



## Poly-thiosemicarbazide membrane for gold recovery



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### ARTICLE INFO

#### Article history:

Received 25 March 2014

Received in revised form 14 August 2014

Accepted 14 August 2014

Available online 6 September 2014

#### Keywords:

Gold recovery

Membrane adsorber

Poly-thiosemicarbazide

Polymeric membrane

Metal-ion capture

### ABSTRACT

A novel polymeric membrane adsorber with a high density of adsorption sites that can selectively capture Au(III) ions, is proposed as an efficient alternative to recover gold from dilute solutions. Poly-thiosemicarbazide (PTSC), a polymer that contains one chelate site per monomeric unit, was used to fabricate the membranes. This polymer can be easily processed into membranes by a phase inversion technique, resulting in an open and interconnected porous structure suitable for high flux liquid phase applications. This method overcomes the usual low capacities of membrane adsorbents by selecting a starting material that contains the adsorption sites within it, therefore avoiding the necessity to add an external agent into the membrane matrix.

The resulting mechanically stable PTSC membranes can operate in a pressure driven permeation process, which eliminates the diffusion limitations commonly present in packed column adsorption processes. This process can selectively recover 97% of the gold present in a solution containing a 9-fold higher copper concentration, while operating at a flux as high as 1868 L/m<sup>2</sup> h. The maximum gold uptake measured without sacrificing the mechanical stability of the membrane was 5.4 mmol Au/g. Furthermore the gold can be easily eluted from the membrane with a 0.1 M thiourea solution and the membrane can be reused for at least three cycles without any decrease in its performance. Finally, the ability of this membrane for recovering metals from real-life samples, like seawater and tap water, was tested with promising results.

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### 1. Introduction

Growing demand for gold and high market prices motivate the development of technologies to recover the precious metal from secondary sources, like scrap (electronic, jewelry, dental), industry waste (spent catalyst, alloy scraps, copper anode slime, mine tailing), and seawater [1]. To put into perspective how realistic it is to consider gold recovery and recycling as a future source of gold, Ogata et al. reported that cellular phone scrap contain around 200 g of gold per ton of scrap, while the gold present in the gold ores used in mining contains between 5 and 30 g of gold per ton of ore [2].

A hydrometallurgical process, the preferred method for recovering gold from secondary sources, consists of three main steps: (i) leaching to extract the gold and bring it into solution, (ii) selective recovery of the precious metal by precipitation, ion exchange, solvent extraction or adsorption, and (iii) refining it to improve the purity. The second step, the bridge between the leaching process and the final metal-winning process, is the key step to make

hydrometallurgy a more efficient process [3]. Concentrating the gold from dilute solutions to appropriate concentrations for the refining process is a challenging endeavor. The leaching solution containing the dissolved metals is quite toxic if cyanide is used as the leaching agent, so technologies are moving away from this technique. Another alternative is the use of halides at low pH's as leaching agents. The most common halide solution for this purpose is called "aqua regia", which is a hydrochloric acid/nitric acid mixture with a ratio of 3:1. Usually the gold concentration in the leaching solution is low and several other unwanted metal ions are present. Especially copper can be found in large excess.

Out of all the possible processes for concentrating the gold, special attention is directed to the use of solid adsorbents, because they are easy to handle and efficient and they produce less amounts of secondary waste compared to other processes. The ideal adsorbent is one that can selectively adsorb gold very fast, with a high capacity and is easy to regenerate.

Several adsorbents with impressive gold uptake capacities ranging from 4 mmol Au/g to more than 40 mmol Au/g can be found in literature [2,4–9]; the time they take to reach their maximum uptake capacity varies from 5 h up to more than 300 h. Capacity is an important characteristic for an adsorbent; however,

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high adsorption rates are crucial for making the process economically viable. To achieve this, the film and pore diffusion limitations must be eliminated or reduced to a great extent [10]. Lam et al. grafted organic amine groups to a mesoporous silica support, the easy access to the adsorption sites through the large cylindrical pores present in the silica allowed this adsorbent to reach equilibrium in just 30 min with a loading of 1.4 mmol Au/g. Similarly Huang et al. immobilized bayberry tannin into a mesoporous silica support resulting in fast adsorption rates with a maximum uptake of 2.21 mmol Au/g. Both of these configurations achieve high adsorption rates, but at the cost of reducing the specific active area available for adsorption.

Tuning the morphology of the adsorbent plays a key role in reducing the pore diffusion limitation. However, this must be done in such a way as to retain the available specific active surface area, so the capacity is not diminished. Membrane technology can be used to reduce or even eliminate the pore diffusion limitation; when a solution is forced to pass through a porous membrane the molecules travel by convective flow through the membrane pores, eliminating the usually present long diffusion time that the molecules or ions take to reach the adsorption sites inside the pores [11]. Adsorption sites can be incorporated inside the membrane pores by different methods: (i) dispersion of adsorbent particles in the membrane matrix, known as mixed matrix membranes (MMMs) [12,13]; (ii) incorporation of a liquid carrier in the membrane matrix by either filling the pores of the membranes with the carrier, known as supported liquid membranes (SLMs), or by mixing the liquid carrier with the polymer solution before membrane casting, known as polymer inclusion membranes (PIMs) [14–18]; (iii) functionalization of polymeric membranes to incorporate chelate-forming groups, ion-exchange groups or affinity ligands [19–23]; (iv) fabrication of membranes from blends between membrane-forming polymers and polymers containing the appropriate functional groups for the adsorption process [24–28]; (v) fabrication of membranes from metal-complexing polymers [29–31]. The latter enables the highest concentration of adsorption sites per membrane volume, because each monomeric unit has at least one adsorption site. It is also the easiest method to fabricate a membrane adsorber and the most scalable one, because it involves the least amount of production steps and the membranes can be fabricated with current industrial manufacturing facilities. In spite of this, this method is not common because it is challenging to find a metal-complexing polymer that has both: good film-forming properties to fabricate a mechanically stable membrane that can withstand the pressure-driven permeation process; and monomeric units with adsorption sites that can form strong chemical complexes with the desired adsorbate.

In this work we propose the use of poly-thiosemicarbazide (PTSC) for the fabrication of asymmetric membranes to recover gold(III) from a solution by permeating the solution through the membrane. Each monomeric unit of this polymer contains two thiosemicarbazide groups that form a chelate site. This site contains several groups that can contribute to the formation of complexes with metal ions; the structure of PTSC is illustrated in Fig. 1. Campbell and Tomic first synthesized poly-thiosemicarbazide in 1962, in their work they demonstrated that this polymer forms chemical complexes with iron, nickel, silver, copper, mercury and lead

[32,33]. Further tests from our group demonstrated its ability to form strong complexes with gold ions, even at extreme acidic conditions. We manufactured this polymer for the first time into a porous asymmetric membrane providing the possibility of performing permeation experiments, in which contact of the gold ions with the chelating group of the polymer is promoted, and all the diffusional limitations of the adsorption process are reduced or eliminated.

## 2. Materials and methods

### 2.1. Membrane fabrication and characterization

Poly-thiosemicarbazide was synthesized according to literature by the reaction of N,N'-diaminopiperazine and methylenebis(4-phenylisothiocyanate) in dimethyl sulfoxide (DMSO). PTSC membranes were prepared by non-solvent induced phase separation (Fig. 2). First a solution of 15 wt% PTSC, 10 wt% 1,4-dioxane and 75 wt% DMSO was stirred for 5 h and allowed to rest for another 5 h until all the air bubbles had escaped. Then a 250- $\mu\text{m}$ -thick polymer solution film was cast on a glass plate. The glass plate was then immersed in a non-solvent bath (water) at room temperature for at least 12 h. Finally, the membranes were cut in circles with diameter of 2.5 cm and an average dry weight of 14.3 mg for the permeation experiments and in squares of 1 cm<sup>2</sup> for the batch experiments. The membranes were stored in a water/ethanol solution until use.

Scanning electron microscope (SEM) images of the membrane surface and cross-section were taken with a FEI Nova NanoSEM. Cross-section samples were prepared by fracturing the membranes right after having been exposed to liquid nitrogen for about 2 min. Surface and cross-section samples were attached to an aluminum support with a conductive aluminum tape and coated with a thin film of Iridium to reduce charging during imaging.

### 2.2. Batch adsorption experiments

Three gold solutions (100, 500 and 1000 ppm Au) were prepared by diluting a mother solution of 1000 mg of gold per liter of 10% HCl solution obtained from Perkin Elmer atomic spectroscopy standards with a 10% HCl aqueous solution. This solution was chosen for all the experiments reported in this work. The concentration of HCl was kept at 10% in all the experiments.

PTSC squares of 1 cm<sup>2</sup> were dried at 45 °C for 24 h and weighted afterwards. Each of the membrane squares was immersed in one of the three previously prepared gold solutions. The solutions were in constant agitation via a shaker and aliquots of 0.2 ml were taken at certain time intervals to measure the progression of gold adsorption. The gold solution aliquots were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian Inc. 720-ES Inductively Coupled Plasma-Optical Emission Spectrometer. All the experiments were done at room temperature unless other temperature is specified.

### 2.3. Dynamic adsorption experiments

For all these experiments PTSC membrane circles with a diameter of 2.5 cm were used. Three circular membranes were dried under vacuum at 45 °C for 24 h and weighted to obtain an average weight value. The permeation experiments were done in a Millipore Stirred Cell model 8010 with an active membrane area of 4.1 cm<sup>2</sup>, a maximum process volume of 10 ml and a hold-up volume of 0.2 ml. Pressurized air was used to force the solutions through the membrane. A non-woven polyester circle of the same size of the membrane was used below the membrane to provide mechanical support during the permeation experiments; the

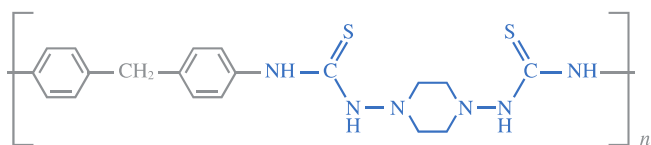


Fig. 1. Poly-thiosemicarbazide structure.

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