



Adsorption Studies of Eu^{3+} from Aqueous Solutions by Poly(*N'*-Isopropyl Acrylamide-co-*N*-Acryloyl-*L*-Phenylalanine) Hydrogel Networks

T.J. Sudha Vani,^{1,2} N. Sivagangi Reddy,¹ K.S.V. Krishna Rao,^{1*}

¹Department of Chemistry, Yogi Vemana University, Kadapa-516 003, India.

²Department of Chemistry, Rayalaseema University, Kurnool, India.

Received 9th April 2014; Accepted 21st April 2014

Editor in Chief: Dr. K.S.V. Krishna Rao; Guest Editors: Dr. Siddaramaiah, Dr. G. M. Shashidhara.

Presented at the POLYCON-2014, 6th National Conferences on Advances in Polymeric Materials [Energy, Environment & Health] (NCAPM), Mysore, India, 25-26 April 2014.

ABSTRACT

The present work reports the synthesis of Amino acid functionalized hydrogel networks (AFHs). *N*-acryloyl-*L*-phenylalanine and *N'*-isopropylacrylamide and were crosslinked by *N,N*-methylene-bis-acrylamide using redox polymerization technique. The diffusion parameters were calculated by swelling kinetics to understand the diffusion mechanism. Equilibrium swelling experiments have been performed on the AFHs in metal ion solutions. The effect of relevant parameters, such as contact time, initial pH, and initial metal ion concentration were investigated to determine the optimum sorption conditions. Adsorption equilibrium data were better fitted by a Langmuir isotherm. The adsorption capacity of Eu^{3+} on the AFHs was 0.89 mM/g. Desorption studies were also performed in acid media and EDTA, to observe whether the gels can be utilized as reusable tool for the metal ion removal. Metal ion sorption studies shows that AFHs can be used for removal of Eu^{3+} ions from aqueous solutions. Adsorption data were modeled using the pseudo-second-order. The experimental data were fitted well the pseudo-second-order kinetics.

Key words: Hydrogels, Toxic metals, Europium, *N*-Isopropyl acryl amide

1. INTRODUCTION

Increasing economic development has been accompanied by one of the most important world problems, environmental pollution. Indeed, metal (radioactive or not) ions, contributed into nature by natural or industrial resources, are of environmental concerns due to their possible detrimental affects associated with radioactivity and/or toxicity to the biological systems, even they are present at trace levels. Therefore, remediation for wastewater becomes necessary and corresponding techniques are needed. Besides this, for more highly specific metal ion-recovery processes have led to increasing interest to develop new technologies. Conventional methods for removing heavy metals from industrial effluents (e.g. precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, electrochemical treatment and evaporation) are often ineffective and costly when applied to dilute and very dilute effluents [1,2]. The adsorption/separation procedures are introduced as a favorable way for the remediation processes, because of its efficacy, practicality, and economical

*Corresponding Author:

E-mail: drksvkrishna@yahoo.com

feasibility, depending on the used adsorbents. The adsorbents possessing lower cost are very abundant in the nature [3,4]. Phosphonic acid grafted on polystyrene resin has been investigated in liquid-solid extraction of europium [5]. Am^{3+} was separated and recovered effectively from Eu^{3+} in nitrate aqueous solution using TPPEN-NIPA gel [6]. The membrane-type and polymer-type adsorbents polyaniline and poly(acrylic acid) grafted alginate and gelatin blends prepared by free radical copolymerization were used for extraction of Cu^{2+} [7].

In the present work, we developed poly (*N*-isopropyl acrylamide-co-acryloyl phenylalanine) hydrogels, studied their swelling studies and removal of Eu^{3+} in aqueous media.

2. EXPERIMENTAL

2.1. Materials

Analytical reagent grade samples of acryloyl phenylalanine (APA), *N'*-isopropylacrylamide (NIPA), *N,N*-methylenebisacrylamide (MBA),

N,N,N',N'-tetramethylethylenediamine (TEMED), $[\text{Eu}(\text{NO}_3)_3] \cdot 6\text{H}_2\text{O}$ and Potassium persulfate (KPS) were purchased from Aldrich Chemicals Co. Ltd., USA. Chemicals were used without further purification and double distilled (DD) water was used throughout the experiments.

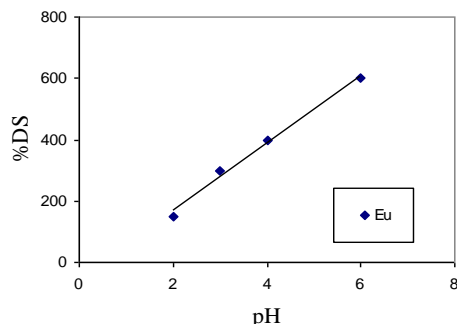


Figure 1. Effect of pH on the swelling of AFH in Eu^{3+} solution

2.2. Synthesis of Poly(NIPA-co-APA) AFHs (Amino acid Functionalized Stimuli Responsive Hydrogel Networks)

N'-isopropylacrylamide (NIPA) (1g), and *N,N'*-Methylene-bis-acrylamide (MBA) (10 mg/ml) were dissolved in distilled water at room temperature while APA acryloyl phenylalanine (APA) (180 mg) dissolved in equi molar concentration of NaOH solution. These two solutions were mixed, then the initiator APS (10 mg/ml) and accelerator TEMED (50 μl) were added to allow the copolymerization for 24 hr at 0 °C to 5 °C temperature. The prepared hydrogel networks were taken out and immersed in distilled water for 2 days at room temperature by changing the water every 12 hr to remove the excess of unreacted monomers and oligomers and were dried at 40 °C to attain the constant weight. The AFHs were synthesized by varying ratios of monomers and crosslinking agent.

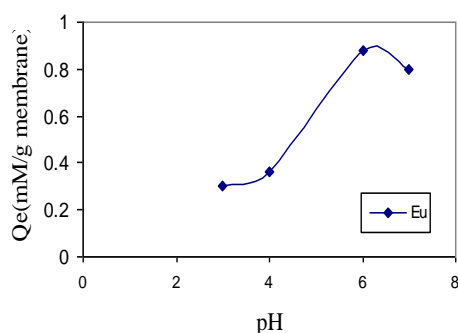


Figure 2. Effect of pH on adsorption of Eu^{3+} on AFH.

2.3. Preparation of Eu^{3+} Solutions

Eu^{3+} solution was prepared by dissolving accurately weighed appropriate amounts of $[\text{Eu}(\text{NO}_3)_3] \cdot 6\text{H}_2\text{O}$ in double distilled water to obtain solutions in the concentration range of 0.2 to 2.5 mM.

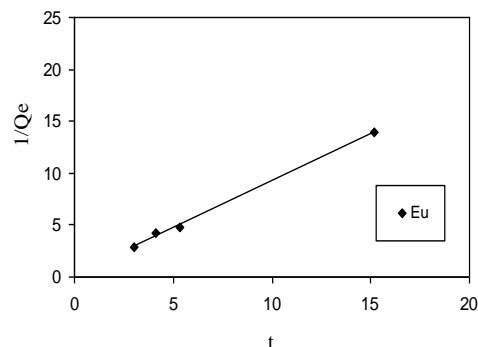


Figure.3. Pseudo second-order kinetics plots of adsorption kinetics of Eu^{3+} ions on AFH.

2.4. Metal ion Sorption Studies

The experiments were carried out by placing weighed circular pieces of gels in 20 mL of 2 mM metal ion solution. After 40 minutes they were removed from the solution. Initial and equilibrium concentrations were calculated from the measured absorbance values using UV spectrophotometer (Shimadzu, JAPAN). The equilibrium adsorption amount, Q_e (mM/g-dry gel) was determined using equation (1).

$$Q_e = (C_o - C_e) \frac{V}{M} \quad (1)$$

Where, C_o is the initial concentration of the metal ion solution (mM L^{-1}), V is the volume of the solution used for the adsorption (L), M is the mass of the dry membrane (g) and C_e is the concentration of the ions remaining in solution (8).

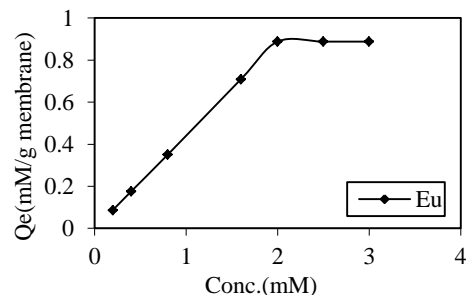


Figure.4. Effect of concentration on adsorption of Eu^{3+} at pH 6 on AFH

3. RESULTS AND DISCUSSION

3.1. Characterization and Swelling Studies

Characterization and swelling Studies were followed as in our previous paper (9)

3.2. Effect of pH on Swelling

The swelling behaviour of poly(NIPA-co-APA) AFHs was observed as pH dependent due to the ionization/deionization of the ionisable functional groups, such as $-\text{NH}_2$ or $-\text{COO}$ (Figure .1). At lower pH values, these groups do not ionize and keep the network at its collapse state. At higher pH values, these groups ionize and their charges repel each other, resulting in the swelling of the AFHs.

3.3. Effect of pH on Metal ion Adsorption

The ionisable functional groups, such as -COOH, -NH- or -C=O on the surface of gel may gain or lose a proton, resulting in a surface charge that varies with pH (Figure.2). At low pH, surface sites are protonated and the surface becomes positively charged, while at high pH the ionisable groups lose their protons and the surface becomes negatively charged. The pH value in aqueous solution is a very critical parameter affecting both the removal capacity and the removal mechanism of Eu^{3+} ions by hydrogels. As pH value increases (pH 2-6) its removal capacity of Eu^{3+} by uptake also increases. The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. As the crosslinked gels contain accessible binding groups (-COO⁻, C=O, -NH-), hence the uptake capacity increases for metal ions.

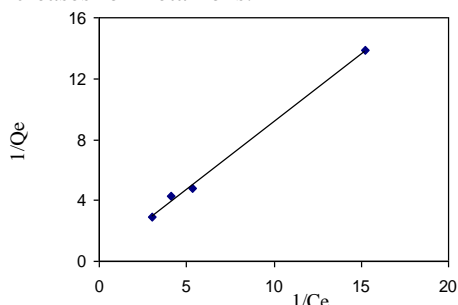


Fig. 5. Langmuir isotherm for adsorption of Eu^{3+} on AFH.

3.4. Effect of Contact Time and Adsorption Kinetics

The adsorption of Eu^{3+} over one gram of solid support was rapid initially and became slower with lapse of time. At the initial stage the process of adsorption was fast due to the availability of abundant free sites near the surface where there is less hindrance for the approaching metal ions. With respect to contact time the gel reached saturation after 40 minutes. The data were used to study the kinetics of adsorption of Eu^{3+} ion on AFHs. Many kinetic models were developed and studied by several researchers to find out kinetic adsorption constants [9, 10]. Kinetics data were modeled using pseudo-second-order model, which assumes that the rate is proportional to the square of the number of remaining free surface sites.

The linearised form of pseudo-second order equation [11] may be expressed as

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (2)$$

where k_2 (g/mg/min) is the rate constant of the second-order kinetic equation, Q_t (mg/g) is the amount adsorbed at time t (min) and Q_e is the amount adsorbed at equilibrium (mg/g).

Fig.3 shows the application of pseudo-second-order model for the experimental data. Obviously, the adsorption process could be well described by the pseudo-second order equation, indicating the process mechanism to be chemical adsorption [12].

3.5. Effect of Initial Metal ion Concentration and Adsorption Isotherm

It is clear from the figure 4 that adsorption amount of metal ions increased with increasing initial ion concentration then reached a plateau value at higher concentration due to the saturation of the chelating sites of the membrane. The adsorption is measured at pH 6. The maximum adsorption capacity of the AFHs was found to be 0.89 mM/g for Eu^{3+} . The high adsorption efficiency was attributed to the hydrophilic nature of AFH due to the presence of carbonyl (-C=O), amine (-NH-) and carboxyl (-COO⁻) groups, which had an adequate affinity to the metal ions.

The equilibrium data were better fitted to Langmuir adsorption isotherm model (Figure .5). The most widely used isotherm equation for modeling equilibrium is the Langmuir equation. In this study, we attempted to analyze adsorption at different concentrations (0.1-3.0Mm) by this model.

$$\frac{1}{Q_e} = \frac{1}{Q^o b C_e} + \frac{1}{Q^o} \quad (3)$$

where Q_e is the amount of metal adsorbed per unit weight of the sorbent (mg/g) and Q^o and b are Langmuir constants indicating the adsorption capacity and energy of adsorption, respectively. The linear plot of $1/C_e$ versus $1/Q_e$, with high correlation coefficient (r^2) values, indicated the monolayer adsorption on AFH. The value of Q^o for Eu^{3+} is 0.89mM g⁻¹.

3.6. Desorption Studies and Reusability

Desorption of Eu^{3+} from gels was studied with HCl and EDTA as regenerants. When 0.01M HCl or EDTA were used desorption was only 60% and 72% respectively of adsorbed ions on gels in to the solutions. As the concentration of the regenerant is increased to 0.1M the desorption of ions increases to 80% and 94% for HCl and EDTA respectively. The cycle of extraction-recovery-regeneration was repeated five times. The uptake performance of regenerated sorbent was found to be close to the freshly prepared sorbents which indicate that the sorbents can be regenerated and reused respectively atleast for five times.

4. CONCLUSION

As the hydrogels contained ionizable functional groups, as their swelling behavior was essentially dependent on pH, leading to a typical pH-sensitive swelling behavior of hydrogels, AFHs were able to

successfully separate Eu^{3+} metal ions from aqueous solutions. The adsorption equilibrium data were fitted to the Langmuir isotherm. The maximum monolayer adsorption capacity of AFH was 0.89mmol/g for Eu^{3+} . It may be proposed that these gels are potential sorbents for the removal of Eu^{3+} metal ions from waste water.

Acknowledgements:

Authors Dr. K.S.V. Krishna Rao and N. Sivagangi Reddy thank the Board of Research on Nuclear Science, Mumbai, India. (B.R.N.S file No: 2010/35C/53/BRNS/2538) for financial support.

5. REFERENCES

- [1]. S.J.T. Pollard, G.D. Fowlerr, C.J. Sollars, R. Perry, (1992) Low-cost adsorbents for waste and waste water treatment: a review. *Science of the Total Environment*, **116** 31-52.
- [2]. A. A. Atia, A. M. Donia, (2005) Studies on the interaction of mercury (II) and uranyl (II) with modified chitosan resins. *Hydrometallurgy*, **80** 13-22.
- [3]. D. Mohan, C.U. Pittman (2006) Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *Journal of Hazardous Materials*, **137** 762-811.
- [4]. M. Casolaro, E. Paccagnini, R. Mendichi, Y. Ito (2005) Stimuli-responsive polymers based and cross-linked hydrogels, *Macromolecules*, **38**, 2460-2468.
- [5]. A. Omar, F. Nacer, D. Mohamed Amine, V. Didier, (2011) A new sorbent for europium nitrate extraction: phosphonic acid grafted on polystyrene resin, *Journal of Radioanalytical and Nuclear Chemistry*, **290** 267-275.
- [6]. T. Kenji, M. Tatsuro, N. Yoshi, (2008) Separation of americium(III) and europium(III) by thermal-swing extraction using thermosensitive polymer gel, *Progress in Nuclear Energy*, **50**, 466-469.
- [7]. T.J. Sudha Vani, N. Sivagangi Reddy, P. Ramasubba Reddy, K.S.V. Krishna Rao, Jayshree Ramkumar, A.V.R. Reddy, (2013) Synthesis, Characterization and Metal Uptake Capacity of New Polyaniline and Poly (acrylic acid) Grafted Sodium Alginate/Gelatin Adsorbent, Desalination Water Treatment doi: 10.1080/19443994.2013.846460.
- [8]. T. J. Sudhavani, N. Sivagangi Reddy, K. Madhusudana Rao, K. S. V. Krishna Rao, Jayshree Ramkumar, A. V. R. Reddy, (2013) Development of Thiourea-Formaldehyde Crosslinked Chitosan Membrane Networks for Separation of Cu (II) and Ni (II) Ions, *Bulletin of Korean Chemical Society*, **34** (5) 513-1520
- [9]. Y. Kim, V. Ramesh Babu, K. S. V. Krishna Rao, Jae-Min Lim, T. Daniel Thangadurai, Yong-Il Lee. (2014) Stimuli-Sensitive Poly(NIPA-co-APA) Hydrogels for the Controlled Release of Keterolac Tromethamine, *Journal of the Korean Chemical Society*, **58** 92-99
- [10]. S. Babel, T.A. Kurniawan, (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *Journal of Hazardous Materials*, **396** (7) 1-25.
- [11]. Z.Aksu, (2002) Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*, *Process Biochemistry*, **38**, 89-99.
- [12]. Y.S. Ho, G. McKay, (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Research*, **34**, (3)735-742.
- [13]. Y.S. Ho, J.C.Y .Ng, G. Me Kay, (2001) Removal of lead(II) from effluents by sorption on peat using second-order kinetics, *Separation Science and Technology*, **36**, 241-261.