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Sorption of Ga(III), Cu(II), Ni(II) and Zn(II) on Synthetic Polymeric Resins

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Poly(acrylamide-acrylic acid-dimethylaminoethylmethacrylate) [P(AM-AA-DMAEM)] and poly(acrylamide-acrylic acid)-ethylenediaminetetracetic acid disodium [P(AM-AA)-EDTANa$_2$] were prepared by γ radiation-induced template polymerization technique. The prepared polymeric materials were used for the sorption of Ga(III), Cu(II), Ni(II) and Zn(II) in aqueous solution. The effect of pH, weight of resins, metal ion concentrations and contact time on the sorption of these metal ions were studied.

Key Words: Sorption, Gallium(III), Zinc(II), Copper(II), Nickel(II) and polymeric resins.

INTRODUCTION

Polymeric substrate are being continuously developed and used for the purpose of complexation with metal ions either for ion-exchange or selective adsorption purpose. These polymeric ligands are tailored synthesized to remove certain metal ions or groups from aqueous media[1-3]. A number of chelating polymers, containing different active groups such as carboxylic, amide, amino amidoxime and hydroxamic groups were prepared by different polymerization techniques[4-7]. The functional groups are interacted with the metal ions through complexation or formation of covalent bonds by ion-exchange mechanism[8,9]. These resins contain as a rule one or more donor atom which can form a coordination bond with the metal ion. The selective ion-exchange phenomenon in a system mainly depends on the combination of three factors, the metal ion chemistry in aqueous solution and the resin, the structure of the functional groups in the resin phase and the macromolecular structure as present under the separation condition[10]. The efficiency of the resins increases by decreasing the degree of crosslinking. The resins can be regenerated and reused for continuous process[11-13]. The removal process of the metal ions from the solution depends on the type of the metal ion, pH of the solution, metal ion concentration and the properties of the ion exchanger such as crosslinking degree, swelling and the type of the ligand[14].

Different polymeric resins were synthesized and used for the separation of the metal ions from aqueous solutions investigated by several authors. Poly(ethyleneimine-vinyl benzaldehyde) was used for the separation of Fe(III) from aqueous solution containing Cu(II), Ni(II), Co(II), Fe(II), Mn(II) and Zn(II)[15], while poly(1-β-acrylamidoethyl-3-hydroxy-2-methyl-4(1*H*)-pyridinone N,N-dimethylacrylamide) was used for chelating of Fe(III) from poisoned blood plasma[16]. Poly(styrene-supported-1-(2-aminoethyl)piperazine was used for the removal of Au(III), Pb(II) from Cu(II), Ni(II) and Fe(III) in 0.1 M HCl[17]. Cu(II) was separated from a solution containing Cd(II), Co(II), Ni(II) and Zn(II) at pH > 2.5 onto poly(glycidyl-methacrylate) modified resins by pyrazole, imidazole and 1,2,4-triazole[18], while Zn(II) was also separated from Cu(II), Ni(II) in aqueous solution at pH > 4.5 onto a modified poly(glycidyl methacrylate)[19]. Poly(amidoxime) was used for the removal of Cu(II), Pb(II), Zn(II), Cr(III) and Ni(II) at pH 5 in aqueous solution[20].

Poly(N-acryloyldethyliminodiacetate-acrylic acid) was used for the removal of ^{152}Eu at pH 4[21]. Poly(hydroxamic acid) used for separation of Fe(III) from solution containing Cu(II) and Ni(II) at pH < 4[22] and poly(methylacrylohydroxamic acid) was also used the separation of metal ions such as Cu(II), Ni(II), Co(II), Pb(II) and Fe(III) at pH 3.5-5.0[23]. Polymeric composite such as poly(acrylamide-acrylic acid)-EDTANa$_2$, poly(acrylamide-acrylic acid)-montmorillonite, poly(acrylamide-acrylic acid)-KNiHCF, poly(acrylamide-acrylic acid)-KZnHCF, poly(acrylamide-acrylic acid-DMAEM)-KNiHCF were used for the removal of metallic ions such as Cu(II) and Cr(II) as test ions from waste water and were also used for treatment of radioactive liquid waste containing radioactive isotopes such as ^{60}Co and ^{152}Eu[24,25]. Generally, acrylamide polymeric material: were used for the removal of various metallic ions, heavy metal and radioactive isotopes from their aqueous solution[26]. In the present work, acrylamide polymeric resins are used for the sorption of Ga(III), Cu(II), Ni(II) and Zn(II).

EXPERIMENTAL

N,N'-Methylenediacrylamide and acrylamide, were obtained from (BDH), acrylic acid monomer and dimethylaminoethylmethacrylate were obtained from Merk (Germany) and $EDTANa_2$ obtained from oxford laboratory reagent.

Preparation of polymeric materials: Polyacrylamide, p(AM), was prepared by γ radiation-initiated polymerization of 10 % acrylamide monomer solution using γ-radiation at a dose 10 kGy[27]. P(AM-AA-DMAEM), [R1], was prepared by template copolymerization of acrylic acid and dimethylaminoethylmethacrylate in presence of N,N methylene-diacrylamide, (DAM) as acrosslinker.

P(AM-AA)-$EDTANa_2$, [R2], was prepared by γ-radiation induced template polymerization of acrylic acid on p(AM) in the presence of $EDTANa_2$ and N,N-methylenediacrylamide, (DAM), as across-linker.

Batch sorption studies: The ion exchange behaviour of the metal ions of Ga(III), Cu(II), Ni(II) and Zn(II) towards the synthesized polymeric materials was studied using the batch technique where, 40 mg of each resin was equilibrated with 20 mL aqueous solution containing the desired metal ion. The uptake percentage of the studied ion on the polymeric materials was determined using ICP-a Jobin Yvon ICP-OES spectrometry model Ultima[2]. The uptake percentage was determined using the following equation[4]:

$$\text{Uptake (\%)} = 100\left[1 - \frac{A}{A_0}\right]$$

where A_0, A are the concentration of the metal ion before and after addition the resin, respectively.

RESULTS AND DISCUSSION

Effect of pH on the metal concentration: The effect of pH on the metal concentration of Ga(III), Cu(II), Ni(II) and Zn(II) in aqueous solution was studied and the result are shown in Table-1. The result showed that the metal concentration is constant at pH < 5 for Ga(III) and Cu(II) and then decreases, while, the metal concentration for Ni(II) and Zn(II) decreases also at pH > 5.5 and 6.0, respectively.

TABLE-1
EFFECT OF pH ON THE METAL CONCENTRATION

Metal ions	Ga(III)	Cu(II)	Ni(II)	Zn(II)
Initial concentration (ppm)	60	92	97	86
pH = 1.5	58	92	97	85
pH = 2.0	59	91	97	85
pH = 2.5	58	90	97	85
pH = 3.0	59	91	96	86
pH = 3.5	57	90	97	85
pH = 4.0	58	91	96	85
pH = 4.5	58	91	97	86
pH = 5.0	58	90	97	85
pH = 5.5	59	89	95	85
pH = 6.0	59	84	90	82
pH = 6.5	56	77	82	79
pH = 7.5	52	42	45	72
pH = 8.5	30	21	25	62.5

Effect of pH on the sorption of metal ions: The sorption of Ga(III), Cu(II), Ni(II) and Zn(II) was studied on polymeric materials of P(AM-AA-DMAEM) and P(AM-AA)-$EDTANa_2$ at different pH values as shown in Figs. 1-4.

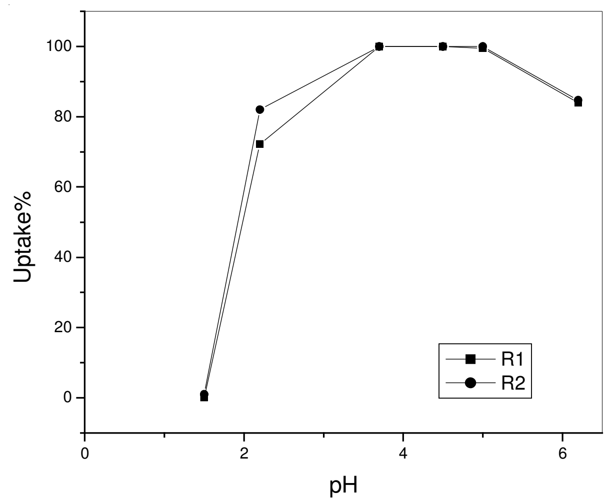


Fig. 1. Effect of H^+ concentration on the uptake of Ga(III) on p(AM-AA-DMAEM) and P(AM-AA)-$EDTANa_2$

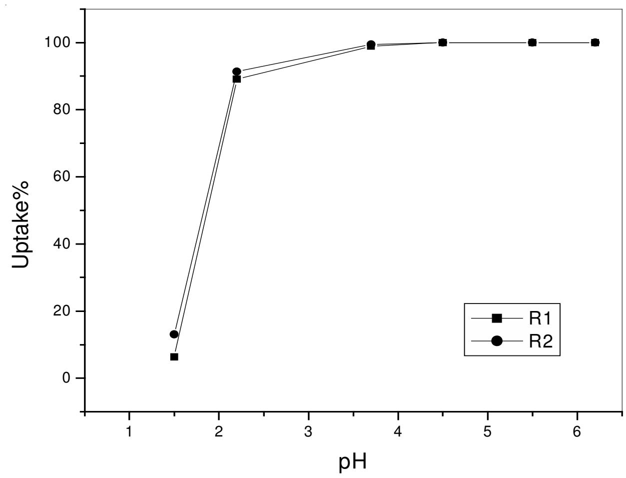


Fig. 2. Effect of H^+ concentration on the uptake of Cu(II) on p(AM-AA-DMAEM) and P(AM-AA)-$EDTANa_2$

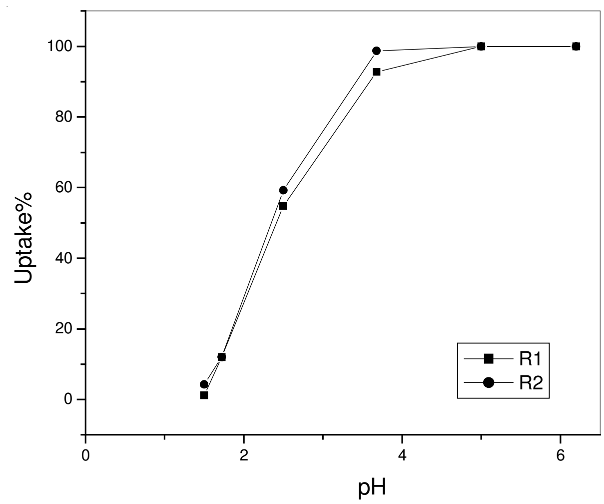


Fig. 3. Effect of H^+ concentration on the uptake of Ni(II) on p(AM-AA-DMAEM) and P(AM-AA)-$EDTANa_2$

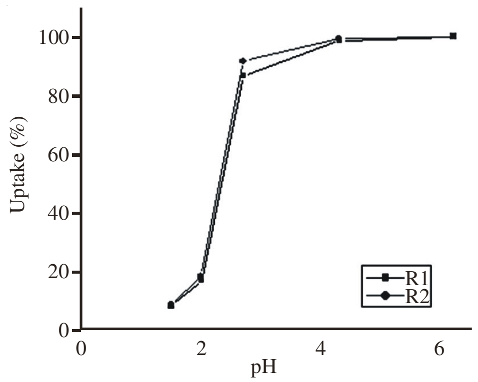


Fig. 4. Effect of H^+ concentration on the uptake of Zn(II) on p(AM-AA-DMAEM) and P(AM-AA)-EDTANa$_2$

The data showed that, the sorption of Ga(III), Cu(II), Ni(II) and Zn(II) on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa$_2$ increases with increasing the pH value. This can be attributed to the effect of pH on the functional groups of the polymeric materials. At low pH value, the amide and amino groups are present in protonated form, leading to imidation of amide groups with the formation of intermolecular cross-linking between polymeric chains, which inhibits their complexation with metal ions. With increasing pH, the degree of protonation decreases which leads to increasing interaction between polymeric materials and metal ions. By increasing pH, the degree of ionization of carboxylate groups (pKa = 2.45) of polymeric materials increases as well, which facilitates the cation exchange. Moreover, at high pH the amide and amino groups of the resins can interact with metal ions. It was found that, the optimum pH values for the removal of Ga(III),Cu(II), Ni(II) and Zn(II) were found to be 3.5, 5, 6 and 4, respectively. This can be attributed to the presence of metal ions as free ions in the solution. At higher pH value > 6, the metal ions form metal hydroxides.

Effect of weight of polymeric materials: Different weights of polymeric materials of p(AM-AA-DMAEM) and p(AM-AA)-EDTANa$_2$ were used for the removal of Ga(III), Cu(II), Ni(II) and Zn(II) individually from aqueous solution at pH = 4.4, 4.5, 5.5 and 5.6, respectively. The results are shown in Figs. 5-8.

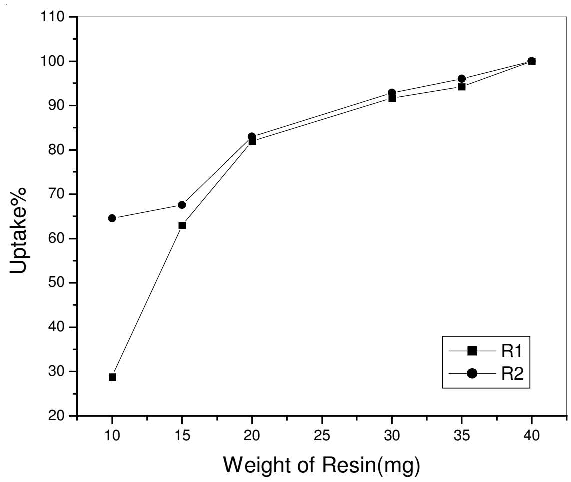


Fig. 5. Effect of resin weight of p(AM-AA-DMAEM) and p(AM-AA)-EDTANa$_2$ on Ga(III)

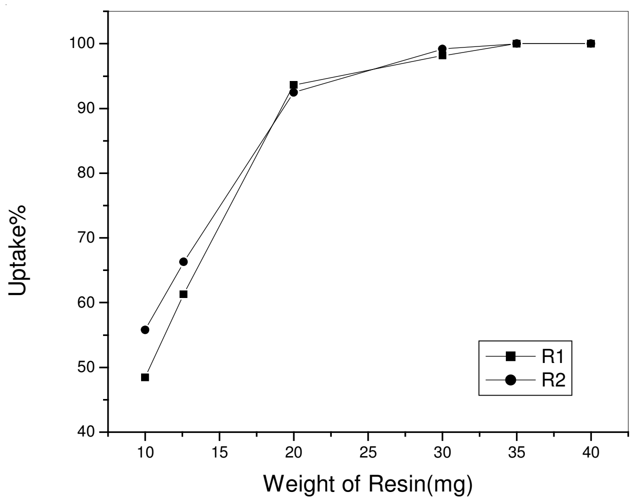


Fig. 6. Effect of resin weight of p(AM-AA-DMAEM) and p(AM-AA)-EDTANa$_2$ on Cu(II)

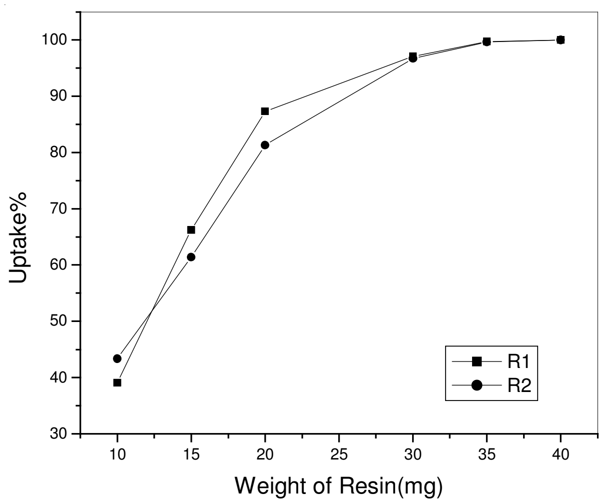


Fig. 7. Effect of resin weight of p(AM-AA-DMAEM) and p(AM-AA)-EDTANa$_2$ on Ni(II)

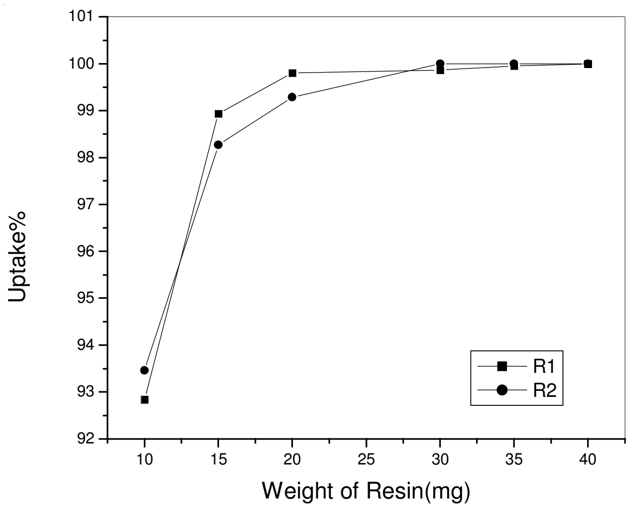


Fig. 8. Effect of resin weight of p(AM-AA-DMAEM) and p(AM-AA)-EDTANa$_2$ on Zn(II)

The uptake percentage increases with increasing the weight of the polymeric materials and reached its maximum value at 40 mg for all metal ions, this means that, this is optimum concentration for the sorption process.

Effect of metal ion concentration: The effect of sorption of Ga(III), Cu(II), Ni(II) and Zn(II) from aqueous solution on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2 was studied. The result are shown in Figs. 9-12, which shows that, the uptake decreases with increasing metal ion concentration due to the specific capacity of the polymeric materials.

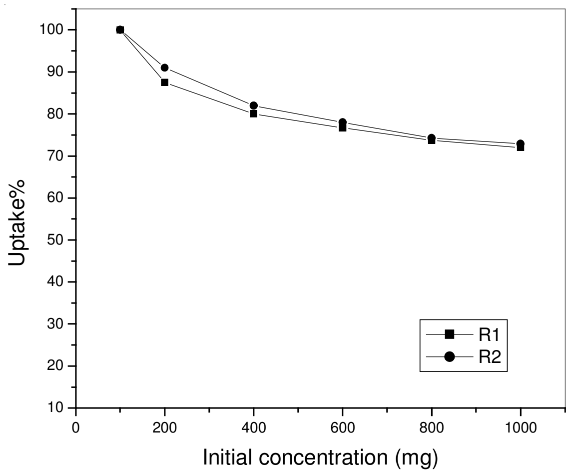


Fig. 9. Effect of initial metal ion concentration on the uptake on Ga(III) on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2

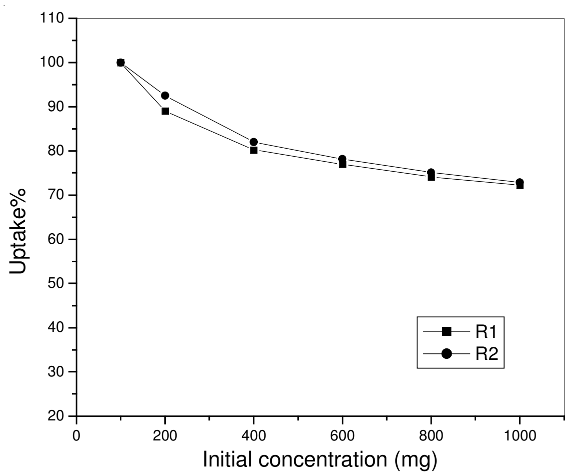


Fig. 10. Effect of initial metal ion concentration on the uptake of Cu(II) on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2

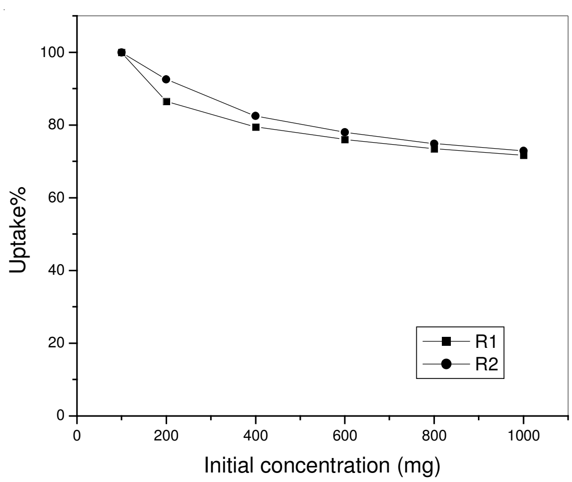


Fig. 11. Effect of initial metal ion concentration on the uptake of Ni(II) on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2

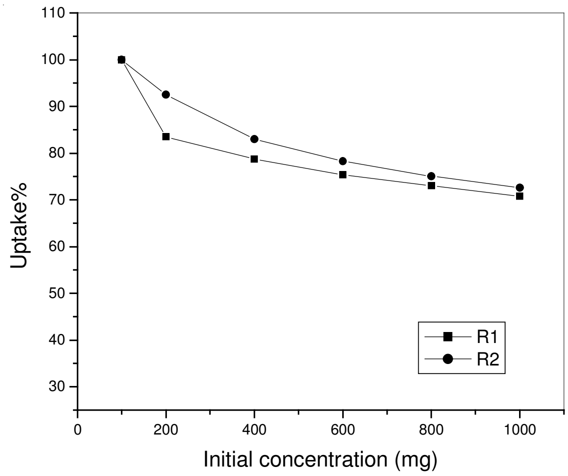


Fig. 12. Effect of initial metal ion concentration on the uptake of zinc(II) on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2

Effect of contact time: The variation of the uptake percentage of Ga(III), Cu(II), Ni(II) and Zn(II) ions (at concentration 100 ppm and constant pH value) from aqueous solution with time was measured by p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2. The results are shown in Figs. 13-16.

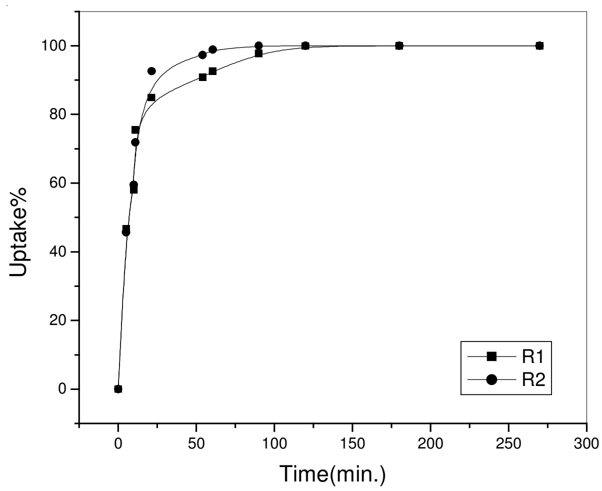


Fig. 13. Effect of contact time on the uptake of Ga(III) on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2

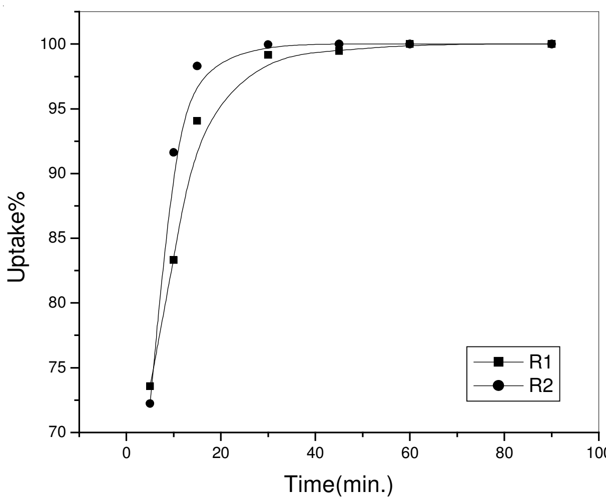


Fig. 14. Effect of contact time on the uptake of Cu(II) on p(AM-AA-DMAEM) and p(AM-AA)-EDTANa_2

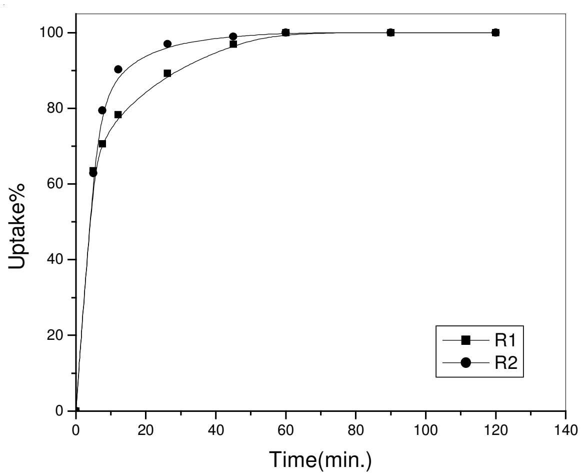


Fig. 15. Effect of contact time on the uptake of Ni(II) on p(AM-AA-DMAEM) and p(AM-AA)-$EDTANa_2$

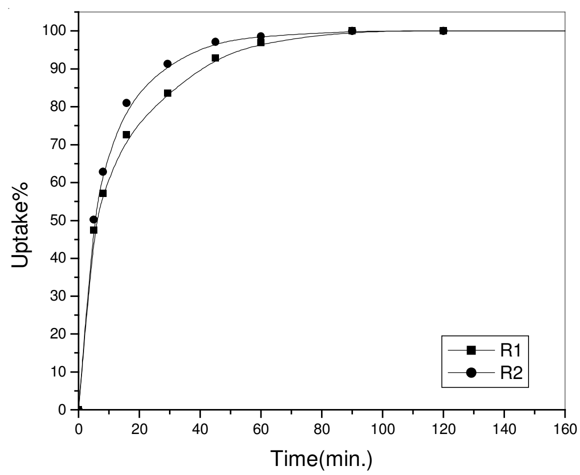
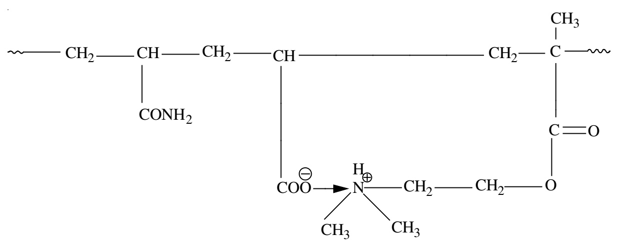


Fig. 16. Effect of contact time on the uptake of Zn(II) on p(AM-AA-DMAEM) and p(AM-AA)-$EDTANa_2$

In all cases, the uptake increases with increasing the time. The equilibrium time for removal of Ga(III), Cu(II), Ni(II) and Zn(II) onto p(AM-AA-DMAEM) and p(AM-AA)-$EDTANa_2$ was found to be (90, 75), (45, 30), (60, 45), (60, 45), respectively. The uptake value for Ga(III), Cu(II), Ni(II) and Zn(II) on the p(AM-AA-DMAEM) and p(AM-AA)-$EDTANa_2$ were in the order: p(AM-AA-DMAEM) < p(AM-AA)-$EDTANa_2$. The higher uptake value for p(AM-AA)-$EDTANa_2$ relative to p(AM-AA-DMAEM) can be attributed the complex formation between the amino- and the carboxylate groups of polymeric chain as shown in the **Scheme-I**. This complexation leads to an increase in the degree of crosslinking between the polymeric chains of the prepared polymeric composite resin, consequently, the efficiency of the resin decreases.



Scheme-I: Complex formation between the amino- and carboxylate groups of the polymeric chains

Conclusion

The sorption process of the studied polymeric materials for investigated metal ions increases by increasing the pH value, weight of resins and initial concentration of the solution. The equilibrium time of Ga(III), Cu(II), Ni(II) and Zn(II) onto p(AM-AA-DMAEM) and p(AM-AA)-$EDTANa_2$ was found to be (90, 75), (45, 30), (60, 45), (60, 45), respectively.

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REFERENCES

1. Ö. Kantoalu, M. Sen and Ö. Guven, *Nucl. Inst. Meth. Phys.*, **151**, 218 (1999).
2. D. Saraydin, Y. Isikver and N. Sahiner, *Polym. Bull.*, **47**, 71 (2001).
3. S.I. El-Dessouky, E.A. El-Sofany and J.A. Daoud, *J. Hazard. Mater.*, **143**, 17 (2007).
4. T. Siyam, M.M. Abdel-Hamid and I.M. El-Naggar, *Macromole. Reports*, **A32**, 871 (1995).
5. T. Siyam, A.H. Youssef and I.M. El-Naggar, Synthesis of Hydrogels of Poly(acrylamide-acrylic Acid) and their Use as Exchanger, 6th Intern. Conf. on Energy and Environmental, 2, 609 (1988).
6. T. Siyam and Z.H. Abd-Elatif, in eds.: P.N. Prasad *et al.*, Template Polymerization of Dimethylaminoethyl Methacrlate in the Presence of Poly(acrylamide-acrylic Acid) induced by Gamma Radiation and its use for Removal of metal ions, Science and Technology of Polymers and Advanced Materials, Plenum Press, New York, pp. 165-173 (1998).
7. T. Siyam, Gamma Radiation-induced Preparation of Some Polyelectrolytes and its use for Treatment of Engineering Polymeric Materials, Marcel Dekker Inc., Ch. 9, pp. 119-135 (1997).
8. T. Siyam, M.M. Abdel-Hamid and I.M. El-Naggar, Recovery of Some Metal Cations on Poly(amido-amines) from Aqueous Solution, Intern. Conf. on Hazardous waste Sources, Effect and Management, HAWA, 98, 12-16 Dec. III, 1159, Cairo, Egypt (1998).
9. T. Siyam, H.A. Youssef and I.M. El-Naggar, *J.M.S.-Pure Appl. Chem.*, **A34**, 2379 (1997).
10. T. Siyam, *Design. Monomers Polym.*, **4**, 107 (2001).
11. T. Siyam and H.A. Youssef, *Radiation Phys. Chem.*, **55**, 447 (1999).
12. T. Siyam, H.M. Abd-Elaziz, A.M. El-Razek and F.H. El-Sweify, Use of Poly(amido-amine)resins for the Separation of Radioactive Isotopes, 7th Arab Intern. Conf. on Polymers Science and Technology, Oct. 5-9, Cairo-Hurghada,I, 62, Egypt (2003).
13. R.A. Beauvais and S.D. Alexandratos, *React. Funct. Polym.*, **36**, 113 (1998).
14. A.A. El-Zahar, H.M. Abdl-Aziz and T. Siyam, 8th Arab Intern. Conf. on Polymer Sci. & Tech., 27-30 Nov., Cairo-Sharm-El-Shiekh, Egypt (2005).
15. Q. Zhao and J. Bartsch, *J. Appl. Polym. Sci.*, **57**, 1465 (1995).
16. A.W. Trochimczuk, *React. Funct. Polym.*, **44**, 9 (2000).
17. M. Chanda and G.L. Rempel, *React. Polym.*, **19**, 213 (1993).
18. M. Feng, L. van der Does and A. Bantjes, *React. Polym.*, **23**, 63 (1994).
19. C. Yi-Yong and Y. Xing-Zhong, *React. Polym.*, **23**, 165 (1994).
20. P.M. van Berkel, W.L. Driessen, J. Reedijk, D.C. Sherrington and A. Zitsmanis, *React. Funct. Polym.*, **27**, 15 (1995).
21. P.M. van Berkel, D.J. Dijkstra, W.L. Driessen, J. Reedijk and D.C. Sherrington, *React. Funct. Polym.*, **28**, 39 (1995).
22. B.W. Zhang, K. Fischer, D. Bieniek and A. Ketnup, *React Polym.*, **20**, 207 (1993).
23. V. Montembault, V. Folliot, J.C. Soutif and J.C. Brosse, *React. Polym.*, **22**, 81 (1994).
24. K.J. Kamble and D.N.J. Patker, *J. Appl. Polym. Sci.*, **52**, 1361 (1994).
25. Y.K. Agrawal and K.V. Rao, *React. Funct. Polym.*, **31**, 225 (1996).
26. A.A. El-Zahhar, H.M. Abdel-Aziz and T. Siyam, *J. Radioanal. Nucl. Chem.*, **267**, 657 (2006).
27. A.A. El-Zahhar, H.M. Addel-Aziz and T. Siyam, *J. Macromole. Sci. A: Pure Appl. Chem.*, **44**, 215 (2007).