Hydrometallurgy 104 (2010) 483–487

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Today's wastes, tomorrow's materials for environmental protection

L.E. Macaskie [a,*], I.P. Mikheenko [a], P. Yong [a], K. Deplanche [a], A.J. Murray [a], M. Paterson-Beedle [a], V.S. Coker [b], C.I. Pearce [b], R. Cutting [b], R.A.D. Pattrick [b], D. Vaughan [b], G. van der Laan [c], J.R. Lloyd [b]

[a] Unit of Functional Bionanomaterials, School of Biosciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
[b] School of Earth, Atmospheric and Environmental Sciences and Williamson Research Centre for Molecular Environmental Science, The University of Manchester, Manchester M13 9PL, UK
[c] Diamond Light Source, Didcot, Oxfordshire, OX11 0DE, UK

ARTICLE INFO

Available online 25 June 2010

Keywords:
Catalyst
Fuel cell
Gold
Iron
Nanomaterial
Palladium
Photovoltaic
Platinum
Selenium
Uranium
Waste treatment

ABSTRACT

Over the past 30 years the literature has burgeoned with bioremediation approaches to heavy metal removal from wastes. The price of base and precious metals has also increased. With the resurgence of nuclear energy uranium has become a strategic resource. Other 'non-carbon energy' technologies are driven by the need to reduce CO_2 emissions. The 'New Biohydrometallurgy' we describe unites these drivers by the concept of conversion of wastes into new materials for environmental applications. The new materials, fashioned, bottom-up, into nanomaterials under biocontrol, can be termed 'Functional Bionanomaterials'. This new discipline, encompassing waste treatment along with nanocatalysis or other applications, can be summarized as 'Environmental Bionanotechnology'. Several case histories illustrate the scope and potential of this concept.

1. Introduction

Heavy metals become dispersed into the environment in many ways, e.g. in run-offs from disused mines, wastes from metal processing or from industrial processes (e.g. tanning) that use metallic components and from deliberately-applied chemical agents (e.g. wood preservatives). Man's mining of traditional energy sources (e.g. coal) can result in iron-rich wastes (Coker et al., 2005–2006) while the nuclear industry has still to resolve the problem of long-term containment of radionuclide wastes and the environmental impact of nuclide migration in the geosphere. Man's lifestyle also impacts on the environment via automobiles; here the use of precious metal (PM)-containing catalytic converters for atmospheric protection has resulted in substantial losses of PMs into road dusts (Jackson et al., 2007) and the car industry is a major global consumer of scarce precious metals (Anon, 2009). Even base metals, previously considered uneconomic to recover, are rising in price such that the economics of metal recovery from wastes should be revisited. More than 20 years ago Brierley et al. (1986) set an 'economic threshold' for solely metal waste remediation using biosorption/bioaccumulation of metals and this has been met or exceeded by only a few bioremediation systems.

Microorganisms accumulate metals via several mechanisms e.g. biosorption, sequestration or various enzymatically-driven mechanisms such as metal oxidation/reduction and precipitation via enzymatic ligand production. These can lead to the formation of biomineral deposits which have useful properties (Lloyd et al., 2005, 2008). This paper presents various examples of applications of biomineralization approaches to convert metal-containing wastes into new nanomaterials for environmental protection.

2. Case histories illustrating bioconversion of wastes into new materials

2.1. Case history 1. Bioremediation of uranium mine-water and nanofilter fabrication for nuclear waste remediation

A *Serratia* sp. originally isolated from a metal-contaminated site has an atypical phosphatase localized within the cellular exopolymeric matrix (Fig. 1A). When provided with a suitable organic phosphate source inorganic phosphate is cleaved enzymatically to deposit heavy metals as their phosphates (Macaskie et al., 2000). Cells immobilized as a biofilm on a suitable porous support comprise a filter that was successfully applied to the removal of uranyl ion, $(UO_2)^{2+}$, from U-mine wastes (Macaskie et al., 1997). The uranium is retained

---

* Corresponding author.
E-mail addresses: L.E.Macaskie@bham.ac.uk (L.E. Macaskie), I.MIkheenko@bham.ac.uk (I.P. Mikheenko), P.Yong@bham.ac.uk (P. Yong), K.Deplanche@bham.ac.uk (K. Deplanche), AJM543@bham.ac.uk (A.J. Murray), M.Paterson@bham.ac.uk (M. Paterson-Beedle), V.S.Coker@manchester.ac.uk (V.S. Coker), Carolyn.Pearce@manchester.ac.uk (C.I. Pearce), Richard.Cutting@Manchester.ac.uk (R. Cutting), Richard.Pattrick@manchester.ac.uk (R.A.D. Pattrick), DavidVaughan@manchester.ac.uk (D. Vaughan), gerrit.vanderlaan@stfc.ac.uk (G. van der Laan), Jon.Lloyd@Manchester.ac.uk (J.R. Lloyd).

0304-386X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.hydromet.2010.01.018

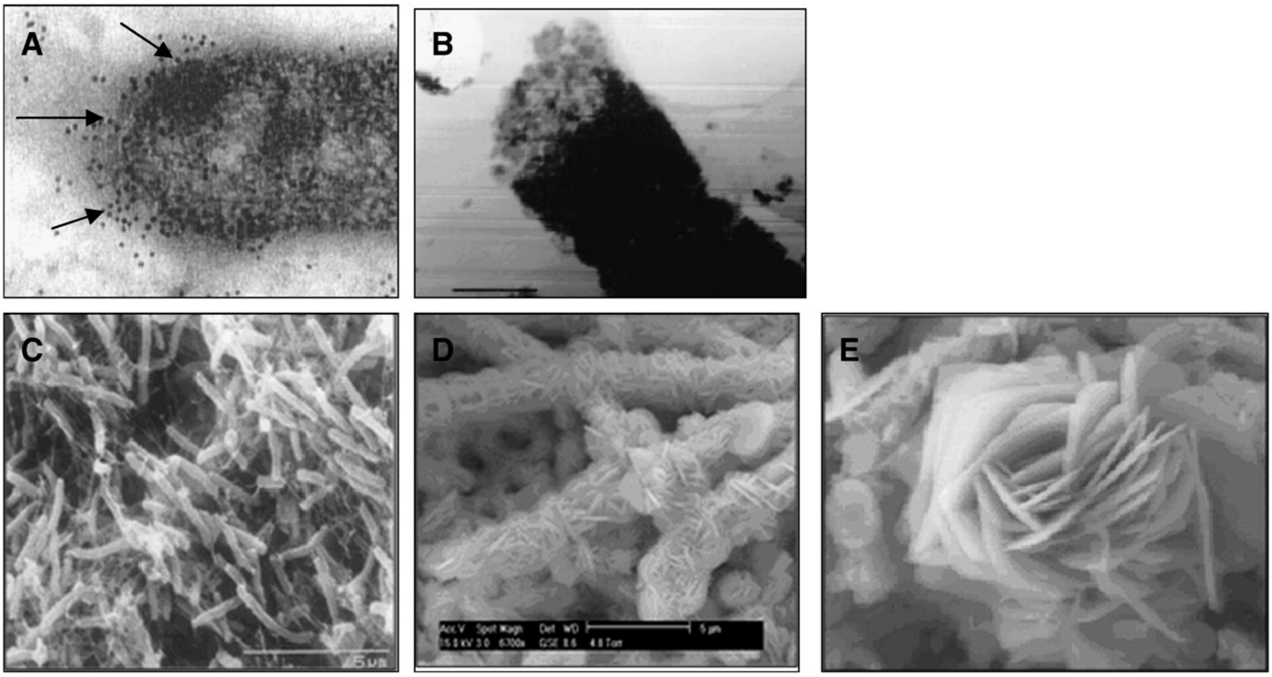

Fig. 1. *Serratia* cell with immunolabelled extracellular phosphatase, arrowed (A) and coated with HUO_2PO_4 (B). Bar is 500 nm. A *Serratia* biofilm (C) forms a meshwork of HUP-encrusted fibrils (D) (bars are 5 μm). (E) Detail of a single HUP lamellar structure.

as cell-bound deposits of hydrogen uranyl phosphate, $HUO_2PO_4.nH_2O$ (HUP) and continuous HUP deposition leads to the accumulation of a biomineral-encrusted meshwork of interwoven cells (Fig. 1), with stacked HUP crystals clearly visible (Fig. 1E).

A noteworthy feature of HUP is that it comprises stacks of lamellae with water molecules bridging adjacent HUP chains. These contain mobile protons that can exchange for metal cations like Ni^{2+}, removing the Ni^{2+} from solution into the HUP lattice via intercalative ion exchange (Bonthrone et al., 1996). This approach was adopted for the removal of radionuclides from contaminated waters (Paterson-Beedle et al., 2006).

Initial tests used Co^{2+}, Sr^{2+} and Cs^{+} as 'surrogates' for the problematic fission products ^{60}Co, ^{90}Sr and ^{137}Cs. Bioreactors (11 ml) containing HUP (~107 (for Co, Sr) or ~61 (for Cs) mg of U) were challenged with flows (10 ml/h) of 1 mM Co^{2+}, Sr^{2+} or Cs^{+}. Complete removal of the target metals into HUP was maintained for ~250 (Co, Sr) and ~350 (Cs) ml until column saturation. The capacity (bed volumes) under realistic flow concentrations at ~10^8–10^9 bed volumes, was more than 1000-fold better than current commercial materials, and the biomaterial was active at pH 3.5–9.3, whereas commercial materials tend to be pH-specific (e.g. for Sr pH$>$10 and for Co pH 4–8). Finally the bio-HUP was tested against a real nuclear waste containing ^{137}Cs at 1.78 Bq/ml (0.26 pM) and ^{60}Co at 0.15 Bq/ml (0.71 pM), where the respective radionuclide removal by the bio-derived filter was 99% and 85%, respectively.

A previous study (EU Final Report, 1995) identified that the limiting economic factor in the fabrication of the bio-HUP from U-wastewater was the cost of the organophosphate feed (glycerol 2-phosphate). Recent studies have shown that phytic acid (inositol phosphate), a natural plant product containing 6 mol phosphate/mol can support HUP deposition and subsequent removal of the surrogate nuclides into the phytic acid-derived HUP; the process then becomes economic (Paterson-Beedle et al., 2009).

A future possibility yet to be explored is use of the bio-HUP as a precursor for the fabrication of nuclear fuels; at a loading of ~tenfold by mass of uranium to the biomass component routinely achieved and with no mineral processing costs the economics of fuel manufacture may be attractive.

2.2. Case history 2. Bioconversion of palladium and platinum-containing industrial and automotive catalyst wastes into catalysts for (a) treatment of environmental contaminants and (b) clean electricity generation

An early study (Lloyd et al., 1998) showed that bacteria can utilize hydrogenase enzymes for the reduction of soluble Pd(II) ions to generate cell-bound nanoparticles of Pd(0). A process was developed for the continuous removal of Pd as well as other precious metals (PM) from spent automotive catalyst leachates (Yong et al., 2003). This involved a continuous-flow electrobioreactor with hydrogen generated electrochemically and fed to the bacteria via a Pd-thimble electrode. The bacteria formed a biofilm on the electrode and Pd(0) was removed from leachates developed via *aqua regia*-leaching of ground spent automotive catalysts (Yong et al., 2003). The recovered PMs sank to the bottom for recovery under gravity. Another approach involved hydrogen gas bubbled from below into a reactor for PM recovery from waste printed circuit board scrap containing 33 ppm of Pd and 79 ppm of Au (Creamer et al., 2006). Other studies showed that 'palladized' bacteria were active in the reduction of Cr(VI) (Mabbett et al., 2004), the dehalogenation of chlorinated aromatic compounds (Baxter-Plant et al., 2003) including the pesticide lindane (Mertens et al., 2007) and the dehalogenation of tris (chloroisopropyl) phosphate (TCPP) a flame retardant introduced as a substitute for polybrominated diphenyl ethers which is starting to accumulate in groundwaters (Deplanche et al., 2009). Since bio-bound Pd(0) is nanoparticulate the obvious question to address was whether 'Bio-Pd (0)' recovered from leachates has catalytic activity against potential environmental contaminants. Zero-valent iron has long been known to have potential in this respect but reports suggest that a Fe/Pd bimetallic is superior (Korte et al., 1997) (Fig. 2).

An initial study showed catalytic activity (in the reduction of Cr(VI) to Cr(III)) of 'Bio-Pd(0)' made from an industrial processing waste

Fig. 2. Palladized cells of *Desulfovibrio desulfuricans*. A non-palladized cell is also shown (inset). Palladization involves pre-incubation with Pd(II) to saturate biosorption sites, followed by addition of H_2 to achieve reduction of Pd(II) to Pd(0) via hydrogenase (Lloyd et al., 1998). Particle growth to the correct size is achieved via autocatalysis via the Pd(0) nanoclusters; cellular viability is not required after the initial nucleation. The laboratory 'workhorse' *Escherichia coli* and other bacterial strains can be similarly used to make catalysts with similar catalytic activities.

(Mabbett et al., 2006), while a subsequent work (Murray et al., 2007) showed activity using 'Bio-Pd(0)' made from a leachate from a secondary waste source (Table 1).

For clean energy production a major focus is on the use of fuel cells (FCs) to produce clean electricity from hydrogen. The most efficient FCs use a precious metal anode and cathode catalyst, usually Pt, which splits H_2 into $2H^+$ and $2e^-$, with the electrons forming the current and the protons being reunited with them at the cathode in air forming water as the only product. Recent studies have shown that precious metal scavenged onto biomass: Pt(0) on yeast (Dimitriadis et al., 2007) and Pd(0) on bacteria (Yong et al., 2007) have been fashioned into active FC catalysts. The PM mixture recovered from the industrial processing waste (see Table 1) also supported electricity production as the anode catalyst in a FC after further treatment (Yong et al., 2009). By using waste biomass from another process (Dimitriadis et al., 2007) (and see below) the catalyst can be made inexpensively while overcoming problems of disposal of organic waste (Table 2).

2.3. Case history 3. Bioconversion of Au-containing jewellery waste into nano-Au catalyst for glycerol oxidation

Initial studies aimed at bio-recovery of gold from printed circuit board scrap (Creamer et al., 2006) revealed that, in addition to hydrogenase-mediated Au(III) reduction, another, undefined mechanism is involved. This is reflected in the different morphology of Bio-Au(0) made in the same way as for Bio-Pd(0) (Fig. 3). To date the secondary 'Au-reductase' is unidentified.

Gold was recovered from jewellery waste (Deplanche and Macaskie, 2008). The concentration of Au(III) in the leachate was ~115 ppm and after 100 min no residual soluble Au(III) was detected (Deplanche and Macaskie, 2008). Au(0) is a potent oxidation catalyst, with the benefits of nanoscale Au(0) recently becoming realized. Bio-Au(0) functioned in the selective oxidation of glycerol to glycerate (Deplanche et al., 2007); this is noteworthy since commercial glycerol oxidation catalysts (supported Pt and Pd) generally give poor selectivity for glycerate. The conversion by both pure Bio-Au(III) and that made from the jewellery waste was ~30% after 3 h (Deplanche et al., 2007).

Table 2
Electricity production in a fuel cell with anodes made using Bio-Pd(0)s.

Pd(0) source	Power output$_{max}$ (milliWatts)
Commercial Pd(0)	99
D. desulfuricans (pure Pd(II) solution)	140
E. coli (pure Pd(II) solution)	114
E. coli (waste PM)	66

The catalytic oxidation of glycerol is foreseen as having an impact in the energy sector. Low-grade glycerol is produced in large quantities from the manufacture of biodiesel (~1 tonne low grade glycerol/tonne of biodiesel) and it has little market value *per se*. Other studies have shown that organic acids can be separated from the mother liquor rapidly and selectively using anion-selective electrodialysis. Organic acids provide an excellent feedstock for the photosynthetically-mediated generation of hydrogen by *Rhodobacter sphaeroides* (via a side reaction of nitrogenase) (Rousset et al., 2007). The bio-H_2 is fuel-cell quality (i.e. it does not require clean-up) and, furthermore, the residual *R. sphaeroides* is active in the manufacture of catalytically-active Bio-Pd(0) (Redwood et al., 2008) or Au(0) (unpublished).

The foregoing examples show real applications of bio-recovered materials in the remediation of environmental contaminants or in the production of 'non-carbon' energy. Several other possibilities exist which have not yet been demonstrated in 'real life' but nevertheless provide good potential for future focus.

2.4. Case history 4. Bioconversion of selenium oxyanions into optically active chalcogenide materials

Selenium is found in waste materials from a broad spectrum of anthropogenic operations including mining, agricultural, petrochemical, electronics, and industrial manufacturing operations (Lemly, 2004). The developing field of nanotechnology includes many Se-based materials, so wastes of the future are also likely to be seleniferous. Bacterially-mediated processes in the environment result in Se transformations, including changes in valence or chemical form (Shrift, 1964). These processes can be used to develop stabilization strategies, in which toxic, bioavailable Se oxyanions are reduced to less available elemental selenium, Se(0), removing them

Table 1
Metal composition and catalytic activity of 'Bio-Pd(0)' made from precious metals (PM) bio-recovered from industrial processing waste (A) and acid leachate from secondary waste (B).

A. From Degussa processing waste		B. From spent automotive catalyst		Catalytic activity[c]		
Waste pH 7, on *D. desulfuricans*		Waste pH 2, on *E. coli*			A	B
Composition of metals on cells (%)[a]		Composition of metal on cells (%)[b]		Pd metal	1.7	12.5
Pd	33%	Pd	28%	Bio-Pd(0)	2.7	31.0
Pt	17%	Pt	4%	Bio-PM	25	530
Ag	6%	Rh	2%	X-fold increase using waste source		
Al	42%	Al	37%			
Mg	3%	Mg	12%			
		Fe	14%		×10	×17

[a] Metals were analysed in the solid material by proton induced X-ray emission (Mabbett et al., 2006).

[b] Metals were estimated in the solid material by loss from the liquid leachate.

[c] Activity is μmol Cr(III) produced/h/mg Pd metal on biomass. 'Pd metal' is commercial Pd(0). 'Bio-Pd' is a catalyst made from pure Pd(II) solution under the same conditions. Bio-PM is a catalyst made from the liquid wastes.

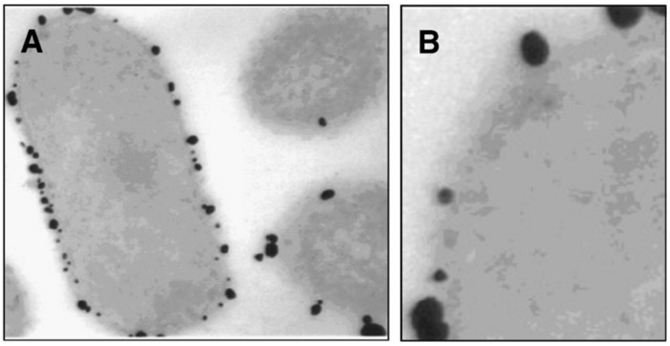

Fig. 3. Formation of Bio-Au(0) on *E. coli* (A). Similar Au-particles were seen on *D. desulfuricans*. Close inspection (B) shows the Au-particles to be embedded in the cell surface layers and not extruded as well defined nanocrystals as with Pd(0) shown in Fig. 2.

from aqueous waste streams, e.g. drinking water, groundwater or wastewater. The products of these reductive transformations include a range of functional bionanominerals with interesting physical properties of potential technological significance (Miller and Webster, 2006; Pearce et al., 2008; Ralston, 2008; Oremland et al., 2004). For instance, these biogenic elemental Se nanospheres have photooptical and semiconducting physical properties, different from their chemically formed counterparts, for application in photocopiers, microelectronic circuits and solar cells (Oremland et al., 2004). Elemental Se is further reduced by some bacterial strains e.g. *Veillonella atypica*, to form reactive soluble selenide, which can be precipitated to produce nanoparticles such as the II–VI semiconductors ZnSe and CdSe, potentially stabilized by proteins present in the biogenic starting material. These materials can be fabricated into optoelectronic devices, light sensors and photovoltaics (Pearce et al., 2008) (Fig. 4).

2.5. Case history 5. Bioconversion of Fe(III)-oxide waste into a nanoscale magnetic material

Wastes containing iron are produced from various industrial activities including the polishing steps used by the water industries and also from mining activities. Under oxic conditions Fe(II) oxidises to Fe(III) to give a colloidal deposit of $Fe(OH)_3$ which settles poorly under gravity to give a high volume wet sludge which is difficult to handle and transport. The low recovery value of iron means that a high value chemical product is not usually a primary consideration. However bioconversion of the substrate from a poorly crystalline amorphous Fe(III) oxide, to a structured magnetic spinel offers a potentially useful remediation strategy for areas impacted with Fe (III)-based industrial reagents and 'one-pot conversion' of the waste into a potentially useful product.

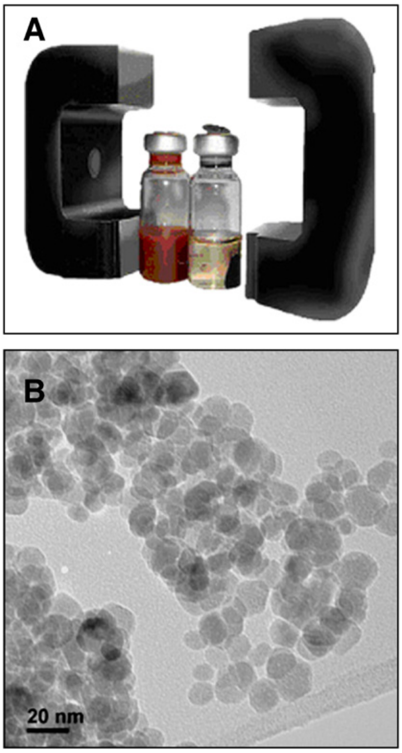

Fig. 5. (A) Conversion of Fe(III)-oxyhydroxide (left vial) to nanoscale magnetite (right vial) using *G. sulfurreducens*. (B) TEM image of nanoscale biogenic magnetite particles.

Fe(III)-reducing bacteria are a group of micro-organisms found in anoxic subsurface sediments that gain energy for growth by reducing metals such as Fe(III) and Mn(VI) coupled to the oxidation of organic matter, causing changes in the mineralogy of the sediments (Caccavo et al., 1994). *Geobacter sulfurreducens* is a bacterium capable of respiring amorphous Fe(III) oxides, converting the iron minerals to nano-sized magnetic particles of magnetite (Fe_3O_4) (Fig. 5A), with a size of about 20 nm (Fig. 5B) (Coker et al., 2007). Such particles have electrical, magnetic, and structural properties that differ from coarse grained materials.

Waste iron oxides can contain other important metals such as cobalt, nickel and manganese, which can be incorporated into the spinel structure changing the chemical formula to $M_xFe_{3-x}O_4$, where *M* is a cation different from iron. This changes the magnetic properties of the particles; therefore it has been important to first study simple synthetic systems in order to understand the more complicated waste nano-magnets. Using *G. sulfurreducens*, we have produced a variety of nanoparticles from iron oxides synthesised in the laboratory, containing just one or two of the above elements (Coker et al., 2008).

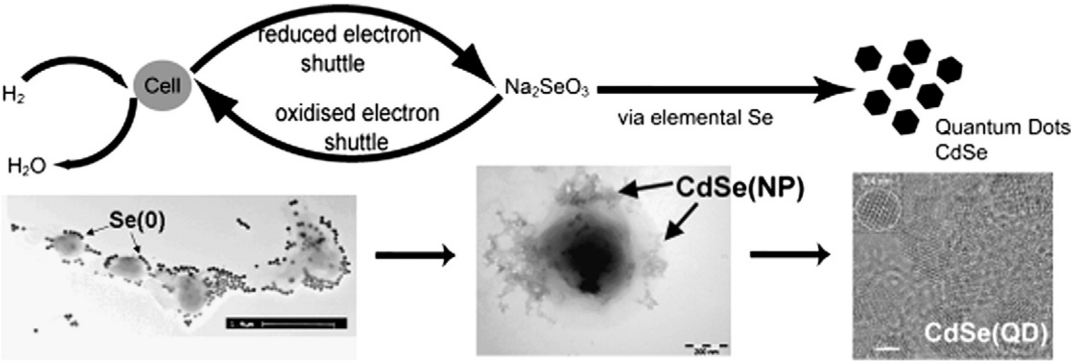

Fig. 4. Microbial synthesis of chalcogenide-based nanoparticles via the reduction of sodium selenite using the metal-reducing bacterium *Veillonella atypica*.

These experiments have confirmed that Fe(III)-reducing bacteria can produce doped nano-sized “designer” magnetic particles via biosynthetic routes, for a range of technological and medical applications. This type of reductive transformation also has potential applications for the recovery and re-use of waste Fe(III) oxides where the magnetic properties of the material do not have to be so carefully controlled. Obvious applications here include the formation of magnetically recoverable functional biominerals for Fe(II)-mediated reactions leading to the bioremediation of redox active organics, metals and radionuclides. To conclude, the method of production of these novel extracellular bionanomagnets is efficient, requires little energy, has no hazardous wastes and can be used to make tailored nano-magnets for a variety of applications.

Acknowledgments

This work was supported by grants from EPSRC (EP/C548809/1; EP/D058767/1; EP/057310/1) and BBSRC (BB/E003788/1; BB/E004601/1). This work was supported by the facilities funded through Birmingham Science City: AM2, an Advantage West Midlands-supported project part funded by the European Regional Development Fund (ERDF).

References

Anon, 2009. Platinum interim review 2008. Platinum Metals Rev. 53, 48–49.

Baxter-Plant, V.S., Mikheenko, I.P., Macaskie, L.E., 2003. Sulphate-reducing bacteria, palladium and the reductive dehalogenation of chlorinated aromatic compounds. Biodegradation 14, 83–90.

Bonthrone, K.M., Basnakova, G., Lin, F., Macaskie, L.E., 1996. Bioaccumulation of nickel by intercalation into polycrystalline hydrogen uranyl phosphate deposited via an enzymatic mechanism. Nat. Biotechnol. 14, 635–638.

Brierley, J.A., Goyak, G.M., Brierley, C.L., 1986. Considerations for commercial use of natural products for metal recovery. In: Eccles, H., Hunt, S. (Eds.), Immobilization of Ions by Bio-sorption. Ellis Horwood, Chichester, England, pp. 105–120.

Caccavo Jr, F., Lonergan, D.J., Lovley, D.R., Davis, M., Stolz, J.F., McInerney, M.J., 1994. *Geobacter sulfurreducens* sp. nov., a hydrogen- and acetate-oxidizing dissimilatory metal-reducing microorganism. Appl. Environ. Microbiol. 60, 3752–3759.

Coker, V.S., van der Laan, G., Pattrick, R.A.D., Lloyd, J.R., 2005–2006. Novel nanomagnets manufactured by friendly bacteria. SRD Annual Report, pp. 46–47.

Coker, V.S., Pearce, C.I., Lang, C., van der Laan, G., Pattrick, R.A.D., Telling, N.D., Schuler, D., Arenholz, E., Lloyd, J.R., 2007. Cation site occupancy of biogenic magnetite compared to polygenic ferrite spinels determined by X-ray magnetic circular dichroism. Eur. J. Mineral. 19, 707–716.

Coker, V.S., Pearce, C.I., Pattrick, R.A.D., van der Laan, G., Telling, N.D., Charnock, J.M., Arenholz, E., Lloyd, J.R., 2008. Probing the site occupancies of Co-, Ni- and Mn-substituted biogenic magnetite using XAS and XMCD. Am. Mineral. 93, 1119–1132.

Creamer, N.J., Baxter-Plant, V.S., Henderson, J., Potter, M., Macaskie, L.E., 2006. Palladium and gold removal and recovery from precious metal solutions and electronic scrap leachates by *Desulfovibrio desulfuricans*. Biotechnol. Lett. 28, 1475–1484.

Deplanche, K., Macaskie, L.E., 2008. Biorecovery of gold by *Escherichia coli* and by *Desulfovibrio desulfuricans*. Biotechnol. Bioeng. 99, 1055–1064.

Deplanche, K., Attard, G., Macaskie, L.E., 2007. Biorecovery of gold from jewellery wastes by *Escherichia coli* and biomanufacture of active Au-nanomaterial. Adv. Mat. Res. 20–21, 647–650.

Deplanche, K., Snape, T.J., Hazrati, S., Harrad, S., Macaskie, L.E., 2009. Versatility of a new bioinorganic catalyst: palladized cells of *Desulfovibrio desulfuricans* and application to dehalogenation of flame retardant materials. Environ. Technol. 30, 681–692.

Dimitriadis, S., Nomikou, N., McHale, A.P., 2007. Pt-based electro-catalytic materials derived from biosorption processes and their exploitation in fuel cell technology. Biotechnol. Lett. 29, 545–551.

EU Final report, 1995. Biological Rehabilitation of Metal Bearing Wastewaters, EV5V-CT93-0251.

Jackson, M.T., Sampson, J., Prichard, H.M., 2007. Platinum and palladium variations through the urban environment: evidence from 11 sample types from Sheffield, UK. Sci. Total Environ. 385, 117–131.

Korte, N., Liang, L., Muftikian, R., Grittini, C., Fernando, Q., 1997. The dechlorination of hydrocarbons: palladised iron utilised for ground water purification. Plat. Metals. Rev. 41, 2–7.

Lemly, A.D., 2004. Aquatic selenium pollution is a global environmental safety issue. Ecotoxicol. Environ. Saf. 59, 44–56.

Lloyd, J.R., Yong, P., Macaskie, L.E., 1998. Enzymatic recovery of elemental palladium using sulfate-reducing bacteria. Appl. Environ. Microbiol. 64, 4607–4609.

Lloyd, J.R., Anderson, R.T., Macaskie, L.E., 2005. Bioremediation of metals and radionuclides. In: Atlas, R., Philp, J. (Eds.), Bioremediation: Applied Microbial Solutions to Real-world Environmental Cleanup. ASM Press, Washington DC, pp. 293–317.

Lloyd, J.R., Pearce, C.I., Coker, V.S., Pattrick, R.A.D., Van der Laan, G., Cutting, R., Vaughan, D.J., Paterson-Beedle, M., Mikheenko, I.P., Yong, P., Macaskie, L.E., 2008. Biomineralization: linking the fossil record to the production of high value functional materials. Geobiol. 6, 285–297.

Mabbett, A.N., Yong, P., Farr, J.P.G., Macaskie, L.E., 2004. Reduction of Cr(VI) by “palladized” biomass of *Desulfovibrio desulfuricans* ATCC 29577. Biotechnol. Bioeng. 87, 104–109.

Mabbett, A.N., Sanyahumbi, D., Yong, P., Macaskie, L.E., 2006. Biorecovered precious metals from industrial wastes: single-step conversion of a mixed metal liquid waste to a bioinorganic catalyst with environmental application. Environ. Sci. Technol. 40, 1015–1021.

Macaskie, L.E., Yong, P., Doyle, T.C., Roig, M.G., Diaz, M., Manzano, T., 1997. Bioremediation of uranium-bearing wastewater: biochemical and chemical factors influencing bioprocess application. Biotechnol. Bioeng. 53, 100–109.

Macaskie, L.E., Bonthrone, K.M., Yong, P., Goddard, D.T., 2000. Enzymatically mediated bioprecipitation of uranium by *Citrobacter* sp.: a concerted role for exocellular lipopolysaccharide and phosphatase in biomineral formation. Microbiology 146, 1855–1867.

Mertens, B., Blothe, C., Windey, K., de Windt, W., Verstraete, W., 2007. Biocatalytic dechlorination of lindane by nano-scale particles of Pd(0) deposited on *Shewanella oneidensis*. Chemosphere 66, 99–105.

Miller, D.C., Webster, T.J., 2006. Anticancer orthopedic implants. In: Nalwa, H.S., Webster, T.J. (Eds.), Cancer Nanotechnology. American Scientific Publishers, pp. 307–316.

Murray, A.J., Mikheenko, I.P., Goralska, E., Rowson, N.A., Macaskie, L.E., 2007. Biorecovery of platinum group metals from secondary sources. Adv. Mat. Res. 20–21, 651–654.

Oremland, R.S., Mitchell, H.J., Switzer Blum, J., Langley, S., Beveridge, T.J., Ajayan, P.M., Sutto, T., Ellis, A.V., Curran, S., 2004. Structural and spectral features of selenium nanospheres produced by Se-respiring bacteria. Appl. Environ. Microbiol. 70, 52–60.

Paterson-Beedle, M., Macaskie, L.E., Lee, C.H., Hriljac, J.A., Jee, K.Y., Kim, W.H., 2006. Utilisation of a hydrogen uranyl phosphate-based ion exchanger supported on a biofilm for the removal of cobalt, strontium and caesium from aqueous solutions. Hydrometallurgy 83, 141–145.

Paterson-Beedle, M., Macaskie, L.E., Readman, J.E., Hriljac, J.A., 2009. Biorecovery of uranium from minewaters into pure mineral product at the expense of plant wastes. Adv. Mats. Res. 71–73, 621–624.

Pearce, C.I., Coker, V.S., Charnock, J.M., Pattrick, R.A.D., Mosselmans, J.F.W., Law, M.N., Beveridge, T.J., Lloyd, J.R., 2008. Microbial manufacture of chalcogenide-based nanoparticles via the reduction of selenite using *Veillonella atypica*: an in situ EXAFS study. Nanotechnology 19, 1–13.

Ralston, N., 2008. Nanomaterials: nano-selenium captures mercury. Nat. Nanotechnol. 3, 527–528.

Redwood, M.D., Deplanche, K., Baxter-Plant, V.S., Macaskie, L.E., 2008. Biomass-supported palladium catalysts on *Desulfovibrio desulfuricans* and *Rhodobacter sphaeroides*. Biotechnol. Bioeng. 99, 1045–1054.

Rousset, M., Casalot, L., De Philip, P., Belaich, A., Mikheenko, I., Macaskie, L.E., International patent PCT/EP200/050942, 2007.

Shrift, A., 1964. A selenium cycle in nature? Nature 201, 1304–1305.

Yong, P., Rowson, N.A., Farr, J.P., Harris, I.R., Macaskie, L.E., 2003. A novel electrobiotechnology for the recovery of precious metals from spent automotive catalysts. Environ. Technol. 24, 289–297.

Yong, P., Paterson-Beedle, M., Mikheenko, I.P., Macaskie, L.E., 2007. From biomineralisation to fuel cells: biomanufacture of Pt and Pd nanocrystals for fuel cell electrode catalyst. Biotechnol. Lett. 29, 539–544.

Yong, P., Mikheenko, I.P., Deplanche, K., Sargent, F., Macaskie, L.E., 2009. Biorecovery of precious metals from wastes and conversion into fuel cell catalyst for electricity production. Adv. Mat. Res. 71–73, 729–732.