

Adsorption of a Gold-Iodide Complex (AuI₂⁻) onto Cellulose Acetate-Polyaniline Membranes: Equilibrium Experiments

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ABSTRACT: The adsorption of AuI₂⁻ complex onto acetate cellulose-polyaniline membranes was investigated. Kinetic experiments showed a rapid adsorption of this complex, which was attributed to an ion-exchange mechanism. Equilibrium adsorption results were represented by the Langmuir model, showing a correlation coefficient of 0.9852. Langmuir parameters *K* and *Q_m* were found to be 0.2937 L mg⁻¹ and

1.2394 mg g⁻¹, respectively. Approximately 94% of AuI₂⁻ was adsorbed when a solid/liquid ratio of 40 g L⁻¹ (grams of membrane/ liter of solution) was used. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2670–2674, 2009

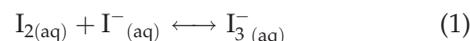
Key words: conducting polymers; separation techniques; membranes; ion exchangers

INTRODUCTION

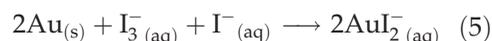
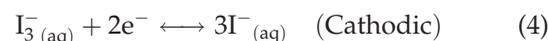
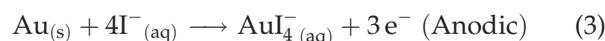
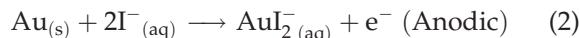
Precious metals, such as silver, gold, and platinum, are recovered from a wide variety of sources. In addition to traditional precipitation processes, solvent extraction and ion-exchange processes are also used.¹ Chlorine was used to dissolve gold from ores and concentrates, during the second half of the 19th century in Australia and North America.² At the beginning of the 20th century, this process was gradually replaced by the more economical alkaline cyanide leaching.³ Alkaline solutions of cyanides are used in large amounts as solvents for gold, which gives rise to a number of potential ecological problems.⁴ Main concerns in the mining industry at the present time are the increase in environmental awareness and more restrictive environmental legislations. Thus, alternative methods become necessary to replace old technologies to comply with new regulations. Although potassium cyanide is the most economical lixiviant at the moment, it raises certain concerns regarding the operators' health. These include the adsorption through the skin and accidental ingestion of cyanide salts by the operators, and the formation of deadly hydrogen cyanide gas. Dangerous situations may occur when cyanide ions form organic and inor-

ganic complexes, which are difficult to destroy by conventional methods contaminate effluent streams.⁵

Based on the above considerations, several researchers have been investigating alternative lixivants, which include the halogen group.^{6–8} From this group, iodine forms the most stable gold complex in aqueous solutions, even up to a pH of 14.⁹ The dissolution of gold in an iodine/iodide solution is an oxide-reduction process (redox), which can be shown in terms of an electrochemical cell, which includes separate anodic and cathodic chemical reactions. This process begins with the formation of the triiodide ion as follows^{10,11}:



This ion serves as an oxidant in the following electrochemical reactions.



The standard potentials of reactions (5) and (6) of gold in iodide solutions are: $E^{\circ}\text{AuI}_{2}^{-}/\text{Au} = 0.578\text{V}$

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and $E^0\text{AuI}_4^-/\text{Au} = 0.550\text{V}$. Therefore, the reaction (5) is the most acceptable mechanism for the dissolution of gold with triiodide ions as an oxidizing agent.¹²

The use of activated carbon for the recovery of gold from leach liquors has gained wide acceptance in the mining industry. The most common method of extraction is the carbon-in-pulp process. The gold adsorption occurs from a slurry containing fine ground rock particles and possibly a number of other metals in solution and organics, which may poison the carbon.¹³ Recently, there has been interest in using ion-exchange resins instead of activated carbon. Lukey et al.¹⁴ investigated the properties of five weak-base type resins that contain a small amount of strong base groups and different aliphatic amino functional groups. The experimental data showed that gold cyanide adsorbed onto each resin in both nonsaline and highly saline solution as $[\text{Au}(\text{CN})_2]^-$ complex. In either of these processes, the adsorbent was in granular form and was contacted with a leached slurry in a series of agitated tanks. From both kinetics and equilibrium points of view, a better way of contacting the adsorbent and the solution is the use of a packed column. In the case of granular adsorbents, the flow of mine slurry through a packed bed is not practical because the slurry blocks the bed. If ion-exchange membranes could be used for treating gold slurries, it would be possible to simulate a packed bed by passing the slurry through a column in which a number of parallel sheets of membrane are placed.¹³ Diniz et al.¹⁵ reported matrices containing polyaniline displaying ion-exchange properties, the matrices being selective to anions based upon their radii, with a cut-off value around 240 pm.

The present authors reported the synthesis of cellulose acetate (CA) membranes coated with polyaniline (PANI)¹⁶ porous membranes with good electrical and mechanical properties were obtained. These membranes showed a potential use in a process to recover gold.

PANI is an intensively studied polymer due to its electrical, electrochemical, and optical properties and its high environmental stability, which confers it potential use in many applications including sensors, rechargeable batteries, anticorrosion coatings, electrochromic displays and selective membranes among others.¹⁷⁻²² CA is commonly used to prepare membranes for different uses and various methods have been developed to control its pore diameter using polyelectrolytes.²³

The property of ion exchange of polyaniline is reported since 1972 by Muller and Jozefowicz.²⁴ By September 2008, 17,073 references containing "polyaniline" as keyword were found, of which only 1.2% of references were found containing "ion exchange" as associated keyword (SciFinder). Thus, there

exists interest to take advantage of this property of PANI. In this article, the ion-exchange properties of CA-PANI membranes synthesized are reported. The goal of this work was to test the membranes as potential ion-exchange adsorbents for the recovery of gold from iodine-iodide aqueous solutions.

EXPERIMENTAL

Materials used in this study included CA powder (Aldrich), poly(acrylic acid, sodium salt) (PAA) 35 wt %, w 15,000 (Aldrich) acetic acid, glacial (Sigma) hydrochloric acid (Merck), ammonium persulfate (Fermont), triphenyl phosphate 99% (TPP) (Aldrich), potassium iodide (Fermont), iodine 99.99% (Fermont), gold, powder 99.99% (Aldrich). Anilina 99% (Merck) was distilled under vacuum in nitrogen atmosphere before use. All other reagents were used as received.

Preparation of CA membranes coated with PANI

CA membranes modified with PAA and plasticized with TPP were prepared. The membrane preparation was performed according to the procedure described in a previous article.¹⁶ CA (4 g) was weighed and dissolved in 50 mL of acetic acid, with constant stirring for 4 h, and subsequently, 5 mL of PAA was added under stirring for one hour. Finally, 1 g of TPP was added to the solution, while keeping stirring for 1 h.

The membranes were prepared by phase inversion in a wet process. An aliquot of the solution corresponding to each batch of membrane was poured onto a flat glass plate of approximately 10 cm diameter. The excess of the solution was removed, leaving the plate covered by a fine layer of solution. The plate was then placed in a coagulation bath (ice water mixture) for 30 s. The plate with the solution was then immersed in the cold water for 15 min. Finally, the membrane was peeled off from the glass plate, washed in water, and dried at 25°C for 24 h on filter paper.

For the coating of membranes with PANI, a solution of 0.5M of aniline was prepared. Aniline was dissolved in 0.02M aqueous solution of HCl. The membranes were cut into strips to facilitate their coating and were placed in a glass vessel containing the aniline solution. The strip was immersed in the solution for 5 min. The strip was removed, drained, and placed in a glass vessel containing a solution of ammonium persulfate 0.5M, for 5 min. Subsequently, the membranes were dried at 25°C for 24 h.

Test of application as ion-exchange membranes

The leaching solution was prepared as follows: 12 g iodine total ($I_2 + KI$) were used, with a KI to I_2 ratio of 2 : 1. The solution of gold-iodide complex (AuI_2^-) was prepared using the leaching solution, to which a predetermined amount of gold was added to achieve the range of concentration 2.5–20 ppm. Total Au concentration was verified by atomic absorption spectroscopy using a Perkin Elmer 3110 atomic absorption spectrometer.

All tests as ion-exchange membranes were made at 25°C. Kinetic experiments were done to determine the time of contact necessary to achieve equilibrium conditions of the membrane-solution system. The membranes were cut into square pieces of 1×1 cm. The pieces were introduced in an Erlenmeyer flask, and submerged in to the solution of AuI_2^- complex, under constant magnetic agitation (155 rpm), after which the pieces of membranes were immediately removed from the solution. The contact time of the membrane with the solution of AuI_2^- complex varied in the range of 0–720 min. One experiment was done per contact time tested. In all the experiments, the initial concentration of total Au was kept at 10 ppm. The solid/liquid ratio used was 10 g L^{-1} (grams of membrane/liter of solution). The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

Equilibrium experiments

In the equilibrium experiments, membranes coated with PANI were used. The effect of the solid/liquid ratio versus percentage of Au adsorption was tested. For these experiments, the membranes were cut into pieces of 1×1 cm. Different amounts of mass membranes, ranges from 1 to 40 g L^{-1} , were introduced in to Erlenmeyer flasks and submerged in the solution of AuI_2^- complex, under constant magnetic agitation (155 rpm) for 12 h, after which the pieces of membranes were immediately removed from the solution of AuI_2^- complex. The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

To obtain the adsorption isotherms, solutions of different concentrations of Au were used (range 2.5–20 ppm). The solid/liquid ratio (grams of membrane/liter of solution) used varied from 1 to 40 g L^{-1} . The membranes were cut into pieces of 1×1 cm and were introduced into Erlenmeyer flasks and submerged into the solution of AuI_2^- complex, under constant magnetic agitation (155 rpm) for 12 h, after which the pieces of membranes were immediately removed from the solution. The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

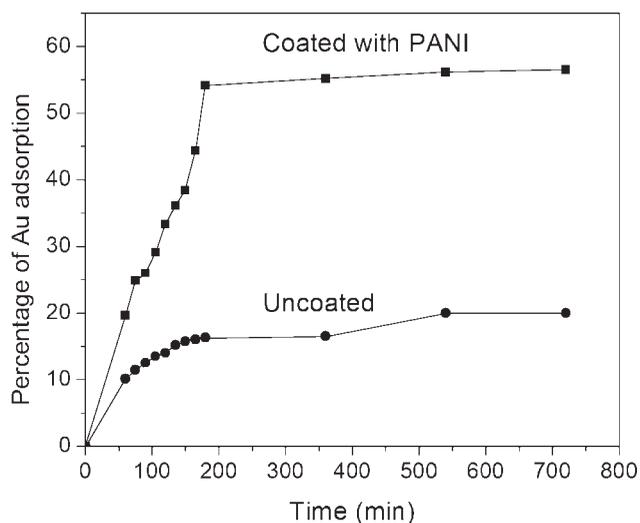


Figure 1 Adsorption kinetics of AuI_2^- complex onto CA membranes without and with coated of PANI, solid/liquid ratio = 10, $[Au_i] = 10$ ppm, $T = 25^\circ\text{C}$.

RESULTS AND DISCUSSION

A detailed description of the porous membranes obtained in this study is presented elsewhere.¹⁶ A summary of their characteristics follows. The pore size varied from 3 to $10 \mu\text{m}$. Uncoated membranes showed a thickness of 0.042 cm, whereas coated membranes of 0.127 cm. The membranes coated with PANI showed electrical conductivity in the order of $10^{-3} \text{ S cm}^{-1}$ and its mechanical properties were acceptable.

CA membranes uncoated and coated with PANI were used in testing kinetic. The results are presented in Figure 1, where the percentage adsorption of Au was calculated according to the following expression

$$\text{Percentage adsorption of Au} = \frac{(C_0 - C) \times 100}{C_0} \quad (7)$$

Where C_0 is the initial concentration of total Au (ppm), and C is the concentration of Au (ppm) in the solution at time t .

Figure 1 shows that the percentage adsorption of Au increases with time and achieves equilibrium at about 180 min for membranes coated with PANI, and 540 min for membranes uncoated for an initial Au concentration of 10 ppm. It shows that the adsorption of Au remained constant, implying equilibrium has been reached. To verify the equilibrium conditions has been obtained, a sample of one of the experiments was left sealed over a week, upon which the chemical analysis of this solution was repeated. The results verified that the solution concentration remained constant.

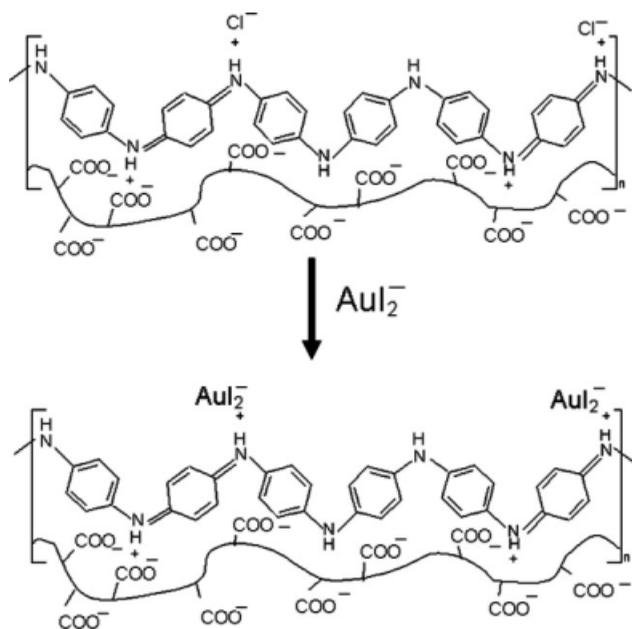


Figure 2 Schematic representation of the ion-exchange process of AuI_2^- onto CA-PANI membranes.

The results in Figure 1 indicate that the adsorption kinetics is faster than those reported for commercial resins and membranes of anion exchange, and activated carbon using cyanide as leaching solution for Au, which attained conditions equilibrium in the range of 1200–2500 min.¹³ Membranes coated with PANI presented adsorption kinetics faster and with higher gold recovery than those obtained with uncoated membranes. These results are attributed to the presence of PANI. CA membrane contains PAA, which serves as a template for PANI chains. These chains get doped with chloride ions, which are used to give electrostatic stability, these chloride ions may be interchanged with other anions, such as the AuI_2^- complex. We proposed this mechanism to explain these results. Figure 2 shows a schematic drawing of our model of ion exchange. Wang²⁵ reported that the relative anion-exchange selectivity decreased in the following order: $I^- > SCN^- > NO_3^- > Br^- > Cl^- > F^-$. This sequence agrees with that for quaternary ammonium anion exchangers. To verify that Cl^- was indeed exchanged during the process by AuI_2^- complex, the concentration of Cl^- was determined before and after the contact by ion chromatography. The concentration of Cl^- in solution before and after the process was less than 1 ppm and 15 ppm, respectively. Hence, an ion exchange between Cl^- and AuI_2^- complex is likely to have occurred.

In the equilibrium experiments, only membranes coated with PANI were tested. This was based on the fact that the percentage of Au adsorption was higher than for uncoated membranes. Figure 3 shows the effect of the solid/liquid ratio; grams of mem-

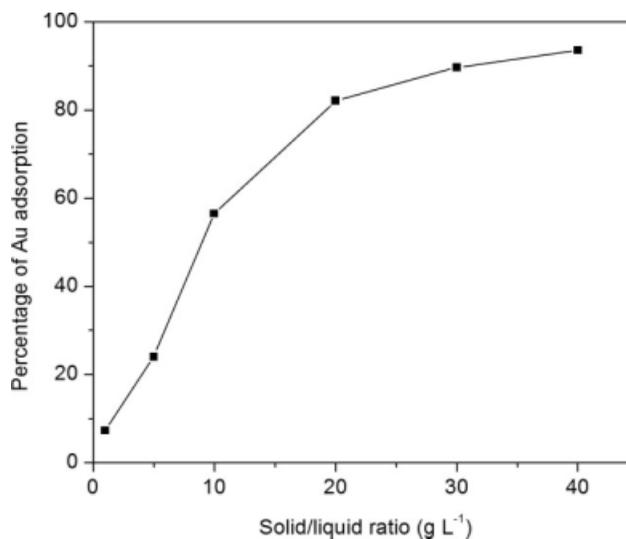


Figure 3 Effect of the solid/liquid ratio; grams of membrane/liter of solution, on the percentage adsorption of AuI_2^- complex of membranes coated with PANI.

brane/liter of solution on the percentage adsorption of AuI_2^- complex of membranes coated with PANI. It is noted that the percentage of extracted gold increases as the amount of adsorbent material increases. This is an expected result because the larger the amount of membrane, the greater capacity of adsorption is available. The percentage adsorption of Au, using a solid/liquid ratio of membrane of 40 g L⁻¹ was about 94%. Value is acceptable, and over 90% of published by Wang and Liang²⁶ in the adsorption of gold ions onto chitosan and *N*-carboxyl methyl chitosan.

The equilibrium experimental data were adjusted in the linear forms of isotherms of Langmuir and

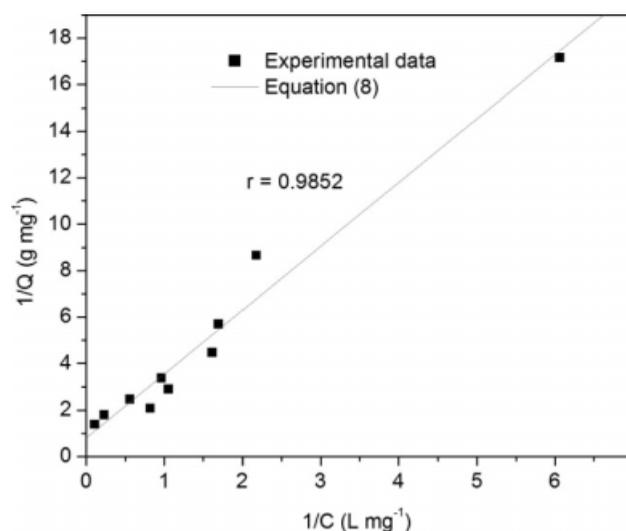


Figure 4 Adsorption isotherm of Langmuir for AuI_2^- complex on CA-PANI membranes.

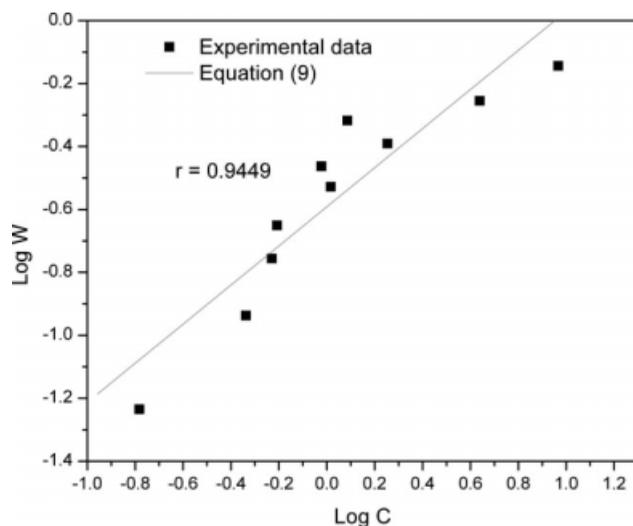


Figure 5 Adsorption isotherm of Freundlich for AuI_2^- complex on CA-PANI membranes.

Freundlich. The equations are shown in (8) and (9), respectively.

$$\frac{1}{Q} = \frac{1}{Q_m K C} + \frac{1}{Q_m} \quad (8)$$

$$\text{Log} Q = \text{Log} c_1 + \frac{1}{c_2} \text{log} C \quad (9)$$

where Q is the amount of Au adsorbed per unit weight of membrane at equilibrium concentration (mg/g), C is the equilibrium concentration of Au (ppm) in the aqueous solution, Q_m is the maximum capacity of adsorption, K is the constant of the isotherm of Langmuir; c_1 and c_2 are empirical constants of Freundlich. Figures 4 and 5 show the equilibrium isotherms of Langmuir and Freundlich, respectively. The best linear fit of experimental data was obtained by the Langmuir isotherm. The values for K and Q_m were found to be 0.2937 L mg^{-1} and 1.2394 mg g^{-1} , respectively. The linear fitting showed a correlation coefficient (r) of 0.9852. Therefore, these results suggest a monolayer adsorption process, without lateral interactions between the adsorbed molecules.²⁷

CONCLUSIONS

CA-polyaniline membranes are effective adsorbents for recovery of AuI_2^- complex. The adsorption of Au

on CA-polyaniline membranes was attributed to the exchange of Cl^- and AuI_2^- complex ions. The adsorption equilibrium data were found to obey the Langmuir isotherm model. Kinetics and equilibrium experiments showed that CA-PANI membranes represent a promising alternative for a gold recovery process without the use of cyanide solutions. Through this analysis we show the application of the polymeric material prepared.

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