

Removal of Cu^{2+} and Zn^{2+} from aqueous medium using ionic polyacrylamides

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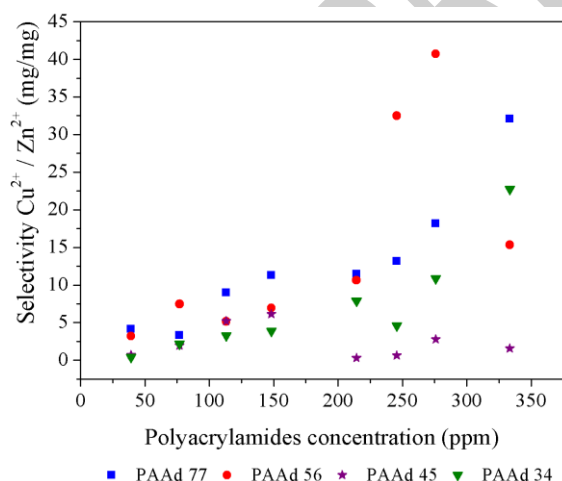
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Abstract

The wastewater produced by the galvanoplasty industry is a serious environmental problem due to the high concentrations of heavy metals. In this study polymers were used in ionic flocculation to treat synthetic wastewater containing metals, applying four types of polyacrylamides with different ionic loads as agents to remove copper and zinc. Metal removal efficiency was assessed considering the influence of polymer concentration, ionic load and pH. Selectivity ($\text{Cu}^{2+}/\text{Zn}^{2+}$) at different polymer concentrations was also evaluated. The results confirm that polyacrylamide is efficient in treating wastewater containing heavy metals. These experiments exhibited removal efficiency of around 40% and $\text{pH}=4.5$; however, efficiency was more than 80% with $\text{pH}=7.0$ under the same conditions, when polyacrylamides with average ionicity were used.

Keywords: Heavy metals removal; ionic polyacrylamides; ionic flocculation; Analysis of pH; Selectivity ($\text{Cu}^{2+}/\text{Zn}^{2+}$).



1. Introduction

The removal of metal ions from wastewater requires controlling different parameters, such as pH and temperature, the main problem being their high solubility in water [1]. Free inorganic particles such as metal ions are not susceptible to degradation, as occurs with organic

substances [2], and are therefore potentially dangerous. Accordingly, the presence of heavy metals in the environment [3,4], whether in animals [5] or plants [6] used as food, at concentrations beyond that stipulated by law, can trigger serious health problems for humans.

The disposal of untreated industrial wastewater in water bodies or soil is a significant threat to healthy environmental equilibrium [7]. The variety and high concentration of metals are characteristics of industries that work with galvanoplasty, one of whose applications is metal electrodeposition to protect surfaces. This type of industry uses tanks containing solutions of metals at high concentrations that may generate environmentally hazardous wastewater if left untreated.

Thus, efficient treatment of all these wastewaters is important in order to reduce the concentration of dangerous agents as much as possible before their final disposal. Adsorption is a highly recommended technique for properly treating wastewater, when there are ions in solution. Traditionally used materials such as chitosan [8,9], activated carbon [10,11], inorganic ion exchange resins [12,13], zeolites [14,15], or some combination of these [16,17], can be used to remove metal ions, such as Ag, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn from an aqueous medium.

Liquid-liquid extraction is also widely used and highly efficient. Separation, achieved by selecting the solvent used with a determinate species, is employed to remove ions such as Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Pt, Sn and Zn. A disadvantage is the use of an organic solvent that is harmful to human health and the environment [18,20]. Another alternative is also chemical precipitation, whereby an insoluble solid is obtained from species initially dissolved by changing their solubility equilibrium, thereby hindering their stay in solution. A number of applications of this technique are possible, since they are based on the formation of flakes rich in the dissolved metal. During the process, small dispersed particles are observed initially, but these soon aggregate, forming flakes that increase in volume and then decant, facilitating their removal. Thus, this technique is important in metal ion removal and can be used to remove Cu, Cr, Ir, Ni, Pb and Zn [21-23].

The present study aimed at using an agent that simultaneously allowed ionic interaction with the metal ion, via its chemical structure, and phase separation obtained by ionic flocculation. To that end, ionic polyacrylamides (PAA_d) are an alternative for this process. This polymer is soluble in water, even in environmental conditions, which allows good interaction with the wastewater. Figure 1 shows that the polyacrylamide monomer has a structure formed by a carbon chain containing an amine group, without load, and a carboxyl group, with a negative load that allows interaction with the metal cation.

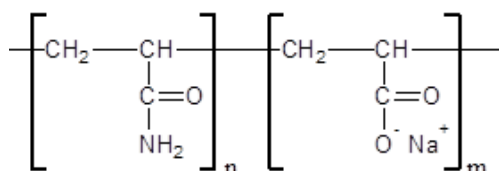


Figure 1. Polyacrylamide monomer

The proportion “n” and “m” defines the ionicity of the polyacrylamide such that the greater the percentage of “m”, the greater the occurrence of active points in which interaction takes place between opposite loads.

The metals used in this study were zinc, since it resists flake formation, making it difficult to remove from wastewater, and copper, both in the form of salts.

2. Materials and methods

2.1. Materials

The experiment used 4 types of polyacrylamides with ionic load ranging from 30 to 70% (Table 1).

Table 1. Polyacrylamides used and their respective ionic charge

Kinds of polymer	Ionic charge (% molar)	CAS
PAAd77	70	9003-05-8
PAAd56	50	
PAAd45	40	
PAAd34	30	

The synthetic wastewaters were prepared from a stock solution with initial concentrations of 20 ppm of ZnSO₄·7H₂O (CAS 7446-20-0) and 200 ppm of CuSO₄·5H₂O (CAS 7758-99-8). Both solutions have a pH of around 4.5. Polyacrylamide solutions were used because it is soluble in water. In the case of trials with zinc, the initial concentration of the stock solution of polymers was 200 ppm and for copper was 2.000 ppm.

2.2. Methodology

2.2.1 Assessment of polymer concentration

The entire removal process was carried out at a temperature of 25 °C, regardless of the type of polymer used. To remove ions from the aqueous solution, equal volumes of each of the polyacrylamide solutions were mixed at different volumes of the wastewater solution for

a contact time of 5 minutes under constant agitation. This mixture was then separated by filtration and the filtrate analyzed in a Varian AA240 (flame AA) atomic absorption spectrometer to determine residual metal concentration. The procedure was replicated in duplicate, and when necessary, in triplicate.

To do spectrophotometric analysis, each metal was evaluated separately. In this case, the equipment uses a suitable lamp to each metal and working range according to the methodology indicated in the equipment’s manual.

2.2.2 Operation time and kinetic study

The floc formation takes place immediately after the contact between the two solutions. Five minutes is sufficient time for the complete homogenization of the solutions and to provide maximum metal removal. Therefore, this system reaches the equilibrium rapidly and kinetic study is impractical.

2.2.3 Analysis of pH variation

The influence of pH on the removal of dissolved metals is well known [24]. Therefore, tests with neutral pH and in acid medium (pH= 3.0) were conducted in order to improve the zinc ion removal process. The pH adjustment stage was carried out using solutions of chloridric acid (1.0 M) (CAS 7647-01-0) and sodium hydroxide (1.0 M) (CAS 1310-73-2) in the zinc solution, followed by the addition of a polymer solution, thereby preventing the formation of precipitate before adjusting the pH.

2.2.4 Assessment of Cu²⁺/Zn²⁺ selectivity

In the case of the galvanoplasty industry, wastewater normally contains a range of metals. Thus, experiments were performed to analyze the anionic polyacrylamide selectivity of two metals (zinc and copper).

The experiments were conducted varying the initial concentrations of Zn²⁺ and Cu²⁺ between 40 and 330ppm, and polymer between 40 and 460 ppm. The two solutions of metals were prepared by dilution from a stock solution and then a polymer solution was added to the desired concentration.

3. Results and discussions

3.1. Removal efficiency

To assess the effect of polyacrylamide on zinc and copper removal, experiments were carried out at concentrations ranging from 25 to 110 ppm for zinc and 40 to 460 ppm for copper. In cases of concentrations below this established range, significant removal was not obtained and these were therefore not studied. On the other hand, at concentrations above this range, no significant increase in removal was achieved, remaining practically constant. Figures 2 and 3 show removal efficiency as a function of variation in polymer concentration, pH= 4.5, at a temperature of 25 °C.

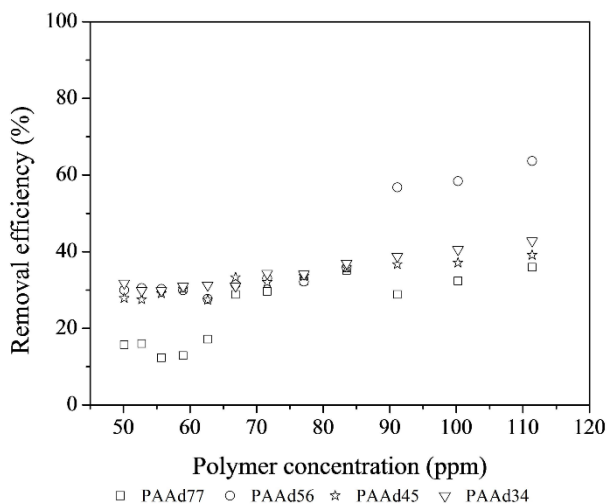


Figure 2. Removal efficiency of Zn^{2+} as a function of initial polyacrylamide concentration, at pH= 4.5 and temperature of 25 °C.

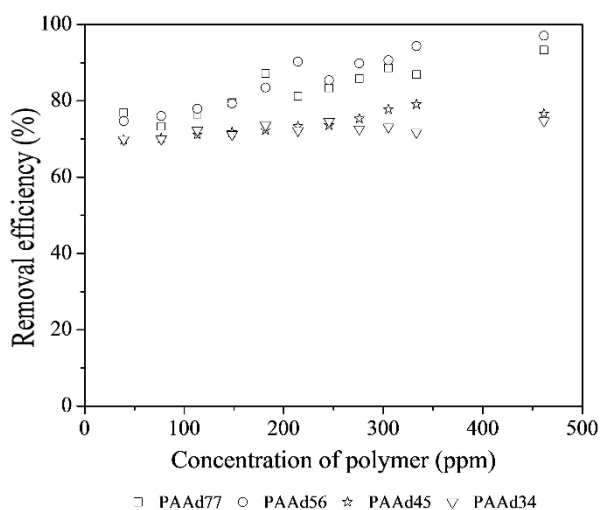


Figure 3. Removal efficiency of Cu^{2+} as a function of initial polyacrylamide concentration, at pH= 4.5 and temperature of 25 °C.

Figures 2 and 3 demonstrate that the removal of Zn^{2+} and Cu^{2+} ions from an aqueous medium is entirely possible with the use of anionic polyacrylamides. All polymers are capable of lowering the ion concentration in a solution. The presence of anionic charge in the carbon chain of the polymer attracts dissolved metal ions, successfully promoting removal. Even without changing the pH, mean removal efficiency was between 15 and 60% for Zn^{2+} and between 70 and 95% for Cu^{2+} . It is important to underscore that in all cases removal capacity depends on the affinity between the polyacrylamide and the ions.

In a medium with a high concentration of heavy metals, interaction between metal ions and the polymer is evidenced by the immediate formation of flakes that tend to be deposited at the bottom of the receptacle. However, this phase can be slightly compromised when the system is in regions with a high concentration of polyacrylamide, since this polymer increases the viscosity of the medium, which may hinder its passage through a filtering membrane.

3.2 Effect of pH

The effect of pH on the flocculation of metal ions was studied for zinc, in order to obtain the best removal efficiency. The pH values assessed were 3.0 and 7.0 under the same conditions. The study of the process in basic medium was not conducted, since before the addition of the polymer, metal flocculation had already been observed. The samples of synthetic wastewater exhibited a natural pH of 4.5. Figure 4 shows zinc removal for the different polymers and pH.

The results presented in Figure 4 demonstrate that zinc removal increases considerably at pH 7. In the case of polymer PAAAd45, this change caused removal of up to 90% of the zinc. This increased removal efficiency is attributed to greater interaction between the polymer and the metal, due to the rise in pH, given that a high removal percentage is found in divalent and trivalent metal ions in pH above 3 [25], as observed in Figures 2, 3 and 4. In polymers PAAAd34 and PAAAd45, those with the lowest ionic charge, the increase in pH led to a considerable rise in removal efficiency (mean of 50% and 80% for PAAAd34 and PAAAd45, respectively).

The results obtained at pH 3.0 showed very low mean removal efficiency of 10%. This is due to the competition between acid protons and the metal ion, which nullifies the negative charge of the polymer before it interacts with the metal, diminishing its capacity to attract dissolved ions. This may also explain the fact that removal is enhanced at neutral pH, since the solution originally exhibits an acidic pH.

3.3 Selectivity

The experimental data of selectivity are illustrated in Figure 5 and were obtained at a temperature of 25 °C and pH 4.5.

Figure 5 shows that Cu^{2+}/Zn^{2+} selectivity exhibits values greater than 1, indicating that copper has more affinity with polymers than with zinc. In the region in which polymer concentration is in the range between 250 and 330 ppm, selectivity obtains better results, reaching a maximum of around 40 $mgCu^{2+}/mgZn^{2+}$ for polymer PAAAd56 at a concentration of 275 ppm. Furthermore, PAAAd77 and PAAAd56, with higher ionic load, show greater selectivity when compared to PAAAd45 and PAAAd34. The increase in selectivity as polymer concentration rises is related to greater copper removal under these conditions, possibly a result of the characteristics of d electrons in copper, which are more firmly maintained, less available for π bonds and require excess polymer [26].

Stringent environmental laws have stimulated research in the development of new materials and in the improvement of those already used. In the research for new materials, those that combine low cost and high removal efficiency have been gaining strength, with a focus on regional materials. Among the new adsorbents can be highlighted a sporopollenin, a biopolymer of vegetal origin, in the

removal of Cu^{2+} ($0.0195 \text{ mmol.g}^{-1}$)*, Pb^{2+} ($0.0411 \text{ mmol.g}^{-1}$)* and Cd^{2+} ($0.0146 \text{ mmol.g}^{-1}$)* [27]; the rice husk in the removal of Cd^{2+} (II), in this case the removal efficiency varied from 18 to 99% when the amount of adsorbent increased from 0.5 to 30 g [28]; the bentonite, a mineral with interesting physicochemical properties such as high specific area, excellent cation exchange capacity and affinity for organic and inorganic compounds, in the

removal of Pb^{2+} (0.07 mmol.g^{-1})* and Ni^{2+} ($0.0736 \text{ mmol.g}^{-1}$)* [29]; a combination of zeolite and nanofibers to remove Ni^{2+} (342.8 mg.g^{-1})* and Cd^{2+} (838.7 mg.g^{-1})* [30]; Magnetic nanoparticles of Fe_3O_4 impregnated with 1,6-hexadamine in the removal of Cu^{2+} (25.77 mg.g^{-1})* [31]; nanotubes of carbon coated with magnesium oxide in the removal of Pb^{2+} (78.74 mg.g^{-1})* [32]. In all these studies pH and temperature analyzes were fundamental.

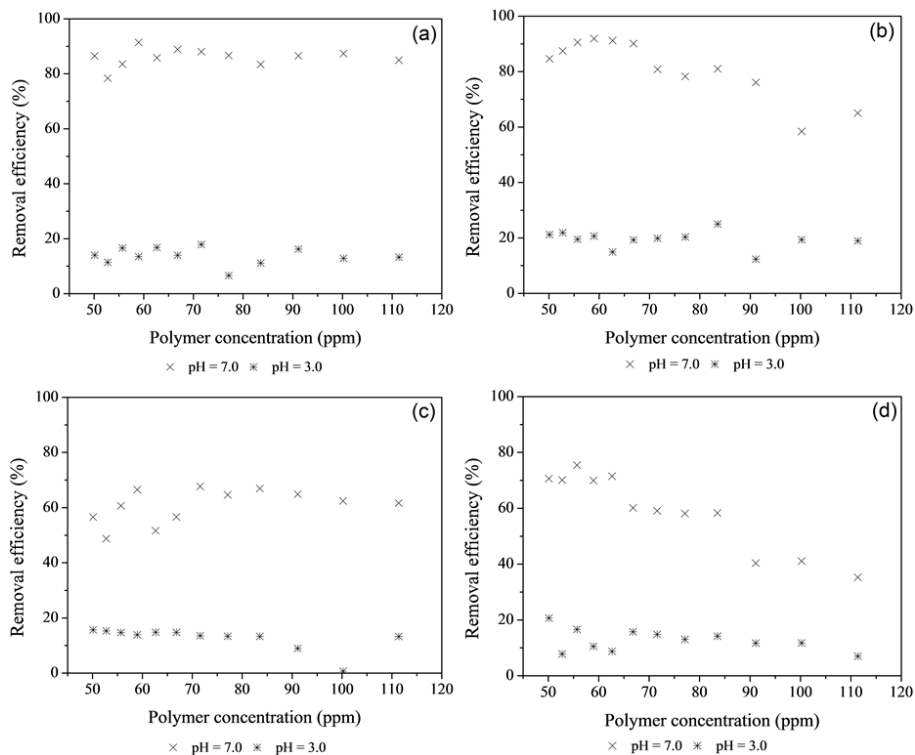


Figure 4. Removal efficiency of Zn^{2+} as a function of initial polyacrylamide concentration, at pH = 3.0 and pH = 7.0 for polymers PAAAd34 (a), PAAAd45 (b), PAAAd56 (c) and PAAAd77 (d) and temperature of 25 °C

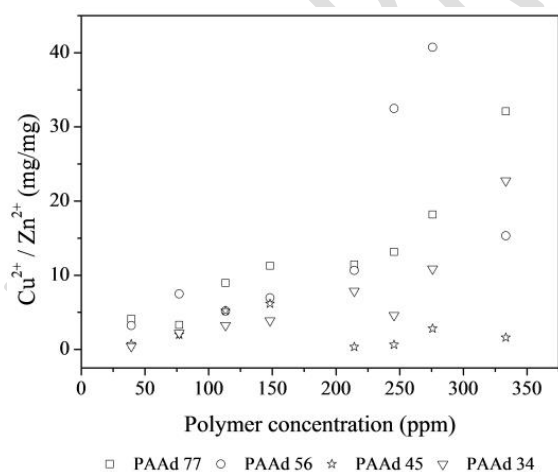


Figure 5. $\text{Cu}^{2+}/\text{Zn}^{2+}$ selectivity for different polymers at various concentrations

4. Conclusion

In this study 4 different types of polyacrylamide were used to remove copper and zinc ions from synthetic wastewater.

All were efficient in this process. The main conclusions obtained in this study were:

- Copper and zinc removal depends on the concentration and ionic load of the polymer;
- An increase in pH favors greater removal efficiency, primarily for zinc;
- By contrast, the decrease in pH for a lower value than that measured in the original wastewater solution considerably hindered the removal process;
- In the case of the wastewater containing the two metals, polymer selectivity is preferentially for copper;
- Applying the polymer to individual copper and zinc wastewater shows greater affinity of the polymer for copper to the detriment of zinc.

The anionic polyacrylamide presented in this work shows to be an alternative for the removal of ions in solution, because it is a commercial polymer of easy access and considerable efficiency in the removal of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ ions in aqueous solution.

*Maximum adsorption capacity

The flakes produced cannot be discarded in an unsuitable place. This solid residue, obtained at the end of the removal process, contains a high concentration of the pollutant so that it cannot be disposed of directly into the environment, the impact caused may be even greater than its presence in the previously treated effluent. Thus, it is necessary to search for an alternative disposal for this residue. One way to do this is to stabilize this material by adding it to the concrete used in construction. After the period of curing, the concrete makes the metal ion stable, preventing its migration out of the matrix [33-35].

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