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# (Sodium Alginate/Acrylamide) Semi-Interpenetrating Polymer Networks and their Usability on Removal of Lead, Cadmium, Nickel Ions

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*In this study, (sodium alginate (NaAlg)/acrylamide (AAm)) interpenetrating polymer networks (IPN) have been prepared at three different compositions, where the sodium alginate composition varies 1, 2, and 3% (w/v) in 50% (w/v) acrylamide solutions. These solutions have been irradiated with a* $^{60}Co$-$\gamma$ *source at different doses. The percent conversion was determined gravimetrically and 100% gelation was achieved at the 10.0 kGy dose. The swelling results at pH 7.0 and 9.0 indicated that (NaAlg/AAm)3IPN hydrogel, containing 3% NaAlg showed maximum % swelling in water, with swelling increasing in the order of* $Ni^{2+} > Cd^{2+} > Pb^{2+}$. *Diffusion in aqueous solutions of metal ions within (NaAlg/AAm)IPN hydrogels was found to be Fickian character. Diffusion coefficients of (NaAlg/AAm)IPN hydrogels in water and aqueous solutions of metal ions were calculated. The maximum weight loss temperature and half life temperature for NaAlg, PAAm, (NaAlg/AAm)IPN and (NaAlg/AAm)IPN-metal ion systems were found from thermal analysis studies. In the adsorption experiments, the efficiency of (NaAlg/AAm)IPN hydrogels to adsorb nickel, cadmium and lead ions from water was studied. (NaAlg/AAm)IPN hydrogels showed different adsorption for different aqueous solution of metal ion at pH 7.0. Adsorption isotherms were constructed for the (NaAlg/AAm)IPN-metal ion systems. S type adsorption in the Giles classification system was found.*

**Keywords** gamma-irradiation, semi-interpenetrating polymer networks, hydrogels, adsorption, heavy metal ions

## Introduction

The efficient removal of toxic metal ions from water is an important and widely studied research area. A number of technologies have been developed over the years to remove toxic metal ions from water. The most important of these technologies include filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and membrane systems. All of these technologies have their inherent advantages and limitations. Filtration is very low-cost and effective for removing particulate and other insolubles. Chemical precipitation is low-cost and quite effective for the removal of large quantities of metal ions quickly. Neither of these technologies, however, is capable of removing trace

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levels of metal ions. Ion exchange is also a mature and cost-effective procedure that is capable of reducing metal ion concentrations to part per million levels. However, in the presence of large quantities of competing mono-and divalent ions such as sodium and calcium, ion exchange is almost totally ineffective.

Adsorption, such as with activated carbon, while widespread in use, is ineffective for very low concentrations of metal ions. Electrodeposition possesses the significant advantage of allowing for the recovery and recyling of metals from solution. Membrane systems can also lower toxic metals to part per million levels. However, these systems are expensive and sophisticated, requiring a higher level of technical expertise to operate.

A technique which has been used is the use of (sodium alginate/acrylamide) interpenetrating polymer networks to remove the heavy metals from water. Interpenetrating polymer networks (IPN) take advantages of two polymers to remove ions of a specific size in the presence of large quantities of other ions. This approach is inherently attractive since only the metal ions are removed while the harmless ones move on into the environment. Some of the best IPN systems contain polysaccharides.

Polysaccharides, which are capable of lowering metal ion concentrations to part per billion concentrations, are widely available and are environmentally safe. Such materials include cellulosics, alginates, carrageenans, lignins and chitin derivatives. Another attractive feature of polysaccharides is that they possess a number of different functional groups, such as hydroxyls and amines, to which other chemical moieties can be reacted and which can increase the efficiency of metal ion uptake and/or the maximum chemical loadings possible (1, 2). Rather than being competetive with the above described, more classical techniques, polymer-metal complexes and adsorption of heavy metal ions on polymer and/or IPN based on sodium alginate is compatible with them, especially as a polishing step after the majority of the metal ions have been removed. In this study, (sodium alginate/acrylamide) interpenetrating polymer networks were synthesized by gamma-radiation and these IPN's were used to remove some heavy metals from water.

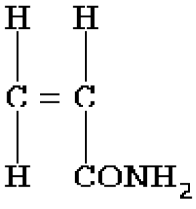
## Experimental

### *Materials*

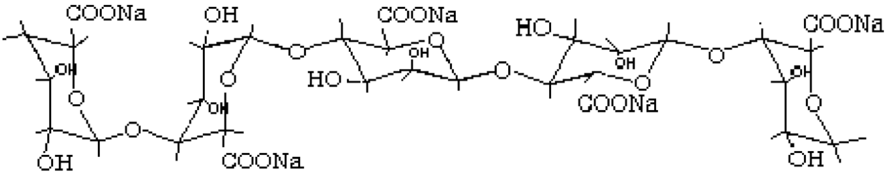
A medium viscosity sodium salt of alginic acid (NaAlg) (A-2023, Sigma Chemical Co., St Louis, MO), obtained from Macrocystitis pyrifera, was used in all studies. The monomer used in this study, namely acrylamide (AAm) was obtained from BDH. Lead nitrate [$Pb(NO_3)_2$], nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] and cadmium nitrate tetrahydrate [$Cd(NO_3)_2 \cdot 4H_2O$] were obtained from Aldrich and BDH, respectively. Sodium phosphate, di-sodium hydrogen phosphate-2-hydrate and phosphoric acid used to prepare phosphate buffer solutions were obtained from BDH. Nitric acid and sodium hydroxide used to adjust pH of the medium were obtained from Merck. All materials were used without any further purification. Some properties of acrylamide and sodium alginate are listed in Scheme 1.

### *Preparation of Interpenetrating Polymer Network (IPN) Hydrogels*

Three concentrations of alginate solution were prepared: 1, 2, and 3% (w/v) in 50% (w/v) acrylamide solution. These solutions were irradiated in air at ambient temperature in a Gammacell 220 type $\gamma$ irradiator. Doses of 2.0–20.0 kGy were applied at a fixed dose rate of 0.14 kGy/h. IPN hydrogels obtained in long cylindirical shapes were cut,



Acrylamide



Sodium Alginate

**Scheme 1.** Chemical formula of acrylamide and sodium alginate.

washed with distilled water for removal of unreacted monomers (if any) and dried in air under vacuum and stored for later evaluations. The percent conversion was determined gravimetrically.

### *Determination of Percent Gelation*

The obtained IPN hydrogels were cut into pieces of $\approx 2$ mm long. The prepared IPN gels were washed in deionized water for a week to remove uncrosslinked polymer and low molecular weight substances. The IPN gels were then dried in a vacuum oven until a constant weight was reached for each sample. Percent conversion of (NaAlg/AAm) (1–3) IPN hydrogels as insoluble networks were determined by using the weight of the hydrogel according to its initial weight. The percent gelation of (NaAlg/AAm) (1–3) IPN hydrogels obtained from AAm and NaAlg was calculated by using Equation (1).

$$\%\ \text{Gelation} = \frac{\text{weight of dry IPN hydrogel}}{\text{initial weight of IPN hydrogel}} \times 100 \qquad (1)$$

### *Spectroscopic and Thermal Analysis*

Fourier Transform Infrared (FTIR) spectra of the homopolymers, IPN hydrogels, aqueous solutions of metal ions and IPN hydrogels which contain metal ions were recorded between 4000–400 $\text{cm}^{-1}$, using a Nicolet 520 FTIR spectrometer and KBr pellets. The IPN hydrogels and IPN-metal ion systems were characterized by comparing the FTIR spectra of IPN hydrogel and IPN-metal ion systems. A DuPont 910 model thermogravimetric analyser (TGA) was used for determination of the thermal stabilities of homopolymers and IPN hydrogels. Samples weighing 5–10 mg were heated in a dynamic nitrogen atmosphere from 20°C–800°C at a heating rate of 10°C $\text{min}^{-1}$.

### Swelling Studies

Dried IPN hydrogels were weighed and then they were immersed to swell in a solution of desired pH (3–9), at a temperature of 25°C. Periodically, the IPN hydrogels were withdrawn from the solution and weighed after removing the excess surface water. This procedure was continued until the weights of the IPN hydrogels reached a constant value. The percent swelling of each IPN hydrogel was calculated from the following relation Equation (2):

$$\%\ \text{Swelling} = \frac{(m_t - m_0)}{m_0} \times 100 \tag{2}$$

where $m_t$ is the mass of swollen IPN at time t, and $m_0$ is the initial mass of dry IPN. Some parameters (diffusion characters, equilibrium water content, etc.) were calculated by using swelling data.

### Adsorption Studies

The effects of the initial concentration of $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ and pH of the medium on the adsorption rate and capacity were studied. Aqueous solutions of $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ were prepared at (0.4–600.0 ppm) concentrations. (NaAlg/AAm)(1–3)IPN hydrogels were added to 25 mL of metal ion solutions at different pH values. The solutions were shaken in closed flasks at 25 ± 1°C for 48 h. During the shaking process, aliquots of 0.5 $cm^3$ of the solution were collected periodically for the determination of remaining lead, cadmium and nickel ion concentrations. The lead, cadmium and nickel ion concentrations in the liquid phase were determined with an atomic absorption spectrophotometer, (Perkin-Elmer, GFAAS Analyst 100). The amount of adsorption per unit mass of (NaAlg/AAm)(1–3)IPN hydrogels was evaluated by using the following expression Equation (3):

$$q_e = \frac{[(C_0 - C_e)V]}{W} \tag{3}$$

where, $q_e$ is the amount of heavy metal ion adsorbed onto unit dry mass of the (NaAlg/AAm)(1–3)IPN hydrogels (mg $g^{-1}$), $C_0$ and $C_e$ are the concentrations of the metal ion solutions in the initial solution and in the aqueous phase after treatment for a certain period of time, respectively (mg$L^{-1}$), V is the volume of the aqueous phase (L) and w is the amount of dry (NaAlg/AAm)(1–3)IPN hydrogels used (g).

## Results and Discussion

Natural polymers from marine resources such as chitin and alginate have attracted more and more attention owing to their abundant sources, friendliness to the environment and potential to substitute for some petrochemicals. Cellulose/alginate and poly(vinylalcohol)/sodium alginate blend membranes were prepared by Zhang and his group (3) and Yeom and his group (4). The adsorption characteristics of toxic heavy metals, lead and cadmium ions were investigated with sodium alginate (5).

The percent gelation of (NaAlg/AAm)IPN hydrogels are presented in Table 1. Approximately 100% gelation occured at an irradiation dose of 10.0 kGy. As can be seen from this table, the percent gelation of IPN hydrogels decreased with the increasing irradiation doses after the 10.0 kGy irradiation doses. The IPN hydrogel irradiated at the 10.0 kGy was used in this study. (NaAlg/AAm)1IPN hydrogel, (NaAlg/AAm)2IPN

**Table 1**
The percent gelation of (NaAlg/AAm) mixtures irradiated at various doses for (NaAlg/AAm) (1–3) IPN hydrogels. Dose rate: 0.14 kGyh$^{-1}$

| Dose (kGy) | % Gelation | | |
|---|---|---|---|
| | (NaAlg/AAm)1 | (NaAlg/AAm)2 | (NaAlg/AAm)3 |
| 2.0 | 64 | 62 | 65 |
| 5.0 | 71 | 72 | 71 |
| 7.5 | 81 | 74 | 63 |
| 10.0 | 100 | 100 | 91 |
| 12.5 | 100 | 92 | 82 |
| 15.0 | 81 | 81 | 81 |
| 17.5 | 72 | 70 | 68 |
| 20.0 | 61 | 65 | 60 |

hydrogel and (NaAlg/AAm)3IPN hydrogel have been used for three different compositions of (NaAlg/AAm)IPN hydrogels obtained by using NaAlg contents at 1, 2, and 3% (w/v), respectively.

### *Spectroscopic Analysis of (NaAlg/AAm)IPN-metal Ion Systems*

To examine the nature of the interaction between the metal ions and (NaAlg/AAm)IPN hydrogel, FTIR spectra of (NaAlg/AAm)3IPN, (NaAlg/AAm)3IPN-Cd$^{2+}$, (NaAlg/AAm)3IPN-Pb$^{2+}$, (NaAlg/AAm)3IPN-Ni$^{2+}$ systems are shown in Figure 1. In the FTIR spectrum of the (NaAlg/AAm)3IPN the absorption peaks at 1633 cm$^{-1}$, 1440 cm$^{-1}$ shifted to lower frequencies at 1590 cm$^{-1}$ and 1416 cm$^{-1}$, respectively. Upon coordination, the –COO$^{-}$ stretching frequency is lowered to 1590 cm$^{-1}$ and 1416 cm$^{-1}$, indicating complexation with metal ions as well as an increase in intensity. This peak is specific to ionic binding. The peaks in the region 400–800 cm$^{-1}$ can be assigned to M–O stretching of the metal carboxylic-acid bond. For the (NaAlg/AAm)3IPN-metal ion systems, the lowering of the bonds at 1633 cm$^{-1}$ and 1440 cm$^{-1}$ were not very significant. As metal ions are between the alginate blocks, the radius and the atomic weight of the cation are changed, creating a new environment around the carbonyl group thus a peak shift may be expected. In the region at 1150–1000 cm$^{-1}$, one can observe a set of three sharp peaks. The first two peaks have been assigned to C–C and C–O stretching, however, no assignment is available for the third peak. All these peaks show shifts towards lower wavenumbers as the metal ions are placed between the alginate blocks. This shift to lower frequencies is an indication of a weakening in the C–C and C–O bonds, most likely due to the sharing of these bonds between metal ions.

### *Thermal Analysis of (NaAlg/AAm)IPN-metal Ion Systems*

In order to determine the thermal properties of (NaAlg/AAm)IPN-metal ion systems, the temperature for maximum weight loss ($T_{max}$) and the temperature for half life ($T_{1/2}$) and the decomposition temperatures were investigated to determine the change in the stabilities of (NaAlg/AAm)IPN-metal ion systems. For this purpose, the thermograms of (NaAlg/AAm)3IPN-Cd$^{2+}$, (NaAlg/AAm)3IPN-Pb$^{2+}$ and (NaAlg/AAm)3IPN-Ni$^{2+}$ were examined as shown in Figure 2.

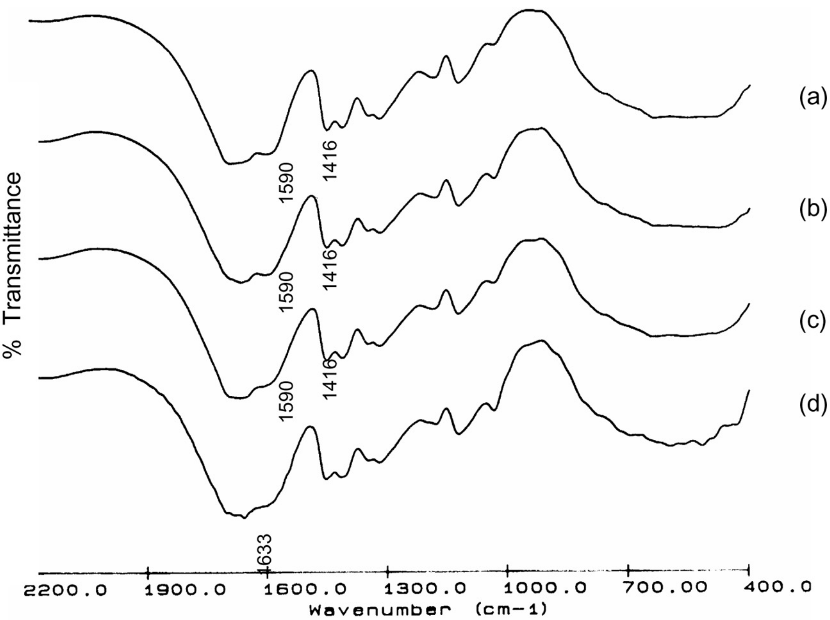


**Figure 1.** FTIR spectra of (a) (NaAlg/AAm)3IPN-$Ni^{2+}$ system, (b) (NaAlg/AAm)3IPN-$Cd^{2+}$ system, (c) (NaAlg/AAm)3IPN-$Pb^{2+}$ system, (d) (NaAlg/AAm)3IPN hydrogel.

Thermogravimetry of (NaAlg/AAm)3IPN-metal ion systems reveals the variation of thermal stability by complexation with metal ions. The thermal decomposition behavior of a (NaAlg/AAm)3IPN-metal ion complex depends on the macromolecular characteristics of the polymer support and the type of coordination geometry (6).

The decomposition of (NaAlg/AAm)3IPN hydrogel occured in a five-stage process. In the thermogram of (NaAlg/AAm)3IPN-metal ion systems, there are three decomposition stages and $T_{max}$ values appear at 374°C, 364°C, and 362°C for (NaAlg/AAm)3IPN-$Cd^{2+}$, (NaAlg/AAm)3IPN-$Pb^{2+}$ and (NaAlg/AAm)3IPN-$Ni^{2+}$ systems, respectively. The thermograms of (NaAlg/AAm)3IPN-metal ion systems are similar to each other. The thermograms of all (NaAlg/AAm)3IPN-metal ion systems are given in Figure 2. In all these cases, the first-stage decomposition corresponds to decomposition of the carboxylate groups/uncomplexed ligands. The second-stage decomposition of (NaAlg/AAm)3IPN-$Cd^{2+}$, (NaAlg/AAm)3IPN-$Pb^{2+}$, and (NaAlg/AAm)3IPN-$Ni^{2+}$ systems occurs at 376°C, 364°C and 362°C, respectively. In all cases, the second stage is the major decomposition and in (NaAlg/AAm)3IPN-metal ion systems, during the major decomposition, the polymer chain breaks and the chains rupture giving only the metallic residue. Consequently, it may be explained that the thermal stabilities of (NaAlg/AAm)3IPN-metal ion systems are somewhat more stable than the (NaAlg/AAm)3IPN hydrogel.

### *Swelling and Diffusion Studies of (NaAlg/AAm)IPN Hydrogels in Aqueous Solutions of Metal Ions*

The effect of metal ion on swelling capacity of (NaAlg/AAm)IPN hydrogels was investigated. The swelling curves of (NaAlg/AAm)IPN hydrogels in water and aqueous

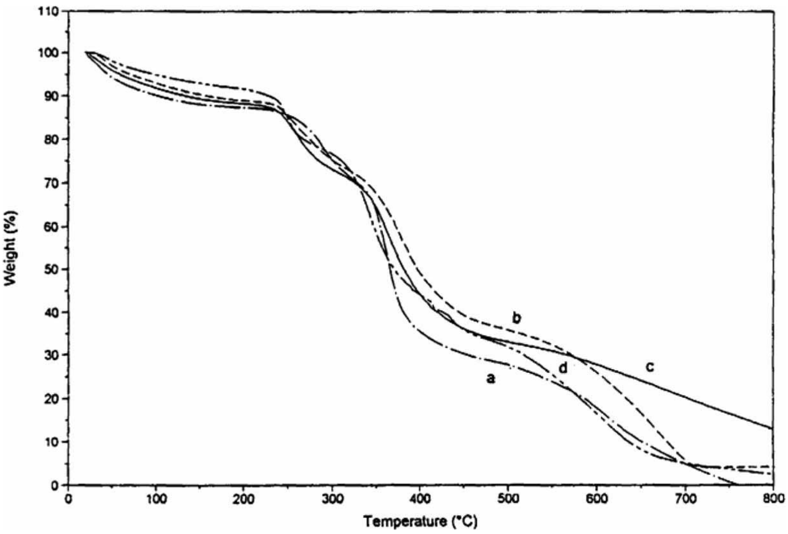


**Figure 2.** The thermograms of (a) (NaAlg/AAm)3IPN-$Ni^{2+}$ system, (b) (NaAlg/AAm)3IPN-$Cd^{2+}$ system, (c) (NaAlg/AAm)3IPN-$Pb^{2+}$ system, (d) (NaAlg/AAm)3IPN hydrogel.

solutions of metal ions are given at pH 7.0 for $Pb^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ in Figures 3 and 4. As shown, the swelling capacities of the (NaAlg/AAm)3IPN hydrogels are in the range of 1458–2656% and 600–900% in water and the aqueous solutions of $Pb^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ ions at pH 7.0. These figures show that the swelling behaviors of the (NaAlg/AAm)3IPN hydrogel in water and aqueous solution of metal ions are similar to each other. The

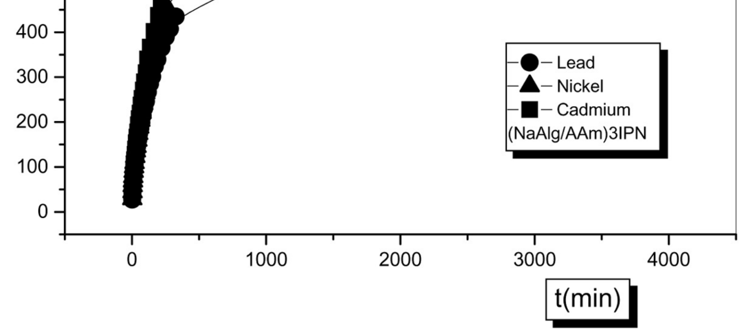


**Figure 3.** Swelling curves of (NaAlg/AAm)3IPN hydrogels in aqueous solution of $Ni^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ at pH 7.0 and 25°C. $[Ni^{2+}] = [Cd^{2+}] = [Pb^{2+}] = 600$ ppm, I: 0.05, dose: 10.0 kGy.

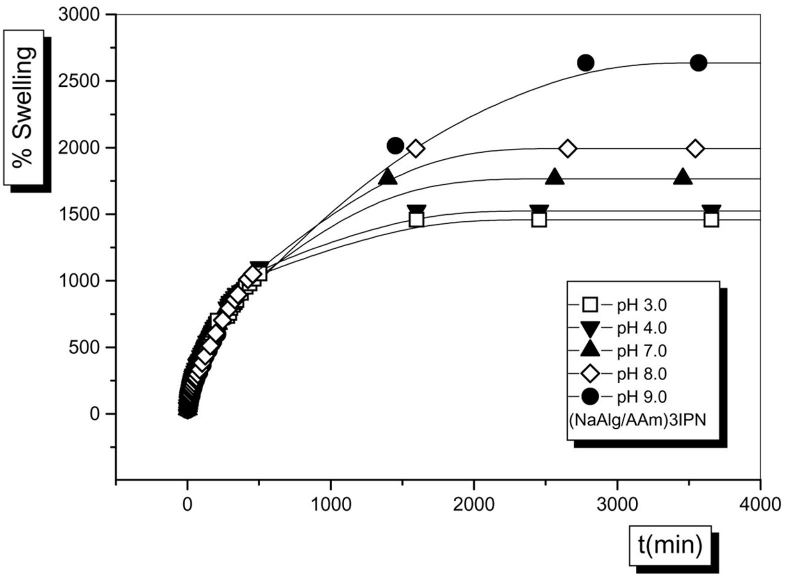


**Figure 4.** Effect of pH on swelling behavior of (NaAlg/AAm)3IPN hydrogel in water at 25°C. I: 0.05, dose: 10.0 kGy.

equilibrium swelling of (NaAlg/AAm)3IPN hydrogel in metal ion solution is given in Figure 5 as a function of pH at 25°C and 0.05 M ionic strength. The equilibrium swelling for (NaAlg/AAm)(1–3)IPN hydrogels is found to be minimum at pH 7.0. The equilibrium swelling of (NaAlg/AAm)IPN hydrogels increases as the pH of the surrounding liquid is lowered at constant ionic strength (Figure 5) and the equilibrium swelling of (NaAlg/AAm)3IPN hydrogels decreases as the pH increases, achieving the lowest values at pH 7.0. This behavior is similar for all the metal ions. It can be attributed to the interactions between the metal ions and (NaAlg/AAm)3IPN hydrogel through electrostatic interactions which depend on the dissociation degree of carboxyl groups in NaAlg. The dissociation increases with increasing pH. This coincides with the deprotonation reactions of the carboxyl groups (pK 3.5–4.5). The equilibrium swelling values for (NaAlg/AAm)3IPN hydrogel in metal ion solutions reach a steady state at a pH of approximately 5.5–7.0 (7–10). The metal ions interact with the carboxyl groups of NaAlg in (NaAlg/AAm)3IPN hydrogel, so the hydrophilic groups of the (NaAlg/AAm)IPN hydrogels can not bond with water. Thus, swelling of the hydrogel increases in the aqueous solutions of metal ions in an acidic medium. At the end of these evaluations, (NaAlg/AAm)IPN hydrogel in aqueous solutions of metal ions were swollen in the following order in the acidic medium.

$$Ni^{2+} > Cd^{2+} > Pb^{2+}$$

In order to study the diffusion phenomena in (NaAlg/AAm)IPN hydrogels, the swelling curves of (NaAlg/AAm)IPN hydrogels were used to determine the nature of the diffusion of water and aqueous solution of metal ions into hydrogels by the following equation (11):

$$F = M_t/M_\infty = kt^n \quad (4)$$

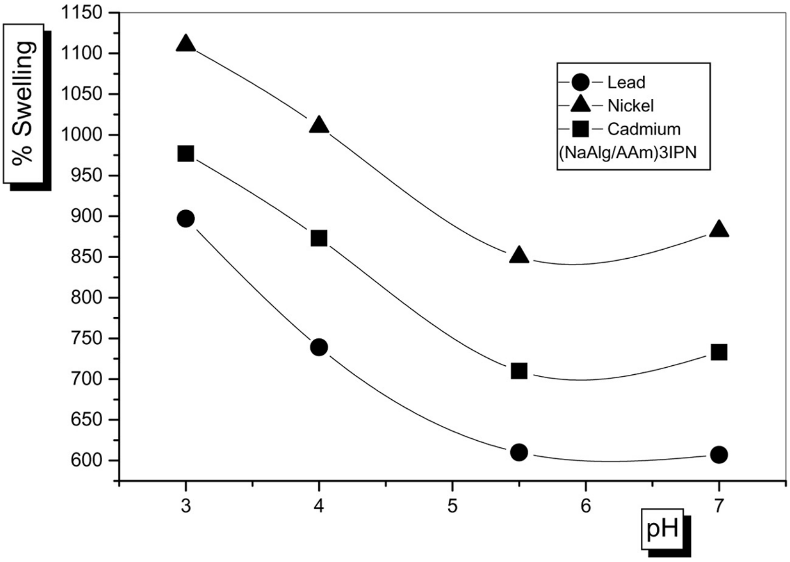


**Figure 5.** Effect of pH on swelling behavior of (NaAlg/AAm)3IPN-metal ion systems at 25°C. $[Ni^{2+}] = [Cd^{2+}] = [Pb^{2+}] = 600$ ppm, I: 0.05, dose: 10.0 kGy.

where $M_t$ and $M_\infty$ denote the amount of solvent diffused into the gel at time t and infinite time (at equilibrium), respectively, k is a constant related to the structure of the network, and the exponential n is a number used to determine the type of diffusion. This equation was applied to the initial stages of swelling. Diffusion coefficients were calculated from the relation (12).

$$D = 0.049/(t/4r^2)^{1/2} \tag{5}$$

where D is in $cm^2 min^{-1}$, t is the time at which the swelling is one-half the equilibrium value ($V/Vo = 1/2$), and r is the radius of the swollen cylindirical sample.

The nature of diffusion of water and aqueous solution of metal ions into (NaAlg/AAm)IPN hydrogels was also determined by Equation (4). Diffusion coefficients were calculated for water and aqueous solution of metal ions according to Equation (5). ln(F) vs. ln(t) and F vs. $t^{1/2}$ graphs are given for aqueous solution of metal ions at pH 7.0 in Figures 6 and 7, respectively. The values n, k, and diffusion coefficient, D, are listed in Table 2. Diffusion coefficients are important parameters about the penetration of some metal ions into (NaAlg/AAm)IPN hydrogels. The n values in this table are ranged between 0.36–0.40. The diffusion of aqueous solution of metal ions into (NaAlg/AAm)IPN hydrogels was shown to have Fickian character. The penetration of the metal ion, which has a lower ionic radius into the (NaAlg/AAm)IPN hydrogel, is much easier than that of the other metal ions. Since the carboxyl groups are deprotonated after pH 5.5, the possibility of interaction between carboxyl groups in NaAlg and amide group in PAAm for the higher ionic radii in $Cd^{2+}$ and $Pb^{2+}$ the equilibrium swelling is lower than the aqueous solution of $Ni^{2+}$. As can be seen from this table, diffusion coefficients increased in the following order at pH 7.0.

$$\text{Water} > Ni^{2+} > Cd^{2+} > Pb^{2+}$$

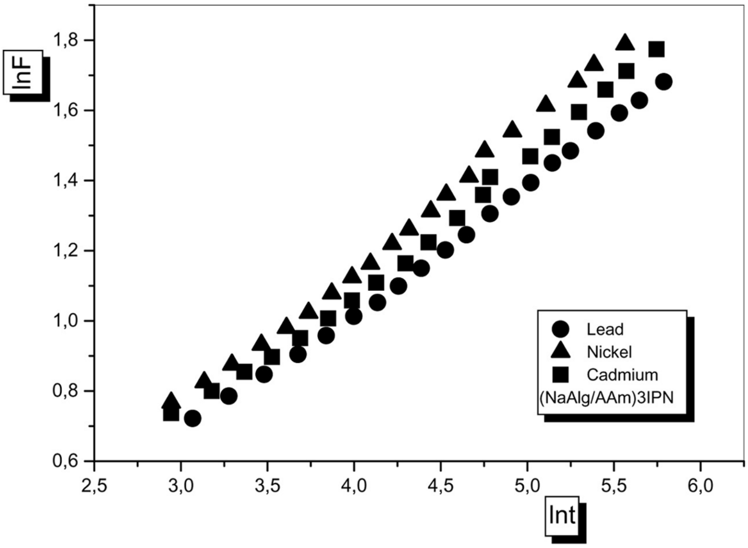


**Figure 6.** Linear fit line lnF vs. lnt for (NaAlg/AAm)3IPN-metal ion systems at pH 7.0 and 25°C. $[Ni^{2+}] = [Cd^{2+}] = [Pb^{2+}] = 600$ ppm, I: 0.05, dose: 10.0 kGy.

## *Adsorption Studies*

For many toxic metals that may be present as contaminants in natural water and wastewaters, several acidic polysaccharides have demonstrated superior metal-binding properties and have been tested for their abilities of recovering metals from aqueous media.

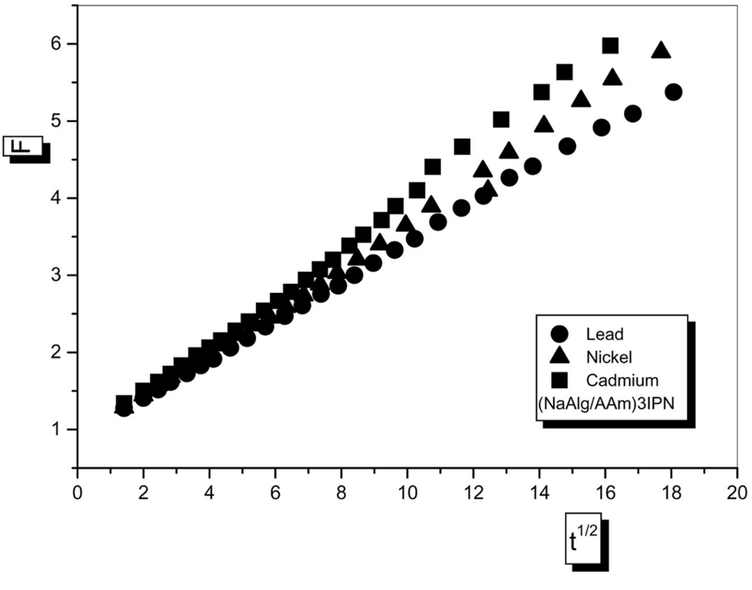


**Figure 7.** Plots of F vs. $t^{1/2}$ of (NaAlg/AAm)3IPN-metal ion systems at pH 7.0 and 25°C. $[Ni^{2+}] = [Cd^{2+}] = [Pb^{2+}] = 600$ ppm, I: 0.05, dose: 10.0 kGy.

**Table 2**

Swelling and diffusion parameters of (NaAlg/AAm)3IPN hydrogels in water and aqueous solution of metal ions at pH 7.0 and 25°C. I: 0.05 dose: 10.0 kGy

| Metal ion | k | n | D ($cm^2\ min^{-1}$) |
|---|---|---|---|
| $Ni^{2+}$ | 1.56 | 0.38 | 0.038 |
| $Cd^{2+}$ | 1.60 | 0.40 | 0.034 |
| $Pb^{2+}$ | 1.52 | 0.36 | 0.027 |
| Water | 2.24 | 0.62 | 0.172 |

Many polysaccharides derived from microbes and plants are known to strongly bind metals. The capability of biomaterials, especially biopolymers, to chelate heavy metals has been applied to the recovery or removal of heavy metals from mine drainages and industrial wastewaters (9, 13). The selectivity of various polysaccharides for Groups IIA, IIB and transition metals is very high. Alginic acid has been shown to be effective at removing many cationic metals from solution including $Pb^{2+}$ and $Cu^{2+}$ (14), $UO_2^+$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ (15), $Nd^{3+}$ and $Yb^{3+}$ and $^{226}Ra$ (16).

The factors affecting the capacity and affinity of a polysaccharide to bind a metal from aqueous media include the chemical nature of the metal ion (e.g., size, valence, electron orbital structure, and stable chemical forms in the nature) and the biopolymer (e.g., charge density and structure of the polymer chain, constituent sugar units and proteins, and functional groups), environmental conditions (e.g., pH, temperature, ionic strength, and existence of competing organic or inorganic metal chelators), morphology (e.g., orientation of metal binding groups, sizes of the metal ion and the metal-binding "cavity" formed by metal-binding groups, and the existence of stabilizing groups in the cavity), and thermodynamics of binding process (e.g., ordering effect that results in a decrease of entropy upon binding) (17).

In this study, we tried to develop the mechanical and thermal stability together with the other physical properties of alginates by preparing IPN hydrogels with sodium alginate and acrylamide. The adsorption of aqueous solutions containing metal ions such as $Pb^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ into (NaAlg/AAm)(1–3)IPN hydrogels was investigated. A possible interaction between negative charges of NaAlg and positive charges of metal ions are shown in Figure 8.

To observe the uptake of some heavy metal ions ($Ni^{2+}$, $Cd^{2+}$, $Pb^{2+}$), (NaAlg/AAm)(1–3)IPN hydrogels were placed in solutions of $Ni(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ and allowed to equilibrate for two days. Effects of the initial concentration of heavy metal ion solutions on the adsorption rate and capacity were studied. The heavy metal ion solutions were prepared in the concentration ranges between 0.4–600.0 $mgL^{-1}$ for $Ni^{2+}$, $Cd^{2+}$, $Pb^{2+}$. Approximately, 0.1 g (NaAlg/AAm)(1–3)IPN hydrogels containing 1, 2, 3% NaAlg were transferred into 25 mL of heavy metal ion solutions at pH 7.0 and after reaching saturation of adsorption (2 days), the amount of adsorbent per unit mass of the (NaAlg/AAm)(1–3)IPN hydrogels was evaluated by using Equation (3).

To determine the effect of concentration of heavy metal ion solutions on adsorption, the graphs were plotted for the amount of heavy metal ion adsorbed per unit dry mass of (NaAlg/AAm)(1–3)IPN hydrogels, $q_e$, against initial concentration of the heavy metal ion. As can be seen from Figures 9, 10 and 11, the adsorption of nickel, cadmium and

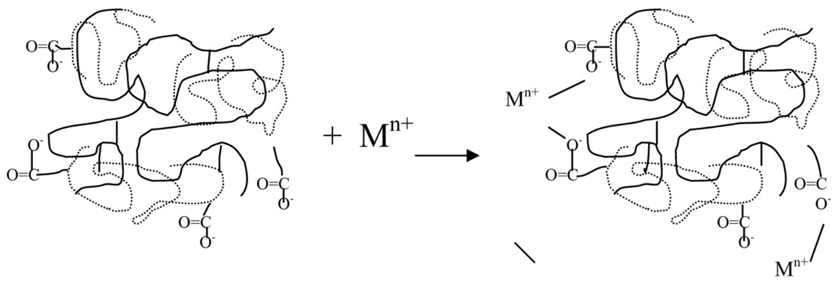


**Figure 8.** Possible IPN hydrogel-metal ion interaction mechanism.

lead ions onto the hydrogels increase with an increase of NaAlg content in the hydrogels and heavy metal ion concentration. The increase of carboxyl groups in the hydrogels with the increase of NaAlg content is due to the electrostatic interactions between the cationic ions of nickel, cadmium and lead and the anionic groups of alginic acid in the IPN hydrogels.

The capacity of (NaAlg/AAm)(1–3)IPN hydrogels for the adsorption of nickel, cadmium and lead ions can be determined by constructing adsorption isoterms (18). The curves shown in Figures 9, 10 and 11 show that adsorptions of heavy metal ions within different compositions of (NaAlg/AAm)(1–3)IPN hydrogels correspond to S type adsorption isotherms in the Giles classification system concerning the adsorption of a solute from its solution (19).

When the adsorption capacity of (NaAlg/AAm)(1-3)IPN hydrogels for nickel, cadmium and lead ions was compared, it was determined that the adsorption of nickel

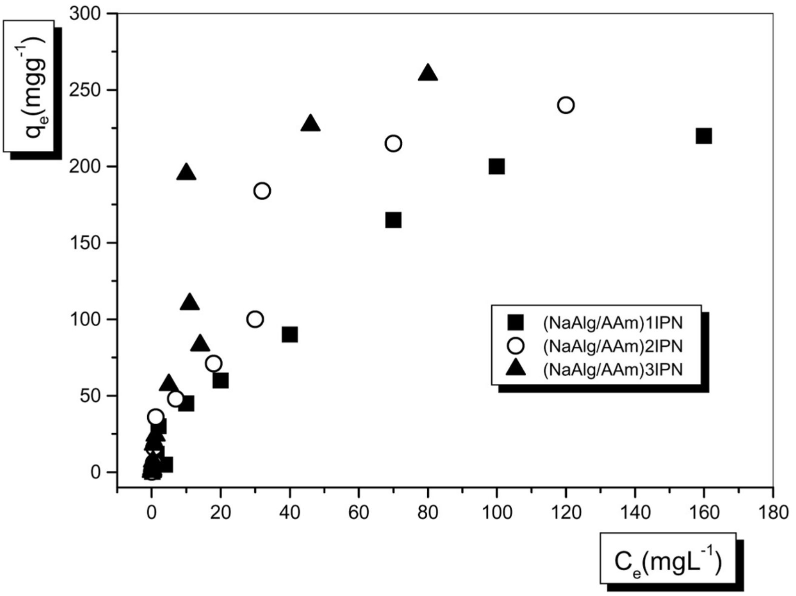


**Figure 9.** Effect of nickel ion concentration on the adsorption capacity of (NaAlg/AAm)IPN hydrogel at pH 7.0 and 25°C. I: 0.05, dose: 10.0 kGy.

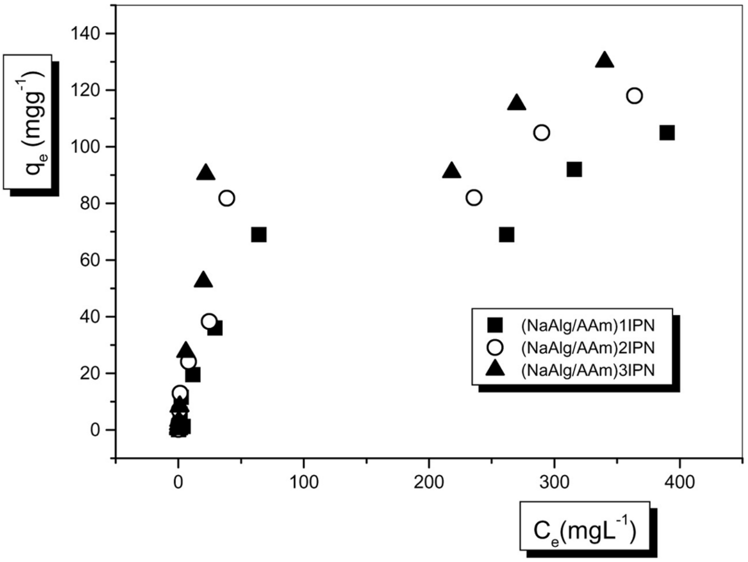


**Figure 10.** Effect of cadmium ion concentration on the adsorption capacity of (NaAlg/AAm)IPN hydrogel at pH 7.0 and 25°C. I: 0.05, dose: 10.0 kGy.

ions onto (NaAlg/AAm)(1–3)IPN hydrogels is higher than that of cadmium and lead ions due to the lower atomic mass and molecular size of these ions since adsorbent-adsorbate interaction would be reduced with regard to the weak dispersion energy of water with other heavy metal ions.

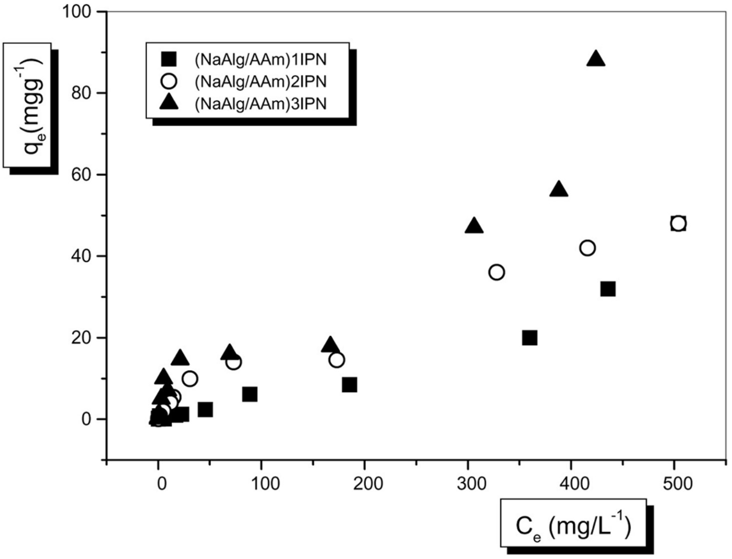


**Figure 11.** Effect of lead ion concentration on the adsorption capacity of (NaAlg/AAm)IPN hydrogel at pH 7.0 and 25$^0$C. I: 0.05, dose: 10.0 kGy.

## Conclusions

(NaAlg/AAm)(1–3)IPN hydrogels have been prepared at three different compositions and irradiated in $^{60}$Co-$\gamma$ source at different doses.

Spectroscopic analyse were achieved to investigate the interaction of (NaAlg/AAm)IPN with metal ions.

The thermal stabilities of (NaAlg/AAm)IPN-metal ion systems were higher than those of (NaAlg/AAm)IPN.

(NaAlg/AAm)3IPN hydrogel containing more NaAlg showed maximum percent swelling in distilled water at pH 7.0 and in aqueous solution of metal ions at acidic medium. Swelling increased in the order of $Ni^{2+} > Cd^{2+} > Pb^{2+}$ at pH (3.0–7.0).

The diffusion of aqueous solutions of metal ions into (NaAlg/AAm)IPN hydrogels was found to be of Fickian character.

Diffusion coefficients were calculated for (NaAlg/AAm)IPN in aqueous solutions of nickel, cadmium and lead.

(NaAlg/AAm)IPN hydrogels are pH sensitive. They swell in the range of pH 7–9 in water but for aqueous solution of metal ions at lower pH values.

Adsorption capacity of (NaAlg/AAm)IPN hydrogel was determined and adsorption isotherm of (NaAlg/AAm)IPN-metal ion systems was observed to be S type.

For removing nickel, cadmium and lead ions from water, the optimum conditions are 0.1 g (NaAlg/AAm)IPN hydrogel, at an ionic strength of 0.05, at 25°C and pH 5.5–7.0.

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