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Electroless recovery of silver by inherently conducting polymer powders, membranes and composite materials

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Abstract

A wide variety of inherently conducting polymers, including polypyrroles and polyanilines, were shown to reduce silver ion in aqueous solution, demonstrating that these materials may form the basis of a novel approach to silver recovery. The effect of varying the polymer, dopant, and underlying substrate (reticulated vitreous carbon or fabric) was investigated, as was the effect of changing the pH of the solution containing silver. Silver recovery was found to proceed more readily from solutions with near neutral pH than from solutions with strongly acidic pH, and to occur selectively from solutions containing both silver and iron. Scanning electron microscopy (SEM) showed deposits that formed on polymeric materials after prolonged exposure to concentrated silver nitrate solutions were partially crystalline in nature. XPS spectra provided support for a mechanism of silver recovery involving a redox reaction between the polymer and silver ions leading to the formation of silver metal.

Keywords: Inherently conducting polymer; Polypyrrole; Silver

1. Introduction

Silver is a precious metal widely used in the photographic, electrical, electronics, chemical and jewellery industries. While it is not as expensive as gold or platinum, silver is still only present in limited amounts in nature, which contributes to the need for efficient methods of recycling the metal from waste generated by the above industries. There are currently a variety of methods that can be used for recovery of silver from different sources, including electrolysis, precipitation, metal replacement, ion-exchange and reverse osmosis [1–3]. Of these methods the most widely used for recovery of silver from photographic waste are metal replacement (cementation) and electrolysis. Several authors have reviewed the chemistry of silver recovery by metal replacement, which typically uses steel wool, iron, zinc, copper or aluminium to reduce silver ions to silver metal [4–8]. A disadvantage of the metal replacement method is that the solution being recycled becomes contaminated by metal ions derived from the reducing agent. This does not happen in the case of electrolysis, which is probably the most widely used method for silver recovery, and often employs a rotating cylinder electrode. Electrolytic methods can be readily adapted to high throughput applications and yield silver of high purity [9–12]. However, the electrolytic method requires large amounts of waste in order to be economically viable, and must be combined with another method in order to achieve near quantitative recoveries. While some other methods offer greater silver recoveries, they generally suffer from one or more disadvantages including medium to high capital costs, the ability to be applied chiefly only to dilute silver solutions, and the need to employ hazardous chemicals. There is, therefore, a need for alternative methods of silver recovery that are efficient, selective, and use environmentally benign materials or processes. A variety of new approaches are currently being explored, including adsorption onto agricultural by-products [13] and combining ultrasound with electrochemical methods [14].

Inherently conducting polymer (ICP) materials including membranes, powders and composites have been shown to rapidly recover gold from solutions containing $[AuCl_4]^-$ [15–22]. Gold recovery is selective, and occurs by a mechanism in which the conducting polymer is oxidized with concomitant reduction of $[AuCl_4]^-$ to gold metal on the surface of the polymer. Under acidic conditions the oxidized polymer is spontaneously returned to a lower oxidation state, allowing the gold recovery process to continue until the polymer surface is completely covered by metal. The key to the mechanism of gold recovery is the high redox potential for the Au(III)/Au(0)

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couple (1.0 V vs SHE). The redox potential for the $Ag^+/Ag(0)$ couple of 0.80 V (vs SHE) is lower than that for Au(III)/Au(0), but still suggests that silver metal might also be recovered from aqueous solutions containing Ag^+ by an analogous mechanism to that found for $[AuCl_4]^-$. This was confirmed by a recent study that showed that chemically or electrochemically prepared polyaniline recovered significant amounts of silver ion from nitric acid solutions [23]. X-ray diffraction was used to confirm that silver metal deposited onto polyaniline powders used in these experiments.

In this paper, we further demonstrate the potential of inherently conducting polymers (ICPs) to recover silver ions from aqueous solution. Such an approach to recovery of silver from, for example, photographic waste, would be extremely novel, as it does not involve the use of an external electrical source or inorganic reductants. ICPs are inexpensive and readily prepared. Their redox properties can be varied by changing the monomer or dopant, which provides opportunities for developing selective reductants for use with metal ion mixtures. Here we report the effect of changing the ICP and the underlying substrate (RVC or fabric) present in ICP composite materials on the extent of silver recovery, and the ability of ICP powders to selectively recover silver from solutions also containing iron.

2. Experimental

2.1. Reagents

Pyrrole and aniline were obtained from Aldrich and distilled before use. Anthraquinone-2-sulfonic acid, sodium salt monohydrate (AQSA), 1,5-naphthalenedisulfonic acid (NDSA), sodium *p*-toluenesulfonic acid (pTS), poly(vinyl)sulfonic acid, sodium salt (PVS), 4,5-dihydroxy-1,3-benzenedisulfonic acid (Tiron), acetonitrile and propylene carbonate were also obtained from Aldrich. Reticulated vitreous carbon (RVC) was obtained from ERG Materials and Aerospace Corporation, Oakland, CA, USA. The true surface area of the RVC was 65 cm^2/cm^3 (data supplied by manufacturer) Fabrics (2–4 m^2) were obtained from a local drapery (Spotlight, Wollongong, Australia). Silver solutions were prepared by appropriate dilution of a 1000 ppm Ag^+ stock solution, prepared by dissolving 1.0000 g of analytical grade silver nitrate (Aldrich) in 1000 mL of either Milli-Q water (18 MΩ cm) or 0.1 M HNO_3. In order to reduce photodecomposition all silver solutions were prepared using brown volumetric flasks and all recovery experiments were performed using brown sample vials.

2.2. Preparation of inherently conducting polymer membranes and powders

Membranes consisting of polypyrrole (PPy) were prepared using a three-electrode electrochemical cell, consisting of a stainless steel plate measuring $7\times 6\ cm^2$ as the working electrode, a Ag/AgCl(3 M $NaCl_{(aq)}$) reference electrode, and an auxiliary electrode consisting of a block of RVC measuring $10\times 4\times 1\ cm^3$. Polymerizations were performed using a Princeton Applied Research (PAR) model 363 potentiostat/galvanostat to apply a constant current density of 1.0 mA/cm^2 for 1 h at room temperature to aqueous solutions containing 0.2 M pyrrole and 0.05 M dopant in a 600 mL beaker. Membranes prepared in this manner were rinsed thoroughly with water, carefully peeled away from the working electrode and allowed to dry in air.

Powders composed of polypyrrole doped with chloride (PPy/Cl) were prepared by stirring aqueous solutions containing 0.025 M pyrrole and 0.075 M $FeCl_3$ at room temperature for 4 h. In these reaction mixtures $FeCl_3$ acted as the oxidant and the source of the dopant anion. Powders composed of polyaniline doped with chloride (PAn/Cl) or sulfate (PAn/SO_4) were prepared by stirring aqueous solutions containing 0.20 M aniline, 0.15 M $(NH_4)_2S_2O_8$ and either 1 M HCl or 1 M H_2SO_4 for 16 h at room temperature.

2.3. Preparation of inherently conducting polymer coated fabrics

Inherently conducting polymer coated fabric composites were prepared at room temperature by coating seven different fabrics with PPy/NDSA to give PPy/NDSA/fabric. These were prepared by first soaking circular pieces of uncoated fabric measuring 17 cm in diameter in a large crystallising dish (20 cm diameter) containing 250 mL 0.03 M pyrrole and 0.01 M NDSA for 30 min. They were then transferred to a second crystallising dish containing 250 mL 0.08 M $FeCl_3$, and polymerization allowed to proceed at room temperature for 4 h in all cases except when nylon was the underlying substrate. Owing to the very low wettability of this fabric, polymerization was allowed to proceed for 5 days to ensure an even coating of polymer was deposited. After synthesis the ICP coated fabrics were rinsed with Milli-Q water and dried at room temperature for 24 h. The mass of conducting polymer that had deposited on the fabrics was then calculated by subtracting the initial mass of the fabric from that after polymerization.

2.4. Preparation of inherently conducting polymer coated RVC

Inherently conducting polymers were deposited onto RVC electrochemically using a three-electrode cell described previously [22]. A Ag/AgCl (3 M $NaCl_{(aq)}$) reference electrode was used together with an auxiliary electrode consisting of a 5 cm high hollow RVC cylinder with a wall thickness of 0.5 cm and internal diameter of 3 cm. The working electrode was a block of RVC measuring 3 cm × 1 cm × 1 cm. Both the working and reference electrodes (and associated salt bridge) were placed in the electrochemical cell (25 mL beaker) inside the auxiliary electrode. Synthesis of polymers was performed in a 25 mL beaker at room temperature using solutions containing the same concentrations of monomer and dopant used for preparing the analogous polymer membranes. Polymerizations were carried out galvanostatically, by applying a constant current density of 1.0 mA/cm^2 for 10 min. A total current of 195 mA was used to provide sufficient charge

(39,000 mC/cm^3) to cover the working electrode with conducting polymer. This resulted in deposition of between 30 and 40 mg of conducting polymer in the case of polypyrroles, and between 5 and 10 mg of conducting polymer for polyanilines. After polymerization all polymer coated RVC composites were washed thoroughly with Milli-Q water and then allowed to dry in air.

2.5. Silver recovery experiments

All silver recovery experiments were performed at room temperature. Initial experiments were performed using rectangular pieces of polymer coated fabric or membrane measuring 5 cm × 2 cm, 30 mg of polymer powder, or rectangular polymer coated RVC blocks measuring 3 cm × 1 cm × 1 cm. The mass of powder used was chosen because it corresponded roughly to the average mass of polymer membranes used in these experiments. Experiments were performed in brown vials that had been rinsed with 0.1 M HNO_3 and Milli-Q water, before being dried in an oven prior to use. Pre-weighed pieces of polymer membrane, coated fabric, coated RVC or powder were placed in the vials and 20 mL of 100 ppm $AgNO_3$ added. This resulted in the entire surface area of each type of polymer material being exposed to the silver solution during the recovery experiment. The concentration of residual silver in the solutions was then determined in triplicate after 2 h, 1 day, 4 days and 7 days. Experiments were performed using silver nitrate solutions prepared in Milli-Q water (pH 6.5) and 0.1 M HNO_3 (pH 1.0). The concentration of silver in solutions was determined by AAS at 338.3 nm using a Perkin–Elmer PE-5000 atomic absorption spectrophotometer. Control experiments were also performed using pieces of uncoated fabric or RVC with identical dimensions to that of the polymer coated materials.

The capacity of the different polymer materials to recover silver was further explored in a second series of experiments using 20 mL of solution containing 1000 ppm Ag^+. These experiments were performed using identical sized pieces or quantities of polymer membrane, polymer coated RVC or fabric, and polymer powder to those used in the initial experiments.

The selectivity of silver recovery was investigated using a solution containing 1000 ppm $AgNO_3$ and 1000 ppm Fe. The iron present in this solution was derived from a commercial inductively coupled plasma standard solution, that was prepared by dissolving iron metal in 5% HNO_3, and consists of a mixture of iron in the 2+ and 3+ oxidation states.

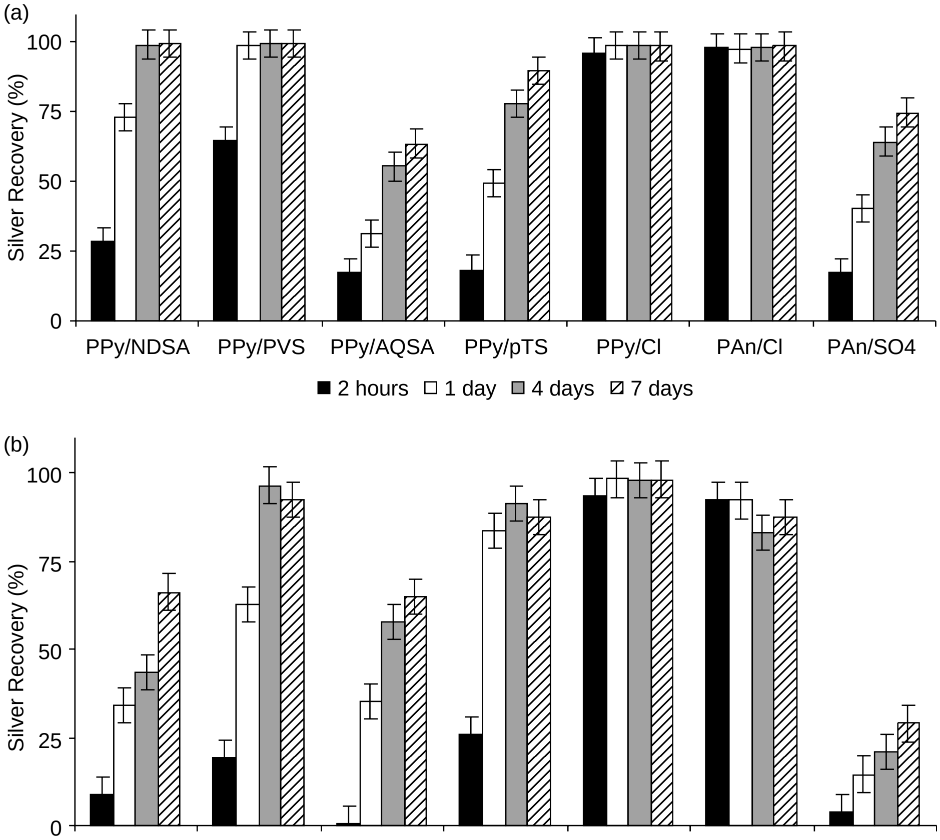

Fig. 1. Recovery of silver from 20 mL aqueous solution containing: (a) 100 ppm $AgNO_3$ or (b) 100 ppm $AgNO_3$ and 0.1 M HNO_3, by ICP powders and ICP coated membranes. Experiments were performed using either 30 mg of PPy/Cl, PAn/Cl or PAn/SO_4 powder, or pieces of ICP coated membrane measuring 5 cm × 2 cm.

2.6. Instrumentation

Scanning electron micrographs were obtained using either a Hitachi S-4500 scanning electron microscope at the University of New South Wales electron microscopy unit, or a Leica Cambridge 440 scanning electron microscopy located within the Department of Materials Engineering at the University of Wollongong. X-ray photoelectron spectra were obtained by Dr Bill Bin Gong of the University of New South Wales, using a VG Scientific ESCALAB 220i-XL spectrometer. A monochromatic A1 Kα source (energy = 1486.6 eV, power = 120 W) was used on spots measuring approximately 0.5 mm in diameter. The pass energy was 100 eV for wide scans and 20 eV for narrow scans. All spectra were obtained under ultra high vacuum conditions ($<2\times10^{-9}$ mbar).

3. Results and discussion

3.1. Silver recovery using polymer membranes and powders

Attempts to prepare stand alone PPy-Tiron membranes were not successful and this material was not pursued further. In all other cases depending on the synthesis approach used either robust stand alone membranes or finely divided powders were produced. All recovery experiments performed using polypyrrole or polyaniline powders used 30 mg of material. However, the masses of pieces of membrane composed of different ICPs varied between 15 and 30 mg, owing to differences in thickness and/or density of the different polymers. The mass of pieces of a specific ICP membrane cut to the same dimensions had approximately the same mass (±2 mg).

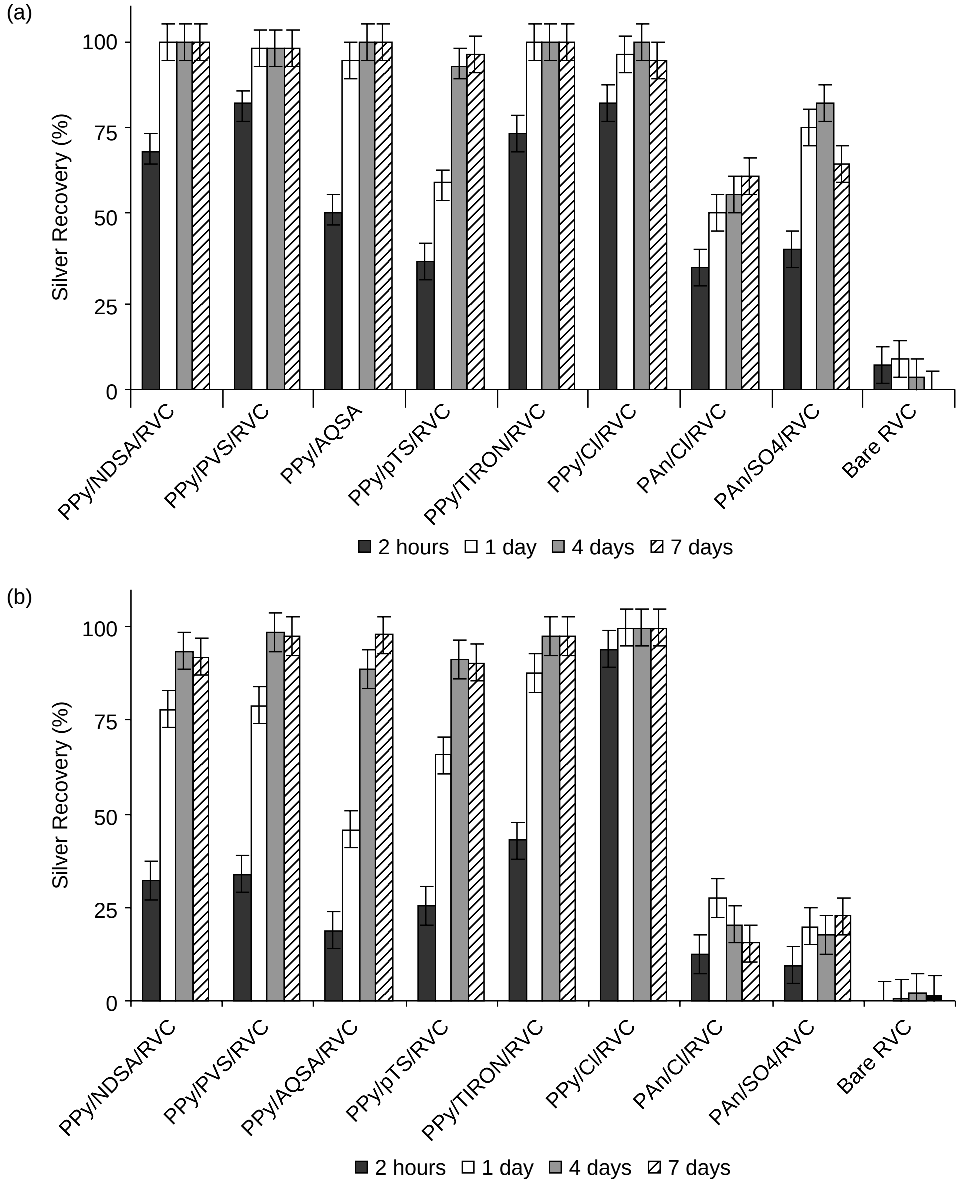

Fig. 2. Recovery of silver from 20 mL aqueous solution containing: (a) 100 ppm $AgNO_3$ or (b) 100 ppm $AgNO_3$ and 0.1 M HNO_3, by ICP coated RVC. Experiments were performed using pieces of ICP coated RVC measuring 3 cm × 1 cm × 1 cm.

The results of silver recovery experiments performed using solutions containing 100 ppm Ag^+ and ICP membranes and powders are shown in Fig. 1. For most systems a consistent trend towards greater silver recovery after longer exposure to the ICP was observed. Significant variations in the ability of the different materials to recover silver are also evident. For example, PAn/Cl and PPy/Cl powders showed silver recoveries of more than 90% from both low and near neutral pH solutions after just 2 h, while at least five other materials displayed recoveries of less then 30% under the same conditions. After 7 days most membranes and powders had recovered more than 60% of the silver initially present in either type of solution. However, PAn/SO_4 showed very poor recoveries from acidic solutions. Comparison of the data obtained at different pH values shows that in most cases lowering the pH resulted in a significant decrease in silver recovery. The exceptions to this were PAn/Cl and PPy/Cl powders, which appeared to be almost equally efficient at recovering silver from both types of solutions. While this suggests that the use of ICP powders might offer advantages for silver recovery, it is important to note that the results shown in Fig. 1 also reveal significant variations in recovery caused by changing the dopant present in ICP membranes and powders. For example, PAn/SO_4 powder recovered less than 5% of the silver present in a 0.1 M HNO_3 solution after 2 h, compared to more than 90% for PAn/Cl.

3.2. Silver recovery using polymer coated RVC

One of the many useful properties of ICPs is that they can be deposited onto a variety of substrates to give composite materials that share the properties of both the polymer and the underlying substrate. Reticulated vitreous carbon is a highly porous substrate with good electrical conductivity, allowing it to function as an electrode that can be coated with ICPs. We have previously explored whether the high surface area of composite materials consisting of ICPs deposited onto RVC show superior properties for the recovery of either $[AuCl_4]^-$ or $[Au(CN)_2]^-$ from aqueous solution [22,24]. In the case of solutions containing $[AuCl_4]^-$, the composite materials were shown to recover gold in a highly facile and selective fashion, and to possess comparable gold capacities when expressed as mg Au/g polymer, to ICP membranes [22]. The ability of ICP coated RVC to recover silver was investigated here. In all cases uniform adherent ICP coatings were obtained on the RVC substrate, which did not appear to affect RVC porosity. The amount of polymer deposited onto RVC varied between ICPs, and especially between polypyrroles and polyanilines. While the mass of polypyrroles deposited onto RVC was typically equal to or greater than the mass of PPy membranes used in silver recovery experiments, the mass of polyaniline present in the PAn/RVC composites used was considerably less than that of polyaniline powder used.

Fig. 2 illustrates the results of experiments performed using both acidic and near pH neutral solutions containing 100 ppm Ag^+. The amounts of silver recovered by uncoated RVC were minimal. Comparison of Figs. 1 and 2 suggest ICP/RVC composites were just as efficient or perhaps slightly more efficient than ICP membranes for recovery of silver. Six of the eight ICP/RVC composites examined recovered more than 90% of the silver present in either acidic or neutral solution, and the majority of ICPs that formed efficient membranes for recovery of silver, such as PPy/Cl, PPy/NDSA and PPy/PVS, also recovered the metal in a facile fashion when coated onto RVC. While it is tempting to attribute this to the tremendous surface area of RVC, it must be remembered that the amount of polypyrrole deposited onto this substrate was in some cases greater than that present in the corresponding PPy membranes. One exception to the generally observed trend of superior recovery shown by ICP/RVC composites was PAn/Cl/RVC. Powders composed of PAn/Cl recovered more than ~90% of the silver initially present in solution. However, the silver recoveries obtained using PAn/Cl/RVC were only between 50 and 60% from near neutral pH solutions, and less than 30% from acidic solutions. This may be attributed to the exceptionally small amounts of polymer present in this composite material, which was significantly lower than for any of the other ICPs examined, including PAn/SO_4/RVC. Comparison of the results obtained using ICP/RVC composites and silver solutions with different pH values, showed that increasing acidity resulted in small reductions in metal recovery by ICP coated RVC in most instances. However, for both PAn/SO_4/RVC and PAn/Cl/RVC, which displayed two of the poorest sets of recovery results among the composite

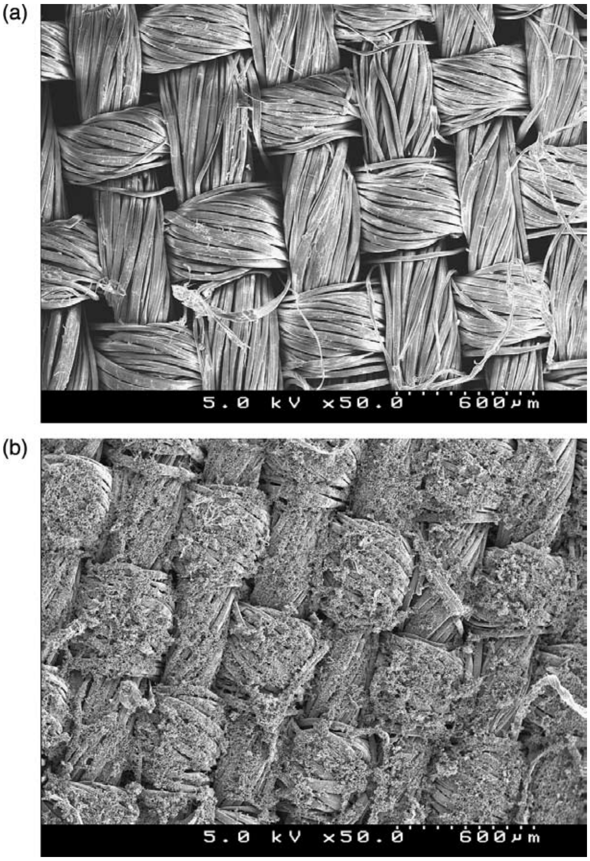

Fig. 3. Scanning electron micrographs of: (a) linen and (b) PPy/NDSA/linen. Both micrographs were obtained using a magnification of 50×.

materials, the decrease was significantly greater. This may again be attributed to the very low polymer loadings of both materials.

3.3. Silver recovery using polymer coated fabrics

The attractiveness of RVC as a substrate for producing composite materials lies in its combination of properties, including very high surface area and suitability as an electrode, which facilitates controlled electrochemical deposition of ICPs. The previous set of results illustrate that these properties can be harnessed to produce ICP/RVC composite materials that display comparable or perhaps even superior silver recovery properties to ICP membranes. Two drawbacks associated with the use of RVC as a substrate for ICP composites are its high cost and brittleness. An alternative set of substrates that do not have these disadvantages, but can still be used to produce ICP composite materials, are natural and synthetic fabrics such as cotton, linen and nylon. ICP/fabric composites can be readily prepared on relatively large scales using simple chemical polymerisation methods, and have been shown previously to be effective for recovery of gold from solutions containing

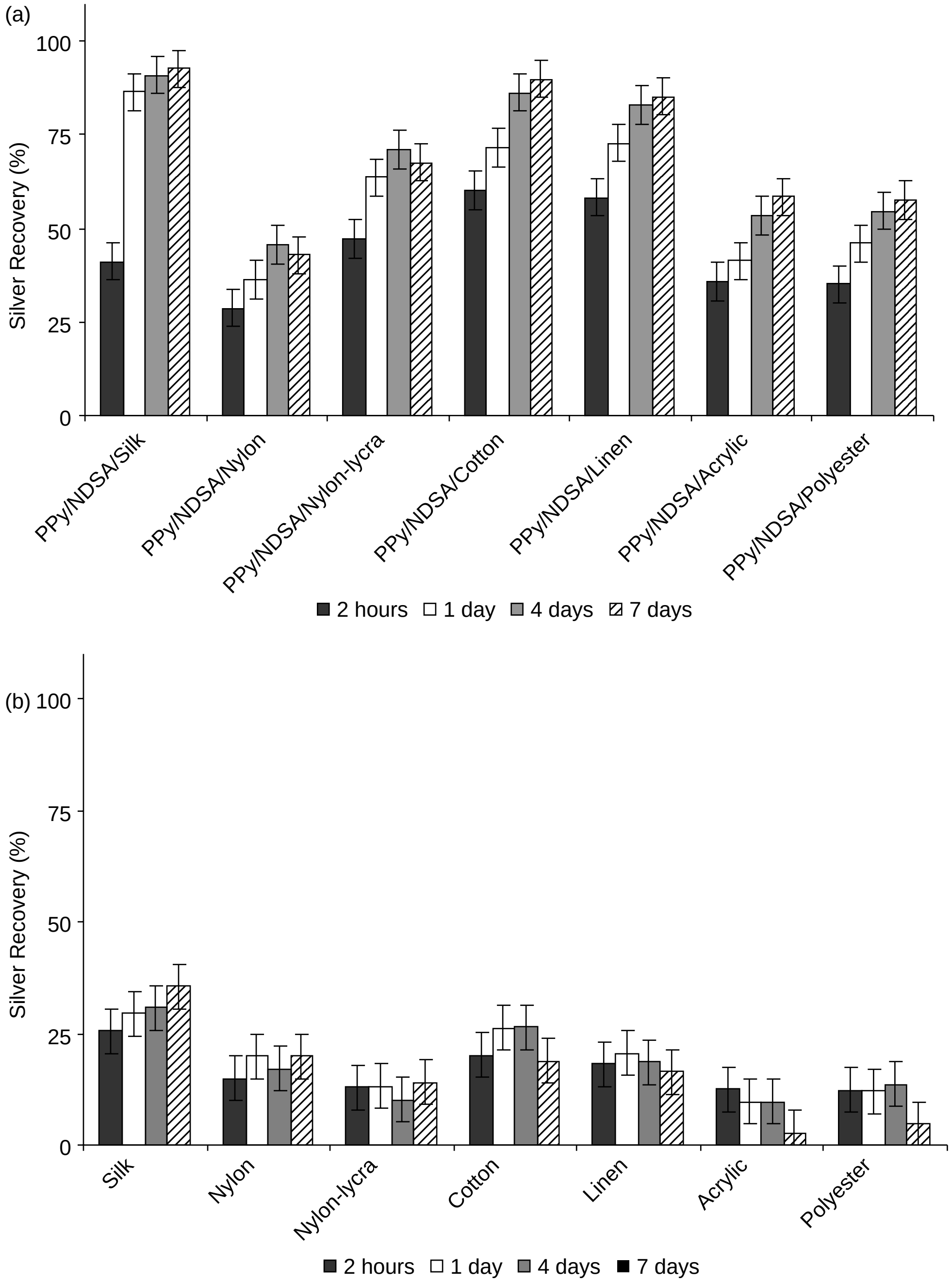

Fig. 4. Recovery of silver from 20 mL aqueous solution containing 100 ppm $AgNO_3$ by: (a) PPy/NDSA coated fabrics or (b) bare fabrics. Each experiment was performed using pieces of PPy/NDSA coated fabric or bare fabric measuring 5 cm × 2 cm.

$[AuCl_4]^-$ [20,21]. In this work, we have examined the ability of composite materials containing PPy/NDSA coated onto different fabrics to recover silver from solution. NDSA was chosen as the dopant for these systems as it has been shown previously to be an effective dopant when coating textiles with ICPs [21,25]. Fig. 3 shows SEM images of linen before and after coating with PPy/NDSA, which shows that the surface of the fabric is coated evenly with conducting polymer.

Fig. 4 compares the amount of silver recovered from aqueous solutions containing 100 ppm Ag^+ (pH 6.5) by PPy/NDSA/fabric composite materials, with that recovered by the uncoated fabrics. The mass of PPy/NDSA deposited onto different fabrics varied between 10 and 35 mg. This was slightly less than the amount of polymer present in PPy/NDSA/RVC composites used for silver recovery experiments, but comparable to the mass of PPy/NDSA membranes used previously (15–19 mg). The only exception to this was PPy/NDSA/linen, which had a mass of polymer (30–35 mg) significantly greater than that of PPy/NDSA membranes used for silver recovery, but still less than that of PPy/NDSA/RVC. Fig. 4(a) shows that all of the PPy/NDSA/fabric composites had recovered $>40\%$ of the silver initially present after 7 days, with the amount of metal recovered being $>80\%$ in some instances. Similar trends to those shown in Fig. 4(a) were observed in experiments using acidified solutions containing Ag^+, although the absolute amounts of silver recovered by the composite materials were typically $\geq 20\%$ lower.

Fig. 4(b) shows that all of the uncoated fabrics recovered generally between 10 and 20% of the silver initially present. While this is considerably less than the amounts recovered by the PPy/NDSA/fabric composites, it is still significant and merits further comment. Inspection of Fig. 4(a) shows that the three composite materials with the highest recoveries were PPy/NDSA/silk, PPy/NDSA/cotton and PPy/NDSA/linen, while the two uncoated fabrics which showed the greatest ability to recover silver were silk and cotton. Most of the silver recovered by the uncoated fabrics is probably a result of absorption of water and dissolved metal ion into the fabric, or adsorption of metal ion onto its surface. This is supported by SEM analysis of uncoated fabrics after exposure to concentrated silver solutions for 7 days, which showed an absence of particles that might be attributable to metallic deposits formed by a redox mechanism. Therefore, the slightly greater silver recoveries displayed by uncoated silk and cotton may reflect more open and/or hydrophilic structures, which permit greater penetration of solvent and dissolved solutes compared to synthetic fabrics such as nylon and polyester.

The higher silver recoveries displayed by uncoated cotton and silk would be expected to contribute to the greater performance of PPy/NDSA/silk and PPy/NDSA/cotton compared to the other composites. However, the majority of the silver recovered by these materials is probably a result of redox reactions between the ICP surface layer and Ag^+. Evidence in support of this was provided by the observation of silver particles on the surface of PPy/NDSA/fabric composites immersed in solutions containing 1000 ppm Ag^+ (see below). Significant differences in silver recovery between some composites, such as PPy/NDSA/silk and PPy/NDSA/nylon, are probably due to differences in contact between the polymer and metal ion, rather than differences in redox potential of the composites, which would not be expected to vary greatly. A comparison of the amount of silver recovered with the mass of polymer present in the composite material showed no correlation, further suggesting that factors such as surface morphology may be important.

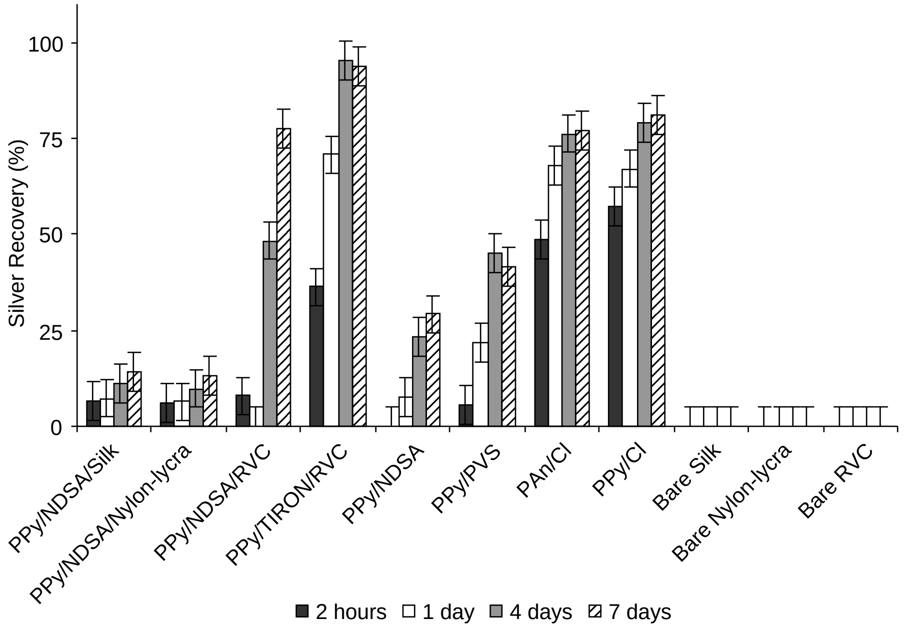

Fig. 5. Recovery of silver from 20 mL aqueous solution containing 1000 ppm $AgNO_3$ by ICP powders, membranes, coated RVC and coated fabrics. Each experiment was performed using 30 mg of ICP powder, pieces of ICP membrane or ICP coated fabric measuring 5 cm × 2 cm, or pieces of ICP coated RVC measuring 3 cm × 1 cm × 1 cm.

3.4. Silver recovery from concentrated solutions

Many of the materials prepared showed very high recoveries in experiments with solutions containing 100 ppm Ag^+, making it impossible to determine accurately their silver capacities. Therefore, a second series of experiments were performed in which selected high performing polymer membranes, powders and composites were allowed to react with solutions containing 1000 ppm Ag^+ (pH 6.5) for 1 week. The results of these experiments are presented in Fig. 5. It is immediately apparent that the performance of the fabric composites was significantly poorer than that of the other materials tested, as silver recoveries with the former were $<20\%$. PPy/NDSA and PPy/PVS membranes showed slightly greater silver recoveries, however, this was surpassed by the performance of ICP/RVC composites and ICP powders, which showed silver recoveries above 75%. While the results shown in Fig. 5 suggest the latter materials are superior silver recovery reagents, it must be borne in mind that comparison between different classes of materials are problematic, owing to variations in surface area, morphology and polymer loading.

In order to shed further light on the reasons behind the variations in silver recovery shown in Fig. 5, the data obtained after 7 days was used to provide an estimate of the absolute capacity of each material for silver. These values, which are the average of duplicate measurements expressed as mg Ag/g polymer are shown in Table 1, together with the mass of polymer present in each material. Table 1 shows that the maximum silver capacity of the different types of materials is between 500 and 600 mg Ag/g polymer, and variations in the identity of both the polymer and underlying substrate can result in significant variations in ability to recover silver. The latter points are illustrated by comparison of the silver capacity for PPy/NDSA membranes, with that for PPy/PVS membranes and PPy/NDSA composites with RVC, silk and nylon-lycra. The two polymer membranes differ in silver capacity by a factor of two, despite identical sized pieces being used in the metal recovery experiment. The greater silver capacity of PPy/PVS membranes may be attributed to their lighter mass, and the fact they recovered almost 50% more silver. In order to investigate the origin of this effect, cyclic voltammetry studies were performed using PPy/NDSA and PPy/PVS coated glassy carbon electrodes immersed in 0.1 M aqueous $NaNO_3$. The resulting cyclic voltammograms showed that the two ICPs did not differ significantly as reducing agents, suggesting that the differences in silver recovery are most likely a result of differences in surface morphology or surface area of the polymer exposed to the silver solution. Support for this hypothesis is provided by a comparison of the SEM images of PPy/NDSA and PPy/PVS membranes shown in Fig. 6. SEM shows that the surface of the latter membrane has a smooth and uniform surface morphology. In contrast, the surface of the PPy/NDSA membrane is covered by numerous nodule-shaped structures, many with diameters between 10 and 15 μm. These nodules may have a detrimental effect on the silver capacity of the polymer. This could be because a large spherical nodule contains less ICP and/or has a lower surface area than an aggregate of much smaller nodules with the same diameter. Table 1 also reveals that the underlying substrate can have a significant effect on silver capacity. This is best illustrated by comparison of the values for PPy/NDSA, PPy/NDSA/RVC, PPy/NDSA/silk and PPy/NDSA/nylon-lycra, which are 250, 500, 260 and 130 mg Ag/g polymer, respectively.

Table 1
Silver capacities and polymer loadings for selected ICP membranes, powders, and composite materials

Material	Mass of polymer (mg)	Silver capacity (mg Ag/g polymer)
Membranes		
PPy/NDSA	23	260
PPy/PVS	16	510
Powders		
PAn/Cl	30	520
PPy/Cl	32	510
RVC composites		
PPy/NDSA/RVC	31	500
PPy/Tiron/RVC	34	550
Fabric composites		
PPy/NDSA/silk	9	260
PPy/NDSA/nylon-lycra	21	130

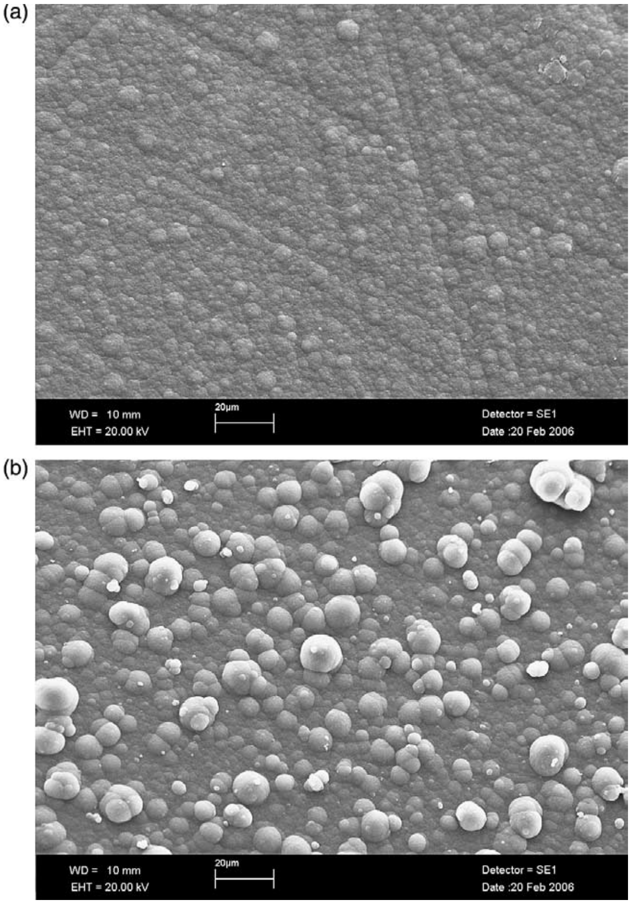

Fig. 6. Scanning electron micrographs of: (a) a PPy/PVS membrane and (b) a PPy/NDSA membrane. In both cases the images shown are of the side of the membrane exposed to the solution during polymer growth, and were obtained using a magnification of 1000×.

While the silver capacities shown in Table 1 indicate that all the materials examined have a strong ability to recover silver, they are still considerably less than values obtained in experiments examining recovery of gold from solutions containing $[AuCl_4]^-$. For example, PPy/PTS membranes, PPy/PTS/RVC and PPy/PTS/NL were previously shown to have gold capacities of 5000, 2900 and 7000 mg Au/g polymer, respectively [21,22]. These values are generally an order of magnitude greater than the capacities shown in Table 1, a fact that may be attributed to the unique nature of the gold recovery mechanism. Reduction of $[AuCl_4]^-$ by ICPs is accompanied by over-oxidation of the polymer, which then spontaneously undergoes reduction under the acidic conditions present to regenerate the original ICP so that it can participate further in the gold recovery process [15–17]. In contrast calculations show that the number of moles of silver recovered by either PPy/Cl powder or PPy/NDSA membranes is approximately only 1.5 times what would be expected based on the number of polymer repeat units present, which suggests that there is little, if any, recycling of the polymer during silver recovery. It is not clear why the mechanism of silver recovery is different to that for gold, since identical polymers were used and the pH of the solutions were similar.

3.5. Selectivity of recovery

The ability of two ICP powders to recover silver selectively from aqueous solutions containing 1000 ppm $AgNO_3$ and 1000 ppm Fe was investigated. After just 2 h both PPy/Cl and PAn/Cl had already recovered $>45\%$ of the silver initially present, while the amount of iron recovered was less than 2%. This illustrates that the mechanism of silver recovery by ICPs is selective, in a similar fashion to that seen previously with solutions containing gold and iron [22]. The origin of this selectivity is the higher redox potential of the $Ag^+/Ag(0)$ couple ($+0.80$ V) compared to both the $Fe^{3+}/Fe(0)$ (-0.037 V) and $Fe^{2+}/Fe(0)$ couples (-0.447 V), which results in only Ag^+ being able to oxidise ICPs and be reduced to the metallic state.

3.6. Characterisation of the products of silver recovery

Exposure of different ICP materials to solutions containing 1000 ppm Ag^+ resulted in the appearance of bright metallic deposits that suggested the formation of silver metal by reduction. Closer inspection of these deposits using scanning electron microscopy (Fig. 7) revealed the presence of well-defined crystalline regions of a white-coloured material. Comparison of the low magnification image of PPy/NDSA/linen after exposure to silver for 7 days (Fig. 7(a)), with that of PPy/NDSA/linen that had not been exposed to the metal (Fig. 3(b)), also reveals that the uniformity of the polymer coating deteriorates significantly upon standing for long periods of time in silver solutions.

Evidence that the crystalline deposits formed after long term exposure to silver ion contained silver metal was provided by X-ray photoelectron spectroscopy. Fig. 8 compares the 3d5/2 region of the X-ray photoelectron spectra of a sample of pure silver metal with that of the crystalline material that had deposited onto PPy/NDSA coated linen, polyester and acrylic after the materials were allowed to stand in 1000 ppm Ag^+ for 7 days. The spectrum of pure silver metal (Fig. 8(a)) shows a single symmetrical band with a binding energy of 368.3 eV, consistent with values reported

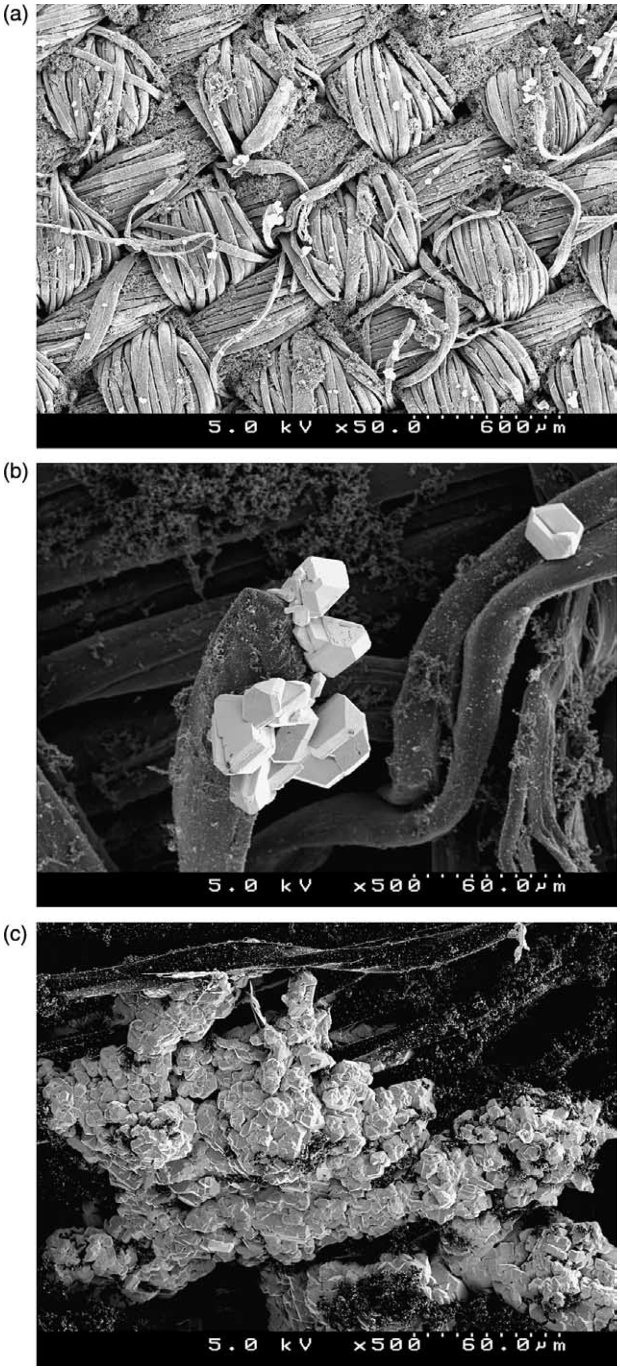

Fig. 7. Scanning electron micrographs of metallic deposits formed on ICP coated fabrics after exposure to solutions containing 1000 ppm $AgNO_3$ for 7 days: (a) 50× image of PPy/NDSA/linen; (b) 500× image of PPy/NDSA/linen; (c) 500× image of PPy/NDSA/polyester.

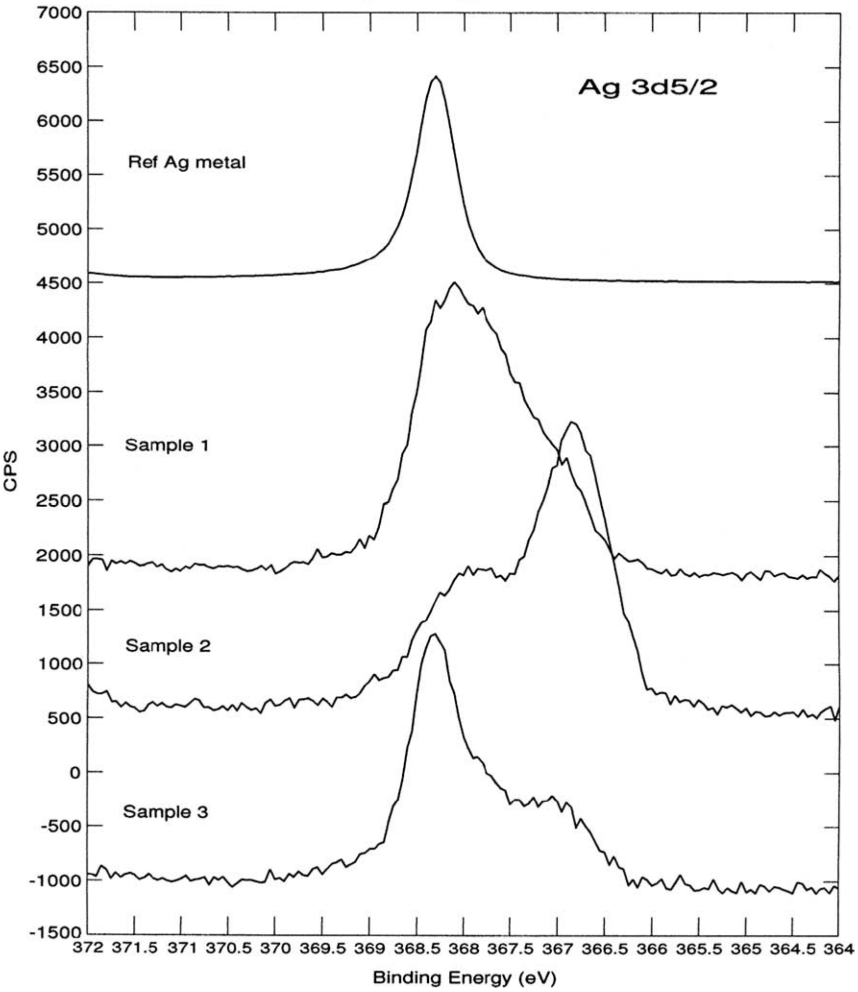

Fig. 8. X-ray photoelectron spectra of the Ag 3d5/2 spectral line of pure silver and metallic deposits formed on ICP coated fabrics after exposure to solutions containing 1000 ppm $AgNO_3$ for 7 days. Sample 1 = PPy/NDSA/linen, sample 2 = PPy/NDSA/polyester, sample 3 = PPy/NDSA/acrylic.

in the literature. The spectra of the three deposits all consisted of broader unsymmetric features that were shown to consist of two overlapping bands. The major bands in the spectra of the deposits on PPy/NDSA coated linen and acrylic had binding energies of 368.1 and 368.3 eV, respectively. These bands as well as the minor band in the spectrum of the deposit on PPy/NDSA/polyester (368.0 eV) are all consistent with assignment to silver metal, and provide strong support for a mechanism of silver recovery involving reduction of the metal ion by the ICP. The second band in the spectra of the deposits on each of the ICP coated fabrics had binding energies ranging from 366.8 to 367.3 eV. Assignment of these additional bands is difficult owing to the general insensitivity of the silver 3d5/2 band to changes in the chemical environment of the metal, which results in the most plausible candidates having very similar binding energies to that of silver metal. For example, the 3d5/2 binding energy for $AgNO_3$ has been reported to be 368.2 eV, while values of between 367.7 and 368.2 eV have been reported for Ag_2O [26]. The most likely explanations for the additional band in each XPS spectrum are the presence of an oxide of silver formed by aerial oxidation of the elemental metal or, less likely, the presence of an amorphous form of Ag(0).

4. Conclusions

This work demonstrates that a variety of ICP materials, including powders, membranes and composite materials with RVC or fabrics, are able to efficiently recover silver from aqueous solutions. The extent and rate of silver recovery from concentrated solutions is not as great as that seen previously for recovery of gold from solutions containing $[AuCl_4]^-$ [22]. Both observations may be attributed to one very important difference between the mechanisms of recovery of both metals. In the case of gold recovery, metal reduction and recovery occurs concomitantly with polymer over-oxidation. However, under acidic conditions the over-oxidised polymer is returned to its initial oxidation state, allowing quantities of gold comparable to or greater than that of the ICP to be recovered [15–17]. X-ray photoelectron spectroscopy provided evidence that the mechanism of recovery of silver by ICPs also involves redox chemistry. However, it is not possible to totally rule out the possibility that at least some of the silver recovered by PPy/Cl and PAn/Cl powders was a result of the dopant slowly leaching out of the polymer and forming $AgCl_{(s)}$.

Quantitative calculations show that there is a near stoichiometric relationship between the amount of ICP used and the quantity of silver recovered, even under acidic conditions. In fact the amount of silver recovered from more strongly acidic solutions was generally less than that from solutions with near neutral pH levels, which may be attributed to the oxidising nature of dilute HNO_3.

Changes to the polymer, dopant and underlying substrate were all found to have significant effects on the extent of silver recovery. It was shown that differences in redox potential was not a major contributing factor to the difference in silver capacities displayed by PPy/NDSA and PPy/PVS membranes. However, this is likely to be significant when comparing other systems, particular those containing different ICPs (e.g. polypyrroles and polyanilines). ICP coated RVC and powders displayed a far greater propensity to recover silver from solutions containing 1000 ppm $AgNO_3$ than ICP membranes or fabric composites. This highlights the potential role that other factors such as polymer surface area and morphology may play in determining overall silver capacity. The most efficient material for recovering silver from concentrated solutions was found to be PPy/TIRON/RVC, which recovered over 70% of the silver initially present after exposure for 1 day, and over 90% after 4 days. The results obtained for this material and the other RVC composites and ICP powders provides further impetus in the search to find materials that display comparable or better silver capacities, as well as enhanced kinetics of metal recovery. However, it should be remembered that many sources of recyclable silver contain the metal at relatively low concentrations. In preliminary studies involving solutions containing 20 mL of 10 ppm $AgNO_3$, we found that all seven PPy/NDSA/fabric composites examined recovered more than 85% of the silver after just 2 h, while three of the composites showed essentially quantitative recovery. It will be of interest to see if the other classes of ICP materials show similar effectiveness at recovering silver from dilute solutions. Additional experiments are also planned to investigate more fully the selectivity of the recovery process, and to make a detailed comparison of recovery efficiency with other adsorbents such as activated carbon.

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