

Competitive Removal of Nickel (II), Cobalt (II), and Zinc (II) Ions from Aqueous Solutions by Starch-Graft-Acrylic Acid Copolymers

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ABSTRACT: Graft copolymerization of acrylic acid (AA) onto starch was carried out with ceric ammonium nitrate as initiator under nitrogen atmosphere. The grafting percentages (GP%) of starch-graft-acrylic acid (St-g-AA) copolymers were determined. The effect of GP% of St-g-AA copolymers on the competitive removal of Co^{2+} , Ni^{2+} , Zn^{2+} ions from aqueous solution was investigated at different pH (2, 4, 6). The concentrations of each ion in aqueous solution 5 mmol/L. Effects of various parameters such as treatment time, initial pH of the solution and grafting percentage of starch graft

copolymers were investigated. Metal ion removal capacities of St-g-AA copolymers increased with GP% of the copolymers and pH. The results show that the removal of metal ions followed as given in the order $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$. In this study, metal ion removal capacities were determined by atomic absorption spectrophotometer (AAS). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1800–1805, 2007

Key words: starch; acrylic acid; heavy metal ion removal; graft copolymers

INTRODUCTION

Starch has been the raw material of scientific and industrial studies for many decades, due to its low cost and biodegradability. Many chemical modifications of starch have been carried out for its use. Chemical modification of starch via grafting of vinyl monomers is one of the most effective methods to incorporate desirable properties into starch without sacrificing its biodegradable nature.¹ Grafting of acrylamide,^{2–5} acrylonitrile,^{3,6,7} methylacrylonitrile,¹ alkyl methacrylates,^{8,9} vinyl ketones,¹⁰ 2-(dimethylamino)ethyl methacrylate,¹¹ acrylic acid (AA)^{12–14} onto starch has been investigated. Starch graft copolymers have been used as hydrogels,¹⁴ flocculants,^{15,16} ion exchangers.^{17,18}

The removal of toxic and polluting heavy metal ions from aqueous solutions has been given much more attention over the past few years. The removal of heavy metal content of waters because of their toxic effects on living organisms is extremely important. The toxic nature of heavy metals, even at trace level in natural waters has been a public health problem for many years. The presence of heavy metal ions in industrial waste waters has been of great concern in terms of environmental protection because of toxic properties and other harmful effects on living organisms.¹⁹ Various

methods exist for the removal of heavy metals from industrial water and natural water such as chemical precipitation, ion-exchange, and reverse osmosis techniques.²⁰ Graft copolymers of natural polysaccharides such cellulose^{21–23} and starch^{24–28} have been used in removal of heavy metal ions.

In this work, we describe the competitive removal of nickel (II), cobalt (II), and zinc (II) ions from aqueous solutions. Competitive ion removal was aimed since the natural and industrial water rarely contain a single metal. For this purpose, various factors affecting the removal of heavy metal ions, such as treatment time with the solution, initial pH of the solution, and grafting percentage of starch graft copolymers, were investigated. The concentration of each ion in aqueous solution was 5 mmol/L.

EXPERIMENTAL

Materials

Maize starch (food grade) was dried at 110°C and then was stored in vacuum desiccator. Acrylic acid (AA) (Merck, Germany) was purified by vacuum distillation, and then was stored in refrigerator. Ceric ammonium nitrate (CAN) (Merck, Germany) was dried at 110°C and then was stored in vacuum desiccator. Nickel(II), cobalt(II), and zinc(II) nitrate (Merck, Germany) were analytical grade. Rest of the materials was chemically pure grade. All solutions and standards were prepared using distilled water.

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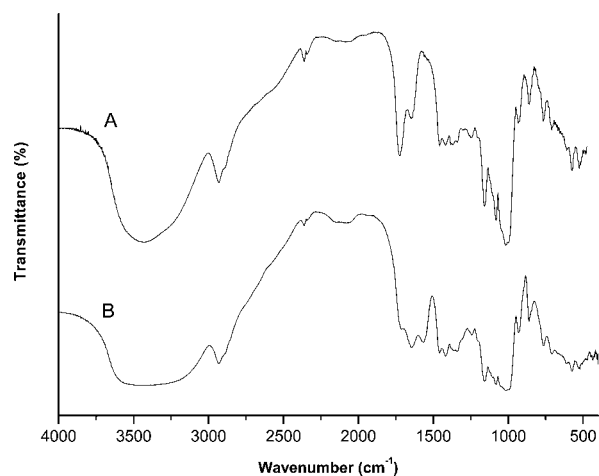


Figure 1 FTIR spectra of St-g-AA copolymer (A) before the removal of heavy metal ions (B) after the removal of heavy metal ions.

Graft copolymerization

The graft copolymerization of AA onto starch was carried out under nitrogen atmosphere in a 500 mL round bottom flask. A mixture of 4 g of dried starch and 140 mL of distilled water was stirred magnetically under nitrogen atmosphere and was then treated with CAN (0.004 mol/L) for 15 min to facilitate free radical formation on starch.^{12,29} This treatment was followed by the addition of AA (0.1, 0.3, 0.5 mol/L) and then the total volume of the reaction mixture was made to 200 mL with distilled water. The reactions were maintained at optimum temperature (35°C) and optimum reaction time (240 min)¹² under nitrogen atmosphere. After 240 min the reactions were stopped by addition of hydroquinone. The product was treated by water by changing the washing water at least three times to remove homopolymer. The residue was separated and was dried under vacuum at 70°C.

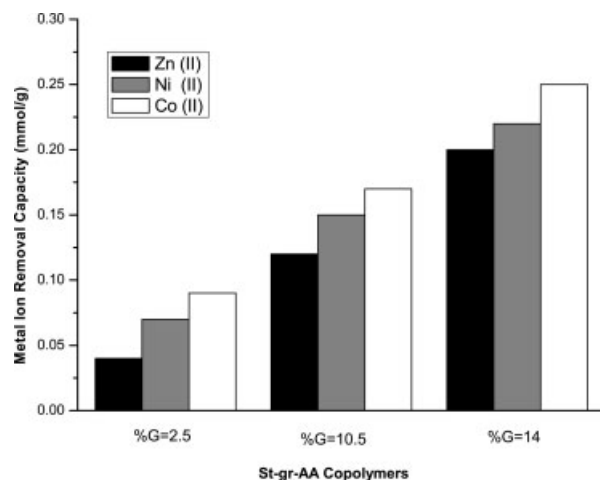


Figure 2 Ni(II), Co(II), and Zn(II) ions removal capacities of St-g-AA copolymers.

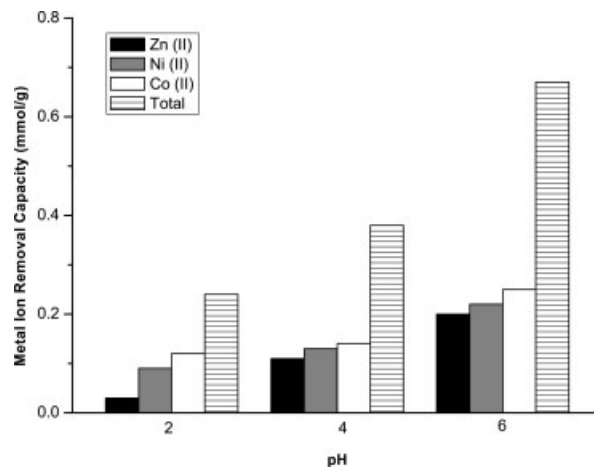


Figure 3 The effect of the pH on the Ni(II), Co(II), and Zn(II) ions removal capacities of St-g-AA-3 copolymer.

Grafting percentage determination

Grafting percentage (GP%) was determined by titration method.³⁰ The graft copolymer in 0.1N NaBr solution was titrated with 0.1N NaOH solution in presence of phenolphthalein indicator and calculated to the following equation.

$$GP\% = \frac{M_1}{M_2} \times 100$$

where M_1 , amount of grafted AA (g) (calculated from result of titration); M_2 , amount of graft copolymer (g).

Removal of heavy metal ions

Stock solution containing Ni²⁺, Co²⁺, Zn²⁺ ions all together with equal concentration, 5 mmol/L, was prepared by dissolving metal nitrate salts in distilled water. pH of stock solution was adjusted to 2, 4, and 6 by using diluted HNO₃ solution. St-g-AA copolymer (0.5 g) was added in 50 mL of stock solution and the mixture was stirred with a magnetic stirrer. The amount of residual metal ions in the aliquots of

TABLE I
The Effect of the pH on the Total Metal Ion Removal Capacity of St-g-AA-3 Copolymer

Time (h)	Total metal ion removal capacity (mmol/g)		
	pH = 2	pH = 4	pH = 6
0.25	0.21	0.24	0.43
0.50	0.21	0.26	0.48
1.00	0.21	0.28	0.55
2.00	0.21	0.32	0.63
3.00	0.23	0.37	0.67
5.00	0.24	0.38	0.67
8.00	0.24	0.38	0.67

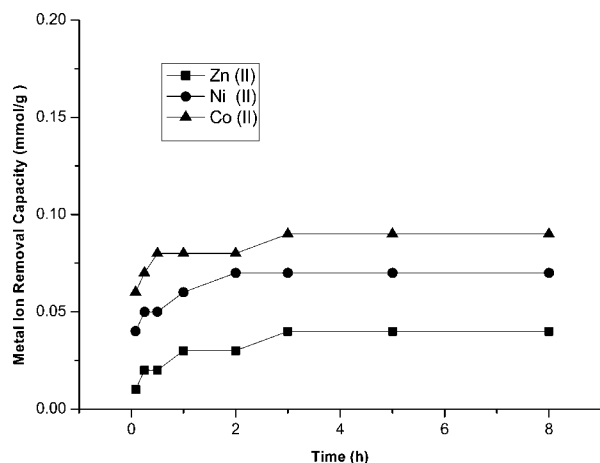


Figure 4 Competitive removal of Ni(II), Co(II), and Zn(II) ions by St-g-AA-1 copolymer.

withdrawn solution was followed by atomic absorption spectrometer (AAS) (Varian SpectrAA FS-220) up to 8 h. Metal ion removal capacities of the copolymers were calculated as follows:

$$\text{Metal ion removal capacity (mmol/g copolymer)} = \frac{(C_i - C_t)V}{M_{\text{copolymer}}}$$

where C_i , initial concentration of metal ions in the solution (mmol/L); C_t , the concentrations of metal ions in the solution after metal ion removal (mmol/L); V , Volume of the solution (L); $M_{\text{copolymer}}$, the weight of St-g-AA copolymer (g).

Used St-g-AA copolymers were regenerated with 1M HCl for 2 h and then they were reemployed in heavy metal ion removal.

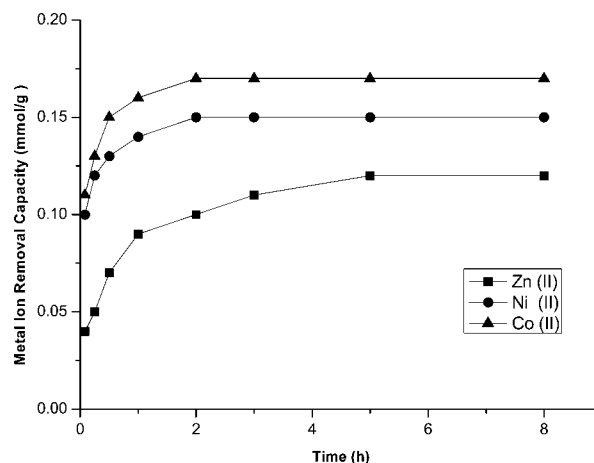


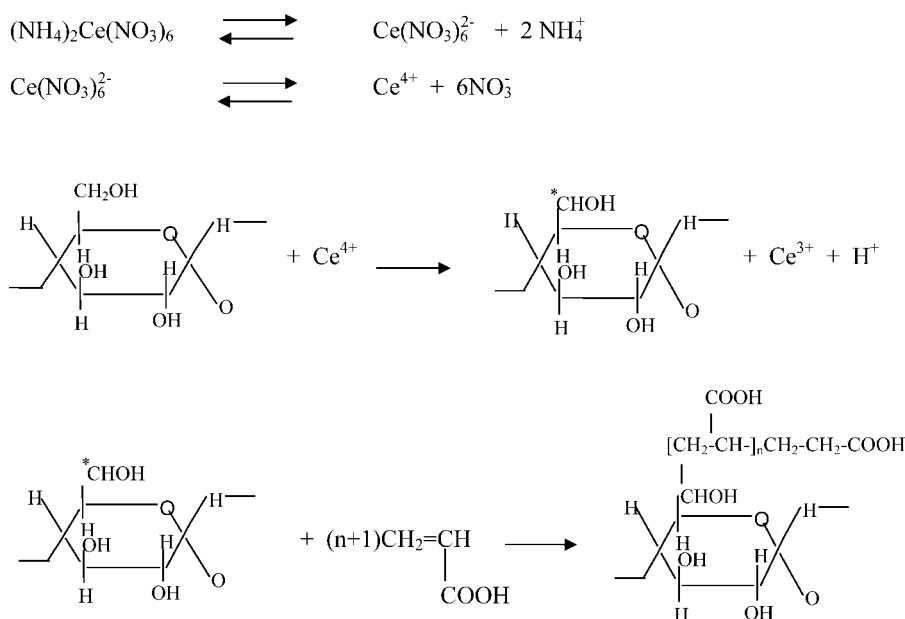
Figure 5 Competitive removal of Ni(II), Co(II), and Zn(II) ions by St-g-AA-2 copolymer.

FTIR analysis

The infrared spectra of St-g-AA copolymers were taken with Digilab Excalibur-FTS 3000MX model FTIR spectrophotometer using KBr pellets.

RESULTS AND DISCUSSION

The graft copolymerization of AA onto starch was carried out with monomer concentration of 0.1–0.5 mol/L. CAN was used as initiator. The grafting reaction initiated by the CAN is characterized with first producing free radicals on the starch backbone and then adding AA molecules to the starch macroradicals formed. The GP% of St-g-AA-1, St-g-AA-2, St-g-AA-3 copolymers were 2.5, 10.5, 14%, respectively. The grafting reaction onto starch is as follows²⁴:



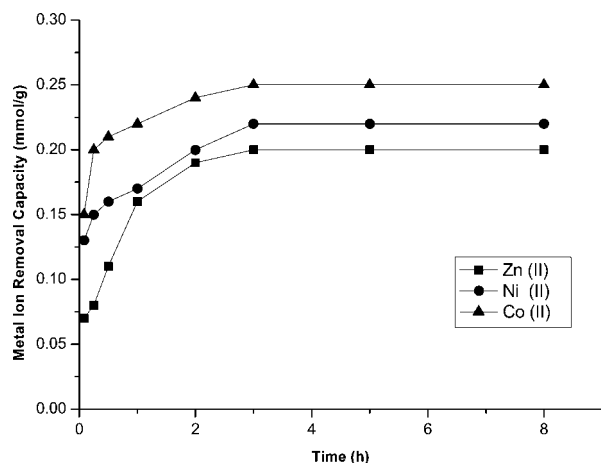
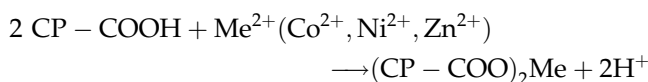


Figure 6 Competitive removal of Ni(II), Co(II), and Zn(II) ions by St-g-AA-3 copolymer.

There are several works about removal of heavy metal ions with modified natural polysaccharides as cellulose^{21,22} and starch.^{24–27} In this work, starch-g-acrylic acid copolymers (St-g-AA-1, St-g-AA-2, and St-g-AA-3) obtained from graft copolymerization of AA onto starch have been used for the first time in the competitive removal of Ni²⁺, Co²⁺, Zn²⁺ ions from aqueous solutions. St-g-AA copolymers and metal loaded copolymers were characterized by FTIR. Figure 1 shows the changes in the spectrum of St-g-AA-3 copolymer before and after removal of heavy metal ions. The peaks at 1715 cm⁻¹ attributed to carboxyl groups shifts to the lower peaks at 1643 cm⁻¹ after the metal binding. In the case of the removal of the metal ions by St-g-AA copolymers, reaction equation can be written as follows²³:



where CP— is the copolymer chain.

The effects of grafting percentage of St-g-AA copolymers, treatment time with metal solution, initial pH of the solution and regeneration of the copolymers on the metal ion removal capacities were investigated.

Effect of grafting percentage

Figure 2 shows the effect of GP% of the St-g-AA copolymers on the metal ion removal capacities from aqueous solutions. It is obvious that Ni²⁺, Co²⁺, Zn²⁺ ions removal capacities increased with increasing grafting yield. The selectivity can be ordered as Co²⁺ > Ni²⁺ > Zn²⁺.

TABLE II
Heavy Metal Ion Removal Capacities of S-g-AA-1 Copolymer

Time (h)	Original S-g-AA-1 copolymer			
	Co ²⁺ (mmol/g)	Ni ²⁺ (mmol/g)	Zn ²⁺ (mmol/g)	Total (mmol/g)
0.25	0.07	0.04	0.01	0.12
0.50	0.08	0.05	0.02	0.15
1.00	0.08	0.05	0.02	0.15
2.00	0.08	0.06	0.03	0.17
3.00	0.09	0.07	0.03	0.19
5.00	0.09	0.07	0.04	0.2
8.00	0.09	0.07	0.04	0.2

Effect of pH

Copolymer sample (St-g-AA-3) was added to the metal stock solution of pH = 2, 4, and 6 to investigate the effect of pH. The metal stock solution containing Ni²⁺, Co²⁺, Zn²⁺ ions all together was prepared by dissolving metal nitrate salts in distilled water. The results for competitive removal of Ni²⁺, Co²⁺, Zn²⁺ ions at different pH are shown in Figure 3 and total ion removal capacities are summarized in Table I. The metal ion removal capacities of copolymers increased with increasing pH. The presence of ionizable group such as carboxyl group on the copolymer structure, pH will affect the metal ion removal capacities of this copolymer, because of the changing of ionization degree with pH. At low pH, the carboxyl groups are present in nonionized form and no interaction can occur between the carboxyl groups and the metal ions. On increasing the pH, the carboxyl groups are ionized and increase the probability of interaction between the carboxylic groups and the metal ions in the solution.³¹ As a result, since the dissociation of the carboxyl group will be favored in the alkaline pH, higher metal ion removal capacity should be observed at higher pH values.³² pH 6 is considered to be optimal pH value since these metals precipitate at pH > 6.

TABLE III
Heavy Metal Ion Removal Capacities of St-g-AA-2 Copolymer

Time (h)	Original S-g-AA-2 copolymer			
	Co ²⁺ (mmol/g)	Ni ²⁺ (mmol/g)	Zn ²⁺ (mmol/g)	Total (mmol/g)
0.25	0.13	0.12	0.05	0.3
0.50	0.15	0.13	0.07	0.35
1.00	0.16	0.14	0.09	0.39
2.00	0.17	0.15	0.10	0.42
3.00	0.17	0.15	0.11	0.43
5.00	0.17	0.15	0.12	0.44
8.00	0.17	0.15	0.12	0.44

TABLE IV
Heavy Metal Ion Removal Capacities of S-g-AA-3 Copolymer

Time (h)	Original S-g-AA-3 copolymer				Regenerated S-g-AA-3 copolymer			
	Co ²⁺ (mmol/g)	Ni ²⁺ (mmol/g)	Zn ²⁺ (mmol/g)	Total (mmol/g)	Co ²⁺ (mmol/g)	Ni ²⁺ (mmol/g)	Zn ²⁺ (mmol/g)	Total (mmol/g)
0.25	0.20	0.15	0.08	0.43	0.18	0.14	0.08	0.4
0.50	0.21	0.16	0.11	0.48	0.19	0.15	0.11	0.45
1.00	0.22	0.17	0.16	0.55	0.21	0.17	0.15	0.53
2.00	0.24	0.2	0.19	0.63	0.22	0.19	0.19	0.6
3.00	0.25	0.22	0.20	0.67	0.23	0.21	0.20	0.64
5.00	0.25	0.22	0.20	0.67	0.23	0.21	0.20	0.64
8.00	0.25	0.22	0.20	0.67	0.23	0.21	0.20	0.64

Effect of the treatment time

Heavy metal ion removal capacities of the copolymers were determined at pH = 6. All of the experiments were occurred at room temperature. Figures 4–6 and Tables II–IV give the effect of treatment time on the removal of Ni²⁺, Co²⁺, Zn²⁺ ions with St-g-AA-1, St-g-AA-2, and St-g-AA-3 copolymers. As seen, the removal capacity of Ni²⁺, Co²⁺, Zn²⁺ ions increased with the treatment time during the 5 h. All the three copolymers containing different amounts of –COOH groups removed Co²⁺ ion the most preferentially, followed by Zn²⁺ and Ni²⁺ ions. The metal ion removal capacities of St-g-AA copolymers show a rapid increase with increasing treatment time during the 2 h and then slow down and reach an equilibrium value (Figs. 4–6). The results indicate that the metal ion removal capacities almost reach equilibrium within 3 h.

Regeneration of St-g-AA copolymers

By treatment of the metal ion-loaded St-g-AA copolymer with 1M hydrochloric acid it is possible to remove almost completely Ni²⁺, Co²⁺, Zn²⁺ ions

from loaded copolymer. Removal of the adsorbed metal ions from copolymers was studied with a batch equilibrium technique.

St-g-AA-3 copolymer was contacted with 1M HCl for 2 h and then filtered, washed for removal of excess HCl. After the regeneration, we determined metal ion removal capacity of regenerated St-g-AA-3 copolymer. As seen in Table IV and Figures 7–9, the metal ion removal capacities of copolymers have very little change and St-g-AA copolymers can be used repeatedly after regeneration process.

CONCLUSION

St-g-AA copolymers were obtained with graft copolymerization of AA onto starch by CAN as initiator. The main purpose of this work is investigation of competitive removal of Ni²⁺, Co²⁺, Zn²⁺ ions from aqueous solutions with St-g-AA copolymers. The metal ion removal capacity of these copolymers increased with increasing grafting percentage, treatment time and pH of the initial metal ion solution. pH 6 is considered to be optimal pH value since these metals precipitate at pH > 6. The observed

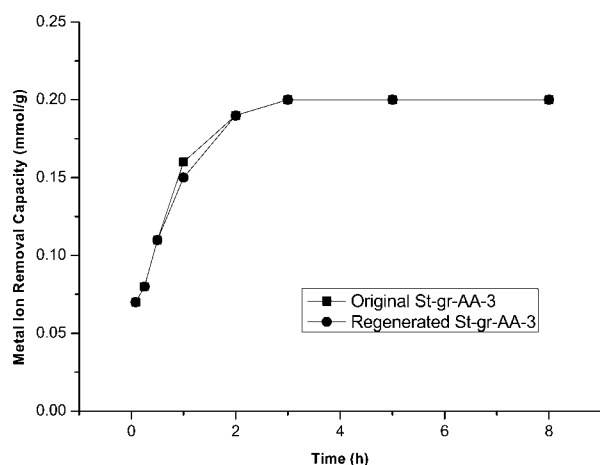


Figure 7 Removal of Zn(II) ion by St-g-AA-3 original and regenerated copolymers.

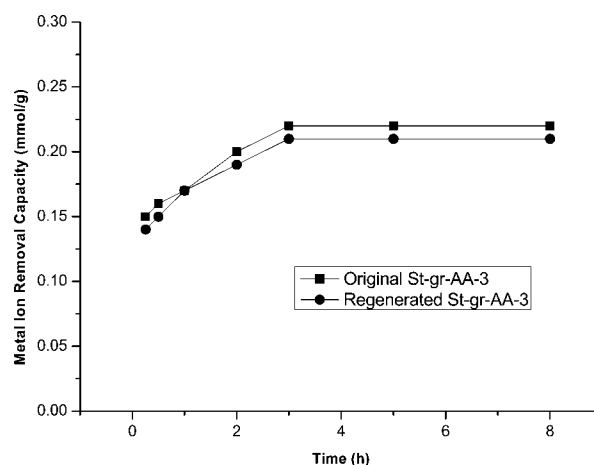


Figure 8 Removal of Ni(II) ion by St-g-AA-3 original and regenerated copolymers.

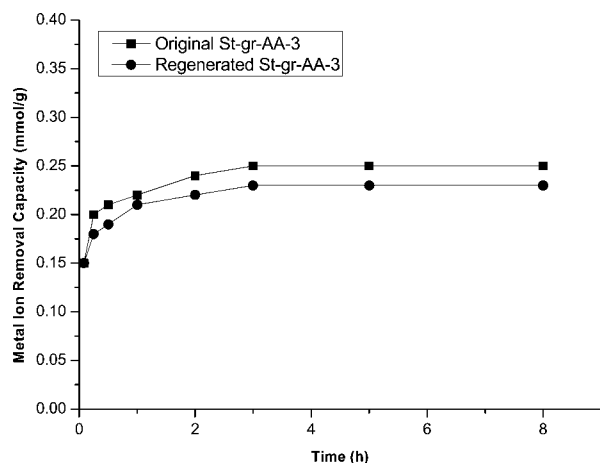


Figure 9 Removal of Co(II) ion by St-g-AA-3 original and regenerated copolymers.

affinity order in removal of heavy metals was found $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$. Additionally, the effect of the regeneration of the St-g-AA copolymers was investigated in this work and no important change was observed in the metal ion removal capacity of St-g-AA copolymers.

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