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Biorecycling of Precious Metals and Rare Earth Elements

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1. Introduction

The six platinum group elements (PGEs), also known as the platinum group metals (PGMs) are platinum, palladium, rhodium, ruthenium, iridium and osmium. These, together with gold and silver, are considered to be "precious" metals due to their high demand coupled with relatively low abundance. Complex processing is required for their extraction and refining from primary ores (Bernardis *et al.,* 2005). Relative to the other precious metals PGMs have high technological importance. Valuable for their resistance to corrosion and oxidation, high melting points, electrical conductivity and catalytic activity, these elements have wide industrial applications (Xiao & Laplante, 2004). The major uses are found in the chemical, electrical, electronic, glass and automotive industries. For example their high catalytic activity for a wide range of substrates has resulted in their use in many industrial synthetic processes, reforming reactions in the petroleum refining industry, hydrogenation and dehydrogenation reactions in the pharmaceutical industry, and both organic and inorganic oxidation reactions (Bernardis *et al.,* 2005) to name but a few. The catalytic properties of PGM are also having a positive impact on the environment through the implementation of automotive emission control catalysts (Whiteley & Murray, 2003, Ek *et al.,* 2004, Zereini & Wiseman, 2009).

South Africa is currently the largest producer of PGMs, followed by Russia and North America. In 2008 South Africa supplied 76% of the worlds platinum, 33% of its palladium and 82% of its rhodium. Russia supplied more palladium than South Africa (51%) but its contribution of the other two metals was much smaller. With the exception of 2006 demand for PGMs has constantly exceeded supply, resulting in large price increases within the industry. The disparity in 2006 is thought to have been caused by significantly lower platinum usage in jewellery compared with previous years (in fact the lowest usage since 1993).

The last 75 years have seen the overall consumption and uses of platinum expand dramatically. Demand (and hence also its price) and uses are impossible to predict far into the future, but the resources and potential supply of platinum and palladium can be calculated with some degree of confidence. Cawthorn's calculations (Cawthorn, 1999) indicate about 204 and 116 million ounces of proven and probable reserves of platinum and palladium, respectively, and 939 and 711 million ounces of inferred resources, down to a depth of 2 km. These figures represent about 75 and 50% of the world's platinum and palladium resources, respectively. These figures for proven and probable reserves in the Bushveld Complex are sufficient for the next 40 years at current rate of production.

However, it has been estimated that if all 500 million vehicles in use today consuming fossil fuels, were substituted with hydrogen driven fuel cells, operating losses would mean that all the world's sources of platinum would be exhausted within 15 years (Gordon *et al.,* 2006, Anon., 2007). As we are moving away from a fossil fuel based economy into a hydrogen economy, it will be vital to conserve stocks of these metals by increasing recycling technologies and preferably by methodologies that remanufacture new materials within the same process.

The environmental impact of mining, extraction and primary production is uncertain but is likely to be large. The Resource Efficiency KTN (Anon., 2008) estimates that worldwide mining activities (of all minerals) are responsible for around 5% of global carbon dioxide emissions. A 2004 report by Earthworks (Anon. 2004) calculated a larger figure, stating that the metals mining industry is responsible for 7-10% of global energy consumption. Either figure demonstrates that the overall environmental impacts of the extractive industries are highly significant.

According to research commissioned by the UK Department for Transport (2006) 12.7 tonnes of ore is extracted per troy ounce of platinum produced. The Resource Efficiency KTN (2008) puts this figure at approximately 10 tonnes per ounce, depending on ore concentration and mining depth. This leads to large spoil heaps and high energy consumption. In fact 65 – 75% of the total cost of producing pure PGMs is accrued at the mining stage due to the large energy demand (Pincock, 2008). In the long-term carbon intensities will grow, as more energy is required to process lower grades of ore, unless technological change can offset the impact.

In contrast to PGMs and despite their name, Rare Earth Elements (REE) are relatively abundant in the earth's crust. Consisting of the 15 lanthanide elements of the periodic table (with the addition of yttrium and scandium), these metals have similar geochemical properties and, consequently, are often found together in mineral deposits. Although their average concentration in the earth's crust is similar to other commonly used industrial metals (e.g. chromium, nickel, zinc), these metals are often difficult to extract economically because of their low local concentrations.

The use of REE ranges from their incorporation in alloys for the metallurgy sector to "high-tech" applications such as laser-guided weapons and hybrid-car batteries. Their widespread incorporation in electronic devices (e.g. computers, mobile phones, digital cameras) and increasingly popular consumer goods (e.g DVDs) has caused demand to increase significantly in the past 5 years. As demand is expected to increase further with the development of electric cars and hybrid vehicles, there is growing concern that the world may soon face a shortage of the REE.

These concerns have recently intensified in response to the recent decrease in REE exports from China, who currently produces over 97% of the world's REE supply and is estimated to possess about half of the 110,000 metric tons of REE currently available worldwide. In the coming years, China is expected to build strategic reserves in REE to meet the rise in their domestic demand and potentially to influence global market prices. Alternative sources of REE are being sought, notably in Australia and California, but mining operations are still limited to date.

Significant amounts of REE can be found in the waste electronic equipment (WEE) network and, as such, these could form a partial answer to REE sourcing problems. In Japan alone, there is a very substantial amount of REE stored in electronic wastes. At present, REE are not often recycled, because of the small quantities present in many commercial products

both on a total and a per-unit basis. In addition, their low market price per-kilogram relative to precious metals means that many common recycling technologies are not cost effective.

One alternative to traditional physicochemical reclaiming processes for PGM and REE is to use the ability of specialised bacteria to reduce or mineralise metals. Many studies have demonstrated that challenging bacteria with oxidised metal species resulted in the precipitation of solid phases of the metal. In the case of precious metals and gold, several studies showed that sulfate-reducing bacteria (SRB) and Fe(III) reducing bacteria are able to reduce palladium (Pd), platinum (Pt) and gold (Au) to the zerovalent form of the metal (Lloyd *et al.,* 1998; Kashefi *et al.,* 2001; Yong *et al.,* 2002a).

Bioreduction is a system involving enzymatically-assisted metal precipitation from a high valence to a zerovalent state. The identification of the enzymatic step responsible for metal deposition may permit its deposition in a growth-decoupled mode (Yong *et al.,* 2002b). Enzymatic systems may promote metal reduction under favourable conditions, independently of cell metabolism. In some cases, metal reduction to lower valence states is directly involved *via* electron transport reactions giving crystals of metal oxide or base metal coated on the cell surface. Bioreduction of metals is a relatively recent addition to the portfolio of metal biorecovery processes. Investigations into new recovery technologies were prompted by the increased market value of many precious metals and more recent studies showed a potential for bioreductive recovery of Pd (Lloyd *et al.,* 1998), Pt (Yong *et al.,* 2002a, b), Ag (Fu *et al.,* 2000) and Au (Kashefi *et al.,* 2001; Konishi *et al.,* 2006). The microbial reduction of Pd(II) to insoluble Pd(0) has attracted much interest as this process was not only successfully applied to the recovery of Pd from industrial automotive catalyst leachates (Yong *et al.,* 2003) but could also be coupled to synthesize nanoscale bioinorganic catalysts of considerable commercial potential (Mabbett *et al.,* 2006, Macaskie *et al.,* 2010). Studies on Au recovery (Lovley *et al.,* 1993) suggested that *c*-type cytochromes of the Fe(III) reducer *Geobacter metallireducens* transferred electrons to soluble Au(III); other work (Deplanche & Macaskie, 2008) has suggested the involvement of hydrogenase activity, in conjunction with another unidentified mechanism, in Au(III) reduction and the formation of Au(0) nanoparticles on the biomass. Other investigations showed the potential of a wide range of dissimilatory Fe(III) reducing mesophiles (*Geobacter ferrireducens*, *Shewanella alga*), thermophiles (*Thermotoga maritime*) and some Archea (*Pyrobacter* sp.) to reduce Au(III) to Au(0) (Kashefi *et al.,* 2001). As most strains precipitated Au(0) on the cell surface, bacterial Au recovery has the potential to become an easy, cheap and attractive process, especially since readily-available jewellery waste rich in Au provided an adequate source of the metal for biorecovery and conversion (Deplanche *et al.,* 2007)., while some urban road dusts were surprisingly rich in Au (H. Prichard and L.E. Macaskie, unpublished) adding to the concept of "urban biomining" (see later).

Research on bacterial metal reduction has been driven forward by the range of biotechnological applications that could derive from harnessing this unique microbial feature. Such applications include the remediation of radioactive contaminants (Lovley, 1991), immobilisation of problematic wastewater pollutants (Chen and Hao, 1998), degradation of xenobiotics (Larsson *et al.,* 1988), the development of new technologies in metal mining (Rawlings and Johnson, 2007) and metal recovery (Lloyd *et al.,* 1998; Kashefi *et al.,* 2001; Konishi *et al.,* 2006). Indirect applications could also include the development of biomagnets (J. R. Lloyd, personal communication) and manufacture of novel biocatalysts (see later), in addition to generation of electricity from sediments (Lloyd, 2003) and indeed from the bionanoparticles (Yong *et al.,* 2010) as well as the creation of metal detecting biosensors (Eccles *et al.*, 1997).

In metal and radionuclide remediation, dissimilatory reduction of Se, Tc, V, U and also possibly other metals (like plutonium (Pu) and neptunium (Np)) would convert soluble metal species to insoluble forms that can readily be removed from contaminated water and waste streams. So far, flow-through bioreactors containing immobilised cells of dissimilatory iron- or sulfate reducing bacteria have been shown to reduce and precipitate Cr(VI), Mo(VI), Tc(VII) and U(VI) (Lovley and Phillips, 1992; Lloyd *et al.,* 1997; Lloyd *et al.,* 1999; Mabbett *et al.,* 2002). Simple electron donors (formate, lactate or H_2) are fed to immobilised cells, which support continuous metal reduction and precipitation over many days. Lovley and coworkers demonstrated that *G. metallireducens* and *S. oneidensis* could couple U(VI) reduction to energy generation and thus could be ideal candidates for large scale remediation process (Lovley *et al.,* 1991). However, U(IV) is adsorbed by Fe(III) oxides forming large volumes of uranium-containing solid waste. Sulfate-reducing bacteria (SRB) were found to possess the same U(VI) reducing activity as Fe(III) reducers and can be cultured more quickly and cheaply, making them potential candidates for U(VI) remediation strategies although the production of H_2S may be problematic. Uranium exists mainly as U(VI) and U(IV) although some actinide contaminants can be stable and predominate as the intermediate (V) oxidation state. A novel approach to the remediation of Np(V) and its capture as biomineral phosphate was shown by Lloyd and Macaskie (2000). Although multiple electron transfer steps are involved in metal reduction, the exact mechanism remains unclear. A study by Renshaw *et al.,* (2005) showed that reduction of U(VI) proceeded *via* a U(V) intermediate showing single electron transfer.

The direct role of periplasmic hydrogenases of *D. desulfuricans* in Tc(VII) reduction was also demonstrated by Lloyd *et al.,* (1999a). In this study, cells treated with Cu(II) (a selective inhibitor of periplasmic -but not cytoplasmic- hydrogenases) lost their ability to reduce Tc(VII). Comparison of Tc(VII) reduction rates by *E. coli* and *D. desulfuricans* demonstrated the greater potential of the latter, and this was attributed to the high activity of the soluble, more accessible, periplasmic hydrogenases in the SRB. A subsequent study (Lloyd *et al.,* 1999b) identified *D. desulfuricans* as the ideal candidate for Tc(VII) reduction. H_2-supplied cells carried out continuous Tc(VII) reduction at far higher rates than shown in similar studies using *E. coli* (the rate of Tc(VII) reduction was 64-fold greater), *S. putrefaciens* (28-fold improvement) or *G. metallireducens* (36-fold improvement). Similarly, selenium has been shown to serve as terminal electron acceptor to support growth of some organisms with concomitant reduction of Se(VI) to Se(0) (Roux *et al.,* 2001; Yee *et al.,* 2007, Macaskie *et al.,* 2010). An economic evaluation of the use of selenate and selenite reducing microorganisms to remove selenium from waste waters concluded that the microbial process could potentially be cheaper than chemical reduction if a nutrient cheaper than peptone could be used in the culturing of the metal-reducing bacterial consortium (Lovley, 1994).

A second alternative to traditional physicochemical recycling techniques is to use bacterial enzymes to immobilise metallic species as metal precipitates. These can be as (e.g.) sulfides, carbonates and phosphates. Such metal 'biomineralisation' is a well-established technology for metal removal from wastewaters but until now the low value of the recovered metal has made such processes largely uneconomic. With the value of REEs (and also uranium) rising rapidly these biotechnologies are becoming attractive. With a view to metal recovery from metal-bearing wastewaters in a form that can be readily processed for subsequent re-use and avoiding energy-expensive commercial refining, an example of this technology has been demonstrated using a *Serratia* sp. originally isolated from metal polluted soil (Macaskie & Dean, 1982) for the recovery of heavy metals such as uranyl ion, lead, copper, cadmium,

lanthanum, strontium, manganese, thorium, americium and plutonium (Macaskie & Dean, 1984; Macaskie & Dean, 1985; Tolley *et al.,* 1991; Macaskie, 1992; Macaskie *et al.,* 1994; Yong *et al.,* 1998; Forster & Wase, 2003; Paterson-Beedle *et al.,* 2004). In the case of uranium the deposited material can be used as nanocrystalline ion exchanger for the removal of radionuclides from nuclear wastes (Paterson-Beedle *et al.,* 2006), while a similar function can be achieved via biogenic hydroxyapatite (calcium phosphate) (Handley-Sidhu *et al.,* 2011) which has a crystallite size much smaller than that of commercial HA, and hence a much higher surface area for interaction with the 'target' metallic species.

The metal-accumulating *Serratia* strain (NCIMB 40259) atypically overproduces a PhoN acid type phosphatase. In the presence of heavy metals the phosphatase enzyme liberates inorganic phosphate ligand (HPO_4^{2-}) from a phosphate donor e.g. glycerol-2-phosphate (G2P) and deposits metal (M) as polycrystalline cell bound $MHPO_4$ (Macaskie *et al.,* 1992, Macaskie *et al.,* 2000).

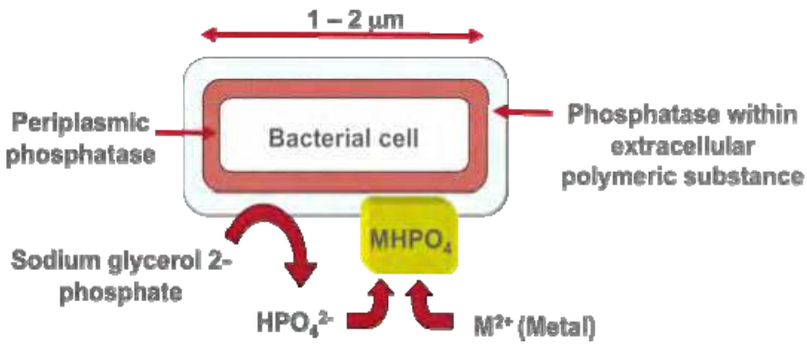


Fig. 1. Mechanism of metal phosphate accumulation by the action of acid phosphatase.

In order to achieve metal removal from solution, *Serratia* cells are immobilised on a support such as polyurethane foam and incorporated into a flow through column. Metal precipitation and crystallisation is *via* the production of locally high concentrations of phosphate ligand, which exceeds the solubility product of the metal phosphate in the vicinity of nucleation sites on the cell surface (Bonthrone *et al.,* 1996; Macaskie *et al.,* 1994). Studies using ^{31}P NMR attributed the nucleation sites to phosphate groups in the lipid A component of cell-surface lipopolysaccharide (Bonthrone *et al.,* 2000; Macaskie *et al.,* 2000). All heavy metals having insoluble phosphates should be amenable to bioremediation in this way.

As an alternative approach to the economic provision of phosphate ligand into the crystalline metal phosphate an interesting study exploited features of the 'enhanced biological phosphate removal' waste water treatment process, in which some bacteria (e.g. *Acinetobacter* spp) grown aerobically deposit intracellular reserves of polyphosphate (polyP). Upon transfer to anaerobic conditions (which can be spatial or temporal) the polyP is mobilised and inorganic phosphate is released from the cells. This was harnessed to the deposition of uranium (Dick *et al.,* 1995) and lanthanum (Boswell *et al.,* 2001) phosphates in a similar way to those biomanufactured using the phosphatase route (above), in a continuous process (Boswell *et al.,* 2001). As a third approach, the use of phytic acid (inositol phosphate, a component of plant wastes and a by product from biodiesel production) as the phosphate donor molecule has been shown to have good economic potential for metal biorecovery (Paterson-Beedle *et al.,* 2010)

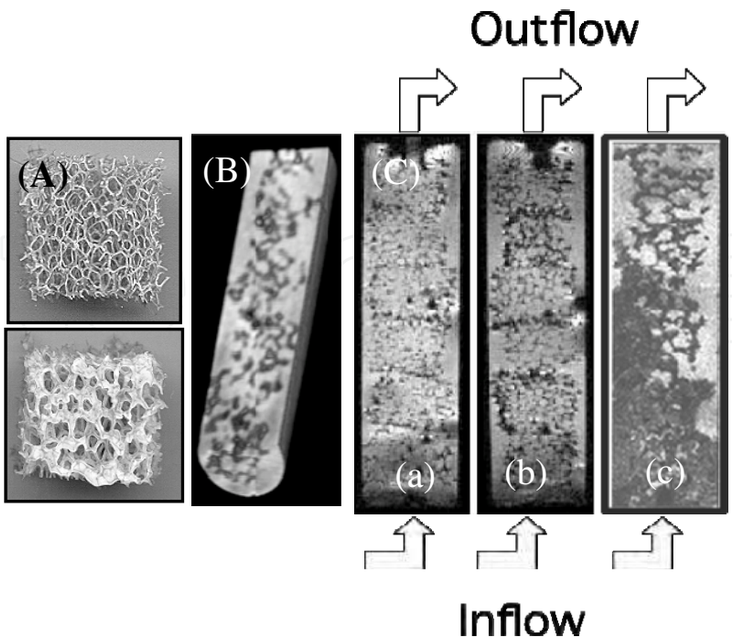


Fig. 2. (A) Polyurethane reticulated foam cubes before and after coating with biofilm of *Serratia* NCIMB 40259. (B) 3-D image of a flow- through a *Serratia* metal recovery column viewed using magnetic resonance imaging (Paterson-Beedle *et al.,* 2001). The reticulated foam matrix is clearly visible. (C) shows the centre of the column imaged in a 2-D slice: (a) before metal addition (glycerol 2-phosphate alone); (b) with metal and no substrate and (c) with metal and substrate. Metal phosphate deposition is shown as dark areas (Macaskie *et al.,* 2005).

Focusing on precious metal biorecovery for subsequent applications ('biorefining'), we now demonstrate in separate case studies the two potential pathways of biorecovery of PGMs *via* bioreduction (case study 1) and REE biorecovery *via* metal phosphates (case study 2).

2. Case study 1: Biorecovery of PGMs from spent car catalyst and biofabrication of new catalysts

Since the 1970s and the implementation of vehicle emissions regulations, worldwide consumption and market price of PGM have increased in parallel, driven by the widespread incorporation of Pd, Pt and rhodium (Rh) in automotive catalytic converters. The finite nature of PGM resources has led to the development of various recovery techniques which commonly include chemical processing of wastewaters but these treatments are often made difficult by unusual solution chemistry as these metals are usually present as complexes in solution (Demopoulos, 1989). Direct precipitation is often not readily applicable while electrochemical recovery requires electrodes with very large surface area for satisfactory metal deposition. Solvent extraction is often costly and non-selective; chelating ion exchange resins have been developed to increase separation of PGM from other metals (Streat and Naden, 1983) but, once eluted, individual metals still require separation using hydrometallurgical techniques. Until recently, there was no "clean" simple, selective and/or efficient system for precious metals recovery (Yong *et al.,* 2002b).

This goal remains elusive. It was shown (Dalrymple *et al.,* 2005) that while bacteria can selectively recover Pd(II) over Pt(IV), the period of selectivity before Pt(IV) is catalytically reduced by the Pd(0) seeds formed on the biomass is too short to form the basis of an industrial process. A selective process for metal recovery from electronic scraps was illustrated by Creamer *et al.,* (2006) but is probably too complex for industrial adoption. However, mixed metal deposits supported on bacterial cells have been reported to be catalytically active in reductive processes (Mabbett *et al.,* 2006) and as fuel cell electrocatalysts (Yong *et al.,* 2010). It is now accepted that biofabrication of new materials from wastes dictates the unavoidability of metal mixtures given the nature of the feedstocks. Since the ground-breaking work of Baxter-Plant *et al.,* (2003) and Mabbett *et al.,* (2006), the literature abounds with reports of using PGM-coated bacteria as catalysts in reactions of increasing complexity and industrial interest. Table 1 summarises the applications of bio-PGMs catalysts found in the literature biomanufactured from pure metal salts.

Metal	Microorganism support	Catalytic test	Comments	References
Au	*Desulfovibrio desulfuricans*	Selective oxidation of glycerol		Deplanche *et al.* (2007)
	Escherichia coli	Selective oxidation of glycerol Selective oxidation of alcohols		Deplanche *et al.* (2007) Deplanche *et al.* (2010b, 2011)
Au/ Pd	*Desulfovibrio desulfuricans*	Selective oxidation of alcohols	Au/Pd core/shell NPs	Deplanche *et al.* (2010, 2011)
	Escherichia coli	Selective oxidation of alcohols	Au/Pd core/shell NPs	Deplanche *et al.* (2010, 2011)
Pd	*Arthrobacter oxydans*	Cr(VI) reduction Mizoroki–Heck coupling Hydrogenations		Deplanche *et al.* (2008a), Wood *et al.* (2010)
	Bacillus sphaericus	Hydrogenations		Creamer *et al.* (2007)
	Clostridium pasteurianum	Cr(VI) reduction	Process coupled to microbial H_2 production	Chidambaram *et al.* (2010)
	Cupriavidus necator	H_2 evolution from hypophosphite Suzuki–Miyaura and Mizoroki–Heck couplings Hydrogenations Reductive dechlorination		Søbjerg *et al.* (2009), Bunget *et al.* (2010), Søbjerg *et al.* (2011)
	Cupriavidus metallidurans	Cr(VI) reduction Mizoroki–Heck coupling Fuel cell electrocatalyst		Deplanche *et al.* (2008a), Yong *et al.* (2010)

Metal	Microorganism support	Catalytic test	Comments	References
Pd	*Desulfovibrio desulfuricans*	H_2 evolution from hypophosphite	Free cells, flow through reactors, immobilised cells, e- donor provided by fermentation of sugar wastes	Yong *et al.* (2002b, 2007, 2010), Mabbett *et al.* (2002, 2004, 2006), Baxter-Plant *et al.* (2003), Macaskie *et al.* (2005), Humphries et *et al.* (2006), Deplanche *et al.* (2007, 2008, 2009), Harrad *et al.* (2007), Redwood *et al.* (2008). Bennett *et al.* (2010), Harrad *et al.* (2007)
		Cr(VI) reduction		
		Reductive dechlorination		
		Reductive debromination		
		Suzuki–Miyaura and Mizoroki–Heck couplings		
		Hydrogenations		
		Fuel cell electrocatalyst		
	Desulfovibrio vulgaris	Reductive dechlorination	Free cells, flow through reactors, immobilised cells	Baxter-Plant *et al.* (2003, 2004), Humphries *et al.* (2006)
		Cr(VI) reduction		
	Desulfovibrio sp. Oz-7	Reductive dechlorination		Baxter-Plant *et al.* (2003, 2004)
	Escherichia coli	Reductive dechlorination		Deplanche (2008), Yong *et al.* (2010)
		Cr(VI) reduction		
		Mizoroki–Heck coupling		
		Fuel cell electrocatalyst		
	Micrococcus luteus	Cr(VI) reduction		Deplanche (2008)
		Mizoroki–Heck coupling		
	Paracoccus denitrificans	H_2 evolution from hypophosphite		Søbjerg *et al.* (2009), Bunge *et al.* (2010)
		Suzuki–Miyaura and Mizoroki–Heck couplings		
	Pseudomonas putida	H_2 evolution from hypophosphite		Søbjerg *et al.* (2009), Bunge *et al.* (2010)
		Suzuki–Miyaura and Mizoroki–Heck couplings		
	Rhodobacter capsulatus	Hydrogenations		Wood *et al.* (2010)

Metal	Microorganism support	Catalytic test	Comments	References
Pd	*Rhodobacter sphaeroides*	Reductive dechlorination Fuel cell electrocatalyst		Redwood *et al.* (2008), Yong *et al.* (2010)
	Serratia sp.	Cr(VI) reduction Mizoroki–Heck coupling		Deplanche (2008)
	Shewanella oneidensis	Cr(VI) reduction Mizoroki–Heck coupling Reductive dechlorination	e- donor supplied by microbial fuel cell	DeWindt *et al.* (2005, 2006), Merten *et al.* (2007), Deplanche (2008), Hennebel *et al.* (2011).
	Staphylococcus sciuri	Suzuki–Miyaura and Mizoroki–Heck couplings Hydrogenations Reductive dechlorination		Søbjerg *et al.* (2011)
Pt	*Desulfovibrio desulfuricans*	Fuel cell electrocatalyst		Yong *et al.* (2010)

Table 1. Applications of precious metal catalysts supported on bacteria and fabricated from metal salt precursors

Biosorption of precious metals onto biomass has been considered as an attractive alternative to traditional recovery techniques. Microorganisms used for biosorption processes include bacteria, fungi, yeasts and algae. Differences in metal uptake are due to the properties of each microorganism such as cell wall structure, nature of functional groups and surface area (Palmieri *et al.,* 2000). Beveridge (1989) showed that bacteria make excellent biosorbents because of their high surface-to-volume ratios and a high content of potentially active chemisorption sites such as teichoic acid present in the cell walls of Gram-positive bacteria. Various microbial species have been shown to be relatively efficient in the biosorption of metal ions from polluted effluents. The biosorption literature is very large over the last 30 years and the reader is referred to key reviews by Volesky (2007) and Gadd (2009). The application of biosorption to precious metals is less well developed due to their complex solution chemistry.

Volesky (1999) reported the effective utilisation of *Bacillus* biomass (the main active ingredient of the commercial biosorbent AMT-Bioclaim) in the biosorption of Au(III) from cyanide solution. In an early study, Yong *et al.,* (2002b) defined the optimum Pd(II) sorption pH to be between 2 to 4 and achieved Pd recovery using a combination of both biosorption and bioreduction. *D. desulfuricans* was shown to possess a high capacity towards Pd(II) biosorption. Cells challenged with acidic Pd(II) solution (2 mM) showed rapid uptake of metal ions (85% uptake after 10 mins) and up to 15% of the biomass dry weight. Saturation of the biosorption capacity was observed within 35 minutes. The effect of the nature of the Pd(II) complex on the bacterial biosorption capacity was also demonstrated. Optimum

uptake from chloride salt ($PdCl_4^{2-}$) was at pH 4 and up to 50% of uptake from a 2 mM solution was observed at pH 2 but only 10% Pd was removed at neutral pH. Uptake from the amine salt ($Pd(NH_3)_4^{2+}$) was pH-independent but was lower; this was attributed to the strong complexing ability of ammonium ions for Pd(II). Furtermore, it was shown that cells of *D. desulfuricans* had greater affinity for Pd(II) than Pt(IV) and Rh(III) and it was suggested to exploit this hierarchy in a new "biological" separation technique (Yong *et al.,* 2002a; Yong *et al.,* 2002b). DeVargas *et al.,* (2004), investigated Pd(II) and Pt(IV) biosorption kinetics by three separate species of the genus *Desulfovibrio* and identified *D. desulfuricans* as the best biosorbent. A low pH is required for the protonation of cell surface functional groups to attract negatively charged species such as $PdCl_4^{2-}$ and the mechanism is probably an ion exchange of $PdCl_4^{2-}$ for biomass Cl^- groups (DeVargas *et al.,* 2005).

Other kinds of high metal-sorbing biomass such as yeast, fungi and algae have also been considered for precious metal recovery. Some chemical compounds of yeast cells can act as ion exchangers with rapid, reversible binding of cations whereas for metal removal and recovery from aqueous solutions, dead fungal biomass seems to offer several advantages; such biomass is often a by-product of industrial processes and may be obtained inexpensively, biosorption kinetics are not affected by metal toxicity since there is no metabolic activity, the biomass does not require nutrient supply and is not affected by the recovery of surface-bound metals (Volesky and Holan, 1995; Vieira and Volesky, 2000). Some studies (Volesky *et al.,* 1994) indicate that the most common yeast biomass (*Saccharomyces cerevisiae*) is an effective biosorbent material and it has been used for Pt(IV) recovery into a proton-exchange membrane fuel cell (PEMFC) to generate electricity following reduction of sorbed Pt(IV) (Dimitriadis *et al.,* 2007). Another industrially important organism, the fungus *Penicillium chrysogenum*, has been shown to extract Au(III) from cyanide solution through anionic gold cyanide species adsorption onto N^-, P^- or O^- containing functional groups on the biomass. However, the biosorption capacity was not encouraging (Niu and Volesky, 1999). Chitosan, which can be extracted from the cell wall of Zygomycetes (a group of phytopathogenic fungi) has a markedly cationic character and a positive charge at most pHs due to its significant content of free amino groups. Thus, chitosan has been found to be an excellent sorbent for the removal of numerous trace metals from wastewaters including Pd(II) and Pt(IV) in addition to base metal ions (see Schmuhl *et al.,* 2001). Catalytically active precious metal nanoparticles supported on chitosan have been reported previously (Guibal *et al.,* 2009 and references therein).

Despite the apparent promise of this type of technology, industry has been slow to endorse biosorption strategies. In addition to economic competitiveness, disadvantages include the perceived variation between batches of the biological product, a lack of specificity and sensitivity to changes in pH (Gavrilescu, 2004). Following discussions at both 2005 and 2007 International Biohydrometallurgy Symposia, the scientific community recognised the lack of commercial potential of biosorption despite extensive attempts and advised for a move towards alternative technologies. This position may, however, change in the case of highly valuable metals and in view of the increasing scarcity of resources.

The work of Lloyd *et al.,* (1998) first showed the potential of a Pd(II) bioreduction process using resting cells of *D. desulfuricans*. When contacted with Pd(II) solution, this organism was shown to precipitate soluble Pd(II) ions to elemental cell-bound Pd(0) using pyruvate, formate or H_2 as the electron donor. Under electron microscopy, opaque deposits of approximatively 50 nm were observed on the surface of challenged cells and these were confirmed to be elemental Pd(0) by energy-dispersive X-ray microanalysis. The authors gave

an insight into the enzymatic nature of the Pd(II) reduction mechanism as cells pre-treated with Cu(II), a known inhibitor of periplasmic hydrogenases, lacked Pd(0) crystals. The role of periplasmic hydrogenases toward Pd(II) reduction was further investigated by Mikheenko *et al.,* (2008) and Deplanche *et al.,* (2010). In studies using several mutants of *D. fructosovorans* and *E. coli* with deleted periplasmic and/or cytoplasmic membrane-bound hydrogenases, mutants lacking periplasmic soluble hydrogenases reduced Pd(II) only at the site of the remaining cytoplasmic membrane-bound hydrogenase, confirming the role of the latter in the nucleation and growth of Pd(0) crystals.

Bioreduction of Pd(II) is affected not only by the same parameters affecting biosorption (e.g. pH, metal salt, competitive ions) but also by other factors such as the choice and concentration of the electron donor, the cell concentration and the presence/absence of O_2. In a study investigating the effect of both the electron donor and the cell concentration on the bioreduction of Pd(II) to cell bound Pd(0) by *D. desulfuricans*, Yong *et al.,* (2002a) found that reduction at the expense of H_2 was slower than when using formate. This was attributed to mass transfer limitations between gas in headspace and liquid. They also showed that the effect of the electron donor and cell concentrations synergistically affected reduction rates. Bioreduction was negligible when both cell and formate concentrations were low up to a threshold value (0.13 mg ml^{-1} of cells, 20 mM formate) where bioreduction dramatically increased. This was explained by the ability of Pd(0) to trap H_2 and hold it as stable, highly reactive atomic H•. Deposited Pd(0) on cells has a very high affinity for H_2 liberated from formate and itself acts as a catalyst in the chemical degradation of more formate (Yong *et al.,* 2002b). Thus, the initial biodeposition reaction is hydrogenase(s)-mediated until autocatalytic reduction takes over. This has been exploited in the recovery of Pd(0) from highly aggressive waste using cells lightly pre-palladised in an intial step under more permissive conditions (Table 2).

The rate of Pd(II) bioreduction was shown to be pH-dependent in at least two studies (Yong *et al.,* 2002a; Yong *et al.,* 2002b). However, the pattern differed according to the electron donor used. Bioreduction of Pd(II) at the surface of *Desulfovibrio* sp. using formate decreased to 50% when the pH was decreased from 7 to 6 and no reduction occurred at pH 2. H_2 allowed reduction at lower pH (optimum 4-7) with 50% reduction still retained at pH 2. The same pattern was observed with the influence of anions on bioreduction. Formate-supported reduction was inhibited up to 50% in the presence of low nitrate/chloride concentrations while H_2-supported reduction remained unaffected by 1 M nitrate at pH 2 and 75% activity was retained in 1 M chloride. Bioreduction was also shown to be O_2 sensitive with formate but not with H_2.

The early studies helped to define conclusively the role of microbial cells and enzymatic mechanisms in Pd reduction and inspired a large number of subsequent studies in this area (Table 1). Three key roles could be attributed. Cells were thought to: 1) act as an enzyme catalyst (formate dehydrogenase and hydrogenase(s) providing an initial pool of electrons), ;2) provide foci of metal deposition for subsequent growth of Pd(0) crystals and 3) act as a scaffold for Pd(0), the primary crystals ("seeds") of which autocatalysed further reaction, leading to stable Pd(0)-nanocluster growth.

Other early studies (Mikheenko *et al.,* 2003; Humphries *et al.,* 2004) suggest that the choice of an organism possessing a high number of active hydrogenases is a requisite to improve Pd recovery yields. Hence most studies on Pd biorecovery have used SRB and notably *Desulfovibrio* spp. as organisms of choice for Pd(II) precipitation. As mentioned earlier, *Desulfovibrio* spp. are known to have a high metal-reduction capacity *via*

hydrogenases and/or c_3-type cytochrome with broad metal specificity coupled with the possibility to use a large spectrum of compounds as electron donors. However, theoretically, most organisms with strong hydrogenase(s) activity could be potential candidates to be used in Pd biorecovery systems. The attempt to move away from SRB reflects the fact that, to be used at industrial scale, the ideal organism should be non-pathogenic, easily culturable and fast-growing, in addition to having strong hydrogenase activity. Furthermore, H_2S, a by-product of dissimilatory sulphate reduction, is a powerful human and catalyst poison. Use of SRB as supports for making Pd catalysts hence requires extensive washing steps to remove H_2S. However, on the other hand, in the case of gold, "partial" poisoning of the catalyst by S- groups can sometimes be beneficial to catalyst activity but this is difficult to control by chemical methods and hence is not used industrially to date.

Pd(0) biodeposition has been observed in e.g. the Fe(III)-reducer *S. oneidensis* and the photosynthetic organism *Rhodobacter sphaeroides* by mechanisms which are still not elucidated (Table 1, DeWindt *et al.,* 2005; Redwood *et al.,* 2005; 2008). The facultatively anaerobic Gram-negative bacterium *E. coli* has been shown to possess the ability to reduce Pd(II) to Pd(0) in a similar manner to *D. desulfuricans* (Mikheenko, 2004) and waste *E. coli* biomass from fermentation, when palladised, was shown to be effective in the hydrogenation of soybean oil (Zhu et al., 2011). As anaerobic conditions are required for expression of hydrogenases, the use of a facultative anaerobe in a Pd recovery system would be divided into two-steps: 1) aerobic pre-growth to high biomass density followed by 2) anaerobic induction of hydrogenases prior to Pd(II) bioreduction. This possibility does not exist with SRB which are strict anaerobes. The above discussion relates Pd(0) deposition to the function of anaerobic enzymes but this is by no means exclusive. Hence, *Serratia* sp. pre-grown in an airlift fermenter produced catalytically active Pd(0) (Deplanche, 2008) while studies using *E. coli* grown aerobically attributed reduction of Pd(II) to formate dehydrogenases FDH-O and FDH-N (Foulkes, J., personal communication). Extensive studies of Pd(0) deposition on cells of the aerobic *Bacillus sphaericus* assumed metal deposition onto the cell surface S-layer (Fahmy *et al.,* 2006) and the resulting material had a similar catalytic activity in hydrogenation of itaconic acid as *Desulfovibrio* bioPd(0) (Creamer *et al.*, 2007). However, further study showed deposition of Pd(0) below the S-layer and within the inner cell surface layers (Skibar *et al.,* 2005) and an additional mechanism was implicated. Other Gram positive organisms have been used for the production of Pd(0) (Deplanche, 2008; Gauthier *et al.,* 2009) but the mechanisms of metal deposition are less well elucidated as compared to Gram negative Enterobacteria and Pseudomonads.

The bioreductive route has been successfully exploited to recover metals from various waste sources containing dilute amounts of PGMs. The metallic nanoparticles formed on the biomass are catalytically active and several studies have shown the potential of a one-step conversion of PGM wastes into bioinorganic catalysts (Table 2).

In this first case study, the ability of the common enterobacterium *Escherichia coli* to precipitate metallic species is used to demonstrate the recovery of PGMs from model solutions containing palladium and platinum mixtures. Biorecovery is then applied to a leachate obtained from a spent car catalyst containing various metallic species. Characterisation of the biorecovered material shows that discrete metallic nanoparticles (NPs) are formed on the cell surface. The catalytic activity of biomass-supported metallic NPs is described, demonstrating a one-step conversion of car catalyst waste into a new product.

Waste source	Metal(s) biorecovered	Microorganism	Catalytic test	Comments	References
Jewellery	Au	*Desulfovibrio desulfuricans, Escherichia coli*	Selective oxidation of glyerol		Deplanche *et al.,* (2007)
Electronic scrap leachate	Au, Pd, Pt	*Desulfovibrio desulfuricans*	NT	Pre-palladised cells used to recover other metals	Creamer *et al.,* (2006)
PGM reprocessing waste	Pd, Pt, Rh	*Desulfovibrio desulfuricans, Escherichia coli, Cupriavidus metallidurans*	H_2 evolution from hypophosphite, Cr(VI) reduction, Fuel cell electrocatalyst		Yong *et al.,* (2002a, 2010), Mabbett *et al.,* (2006)
PGM leachate from secondary sources	Au, Pd, Pt, Rh	*Escherichia coli*	Cr(VI) reduction	Leachate produced using microwave technology Pre-palladised cells used to recover other metals	Murray *et al.,* (2007)
Industrial effluent	Pd	*Cupriavidus necator*	Suzuki–Miyaura coupling		Gauthier *et al.,* (2010)

Table 2. Applications of precious metals bioinorganic catalysts fabricated from wastes

2.1 Materials and methods

2.1.1 Organism and culture conditions

Escherichia coli MC4100 cells were cultured in 12 litres of nutrient broth under anaerobic conditions (Mikheenko, 2004). Cells were harvested by centrifugation, washed three times in MOPS-NaOH buffer pH 7.0 and resuspended in a known volume of buffer. The cell density was checked at an optical density (OD) of 600nm; the OD_{600} was converted to bacterial dry weight by a previously determined calibration. With a dry weight of cells between 20-30 mg/ml the cell cultures were then split into six aliquots in preparation for pre-metallisation

2.1.2 Preparation of leachate from crushed automotive catalyst

Automotive catalysts are generally available in the form of monoliths. Monolithic catalysts employ a high surface area washcoat on the top of a honeycomb structure. The honeycomb is generally composed of magnesium cordierite $2MgO.2Al_2O_3$. The washcoat consists of ɣ-alumina as a substrate for the valuable metals (PGMs) and a variety of additives to improve the catalytic action and to stabilise alumina and active metals at exhaust operating conditions (Angelidis and Sklavounos, 1995). The channels of the monolith are small, on the order of 1 mm, which allows for a large number of channels, increasing the surface area to volume ratio and conversion rates (Depcik and Assanis, 2005).

The outer steel casing was removed and the used autocatalyst was processed by jaw crushing, ground using a Rolls crusher and then passed through a 1mm screen. Any oversize material was reground in the Rolls crusher so that all test material was of diameter d ≤ 1mm. The automotive catalyst used for leachate production had 600 channels per square inch, thus each channel was 1.04 mm wide. Any material greater than 1mm was reground in order to avoid over-crushing but to facilitate maximum acid - washcoat interaction. *Aqua regia* (60 ml; 3 parts 37% HCl to 1 part 70% HNO_3) was added to 6 g of milled catalyst and allowed to stand in an open vessel (30 min). The vessel was then sealed and placed in a microwave (CEM Microwave Accelerated Reaction System 5) set to ramp (109^oC in one min using a power of 600 W), maintain that temperature (15 min), then undergo a cooling cycle (5 min). The contents of the vessel were transferred with washings (half the volume of distilled water to *aqua regia*), centrifuged (4000 rpm; 10 min) and the supernatant was retained for biomass metallisation tests. Commercial analysis of the leachate by Engelhard Corporation gave 24 ppm Pd, 4 ppm Rh and <1 ppm Pt. Stated ICP limit of detection is 0.1 ppm for PGMs. Subsequent analysis of the leach residue solids (by copper collection and XRF of copper button) confirmed >95% Pd extraction during leaching but only 50% Rh extraction.

Analysis of the catalyst used in this study against other typical spent automotive catalysts showed that PGM levels were unusually low, with Pd being approximately 10% of the value of another catalyst processed under the same conditions for alternative testing. Thus the decision was taken to spike the leachate with Pd(II) salt (Na_2PdCl_4, Sigma Aldrich, 98% pure) to a final concentration of 400 ppm in order to increase the Pd(II) level to that more representative of a "typical" catalyst, while still providing the solubilised washcoat background matrix of a "real" leachate. For biorecovery experiments, the leachate was diluted 1:9 with dH2O and the pH was brought to pH 2.2 using 6 M NaOH.

2.1.3 Assay of metals

Removal of PGM from test solution was monitored by a spectrophotometric method using $SnCl_2$ (Dasages, 1978). The reagent solution contained 5.98 g of $SnCl_2$/100 ml of concentrated HCl. For PGM assay sample (200 µl) was added to $SnCl_2$ solution (800 µl) and A_{463} for Pd(II) and A_{401} for Pt(IV) was determined after one hour. It was not possible to estimate accurately the concentrations of metals in mixed metal solutions due to cross-interferences, but the assay was a convenient indicator of the presence of residual non-reduced metal in solution.

2.1.4 Bioreduction experiments

Solutions of 2 mM Pd and Pt were prepared in 1 mM HNO_3 using Na_2PdCl_4 and K_2PtCl_4 salts respectively. Cells were metallised with Pd or Pt (see below) as follows. The required volume of metal solution was calculated then added to aliquots of cells to achieve the desired varied metal loadings, H_2 was bubbled through the suspension for 30 minutes and suspensions were incubated at 30^oC to allow reduction of metal onto the cells. Metal reduction was confirmed as loss from solution using the $SnCl_2$ assay of sample supernatants as described previously (Creamer *et al.,* 2008). Following full reduction of metals cells were harvested by centrifugation, washed once using distilled water and then resuspended in 30 ml of distilled water.

For PGM pre-loading as above, batches of cells were split into 6 aliquots and exposed to 2 mM solutions of Pd and Pt in the correct volume as above to give metal loadings of 5%, 2%

and 1% on the cells. With the cells pre-loaded to the desired levels samples (16 mg of pre-metallised cells; weight before metal deposition) were then exposed to a mixed solution of 0.34 mM Pt and 0.42 mM Pd (model leachate), which gave final metal loadings after reduction of 15 wt%, 16 wt% and 20 wt%. Hydrogen was used as the reducing agent, here via catalysis due to the metals already present on the cells rather than hydrogenase activity. Samples were taken at 0, 0.5, 1, 2 and 5 minutes, with $SnCl_2$ assay of sample supernatants. The results were expressed as percentage of target metal reduction against time. Following full reduction the cells were harvested by centrifugation, washed once in H_2O and once in acetone, dried and ground in an agate mortar. The resultant powder was passed through a 100 micron sieve to obtain a fine powder catalyst.
For experiments on PGM recovery from the spent car catalyst leachate, 1 ml aliquot of the best candidate catalyst (5% BioPd as identified via preliminary catalytic testing using Cr(VI) was suspended in 77.5 ml of leachate as to give a final total metal loading of 20% w/w on cells.

2.1.5 Transmission electron microscopy (TEM)

Pellets of Pd-loaded bacteria were rinsed twice with distilled water, fixed in 2.5% (wt/vol) glutaraldehyde, centrifuged, resuspended in 1.5 ml of 0.1 M Na-cacodylate buffer (pH 7) and stained in 1% osmium tetroxide in 0.1 M phosphate buffer, pH 7 (60 min) for transmission electron microscopy (TEM). Cells were dehydrated using an ethanol series (70, 90, 100, 100, 100% dried ethanol, 15 min each) and washed twice in propylene oxide (15 min, 9500 g). Cells were embedded in epoxy resin and the mixture was left to polymerize (24 h; 60 °C). Sections (100-150 nm thick) were cut from the resin block, placed onto a copper grid and viewed with a JEOL 1200CX2 TEM; accelerating voltage 80 kV. The identity of electron opaque deposits was previously confirmed as Pd using energy dispersive X-ray analysis (Lloyd *et al.*, 1998).

2.1.6 Cr(VI) reduction tests

The catalytic activity of dried, ground catalyst made from each solution (i.e. pre-metallised cells with subsequent loading of additional metal from either model leachate or real leachate) was estimated by the reduction of Cr(VI) to Cr(III). The catalyst (10 mg) prepared as described above was accurately weighed and added to a 12 ml serum bottle. 5 ml 0.5 mM $N_aC_rO_4.4H_2O$ in 20 mM MOPS-NaOH buffer pH 7.0 was then added and reactors were sealed with butyl rubber stoppers. Recators were degassed under vacuum, sparged with nitrogen for anaerobiosis and placed onto a rotary shaker (10 min) to ensure good mixing and distribution of catalyst. Sodium formate (1 ml; to 25 mM) was added, reactors were left bubbling under nitrogen to maintain anaerobic conditions and placed on a shaker (180 rpm). Samples were taken at 30 minute intervals, centrifuged (13000 rpm; 4 min) and residual Cr(VI) in solution was analysed using a diphenylcarbazide (DPC) assay method as described previously (Humphries *et al.*, 2006).

2.2 Results and discussion

2.2.1 Biorecovery of Pd and Pt from model solutions

Leachates produced from spent car catalysts are too aggressive to apply the bioreductive route directly using live cells. To overcome this limitation, we designed a 2-step process in which resting cells of *E. coli* are first pre-metallised under biocompatible conditions with a

low amount of Pd or Pt. This bioinorganic catalyst is then used to reduce and precipitate chemically PGMs from spent leachates.

A first series of experiments aimed to identify the best system to recover PGMs from model solutions (Pd, Pt). *E. coli* cells were pre-metallised at 1, 2 and 5% using Pd or Pt. Aliquots of each suspension were subsequently exposed to a solution containing both Pd(II) and Pt(IV) at concentrations of 0.42 mM and 0.34 mM respectively to reflect the amounts found in typical car catalyst leachates. The removal of Pd(II) and Pt(IV) from the mixture was rapid; no metallic species were detected by assaying the supernatants of reactors with $SnCl_2$ after 1 min of exposure to H_2. There was no significant difference of reduction rates between cells pre-metallised with Pd or Pt, i.e. both metals autocatalytically reduced free metal ions in solution. Similarly, no significant increase in Pd(II) or Pt(IV) reduction rate was observed when the initial loading on cells was increased from 1 to 5%. This suggests that *E. coli* cells loaded with metal "seeds" can precipitate large amounts of metals. The final PGM loadings on cells following complete reduction of Pd and Pt from the mixture was estimated at 15 wt%, 16 wt% and 20 wt% for initial loadings of 1 wt%, 2 wt% and 5 wt% respectively. TEM micrographs of pre-metallised *E. coli* cells before and after contact with the PGM mixture is shown in Fig. 3. The precipitated metals can be seen as discrete electron opaque particles before treatment (intial loading of 5wt% on cells, fig 3A) and as more numerous, larger aggregates following PGM precipitation from the Pd/Pt mixture (fig. 3B, arrowed)

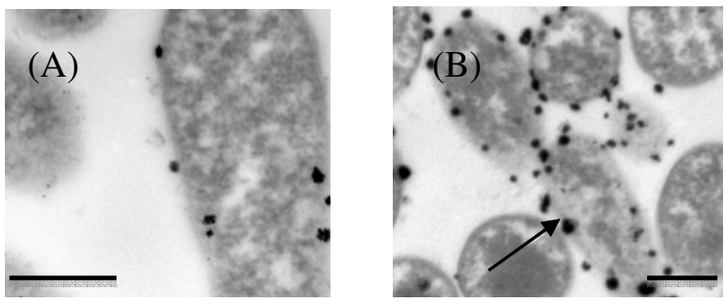


Fig. 3. TEM micrographs of pre-palladised *E. coli* cells before and after the recovery of PGMs from a model solution. The initial Pd loading was set to 5 wt% (A) and increased to 20 wt% (total metal loading) following exposure to the Pt/Pd mixture (B). Scale bars are 500 nm.

From these results the use of 1% Pd pre-loaded cells would be optimum for future use as they offer a near identical reduction rate to that of the cells with higher pre-loadings, with minimal 'sacrificial' metal and with Pd being the metal of choice as it is generally a lower cost than Pt. However, a previous study showed that catalysts made from cells pre-metallised with 2% or 5% Pd were significantly more active catalytically in the reduction of Cr(VI) to Cr(III) (Taylor *et al.*, 2011). Hence, cells pre-loaded with 5% Pd were retained for use in subsequent tests on PGM recovery from a real car catalyst leachate and catalytic testing of the resulting material.

2.2.2 Biorecovery of Pd and Pt from spent car catalyst

The majority of previous PGM biorecovery research has focused on either using model solutions or "real" leachates from mixed metal wastes e.g. spent furnace lining that contained many different metals in addition to the desired PGMs (Murray *et al.*, 2007).

Model solutions are considered too simple (and therefore non-representative of real world wastes) as they contain only the metals of interest. Conversely complex "real" leachates are difficult to study due to interference effects in accurate analysis of the metals and hence the difficulty and expense of the latter. The leaching of autocatalysts provides a good intermediate step between model solutions and complex waste leachates as the cordierite honeycomb is insoluble and hence the leachate is composed of the alumina washcoat and the solubilised PGMs i.e. it is relatively simple with respect to the number of components.

The microwave leaching process used in this study yielded 30 ppm PGM in 67% *aqua regia*. The PGM concentration was unusually low for this type of catalyst and, consequently, the leachate was spiked to 400 ppm with Pd(II) (see materials and methods). The leachate was then diluted 10x in H_2O to lower the concentration of acids and brought to pH 2.2 with 6 M NaOH. Pre-palladised cells of *E. coli* (1 ml, 5 wt% initial Pd loading) were added to 77 ml of leachate and H_2 was bubbled through this mixture for two hours. Samples were taken at 12 h intervals and the residual concentration of PGM was estimated using the $SnCl_2$ assay. Figure 4 shows the time course of PGM reduction from the spent automotive catalyst leachate.

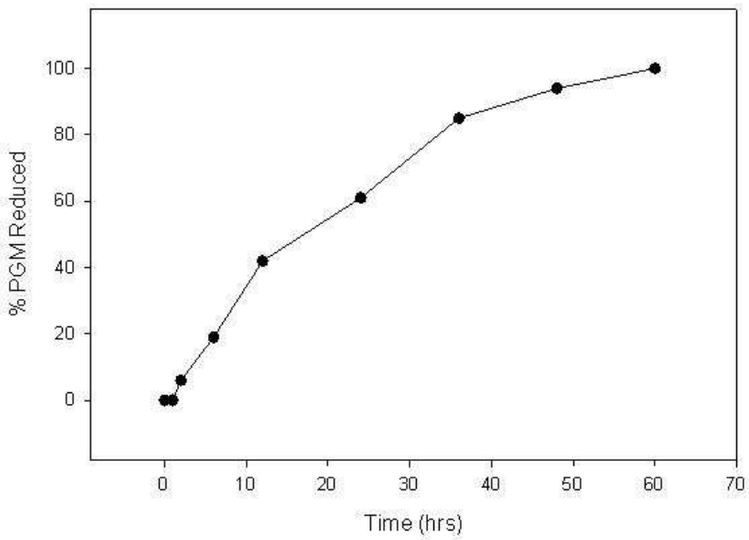


Fig. 4. Time course of PGM reduction from spent automotive catalyst leachate using *E. coli* cells pre-palladised to 5 wt%.

In contrast to model solutions (where total metal removal was obtained within 1 min), PGM reduction from the catalyst leachate by the pre-palladised *E. coli* cells was slow, and proceeded in three distinct phases (Fig. 4). An initially rapid rate of metal removal (0-10h) was followed by a ~ halving of the rate between 10-35 h; selectivity of metal removal was not tested. Removal of the final ~20% of the metals was very slow over the final 20h. Full disappearance of Pd(II) in solution was achieved after ~60 hours of contact

In order to implicate the compound responsible for the inhibition of PGM reduction a simple test was carried out. Model leachates (Pd(II) and Pt(IV)) were prepared as before using fresh *aqua regia* and aliquots were spiked with Pd(II) (400 ppm final concentration), neutralised and diluted as before. The pH was adjusted to 2.0. Aliquots of model leachates were spiked with silica (SiO_2 and Al_2O_3 to 173 ppm final concentration) and a mixture of

both. The bioinorganic catalyst was added in each reactor and the rates of PGM reduction were followed as previously. Addition of either Al and/or Si promoted a significant decrease of the rate of PGM reduction; Pd(II)/Pt(IV) disappearance from the model solution was observed after 6 and 14 hours of contact with the bioinorganic catalyst respectively. Full PGM removal was not observed in the solution supplemented with both Si and Al even after 48 h exposure, whereas metal was removed from the control (leachate + H_2O) within 5 mins as per the model solutions. These results suggest that the presence of Al and Si inhibits PGM recovery and they are responsible for a substantial increase in reduction time observed with the spent car catalyst leachate.

The catalytic activity of the material obtained following PGM recovery from spent car catalyst leachate was estimated in the reduction of Cr(VI) to Cr(III) in the presence of formate. This was tested alongside the catalyst made from PGM recovered from model solutions (see above). Both catalysts were manufactured using *E. coli* cells pre-palladised to 5 wt% and had a similar final metal loading (after PGM recovery) estimated to be 20 wt% PGM.

Both catalysts were active in Cr(VI) reduction tests (Fig. 5) and showed similar initial reaction rates. Near-complete Cr(VI) reduction was obtained with the catalyst made from model leachate after 120 min whereas the catalyst obtained from real leachate showed a slower rate after 30 min, probably attributable to the presence of non-PGM contaminants (possibly Si and Al) which could partially poison catalytic PGM nanoparticles. Nevertheless, more than 90% of the Cr(VI) was reduced by 180 min by the biorecovered material.

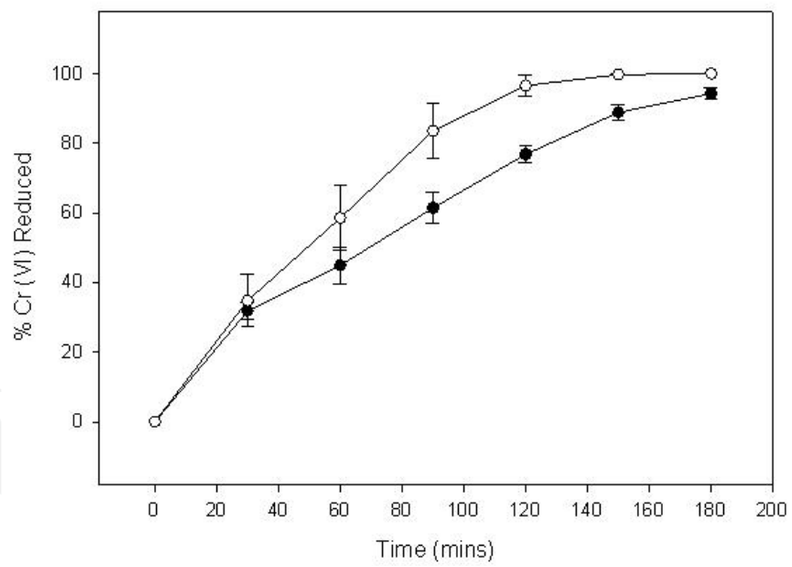


Fig. 5. Time course of the catalytic reduction of Cr(VI) to Cr(III) over two bioinorganic catalysts fabricated from (❍) a model leachate and (●) a spent car catalyst leachate. Results are expressed as percentage Cr(VI) reduced over time. Data are from two separate experiments. When no error bars are shown, these were within the dimensions of the symbols.

These experiments demonstrate the potential of bioreductive processes towards PGM recovery and a one-step conversion of waste material into novel bioinorganic catalysts. The range of reactions amenable to bioPGM catalysis is constantly being expanded (Table 1) and

work is on-going to optimise the formulation of bioinorganic catalysts made from wastes for specific applications. It should be noted that in some cases (Macaskie *et al.,* 2011) the presence of metallic impurities in the biorecovered materials can increase the catalytic activity (c.f. Fig. 5) and a full survey of bionanocatalysts from wastes for particular applications needs to be approached systematically on a case by case basis, applying metal thrifting by decreasing as far as possible the initial metal expenditure in the seeding step.

3. Case study 2: Biorecovery of Rare Earth Elements (REE)

In contrast to PGMs, the REE are not scarce due to low natural abundance but to the complexity of their extraction and refining. In this, China is world-leading and this near monopoly means that REE abundance is controlled socio-economically and REEs, due to their numerous high-tech applications, could become a strategic geopolitical resource.

Traditional extraction/recycling processes of REE require several steps of pre-treatments with strong acids and alkali followed by extraction using organic solvents which, if not recovered, can create extensive environmental damage often leading to the contamination of natural water streams.

Although pre-2010 there was no major study of focused microbial REE recovery the problem of legacy nuclear wastes, the decline of nuclear power in the 1990s and the current decommissioning of first generation nuclear reactors prompted an early focus on the use of microorganisms to remove radionuclides from waste streams. Due to the difficulties of handling the latter, extensive use was made of surrogate elements whose behaviour mimics the radionuclide of interest. Hence, La^{3+} was chosen to provide a convenient surrogate for Am^{3+} and, indeed, the trivalent states of Np and Pu where these would occur (under reducing conditions). An early study (Plummer & Macaskie 1990) established that by using the bacterial phosphatase mechanism (see earlier) La^{3+} was accumulated to 17% of the bacterial dry weight after only 4 h at pH 7, being twice as effective as uranium recovery. This was attributed to the reduced ability of La^{3+} to bind to citrate as compared to UO_2^{2+}; many metal ions form insoluble colloidal hydroxides in solution and incorporation of citrate reduces this. In the 'real world' a pure solution is improbable and most would contain various species capable of forming complexes with metals. Such complex formation holds the metal in a soluble form but, on the other hand, the lower free metal ion concentration (defined by the binding constant) also retards the rate of metal phosphate formation on the bacteria (see Plummer & Macaskie 1990 for discussion). The elemental ratio of La:P in the precipitate was determined as 1:1 by proton induced X-ray emission and the material was suggested to comprise $LaPO_4$; the same study also showed removal of Eu^{3+} (Macaskie *et al.,* 1994). Yong *et al.,* (1998) obtained X-ray powder diffraction data of bio-$LaPO_4$ to show that this contained crystalline components but no further analysis was attempted. The peaks were not well defined, suggesting that the material was possibly nanocrystallline in nature.

Working towards development of a continuous process for Pu removal, Yong & Macaskie (1998) used polyacrylamide gel-immobilised cells in a flow through column, where the imposition of a time constraint in each voxel (volumetric element) by the application of increasing flow rate (F; t = 1/F; F = flow rate in ml/min) showed that at a flow rate of 1 ml/min (total column volume ~ 30ml) and with 0.3 mM La^{3+} or UO_2^{2+} (pH 7 with 5 mM citrate) the removal of La^{3+} and UO_2^{2+} was 80% and 60% respectively, which is less of a difference than that reported by Plummer and Macaskie (1990; above) using cell

suspensions. However increasing the flow rate by 50% (i.e. halving the flow residence time per voxel: Yong *et al.,* 1998) gave corresponding removals of 70% and 40%, suggesting that there is a time element to the metal deposition process (probably the time required for metal phosphate deposition from the liquid phase); Plummer and Macaskie (1990) did not give full metal removal profiles over time.

Additional caution needs to be exercised in applying directly the results obtained using one REE to another. For example Bonthrone & Macaskie (in Diels *et al.,* 1996), using cell suspensions, found the UO_2^{2+} removal after 2 h to be 7 times greater than that of Y^{3+} at both high (~ 900 units) and low (34 units) phosphatase activities, showing that phosphate availability was not rate-limiting. This study also reported the continuous removal of Y^{3+} by cells immobilized in polyacrylamide gel but details were not given.

La^{3+} is a very useful model REE element in another key aspect. Unlike, for example, Gd^{3+}, its nucleus is 'NMR-silent'. Use was made of this to examine the flow-through column system in three and four dimensions to follow the progression of flows and blockages within the column at any spatial position using a flow-through bioreactor containing biofilm of the metal-accumulating *Serratia* sp. (reassigned from *Citrobacter*) using magnetic resonance imaging (MRI) (Fig. 2: Paterson-Beedle *et al.*, 2001; Nott *et al.,* 2001; 2005 a, b). The methodology was described by Paterson-Beedle *et al.* (2001). Nott *et al.* (2001) chose polyurethane reticulated foam as the best support (as compared to glass or ceramic) as this gave the best signal to noise ratio for MRI. An initial study showed the suitability of MRI for obtaining spatial information (Nott *et al.,* 2001) and subsequent studies using the columns in a flow through system gave numerical information which was described in terms of a chemical engineering model (Nott *et al.,* 2005 a,b). For design of a metal removing and recovery process it is vital to a have a robust mathematical description as scale-up predictions can be made from small pilot studies. In particular, for REE recovery from wastes (see later) a low pH may be unavoidable and, by using the tools of MRI, it would become possible to predict the outcome of low pH or high salt (and competing ions) with a greater degree of insight than by measuring column inputs and outputs alone.

Moving towards the goal of metal recovery at low pH Tolley *et al.,* (1995) investigated La^{3+} removal at pH 5, prompted by an earlier study (Macaskie *et al.,* 1990) that suggested that a reduction in metal removal efficiency at pH 5 was attributed to increased metal solubility at low pH. Like the MRI work (above) this study placed metal removal into a mathematical definition, showing that decreased metal removal at acidic pH could not only be compensated by an increased phosphate supply, but the extent to which this was achievable; essential tools for the design of an industrial REE recovery process. Tolley *et al.,* (1995) found that La^{3+} removal was abolished at pH 4 (at which pH the activity of the mediating phosphatase was reduced by 50%). However another study looking at uranium removal from acidic mine wastewater (Macaskie *et al.,* 1996; 1997) showed that, following a period for metal phosphate nucleation, the initially low metal removal gave way to a sustained removal of ~70% of the input UO_2^{2+} (35 ppm; ~ 0.15 mM) (Macaskie *et al.,* 1997) at a pH as low as 3.5 (Macaskie *et al.,* 1996). Importantly, the process could be accurately defined mathematically (Macaskie *et al.,* 1997) but an extensive modeling study in real U-wastewater was not done. In the case of La^{3+} removal at pH 5 the enzymatically-mediated release of phosphate from the organic donor molecule was identical to that at pH 7 but La^{3+} removal was reduced (Tolley *et al.,* 1995). Using a flow through column system and polyacryamide gel-immobilised cells the metal removal (input concentration 1 mM) was 83% and 55% at pH 7 and 5, respectively in 5 mM citrate buffer at the same flow rate

(308 ml/h). Reasoning that the solubility of metal phosphate would be higher as the pH was reduced (i.e. less tendency to form mineral deposits) the activity of the phosphatase was increased by the use of a phosphatase overproducing mutant (approx. twice the activity of the parent strain) and by the use of carbon-limited continuous culture, which increased the activity to ~ 2000 units. The latter compensated to some extent; the respective $FA_{1/2}$ (that flow rate at which 50% metal removal was achieved) values at pH 5 and 7 were 120 ml/h and 600 ml/h respectively. This meant that, in this example, increasing the phosphatase production by four-fold resulted in an increase in bioreactor efficiency of two-fold at the lower pH. This work defined the lowest useful operating pH of the enzymatically-mediated metal recovery system as ~ pH 4 and also concluded that the metal solution chemistry and desolubilisation behavour are the limiting factors at low pH, which is of major importance in the application to recovery of REE from acidic leachates.

However it is also worth noting that the choice of metal-donating substrate is also contributory; the effect of high flow rate on the phosphate release is attributable in part to the affinity of the enzyme for its substrate (K_m; that substrate concentration giving half-maximal reaction rate). The K_m in the column system is, in part, responsible for the 'resistance' of the column to high flow rates and it was found (Tolley *et al.,* 1995) that the effect of the pH on the apparent K_m is, to some extent, substrate-dependent. Since the model substrate glycerol 2-phosphate is unattractive at industrial-scale a cheaper substrate like phytic acid (inositol phosphate) would be more appropriate. The latter was shown to support metal removal (Paterson-Beedle *et al.,* 2010) and it contains 3 moles phosphate per mole, with the phosphate groups removed sequentially via phytase activity (see Paterson-Beedle *et al.,* 2010). Hence a phytic acid-based column system may have three K_m values and be more difficult to describe mathematically, but this represents a potentially attractive route for potential metal recovery from wastes.

A recent study (Jiang *et al.,* 2010) has shown another route to REE biomineralisation. This used the yeast *Saccharomyces cerevisiae* and Ce(III). (Ce(III)/(IV) is a surrogate for Pu(III)/IV) and Np(III)/(IV), and a comprehensive suite of analytical methods, including synchrotron-based X-ray absorption fine structure (XAFS), showed conclusively that Ce(III) was deposited on the yeast cell surface as needle-shaped Ce(III) phosphate nanocrystals with a monazite structure. Importantly, no exogenous phosphate was added and the mobilisation of intracellular phosphate reserves to supply inorganic phosphate into the growing crystals was concluded (Jiang *et al.,* 2010). Since yeast is well known to store phosphate in the form of polyphosphate (which is known to support metal desolubilisation when mobilised: see earlier) it seems likely that the yeast phosphate was derived from this source, with metal phosphate deposition via polyP mobilisation and phosphate efflux processes.

The yeast system of Jiang *et al.,* (2010), unlike *Acinetobacter* spp, (Boswell *et al.,* 2001) needs no aerobic/anaerobic cycling and is thus intrinsically a more useful process for industrial REE recovery but the limit of metal deposition needs to be established. Importantly, and as also found for the bacterial system with UO_2^{2+} at pH 4 (Macaskie *et al.,* 2007), removal of Ce(III) (0.18 mM) by the yeast was initially negligible (up to 96 h at pH 3) and then proceeded abruptly to 60% of the initial concentration after 120 h. Phosphate was produced by the cells at pH 3, again indicating that metal phosphate solubility and not biochemical activity, is the limiting factor in biomineral formation at low pH. Since, following a delay, metal removal can proceed effectively at pH 3 (Macaskie *et al.,* 1997; Jiang *et al.,* 2010) is can be suggested that nucleation, and not biomineral formation, is the limiting step. This was also suggested in a study of bio-hydroxyapatite (HA) formation by *Serratia* sp. where a pH

of above 8 was needed for effective HA-biomineral formation. However, following a nucleation period Ca^{2+} was removed from a phosphate-containing wastewater into bio-HA at neutral pH (Yong *et al.*, 2004).

Ce(III) removal at low pH by *S. cerevisiae* (Jiang *et al.*, 2011) was similar to La(III) removal by *Serratia* sp. (Tolley *et al.*, 1995), showing good REE removal at pH 5 and less so at pH 4. Production of phosphate by the yeast cells was very similar at pH 3 and at pH 5, indicating that the anomalous behaviour was attributable to metal speciation, as was concluded in the case of La^{3+} in the bacterial system (above). Notably, phosphate release was promoted from the yeast cells by the addition of H^+ ions (Jiang *et al.*, 2010); this may reflect possible different physiological functions of polyP: as a pH control agent in yeast (phosphate is a strong buffer with three pK_a values) and as a reserve of cellular energy in the bacterial system, providing the means to metabolise anaerobically where the cells are not able to grow (see Boswell *et al.*, 2001 and references therein).

The development of methodologies using Ce(III) and La(III) as surrogates for the tri/tetravalent actinide elements has provided a good platform from which to develop effective methods targeted specifically towards recovery of REE. A study by Jiang *et al.*, (2010) has shown formation of cerium (Ce(III)) nanoparticles on the surface of the *Saccharomyces* cells (Fig. 6).

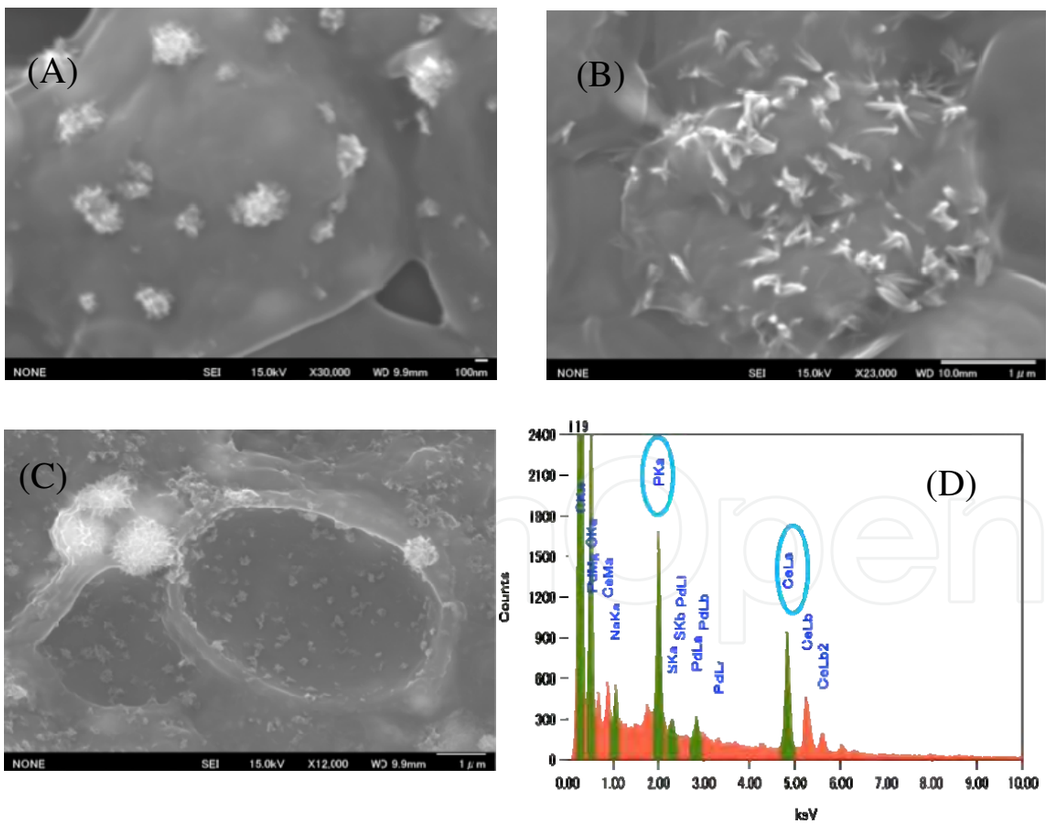


Fig. 6. Cerium phosphate deposition on cells of *Saccharomyces cerevisiae*. Cells were washed 3 times in MilliQ water and then incubated in Ce^{3+} solution for 5 days. (A), (B), (C): formation of nanoparticles on the cells. (D) Energy dispersive X-ray microanalysis shows the cellular deposits to comprise Ce and phosphate.

An SEM and TEM study of $CePO_4$ crystal development is shown in Figs 6 and 7. The deposits formed after 4-5 days, identified as containing cerium and phosphorus by energy dispersive X-ray microanalysis (Fig. 6D), did not give an interpretable X-ray diffraction pattern and were concluded to be nanocrystalline, as suggested by the high resolution TEM images (Fig. 7A,B). An unpublished study (M. Jiang *et al.*,) of Yb-phosphate nanocrystallisation on *S. cerevisiae* included X-ray extended fine structure (EXAFS) analysis which showed subtle differences in 'early' deposits (30 mins) at the three pH values, with the Yb L_{III}-edge appearing similar for samples at pH 4 and 5, but not at pH 3, while with more 'mature' samples (120h) the pH 5 material showed a similarity in its Yb-P site to a $YbPO_4$ reference which was less pronounced in samples at the lower pH values. A 48 h sample at pH 5 appeared similar to a pH 4 sample at 120 h, suggesting an evolution of the crystals which was time- and pH-dependent.

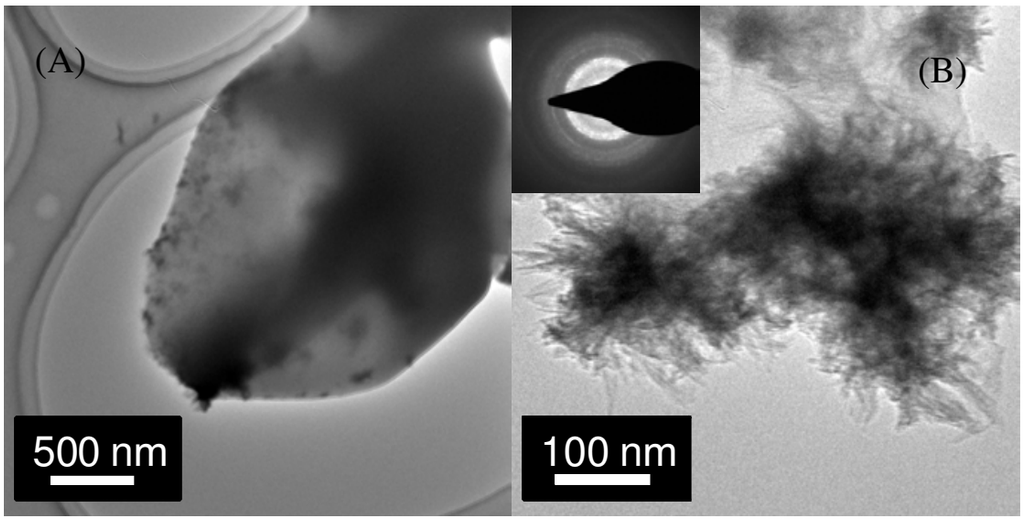


Fig. 7. (A) Development of $CePO_4$ crystals (monazite) on the surface of *Saccharomycese cerevisiae* cells after 48 hours at pH 5; enlarged image of a single particle reveals that this particle consists of needle-shaped Ce-phosphate nanocrystallites (B) (Jiang *et al.,* 2010).

In this second case study, we report pilot experiments on the continuous recovery of two model REE (europium and neodymium) in flow-through columns containing immobilised cells of a *Serratia* sp. The recovered metals are available for further reprocessing in yields exceeding by several-fold the mass those of the bacteria themselves.

3.1 Materials and methods

3.1.1 Microorganism, support and biofilm production

Serratia sp. (NCIMB 40259) was used under license from Isis Innovation, Oxford, UK. Cells were grown as biofilm on polyurethane reticulated foam (Filtren TM30, discs: diameter 2 cm and depth = 0.5 cm, 1.57 cm^3), supplied by Recticel, Belgium. The biofilm was grown in an air-lift fermenter under carbon limiting continuous culture with the phosphatase activity of the cells from the fermenter outflow determined as described previously (Paterson-Beedle & Macaskie 2004). Even colonisation of the foam within the matrix and metal deposition thoughout was confirmed using magnetic resonance imaging (Macaskie *et al.,* 2005).

3.1.2 Preparation of reactor packed-bed systems for neodymium and europium bioaccumulation

Serratia sp. biofilm immobilised onto polyurethane foam discs (Fig. 8) was packed in cylindrical glass reactors (height, 5 cm, i.d. 2 cm). Reactors were exposed to the solutions below (all experiments were done in duplicate):

Solution 1: $N_3NdO_9.6H_2O$ (1 mM), glycerol-2-phosphate (G2P) (5 mM) and sodium citrate buffer (2 mM), pH (5.5). Solution 2: as solution 1 but substituting $EuN_3O_9.xH_2O$ (1 mM) for the neodymium salt. Reactors were exposed to a continuous upward flow (ca. 5 ml/h, 54.5 h) via an external peristaltic pump (Watson-Marlow, 323).

The outflow solutions of reactors were analysed for either Nd or Eu as appropriate (see below). Controls were set up as above using biofilm autoclaved for 15 min (121°C) prior to metal treatment. The controls determined the amount of metal removal attributable to biosorption alone.

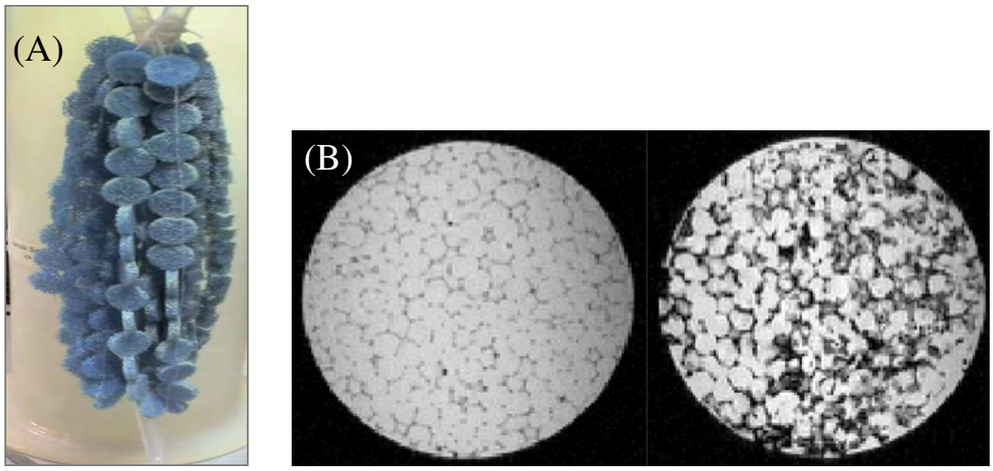


Fig. 8. (A) *Serratia* sp. biofilm grown on polyurethane reticulated foam discs. (B) Magnetic resonance imaging of discs with or without *Serratia* biofilm. MRI image of discs (diameter 20 mm, left) containing polyurethane foam only and *Serratia* sp biofilm coated polyurethane foam (right). The biofilm in a T_2-weighted spin-echo image is the darker regions, due to a reduced T_2 of water (P. Yong, M.L. Johns and L.E. Macaskie, unpublished).

3.1.3 Spectrophotometric analyses of metals

Spectrophotometric determination of Nd and Eu from column outflows was as described by Onishi (1986) using the Arsenazo(III) method with some modification, as follows. For analysis, Nd or Eu sample or standard (standard concentrations 30 µl) was added to a 1.5 ml cuvette followed by ammonium acetate buffer (1.97ml, 1M, pH 3.3). Metal was visualised after mixing by the addition of 0.1 ml of 0.15% (w/v) arsenazo (III). The absorbance was measured at A_{660} against a reagent blank.

3.2 Results and discussion

Reactors containing immobilised biofilms of *Serratia* sp. were challenged with solutions containing Eu or Nd (1 mM) for 54.5 hours at a flow rate of 5 mL/h. The outflow from each reactor was assayed for residual metals and the percentage of metal removed is shown in (Fig. 9).

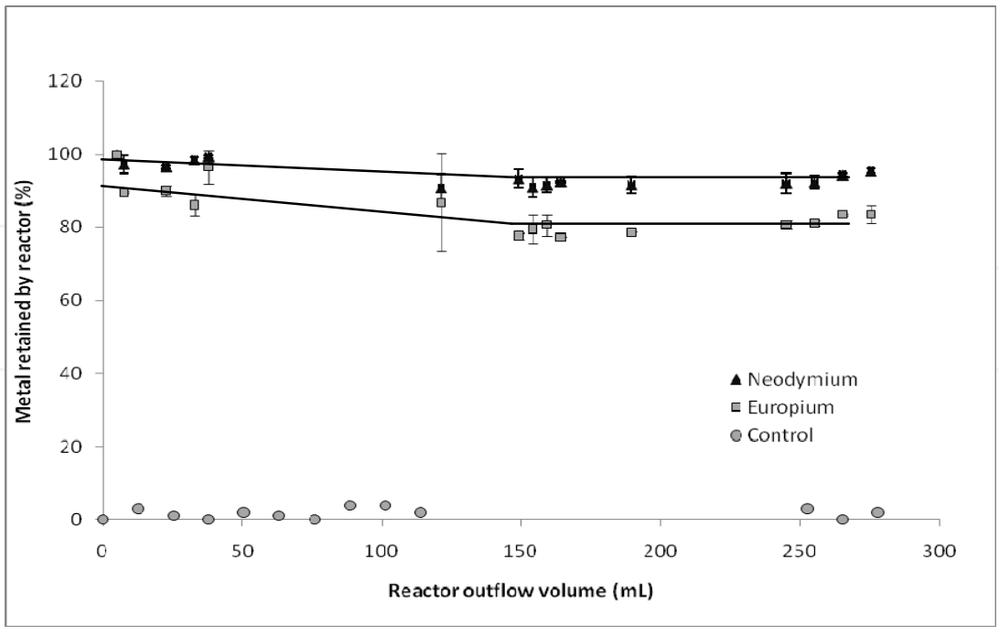


Fig. 9. Biorecovery of neodymium (▲) and europium (□) using cells of *Serratia* sp. in a flow-through reactor with corresponding killed-biofilm controls (○). Results were taken from two reactors, each containing 8 discs of foam with immobilised *Serratia* sp. biofilm. Reactors were challenged with a solution containing neodymium (III) or europium (III) (1 mM) as described at pH 5.5 for 54.5 hours at a flow rate of 5 ml/h. Where no error bars are shown these are within the dimensions of the symbols.

The removal of both metals fell slightly initially (c.f. earlier discussion about the need for a nucleation period at acidic pH) and then stabilised (from 100-150h) at steady-state removal of ~ 85% (Eu^{3+}) and more than 90% (Nd^{3+}), with no loss of activity at completion of the tests. Control reactors containing killed biofilm removed little metal, showing that live *Serratia* cells were required for metal deposition. Solid-state analysis of the metallised biofilms and comparison with, and co-development of, the bacterial and yeast systems, is ongoing in the UK and Japanese laboratories.

In particular, the promising results obtained in the preliminary studies we describe here justify a more prolonged study to determine the total biomass and column capacities since Fig. 10 shows that by the 300 ml stage (54.5 hours exposure), only the bottom layers of the column show the accumulation of metal deposits, indicating substantial unused capacity.

An early study using U showed the total capacity of the bacterial column to be 9 g uranium per g bacterial dry weight (Macaskie, 1990). The limitation of this process is usually an unacceptable back-pressure due to column blockage at high local metal loadings (i.e. at the base of the column, Fig. 10). This probably can be overcome if several column are linked in a series with the first column removed periodically and replaced with a fresh column distally. More critical to industrial application is the recovery of REE from real industrial wastes and the downstream processing required to convert the high yield product into new material. The presence of Fe in wastes may be problematic since the *Serratia* system described here removes all metals with insoluble phosphates. However previous studies treating uranium mine water containing a large excess of iron showed that Fe removal could be achieved by a simple increase in pH to precipitate-out $Fe(OH)_3$. The bioreactor was then run at pH 3.5-4.0

and uranium phosphate product was recovered (Macaskie *et al.*, 1997). A similar strategy could be envisaged for REE recovery. A study has not been made into the nature of the REE precipitate but on the basis of the La^{3+} study reported previously (see earlier) and the detailed solid state analysis of the corresponding $YbPO_4$ on yeast cells (above) it seems likely that the deposit comprises nanocrystalline REE phosphate. It is not yet known what, if any, particular advantages could be conferred by recovery of REE nanoparticles (as compared to large crystals); these are under current consideration in current work. (L.E. Macaskie and T. Ohnuki, current studies).

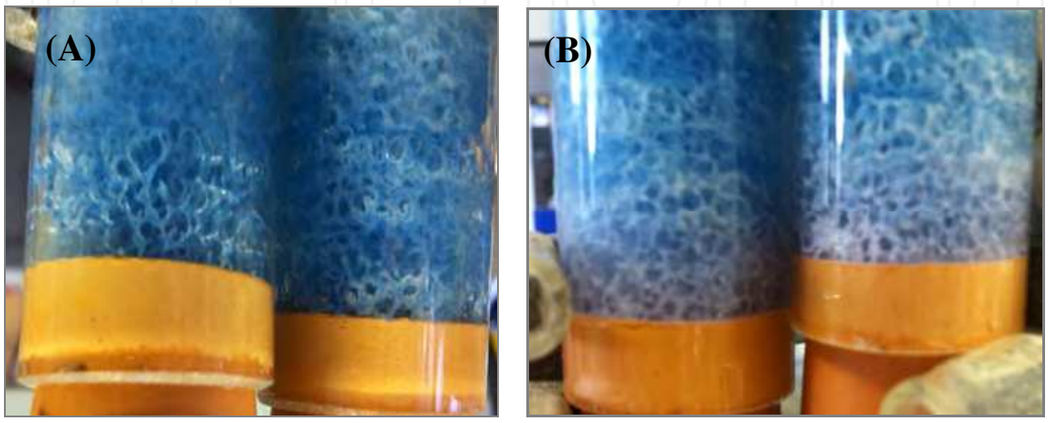


Fig. 10. Reactors containing *Serratia* sp. biofilm on polyurethane foam (A) before and (B) after treatment with $N_3NdO_9.6H_2O$ (54.5 hours); a purple colour can be seen at the bottom of the reactors, in B.

4. Conclusion

In this chapter, we describe two distinct biological routes for the recovery of PGM and REEs. First, the ability of bacterial cells to precipitate metallic ions to the elemental state *via* specific enzymes (bioreduction) is shown to be a potential alternative route for PGM recovery from dilute waste streams. The use of pre-metallised cells as catalysts for metal precipitation allows the process to be applied on aggressive leachates under conditions which are non-permissive for traditional biological treatments. The recovered material (PGM nanoparticles supported on biomass) can be utilised as a catalyst in reactions of increasing complexity.
In the second case study using a yeast and a bacterial system, the recovery of four model REE (Ce, Nb, Eu and Nd) REE was successfully demonstrated. All were precipitated as metal phosphates on the surface of the cells and immobilised cells of *Serratia* sp. recovered Nd and Eu continuously in flow through columns.

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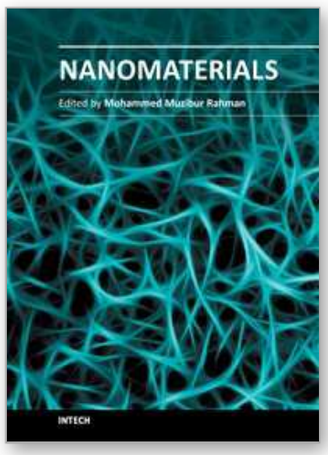
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