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Research Article

HEAVY METAL ADSORBENTS BASED ON CHELATING AMIDOXIMATED GRAFTED CELLULOSE

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ABSTRACT

Modification of cellulose through graft copolymerization with diaminomaleonitrile afforded cellulose grafts (DAMN-g- Cellulose). Ceric ammonium nitrate (CAN) was used as initiator under N_2 atmosphere. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 1.4 M, [CAN] = 6 $x10^{-2}$ mol/L, T = 60 ºC and t = 3 h for 0.5g cellulose. The imparted cyano groups of the grafted cellulose polymer chains (with degree of grafting up to 176 %) were converted into amidoxime groups by the reaction with hydroxylamine hydrochloride. The complexing ability of amidoximated DAMNgraft-Cellulose 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.

Key Words: *Graft Copolymerization, Cellulose, Amidoximation, Metal Adsorbents*

INTRODUCTION

Cellulose is the world's most abundant flexibile, low cost and natural polymer. Cellulose is frequently modified in the preparation of a wide range of new materials that have proved to be very useful in several and diverse fields of application (Onishi *et al.,* 2004; Heinrich and Mischnick, 1999). The presence of three reactive hydroxyl groups on each glucan unit of cellulose makes it relatively easy to modify. One method of modifying cellulose that has been studied extensively is graft copolymerization (Ouajai, 2004). Cellulose graft copolymers are very attractive because their products can readily be made to posses any number of the required properties (Hodano *et al.,* 2003; Okieimen, 2003). Great numbers of grafting methods have been developed, but the free radical methods of generating radicals on the cellulose backbone before grafting have received the greatest attention (Fernandez *et al.,* 1990). The use of ceric ions to generate free radicals which initiate grafting reactions has been one of the most reported (Gupta and Khandekar, 2002). The nontoxic, biodegradable and biocompatible properties 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 (Tarashima *et al.,* 1986). 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. Also, chitin, its derivatives (Yang and Shao, 2000) and modified cellulose (Padilha *et al.,* 1997) have been studied with respect to their ability to remove heavy metals from aqueous solution.

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 (Xu *et al.,* 2004; Xu *et al.,* 2005). 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 carboxylic acid, amine, amide, nitrile, oxime groups, etc. 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. The newly-synthesized 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 (Kavakli *et al.,* 2011). Adsorption efficiency of a new adsorbent towards uranium and vanadium ions was synthesized by radiation-induced graft polymerization affording a new type of fibrous adsorbent with excess amidoxime groups (Kavakli and Guven, 2004). Synthesis, characterization and amidoximation of diaminomaleonitrile-functionalized polyethylene terephthalate (PET) grafts were studied (Abdel-Razik, 2008). Azobisisobutyronitrile (AIBN) was used as an initiator. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 0.5 M, [AIBN] = 1.50 x10^{-3} mol/L, T = 80 ºC and t = 3 h. Diaminomaleonitrile-functionalized polyvinyl alcohol grafts and amidoximation of grafted copolymer to investigate its properties in removing heavy toxic metals from waste water were reported (Abdel-Razik *et al.,* 2012). Preparation of amidoxime-modified polyacrylonitrile (PANoxime) nanofibers and their applications to metal ions adsorption have been investigated intensively due to their potential applications in many areas especially in environmental applications for removal of heavy metals ions (Saeed *et al.,* 2008). Preparation of cellulosic membrane containing pyrrolidone moiety via radiation induced grafting and its application in wastewater treatment were studied (Rocha *et al.,* 2001). Synthesis, characterization and amidoximation of diaminomaleodinitrile-functionalized polyethylene terephthalate grafts for collecting heavy metals from wastewater were investigated (Abdel-Razik and Kenawy, 2012). Molecular structure and Ion exchange of amidoximated cellulosic materials were reported (Nada and El-Wakeel, 2006). In this work the complexing ability of amidoximated DAMN-graft-cellulose copolymer was investigated with respect to the adsorption of some heavy metals from aqueous solution.

MATERIALS AND METHODS

Materials

Commercially available cellulose: (Surapon Foods Public Co., Ltd., Thailand). 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 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 cellulose 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 measurements 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

Diaminomaleonitrile (1.4 mole/L) was added with 0.5 g of cellulose in water (10 mL) and left overnight. Next, 50 mL of dilute nitric acid (0.01N) was added at 80-90 °C. After cooling to room temperature, 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. Then the requisite amount of ceric ammonium nitrate (0.16 M) was added rapidly and the reaction was allowed to proceed for 30 minutes at 60 °C to initiate the polymerization reaction.

The reaction mixture was continuously stirred for 3 hours and nitrogen gas was allowed to pass through the solution. At the end, the grafted cellulose 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 cellulose – dry wt. of original cellulose)/ dry wt. of original cellulose] 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, DAMN176-g-Cellulose, 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 DAMN176-g-Cellulose) 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}.

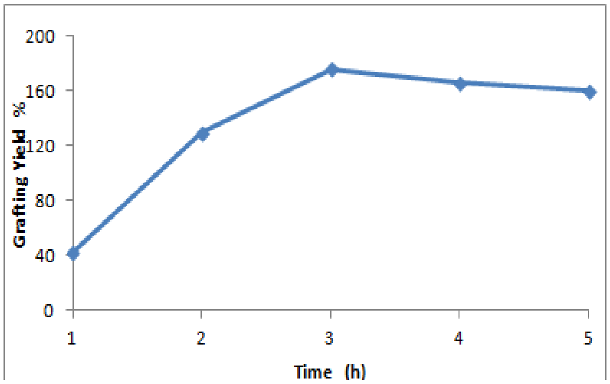


Figure 1: Effect of time on grafting yield and grafting efficiency. [DAMN] = 1.4 M, [CAN] = 6X10^{-2} mol/L, T = 60 ^{0}C.

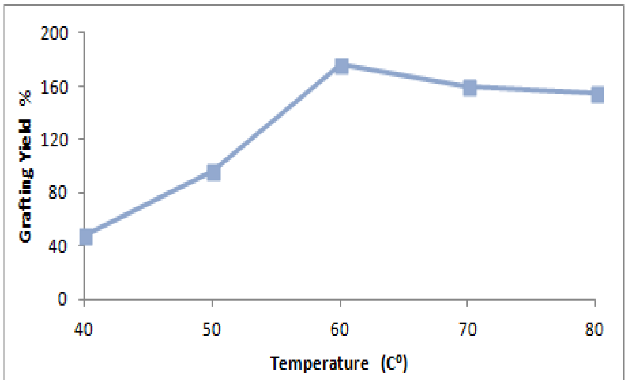
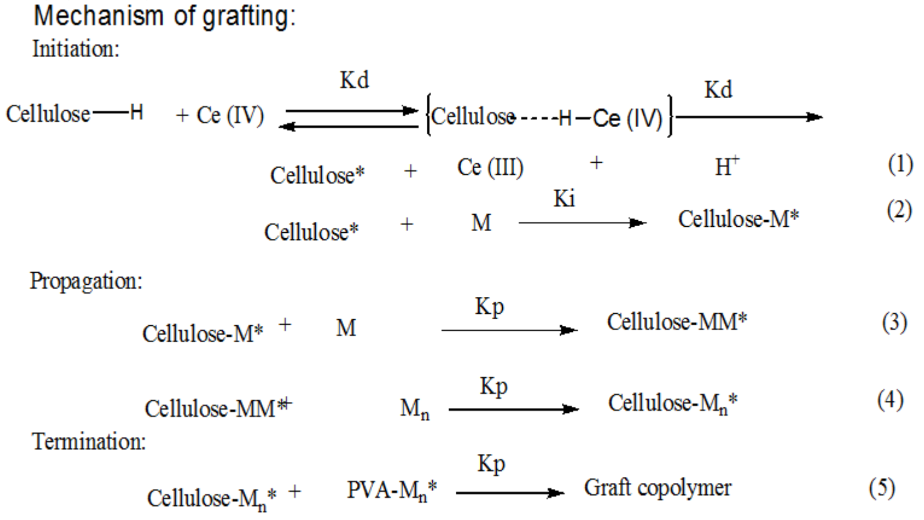


Figure 2: Effect of temperature on grafting yield and grafting efficiency. [DAMN] =1.4 M, [CAN] = 6X10^{-2} mol/L and t = 3 h

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.

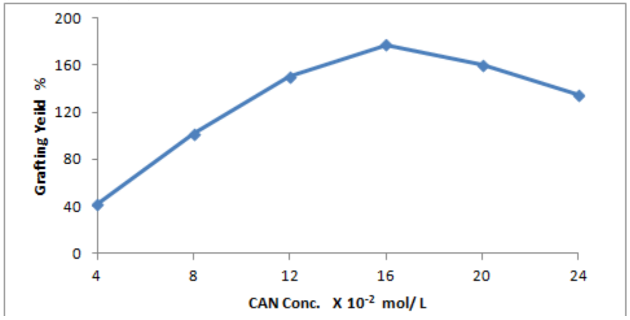
RESULTS AND DISCUSSION

Graft copolymerization of cellulose was achieved at various polymerization times, keeping the monomer, initiator and temperature constant at [DAMN] = 1.4 M, [CAN] = 16 x10^{-2} mol/L and T = 60 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 176 % at 3 h. This is attributed to the diffusion of monomer and initiator molecules into cellulose chains. Within the range of 40-80 ºC, keeping monomer, initiator and polymerization time constant, figure 2 shows an increase in the graft copolymerization yield value to about 176 %. The enhancement in the grafting yield with increasing temperature may be due to the enhancement of cellulose swellability and the diffusion of the initiator and the monomer into cellulose chains. Also, formation of homopolymer indicates the leveling off of the grafting yield beyond 60 ºC. The effect of initiator concentration on grafting yield was illustrated in figure 3 which demonstrate that the graft yield increases with the increase in ceric ammonium nitrate (CAN) concentration in the range from 4 x 10^{-2} to 16 x 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 cellulose back-bone, yielding a cellulose radical capable of initiating grafting.



Scheme 1: Cellulose macroradicals by redox reaction

However, when the initiator concentration increased beyond 16 x10^{-2} mol/L, termination reactions of the graft copolymerization takes place.



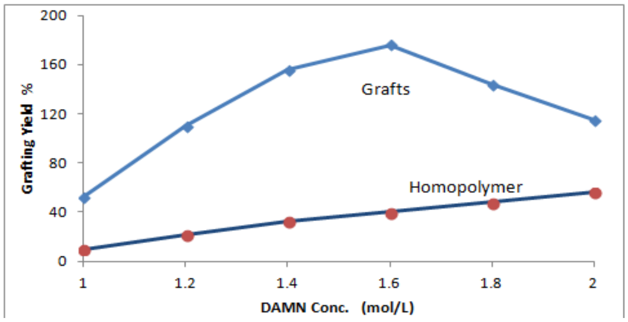


Figure 3: Effect of initiator concentration on grafting yield. [DAMN] = 1.4 M, T =60 C^0 and 3 h

Figure 4: Effect of monomer concentration on grafting yield. [CAN] = 6x10^{-2}mol/L, T = 60 ^{0} C and t = 3h

The effect of monomer concentration on graft copolymerization is illustrated in figure 4 which shows that the graft copolymerization yield rises with increasing DAMN concentration up from 1 - 1.6 mol/L, producing 176 % 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 cellulose surface in excessive amounts, which prevents diffusion of the initiator molecules inside the cellulose 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.

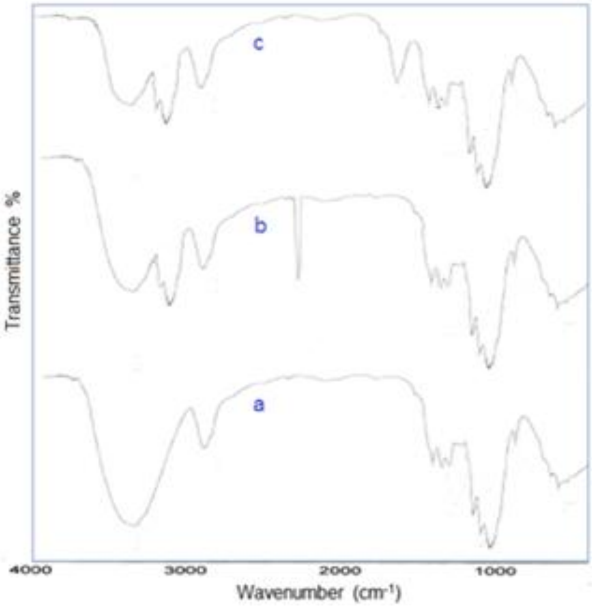


Figure 5: FTIR spectra of ungrafted-Cellulose (a), DAMN176-g-Cellulose (b) and amidoximated Cellulose (c)

Conversion of cellulose 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. There are two attempts (Pourjavadi *et al.,* 2004; Tokura *et al.,* 1996) of preparation of resins with diamidoxime units per repeating unit so far all of which completely differ from our approach. FTIR spectroscopy of ungrafted, grafted and amidoximted cellulose is shown in figure 5 which showed a peak at 3312 and 2248 cm^{-1} assignable to (NH_2) and (CN) groups, respectively, in the grafted cellulose. Presence of a peak assignable to CN group in the grafted cellulose indicated high efficiency of grafting process. Bands were revealed at 2868 cm^{-1} (C-H stretching), 1442, 1036 and 1782 cm^{-1} (arising from C-C, C-O and C=O, respectively) for amidoximated cellulose. The absence of CN band and the presence of C=O band as well as NH_2 band prove amidoximation of all CN groups. Also, a peak at 2873 cm^{-1} assignable to CH stretching of CH_2 was found. Glass transition temperatures (Tg) for cellulose (220 ºC) (Ludwik *et al.*, 2008), cellulose graft 192 ºC and amidoximated cellulose 168 ºC are illustrated in figure 6 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 cellulose is lower than glass temperature of ungrafted cellulose. 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 7 shows TGA thermograms of ungrafted cellulose, DAMN176-g-Cellulose and amidoximated cellulose. The TGA curve for parent cellulose shows that, loss in cellulose weight occurred, attributed to the actual pyrolysis by a minor decomposition reaction at about 260 and 290 °C, and to a major decomposition at 320 and 400 °C. The actual decomposition for DAMN176-g-Cellulose occurred between 340-430 °C. This means that cellulose grafts are more thermally stable than the ungrafted cellulose. Amidoximated cellulose, however, shows better thermal stability having main degradation step recorded at 382 °C. This thermal stability would make the amidoximated cellulose suitable for many practical applications.

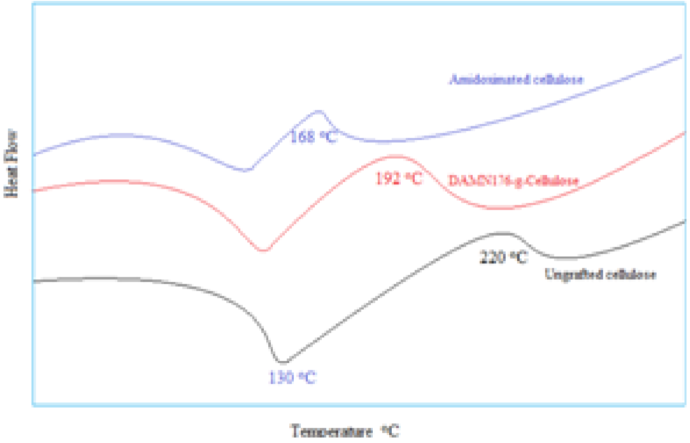


Figure 6: DSC thermograms of ungrafted Cellulose, DAMN 176-g-Cellulose and amidoximated DAMN 176-g-Cellulose

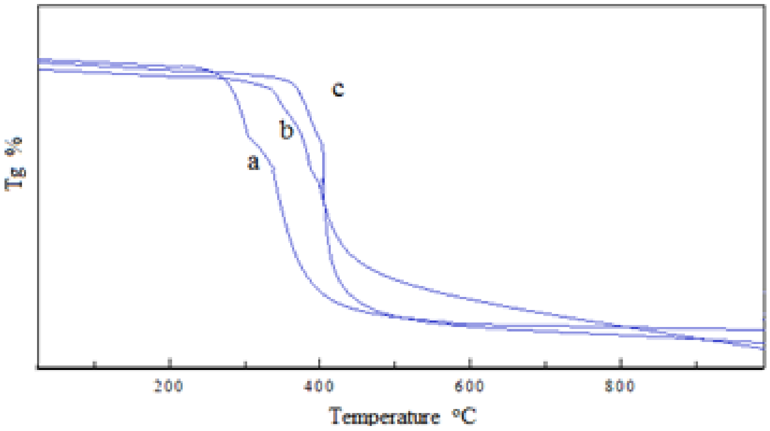


Figure 7: TGA thermograms of ungrafted Cellulose (a), DAMN 176-g-Cellulose (b) and amidoximated DAMN 176-g-Cellulose (c)

Recovery and Separation of Heavy Metals

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 in experimental section. The results in (Table 1) show that the metals can be enriched quantitatively by the resin with recoveries of 94–99%. It can be seen that the amidoximated cellulose 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	94	96	99	96	91	83	62
Cd	92	95	98	91	80	73	58
Zn	93	94	96	88	80	74	61
Fe	94	95	99	91	83	75	63
Cu	91	93	95	87	79	65	59
Ni	90	92	94	85	76	67	56
Co	92	96	97	89	81	70	53

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 (Pourjavadi *et al.*, 2004). 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 again for enrichment of analyte ions. The results show that the recoveries of the metals are > 94 %. The regenerated amidoximated cellulose is once again effective for resorption.

Conclusion

A novel diaminomaleonitrile-functionalized cellulose grafts (DAMN-g-Cellulose) were synthesized. Ceric ammonium nitrate (CAN) was used as initiator under N_2 atmosphere. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 1.4 M, [CAN] = 6 x10^{-2} mol/L, T = 60 ºC and t = 3 h for 0.5g cellulose. The results indicate that amidoximated product of the obtained graft copolymer DAMN176-g-Cellulose 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 > 94 %.

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REFERENCES

Abdel-Razik HH (2008). Synthesis and Characterization of Diaminomaleonitrile-Functionalized Polystyrene Grafts for Application in Pervaporation Separation. *Chemical Papers* **62**(4) 404-409.

Abdel-Razik HH and Kenawy E (2012). Synthesis, characterization and amidoximation of diaminomaleodinitrile-functionalized polyethylene terephthalate grafts for collecting heavy metals from wastewater. *Journal of Applied Polymer Science* **125** 1136-1145.

Abdel-Razik HH, Abboo M and Almahy H (2012). Polymer-based Metal Adsorbents via Graft Copolymerization of Polyvinyl Alcohol with Diaminomaleonitrile: a Green Chemistry Approach. *Journal of Applied Polymer Science* **125** 2102-2109.

Fernandez MJ, Casinos I and Guzman GM (1990). Effect of the way of Addition of the Reactants in the Graft Copolymerization of a Vinyl Methyl Acrylate mixture onto Cellulose. *Journal of Polymer Science Part A* **28** 2275-2292.

Gupta KC and Khandekar K (2002). Graft Copolymerization of Acrylamide-Methylacrylate Comonomers onto Cellulose using ceric ammonium nitrate. *Journal of Applied Polymer Science* **86** 2631-2642.

Heinrich J and Mischnick P (1999). Determination of the Substitution Patterns in the Polymer chains of Cellulose acetates. *Journal of Polymer Science Part A* **37** 3011-3016.

Hodano S, Onimura K, Tsutumi H, Yamasaki H and Oishi T (2003). Synthesis of Chemical modified Cellulose obtained from Waste pulp. *Journal of Applied Polymer Science* **90** 2059-2065.

Kavaklı PA and Guven O (2004). Removal of concentrated heavy metal ions from aqueous solutions using polymers with enriched amidoxime groups. *Journal of Applied Polymer Science* **93** 1705-1713.

Kavaklı PA, Seko N, Tamada M and Guven O (2011). Adsorptive removal of 2, 4-dichlorophenol from aqueous solution by low-cost carbon from an agricultural solid waste: coconut coir pith. *Separation Science and Technology* **39** 1631.

Ludwik Szcześniak, Adam Rachocki and Jadwiga Tritt-Goc (2008). Glass transition temperature and thermal decomposition of cellulose powder. *Cellulose* **15** 445-451.

Nada AMA and El-Wakeel N (2006). Molecular structure and Ion exchange of amidoximated cellulosic materials. *Journal of Applied Polymer Science* **102** 303-311.

Okieimen FE (2003). Preparation, Characterisation and Properties of Cellulose-polyacrylamide Graft Copolymers. *Journal of Applied Polymer Science* **89** 913-923.

Onishi Y, Butler GB and Hogen-Esch TE (2004). 1, 2-propanediol-cellulose- acrylamide Graft Copolymers. *Journal of Applied Polymer Science* **92** 3022-3029.

Ouajai S, Hodzic A and Shanks RA (2004). Morphological and Grafting Modifications of Natural Cellulosic fibres. *Journal of Applied Polymer Science* **94** 2456-2465.

Padilha PM, Pacha JC and Moreira JC (1997). Preconcentration of heavy metals ions from aqueous solutions by means of cellulose phosphate: an application in water analysis. *Talanta* **45** 317-323.

Pourjavadi A, Zohuriaan-Mehr MJ and Mahdavinia GR (2004). Modified Chitosan III. Superabsorbency, Salt- and pH-Sensitivity of Smart Ampholytic Hydrogels from Chitosan-g-PAN. *Polymers for Advanced Technologies* **15** 173-180.

Rocha JA, Pach EE, Parrak ER and Queiroz AA (2001). Preparation of cellulosic membrane containing pyrrolidone moiety via radiation induced grafting and its application in wastewater treatment. *Material Research* **4** 53-57.

Saeed K, Haider S, Oh TJ and Park SY (2008). Preparation of the chitosan containing nanofibers by electrospinning chitosan-gelatin complexes. *Journal of Membrane Science* **322** 400-405.

Terashima Y, Ozaki H and Sekiue M (1986). Removal of dissolved heavy metals by chemical coagulation, magnetic seeding and high gradient magnetic filtration. *Water Research* **20** 537-545.

Tokura S, Nishimura S, Sakairi N and Nishi N (1996). Biological activities of biodegradable polysaccharide. *Macromolecular Symposia* **101** 389-396.

Xu SM, Feng S and Peng G *et al.*, (2005). Removal of Pb (II) by crosslinked amphoteric starch containing the carboxymethyl group. *Carbohydrate Polymers* **60** 301-305.

Xu SM, Feng S and Yue F *et al.*, (2004). Adsorption of Cu(II) ions from an aqueous solution by crosslinked amphoteric starch. *Journal of Applied Polymer Science* **92** 728-732.

Yang Y and Shao JJ (2000). Synthesis of sulfhydryl chitin and its adsorption properties for heavy metal ions. *Journal of Applied Polymer Science* **77** 151-155.