversion to amidoxime structure was followed by determining the changes in CN triple bonds of polymer from respective FTIR spectra. After amidoximation reaction was completed, the amidoximated polymer taken from reaction vessel was washed with distilled water and then dried at 40°C in a vacuum oven.

Analytical procedure

The mixed standard solutions of Pb^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+} are pipetted into beakers (100-500 mL). The solutions are passed through the adsorbing columns (containing DAMN84-g-chitosan) at a flow rate of 4 mL min^{-1} . The analyte is desorbed from each column with 10 mL of 2 M HCl solution at a flow rate of 1.0 mL min^{-1} . Subsequently, the ions in the 10 mL of elute are determined by ICP spectrometer. The conditions for analysis by ICP-AES are: forward power 1100 W, argon plasma gas flow rate 14 L min^{-1} ,

argon nebulizer gas flow rate 1.0 L min^{-1} , argon intermediate gas flow rate 0.6 L min^{-1} ; wavelengths: Pb^{2+} 220.350 nm, Cd^{2+} 226.499 nm, Zn^{2+} 213.855 nm, Fe^{3+} 259.933 nm, Cu^{2+} 324.747 nm, Ni^{2+} 231.602 nm and Co^{2+} 228.612 nm.

RESULTS AND DISCUSSION

Effect of time on grafting yield

Graft copolymerization of chitosan was achieved at various polymerization times, keeping the monomer, initiator and temperature constant at $[\text{DAMN}] = 1.4 \text{ M}$, $[\text{CAN}] = 5 \times 10^{-2} \text{ mol/L}$ and $T = 70^\circ\text{C}$, respectively. Grafting yield percentage first increased with increasing polymerization time; and then leveled off, reaching to a maximum grafting value of 84% at 3 hr (Fig. 1). This is attributed to the diffusion of monomer and initiator molecules into chitosan chains.

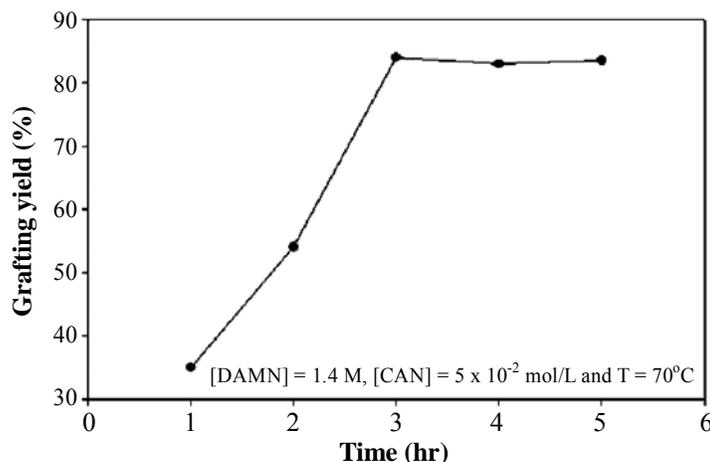


Fig. 1: Variation of graft yield with time

Effect of temperature on grafting yield

Within the range of $40\text{--}80^\circ\text{C}$, monomer, initiator and polymerization time was kept constant, Fig. 2 shows an increase in the graft copolymerization yield value to about 84%. The enhancement in the grafting yield with increasing temperature may be due to the enhancement of chitosans well ability and the diffusion of the initiator and the monomer into chitosan chains. Also, formation of homopolymer indicates the leveling off of the grafting yield beyond 70°C .

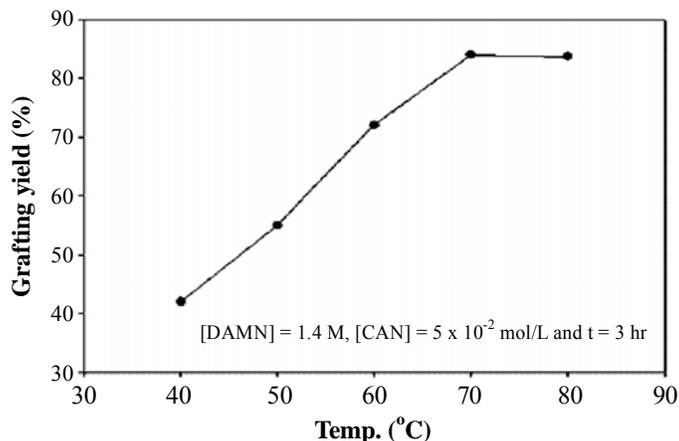


Fig. 2: Variation of grafting yield with temperature

Effect of initiator concentration on grafting yield

The effect of initiator concentration on grafting yield was illustrated in Fig. 3, which demonstrates that the graft yield increases with the increase in ceric ammonium nitrate (CAN) concentration in the range 2×10^{-2} to 6×10^{-2} mol/L, and then decreases with further increase in the CAN concentration. The increase of grafting yield by increasing the CAN concentration to a certain limit prove that free-radical species produced by the dissociation of CAN molecules may participate essentially in the abstraction of hydrogen atoms from chitosan back-bone, yielding a chitosan radical capable of initiating grafting. However, when the initiator concentration was increased beyond 5×10^{-2} mol L⁻¹, termination reactions of the graft copolymerization takes place.

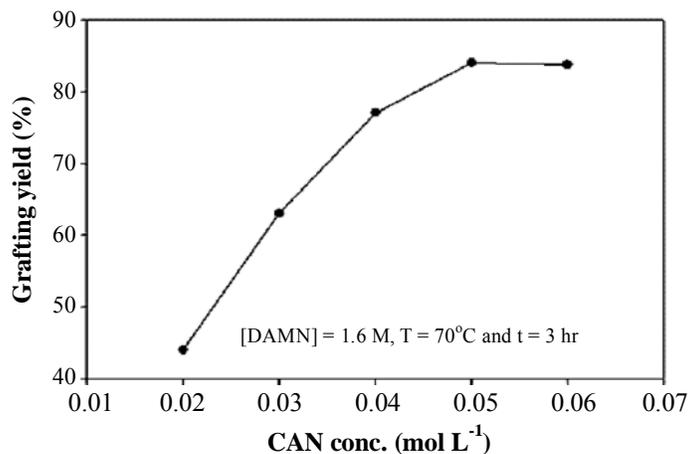


Fig. 3: Grafting yield dependence on CAN concentration

Effect of monomer concentration on grafting yield

The effect of monomer concentration on graft copolymerization is illustrated in Fig. 4, which shows that the graft copolymerization yield rises with increasing DAMN concentration up from 1-1.6 mol L⁻¹, producing 84% grafting yield. With further increase in diaminomaleonitrile concentration, the grafting yield decreases. The decrease in the grafting yield at higher DAMN concentrations may be due to the adsorption of monomer on the chitosan surface in excessive amounts, which prevents diffusion of the initiator molecules inside the chitosan resulting in lowering the graft yield. It may be also attributed to the increase of the homo-polymerization rather than grafting at these high monomer concentrations.

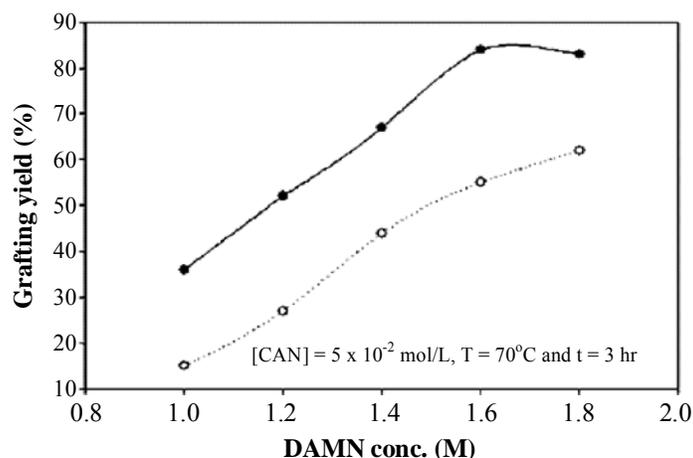


Fig. 4: Variation of grafting yield with DAMN concentration
Grafting efficiency % vs DAMN concentration

Conversion of chitosan into graft copolymer using diaminomaleonitrile as monomer in the presence of initiator (CAN) and further modification into amidoxime structure are achieved. The final step is the amidoximation of nitrile groups of grafted polymer. Nitrile groups were converted to amidoxime groups by reacting with hydroxylamine hydrochloride in the presence of triethylamine. The unique advantage of this polymer is that it contains double amidoxime groups per repeating unit and an additional diethylene spacer unit between neighboring amidoxime groups in each monomeric unit. Our attempts¹⁸⁻²¹ of preparation of resins with diamidoxime units per repeating unit were reported.

FTIR Spectroscopy

FTIR spectroscopy of un-grafted, grafted and amidoximated chitosan is shown in Fig. 5, which showed a peak at 3363 and 2232 cm⁻¹ assignable to (NH, OH) and (CN)

groups, respectively, in the grafted chitosan. Presence of a peak assignable to CN group in the grafted chitosan indicated high efficiency of grafting process. Bands were revealed at 2927 cm^{-1} (C-H stretching), 1084 and 1463 cm^{-1} (arising from C-O and amide C=O, respectively) for amidoximated chitosan. The absence of CN band and the presence of C=O band as well as NH_2 band prove amidoximation of all CN groups.

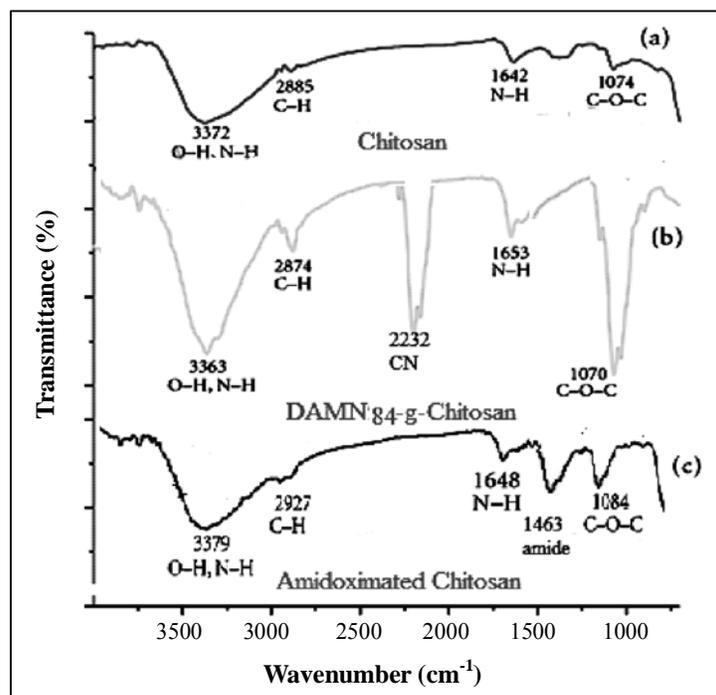


Fig. 5: FTIR spectra of un-grafted chitosan (a), DAMN84-g-chitosan (b), Amidoximated chitosan (c)

Glass transition temperatures (T_g) for chitosan (203°C),²² chitosan graft (187°C) and amidoximated chitosan (168°C) are illustrated in Fig. 6, which show only one T_g for each copolymer. It is postulated that the wide endothermic peak at temperatures below 150°C was a result of the loss of moisture. Glass transition temperature of the grafted chitosan is lower than glass temperature of un-grafted chitosan. This is due to a variation of chain flexibility inherited from methylene length. A decrease in T_g values is observed as a result of grafting indicating the incorporation of polydiaminomaleonitrile chains in amorphous copolymers with higher thermal stability. Besides, the presence of side groups along the chains can also make the chains stand off from one another and lead to the increase of the distance of chains and free volume reducing T_g . This allows the polymer chains to become more flexible and move past one another easily at lower temperature.

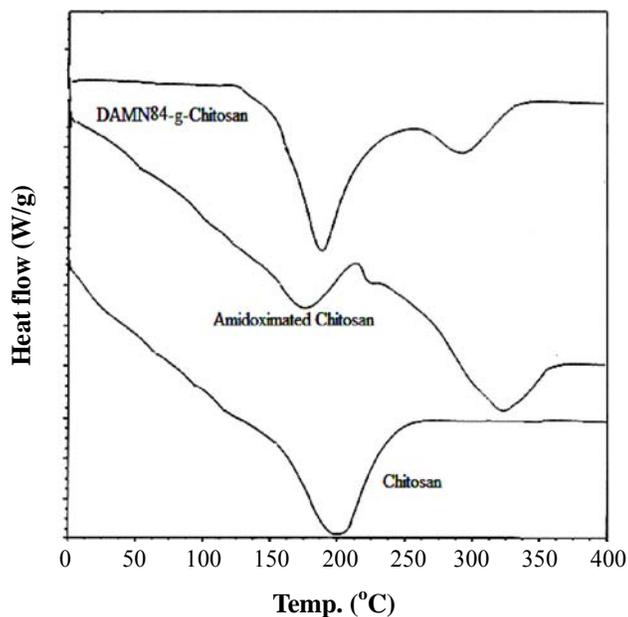


Fig. 6: DSC thermogram of chitosan, DAMN84-g-chitosan and amidoximated chitosan

The effect of grafting on the thermal stability of the prepared copolymers was studied using thermo-gravimetric analysis (TGA). Fig. 7 shows TGA thermograms of un-grafted chitosan, DAMN84-g-chitosan and amidoximated chitosan.

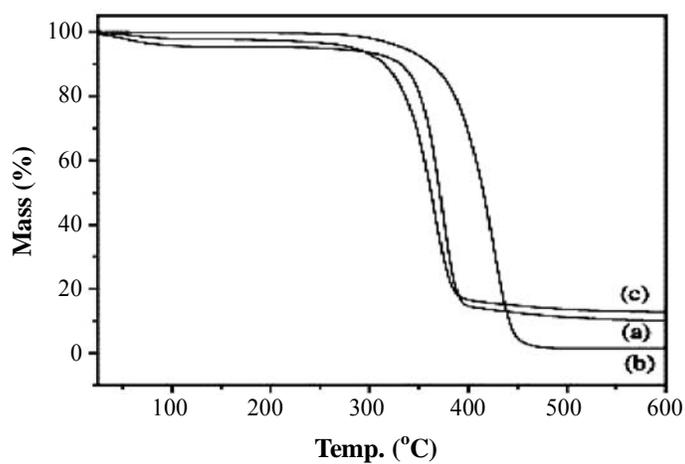


Fig. 7: TGA thermogram of chitosan (c), DAMN84-g-chitosan (a) and amidoximated chitosan (b)

The TGA curve for parent chitosan shows that loss in chitosan weight occurred, which is attributed to the actual pyrolysis by a major decomposition at 320 °C. The actual decomposition for DAMN84-g-chitosan occurred at 340°C. This means that chitosan grafts are more thermally stable than the un-grafted chitosan. Amidoximated chitosan, however, shows better thermal stability having main degradation step recorded at 388 °C. This thermal stability would make the amidoximated chitosan suitable for many practical applications.

Recovery and separation of heavy metals

The obtained material (amidoximated chitosan) was evaluated over several sorption/desorption cycles. Kinetics of sorption/desorption of metal ions could not be followed by gravimetric studies because that requires removal and drying of the samples periodically, which affects the accuracy of the results. Thus, a spectrophotometric technique was applied. With this technique, it is easy to determine the absorbed/desorbed amounts of metal ions without removing and drying the samples. Equal concentrations of mixed standards are diluted to equal volumes and enriched through the columns as described in experimental section. The results in Table 1 show that the metals can be enriched quantitatively by the resin with recoveries of 93-98%. It can be seen that the amidoximated chitosan is characterized by a considerably greater binding ability with respect to heavy metals.

Table 1: Effect of flow rate on enrichment recovery

| Flow rate (mL min ⁻¹) | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 | 8.0 |
|-----------------------------------|------------|-----|-----|-----|-----|-----|-----|
| Element | Recovery % | | | | | | |
| Pb | 87 | 98 | 96 | 96 | 90 | 83 | 61 |
| Cd | 89 | 96 | 95 | 91 | 82 | 71 | 59 |
| Zn | 91 | 96 | 94 | 88 | 78 | 70 | 61 |
| Fe | 89 | 98 | 95 | 91 | 81 | 73 | 63 |
| Cu | 93 | 97 | 93 | 87 | 77 | 65 | 59 |
| Ni | 88 | 93 | 92 | 85 | 75 | 62 | 53 |
| Co | 90 | 95 | 96 | 89 | 81 | 72 | 51 |

The nature of the metal ion also has great importance in the amount binding to the polymeric material. Meanwhile, at pH 1-6, the chelating resin hardly enriched such metal ions.²³ When using the recommended procedure, the flow rate for preconcentration of the analyte on the resin columns was varied between 2.0 and 8.0 mLmin⁻¹. The results in Table 1 show that metal ions can be enriched quantitatively at flow rate of 3.0 mL min⁻¹. After the chelating resin is treated with strong acids, the resin is washed to neutrality with distilled water and used again for regenerated amidoximated chitosan is once again effective for resorption.

CONCLUSION

A novel diaminomaleonitrile-functionalized chitosan grafts (DAMN-g-chitosan) were synthesized. Ceric ammonium nitrate (CAN) was used as initiator under N₂ atmosphere. The study was forwarded to establish the optimum conditions for grafting. The results indicate that amidoximated product of the obtained graft copolymer DAMN84-g-chitosan is a potentially powerful ion exchanger that can be employed for heavy metals removal from waste water effluents. The results show that the recoveries of the metals are ~ 93%.

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