Donnan dialysis based separation of gold(III) from electronic waste solutions using an anion exchange pore-filled membrane

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ABSTRACT

Donnan dialysis technique was employed for the recovery of Au(III) from aqua regia solutions of electronic waste containing low concentrations of Au(III) in the presence of much higher concentrations of Cu(II) and Ni(II). The anion exchange pore-filled membrane was synthesized using in-situ photo-polymerization with polypropylene as the host membrane and (3-acrylamidopropyl)trimethyl ammonium chloride and (3-acryloxy-propyl)trimethoxysilane as the monomer and spacer, respectively. Photo-polymerization was carried out with ethylene glycol dimethacrylate as the cross-linker and 2,2-di-methoxy-2-phenyl acetophenone as the UV-initiator. The transport of Au(III) through this anion-exchange pore-filled membrane was studied using a two compartment cell where the receiver solution contained NaCl as the stripping reagent. Cu(II), which is the dominant metal ion in electronic waste solutions, did not interfere with the transport of Au(III) even at Au(III): Cu(II) mass ratios of up to 1:500. Gold from 100-fold diluted electronic waste solutions in aqua regia was successfully recovered (96.3%) after 4 cycles of Au(III) transport while at the same time insignificant fractions of the dominant metals in the electronic scrap (Cu and Ni) were transported. This study shows that Au(III) can be selectively recovered from diluted aqua regia solutions of electronic waste based on the proposed Donnan dialysis process.

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1. Introduction

Gold is a precious metal and apart from being used in jewelry, it has a large number of applications in the chemical, electrical and electronic industries. In the chemical industry, gold is pre-dominantly used as a catalyst. In the electrical and especially in the electronic industries, gold is used for gold plated contacts owing to its high electrical conductivity and outstanding corrosion resistance [1]. With increasing demand for electrical and electronic devices, there is a continuously growing amount of electronic waste. This waste can be viewed as an important secondary source of gold. This precious metal is generally leached from electronic waste using different leaching agents such as cyanide, aqua regia, thiourea, or thiosulfate [2]. However, due to the nonselective nature of these leaching agents and the presence of copper and nickel in relatively high concentrations, gold is generally accompanied in the leachate by large amounts of these two base metals. Other methods reported in the literature for gold separation employ processes such as cementation, solvent extraction,

adsorption, biosorption, or ion-exchange [2]. Among them ion-exchange separation deserves special attention owing to its simple and cost effective nature and the availability of various ion-exchange resins which are suitable for the separation of gold [3–9]. However, there is a limited amount of research on the separation of Au(III) using ion-exchange membranes. Ion-exchange membranes have been used extensively in separation processes involving electrodialysis and Donnan dialysis. Donnan dialysis is a technique which can be used for separation of ions based on the difference in salt concentrations on the two sides of the ion-exchange membrane. This technique has been implemented in several eco-friendly applications as described by Sarkar et al. [10], which include preconcentration of nitrate [11], copper [12–15], nicke1 [16,17], cobalt [16], lead [18], and uranium [19] in the presence of other ionic species. Pyrzynska [20] used Donnan dialysis involving a cation-exchange membrane for preconcentration of Au(III) prior to its measurement by atomic absorption spectrometry (AAS). Doker et al. [21] used poly((N-(hydroxymethyl)methacryl-amide)-1-allyl-2-thiourea) hydrogels for the recovery and preconcentration of Au(III) from its solutions.

In addition to commercially available ion-exchange membranes (e.g. Selemion), ion-exchange membranes can be prepared in-house by covalently anchoring the required functional groups onto

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the polymer chains of commercially available polymer membranes [22]. Such fixed-site membranes (FSM) or pore-filled membranes (PFM) have been examined for their ability to provide facilitated transport of target ions [23–26]. This class of membranes is prepared by grafting required monomers within the pores of a robust microporous host membrane by using a free radical mechanism. The microporous host membrane provides mechanical strength that mitigates the impact of osmotic forces. The main advantage of pore-filled membranes over supported liquid membranes (SLM) and polymer inclusion membranes (PIM) is their higher stability owing to the chemical immobilization of the ion-exchange groups within the polymer matrix.

In the present work, a pore-filled anion exchange membrane was synthesized using in-situ photo-polymerization. The transport of Au(III) across this membrane was studied using NaCl as the stripping agent in the receiver solution. The influence of the NaCl and Au(III) concentrations in the receiver and feed solutions, respectively, and the solutions' pH on the transport of Au(III) across the newly developed membrane was investigated. Also, the possibility of separating Au(III) from its acidic solutions containing Cu(II) in mass concentrations of up to 500 times higher than that of Au(III) was explored. The newly developed membrane was applied to the selective separation of Au(III) from an aqua regia solution of electronic waste containing high concentrations of Cu(II) and Ni(II).

2. Experimental

2.1. Materials

Microporous poly(propylene) (PP) membranes (Accurel®PP 1E: pore-size=0.1 μm, Membrana GmbH, Germany) were used for the preparation of pore-filled membranes. The monomer - (3-acrylamidopropyl)trimethyl ammonium chloride (APMAC), spacer - (3-acryloxypropyl)trimethoxysilane (APTMS), crosslinker - ethylene glycol dimethacrylate (EGDMA), and UV-initiator - 2,2-dimethoxy-2-phenyl acetophenone (DMPA) were purchased from Sigma-Aldrich and used as received. N,N-dimethylformamide (DMF) and methanol were purchased from Merck. Analytical grade chemicals (NaCl, HCl, HNO$_3$,) from S. D. Fine Chemicals (India) and deionized water (18 MΩ cm^{-1}, Gradient A-10 model, Milli-Q, USA) were used in all experiments. Au(III) solutions used in the transport experiments were prepared from NaAuCl$_4$ (Sigma-Aldrich). Au(III) calibration standards were made from a 1000 mg L^{-1} Au(III) standard solution (BDH Spectrosol).

2.2. Synthesis of the anion-exchange pore-filled membrane

The polymerizing solution was prepared by dissolving the monomer APMAC, spacer APTMS in a 1:1 mol ratio and the crosslinker EGDMA (5 mol% of the monomer) in a 1:1 (v/v) mixture of DMF and methanol. The chemical structures of the monomer, spacer and crosslinker used in the preparation of the pore-filled membrane are shown in Fig. 1.

The grafting was done by in-situ photo-polymerization using UV radiation. The choice of this procedure was based on the fact that UV radiation leads to uniform polymerization throughout the polymer matrix unlike plasma grafting and does not affect the host membrane unlike gamma radiation and e-beam induced polymerization [27,28]. Also, UV radiation grafting requires less stringent conditions for obtaining pore filling unlike heat initiator induced polymerization [29]. For UV induced polymerization, the minimum amount of UV-initiator DMPA required to initiate bulk polymerization (i.e. 1 wt%) was added to this solution. The spacer APTMS was used to minimize dimensional changes in the membrane in its wet and dry states (< 15%). The host microporous membranes (6 × 6 cm^2 area) were immersed in a polymerizing solution overnight. Excess of polymerizing solution adhering on the membrane surface was removed. These solution filled membranes were sandwiched between two transparent polyester sheets to prevent any possible loss of the solution filling the pores. Finally, the sandwiched membranes were exposed to 365 nm UV light for a period of 15 min in a multi-lamp photoreactor (model No. HML-SW-MW-LW-888, Heber Scientific) having six UV lamps (8 W each) arranged in a circle. After exposure in the photoreactor, the membranes were washed thoroughly with hot DMF, methanol and deionized water to remove unpolymerized components. A membrane sample was dried under vacuum at 60 °C for 4 h before weighing. The percentage of crosslinked gel anchored in a host membrane (grafting yield) was determined gravimetrically using the following equation:

$$\% \text{ Grafting yield } = \ (m_f - m_i) \times 100/m_i \tag{1}$$

where m_i and m_f are the dry masses of the nascent and final membrane, respectively.

2.3. Membrane characterization

2.3.1. Ion-exchange capacity

The membrane was first converted completely to the chloride form by immersing it in a 0.1 mol L^{-1} NaCl solution. This was followed by equilibrating it with a sodium nitrate solution with a concentration sufficiently high that it was not affected appreciably by the ion-exchange process. The concentration of the chloride ion in the sodium nitrate solution was measured by ion chromatography (IC, DX 120 ion chromatograph, Dionex, USA). Measurements were performed in triplicate and excellent repeatability was observed.

2.3.2. Morphology

The change in morphology of the membrane before and after grafting was observed using scanning electron microscopy (SEM, Quanta 200 microscope, FEI, USA). Measurements were carried out at 20 kV in high vacuum. The resolution of this instrument as stated by the manufacturer is between 1.2 nm and 3.0 nm at 30 kV and 1 kV, respectively.
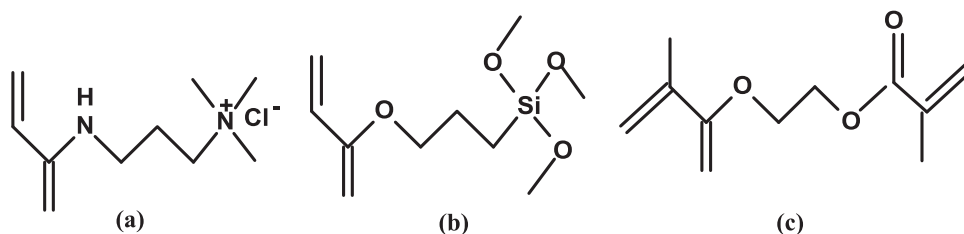

Fig. 1. Chemical structures of APMAC (a), APTMS (b) and EGDMA (c).