

Gold Recovery Using Inherently Conducting Polymer Coated Textiles

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Abstract: The ability of inherently conducting polymer (ICP) coated textiles to recover gold metal from aqueous solutions containing $[\text{AuCl}_4]^-$ was investigated. Nylon-lycra, nylon, acrylic, polyester and cotton were coated with a layer of polypyrrole (PPy) doped with 1,5-naphthalenedisulfonic acid (NDSA), 2-anthraquinonesulfonic acid (AQSA) or *p*-toluenesulfonic acid (*p*TS). Textiles coated with polyaniline (PAn) doped with chloride were also used. The highest gold capacity was displayed by PPy/NDSA/nylon-lycra, which exhibited a capacity of 115 mg Au/g coated textile, or 9700 mg Au/g polymer. Varying the underlying textile substrate or the ICP coating had a major effect on the gold capacity of the composites. Several ICP coated textiles recovered more than 90 % of the gold initially present in solutions containing 10 ppm $[\text{AuCl}_4]^-$ and 0.1 M HCl in less than 1 min. Both PPy/NDSA/nylon-lycra and PAn/Cl/nylon-lycra recovered approximately 60 % of the gold and none of the iron present in a solution containing 1 ppm $[\text{AuCl}_4]^-$, 1000 ppm Fe^{3+} and 0.1 M HCl. The spontaneous and sustained recovery of gold metal from aqueous solutions containing $[\text{AuCl}_4]^-$ using ICP coated textiles has good prospects as a potential future technology.

Keywords: Gold recovery, Conducting polymer, Textiles

Introduction

The majority of industrial procedures for recovery of gold from auriferous ores begin with a leaching process known as cyanidation, which yields solutions containing the gold cyanide complex $[\text{Au}(\text{CN})_2]^-$ [1,2]. This is then usually adsorbed onto activated carbon or an ion-exchange resin and subsequently eluted to produce a concentrated solution of $[\text{Au}(\text{CN})_2]^-$. Several processes can be used to obtain gold metal from these solutions including electrowinning and zinc cementation. Owing to the adverse environmental effects associated with the use of cyanide, there is considerable interest in the development of alternative procedures that use less harmful gold extractants. One such reagent is *aqua regia*, which reacts with gold to give solutions containing $[\text{AuCl}_4]^-$. In order for this process to be useful it is important to have highly efficient and selective methods for recovery of gold from these solutions. Further interest in these methods stems from the presence of $[\text{AuCl}_4]^-$ in waste produced by the jewellery, dental and semiconductor industries.

The recovery of gold metal from aqueous solutions containing $[\text{AuCl}_4]^-$ using polyaniline (PAn) powders and films has been reported [3]. Recovery was both rapid and extensive, with PAn films recovering more than five times their own weight in gold metal. The rate of recovery was highest for the fully reduced leucoemeraldine form of PAn, demonstrating that the rate of gold uptake was dependent on the oxidation state of PAn. The mechanism of gold recovery involved the reduction of Au(III) to Au(0), with simultaneous oxidation of PAn to higher oxidation states. Under the acidic conditions used the oxidised PAn was reduced to lower

oxidation states, thereby allowing the sustained recovery of gold metal until limited by coverage of the PAn surface by metal.

Polypyrrole (PPy) films, powders and nanocomposites have also been shown to recover gold metal from solutions containing $[\text{AuCl}_4]^-$ [4-6]. The amount of gold recovered was several times greater than the amount of PPy used, and the mechanism of recovery proposed to involve similar redox processes to that outlined above for PAn. One of the most promising aspects associated with gold metal recovery using inherently conducting polymers (ICPs) such as polypyrrole and polyaniline is the selectivity of the process [7]. This is attributable to the reduction potentials of common contaminant metal ions such as copper and iron being too low to over-oxidise ICPs. Recently we showed that composite materials consisting of ICPs deposited onto reticulated vitreous carbon (RVC) selectively recover gold from solutions containing $[\text{AuCl}_4]^-$, even in the presence of a one thousand fold excess of iron [8].

Textiles are less expensive, more flexible substrates than RVC for coating with ICPs to produce composite materials for gold recovery. Textile coatings are achieved using a chemical oxidation process as described by Kuhn and Child [9] rather than an electrochemical method as used for RVC. In an initial investigation, it was found that gold could be recovered using composite materials consisting of commercial silk, linen or cotton coated with polypyrrole doped with NDSA [10]. Gold recovery was found to be facile with over 90 % of the gold initially present in solution being recovered in 30 minutes in some instances. Some of the textiles studied also slowly recovered gold from solution even without an ICP coating. However, the rate and amount of gold recovered was generally much less efficient than with the ICP coated materials.

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The aim of the current work was to determine the gold capacities of ICP coated textiles, and whether gold recovery is selective, as observed previously using an RVC substrate. The effect of using different counterions (dopants) with the ICP on gold recovery was also studied. The results presented here enable a more complete comparison of the performance of the ICP coated fabrics with the RVC composites studied previously.

Experimental

Reagents

Pyrrole was obtained from Aldrich and used as received. Aniline was obtained from Aldrich and distilled before use. All textiles, namely nylon-lycra, nylon, acrylic, polyester and cotton, were obtained from a local retail source and used without prior treatment. Ammonium persulfate, hydrogen tetrachloroaurate (III) trihydrate ($\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$), 1,5-naphthalenedisulfonic acid (NDSA), 2-antraquinonesulfonic acid (AQSA) and *p*-toluenesulfonic acid (*p*TS) were obtained from Aldrich. Anhydrous ferric chloride was obtained from BDH. Analytical grade hydrochloric acid (32 %) was obtained from Ajax. All gold solutions were prepared by appropriate dilution, using 0.1 M HCl, of a 1000 ppm Au^{3+} stock solution, which was prepared by dissolving 0.500 g of $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ in 250 ml of 0.1 M HCl. All solutions were prepared using deionized MilliQ water.

Preparation of Inherently Conducting Polymer Coated Textiles

Polypyrrole/textile composites were prepared according to the following procedure using nylon-lycra, nylon, acrylic, polyester and cotton substrates. Circular pieces of uncoated textile (diameter = 19.2 cm) were soaked in 250 ml of solution containing 0.03 M pyrrole, and either 0.01 or 0.02 M dopant for 30 min. For the monosulfonated AQSA and *p*TS dopants the concentration employed was 0.020 M, while for the disulfonated NDSA the concentration was 0.010 M. 250 ml of aqueous 0.08 M FeCl_3 was then added and polymerisation allowed to proceed for 2 h, at 30 °C (thermostatted water bath). In some cases no dopant was present in the pyrrole solution, resulting in a coating of PPy/Cl on the textile. After synthesis ICP/textile composites were washed with Milli-Q water and allowed to dry overnight.

Circular pieces of nylon-lycra measuring 19.2 cm in diameter were coated with polyaniline doped with chloride using the following procedure. The nylon-lycra substrate was first sonicated in isopropanol for 1 h to remove manufacturing oils and improve the PAN/Cl coating. The nylon-lycra was soaked in 250 ml of 0.18 M aqueous ammonium persulfate for 1 h and then 250 ml of 0.12 M aniline added. Polymerisation was allowed to proceed for 24 hrs at 30 °C using a thermostatted water bath. The final product was rinsed using 100 ml of 0.1 M HCl to prevent de-doping of the PAN/Cl coating.

Characterisation of Inherently Conducting Polymer Coated Textiles

Polymer Loading

The % polymer loading of ICP coated textiles was determined by weighing textile substrates before and after polymerisation and using the following equation:

% polymer loading =

$$\frac{(\text{mass coated textile}) - (\text{mass bare textile})}{(\text{mass bare textile})} \times 100 \quad (1)$$

Cyclic Voltammetry

Cyclic voltammetry experiments were performed using a 3-electrode electrochemical cell, and a Princeton Applied Research Model 363 potentiostat/galvanostat coupled to an AD Instruments MacLab/400ICP analogue/digital converter. The working electrode consisted of pieces of ICP coated textile measuring 2 mm × 2 mm adhered to a glassy carbon electrode using conducting carbon paint. The reference and auxiliary electrodes used were Ag/AgCl (3 M NaCl) and Pt mesh, respectively. The supporting electrolyte was 1 M HCl, which was purged with nitrogen gas for 5 min prior to use. The lower and upper potential limits used were -0.8 V and +1.2 V, respectively, and the scan rate was 50 mVs⁻¹.

Gold Recovery

Gold Capacity

Gold capacities were determined using pre-weighed samples of uncoated or ICP coated textile measuring 1 cm × 1 cm. These were added to acid-washed glass vials containing 20 ml of 200 ppm Au^{3+} [as AuCl_4^-] and 0.1 M HCl. The samples were removed after 7 days and the concentration of gold remaining in solution determined using atomic absorption spectroscopy (AAS) using a Varian SpectrAA Atomic Absorption spectrophotometer. All gold capacities reported here are mean values obtained from experiments performed in triplicate.

Rate of Gold Recovery

Pieces of ICP coated textile measuring 2 cm × 2 cm were added to acid-washed glass vials containing 10 ml of aqueous solution containing 0.1 M HCl and either 1 ppm or 10 ppm Au^{3+} [as AuCl_4^-]. After pre-determined periods of time the ICP coated textile samples were removed and the concentration of gold remaining in solution analysed using AAS.

In order to investigate the rate of gold recovery from solutions containing a very low gold concentration a different method was employed. In this case PPy/NDSA/nylon-lycra samples measuring 1 cm × 1 cm were added to acid-washed volumetric flasks containing 100 ml of 0.1 ppm Au^{3+} [as AuCl_4^-] solution. The samples were removed after either 10 min, 1 hr or 1 day and the amount of gold metal

that had deposited on their surfaces was determined using Neutron Activation Analysis (NAA) (Becquerel Laboratories, Lucas Heights, New South Wales, Australia). The amount of gold recovered after each period of time was determined in triplicate.

Selectivity of Gold Recovery

Gold selectivity experiments were performed using pieces of PPy/NDSA/nylon-lycra and PAn/Cl/nylon-lycra measuring 2 cm × 2 cm. These were added to 10 ml of solution containing 0.1 M HCl, 1 ppm Au³⁺ [as AuCl₄⁻] and 1000 ppm Fe³⁺ present in acid-washed glass vials. After pre-determined periods of time the ICP coated textile samples were removed and the concentrations of gold and iron remaining in solution were analysed using AAS.

Results and Discussion

Characterisation of ICP Coated Textiles

A thin, uniform and adherent coating of ICP was obtained using all of the textiles under investigation. The gold capacities and polymer loadings for the different ICP coated textiles are presented in Table 1. The amount of ICP deposited onto the textiles is reflected in the % polymer loadings. Most ICP coated textiles showed % polymer loadings between 1 and 5 % (w/w), which are similar to values reported previously [9]. The only exception to this was PPy/Cl/nylon, which showed a polymer loading of only 0.1 %. This low value may be a result of the hydrophobic nature of the nylon substrate, which reduced its wettability. The greatest polymer loading (4.5 % w/w) occurred when a cotton substrate was used. Small variations in polymer loading were observed when nylon-lycra was used and different dopants employed. The greatest polymer loading achieved on the nylon-lycra substrate was when AQSA was used as the dopant.

Table 1. Polymer loadings and gold capacities of ICP coated textiles

ICP coated textile	% (w/w) Polymer loading	Gold capacity ¹ of ICP coated textile (mg Au/g composite)	Gold capacity ¹ of ICP coated textile (mg Au/g polymer)
PPy/Cl/cotton	4.5	90	2000
PPy/Cl/acrylic	2.1	35	1700
PPy/Cl/polyester	1.2	10	830
PPy/Cl/nylon	0.1	70	70000
PPy/Cl/nylon-lycra	1.2	100	8300
PPy/NDSA/nylon-lycra	1.2	115	9600
PPy/AQSA/nylon-lycra	2.7	110	4100
PPy/pTS/nylon-lycra	1.0	70	7000
PAn/Cl/nylon-lycra	1.2	85	7100

¹Capacity determined as described in the experimental section.

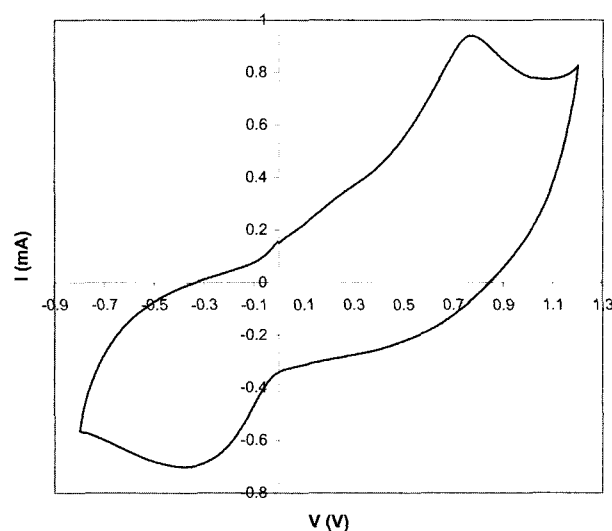


Figure 1. Cyclic voltammogram obtained using a working electrode consisting of a piece of PPy/AQSA/nylon-lycra adhered to a glassy carbon electrode using conducting carbon paint. Supporting electrolyte = 1 M HCl; scan rate = 50 mVs⁻¹.

The cyclic voltammogram (CV) obtained using a working electrode consisting of a piece of PPy/AQSA/nylon-lycra adhered to glassy carbon, and a supporting electrolyte consisting of 1 M HCl, is shown in Figure 1. The CV shown is typical of those obtained using other ICP coated fabrics, and confirms that they are electroactive undergoing the normal oxidation reduction processes previously observed for polypyrrole (PPy).

Gold Recovery

The results presented in Table 1 demonstrate that each of the five PPy/Cl coated textiles examined have a significant capacity to recover gold from solutions containing [AuCl₄⁻]. In addition to the data presented in Table 1, uncoated nylon-lycra and nylon showed some capacity to recover gold. The greatest capacity was obtained when using PPy/Cl coated onto nylon-lycra. While PPy/Cl/nylon displayed only the third highest gold capacity when expressed as mg Au/g composite, the very low polymer loading of this material resulted in the extraordinary capacity of 70000 mg Au/g of ICP. This suggests that only a very thin layer of ICP is needed on the surface of the textile in order to recover gold by a redox mechanism. Consistent with this is the lack of a relationship in Table 1 between gold capacity and polymer loading. Other factors therefore play a significant role in determining gold capacity, including differences in ICP surface area exposed to the gold solution.

Considering the capacity data obtained for nylon-lycra (Table 1) variations in the dopant incorporated during synthesis had a smaller effect on gold capacity than changing the textile itself. When nylon-lycra was used as the substrate the greatest amount of gold recovered, when expressed as

either mg Au/g composite or mg Au/g polymer, was when the polymer used to coat the surface was PPy/NDSA. The lowest gold capacity on a mg Au/g composite basis for this series of materials was observed for PPy/pTS/nylon-lycra. Several factors are likely to be important in determining gold capacity, including differences in morphology and surface area of the polymer coating on the textile surface.

The gold capacities obtained for PPy/Cl, PPy/pTS and PAN/Cl on nylon-lycra were 8300, 7000, and 7100 mg Au/g polymer, respectively. These values compare favourably with those for composite materials prepared by depositing the same ICPs onto reticulated vitreous carbon (RVC). For PPy/Cl, PPy/pTS and PAN/Cl gold capacities of 2700, 2900, and 3100 mg Au/g polymer, respectively have been reported [8].

The effect of varying the ICP used to coat nylon-lycra on the rate of gold recovery from a solution containing 0.1 M HCl and 10 ppm Au³⁺ [as AuCl₄⁻] is shown in Figure 2. After exposure to either PPy/NDSA or PPy/AQSA coated on nylon-lycra for 1 minute the concentration of gold remaining in solution had decreased by between 90 and 95 % of its initial value. This shows that ICP coated textiles can recover gold from solutions containing [AuCl₄⁻] in an extremely facile manner, analogous to that displayed by composite materials consisting of ICPs deposited onto RVC. Slower rates of gold recovery were displayed by the remaining two composites. In the case of PPy/pTS on nylon-lycra more than 95 % of the gold initially present had been recovered after 10 min, while for PPy/Cl on nylon-lycra 4 hours elapsed before the same level of recovery was observed. Despite the slower rate of recovery using these latter materials, the final quantities of gold recovered were extremely high, and comparable to that displayed by either PPy/NDSA or PPy/AQSA on nylon-lycra. When the above experiment was repeated using a solution containing 0.1 M HCl and 1 ppm Au³⁺ [as AuCl₄⁻] similar results were obtained, with each

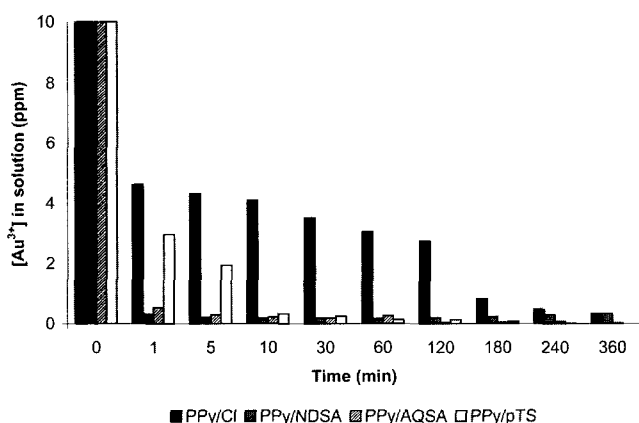


Figure 2. Effect of varying the dopant used in ICP coated onto nylon-lycra on the rate of gold recovery from solutions containing 0.1 M HCl and 10 ppm Au³⁺ [as AuCl₄⁻].

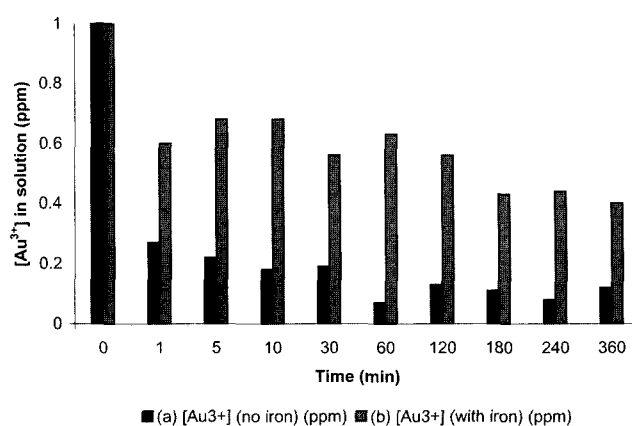


Figure 3. Recovery of gold by PPy/NDSA/nylon-lycra from: (a) a solution containing 1 ppm Au³⁺ and 0.1 M HCl, and (b) a solution containing 1 ppm Au³⁺, 1000 ppm Fe³⁺ and 0.1 M HCl.

composite recovering $\geq 90\%$ of the gold initially present after 1 hour of uptake.

One of the most important properties a material must possess if it is to be useful for recovery of gold or any other precious metal is selectivity. We have previously shown that ICP coated RVC composite materials selectively recover gold from solutions containing low concentrations of gold and much higher concentrations of iron, a common contaminant [7]. Figure 3 shows the removal of AuCl₄⁻ from solution by PPy/NDSA coated onto nylon-lycra. The first solution contained 1 ppm Au³⁺ and 0.1 M HCl only, while the second solution containing 1 ppm Au³⁺, 0.1 M HCl and 1000 ppm Fe³⁺. After 3 hours approximately 60 % of the gold initially present had been removed from the latter solution, while the concentration of iron had not decreased at all. This demonstrates that the selectivity for gold seen previously with ICP/RVC composites is also displayed by ICP/textile composites. However, the extent of gold recovery by the ICP coated textiles is adversely affected by the presence of iron. A similar phenomenon has been observed previously for ICP/RVC composites, where the rate and extent of gold recovery were slightly diminished by the presence of iron [8]. Here this is shown by the much greater recovery of gold from the solution containing 1 ppm Au³⁺ and 0.1 M HCl alone. After 3 hours approximately 90 % of the gold initially present in this solution had been recovered, compared to only 60 % when iron was also present. The most likely explanation for a decrease in gold recovery from the solution also containing iron is that some of the redox capacity of the polymer is exhausted in reducing Fe³⁺ → Fe²⁺. Alternatively, some of the gold metal that deposited onto the surface of the coated textile may have been re-oxidised by Fe³⁺. Measurements performed on the solution containing both gold and iron after 1 and 2 days indicated that there were no further significant changes in the amount of gold recovered. Similar results were also obtained when this study was repeated using PAN/Cl/nylon-lycra.

Conclusion

Common textiles such as nylon-lycra, nylon, acrylic, polyester and cotton can be easily coated with conducting polymers to form a range of composite materials that combine excellent mechanical properties with the ability to recover gold metal from solutions containing $[\text{AuCl}_4]^-$. Changing the underlying textile substrate or conducting polymer present in the composites was found to have a major influence on their gold capacities. Comparison of gold recovery data for ICP/textile composites with that for ICP/RVC composites containing the same conducting polymers showed that the former have superior gold capacities. In addition ICP/textile composites showed excellent rates of gold recovery and the ability to selectively recover gold in the presence of much higher concentrations of another metal. Overall these materials appear to have excellent prospects for applications involving recovery or recycling of gold from waste solutions, and possibly other precious metals as well.

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