



Sorption and filtration of Hg(II) ions from aqueous solutions with a membrane containing poly(ethyleneimine) as a complexing polymer

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ABSTRACT

The performances of a PVA/PEI complexing membrane for the removal of Hg(II) from aqueous solutions were investigated by performing sorption and filtration experiments. This membrane, that was previously shown to ensure efficient sorption of the heavy metal ions Pb(II), Cd(II) and Cu(II) at pH 5, presented a higher affinity for Hg(II) at pH 2.5. The sorption equilibrium was satisfactorily represented by the Langmuir model. In view of possible application to the treatment of industrial wastewaters, the effects of parameters such as pH, temperature, water hardness, and the presence of complexing chloride anions were investigated. The effect of increasing temperature was not straightforward: the complexation equilibrium constant decreased, but the mass of mercury sorbed increased, probably due to the higher mobility of the polymer chains that made internal sites available for complexing mercury. The maximum retention capacity of the membrane was 311 mg Hg g⁻¹. Also, operating at large calcium or chloride concentrations was not detrimental to the membrane performances. For regeneration of the membrane, a 0.05 M solution of EDTA is recommended on the basis of limited performance loss. When used in the filtration mode, the elimination ratio of Hg(II) was close to 99%.

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1. Introduction

Heavy metal pollution represents an important environmental problem due to the toxic effects of metals even at very low concentrations. The accumulation of heavy metals throughout the food chain leads to serious ecological and health problems [1]. Mercury is universally recognized as one of the most toxic, dangerous and non-biodegradable inorganic pollutants present in aquatic systems [2–8]. Mercury is present in many products of common use (e.g. thermometers, batteries, medical drugs, etc.). Hg ions are generated in wastewater by several industrial processes (e.g. chloro-alkali production, pharmaceutical and cosmetic preparations, combustion of fossil fuels, electrical and electronics manufacturing plants, metal processing, metal plating, metal finishing, pulp and paper industries, etc.), resulting in contamination of aquatic systems [2–5,7,8]. In natural waters, mercury occurs under various forms including elemental mercury (Hg⁰), ionic mer-

cury (Hg⁺, Hg²⁺), and methylated mercury [CH₃Hg⁺, (CH₃)₂Hg] [6].

Hg ions are known to bind proteins and to mainly affect the renal and nervous systems [2,5,9]. Because of its high toxicity, the European Union considers mercury ions as a priority hazardous pollutant and has defined a maximum permissible concentration of total mercury as low as 1 µg L⁻¹ for drinking water and 5 µg L⁻¹ for wastewater discharge [8]. Moreover, by European Directive 2000/60/CE, the European Union states the cessation or phasing out of discharges, emissions and losses within 2020. Before this deadline, the complete remediation of polluted water bodies must be fulfilled.

In this context, research on the removal of heavy metals, and especially mercury, from aqueous solutions has grown rapidly [2–10]. Conventional treatment techniques are precipitation–neutralization, coagulation, reduction, solvent extraction, ion-exchange, adsorption [2], electro-deposition, foam-flotation, cementation, and complexation/sequestration [5,8–10]. Membrane processes are probably the most attractive and efficient methods [11]. The use of membrane technologies (ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)) for water treatment allows reduction of costs and overall consumption of energy [12]. Among the membrane techniques, those based on complexation show a high efficiency [2,3]. The use

Abbreviations: AAS, atomic absorption spectroscopy; DBE, 1,2-dibromoethane; PAUF, polymer-assisted ultrafiltration; PEI, poly(ethyleneimine); PVA, poly(vinyl alcohol); s-IPN, semi-interpenetrating polymer network.

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of chelating polymers would be advantageous in environmental applications because metal uptake would take place in the bulk of the membranes and not only at their surfaces [2,13,14].

The subject of this work was the use of UF membranes in which a complexing water-soluble polymer is integrated, in order to group the complexation and filtration steps in a single operation. Thus, the membranes would retain the metal ions during the filtration. This technique is an improvement of the method named polymer-assisted ultrafiltration (PAUF) [5,14,15], which consists in adding a complexing water-soluble polymer that binds with the cations to be removed, forming complexes of large size that are subsequently retained by an UF membrane. The first advantage of complexing membranes is that the amount of polymer used is much lower than in PAUF. A second advantage is that the method should retain the selectivity of PAUF, if provision is made for the appropriate choice of the complexing polymer.

Because the complexing polymer is water-soluble, it must be immobilized in the membrane for application to aqueous solutions. For this goal, the semi-interpenetrating polymer network (*s*-IPN) technique was employed. In this technique, chains of the complexing polymer are entrapped in a crosslinked polymeric matrix. Considering previous work performed in the laboratory [16], we selected the use of a poly(vinyl alcohol) (PVA) matrix crosslinked by a treatment with gaseous 1,2-dibromoethane (DBE).

A large number of polymeric supports incorporating a variety of metal-chelating ligands including polyethyleneimine (PEI), acrylamide and amino acids have been investigated [5,11,14,17–25]. Many reports have shown PEI to be a specific ligand for various metal ions [2,13–15,26–28], and this ligand has been reported to retain interesting complexing ability in a PVA matrix [29].

In the present study, the characteristics of a PVA/PEI membrane for Hg(II) removal from aqueous solutions were determined. Because real wastewaters exhibit large variability, the effects of pH, mass of membrane, temperature, sorption time, water hardness, ionic strength and initial mercury concentration on the performances of this membrane for the filtration of aqueous solutions were studied. Throughout this paper, the binding of Hg(II) ions with the membrane will be referred to as sorption rather than adsorption, because there is no proof that it takes place only at the membrane surface, and experimental data suggest that at least part of the complexing sites present within the membrane are involved in metal removal. The retention of Hg(II) ions from aqueous solutions was investigated under static conditions, i.e. in batch equilibrium experiments, and also studied under dynamic conditions, i.e. in frontal filtration experiments. Sorption kinetics and isotherms were performed with appropriate modelling. Thermodynamic data were calculated to interpret the results.

2. Experimental

2.1. Chemicals and materials

PVA (99% hydrolysed, $\overline{M}_w = 124,000\text{--}186,000\text{ gmol}^{-1}$) and PEI ($\overline{M}_w = 70,000\text{ gmol}^{-1}$) in 50 wt/v% aqueous solution were provided by Sigma–Aldrich. 1,2-dibromoethane (DBE) (99%) (Sigma–Aldrich) and ethylenediaminetetraacetic acid (EDTA) (99%) (Labosi) were used without further purification. All other chemicals were supplied by Sigma–Aldrich as used as received.

The solutions of Hg(II) ions were prepared by dissolving weighed amounts of mercury nitrate (Aldrich) in purified water (Millipore). The pH was measured with a Tacussel LPH-230T pH-meter fitted with a combined glass electrode.

Atomic absorption spectroscopy (AAS) was performed with a Spectra AA 10/20 flame atomic spectrometer from Varian, Mulgrave, Australia. A mercury standard solution (1% wt/v in HNO₃) from Sigma–Aldrich was used for the calibration of the spectrophotometer. All AAS measurements were duplicated and were reproducible within 0.4% accuracy. The wavelength value for mercury measurements was 253.5 nm.

The preparation and structural characterization of the membranes were described elsewhere [16,30].

2.2. Sorption experiments

Membrane samples (5 cm × 5 cm) were weighed (*m*) when dry. They were placed into aqueous solutions of Hg(II) (volume *V*, initial concentration *c*₀) previously brought to the desired pH (±0.1 units) by adding either NaOH or HNO₃. In all experiments, contact between the membrane and the solution was ensured for 24 h, time necessary for complete equilibration, on a horizontal shaking table (10.4 rad s⁻¹). For kinetic studies, samples of 5 cm³ were withdrawn at known times. The concentrations of these samples and of the solution at equilibrium were determined by AAS. All experiments were performed at room temperature (*T* = 294 ± 3 K).

In order to determine the thermodynamic parameters (enthalpy and entropy) of sorption of Hg(II), batch sorption experiments were carried out at various *T* (288, 298, 318, 328 and 338 K). The temperature was controlled (±1 K) by a thermostated Friocell closet (Fisher Bioblock Scientific). Samples of the PVA/PEI membrane (*m* = 100 mg) were equilibrated during 24 h with 50 mL of Hg(II) solutions (*c*₀ = 100–2000 mg L⁻¹) at pH 2.5.

For the study of the effect of water hardness, samples of the same membrane (*m* ≈ 100 mg) were immersed in stirred solutions (*V* = 50 cm³) of Hg(II) (*c*₀ = 100 mg L⁻¹) containing Ca(II) ions at different concentrations (0–200 mg L⁻¹). After 24 h, the solutions at equilibrium were analysed for Hg(II) by AAS.

The effect of chloride ions was studied by carrying out a series of sorption isotherms at constant Hg(II) ion initial concentration (*c*₀ = 100 mg L⁻¹) in solutions (*V* = 50 cm³) containing 0.005, 0.05, 0.5 and 10 g L⁻¹ NaCl concentrations.

2.3. Regeneration experiments

Five cycles of sorption–desorption were carried out on a single membrane sample (*m* ≈ 100 mg). The times were 24 h for sorption and 24 h for desorption. For the sorption step, the membrane was immersed in a stirred Hg(II) solution (*c*₀ ≈ 100 mg L⁻¹, pH 2.5, *V* = 50 cm³). Desorption of Hg(II) ions was performed with 50 cm³ of 0.05 M HCl, 0.05 M HNO₃ and 0.05 M EDTA solutions. The membrane containing Hg(II) ions was placed in the desorption medium and stirred at 100 rad s⁻¹ at 273 K. The amounts of Hg(II) liberated during each desorption step in the desorption medium were determined by AAS.

Desorption kinetics were studied by recovering the membrane (*m* ≈ 100 mg) after sorption of Hg(II) ions (*c*₀ ≈ 100 mg L⁻¹, pH 2.5, *V* = 100 cm³) for 24 h, wiping and immersing in an aqueous solution of 0.05 M EDTA (*V* = 100 cm³). Aliquots of the EDTA solution were withdrawn at known time intervals and analysed.

2.4. Filtration experiments

The filtration experiments were performed using the thermostated (273 ± 0.5 K) two-chamber cylindrical cell previously described [30]. The membrane was weighed (*m*) when dry and then swollen in water before being placed in the cell (active area, 28.3 cm²). The upstream chamber (*V* = 450 cm³) was filled with 400 cm³ of aqueous solution containing the Hg(II) ions to

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