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Copper and Zinc removal from aqueous solutions by polyacrylic acid assisted-ultrafiltration

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HIGHLIGHTS

- Zinc and Copper solutions were treated using ultrafiltration process.
- Transmembrane pressure, PAA concentration, pH and ionic strength were optimized.
- Selectivity was studied using a solution containing the two metal ions.

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ABSTRACT

Copper and Zinc removal from aqueous solution by polyelectrolyte enhanced ultrafiltration (PEUF) process was investigated using poly(acrylic acid) (PAA) with average molecular weight 100 kDa. The ultrafiltration studies were carried out using a tangential cell system, equipped with 10,000 MWCO regenerated cellulose. Several parameters have been studied such as: transmembrane pressure, PAA concentration, pH and ionic strength to improve the retention of the metal ions. The removal of Zn^{2+} and Cu^{2+} is respectively more than 70% and 93%. A better retention was observed at $2 \cdot 10^{-3}$ mol L^{-1} PAA concentration and 3 bar transmembrane pressure. The pH effect on the Zinc and Copper recovery revealed a maximum retention around 75% and 97%, respectively, for pH = 5. The study of the ionic strength effect has shown a retention decrease with the salt concentration increase. Selectivity was studied using a solution containing the two metal ions. Zinc retention decreases compared to single metal solutions, and this is more significant in the case of Copper ions.

1. Introduction

Metal ions play an essential role in many biological processes, and their deficiency, due to unusual accumulation or imbalance, may lead to biological troubles. Some metals, especially heavy metals, do not seem to be essential for mammals. Nevertheless, because of their competition with essential metals in binding with proteins, heavy metal ions become potent enzyme inhibitors, by exerting toxic effects on living systems. Moreover, the toxicity of heavy metal contamination is highly dependent on the chemical form of the metal in question.

For example, Cu^{2+} ions are essential nutrients, but when people are exposed to Copper levels above 1.3 mg L^{-1} for even short periods of time, stomach and intestinal problems occur. Longer exposure leads to kidney and liver damage [1]. The production of DNA mutation is evidence of its carcinogenicity.

Similarly, Zinc is an essential heavy metal for biological functions, but in high concentrations, it can be harmful to people and animals. This metal is naturally present in water, especially in the industrial wastewaters containing Zinc stem from galvanic industries, battery production, etc. The Zinc compounds are used for various purposes, e.g. for parchment production. It is noteworthy that, dissolved free ions are more toxic than metals bound to particles or organic compounds. There are several methods of removing the Zinc from water. To reach a level that meets legal standards, techniques such as coagulation, ion exchange, sand filtration and active carbon may be applied [2].

Copper and Zinc are classified as toxic elements and serious environmental contaminants. Their removal, separation and enrichment in aqueous solutions therefore play an important role for the environmental remediation of wastewater [3].

The removal and rejection of heavy metal ions from aqueous solutions have been conventionally carried out by chemical precipitation, ion exchange, adsorption, etc. Nowadays, the ultrafiltration method, through addition of a polyelectrolyte into the aqueous solutions, has become a significant research area. The principle of ultrafiltration is the possibility

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of linking polymers, with a large molecular weight, with heavy metal ions to form macromolecular complexes. These metal complexes are, subsequently, retained and concentrated by ultrafiltration membranes, unlike unbound metal ions, which will pass through. To date, various polymers, such as poly(vinyl alcohol) [4,5], sulfonated poly(vinyl alcohol) [4,5], poly(ammonium acrylate) [6], poly(acrylic acid) [7–9] and polyethylenimine [9–13] have been used for metal removal from wastewaters.

Polyelectrolyte-enhanced ultrafiltration (PEUF) involves the addition of a soluble polyelectrolyte to the water containing a solute having a charge opposite to that of the polyelectrolyte. The target solute binds to the polyelectrolyte by electrostatic attraction and the solution is treated with ultrafiltration using a membrane having pore sizes small enough to filter the polyelectrolyte from solution [14].

The aim of this study is to evaluate the removal efficiency of Zinc and Copper ions using PAA, with average molecular weight (100 kDa) as polyelectrolyte chelating agent. The effect of transmembrane pressure, polyelectrolyte concentrations, pH and ionic strength on the process efficiency, related to the retention of Cu(II) and Zn(II), is investigated in this paper. Selectivity was studied using a solution containing the two metal ions.

2. Experimental

2.1. Materials

Poly(acrylic acid) (PAA) was used in this study. Its molecular weight is chosen equal to 100,000 Da in order to assure that no polymer passes through the membrane during the filtration. The Cu^{2+} and Zn^{2+} ions are introduced in the solution as Copper chloride ($CuCl_2\cdot 2H_2O$) and Zinc chloride ($ZnCl_2\cdot 2H_2O$). In the study of the effect of pH and ionic strength, sodium hydroxide, chloride acid, sodium chloride and sodium sulfate were respectively used. All chemicals used are of analytical grade supplied by Sigma Aldrich.

Solutions were prepared with ultrapure water produced by Milli-Q gradient unit (Millipore).

Copper and Zinc concentrations in feed and permeate streams were measured by means of atomic absorption spectrophotometry AAS using the Analytical Jena AAS vario 6 atomic absorption spectrophotometer.

2.2. Equipments

Ultrafiltration experiments were carried out with a tangential cell system (Minitan-S Millipore). The inlet flux was held constant (up to 0.5 m s^{-1}) and a transmembrane pressure was varied from 1 to 3 bar by restricting the outlet tube. Regenerated cellulose membrane with molecular weight cut-off (MWCO) of 10 kDa and an effective filtration area of 50 cm^2 were used (PTGC OMS 10, Millipore).

Before each experiment, membrane was conditioned by totally recycling ultrapure water as the permeate and the retentate. A steady state characterized by a stable flow with respect to permeate quality is reached in few minutes under suitable temperature and pressure conditions.

A schematic of the experimental ultrafiltration system is shown in Fig. 1.

3. Theoretical background

Permeate flux was calculated using the following equation:

$$J_v\left(Lh^{-1}m^{-2}\right)=\frac{V_p}{S.t} \quad (1)$$

where V_P is the volume of permeate, S is the effective membrane area and t is the time.

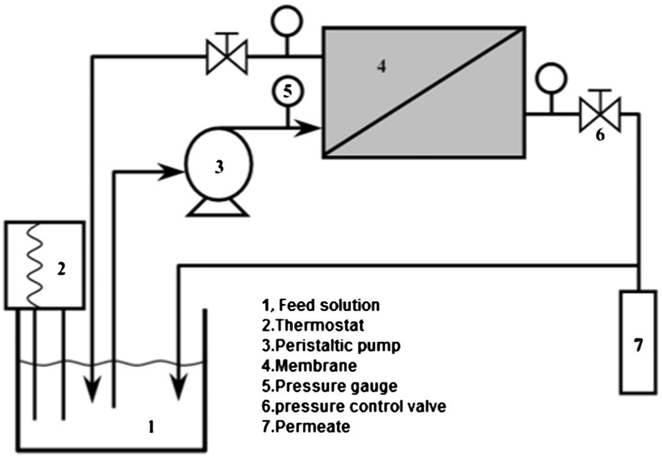

Fig. 1. Experimental ultrafiltration.

The pure water flux through membrane at one particular transmembrane pressure is usually expressed with Darcy's Law:

$$J_w=\frac{\Delta P_m}{\eta R_m}=L_p^0\Delta P_m \quad (2)$$

L_p is the permeability of solvent. It depends on the solvent viscosity (η), and morphologic characteristics of membrane (porosity, specific surface, etc.). ΔP is the transmembrane pressure and R_m is the hydraulic membrane resistance.

$$J_v=\frac{\Delta P_m}{\eta.R_{tot}}=L_p\Delta P_m. \quad (3)$$

The calculation of R_m and R_{tot} values can be made using the above equations and flux data, where R_{tot} is the total filtration resistance (m^{-1}) [15].

To evaluate the filtration efficiency in removing Zinc and Copper ions from the feed solution, we used the observed retention defined as:

$$R(\%)=\left(1-\frac{C_p}{C_f}\right)100 \quad (4)$$

where C_p and C_f are respectively the concentrations of the metal ions in the permeate and the feed.

Low-molecular-weight substances can be bound to macromolecules by intermolecular force, coordinate or ionic bond or a combination of both. The reaction between the polymeric agent (PAA), the proton (H^+) and the metal cation (Cu^{2+} and Zn^{2+}) is represented by the following equilibrium equations.

The reaction of the complex formation between metal ions (Cu^{2+}, Zn^{2+}) and acid groups of macromolecular ligands (PAA) can be written in a simplified form as:

$$2\,RCOOH+M^{2+}\rightarrow(RCOO)_2\,M+2\,H^+ \qquad \beta_2 \quad (5)$$

$$RCOOH\rightarrow RCOO^-+H^+ \qquad K_a \quad (6)$$

$$2\,RCOO^-+M^{2+}\rightarrow(RCOO)_2\,M \qquad K_2 \quad (7)$$

where M^{2+}symbolizes the metal ions (Cu^{2+} and Zn^{2+}).

4. Results and discussions

4.1. Pure water permeability of membrane

The water permeability (J_W) of the membrane was measured to characterize the membrane.

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