Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Pınar Akkaş Kavaklı[a]; Zakir Yılmaz[a]; Murat Şen[a]
[a] Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

To cite this Article Kavaklı, Pınar Akkaş , Yılmaz, Zakir and Şen, Murat(2007) 'Investigation of Heavy Metal Ion Adsorption Characteristics of Poly(N,N Dimethylamino Ethylmethacrylate) Hydrogels', Separation Science and Technology, 42: 6, 1245 — 1254
To link to this Article: DOI: 10.1080/01496390601120490
URL: http://dx.doi.org/10.1080/01496390601120490

Separation Science and Technology, 42: 1245–1254, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390601120490

Investigation of Heavy Metal Ion Adsorption Characteristics of Poly(N,N Dimethylamino Ethylmethacrylate) Hydrogels

Pınar Akkaş Kavaklı, Zakir Yılmaz, and Murat Şen
Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

Abstract: In this study, Poly(N,N dimethyl-amino ethylmethacrylate) (Poly(DMAEMA)) hydrogels with varying compositions were prepared in the form of rods by irradiating ternary mixtures of N,N-dimethylamino ethylmethacrylate/ethyleneglycoldimethacrylate/water with gamma rays at ambient temperature. Swelling studies of poly (DMAEMA) hydrogels were performed at different pH values and maximum swelling values reached at pH 2. The adsorption characteristics of Pb(II), Cd(II), Ni(II), Zn(II), Cu(II), and Co(II) ions to poly(N,N dimethylamino ethylmethacrylate) hydrogels were investigated by a batch process. The order of affinity based on amount of metal ion uptake was found as follows: Cu(II) $>$ Zn(II) $\cong$ Co(II) $>$ Pb(II) $>>$ Ni(II) $>$ Cd(II). In the adsorption studies of Cu(II), Zn(II), Co(II), Pb(II), Ni(II), and Cd(II) ions the Langmuir type adsorption isotherms were observed for all gel systems.

Keywords: Hydrogel, adsorption, swelling, radiation, heavy metal

INTRODUCTION

The removal of heavy metal ions from various water resources is of great scientific and practical interest. Copper, lead, and cadmium are often deposited in lakes and streams from the air near emitting facilities. These substances may also enter waterways from runoff from slag piles, mine drainage,

Received 21 March 2006, Accepted 6 November 2006
Address correspondence to Pınar Akkaş Kavaklı, Department of Chemistry, Hacettepe University, Beytepe, 06532 Ankara, Turkey. Tel./Fax: +90 312 2976083; E-mail: pinar@hacettepe.edu.tr

and industrial effluents. Effluents from electroplating contain a number of heavy metal constituents. Heavy metals, copper in particular, may be toxic to aquatic species as well as harmful to human health. Copper can cause liver and kidney damage when present at high concentrations in the human body. Recently, the removal and recovery of heavy metal ions from industrial wastewater has been a significant concern in all industrial branches owing to economic and environmental factors. Many research studies are devoted to the removal of the metal ions from the waste stream. Different techniques have been investigated for removal of metal ions such as solvent extraction, precipitation, co-precipitation, sorption, and ion exchange. Chelate-forming resins have been widely applied as ion exchangers for various metal ions in different environmental and industrial areas. These resins show higher selectivity (1).

A hydrogel is defined as a cross-linked hydrophilic polymer or copolymer that is capable of imbibing a considerable quantity of water, up to swelling equilibrium. Hydrogels have widespread application in bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology, and other fields (2, 3). The first step in the preparation of hydrogels is the selection of a highly hydrophilic or even water-soluble polymer (4). In recent years, the syntheses of hydrogels with chelating groups have received considerable attention for rapid and inexpensive metal ion separation and concentration (5–10). It was determined that cross-linked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl, amidoxime, and sulfonic acid groups could be used as complexing agents for the removal of metal ions from aqueous solutions (11–14). The main advantages of such materials are easy loading and, in most cases, stripping of cations with simple chemicals and reusability. In this study, the polyDMAEMA hydrogels were synthesized by γ-irradiation and the metal ion uptake of polyDMAEMA hydrogels were investigated in various concentrations of metal ions and pH values.

EXPERIMENTAL

Chemicals

The two monomers used in this study, namely dimethylaminoethyl methacrylate (DMAEMA) and ethylene glycol dimethacrylate (EGDMA) used as a cross-linking agent were obtained from Aldrich (USA) and BDH (UK), respectively.

Preparation of Hydrogels

Three components were used in the preparation of Poly(dimethylamino ethylmethacrylate P(DMAEMA) hydrogels; DMAEMA, EGDMA and water. 35%

water containing aqueous solutions of DMAEMA, were prepared and 0.1, 0.5, and 1.0% volume EGDMA were added into these solutions. Monomer solutions thus prepared were placed in PVC straws of 3 mm diameter and irradiated up to 8.0 kGy in air at ambient temperature in Gammacell-220 type γ-irradiator at a fixed dose rate of 0.16 kGy/h. Hydrogel obtained in long cylindrical shapes were cut into pieces of 2–3 mm and stored for later evaluations.

Monomer-Gel Conversion

The irradiated mixtures were dried in a vacuum oven at 315 K to constant weight and subjected to Soxhlet extraction with water as solvent. The uncross-linked polymer and/or residual monomer were removed with this extraction from the gel structure. The extracted gels were dried again in a vacuum oven at 315 K to constant weight. Percent gelation i.e. percent conversion of the monomer and the cross-linking agent into insoluble networks was based on the total weight of the monomer and the cross-linking agent in the initial mixture. The amount of uncross-linked DMAEMA in monomer, polymer and/or copolymer form was determined by titration of the extract against HCl (0.02 mole/L) to phenolphthalein end point.

Swelling Studies

Dried hydrogels (2–3 mm thickness, 3 mm diameter) were left to swell in a metal ion solution of desired pH (2–9) at 25°C. Swollen gels removed from the swelling medium at regular intervals were dried superficially with filter paper, weighed, and placed in the same medium. The measurements were continued until a constant weight was reached for each sample. This weight was used to calculate the volume fraction of polymer, $\nu_{2m,}$ and the equilibrium degree of swelling (EDS), Q, of the gel in a given gel sample swollen to equilibrium in aqueous solution.

$$\nu_{2m} = \left[1 + \rho/\rho_w(\mathrm{w}^{-1} - 1)\right]^{-1} \tag{1}$$

where ρ and ρ_w are the densities of the swollen gel and water, and w is the weight fraction of the polymer in swollen gel. The equilibrium degree of swelling (EDS) was defined as $Q = 1/\nu_{2m}$. The percent swelling of the hydrogels was calculated by Eq. (2)

$$\%\text{swelling} = \frac{m_t - m_0}{m_0} \tag{2}$$

where m_t is the weight of the swollen gel at time t.

Metal Ion Adsorption

The adsorption ability of the hydrogels towards Pb(II), Cd(II), Ni(II), Zn(II), Cu(II), and Co(II) ions was determined via the batch equilibrium technique, that is, approximately 0.05 gram of the poly(DMAEMA) hydrogels were transferred into salt solutions of metals having various concentrations ranging from 50 to 2000 ppm, and were stirred for 48 hours. Equilibrium concentration of Cu(II) was determined by a Philips PU 8715 UV-Vis spectrophotometer. And equilibrium concentrations of the other metal ions were determined by titration against EDTA using Xylenol Orange indicator for Co(II), Cd(II), Pb(II) and Eriochrome Black–T indicator for Zn(II) and Ni(II).

RESULT AND DISCUSSION

Preparation of PDMAEMA Hydrogels

When pure dimethylaminoethyl methacrylate monomer was irradiated with gamma rays, polymerization and cross-link reactions took place simultaneously. The total dose required for the onset of gelation was determined to be 40 kGy for this monomer. The hydrogels prepared above the gelation dose showed low mechanical stability and ruptured upon swelling. This is probably due to the presence of polymerized, but not cross-linked DMAEMA chains entrapped in the gel structure. Their loss as sol fraction upon contact with water will naturally weaken the mechanical stability of gel. When DMAEMA was irradiated at high doses i.e. 70 kGy, only 10% conversion from monomer to gel structure was observed.

Preparation of P(DMAEMA/EGDMA) Hydrogels

To decrease the gelation dose and increase the cross-link density at the same time, a difunctional cross-linking agent EGDMA was added to the monomer. The hydrogels obtained in the presence of 0–0.1% EGDMA behaved similarly to pure DMAEMA gels, i.e. upon swelling the geometric shape of the gel was destroyed. This is probably due to insufficient formation of cross-linking. The gels prepared with 0.1–1.0% EGDMA, however, were very stable and showed uniform swelling properties in water but disintegrated at low pH values. This behavior was attributed to inhomogeneous cross-link formation within the hydrogel. The internal pressures developed upon the swelling of inhomogeneous network structure may be responsible for the poor mechanical properties of these gels. The effect of the irradiation dose and the amount of EGDMA on the % gelation of DMAEMA are given in Fig. 1. As can be shown from Fig. 1 the percent gelation from the monomer to insoluble network increases with an increasing irradiation dose and after 4.0 kGy, gelation remains almost constant.

Poly-Electrolyte Behavior of Hydrogels

In order to follow the pH response of the DMAEMA hydrogels, dry samples were allowed to swell to equilibrium in phosphate buffers of varying pH at a fixed ionic strength (I = 0.1) and temperature (25°C). Figure 2 shows the changes in the equilibrium degree of the swelling of the DMAEMA hydrogels containing various ratios EGDMA with changing pH values.

Consistent with poly-electrolyte systems, the swelling of these gels is strongly dependent on pH. A decrease in the pH from 8 to 2 caused a significant increase in the equilibrium degree of the swelling of the hydrogel. In all compositions, the maximum extent of swelling were reached at pH 2, this being due to complete protonization of amine groups of DMAEMA at this pH value.

As can be seen from the figures, the values of the swelling of hydrogel systems strongly depend on the concentration of crosslinking agent in the network. Increase in the EGDMA content in the network reduced swelling degree dramatically at all pH values, especially, when the concentration of EGDMA was relatively high.

Adsorption of Metal Ions onto PolyDMAEMA Hydrogels

0.05 gram of polyDMAEMA hydrogel prepared by using 0.1% EGDMA was placed into different concentrations (50–2000 ppm) of six different metal ion

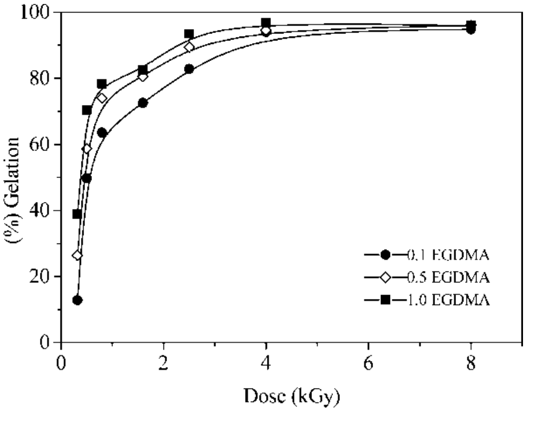

Figure 1. Effect of irradiation dose on the monomer-gel conversion.

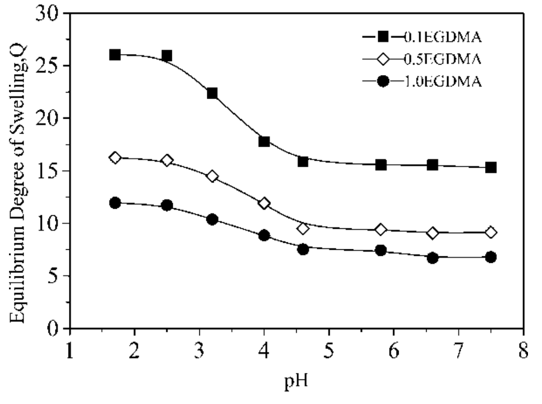

Figure 2. Effect of pH on the swelling characteristics of PDMAEMA hydrogels.

solutions until they reached adsorption equilibrium. The binding properties of these metal ions i.e. Zn(II), Pb(II), Cu(II), Co(II), Ni(II), and Cd(II) with polyDMAEMA hydrogel determined at different concentrations of aqueous metal solutions are given in Fig 3. The adsorption values were displayed as adsorbed M^{2+} (mg M^{2+}/g of gel) versus equilibrium M^{2+} concentration.

It was found that the metal ion uptake by the polyDMAEMA hydrogel gradually increased with increasing initial metal ion concentrations, not reaching adsorption equilibria even at 2000 ppm metal ion concentration as shown in Fig 3. The new hydrogel exhibited a higher affinity for the Cu(II) ion, the highest value found to be 258 mg Cu(II) ion/g dry gel obtained from the initial metal ion solution at 2000 ppm. The adsorption amount of Zn(II), Co(II), and Pb(II) ions corresponded to lower adsorption capacities compared to copper ion. It was found that the adsorption capacities of poly-DMAEMA hydrogel for Zn(II), Co(II), and Pb(II) ions for the initial metal ion solution at 2000 ppm were determined as 204, 199, 142 mg metal ion/g dry polymer, respectively. The adsorption behavior of Ni(II) (95 mg/g dry gel) and Cd(II) (93 mg/g dry gel) ions which have the lowest adsorption capacities, compared to copper ion, shows similar adsorption isotherms with Co(II) ion. The order of adsorption affinity based on the amount of metal ion uptake (mg metal ion/g dry gel) is as follows: Cu(II) $>$ Zn(II) $\cong$ Co(II) $>$ Pb(II) $>>$ Ni(II) $>$ Cd(II). This order was almost in agreement with the stability constants for amine complexes such as ethylene diamine-metal complexes (15). The adsorption capacities given above are the values obtained from the studies performed by using 0.1% EGDMA in hydrogel systems. The experimentally obtained absorption capacities for the 0.5 and 1.0% EGDMA containing hydrogels are very close to the values given above. Thus, the experimental data related with these gels are not given in this study.

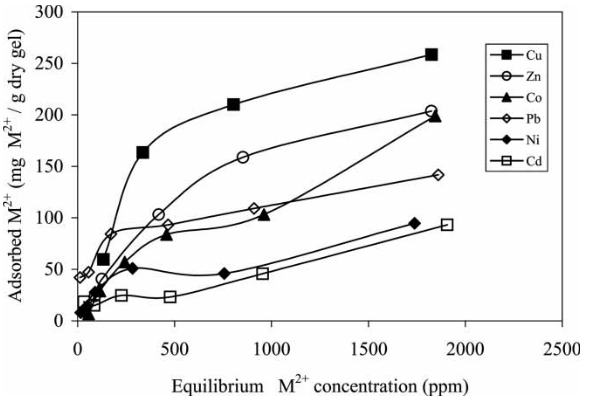

Figure 3. Dependence of metal ion uptake on the equilibrium concentrations of metal ions for polyDMAEMA hydrogel.

During the course of adsorption of metal ions onto polyDMAEMA hydrogels color changes were observed. The colors of the polyDMAEMA hydrogel metal complexes are similar to those of amine complexes. For example Cu(II), Co(II), and Ni(II) complexes were light blue, light pink, and light yellow, respectively. The other colorless metal ion (Zn(II), Pb(II), Cd(II)) complexes were observed as opaque. This color change of the polymer shows that functional groups containing nitrogen atoms interacted with metal ions.

Moreover, applying the data obtained from the adsorption kinetics of Cu(II), Zn(II), Co(II), and Pb(II) ions to different equations, adsorption isotherms were constructed for the polyDMAEMA hydrogel.

Adsorption isotherms of polyDMAEMA were analyzed according to the linear form of the Langmuir isotherms for Cu(II), Zn(II), Co(II), and Pb(II) ions, using the following expression (Eq. (3)),

$$\frac{C_e}{q_e} = (1/K_L q_{mon}) + (1/q_{mon})C_e \tag{3}$$

where C_e is the equilibrium concentration of hydrogel in solution and q_e represents the adsorbed metal ions per unit mass of adsorbent at equilibrium. q_{mon} denotes the amount of adsorption corresponding to complete monolayer coverage. K_L is the Langmuir constant. A plot of C_e/q_e versus C_e would give K_L and q_{mon} (16).

The plots of isotherms are shown in Fig. 4 and appear to be linear over the whole concentration range studied. K_L and q_{mon} values calculated from Langmuir equation are given in Table 1. The constant, K_L, contains enthalphic interaction of the binding of metal ions with the polymer, and can be found from the intercept of the lines given in Fig. 4. q_{mon} is a quantity representing adsorption capacity, also known as monolayer coverage of the surface. q_{mon}

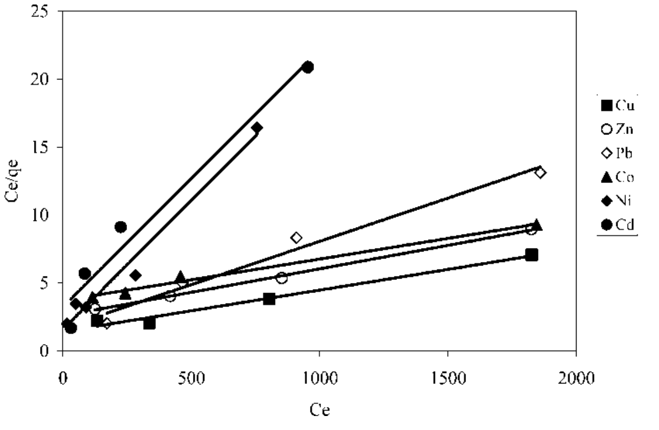

Figure 4. Langmuir isotherms for Cu(II), Zn(II), Co(II), Pb(II), Cd(II), and Ni(II) ions adsorption on polyDMAEMA hydrogel.

values of polyDMAEMA hydrogel from the Langmuir equation for Cu(II), Zn(II), Co(II), and Pb(II) ions were found to be 322, 285, 294, and 156, respectively. This is in good accordance with the results previously found and discussed in this study. However, for Cd and Ni ions the adsorption isotherms could not be fitted in the Langmuir equation after the concentration range of 1000 ppm. The adsorption isotherms up to 1000 ppm are given in Fig. 4. Calculated K_L and q_{mon} values for these metal ions are also exhibited in Table 1.

Swelling of Hydrogel in Metal Ion Solution

For investigating the swelling behavior of polyDMAEMA hydrogels in metal ion solution, hydrogels were swollen in various metal ion solutions. The effect of the metal ion concentrations on the mass swelling value of hydrogels are

Table 1. K_L and q_{mon} values determined from Fig. 3 for the adsorption of Cu(II), Zn(II), Co(II), Pb(II), Cd(II), and Ni(II) ions

Adsorbed ion	K_L	q_{mon}
Cu(II)	2.17×10^{-3}	322
Zn(II)	1.14×10^{-3}	285
Co(II)	8.45×10^{-4}	294
Pb(II)	3.78×10^{-3}	156
Cd(II)	5.88×10^{-3}	53
Ni(II)	1.19×10^{-2}	53

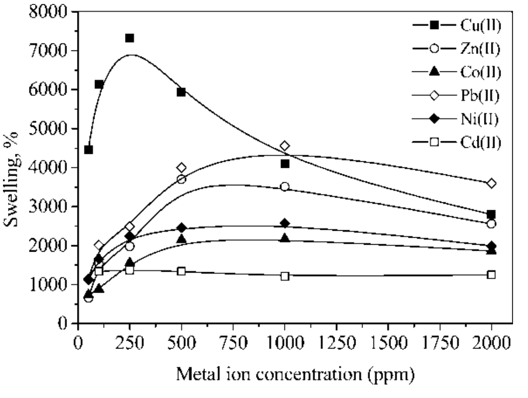

Figure 5. Effect of metal ion concentration on the mass swelling of hydrogels.

given Fig. 5. As can be shown from Fig. 5, for all metal ions, except for the relatively low adsorbed cadmium ion, the mass swelling of hydrogel generally increased with increasing concentration of metal ion after reaching a maximum value, which continued decreasing gradually. This increase was attributed to the electrostatic repulsions between the metal ions in the hydrogel structure and the expansion of the chains. The decrease of mass swelling after reaching a maximum is most probably due to the osmotic pressure constituted by metal ions during the adsorption onto the hydrogel.

CONCLUSION

In conclusion, the adsorption studies clearly showed that external stimuli, pH, and the ionic species in the adsorption medium play an important role on the adsorption behavior of polyDMAEMA hydrogels. It may be proposed that these hydrogels promise to be potential sorbents for the removal of heavy metal ions from wastewater and aqueous effluents.

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