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A novel biorefinery: Biorecovery of precious metals from spent automotive catalyst leachates into new catalysts effective in metal reduction and in the hydrogenation of 2-pentyne

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ABSTRACT

With the aim to recover precious metals (PMs) from spent automotive catalyst leachates into new catalysts, cells of *Escherichia coli* first reduced Pd(II) or Pt(IV) physiologically to nanoparticulate cell-bound Pd(0) and Pt(0). Metallised cells were then used as chemical catalysts for the reductive recovery of precious metals from model solutions and from *aqua regia* leachates of crushed spent automotive catalyst. Metal removal, which was slower from real leachate due to interference by other contaminants, was complete after 60 h. Biofabricated PM catalyst from waste reduced 0.5 mM Cr(VI) to a similar extent to commercial 5% Pd catalyst but at ~half the rate. The hydrogenation of 2-pentyne was examined using commercial Pd on Al_2O_3 catalyst and biofabricated Pd/Pt catalyst, the latter showing more than 3-fold enhanced selectivity towards the desired *cis*-pentene product. Hence, biorefined PMs offer a clean route to waste treatment and effective neo-catalyst biomanufacture.

1. Introduction

Platinum group metals (PGMs) are scarce high value metals with a wide range of applications from jewellery and commercial catalysis to use within car catalytic converters for atmospheric protection (Xiao and Laplante, 2004; Bernardis et al., 2005; Wiseman and Zereini, 2009). No suitable alternative has yet been found for PGM (particularly Pt) in many applications as they have low substitutability, except with other PGMs (Bernardis et al., 2005; Yang, 2009). PGM catalysts are used in low temperature fuel cells (Anon. 2006). This highlights future tensions between today's transport requirements and tomorrow's energy needs. Supply and price of PGM are critical to both (Anon. 2008). To safeguard future supplies of PGMs it is increasingly important to recover and re-use the metals effectively and sustainably.

All new motor vehicles are fitted with a catalytic converter, each containing up to 2.4 g of precious metals which are routinely 'thrifted' by adjusting the catalytic composition according to the PGM market price (Mouza et al. 1995; Johnson Matthey, 2001; Xiao and Laplante, 2004). PGM loadings on catalytic converters are unlikely to decrease in future (Bloxham, 2009) and will probably increase slightly in order to meet stringent standards (Yang, 2009).

Under load the PGMs on the catalytic surface become abraded from the support and become deposited within road dust (Cinti et al., 2002; Schafer and Puchelt, 1998). The PGM levels found within some urban wastes were shown to be equivalent to that of an ore from a low grade mine (Jackson et al.2007) e.g. a small city the size of Sheffield, UK produces around 8000 tonnes of road dust per year. Consideration of such secondary wastes as 'urban mines' is attractive due to the negligible comminution costs of powdered materials as well as the resource they contain. However upgrading of bulk materials to obtain PGM levels that are economic for extraction remains a challenging area (Murray, 2012).

We take automotive catalysts as an example as these are the source material from which environmental PGMs are derived. Yong et al. (2003) showed a new approach to recovery of PGMs from acidic spent automotive catalyst leachates using cells of the bacterium *Desulfovibrio desulfuricans* which deposits precious metals via their reduction from soluble ionic forms. The ability of *D. desulfuricans* and many other bacteria (Deplanche et al., 2011) to reduce various metals, including PGMs, onto their surface through hydrogenase activity is well documented (e.g. see Lloyd et al., 1998; Deplanche et al., 2010; Deplanche et al., 2011). The deposited metals form nanoparticles on the cell surface. This ability has been exploited to create "bionanocatalysts" comprising bacterial cells coated with a well distributed layer of metallic nanoparticles (NPs) (see Deplanche et al., 2011 for review). Studies have illustrated the use of metals biorecovered from wastes to produce

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these catalysts (Mabbett et al., 2006; Murray et al., 2007; Macaskie et al., 2011). Some can produce catalysts with higher activity than those made with just one metal (Yong et al., 2010; see Macaskie et al., 2011). However, although for applications in fine chemicals synthesis an undefined 'dirty' catalyst may be unattractive, for other applications such as decontamination of pesticides (Mertens et al., 2007) or chlorinated organic compounds in groundwater (Deplanche et al., 2009) a mixed metal 'dirty' catalyst may suffice. This approach pioneers a new area of environmental nanotechnology. However the potential hazards of NP migration would need to be minimised. This can be done via the retention of multiple catalytic NPs onto micron-sized 'carrier' bacterial cells that are structurally robust and can be immobilised on bacterial biofilm for continuous use (Beauregard et al., 2010; Yong et al., 2015), with negligible catalyst attrition from bacterially-bound nanoparticles (Bennett et al., 2013).

A continuous biorecovery system for PGMs from waste was pioneered by Yong et al. (2003). These authors used electrochemically-generated hydrogen to supply a film of PGM-reducing bacteria on the outside of a Pd/Ag thimble electrode immersed in PGM solution, with the hydrogen generated at the back-side. When loaded, the bacteria fell from the electrode for harvest (Yong et al., 2003). The bacteria removed more than 80% of the presented Pd and Pt from an industrial processing waste and up to 75% of the presented Rh (Yong et al., 2003).

Recovery of metals from very acidic solutions such as waste leachates is difficult. This is due to the strength of acid required to dissolve PGMs (noble metals typically require *aqua regia*). This is incompatible with biochemical activity. Therefore a two step approach was developed whereby bacteria were first allowed to reduce (e.g.) Pd(II) to Pd (0) 'seeds' under physiologically compatible conditions. These pre-metallised cells then functioned as chemical catalysts in the recovery of PGMs from acidic solutions (Creamer et al., 2006; Mabbett et al., 2006).

An early study showed that 5% by mass loading of Pd(0) onto *D. desulfuricans* gave a hydrogenation catalyst comparable to commercial 5% Pd on carbon (Creamer et al., 2007) but 'thrifting' Pd(0) on cells of *D. fructosovorans* resulted in an inferior catalyst; i.e. cells at 5% and 2% Pd(0) mass loading released, respectively, 0.7 and 0.3 ml H_2/min/mg Pd from hypophosphite, while the respective hydrogenation of 0.4 mM itaconic acid (methylene succinate) to methyl succinate after 1 h was 70% and 50% (Skibar et al., 2005). The discrepancy was even greater in the bio-Pd- catalysed reduction of Cr(VI) (CrO_4^{2-} anion). Here, less than 10% of 0.5 mM Cr(VI) was reduced after 3 h by cells with 2% Pd (0) mass loading whereas 5% loading achieved > 30% reduction (Skibar et al., 2005). Clearly a mass loading of 5 wt% Pd is preferable and a way to reduce this to 2 wt% Pd from a primary source while retaining catalytic efficacy would be useful from an economic viewpoint. One option is to 'top up' the cellular Pd(0) by sourcing the metal from a waste.

The dual aims of this study were firstly to use a microbial biorecovery method to convert a waste leachate into catalytically active biomaterial and secondly to show that the biorecovered metal gave catalytic activity over and above that of metallised bacteria bearing only the initial 'seeds'.

Previous work has focused on Pd (e.g. Creamer et al., 2007). Many PGM wastes and especially catalytic converters and road dusts contain both Pd and Pt (Shelef and McCabe, 2000, Ek et al., 2004) as well as Rh. This study focused on Pd and Pt since these are the major PGM components (Murray, 2012). Hence, cells were 'seeded' using both Pd and Pt to various loadings prior to metal removal from, initially, model metal mixtures and then from real automotive catalyst leachate. Initial studies focused on reduction of Cr(VI) but in order to assess the potential for this approach in chemical manufacturing applications ('green chemistry') the bionanocatalysts were also evaluated with respect to their ability to hydrogenate 2-pentyne, focusing on the ability to produce the preferred *cis*-pentene isomer.

Many studies have reported the application of microbial processes to the recovery of base metals and precious metals from wastes but relatively few have progressed from model solutions to actual wastes, i.e. that contain also other metallic and non-metallic components. Bioconversion of a metal recovered from a waste into a neo-catalyst has received little attention; examples include bioconversion of a relatively benign PGM-processing wastewater into a catalyst for reduction of toxic Cr(VI) (Yong et al., 2015) and a fuel cell electrocatalyst (Yong et al., 2010) but showing the potential for neo-catalysts biomanufactured from an aggressive waste leachate is a novel development. The goal of this study is to illustrate this potential.

2. Materials and methods

2.1. Growth of organisms

Escherichia coli MC4100 cells were cultured in 12 l of nutrient broth under anaerobic conditions (i.e. with exclusion of air: Deplanche and Macaskie, 2008). Cells were harvested by centrifugation, washed three times in 20 mM MOPS-NaOH buffer pH 7.0 and resuspended in a known volume of buffer. The cell density was checked by OD_{600} which was converted to bacterial dry weight by a previously determined calibration, whereby suspended samples of cells at a known OD_{600} and known volume were dried to constant weight after washing with water to remove residual salts. With a dry weight of cells between 20 and 30 mg/ml the cell suspensions were then split into six aliquots in preparation for pre-metallisation.

2.2. Pre-metallisation of cells

Cells were metallised as described by Taylor (2012). Solutions of 2 mM Pd(II) and Pt(IV) were prepared in 1 mM HNO_3 using Na_2PdCl_4 and K_2PtCl_6 salts respectively. The required volume of metal solution was then added to aliquots of cells (known mass: above) to achieve the desired metal loadings of 1%, 2% or 5% by mass as stated. H_2 was bubbled through the suspension (30 min) and suspensions were then incubated at 30 °C under H_2 for reduction of metal onto the cells. Complete metal reduction and removal was confirmed in sample supernatants using a $SnCl_2$ – based assay for residual soluble metal as described previously (Creamer et al., 2007). Following full reduction of metals (within 30 min) the 'seeded' cells were harvested by centrifugation, washed once using distilled water and resuspended in distilled water (30 ml).

2.3. Recovery of target metals from model solution and catalyst production

The seeded cells (1%, 2% or 5% of Pd, or Pt as specified; 16 mg of pre-loaded cells) were exposed to a mixed solution of 0.34 mM Pt(IV) and 0.42 mM Pd(II) in HNO_3 (target metal solution: chosen as an approximation to a real catalyst leachate: Taylor, 2012). The volume of solution added was calculated as that required to give a final loading of metals on pre-palladised cells, following target metal reduction of, respectively, 15 wt%, 16 wt% and 20 wt% in a background of 1 mM HNO_3.

The reducing agent (H_2) was bubbled into the solution as described in the seeding step with metal reduction monitored in withdrawn samples using $SnCl_2$ as above. No attempt was made to assess selectivity of metal removal. The results were expressed as percentage target metal reduction against time, using five independent batches for each test to assess the inter-batch variability (standard error of the mean was within 5%). After complete metal reduction (loss of metals by assay of the spent solution) the cells were harvested by centrifugation, washed once in H_2O and once in acetone. They were then dried and ground in an agate mortar to give a black powder which was passed through a 100 μm sieve to obtain a fine powder catalyst.