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Polypyrrole-Coated Electrospun Nanofibre Membranes for Recovery of Au(III) from Aqueous Solution

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Abstract

In this paper, for the first time, polypyrrole-coated electrospun nanofibre mats have been used as separation membranes to electrolessly recover Au from aqueous $[Au(III)Cl_4]^-$ solutions, based on a continuous-flow membrane separation process. With a $[Au(III)Cl_4]^-$ solution passing through the nanofibre membrane, the Au(III) ions were converted into elemental Au. The gold recovered was deposited on the nanofibre membranes in the form of Au particles, as confirmed by EDX measurements. It has been found that the polypyrrole-coated electrospun nanofibres are good candidate membrane material for the recovery of Au, and the recovery efficiency is affected by the membrane thickness, the permeate flux rate and the initial $[Au(III)Cl_4]^-$ concentration.

KEYWORDS: Electrospun nanofibres, Au recovery, polypyrrole, vapour polymerisation, membrane separation.

1.   Introduction

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As a precious metal, gold has been extensively used in jewelry and many high-technology areas. The demand for gold has been increasing over the last decade, especially due to the explosive production of electronic devices such as computers. Special interest has been devoted to developing highly efficient and environment-friendly methods to recover gold not only from its ore, but also from mine tailings and industrial wastes. Recycled gold from electronic scraps and leaching residues has also been an important gold source. In addition, oceans contain huge quantities of gold. However, the lack of profitable technique to recover trace gold (2~50ppt) from the seawater has left this precious resource undeveloped so far.

Most techniques to recover gold ions from aqueous solution involve an adsorption process in which $[Au(III)Cl_4]^-$ in acidic solution, or $[Au(I)(CN)_2]^-$ in alkali solution, is adsorbed typically by a powder-like adsorbent and spontaneously reduced to elemental Au. For example, activated carbon has been used to recover gold from leaching solution containing high concentrations of ionic gold for more than 30 years. Bio-mass of dead alfalfa[1, 2] and hops[3], photo-catalytic ZnO nano powders[4-6] and chicken egg-shell membrane/conjugated chitosan beads[7] have been reported to have potential to recover gold from dilute Au(III) solutions. Also, live alfalfa plants[8], fungus[9, 10] and algae[11-13] are able to collect trace gold ions from water, and accumulate the recovered Au(0), intra- or extra-cellularly, in the form of gold nanoparticles. However, the powder-like absorbents are usually difficult to separate from liquors, and these absorbents are poor in either recovering efficiency or selectivity.

Ion exchange resins[14, 15] can also be used to concentrate gold ions from aqueous solution, and the ion-selectivity has been improved by using a functional resin that bears specific affinity ligands[16, 17]. However, additional processes are often required to elute the adsorbed gold ions from the resin,

and then convert them into elemental Au. Also, the specific ion exchange resins are normally expensive in the preparation.

The recovery of gold by membrane separation technique is very promising as it is easy to operate and energy efficient. Incorporating an efficient Au-recovering membrane technique into a water treatment system, such as wastewater treatment or seawater desalination, will create added-value to the system through collecting trace gold from the gold-containing water. An ideal membrane technique to recover ionic Au from an aqueous solution should be based on a continuous flow membrane process in which the gold ions are converted spontaneously into elemental gold while the solution is passing through the membrane. The separation should have high recovering yield, excellent selectivity, but minimal influence on flux parameters. Also, the Au recovered should be easily gathered from the membrane. However, to our knowledge, a separation membrane showing such characteristics has not been developed to date.

Polymer nanofibres produced by an electrospinning technique[18-26] have shown enormous potential in areas such as tissue engineering scaffolds[27, 28], control release[29], filtration[30], catalysis carrier[31], nano-composites[32, 33], chemical sensors[34-36] and battery separators[37], because the nanofibre mats have high porosity, excellent pore interconnectivity and high surface-to-volume ratio. Electrospun nanofibre membranes have shown excellent filtration efficiency to collect aerosol particles from air, with a low air pressure drop[30]. However, it is not yet established if an electrospun nanofibre mat can be used as separation membrane to recover metal ions, such as gold ions, from solution media.

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To recover gold ions from an aqueous solution, the nanofibre membrane should be chemically reactive and able to reduce Au ions to Au(0), besides its large surface area and excellent permeability. It has been reported[38-40] that conducting polymers, such as polypyrrole (PPy) and polyaniline (PANi), have outstanding ability to reduce gold ions electrolessly into Au(0), because of their unique redox properties. The recovery shows excellent selectivity for $[Au(III)Cl_4]^-$ in acidic solution[41], but the recovery yield is surface-area dependent. The PPy-coated Reticulated Vitreous Carbon (RVC) has demonstrated an enhanced capability to recover Au from dilute solution[42]. However, using a membrane-based conducting polymer to electrolessly recover ionic Au from a continuous-flow solution has not yet been reported in the research literature.

In this paper, for the first time, we demonstrate the concept of using a polypyrrole modified electrospun nanofibre mats as membranes to electrolessly recover $[Au(III)Cl_4]^-$ from continuous-flow aqueous solutions. We have found that the PPy-coated electrospun nanofibres are good candidate membrane material for Au recovery, and the recovery efficiency is affected by the membrane thickness, the flux rate and the initial $[Au(III)Cl_4]^-$ concentration. This work provides a new membrane technique to collect trace Au ions from aqueous water. The reason for not using pure PPy nanofibres as the membrane is because the PPy has poor electrospinning ability.

2. Experimental

2.1. Materials and Measurements

All chemicals and PVdF-HFP were obtained from Aldrich-Sigma. The $[Au(III)Cl_4]^-$ solutions were prepared using deionzed water containing 0.1M HCl. The nanofibre morphology was observed under the scanning electron microscope (SEM, Leo 1530). The ATR-FTIR spectra were recorded with a FTIR spectrophotometer (Bruker Optics). The ESEM and EDX maps were measured using FEI

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Quanta 2000 ESEM, with a magnification roughly at 1600 and using a Si(Li) X-ray detector in the low vacuum mode. The Au(III) concentration was analysed by an atomic absorption spectrometer (Varian, AA140), and the standard deviation was found to be less than 0.1% of the measured value for all the tests. The cyclic voltametry curves were measured in 1.0 M $NaNO_3$ solution, using Ag/AgCl as the reference electrode and a Pt wire as the counter-electrode. The measurement was performed using PowerLab system controlled by the EChem software (ADInstruments) at 200 mV/s of scan speed. The dependency of the pressure drop on flux rate was measured by a pressure gauge (Cole-Parmer, accuracy 0.01bar) using a digital syringe pump (KD scientific) to control the solution flow rate.

2.2. Electrospinning of PVdF-HFP nanofibres

The electrospinning setup consists of a plastic syringe with a metal syringe needle (21 Gauge), a syringe pump (KD scientific), a high voltage power supply (ES30P, Gamma High Voltage Research) and a metal roller collector. The plastic syringe, needle and the syringe pump were fixed on a movable tackle driven by a motor, forming the moveable nozzle system. In electrospinning, the PVdF-HFP solution (14wt% in DMF-acetone 1:1 v/v) was placed into the syringe and charged with 20kV electrical voltage via connecting the syringe needle to the power supply. The grounded electrode was connected to the metal roller, 15cm away from the needle tip. The flow rate of the PVdF-HFP solution was controlled at 1.0ml/hr. During the electrospinning process, the nozzle moved to-and-fro along the axis direction of the metal roller at the speed of 20cm/min, while the metal roller rotated constantly at the speed of 100 rpm. This system is able to produce relatively large ($20\times30cm^2$) and uniform nanofibre mat.

2.3. Vapor-phase polymerisation

The as-spun nanofibre mat was cut into a round disk (diameter 45mm), and mounted as the filter paper with a vacuum filtration assembly (Aldrich, diameter 47mm). About 20ml $FeCl_3$ ethanol solution (5 wt %) was filtered through the nanofibre membrane, with the aid of low vacuum. The ferric-ethanol solution was thus coated evenly onto the nanofibre surface. Further vacuuming the membrane for 10min removed the ethanol from the membrane, leaving a semi-dry $FeCl_3$ layer on the nanofibre surface. The $FeCl_3$-coated nanofibre membrane was then placed into a small chamber filled with pyrrole-saturated nitrogen. After 10 min of exposure to the pyrrole environment at room temperature, the nanofibre membrane was rinsed with water and ethanol, and finally dried at ambient temperature. After the vapour polymerisation, 0.54g of polypyrrole was loaded on each gram of nanofibres.

2.4. Recovery of Au

A PPy-coated nanofibre membrane disk (diameter 10mm) was mounted with a reusable plastic filter holder (13mm, Aldrich). The Au(III) solution in a plastic syringe was fed through the membrane from the inlet of the filter holder, with the flow rate controlled by a digital syringe pump.

3. Results and Discussion

To prepare the PPy-coated nanofibre membrane, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) was used as the substrate material. The PVdF-HFP nanofibre membrane was produced by electrospinning 14wt% PVdF-HFP solution with the applied voltage, spinning distance and flow rate of 20kV, 15cm and 1.0ml/hr, respectively. The scanning electron microscope (SEM) image (**Figure 1a**) indicates that the as-spun nanofibres have good fiber uniformity, with an average fiber diameter of 420±110 nm.

An *in-situ* vapour-phase polymerisation was used to apply a thin coating of PPy onto the nanofibre surface. During the polymerisation process, the nanofibres were first coated with a thin layer of oxidant (ferric chloride), and then placed in a closed chamber filled with pyrrole-saturated nitrogen. After a short exposure to the pyrrole vapour, the nanofibre mat turned black, indicating the presence of PPy on the nanofibres. The whole membrane looked very uniform, without any colour variations and physical defects. **Figure 1b** shows the SEM image of the PPy-coated nanofibres. All the coated nanofibres maintained the fibrous morphology and the surfaces looked smooth, except that some nanofibres were bonded at the fiber-fiber intersections. A possible reason for the formation of the bonding structure is the capillary effect occurring during application of the $FeCl_3$ solution to the nanofibres, so that the extra $FeCl_3$ was adsorbed at these intersections and therefore more PPy was formed in these areas. After the PPy coating, the average fiber diameter was increased to 480±120nm.

The existence of PPy coating layer can be further confirmed by ATR-FTIR spectra (**Figure 2**). After the vapour polymerisation reaction, new vibration bands occurred at 1558~1541, 1090, 1035, 960, 840, 780 and 670cm^{-1}. The band ranging from 1558 cm^{-1} to 1541 cm^{-1} is assigned to the typical skeletal vibration of the pyrrole ring. The bands at 1090 cm^{-1} and 1035 cm^{-1} correspond to the C-C stretching and the in-plane deformation vibration of the pyrrole ring, respectively. The peak at 960 cm^{-1} is assigned to the =C–H out-of-plane vibration, and the bands at 840 cm^{-1}, 780 cm^{-1} and 670 cm^{-1} represent the out-of-plane deformation of the C-H bond.

To estimate the adhesion of the PPy coating on the nanofibre substrate, standard peel-off test for measuring the adhesion of fabric coating (ISO 2411) and pull-off adhesion test (ISO 4624) were tried but without success, because the tests removed nanofibres from the samples, instead of peeling the

PPy coating from the fibre surface. However, intensively rubbing the PPy-coated nanofibre mat by hand left no black substance on the hand, suggesting that the PPy coating had reasonable bonding with the nanofibres and the adhesion was adequate for the membrane fabrication and separation process.

A basic set-up for membrane-based gold recovery includes a PPy-coated nanofibre disk (diameter 10mm) which was mounted inside a plastic filter holder (**Figure 3a**). An aqueous $[Au(III)Cl_4]^-$ solution containing 0.1M HCl was fed via a plastic syringe through the PPy-coated nanofibre membrane, with the flow rate controlled by a digital syringe pump. The permeate solution was collected in 1ml/fraction.

Atomic absorption spectrometer analysis showed that the Au(III) content in the first permeate fraction was reduced considerably, and the content in the subsequent volume-equivalent permeate fractions showed a gradual increase until it reached the original concentration. This result suggested that the Au(III) was removed while the solution passed through the membrane, and the membrane became less effective as more Au(III) solution permeated. The reduced recovery effectiveness was caused by the PPy unit/molecule losing its electro-activity because of the over-oxidation in reducing Au(III) to Au(0)[43]. As shown in **Figure 4,** before the Au collection the PPy-coating showed well-defined reduction and oxidation responses associated with the polypyrrole backbone, while this redox response was decreased considerably after the Au collection.

After the Au(III) recovering process, a thin layer of reddish brown powders was generated on the membrane surface, indicating the formation of Au particles. SEM observation confirmed that solid particles scattered on the membrane surface, with the particle size in the range of 5~10μm (**Figure

3b). The distance between two adjacent particles can be as far as 20µm, but varied depending on the initial Au(III) concentration and the volume of the Au(III) solution permeated. The deposition morphology could come from a complex mass exchange mechanism during the recovery process.

The existence of Au particles on the PPy-coated membrane was further confirmed by the Environmental SEM (ESEM) and the Energy Dispersive X-Ray Spectroscopy (EDX) mapping images. The EDX measurement showed two signals at E = 2.12 and 9.71 keV, ascribable to Au Mα and Lα, respectively, indicating the exact presence of Au element in areas tested. The EDX map of Au (Mα) (**Figure 5b**) shows the Au particles distributing heterogeneously on the nanofibre membrane, with the pattern exactly the same as the white areas shown in the ESEM image (**Figure 5a**). Also, the EDX maps of elements F and Cl are quite similar to each other (**Figure 5c~d**), which confirms the PPy covers the whole surface of the nanofibres. Dark areas found in the F and Cl maps could derive from the Au particles obstructing the penetration of X-ray in the mapping tests.

Figure 6 shows the XPS spectrum of the nanofibres after the Au collection, corresponding to the 4f region of Au. The binding energies of 83.6 and 87.2eV are typical of $Au4f_{7/2}$ and $Au4f_{5/2}$ of zerovalent metallic gold [44]. No higher valence state of Au occurred in the spectrum. This result was verified by comparing with the XPS spectrum of gold reference (99.999% purity) tested under the same condition.

Because the reduction of Au(III) could form an intermediate Au(I) which is soluble in water, the existence of Au(I) ions in the permeate solution was tested via adding concentrated nitric acid into the permeate solution to oxidize the Au(I) ions back to Au(III) and subsequently measuring the increase of Au(III) content. However the atomic absorption test revealed no change in the Au(III)

concentration after the oxidation treatment. This suggested that the PPy has directly and completely reduced the Au(III) to elementary Au(0).

Reasons for the collection of metallic gold only on the nanofibres membrane were that the gold ions were soluble in water, and the trace Au(III) ions absorbed on the membrane could be reduced to Au(0).

Based on the Au(III) concentration change, the Au recovery yield can be calculated as:

$$\eta(\mathrm{Au})(\%) = \frac{C_0 - C_1}{C_0} \times 100\%$$

Here, the C_0 and C_1 are the Au(III) concentrations of the original solution and the permeate fraction, respectively. It was found that the recovery yield varied in different permeate fractions. With the increase in the number of permeate fractions, recovery yield decreased gradually (**Figure 7**).

Also, the flow rate, the membrane thickness and the initial Au(III) concentration influenced the recovery yield. With the decrease in the flow rate, the Au recovery yield increased (**Figure 7a**). The membrane thickness has been found to have a significant influence on the recovery yield (**Figure 7b**). When the membrane thickness was less than 300μm, the Au recovery yield was relatively low. However, when the membrane thickness was larger than ~500μm, the Au recovery yield reached a very high level. In addition, the recovery yield showed a slight decrease when the initial Au(III) concentration changed from 207.00 to 6.42ppm (**Figure 7c**). A possible reason for this decrease in the recovery yield is that the mass transfer between the solution and membrane surface has lower efficiency in a diluter Au(III) solution.

When a nanofibre membrane with a thickness of 560μm was used to treat 207ppm Au(III) solution with the flow rate at 1ml/min (flux 84 mL·hr^{-1}·cm^{-2}), from the start of recovery until the loss of membrane's recovering capability, the membrane disk (diameter 9.5mm) collected 8.81mg Au(0) from 64ml solution with an overall recovery yield of 66.5%. However, under the same collecting conditions, the membrane of 280μm thickness was able to recover 4.6mg gold from 34ml solution (65.4% recovery yield), even though it showed a relatively low recovery efficiency at the initial fractions (**Figure 7b**). By comparison, a conventional textile coated with PPy took 7 days to recover Au(III) from water, though the recovery yield was higher than that of the nanofibre membrane[45].

During the recovery process, the pressure drop between the two sides of the membrane is affected by the flux and the membrane thickness. With the increase in flux rate, a linear increase in the pressure drop was observed for all membranes used (**Figure 8**). Also, a thicker membrane generated higher pressure drop. However, the pressure drop was typically at a low level. For the membrane of thickness 560μm, a solution flowing through it with 84 mL·hr^{-1}·cm^{-2} flux rate resulted in a pressure drop as low as 0.9bar.

In addition, the content of organic substance in the permeate solution was measured based on the Total Organic Carbon (TOC) test, but the content was beyond the lowest limit of the instrument's detecting ability. It suggested that the polypyrrole did not degrade into small molecules and dislodge from the nanofibre surface during the Au recovery, and therefore would not lead to secondary pollution to the permeate solution.

4. Conclusions

A conducting polymer-coated electrospun nanofibre membrane has been produced successfully via an *in-situ* vapour phase polymerisation process, and the treated nanofibre mat has shown great potential in the recovery of ionic Au from acidic aqueous solution. The recovery yield is dependent on the membrane thickness, the solution flux rate and the initial Au(III) concentration. Higher recovery efficiency can be achieved by using a thicker nanofibre membrane or reducing the solution flux rate. A relatively low pressure drop is generated during the recovery process. The concept of applying a functional coating onto nanofibres can also be used to recover other metal ions, such as heavy metal ions, from water. This technology may have great potential for water purification.

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