

A New Approach for the Recovery of Precious Metals from Solution and From Leachates Derived From Electronic Scrap

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ABSTRACT: A new approach is described for the recovery of precious metals (PMs: Au, Pd and Ag) with >99% efficiency from aqueous solution utilising biogas produced during the aerobic growth of *Klebsiella pneumoniae*. Gold was recovered from electronic scrap leachate (~95%) by this method, with some selectivity against Cu. The recovered PM solids all contained metal and sulphur as determined by energy dispersive X-ray microanalysis (EDX). X-ray powder diffraction analysis (XRD) showed no crystalline metal sulphur compounds but a crystalline palladium amine was recorded. Silver was recovered as a sulphide (found by EDX), carbonate and oxide (found by XRD). EDX analysis of the Au-precipitate showed mainly gold and sulphur, with some metallic Au(0) detected by XRD. The gold compound was shock-sensitive; upon grinding it detonated to leave a sooty black deposit.

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Introduction

The European Waste Electrical and Electronic equipment (WEEE) Directive (2002/96/EC; Anonymous, 2005a) requires that electrical and electronic equipment be recovered and recycled. Manufacturers, sellers and distributors are required to fund the collection, treatment, recovery and disposal of WEEE from private households and stringent targets for EU businesses must be achieved. As an

example ~50,000 tons of printed circuit board scrap is produced in the UK annually, with only ~15% of this being recycled (Pilone and Kelsall, 2006). WEEE scrap (e.g. printed circuit boards) contains, in addition to plastic and general heavy metals (e.g. copper, and tin and lead from solder), a substantial content of precious metals (PMs) (Creamer et al., 2006).

Reprocessing of PMs via traditional hydro- or pyrometallurgical routes is costly and not environmentally friendly and a low cost method of PM recovery is required (Pilone and Kelsall, 2006). The possible contribution of biotechnology as a clean alternative has been addressed. For example, bioreductive recovery of gold was reported (Canizal et al., 2001; Kashefi et al., 2001; Korobushkina and Korobushkin, 1986; Lloyd, 2003; Lloyd et al., 2003; Yacaman et al., 2001) with, in some cases, extracellular deposition (e.g. Mukherjee et al., 2002) or by using cell extracts (Gericke and Pinches, 2005). The biodeposition of silver has also received attention (e.g. see Duran et al., 2005; Fu et al., 2000; Lloyd, 2003; Lloyd et al., 2003). Little has been published on the biotechnology of platinum (except for its widespread use in anti-cancer drugs, exploiting the ability of Pt-based compounds to bind tightly to bioligands such as DNA (e.g. Boulikas and Vougiouka, 2003)). Other than via biosorption, there are few studies of Pt biorecovery. During biosorption of Pt(IV) to cells of *Desulfovibrio desulfuricans* some endogenous bioreduction to lower valence species was observed (De Vargas et al., 2005). Reductive biorecovery of Pt(IV) at the expense of H₂ was observed in the presence of Pd(II) (Yong et al., 2003). It was suggested that Pt(IV) deposition was largely chemical in nature, via Pd(0) bionanoparticles as the reduction catalyst at the expense of H₂ (Mabbett et al., 2006; Sanyahumbi et al., 2005).

In contrast to Pt(IV), the bioreductive recovery of Pd(II) as biomass-bound Pd(0) is well-established, both from

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laboratory solutions (Lloyd et al., 1998, 2003; Yong et al., 2002, 2003), and industrial wastes (Mabbett et al., 2006; Sanyahumbi et al., 2005; Yong et al., 2003). Studies on PM recovery have concentrated on sulphate-reducing bacteria (SRB) because they have high hydrogenase activity, which couples the oxidation of H₂ to Pd(II) reduction (Lloyd et al., 1998, 1999a,b; Mikheenko et al., 2005). However, this approach cannot separate Pd and Pt (Sanyahumbi et al., 2005; Yong et al., 2003) and, accordingly, the solid deposit biorecovered from a PM-wastewater comprised a mixture of Pd, Pt, Ag and other metals suggesting their co-deposition (Mabbett et al., 2006).

Electronic scrap contains, in addition to PMs, ~25% by mass of copper (Creamer et al., 2006). Hydrogenases are sensitive to Cu²⁺, which inhibits Pd(II) reduction (Lloyd et al., 1998) and hence this approach is not applicable per se for the biorecovery of metals from WEEE leachates. Strong mineral acids (*aqua regia*) are required for the dissolution of PMs. Hence, WEEE leachates are aggressive and usually contain a high level of chloride ion. PMs can be removed from acidic leachates by pre-palladisation of biomass under permissive conditions and using this as the reduction catalyst in the acidic solution (Mabbett et al., 2006; Sanyahumbi et al., 2005) but this method is non-selective and does not remove Cu²⁺.

A recent study (Essa et al., 2005, 2006) proposed a new method of metal recovery which precipitates metals from solution using the off-gas from a culture of *Klebsiella pneumoniae* grown aerobically. Here, CO₂ is the respiratory product and, accordingly, analysis of the crystalline components of biogas-precipitated heavy metal (Cd, Pb, Hg) precipitates by X-ray powder diffraction (XRD) showed carbonates (and hydroxides) of all of the metals tested except mercury, which was reduced in part to Hg(I) with precipitation of HgCl (Essa et al., 2006). Energy dispersive X-ray emission analysis (EDX) revealed additional amorphous metal-sulphur components (Essa et al., 2006). Metal sulphide precipitation via volatile H₂S production (Aiking et al., 1982, 1985) was largely discounted since the precipitates were all white and lacked diagnostic colorations. Dimethyl disulphide was found as a significant component in the culture off-gas and it was proposed that the precipitate contained a metal-organothiol (Essa et al., 2006). Metal-organosulphide precipitation was proposed previously as a more effective route for metal removal from wastes than via sulphides per se (see Mühlbacher, 1994), but chemical production of organothiols for waste treatment is uneconomic. A biological method of organothiol synthesis could overcome the problems associated with the use of biogenic H₂S as the metal precipitant (see Essa et al., 2006).

The use of biogas can recover metals from aggressive solutions since no contact between the live bacteria and the metal is required. Furthermore, the biomass-free mineral solid is more economic to transport for further processing, and is also safe microbiologically since the microbial component is retained in the culture vessel.

The objective of this work was to evaluate the potential application of this approach to the removal of PMs from solution, with particular reference to the metals found in printed circuit board scrap, that is Au, Pd, Ag together with an excess of Cu (Creamer et al., 2006).

Materials and Methods

Microorganism and Culture Conditions

K. pneumoniae M426 was described previously (originally obtained from the National Culture Type Collection, Colindale, London) and was routinely grown aerobically in Luria Broth medium (Essa et al., 2005, 2006). The 16S rRNA gene sequence had 99% identity to the gene sequence accession no AF144323.1, confirming its identity as *K. pneumoniae* (see Essa et al., 2003). Metal precipitation used an aerobic 2 L batch reactor system with an off-chamber (50 mL) used for metal precipitation by passing the culture exit gases through metal solution (aq.) via a 0.2 µm filter as described previously (Essa et al., 2005, 2006).

Metal Precipitation Tests and Analysis of Soluble Residual Metals

Heavy metals were introduced as aqueous solutions (AgNO₃, Na₂PdCl₄, NaAuCl₄, Na₂PtCl₆.6H₂O, CuSO₄; 1 M stock solutions; concentrations as specified in individual experiments) in the external precipitation chamber as described by Essa et al. (2005, 2006). The metal precipitate formed after contact with the culture off-gas (2 or 24 h as stated) was removed by centrifugation (1,600g; 15 min). Aliquots (10 mL) of the supernatant were filtered (0.2 µm Nalgene Syringe filters) and analysed for residual soluble metals either using a 1999 Duo HR Iris advanced inductive coupled plasma (ICP) spectrometer (single metal solutions; Matlock et al., 2001), or were analysed by a commercial laboratory (gold solutions and gold/copper mixtures; H₂b Ltd., Capenhurst, UK).

Solid State Analysis

Samples were centrifuged as above and precipitates were washed in 20 mL deionised water three times and dried in air at 30°C. The metal precipitates were examined by scanning electron microscopy with energy dispersive X-ray micro-analysis as described previously (Ag, Pd; Essa et al., 2006) or using a FEI FEG ESEM L30 with an Oxford 'INCA' EDX system (20 kV; Au, Cu). X-ray powder diffraction analysis (XRD) was done on duplicate samples in parallel. Precipitates (a few mg) were washed and dried as above. XRD patterns were recorded on a Siemens D5005 diffractometer using monochromatic high-intensity CuKα radiation (λ = 0.1540598 nm). Where done, elemental ratios were determined using proton induced X-ray

Table I. Survey of metal precipitation by biogas at neutral and acidic initial pH values.

Metal	Precipitation at initial pH 7 (final pH 8–9)	Precipitation at initial pH 2 (final pH 6–7)
Copper ^a	+	+
Silver	+	–
Palladium	+	–
Platinum	–	–
Gold	–	+

The metal salts used were Na₂PdCl₄, Na₂PtCl₆, AgNO₃, NaAuCl₄ and CuSO₄. Concentrations were (mg/mL): Pd, 4.47; Ag, 13.98; Cu, 9.5 (see Table II), Au, 0.99 (see Table III) and Pt, 1.0; pH was adjusted with HNO₃.

^aThe amount of precipitate seen was greater in the samples at an initially neutral pH. Precipitation time was 2 h.

emission (PIXE) as described previously (Basnakova et al., 1998; Essa et al., 2006).

Results and Discussion

Electronic Scrap Composition

The composition of printed circuit board scrap was described previously (Creamer et al., 2006). The average PM contents of 12 solid samples milled in various ways were as follows (ppm): Au, 79; Ag, 68; Pd, 33; Pt 0 (below the limit of detection). The content of non-PMs (wt%) was: Sn, 3.8; Pb, 1.3; Cu, 28.7; Al, 1.7; Fe, 0.6 (Creamer et al., 2006).

Precipitation of Precious Metals Using Off-Gas From *Klebsiella pneumoniae*

The PMs were distinguishable by their pH-affected precipitation behaviour after 2 h (Table I) and diagnostic colorations (Table II). Platinum was not precipitated at either initial pH. Gold was precipitated at an initial pH of 2 only, while silver and palladium precipitated at an initial pH of 7 (Table I). The final pH increased in each case (Table I). This was noted previously and was suggested to occur via production of ammonia or volatile amines by the culture (Essa et al., 2006); *K. pneumoniae* is known to produce these

during growth (Ozugul, 2004). These observations suggest that this approach may have the capability to discriminate between Pt, Au and Pd/Ag, which is a challenge in PMs reprocessing. Since there was negligible platinum present in the printed circuit board waste (above) its recovery was not investigated further. Metal removal was >99% complete within 2 h (Table II). Copper was also removed by this approach, at both initial pH values, therefore selectivity for PMs against an excess of Cu(II) is likely to be problematic.

Solid State Analysis of the Palladium and Silver Precipitates

Palladium and silver had a similar precipitation behaviour (Table I) and they were further examined in parallel using PIXE, EDX and XRD. The ratio of Pd/S found by PIXE analysis was ~1:1; the error was too great to state this unequivocally (Table II) but a form of palladium sulphide was concluded and this was confirmed by EDX analysis (Fig. 1). Silver was present to an excess of ~ sixfold over sulphur (Table II; expected elemental ratio for Ag₂S is 2:1) suggesting additional, non-sulphur, species. The EDX analysis (Fig. 1) detected only metal, sulphur and carbon in each PM sample, with no oxygen (O (K α) emission peak 0.5249 keV). However, EDX is insufficiently sensitive to detect low concentrations of elements. Conversely, XRD detects only crystalline material irrespective of its amount in a bulk sample and hence it is possible to get an apparently different result using the two methods. The powder pattern of the Ag-mineral shows components of Ag₂O and also Ag₂CO₃ (Fig. 2) in accordance with the precipitation of metal carbonates described previously (Essa et al., 2006) but the concentrations were low since the oxygen was not detected by EDX. Since Hg(II) was reduced to Hg(I) by the biogas (Essa et al., 2006) and Au(0) was found in this study (see below) it is possible that Ag(I) was reduced to Ag(0) but this was not sought; metallic silver rapidly tarnishes to the sulphide in air and hence Ag(0) was not expected in significant quantities. As reported previously in the case of heavy metal precipitates (Hg, Pb, Cd: Essa et al., 2006) there was no evidence for any crystalline forms of metal sulphide although in each case small unassigned peaks were visible in the XRD powder patterns (Fig. 2).

Table II. Removal of metals from solution by culture off-gas of *K. pneumoniae* and ratio of metal to sulphur in the precipitate.

Metal	Initial concentration (mg/mL) as metal	Residual concentration (μ g/mL as metal)	% of metal removed	Elemental ^a ratio M/S	Colour of precipitate
Pd	4.47 \pm 0.59	6.4 \pm 1.67	>99%	0.89 \pm 0.68:1*	Brown
Ag	13.98 \pm 0.81	1.9 \pm 1.04	>99%	5.96 \pm 0.28:1	Black
Cu	9.51 \pm 0.53	1.5 \pm 0.78	>99%	NT	Pale blue

The percentage of metal removal from solution was determined after 2 h as described in the text. The salts used were Na₂PdCl₄, AgNO₃ and CuSO₄, at an initial pH value around 7.0 except for Cu which was tested at initial pH values of 2–4 (pH adjusted with HNO₃ or NaOH as appropriate), to prevent spontaneous copper hydroxide formation in the medium. Data are means \pm standard errors for three independent experiments.

NT: not tested.

*The elemental ratio of Pd/S cannot be concluded with confidence due to the large error (see text).

^aElemental ratios in the precipitates were determined by proton-induced X-ray emission analysis (see text).

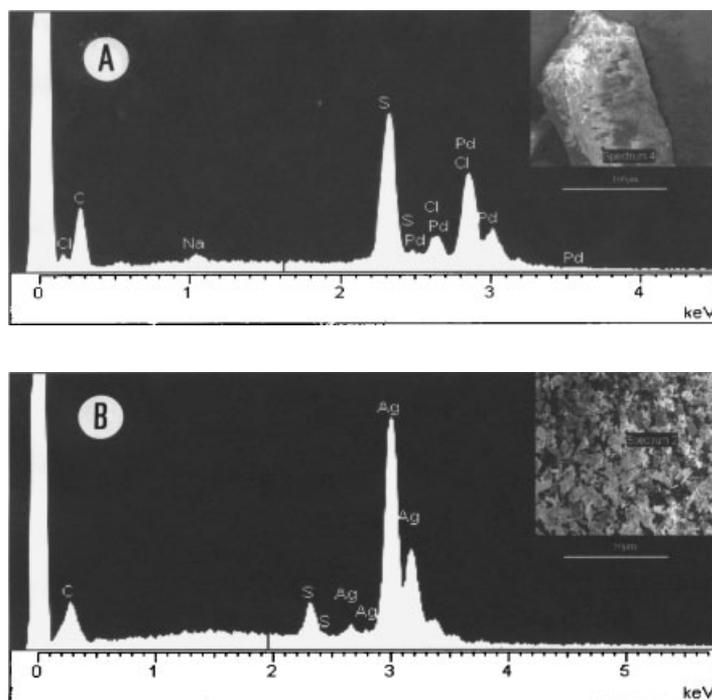


Figure 1. EDX analysis of palladium and silver deposits formed by culture off-gas of *Klebsiella pneumoniae*. The precipitate was recovered from the vessel after 2 h (see Table II). Inset: appearance of the precipitate; bars are 100 μm and 50 μm for the Pd-precipitate (A) and the Ag-precipitate (B), respectively.

The powder pattern for the palladium precipitate shows the presence of a crystalline amine component identified as $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ (Fig. 2), although the nitrogen was not detected by EDX (Fig. 1; N ($K\alpha$) emission peak is 0.3924 keV). This confirms the low-level production of ammonia or a volatile amine(s) by the culture, although analysis of a culture head gas sample for ammonia per se by GC gave this as below the level of detection (M. Paterson-Beedle and L.E. Macaskie, unpublished). The presence of volatile amines was not sought since the main GC peak of the head gas was broad with the only well-defined specie being identified as dimethyl disulphide (Essa et al., 2006). It is well known that Pd (like Pt) has a strong tendency to bind to amine groups via co-ordination to the amine nitrogen. Mertig et al. (1998), investigating the sorption of Pt and Pd complexes onto proteinaceous surfaces, showed a specific adsorption of platinum ions (tetrachloroplatinate) onto the template, with histidine acting as a ligating amino acid, while de Vargas et al. (2005) showed co-ordination of Pd(II) onto unidentified biomass amine groups in whole cells of *D. desulfuricans*. The proportions of palladium amine and sulphide were not determined. The analytical methods do not differentiate between PdS and Pd-organothiols; the latter was suggested to be formed from the head gas in the case of mercury (Essa et al., 2006). A metal-dimethyl disulphide precipitate (Essa et al., 2006) would give an expected elemental ratio of Pd/S of 1:2 (i.e. $(\text{CH}_3)_2\text{S}_2\text{Pd}$; c.f. Table II). If Pd(I) arose via reduction (c.f. above) a compound such as

CH_3SPd would comply with the 1:1 ratio found by PIXE, analogous to the situation suggested with mercury, where Hg(I) was deduced (Essa et al., 2006). A component containing an amorphous form of palladium carbonate could not be discounted since Ag_2CO_3 was found by XRD (Fig. 2) even though oxygen was not detected in either sample by EDX (Fig. 1). Further analysis was beyond the scope of this investigation.

Solid State Analysis of the Gold and Copper Precipitates

More than 99% of the copper was removed from the solution as a chalky pale blue precipitate after 2 h at initial pH values of 2–7 (Tables I and II). The precipitate produced at acidic pH was a more intense blue. The hydrolysis behaviour of copper predominates in solution and precipitation of copper hydroxide starts at pH \sim 5–6 (Hughes and Poole, 1991). Accordingly, analysis of the copper compounds produced at both initial pH values showed the presence of significant amounts of oxygen with, at the lower pH, sulphur, and the formation of needle-like crystals (Fig. 3). A crystalline copper sulphate-hydroxide ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) was confirmed in the latter by XRD (Fig. 4).

In the case of gold the EDX analysis of the golden yellow precipitate obtained showed the presence of Au and S (Fig. 3). The X-ray emission peaks for Au and S overlap (Au

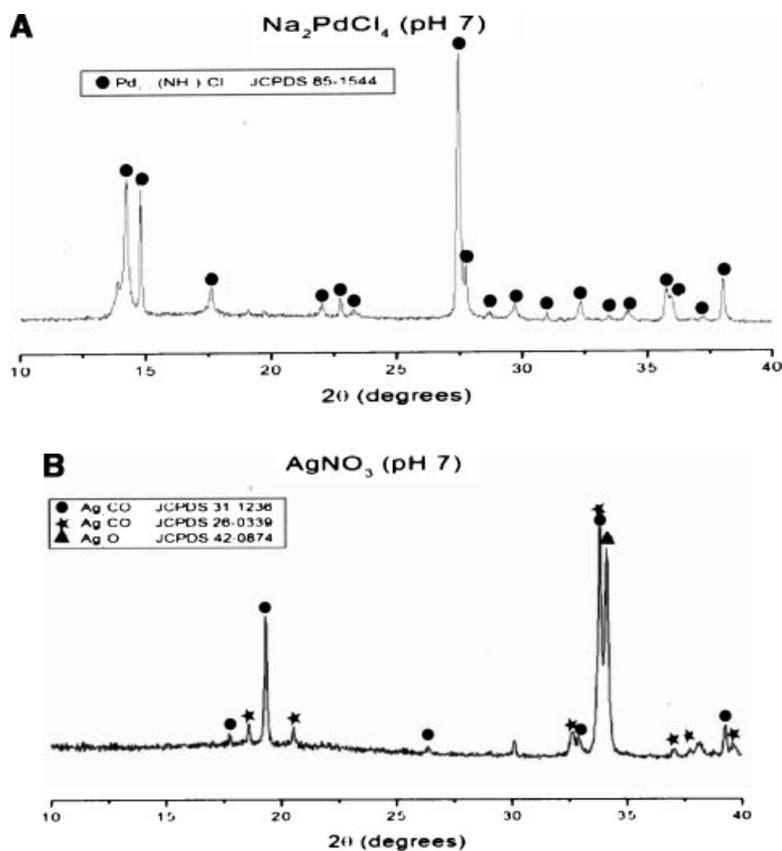


Figure 2. X-ray powder diffraction analysis of precipitates obtained (see Table II) using culture off-gas of *K. pneumoniae*. **A:** palladium; **B:** silver. Inset box: crystalline materials found by reference to the Joint Committee for Powder Diffraction Studies (JCPDS) database.

$M\alpha$ and $S\ K\alpha$ peaks are at 2.1205 and 2.3075 keV, respectively) but the sulphur peak was visible as a ‘shoulder’ on the Au peak (Fig. 3). Small amounts of oxygen, nitrogen and chloride were also detected, in addition to carbon (Fig. 3). The X-ray powder pattern showed only an amorphous or nanocrystalline material, with no crystalline components (not shown). By expansion of the ‘noise’ (Fig. 4B) a peak was identified at a position corresponding to Au(0) (Fig. 4B) which confirms metal ion reduction by a component of the biogas. Some reduction of Au(III) to Au(0) is not surprising since previous work suggested the reduction of Hg(II) to Hg(I) (Essa et al., 2006).

The alkalinisation of the solution, together with the detection of an amine compound of palladium by XRD (see above) indicate the presence of low concentrations of ammonia/amine in the culture off-gas and, accordingly, a small amount of nitrogen was detected in the Au-compound (Fig. 3). Amine compounds of PMs, particularly silver and gold, are explosive. Accordingly, a few mg of the unidentified gold compound detonated when ground in a pestle and mortar, leaving a sooty deposit (presumably the carbon component, but this was not tested). This behaviour is diagnostic of the compound ‘fulminating gold’, a gold-

amine characterised by shock-sensitivity (see Sadler, 1999); indeed, a recent note draws attention to the need to exercise extreme caution when preparing materials using gold salts and ammonia (Fisher, 2003). Clearly future studies must characterise the exact nature of the Au-solid, and its stability, before implementation of this approach for large scale PM recovery.

Removal of Metals From Mixed Gold and Copper Solutions

The above suggests that it would be difficult to separate gold and copper from a mixture by the off-gas precipitation technique per se since they both formed precipitates at an acidic initial pH (Table I). Accordingly, in combination both metals were removed, a co-precipitate formed within 2 h (Table III) and the final pH was found to be ~ 8.3 . Removal of gold also occurred from electronic scrap leachate (see Creamer et al., 2006) supplemented with Au(III) and adjusted to an initial pH of 3; 223 ppm was found by assay initially, with 9 ppm residual after biogas treatment and hence the removal of Au(III) was $>95\%$ but the copper

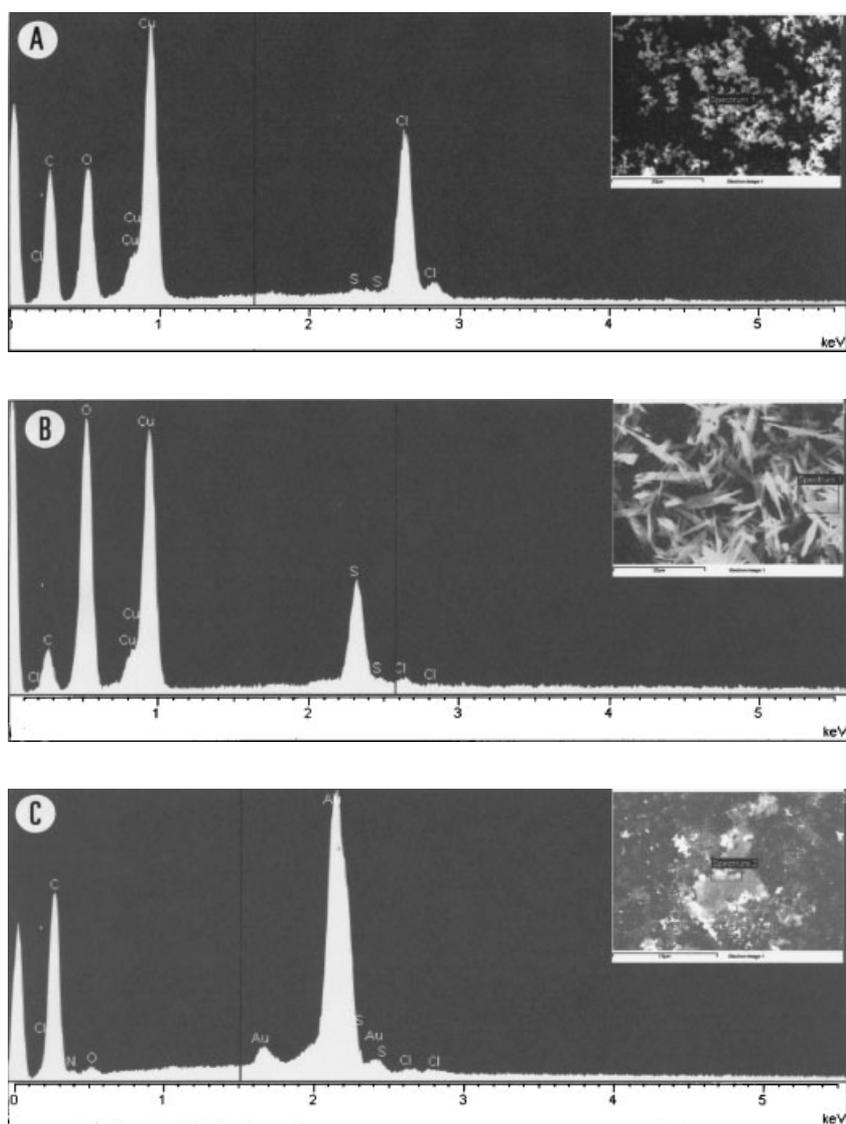


Figure 3. EDX analysis of copper and gold deposits formed by culture off-gas of *K. pneumoniae*. **A:** Cu-precipitate at initial pH of 7. **B:** Cu-precipitate at initial pH of 2. **C:** Au-precipitate at initial pH of 2. Inset: appearance of the precipitates. Bars are 20 μm (A,B) and 10 μm (C).

removal from the leachate was not determined. The pH of the leachate increased by only ~ 2 units, to pH 5, as compared to ~ 6 units in the test solutions. Table III shows that copper was removed from solution effectively at pH 2 after 2 h but less so after 24 h. This effect was reproducible and was maximal at an initial pH of 3.0 (not shown) where only 35% of the Cu(II) was removed after 24 h, under which conditions the removal of Au(III) was 97%. This could be attributed to resolubilisation of the copper component of the co-precipitate by volatile amines/ammonia produced by the culture (see above) since the cuprammonium ion is highly soluble.

In a final series of tests samples of mixed Au(III)/Cu(II) solution (as shown in Table III) at an initial pH of 3 were treated and the precipitate and residual solution were

divided after 2 h. One half was further treated with biogas for 24 h, after which time the residual solution became dark blue, characteristic of the cuprammonium ion, with a final pH of 9.0 ± 0.5 . The other half was withdrawn and treated by careful addition of a few drops of 5% ammonia solution. A dark blue solution characteristic of the cuprammonium complex ion was formed. Quantitative analysis was not done due to the highly hazardous nature of PM amines (see below) but these results suggest that Au could be selectively recovered from a mixed Au(III)/Cu(II) solution by utilising the biogas to selectively resolubilise Cu(II), leaving an insoluble Au-amine/sulphide. However, washing with ammonia is reported to hydrolyse the 'fulminating gold' compound $(\text{ClAuNH}_2)_2\text{NH}$ to the more explosive $(\text{OHAuNH}_2)_2\text{NH}$ (Anonymous, 2005b). Similar tests were

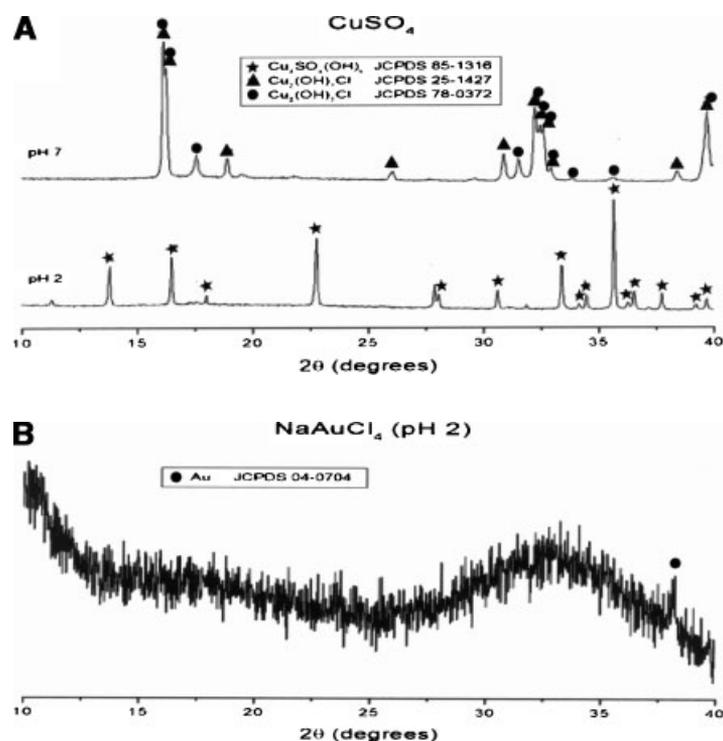


Figure 4. X-ray powder diffraction analysis of the copper (A) and gold (B) precipitates. Inset boxes: crystalline materials found by reference to the Joint Committee for Powder Diffraction Studies (JCPDS) database.

not carried out with Ag and Pd since all PM amines are unstable. The compounds of silver are among the most violently explosive of the nitrogen derivatives of the PMs (Anonymous, 2005b). ‘Fulminating silver’ is formed by the action of ammonia on silver oxide (c.f. Fig. 2) and the black compound (c.f. Table I) is reported to explode violently in the liquid under slight stirring (Anonymous, 2005b).

Conclusions and Future Perspective

This study reports the use of a biogas to recover PMs from solution. The exact composition of the recovered solids remains to be established but they are suggested to comprise

mixtures of metal carbonates, oxides, thiols and amine compounds. The use of biogas can partially separate gold from copper after 24; this is attributable to the production of volatile ammonia or amines by the culture. However, great care needs to be taken to minimise the formation of PM amines which are shock-sensitive. A reaction scheme could be proposed for metal recovery from WEEE leachate (liquid stream 1) using biogas as follows. At pH 2 copper and gold are removed rapidly and separated from the liquor. Further treatment of the solid with biogas can selectively resolubilise Cu(II) as the cuprammino complex (liquid stream 2). The residual liquid (in stream 1) would be adjusted to pH 7 for co-removal of Ag and Pd; any Pt (if present) would remain in solution (liquid stream 3). The solid Pd/Ag will not easily

Table III. Gold and copper removal from pure metal solutions and mixtures.

Initial concentration (ppm)		Residual metal (ppm)		Metal removed (%)	
Au(III)	Cu(II)	Au(III)	Cu(II)	Au(III)	Cu(II)
990 ± 23	0	11 ± 3 (2 h)	0 (2 h)	99%	NT
0	186 ± 0	0 (2 h)	3 ± 1 (2 h)	NT	98%
431 ± 5	196 ± 6	8 ± 1 (2 h)	6 ± 4 (2 h)	98%	97%
437 ± 10	214 ± 26	4 ± 3 (24 h)	42 ± 8 (24 h)	99%	80%

Aqueous solutions of Au(III) and Cu(II) were prepared (nominally to 1000, 500 or 200 ppm) and the initial and final metal concentrations before and after biogas treatment for 2 or 24 h (initial pH of 2.0) were analysed by a commercial laboratory as described in Materials and Methods. Data are means ± SEM from three experiments.

be separated in water via biogas using the reactions described here but other studies have considered the potential for using electrochemistry to separate PMs in WEEE leachates (Pilone and Kelsall, 2006).

For the realistic application of biogas the formation of PM amines must be avoided and it must be stressed that the use of *K. pneumoniae* is unsuitable for further process development because of both its potential to produce biogenic amines (Ozugul, 2004) and also because it is a class 2 pathogen. This strain was originally from a collection of medical isolates (see Essa et al., 2003) and further work would examine the scope for using non-pathogenic strains of related enterobacteria (e.g. see Creamer et al., 2006). We recommend strongly that trials using a copper test solution with spectrophotometric monitoring for formation of the diagnostic soluble dark blue cuprammino ion is carried out before exposure of mixed PM/copper solutions to bacterial off-gases. The proportion of metal amines present is assumed to be small since nitrogen was largely undetectable in the solid state analyses, the main components of the precipitates being attributed to non-crystalline metal thiols.

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