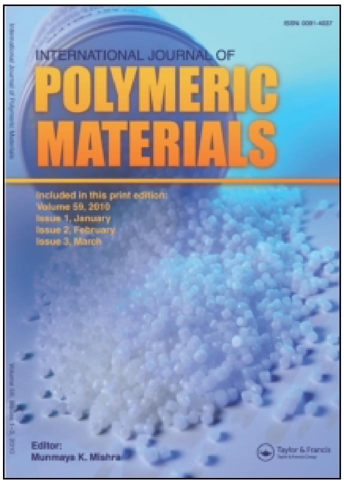
This article was downloaded by:
On: *18 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Preparation of Poly(acrylamide-maleic Acid) Resin by Template Polymerization and Its Use for Adsorption of Co(II) and Ni(II)

H. M. Abdel-Aziz[a]; H. A. Hanafi[b]; S. F. Abozahra[a]; T. Siyam[a]
[a] Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt [b] Cyclotron Project, Nuclear Research Centre, Atomic Energy Authority, Cairo, Egypt

Online publication date: 09 November 2010

To cite this Article Abdel-Aziz, H. M. , Hanafi, H. A. , Abozahra, S. F. and Siyam, T.(2011) 'Preparation of Poly(acrylamide-maleic Acid) Resin by Template Polymerization and Its Use for Adsorption of Co(II) and Ni(II)', International Journal of Polymeric Materials, 60: 1, 89 — 101

To link to this Article: DOI: 10.1080/00914037.2010.504166

URL: http://dx.doi.org/10.1080/00914037.2010.504166

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Journal of Polymeric Materials, 60:89–101, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914037.2010.504166

Preparation of Poly(acrylamide-maleic Acid) Resin by Template Polymerization and Its Use for Adsorption of Co(II) and Ni(II)

H. M. Abdel-Aziz,[1] H. A. Hanafi,[2] S. F. Abozahra,[1] and T. Siyam[1]

[1]Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt
[2]Cyclotron Project, Nuclear Research Centre, Atomic Energy Authority, Cairo, Egypt

Poly(acrylamide-maleic acid) resin P(AAm-MA) was prepared by template polymerization. Polyacrylamide PAAm was used as a template for the polymerization of MA in an aqueous solution using gamma rays as the initiator. The effects on the capacity of P(AAm-MA), such as concentration of maleic acid and amount of template polymer, were investigated. P(AAm-MA) has been utilized as an adsorbent for the removal of Co(II) and Ni(II) ions from an aqueous solution. The effects of time of equilibrium, pH, temperatures, and dosage of the adsorbent on the removal of Co(II) and Ni(II) ions have been studied. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The equilibrium process was described well by the Langmuir isotherm model.

Keywords adsorption, Co(II), Ni(II), radiation, resins, template polymerization

INTRODUCTION

Template or matrix polymerization is defined as a polymerization in which chain propagation occurs along a performed template, i.e., a polymer added to a reactive system. The term "template polymerization" usually refers to

---

Received 15 March 2010; accepted 2 June 2010.

Address correspondence to H. M. Abdel-Aziz, Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt. E-mail: hmabdelaziz@hotmail.com

one-phase systems in which the monomer and the template are soluble in the same solvent or are present in a form of a swollen gel [1–4]. The presence of the template may influence the polymerization kinetics (e.g., polymerization rate, activation energy, reaction order with respected to monomer and initiator), the characteristics of the produced polymer (average molecular weight, molecular weight distribution, microstructure, stereoregularity), and the activity ratios in the case of copolymerization. The nature of interaction between the monomer and the template polymer depends mainly on the nature of the forces acting between monomers and the template. These forces may be covalent bond, hydrogen bond, dipole–dipole bond or electrostatic forces [1,2]. Two types of polymer materials can be obtained as a result of template polymerization: polymers or copolymers with at least partially ladder-type structure, and polycomplexes with a structure of a more ordered form than that obtained by mixing two polymer components.

Over the past decade, the consumption of metals and chemicals in processing industries has increased dramatically. Industrial uses for metals, such as metal plating, tanning, and reaction catalysis, have generated large amounts of aqueous effluents that contain high levels of heavy metals [5]. Methods for the removal of metal ions from aqueous streams, such as chemical precipitation and reverse osmosis, result in incomplete metal removal and have high reagent or energy consumptions. Moreover, they generate toxic sludge that is difficult to dewater and other waste products that require careful disposal [6]. Removal of heavy metal ions by using polymers with different functional groups would be of great importance in environmental applications [7–12] due to their high adsorption capacities, especially regeneration abilities and reuse for continuous processes. For this purpose, different polymeric adsorbents having different functional groups, which have complexing ability with metal ions, have been investigated in the preceding literature [13–17]. Polyamide is an interesting candidate for study based on its unwettability and porosity [13]. The preparation of modified polyamide beads containing predominantly amino and carboxyl groups on their surfaces has been reported by several authors [14–17].

In this study, P(AAm-MA) was prepared by a template polymerization of MA in the presence of PAAm as a template polymer using gamma rays. The influences of MA and PAAm template polymer content in polymer were investigated. This paper also reports about systematic adsorption studies of Co(II) and Ni(II) ions on P(AAm-MA). The effect of equilibrium time, pH and dosage of adsorbent on the adsorption of these metal ions is described. The adsorption isotherm and probable mechanism are explained. In addition, the kinetics of adsorption were determined by the classical kinetic approach to predict the rate constant of the adsorption.

EXPERIMENTAL

Materials

PAAm (average mol. wt. 5,000,000) and MA were obtained from Merck and Aldrich Chemicals, respectively. They were used in polymerization reactions without further purification. N,N′-methylenebisacrylamide (NMBA) was purchased from Merck and used as received.

Adsorbate Solution

The stock solution (1000 mg L^{-1}) of metal ions was prepared by dissolving their corresponding nitrate salts in double-distilled water. The solution was further diluted to the required concentrations before use. All the chemicals used were analytical reagent grade and were obtained from Merck and BDH. We used double-distilled water because these studies provide basic information and the possibilities to implement in a real system, however, for a real system the adsorption studies have to be conducted under natural conditions.

Batch Adsorption Studies

Adsorption experiments were carried out at 25°C, in magnetically stirred (160 rpm) cylindrical glass vessels, in batch conditions. The samples (50 mg) of P(AAm-MA) were added into a metal ion solution (10 ml) with concentration of 10 mg L^{-1} and 100 mg L^{-1} for Co(II) and Ni(II), respectively. The amount of residual in the solution was determined by a Jobin Yvon ICP-AES spectrometer, model Ultima 2. In these experiments, samples were stirred with metal ion solutions under the experimental conditions described above and residual metal ion concentrations were determined at regular time intervals. Dependence of adsorption capacities on time was determined and adsorption kinetics were investigated in detail. Furthermore, adsorption isotherms were obtained by stirring polymers in the metal ion solutions with various initial concentrations for a period of time equal to the respective equilibrium times. The effect of pH of the solution was adjusted either by 1.0 N HCl or NaOH solution. The adsorption capacity, Q (milligram metal ion per gram polymer), of polymer was calculated by using the following expression:

$$Q(mg/g) = \frac{(C_i - C_e)V}{m} \tag{1}$$

where, C_i and C_e are the initial and equilibrium concentrations of metal ion (mg L^{-1}), respectively, V is the volume of the solution added (L), and m is the amount of polymer (g).

Preparation of P(AAm–MA)

Different compositions of maleic acid/polyacrylamide (MA-PAAm) mixtures using water as a solvent were subjected to γ-rays. During the irradiation process, the formation of active free radicals on both the PAAm template polymer and MA monomer are formed. PMA macro-radical chains initiated by the reaction of radicals formed from radiolysis of MA molecules, also, P(AAm–MA) copolymer chains initiated by the reaction of radicals formed from radiolysis of MA and PAAm polymer are obtained. The macro-radicals recombined and new covalent bonds and hydrogen bond between the polymer chains are formed and turn into an insoluble fraction. The amount of these new bonds depends upon the irradiation dose (as the irradiation dose increases the insoluble fraction increases), monomer concentration and template PAAm concentration. After the irradiation process, the resins were cut into small discs. All the prepared samples were immersed twice in excess water for 24 h to remove the unreacted monomer. The resin was then left to dry at room temperature.

RESULTS AND DISCUSSION

P(AAm-MA) resin was prepared by template polymerization of MA monomer on PAAm as a template polymer in the presence of NMBA as a crosslinker using gamma radiation technique. The polymeric resins used for the adsorption of metal ions have a series of practical characteristics. They are hydrophilic, insoluble in water, chemically stable and have a high capacity towards metal ions. Therefore, the present study aims to prepare P(AAm-MA) resin with a high uptake capacity. The experimental factors such as MA content and the concentration of PAAm that affects the capacity of the obtained resin were studied.

IR Analysis

According to the chemical structure of polymers, hydrogen bonding must be between the carboxylic group and amide group. Fourier transform infrared spectroscopy (FTIR) was used for the identification of hydrogen bonds in the complexes as shown in Figure 1.

The IR spectrum of polyacrylamide exhibits several characteristics bands. The absorption band at 1650 cm^{-1}, the so-called amide I mode [18], is a mode with contributions of the $C=O$ stretching modes. N–H stretching, amide II mode, absorbs in the range 3500–3100 cm^{-1} and the C–O stretching absorbs at 1400 cm^{-1}. In the case of copolymers of acrylamide and maleic acid crosslinked with crosslinking agents, the IR spectra showed characteristic bands

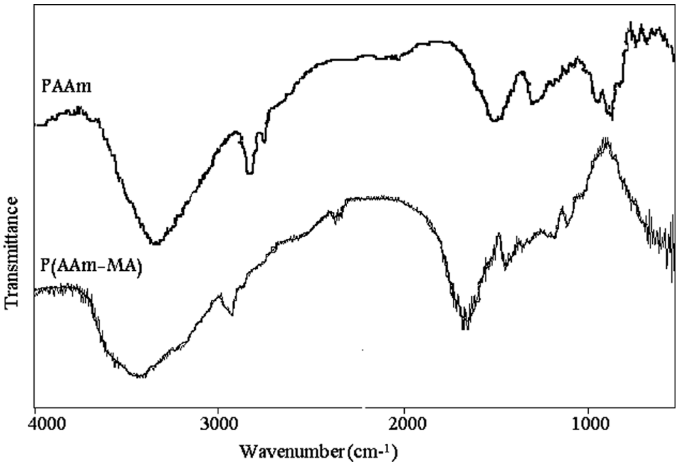


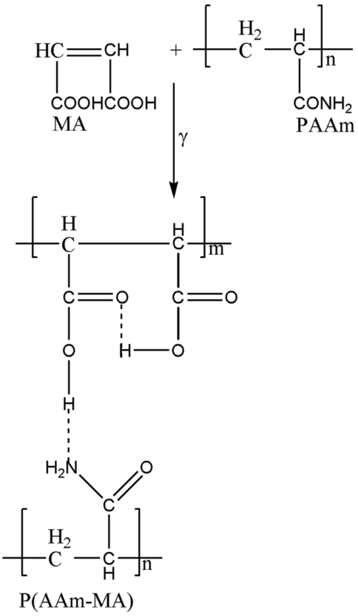
Figure 1: FTIR spectrum of P(AAm-MA).

of maleic acid repeating unit in addition to the characteristic bands of the acrylamide unit but the band appears at shifted position. Hydrogen bonds are formed between the proton–donor and proton–acceptor molecules. The intensity of the hydrogen bond band depends on the acidity of the hydrogen in the proton–donor, the alkalinity of the proton—acceptor and the possibility of their close contact. As a consequence of hydrogen bonding, the covalent bonds in the donor and acceptor are weaker, while the energy barrier for angle deformation becomes higher. In the spectrum of pure PAAm, the υ (C = = O) band lies at 1650 cm^{-1}, whereas in the spectra of the complexes this band appears at the higher frequency of 1675 cm^{-1}.

The bands corresponding to carboxyl groups of maleic acid have overlapped with N-H stretching frequency in the region 3000 cm^{-1}. There are small humps around 1720–1710 cm^{-1} characteristic of thee carbonyl group of maleic acid. In addition to this, other characteristic bands related to OH group of the carboxyl group are observed at 1454, and 1119 cm^{-1} indicating the incorporation of maleic acid units in the copolymer chains. Thus the IR spectra confirm the presence of two repeating units, that is, the acrylamide and maleic acid in the copolymer structure. A possible structure of P(AAm-MA) prepared by template polymerization of MA on PAAm as a template polymer is shown in Scheme 1.

Effect of Maleic Acid Content

The effect of initial MA concentration (wt%) on the capacity of P(AAm-MA) is shown in Figure 2. It is obvious that the capacity increases with the increase of initial MA concentration. Because polyacrylamide is a nonionic polymer,



Scheme 1: Synthesis of the P(AAm-MA).

ionizable groups (COOH) were increased by the addition of MA to the PAAm template polymer. Increasing carboxyl groups in the resins with increasing the MA contents causes electrostatic interactions between the cationic groups of the adsorbate and anionic groups of MA in the resins [19].

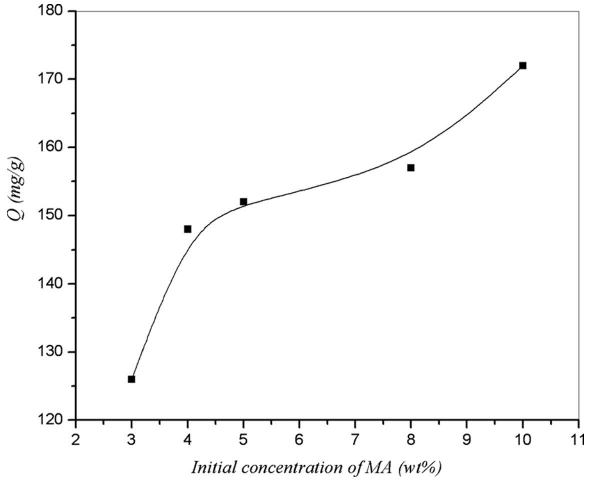


Figure 2: Effect of initial MA concentration on the capacity of P(AAm-MA).

Effect of PAAm Contents

The aim of the present investigation is to study the influence of the template on the capacity of the final resin product. In general the template polymer used in the template polymerization technique may be a homopolymer or copolymer. In our study the template is a polyacrylamide gel that attached to the added MA monomer through hydrogen bonds. The influence of PAAm concentration on the capacity of the obtained resin was studied at MA concentration of 6%, NMBA concentration of 1%, the dose of 30 kGy and dose rate of 3.5 kGy h^{-1} as shown in Figure 3. The obtained results clearly show that the capacity of the obtained resin depends on the concentration of the PAAm employed in the polymerization mixture. Figure 3 shows that the capacity of P(AAm-MA) resin increases by increasing the PAAm concentration. Increasing the amount of the added template polymer PAAm leads to an increase in the number of hydrophilic amide groups on the polymeric resin that can increase interaction with the cation groups of the adsorbate.

Effect of Adsorbent Dose

Figure 4 shows the adsorption of Co(II) and Ni(II) with varying weight of the adsorbent at pH 5.8. It indicates that the uptake of Co(II) and Ni(II) increases in as the adsorbent dose increases from 0.025 to 0.3 g in 10 ml of Co(II) and Ni(II) solution. Beyond 0.2 g of the adsorbent the Co(II) and Ni(II) removal becomes more or less constant. The adsorbent dose of 0.2 g was able to

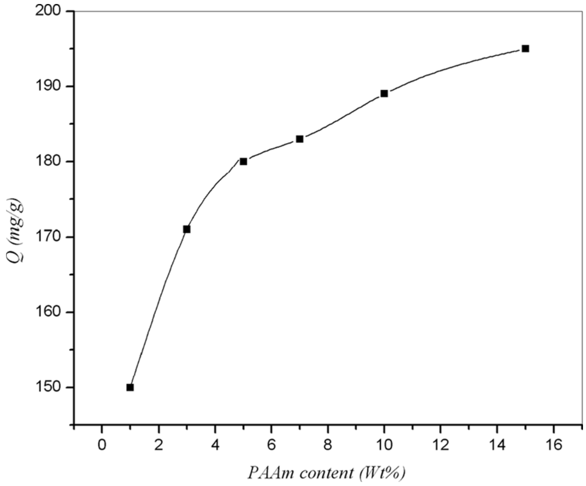


Figure 3: Effect of PAAm content on the capacity of P(AAm-MA).

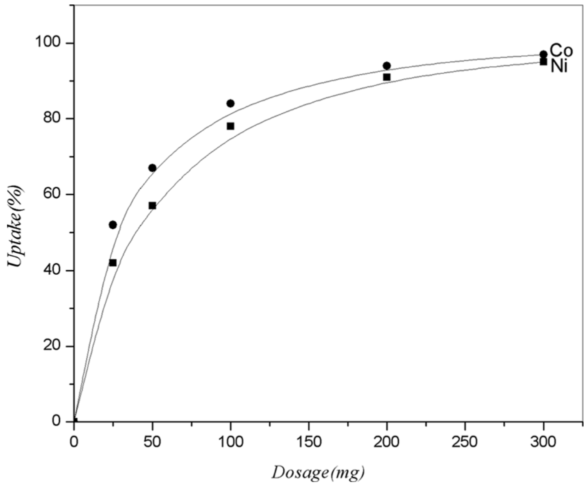


Figure 4: Effect of dosage of P(AAm-MA) on the adsorption of Co(II) and Ni(II).

adsorb 95% Co(II) and Ni(II). This increase of Co(II) and Ni(II) removal may be attributed to increases in the active site of the adsorbent surface.

Effect of Contact Time

The adsorption of Co(II) and Ni(II) ions with time was studied and the results are shown in Figure 5. The adsorption increases with increasing contact time and the equilibrium was attained after shaking for 90 min. It is observed that the adsorption of Ni(II) ions reaches a final plateau after 50 min. The maximum uptake after this time is constant at a value of 98% of adsorption. On the other hand, the behavior of Co(II) ions reaches a value of 97%. However, the time of equilibrium used in all the following studies was set to 1.5 h for the sake of simplicity as well as to ensure a complete adsorption in both cases.

Effect of pH on Sorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process [20] and thus the role of hydrogen ion concentration was examined from solutions at different pH covering a range of 1–6. Both the metal ions show different extent of adsorption at different pH values of P(AAm-MA). The percent adsorption for Co(II) and Ni(II) ions increased with increasing pH and reached the plateau at pH 5–6 for Co(II) and Ni(II) ions as shown in Figure 6.

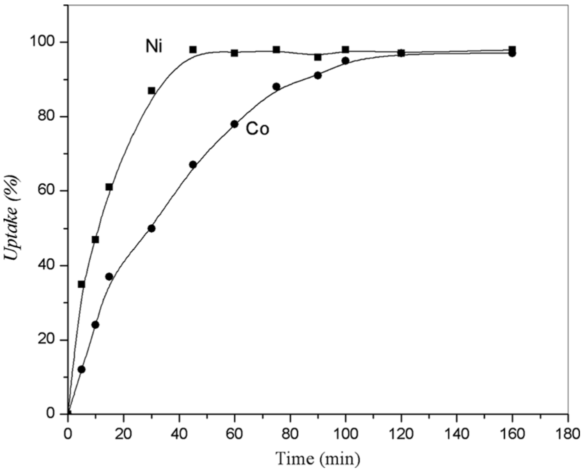


Figure 5: Effect of time on the adsorption of Co(II) and Ni(II) ions on P(AAm-MA).

The adsorption behavior of Co(II) and Ni(II) ions on P(AAm-MA) at different pH values may be explained by ion exchange and complexation mechanisms.

P(AAm-MA) basically contains AAm and MA. The polar functional groups of P(AAm-MA), e.g., amide, and carboxylic group are involved in these processes. They are affected by pH and may undergo protonation and/or deprotonation thereby resulting in the variation in surface charge of the adsorbent [21]. This results in the uptake of metal ions from the solution via complexation and/or ion exchange processes. The investigated ions show similar trends of adsorption, probably because they belong to the same group of the periodic table. Their different extents of adsorption may be attributed to their different effective ionic radii. The ionic radius of Ni(II) ions is 6.6 Ǻ while that of Co(II) ions is 6.7 Ǻ. The smaller ionic size of Ni(II) ions helps in its easy approach to less approachable sites of the adsorbent as compared to that of Co(II) ions. Further, the higher hydration energy of Co(II) ions in comparison to Ni(II) ions restricts its maximum uptake by the adsorbent.

Adsorption Isotherms

Adsorption capacity of an adsorbent is rather depended on the concentration of the adsorbed molecule as well as the other process parameters. In order to investigate the effect of the initial metal ion concentration on the adsorption capacity, experiments were carried out at various initial Co(II) and Ni(II) ions concentrations (10–300 ppm) at 25°C for 2 h as described in the Experimental section.

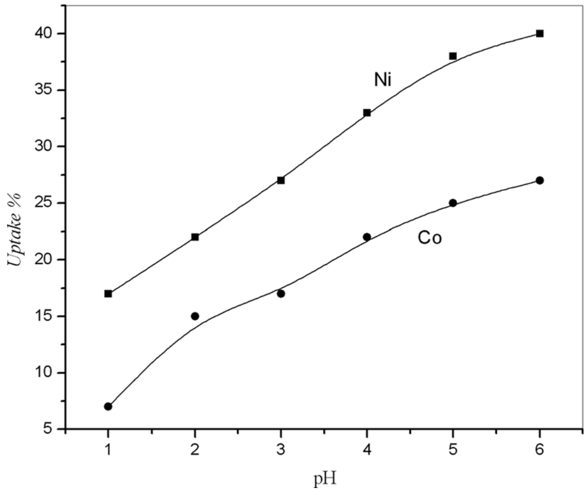


Figure 6: Effect of pH on the adsorption of Co(II) and Ni(II) ions on P(AAm-MA).

Several models have been published in the literature to describe adsorption isotherms. The Langmuir and Freundlich models are the most frequently used models. In this study, the Langmuir and Freundlich models were used to describe the relationship between the amount of Co(II) and Ni(II) ions adsorbed and its equilibrium concentration in solution.

The basic assumption of the Langmuir adsorption model is that sorption takes place at specific homogeneous sites within the adsorbent. The Langmuir isotherm is represented by the following equation [22].

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}} \tag{2}$$

where, Qe ($\mathrm{mg\,g^{-1}}$) is the amount of the adsorbed metal ions per unit weight of adsorbent at the final equilibrium concentration of the metal ion solution (C_e, $\mathrm{mg\,L^{-1}}$). The Q_{max} signifies the maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$) and b is related to the energy of adsorption (L mg). The essential characteristic of the Langmuir equation can be expressed in terms of the dimensionless separation factor R_L, which is defined by

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where, C_0 is the highest initial metal ion concentration ($\mathrm{mg\,L^{-1}}$) and b is the Langmuir constant. The value of R_L indicates the type of the isotherm either to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible

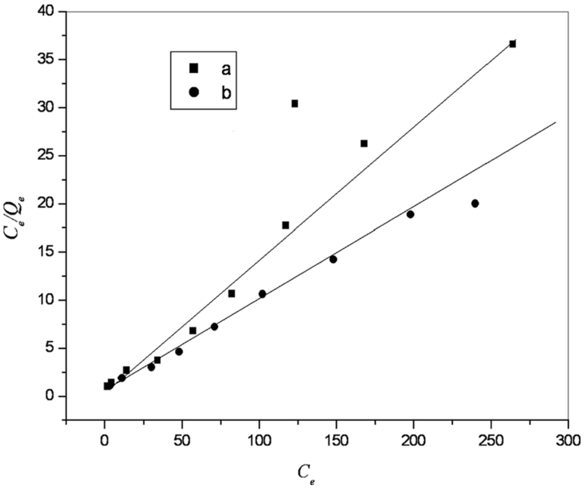


Figure 7: Langmuir adsorption plot for the adsorption of Co(II) and Ni(II) ions by P(AAm-MA).

($R_L = 0$). The Freundlich isotherm model can be represented by the following equation [23].

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where, K_f and n are Freundlich constants that are related to adsorption capacity and intensity of adsorption.

The isotherm data were fitted with Langmuir isotherm model for the both metal ions. The Langmuir isotherms for the adsorption of Co(II) and Ni(II) ions onto P(AAm-MA) are represented in Figures 7(a) and (b). Langmuir constants are given in Table 1. It is seen from the table that the correlation coefficients are 0.9887 and 0.989 for the Co(II) and Ni(II) ions, respectively. The maximum adsorption capacities calculated from the equation are close to the experimental results. The low value of R_L indicates a favorable adsorption. When the Freundlich isotherm model was applied to experimental data, a good fit was not obtained (correlation coefficients are 0.718 and 0.910 for the Co(II) and Ni(II) ions, respectively).

Table 1: Longmuir constants for the adsorption of Co(II) and Ni(II) ions onto the polymer.

		Longmuir constants		
Ions	*b*	*R_L*	*r^2*	*Q_{max}*
Co(II)	1.265	0.00262	0.988	7
Ni(II)	0.1001	0.032	0.989	12

CONCLUSION

P(AAm-MA) resin was prepared by the template polymerization of MA on PAAm as a template polymer using gamma rays as the initiating system in the presence of NMBA as a crosslinker. The influence of maleic acid content and PAAm concentration on the capacity of P(AAm-MA) resin was investigated. The capacity of P(AAm-MA) increases with the increase of MA and PAAm concentration.

The adsorption of Co(II) and Ni(II) was studied by batch technique and it was observed that >90% of metal ions removal was achieved by using 50 mg of P(AAm-MA) resin for an initial metal ion concentration of 10 mg L^{-1} and 100 mg L^{-1} for Co(II) and Ni(II), respectively. The adsorption of Co(II) and Ni(II) was found to be dependent on pH, contact time and adsorbent dosage. The experimental results were analyzed by using Langmuir and Freundlich isotherm models and the correlation coefficients for the Langmuir equation fitted better than the Freundlich equations.

At the end of this study, we can say that P(AAm-MA) resin prepared by gamma rays may be used as an alternative sorbent for the removal of some metal ions from wastewaters.

REFERENCES

[1] Polowinski, S. (1997). *Template Polymerization*, Chem Tec Publishing, Canada.

[2] Polowinski, S. *Prog. Polym. Sci.* **27**, 537 (2002).

[3] Rainaldi, I., Cristallini, C., Ciardelli, G., and Giusti, P. *Macromol. Chem. Phys.* **201**, 2424 (2000).

[4] Cristallini, C., Ciardelli, G., Polacco, G., Villani, A., Lazzeri, L., and Giusti, P. *Polym. Int.* **48**, 1251 (1999).

[5] Leung, W. C., Wong, M. F., Chua, H., Lo, W., Yu, P. H. F., and Leung, C. K. *Wat. Sci. Tech.* **41**, 233 (2000).

[6] Kapoor, A., and Virarghavan, T. *Wat. Res.* **32**, 1968 (1998).

[7] Kaşgöz, H., Özgümüş, S., and Orbay, M. *Polymer* **44**, 1785 (2003).

[8] Saha, B., and Streat, M. *Ind. Eng. Chem. Res.* **44**, 8671 (2005).

[9] Hashem, A., Socker, H. H., Halim, E. S. A., and Gamal, A. *Ads. Sci. Tech.* **23**, 455 (2005).

[10] Zhanhai, Y., Lei, R., and Jun, X. *J. Appl. Polym. Sci.* **83**, 1986 (2002).

[11] Li, W., Zhao, H., Teasdale, P. R., John, R., and Zhang, S. *React. Funct. Polym.* **52**, 31 (2002).

[12] Kaşgöz, H. *Polym. Bull.* **56**, 517 (2006).

[13] El-Aal, S. E. A., Hegazy, E. A., Abutaleb, M. F., and Dessouki, A. M. *J. Appl. Polym. Sci.* **96**, 753 (2005).

[14] Delval, F., Crini, G., Bertini, S., Filiatre, C., and Torri, G. *Carbohyd. Polym.* **60**, 67 (2005).

[15] Essawy, H. A., and Ibrahim, H. S. *React. Funct. Polym.* **61**, 421 (2004).

[16] Jose, J., John, M., Gigimol, M. G., and Mathew, B. *J. Appl. Polym. Sci.* **90**, 895 (2003).

[17] El-Sawy, N. M. *Polym. Int.* **49**, 533 (2000).

[18] Iliopoulos, I., and Audebert, R. *Macromolecules* **24**, 2566 (1991).

[19] Karadag, E., Saraydin, D., and Güven, O. *J. Appl. Polym. Sci.* **61**, 2367 (1996).

[20] Elliot, H. A., and Huang, C. P. *Water Res.* **15**, 849 (1981).

[21] Huang, C. P., and Rhoads, E. A. *J. Colloid Interf. Sci.* **131**, 289 (1989).

[22] Özcan, A., and Özcan, A. S. *J. Hazard. Mater.* **B125**, 252 (2005).

[23] Crini, G., and Peindy, H. N. *Dyes Pigments.* **70**, 204 (2006).