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ORGANIC HYDROGELS AS POTENTIAL SORBENT MATERIALS FOR POSITIVELY CHARGED METAL IONS

BEKIARI V.[1], LINARDATOS G.[1], ZAMPARAS M.[1], BOKIAS G.[2] and AVRAMIDIS P.[3]

[1]Tecnological Educational Institute of Western Greece, Department of Fisheries and Aquaculture Technology, 30200, Messolonghi, Greece
[2]University of Patras, Department of Chemistry, GR26504, Patras, Greece
[3]University of Patras, Department of Geology, GR26504, Patras, Greece
E-mail: mpekiari@teimes.gr

ABSTRACT

Hydrogels are three-dimensional, hydrophilic, polymeric networks capable to adsorb large amounts of water or biological fluids. The networks are composed of homopolymers or copolymers and are insoluble due to the presence of chemical or physical cross-links. Anionic hydrogels bearing negatively charged $-COO^-$ groups were prepared and investigated. These are based on sodium acrylate (ANa), either homopolymerized (poly(sodiumacrylate), PANa) or copolymerized (P(DMAM-co-ANa$_x$)) with N,N Dimethylacrylamide (DMAM). The molar content x of ANa units (expressing the molar charged content of the hydrogel) varies from 0 (nonionic poly(N,N-dimethylacrylamide), PDMAM, hydrogel) up to 1 (fully charged poly(sodium acrylate), PANa, hydrogel). The hydrogels were used to sorb metal cations from water. Some model metal cations such as copper, iron and manganese have been studied and maximum sorption capacity has been calculated. The study showed that crucial factors controlling the sorption efficiency is the charge content of the hydrogel x, as well as the pH of the aqueous solution, since acrylic acid is a weak acid.

Keywords: oragnic hydrogels, sorbent materials, metal ions

1. Introduction

During the recent years as environmental pollution becomes of greater concern a large share in the impressive development of novel high-technology materials has been made by materials used in water purification systems (Bekiari and Lianos, 2006, Kioussis and Kofinas, 2005, Shannon *et al.*, 2008). In this research field the development of various adsorbents for the removal of metallic species from aqueous systems and wastewaters is of great interest because of their toxicity and non-degradable nature (Chauhan *et al.*, 2006). Most heavy metals are toxic even at low concentrations and affect strongly the ecosystems and the human life via bioaccumulation and bio-augmentation in the food chain. Thus, different types of materials have been synthesized for this scope such as dendritic polymers, mesoporous oxides, organically modified silicas, self-assembled nanocomposites and organic hydrogels (Bekiari and Lianos, 2007, Rether and Schuster 2003).

Organic hydrogels are three-dimensional, hydrophilic, polymeric networks that swell by adsorbing water and may increase their size more than hundred times. The networks are composed of homopolymers or copolymers and are insoluble due to the presence of chemical or physical cross-links. When hydrogels come in contact with aqueous solutions, they can effectively sorb and retain the dissolved substances, depending on the nature of the monomeric units comprising the hydrogel.

In the present work, P(DMAM-co-ANa$_x$) hydrogels containing sodium acrylate units (ANa) and nonionic N,N-dimethylacrylamide units (DMAM) have been prepared. The molar content x of the anionic ANa units varies from 0 (nonionic hydrogel) up to 1 (fully charged hydrogel). The chemical structure of the synthesized hydrogels is depicted in Figure 1. The sorption of copper,

iron and manganese was investigated as a function of the charge content of the hydrogel x, as well as the pH of the aqueous solution, since acrylic acid is a weak acid.
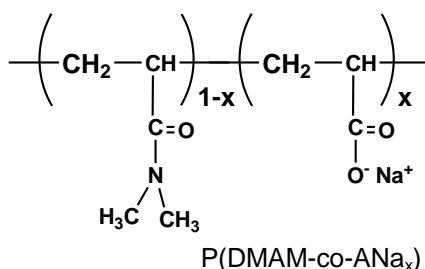

P(DMAM-co-ANa$_x$)

Figure 1: Chemical structure of P(DMAM-co-ANa$_x$) hydrogels used in the present work. The structural units are cross-linked with BIS (not shown).

2. Experimental methods

Materials

Acrylic acid (AA), *N,N*-dimethylacrylamide (DMAM), *N,N,N,N*-tetramethylethylenediamine (TEMED), methylene bisacrylamide (BIS) and ammonium persulfate (APS) were purchased from Aldrich. All reagents were used as received. Standard metal ion solutions (standard 1000 mg/L) were commercially obtained from Perkin Elmer. Water was purified by means of a TKA smart2Pure apparatus.

Synthesis of the hydrogels

The P(DMAM-co-ANa$_x$) hydrogels were synthesized according to the following procedure: x mol AA and y mol DMAM (x+y=1), 0.005 mol BIS (crosslinker, 5 mol% over the total monomer concentration) were dissolved in 20 mL ultrapure water under stirring at room temperature. After deoxygenation of the solution by N$_2$ bubbling for 30 min, 0.1 g APS (dissolved in 2 mL ultrapure water) and 3 drops of TEMED were added. The formation of the gel was almost immediate. The reaction was left to proceed for 24 h and, then, the gels were immersed in ultrapure water. Water was decanted and renewed daily for 1 week. Finally, the purified swollen gel was cut into 2mL pieces and water was removed by heating up to 100ºC. The pH of the solution was adjusted around 7 by addition of an adequate volume of a NaOH 1M solution after the dissolution of the monomers, while the formed gels were fully neutralized by adding an excess of the NaOH 1M solution before purification. A series of hydrogels with five different (0, 0.25, 0.50, 0.75, 1) molar charged contents (negatively charged ANa units) were synthesized according to the experimental procedure outlined previously.

Sorption of metal ions from aqueous solutions

The sorption of metal ions was studied by the following procedure: 40 mL aqueous solutions of varying initial concentrations of metal ions (in mg/L) and sorbent (dry hydrogel samples) dose were left to reach equilibrium for 24h. Then the gels were removed from the solution and the remaining concentrations (C$_e$) of the studied dyes in solution were monitored by UV-Vis absorption spectrophotometry by using a Shimadzu UV-1800 spectrophotometer in the case of high Cu^{2+} concentrations or a HACH DR2800 spectrophotometer with HACH cuvette tests (LCK) in the case of low metal ion concentrations. The removal efficiency (R, %) was calculated by using the following equations:

$$R = \frac{C_0 - C_e}{C_0} 100 \qquad (1)$$

where C$_0$ and C$_e$ (mg/L) are the initial and equilibrium concentrations of metal ions solutions, respectively; V (L) is the volume of the metal ion solution and m (g) is the weight of the hydrogel used for the sorption experiment.

3. Results

3.1. Effect of the charge content of the hydrogel (x)

In Figure 2 the results for Cu^{2+} sorption (%R) by the five different negatively charged P(DMAM-co-ANa$_x$) hydrogels for two different initial concentrations at pH=7 are presented.
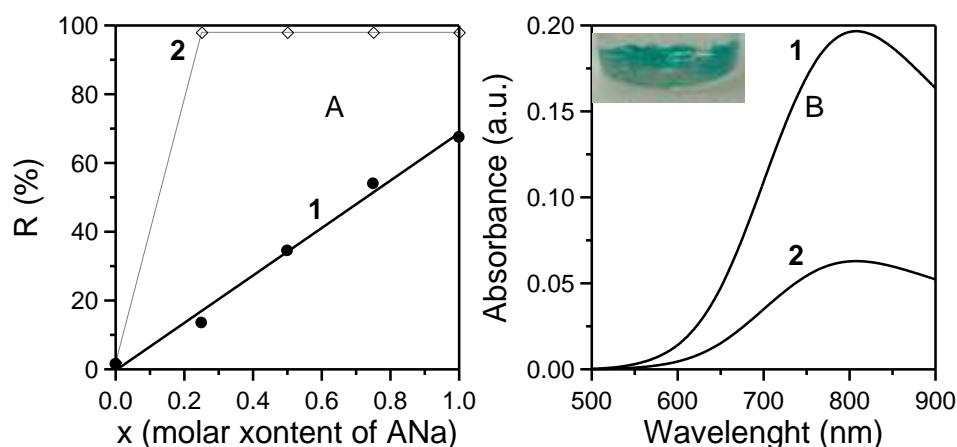

Figure 2: A: R (%) vs. charge content of the P(DMAM-co-ANa$_x$) hydrogels for Cu^{2+} ions. ((1):C_0=1000mg/L, m=0.02g; (2):C_0=20mg/L, m=0.02g), B: Absorption spectra of aqueous 1000 mg/L Cu^{2+} ions before (1) and after (2) equilibration with the hydrogel (x=1). The appearance of the P(DMAM-co-ANa$_1$) hydrogel at the end of the sorption experiment is shown in the inset.

As discussed elsewhere (Zamparas *et al.*, 2014), the aqueous 1000mg/L Cu^{2*} solution is blue-colored, as a result of a large absorption band in the visible region, centered at ~820 nm. After treatment with P(DMAM-co-ANa$_x$) hydrogels, absorbance of the solution decreases proportionally to the charge content (x) of the hydrogel becoming hardly detectable in the case x=1. Moreover, the linear dependence of the sorption on the charge content (x) of the hydrogel indicates that the electrostatic attractions are the driving force for the sorption. In the case of 20mg/L Cu^{2+} all ANa-containing hydrogels have the ability to practically sorb the total amount of the ion.

3.2. Effect of pH

In Figure 3 we compare the sorption efficiency of the hydrogels towards Cu^{2+} ions at pH=2 and pH=7. Since the dissociation of COO^- units is limited at low pH, the amount of the carboxylate anions is much lower leading to considerable decrease of the Cu^{2*} amount sorbed.
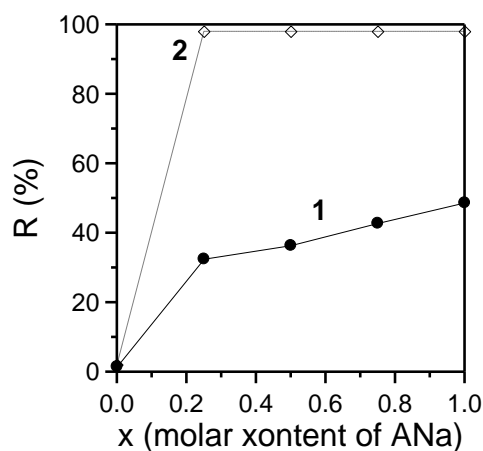

Figure 3: R (%) vs. charge content of the P(DMAM-co-ANa$_x$) hydrogels for Cu^{2+} ions. ((1):C_0=20mg/L, m=0.02g, pH=2; (2):C_0=20mg/L, m=0.02g, pH=7).

3.3. Effect of metal ion

In Figure 4 we compare the sorption efficiency of the hydrogels towards Cu^{2+}, Fe^{3+} and Mn^{2+} ions at pH=2. We see that the hydrogels have significant higher sorption efficiency for Fe^{3+} and Mn^{2+} ions. It is also remarkable that the sorption of manganese and copper ions seems not to be affected by the charge content (x) of the hydrogel, in contrast to iron ions. This probably is related to the ability of carboxylate anions to form complexes with manganese and copper ions, while just electrostatic interaction is the driving force in the case of iron ions.

4. Conclusions

In this work it is shown that anionic hydrogels based on sodium acrylate (ANa), either homopolymerized (poly(sodiumacrylate), PANa) or copolymerized (P(DMAM-co-ANa$_x$)) with N,N Dimethylacrylamide (DMAM) can be employed as efficient sorbents for retaining metal ions from aqueous solutions. Crucial factors controlling the sorption efficiency is the charge content of the hydrogel x, as well as the pH of the aqueous solution, since acrylic acid is a weak acid.
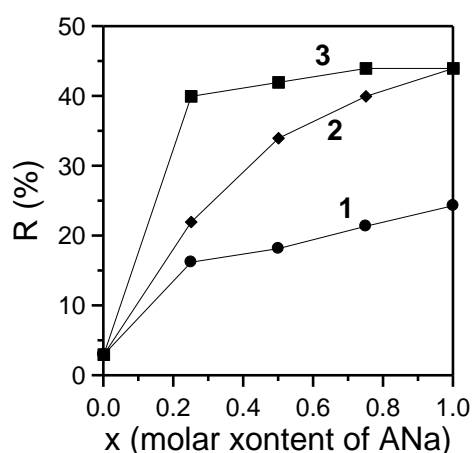

Figure 4: R (%) vs. charge content of the P(DMAM-co-ANa$_x$) hydrogels for Cu^{2+} ions (1), Fe^{3+} ions (2) and Mn^{2+} ions (3) at pH=2 (C_0=20mg/L, m=0.02g)

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