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Preparation of chelating grafted chitin possessing amidoxime moieties and its application in removal of some heavy metals from aquatic samples

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ABSTRACT

Modification of chitin through graft copolymerization with diaminomaleonitrile afforded chitin grafts (DAMN-g-Chitin). Potassium persulphate (KPS) and ferrous ammonium sulphate (FAS) are combined in a redox system and used as initiator under N_2 atmosphere. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 1.4 M, [KPS] = 6×10^{-2} mol/L, T = 75 ºC and t = 2 h for 0.5g chitin. The imparted cyano groups of the grafted chitin polymer chains (with degree of grafting up to 234 %) were converted into amidoxime groups by the reaction with hydroxylamine hydrochloride. The complexing ability of amidoximated DAMNgraft-Chitin copolymer was investigated with respect to the adsorption of Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+} and Co^{2+} from aqueous solution.

KEYWORDS

Graft copolymerization;
Chitin;
Amidoximation;
Metal adsorbents.

INTRODUCTION

Graft copolymerization is a mean of modifying some polymeric materials to impart them new properties suitable for many applications. The nontoxic, biodegradable and biocompatible properties of chitin have been of interest in the past few decades to a wide range of industrial applications. Heavy metal ions resultants of the chemical process industries are pollutants that have received great attention of the governmental organizations since they can be absorbed by plants and animals and then concentrated in the foods. It is well known that heavy metal ions released into the environment are highly toxic to the living organisms and change ecological balance by environmental cycling[1,2]. Various methods including reverse osmosis, ion-exchange, adsorption and electro-dialysis techniques have been developed in order to remove or recover the heavy metal ions from all kinds of waste water[3]. Many different natural and synthetic materials with chelating properties have been developed for use in chemical processes industries plants for preventing operational problems or contamination of the environment[4]. Also, chitin, its derivatives[5] and modified cellulose[6] have been studied with respect to their ability to remove heavy metals from aqueous solution. Grafting of various monomers on plastic chitin can successfully solve the problem of preparation of polyfunctional sorbents and membranes[7-9].

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, crosslinked amphoteric starch with quaternary ammonium groups can effectively remove Cr (VI), Cu (II) and Pb (II) ions in aqueous solution[10,11]. The obtained materials are convenient for waste water treatment applications, since they are able to absorb impurities very fast due to their chelation and/or complexation abilities through their reactive groups, such as carboxylic acid, amine, amide, nitrile, oxime groups, etc. Graft copolymerization of hydroxyethyl methacrylate (HEMA) onto polyethylene terphthalate fibers and fabric using dibenzoyl peroxide as initiator and the conditions affecting on grafting yield were investigated[12]. The capacities of Ni (II) adsorption using vinyl-2-pyrrolidone grafted chitin from aqueous solution have been measured. The graft copolymer VP-g-Ch shows an excellent ability for Ni (II) adsorption[10]. The newlysynthesized starch graft copolymers containing aminoethyl groups was used for removing Cu (II) and Pb (II) ions in the aqueous solution by the effective complexation of amine group with Cu (II) and Pb (II) ions. The effects of various parameters such as metal ions concentration, adsorption time, adsorption temperature and grafting percentage of the starch graft copolymers were investigated. Moreover, the adsorbed Cu (II) and Pb (II) ions can be easily desorbed by treating with HCl solution and the desorption percentage reached above 95% when desorbing with 1 N HCl solution for 1 h at room temperature[13]. Removal of concentrated heavy metal ions from aqueous solutions using polymers with enriched amidoxime groups was evaluated[14]. Synthesis and characterization of diaminomaleonitrile-functionalized polystyrene grafts for application in pervaporation separation were reported[15]. Synthesis, characterization and amidoximation of diaminomaleonitrile-functionalized polyethylene terphthalate (PET) or PVA grafts for collecting heavy metals from wastewater were studied[16,17]. An ICP-AES method using a new spherical macroporous epoxy–polyamide chelating resin to enrich and separate trace Ga (III), In (III), Bi (III), V (V), Cr (III), and Ti (IV) ions from solution samples is established[18]. Graft copolymerization of vinyl acetate with chitin was effected using either the ferrous ion/hydrogen peroxide redox system or gamma radiation for initiation. Results imply that the redox initiation is superior to irradiation; since it gives a much higher graft yield. As with cellulose and starch, the ceric ion has been a useful initiation method for graft copolymerizing chitin and chitosan with typical vinyl monomers[19-21], due to the similarities in the chemical structures of these polysaccharides. Carboxymethyl derivatives of both chitin and chitosan are water-soluble and exhibit a low toxicity[22]. In this work the complexing ability of amidoximated DAMNgraft-Chitin copolymer was investigated with respect to the adsorption of Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+} and Co^{2+} from aqueous solution.

MATERIALS AND METHODS

Materials

Commercially available chitin: (Surapon Foods Public Co., Ltd., Thailand). Diaminomaleonitrile: (Hebei Furan International Co., Ltd.) [Hebei, China (Mainland)] were used. The initiator, potassium persulphate (KPS), ferrous ammonium sulphate $(NH_4)_2Fe(SO_4)_2$ and other reagents were Merck products. Stock solutions of 1mg 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 μg ml^{-1} and the standard solutions were used for all experiments.

Characterization

FTIR spectroscopy of the grafted chitin 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 0.1g 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 measurments were performed in temperature range of 20–450 ºC at the heating rate of 10 ºC /min in a N_2 atmosphere. Thermal gravimetric analysis (TGA) studies were carried out using Perkin-Elmer TGA-7. Thermograms were obtained in temperature range of 50–700 ºC at a constant heating rate of 10 ºC/min under N_2 atmosphere.

Synthesis of graft copolymers

0.5 g of chitin was mixed in 50 ml stopper round-bottomed flask with water–dioxane mixture (1:1) followed by the addition of diaminomaleonitrile (monomer) and left overnight. The reaction mixture was transferred to a 100 mL three-necked flask equipped with a mechanical stirrer. The reaction mixture was purged with nitrogen gas for 30 min. Potassium persulphate (KPS) and ferrous ammonium sulphate are combined in a redox reaction initiator was added in the required order (molar ratio of ferrous ammonium sulphate/potassium persulphate (0.225/0.112 g/g) was added to the reaction flask and the reaction mixture was continuously stirred for 2 hours and nitrogen gas was allowed to pass through the solution at 75 °C. At the end, the grafted chitin was removed and subjected to soxhlet-extraction for 6 h with methanol and distilled water, respectively to remove the homopolymer. At the end of the grafting procedure, homopolymer formed in the grafting medium was precipitated by the addition of excess acetone, collected and dried in an oven at 70 °C. Grafting yield (%) = [(dry wt. of grafted chitin – dry wt. of original chitin)/ dry wt. of original chitin] x 100. Grafting efficiency (GE) was calculated as follows:

GE (%) = [(wt. of graft)/ (wt. of graft + wt. of homopolymer)] x 100.

Amidoximation of pendant nitrile groups

The obtained graft polymer, DAMN234-g-Chitin, was reacted with the methanol solution of hydroxylamine hydrochloride, $NH_2OH.HCl$, at 80 ºC 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 ºC 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 DAMN234-g-Chitin) at a flow rate of 4 mL min^{-1}. The analytes are desorbed from each column with 10 mL of 2M HCl solution at a flow rate of 1.0 mL min^{-1}. Subsequently, the ions in the 10 mL of eluate 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

Graft copolymerization of chitin was achieved at various polymerization times, keeping the monomer, initiator and temperature constant at [DAMN] = 1.4 M, [KPS] = 6 x10$^{"2}$ mol/L and T = 75 ºC, respectively. As shown in (Figure 1), grafting yield percentage first increased with increasing polymerization time; and then leveled off, reaching to a maximum grafting value of 234 % at 2 h. This is attributed to the diffusion of monomer and initiator molecules into chitin chains. Within the range of 40-90 ºC, keeping monomer, initiator and polymerization time constant, Figure 2 shows an increase in the graft copolymerization yield value to about 234 %. The enhancement in the grafting yield with increasing temperature may be due to the enhancement of chitin swellability and the diffusion of the initiator and the monomer into chitin chains. Also, formation of homopolymer indicates the leveling off of the grafting yield at 75 ºC.

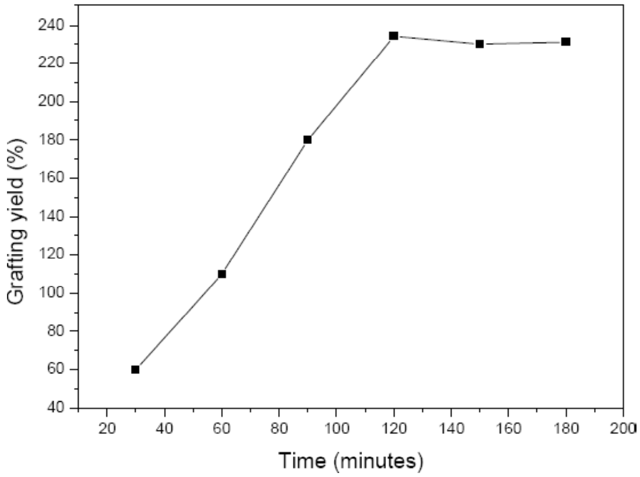

Figure 1: Effect of time on grafting yield and grafting efficiency. [DAMN] = 1.4 M, [KPS] = 6 x10"2 mol/L, T = 75 ºC.

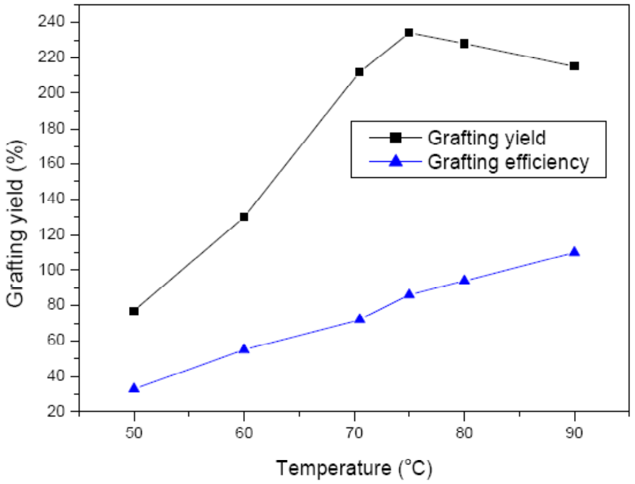

Figure 2 : Effect of temperature on grafting yield and grafting efficiency. [DAMN]=1.4 M, [KPS]=6 x10"2 mol/L and t=2h

Figure 3 revealed that the graft copolymerization yield increases as the initiator (KPS) concentration increases from 3 x $10^{"2}$ to 6 x $10^{"2}$ mol/L, and then decreases with higher KPS concentration. Thus, potassium persulfate (KPS) and ferrous ammonium sulfate (FAS) are combined in a redox reaction that ultimately produces hydroxy radicals being able to form chitin macroradicals (scheme 1) capable of initiating graft copolymerization. However, using initiator concentration higher than 7 x10^{-2} mol/L, lead to termination reactions of the graft copolymerization. The percentage of grafting increases with the increase in catalyst $(NH_4)_2Fe(SO_4)_2$ concentration up to 12x10^{-2} and then starts decreasing (Figure 4). Redox reaction produces Fe (III) ions and active sites on chitin chains, thereby increase the graft yield up to certain concentration of catalyst. But beyond this concentration, the grafting yield decreases. This is attributed to the formation of large number of Fe (III) ion which promote the premature termination of the growing grafted macromolecules[20,21]

$$Fe^{2+} + {}^{-}O_3S—O—O—SO_3^{-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -}$$
$$SO_4^{\bullet -} + H_2O \rightarrow HSO_4^{-} + HO^{\bullet}$$
$$Chitin\%H\ + HO \rightarrow Chitin^{\cdot}$$

Scheme 1: Chitin macroradicals by redox reaction

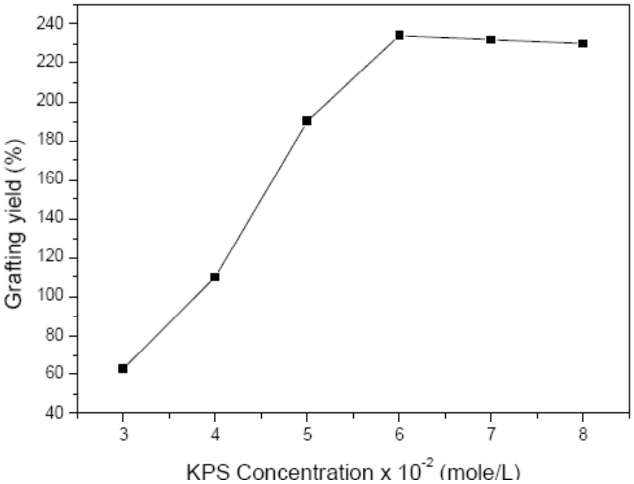

Figure 3 : Effect of initiator concentration on grafting yield. [DAMN] = 1.4 M, T = 75 ºC and t = 2 h.

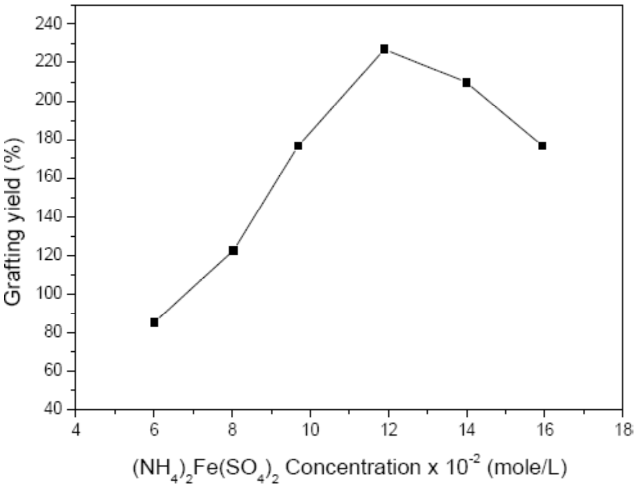

Figure 4 : Effect of catalyst (NH4)$_2$Fe(SO4)$_2$ concentration on grafting yield. [DAMN] = 1.4 M, T = 75 ºC and t = 2 h

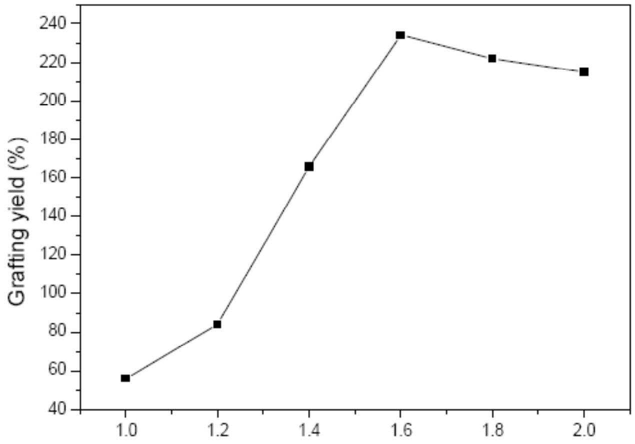

Figure 5 : Effect of monomer concentration on grafting yield. [KPS] = 6 x10"2 mol/L, T = 75 ºC and t = 2 h

The effect of monomer concentration on graft copolymerization is illustrated in Figure 5 which showed that the graft copolymerization yield rises with increasing DAMN concentration up from 1 - 1.6 mol/L, producing 234 % grafting yield. With further increase in diaminomaleonitrile concentration the grafting yield decrease. The decrease in the grafting yield at higher DAMN concentrations may be due to the adsorption of monomer on the chitin surface in excessive amounts, which prevents diffusion of the initiator molecules inside the chitin resulting in lowering the graft yield. It may be also attributed to the increase of the homopolymerization rather than grafting at these high monomer concentrations.

Conversion of chitin into graft copolymer using diaminomaleonitrile as monomer in the presence of initiator (KPS) 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 using 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. There are two attempts[22,23]of preparation of resins with diamidoxime units per repeating unit so far all of which completely differ from our approach. FTIR spectroscopy of chitin and grafted chitin is shown in Figure 6 which showed a peak at 3343, 3407 and 2265 cm^{-1} assignable to (NH_2), (NH) and (CN) groups, respectively. Bands were revealed at 2922 cm^{-1} (C-H stretching), 1436, 1052 and 1736 cm^{-1} (arising from C-C, C-O and C=O, respectively). A characteristic strong band appearing at around 3495 cm^{-1} corresponds to O%H stretching vibrations of the hydroxyl group of chitin disappear in grafted and amidoximated chitin indicating the active site for propagating step. Presence of a peak assignable to CN group in the grafted chitin indicated high efficiency of grafting process. Also, a peak at 2873 cm^{-1} assignable to CH stretching of CH_2 was found. Glass transition temperatures (Tg) for chitin (237 ºC)[24], chitin graft 183 ºC and amidoximated chitin 164 ºC are illustrated in Figure 7 which show only one Tg for each copolymer. It is postulated that the wide endothermic peak at temperatures below150 ºC was a result of the loss of moisture. Glass transition temperature of the grafted chitin is lower than glass temperature of ungrafted chitin. This is due to a variation of chain flexibility inherited from methylene length. A decrease in Tg 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 Tg. This allows the polymer chains to become more flexible and move past one another easily at lower temperature. The effect of grafting on the thermal stability of the prepared copolymers was studied using thermo-gravimetric analysis (TGA). Figure 8 shows TGA thermograms of ungrafted chitin, DAMN234-g-Chitin and amidoximated chitin. A continuous weight

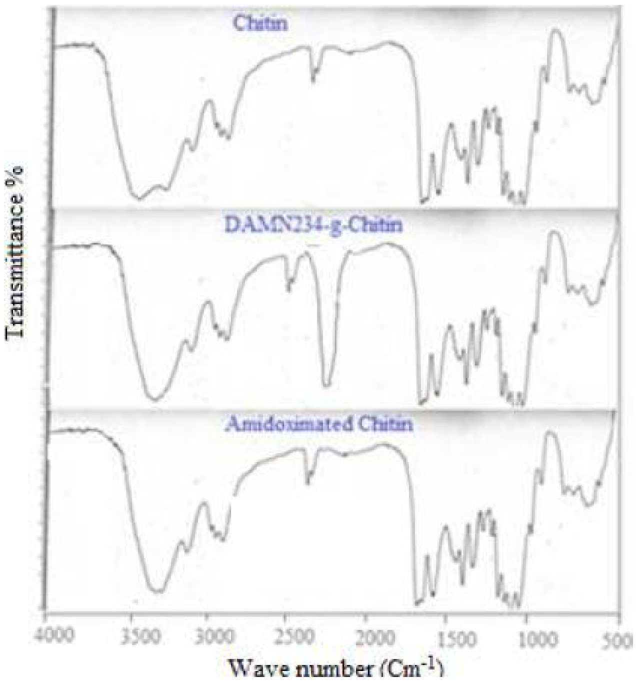

Figure 6 : FTIR spectra of ungrafted- Chitin, DAMN-g- Chitin and amidoximated DAMN234-g- Chitin

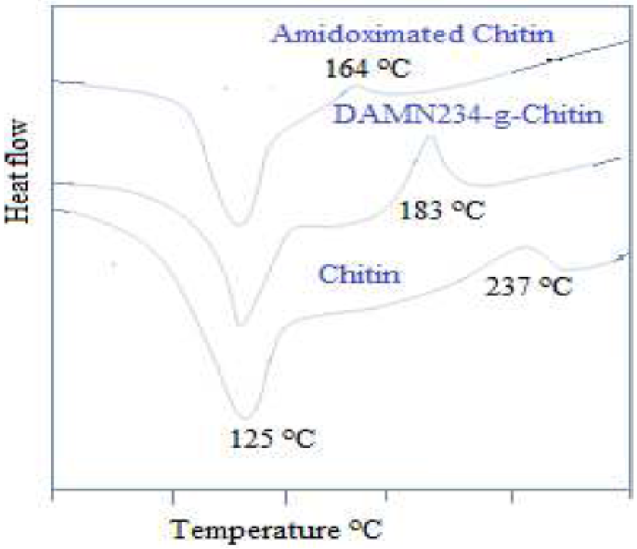

Figure 7 : DSC thermograms of ungrafted chitin, DAMN 234-g- chitin and amidoximated DAMN234-g- chitin

loss confined to a single-step degradation pattern has significantly comparable degradation temperature (Td) vary as a result of grafting. Ungrafted chitin recorded a degradation temperature at 373 ºC, while grafted chitin recorded 395 ºC. This means that chitin grafts are more thermally stable than the un-grafted chitin. Amidoximated chitin, however, shows better thermal stability having main degradation step recorded at 406 °C. This thermal stability would make the amidoximated chitin suitable for many practical applications Figure 7.

Recovery and separation of heavy metals

Since β-chitin is a more hydrated structure than α-chitin, chitin samples with high β-structure content are more hydrophilic supports. Moreover, due to much weaker intermolecular hydrogen bonding ascribable to the parallel arrangement of the main chains, *β*-chitins are more reactive than α-chitins[25]. The possibility of using the obtained materials 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 above. The results in (TABLE 1) show that the metals can be enriched quantitatively by the resin with recoveries of 98–100%. It can be seen that the amidoximated chitin is characterized by a considerably greater binding ability with respect to heavy metals. 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[20]. When using the recommended procedure, the flow rate for preconcentration of the analytes on the resin columns is varied between 2.0 and 8.0 mL min^{-1}. The results in TABLE 1 show that metal ions can be enriched quantitatively at flow rate of 4.0 mL min^{-1}. After the chelating resin is treated with strong acids, the resin is washed to neutrality with distilled water and used for enrichment of analyte ions. The results show that the recoveries of the metals are Ã 95%. The regenerated amidoximated chitin is once again effective for resorption.

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	96	98	99	97	90	77	59
Cd	94	97	100	94	84	75	62
Zn	93	96	98	91	82	71	58
Fe	91	95	98	93	80	72	57
Cu	93	96	99	90	83	69	54
Ni	92	95	100	92	81	70	55
Co	94	97	99	94	84	72	52

CONCLUSION

A novel diaminomaleonitrile-functionalized chitin grafts (DAMN-g-Chitin) were synthesized. Potassium persulphate (KPS) and ferrous ammonium sulphate are combined in a redox system and used as initiator under N_2 atmosphere. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 1.4 M, [KPS] = 6 x10^{-2} mol/L, T = 75 ºC and t = 2 h for 0.5g chitin. The results indicate that amidoximated product of the obtained graft copolymer DAMN234-g-Chitin is a potentially powerful ion exchanger that can be employed for heavy metals removal from waste water effluents.

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