SYNTHESIS OF ACRYLIC ACID/ACRYLAMIDE HYDROGELS FOR REMOVAL OF CUPRIC IONS FOR WATER WASTE TREATMENT.

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Abstract

Some hydrogels have been used as materials that capture different ions in aqueous solutions[1,2]. These polymeric systems have certain functional groups, which are along the polymer chain, and are involved in a physical-chemical complex mechanism for capturing metal ions in aqueous solutions. In this work were synthesized and tested to capture Cu (II), three types of hydrogels with different monomer molar ratios for acrylic acid/ acrylamide (25/75, 50/50 and 75/25). The materials were crosslinked with ethylene glycol dimethacrylate (EGDM) using 1, 4, 6, 8 and 10% wt. The hydrogels were milled and screened for sizes between 0.21 and 1.19 mm. For quantitative removal of the Cu (II), It was prepared an standard solution of 2000 ppm of the ion using CuSO4 • 5H2O. Dilutions were made to obtain mixtures between 100 and 2000 ppm of Cu(II). About ten milligrams of material were in contact with solutions for the capture of the metal by the hydrogels. These samples were were placed in a Erlemeyer flask which is placed in a mechanical agitator (Thermo Scientific ®) by two hours, then samples were filtered and the solution is analyzed for quantification of ion Cu(II) through an Varian® atomic absorption spectrometer. Here, we analyzed the effects of pH, and as function of the concentrations of the solutions for metal removal. Were obtained adsorption isotherms. For the hydrogel of 1% 75/25 gives a maximum removal of 120 mg Cu(II)/g of the hydrogel. Monomer ratio 25/75 with a 10% EGDM had removal of 100 mg Cu(II)/g hydrogel. Apparently functional groups -NH2 provide more hydrophilic power and these groups are directly involved in the capture of Cu(II). The sample of 1% of EGDM content with monomer ratio 75/25, with more hydrophilic groups, has a better removal as well as the monomer ratio of 25/75, that have more amine functional groups.

Introduction

Quelanting polymers have been studied because they have high selectivity for capture specific ions in aqueous solutions. These polymers posses along their chains, different functional groups that form active complexes compounds for

"trapping" metallic ions in solutions. These specific materials could be applied for recovery of precious metals, or for removal of toxic or radioactive elements in water resources.

Metalic absorption is limited for a complex diffusion mecanism of the metal into polymeric network. Generally, ionic interchange resins are used for metal extractions. Swelling properties of the resins are poor, characteristic that restrict movement of ligands and metal-polymer complex formation. Acrylic polymers are highly hydrophilic materials and swell until several thousands times. This swelling behavior has been used in different applications in medicine and agriculture [3-5]. Here, we synthesized acrylic acid/acrylamide copolymers for capture metallic ions in aqueous solutions. These hydrogels could be applied for waste-waster treatment to trap heavy metals. Evidently, hydrogel composition influence caption of metal. Were used, three types of hydrogels with different monomer molar ratios for acrylic acid/ acrylamide (25/75, 50/50 and 75/25) for capture Cu (II).

Experimental Procedure

Purchase from Aldrich Chemical Co., acrylamide (AM) and acrylic acid (AA), were used as monomers with 99 y 98 % purity degree, respectively. Pure $K_2S_2O_8$ and pure $NaHSO_3$ dissolved in water, were compounds used as initiator system. Crosslinking agent, ethylene glycol dimethacrylate (EGDM) was from Aldrich too. For preparation of aqueous solutions doubly distilled and deionized water was used. Standard certified Cu(II) solution for atomic absorption experimets was from Varian Co.

Each synthesis of the hydrogels was realized by aqueous solution polymerization between the acrylic acid and the acrylamide, previous established amount of EGDM as crosslinking agent was then added. Concentrations used of cross-linking agent were from 1, 4, 8, and 16 % wt. All amounts involve in the hydrogel synthesis are illustrate in table 1.

Monomeric ratios AA / AM	Monomers						water
	Acrylic acid (AA)	Acrylamide (AM)	Etilenglycol dimetacrylate (EGDMA)				
			1%	4%	8%	16%	
75 / 25	41.75 g	13.25 g	0.55 g	2.20 g	4.40 g	8.80 g	55 g
50 / 50	28.00 g	27.00 g					55 g
25 / 75	13.25 g	41.75 g					55 g

In a typical synthesis, monomers were dissolved in water, and then pH was rise to a neutral value by addition of 0.2 M KOH solution. The polymerization was

started by addition of the initiators solutions. Mixture was placed in a recirculating bath at 60 °C for two hours. Hydrogel was removed from the reactor and for total consumption of the monomers, material was placed inside an electric oven at 40 °C for 48 hours. After this time, reaction was finished.

Dry hydrogels were milled and screened for sizes between 0.21 and 1.19 mm. For quantitative removal of the Cu (II), It was prepared an standard solution of 2000 ppm of the Cu(II) ion using CuSO4 • 5H2O. Dilutions were made to obtain mixtures between 100 and 2000 ppm of Cu(II). About ten milligrams of material were in contact with solutions for the capture of the metal by the hydrogels. These samples were were placed in a Erlemeyer flask which is placed in a mechanical agitator (Thermo Scientific ®) by two hours, then samples were filtered and the solution is analyzed for quantification of ion Cu(II) through an Varian® atomic absorption spectrometer.
Water uptake could be calculate by relation:

$$mg\,Cu^{+2}/g_{hydrogel} = \frac{Ci - C_{eq}}{m} V_1 \qquad 1$$

where C_i and C_{eq}, are initial and at equilibrium concentrations of the Cu(II) ion, V_1 total volume of metal solutions and m is the mass of the dry hydrogel.

Results and Discussions

Behavior of the swelling for polymeric hydrogels is very important for the capture of the metal. Figure 1 illustrates the swelling in pure water. It can be notice that maximum swelling was obtained for all three types of hydrogels about 60 hours. The hydrogel containing acrylic acid/acrylamide (75/25) crosslinked with 1% of EGDM is the one that captures much water. The maximum value of the swelling is about 28.000%. Although not necessarily the material with maximum swell is not that captures more Cu(II), hydrogel with 1% of EGDM (and for 75/25) was tested.

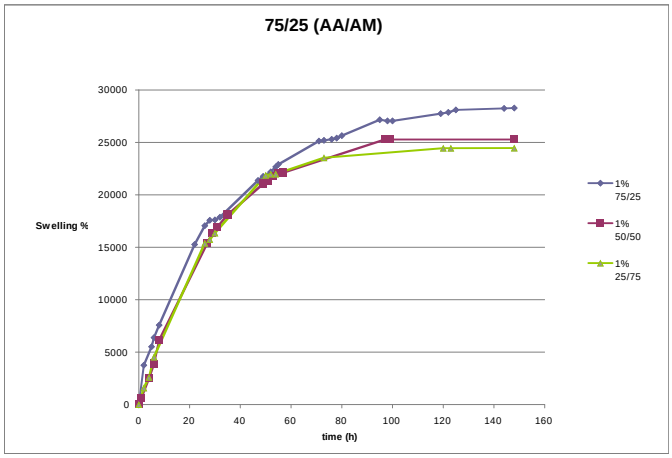

Fig.1. Swelling for the hydrogel in pure water as function of relation of monomers.

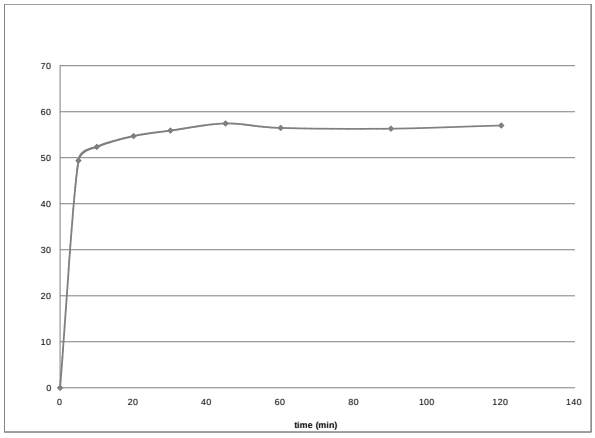

Fig.2. Absortion isotherm for hydrogel with 1% EGDM and for monomer relation 75/25.

To evaluate the uptake of the metal, it is necessary construct absorption isotherms. These isotherms quantifie the metal ions captured by the hydrogel at different concentrations, temperature and pH's. Figures 2 shown typical absortion isotherm, where copper capture take about 30 min until reach equilibrium. This is indicative that hydrogel could “catch” copper ions. To make a complete analysis, samples of the hydrogel were in contact with different concentration solutions, giving the results illustrated at figure 3. In this squeme we observe that hydrogel have a good uptake of metal with solutions from 200 ppm to 1600 ppm, and the maximum uptake varies between 140 to 150 mg of Cu(II) captured per gram of hydrogel.

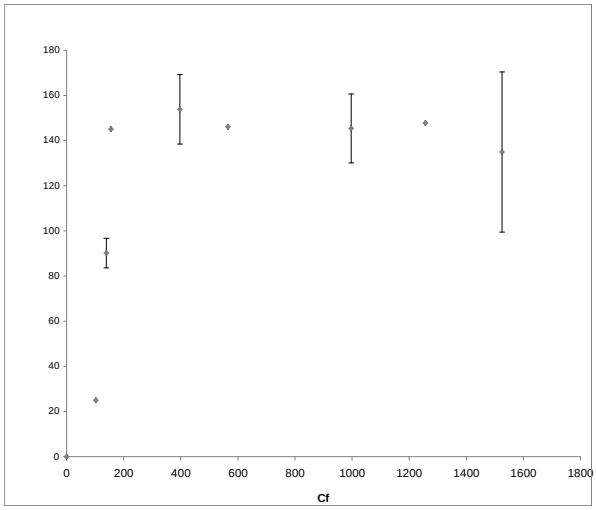

Fig 3. Caption of the Cu(II) as function of the final concentration at low pH.

Conclusions

Ion copper from water solution was uptaken with acrylamide/acrylic acid hydrogel. Improve capture of hydrogel was achieved. About 150 mg de Cu(II) could capture, regardless of the concentration of the solution, either low (200 ppm) or high (up to 1500 ppm). These materials could be tested for industrial waste water or in rivers.

[1] Kasgöz H.; Kasgöz A.; Sahin U.; Temelli Y.; Bayat C., Polymer-Plastics Tech. and Eng., 45, 2006, 117-124.
[2] Katime I. and Rodriguez E., J. Macromol. Sci.-Pure Appl. Chem., A38(5&6), 2001, 543-558.
[3] De Rossi, D.; *et al*.., Eds. *Polymer Gels Fundamental and Biomedical Applications*; Plenum Press: New York, 1991.
[4] Alvarez-Lorenzo C., Concheiro A., Dubovik A.S., Grinberg N.V., Burova T.V., Grinberg V.Y., *Journal of Controlled Release*, *102*, 2005, 629-641.
[5] Park K., Shalaby W.S., Park H. *Biodegradable hydrogels for drug delivery*, Technomic Publishing; Lancaster and Basel, 1993.