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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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With the aim to recover precious metals (PMs) from spent automotive catalyst leachates into new catalysts, cells of *E. 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 Al₂O₃ 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.

Key words: Precious metals. Biorecovery. Automotive catalysts waste. Neo-catalyst. Cr(VI) reduction. 2-pentyne hydrogenation
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 & 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, 2011).

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; 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 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 H2/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) (CrO42− 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 2wt% 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 wastes.

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, 2011). 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. Bio-conversion 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 litres 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 20mM MOPS-NaOH buffer pH 7.0 and resuspended in a known volume of buffer. The cell density was checked by OD<sub>600</sub> which was converted to bacterial dry weight by a previously determined calibration, whereby suspended samples of cells at a known OD<sub>600</sub> and known volume were dried to constant weight after washing with water to remove residual salts. With a dry weight of cells between 20-30 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<sub>3</sub> using Na<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>6</sub> 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<sub>2</sub> was bubbled through the suspension (30 min) and suspensions were then incubated at 30 °C under H<sub>2</sub> for reduction of metal onto the cells. Complete metal reduction and removal was confirmed in sample supernatants using a SnCl<sub>2</sub> –
based assay for residual soluble metal as described previously (Creamer et al., 2008). 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 HNO₃ (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 HNO₃. The reducing agent (H₂) was bubbled into the solution as described in the seeding step with metal reduction monitored in withdrawn samples using SnCl₂ 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 H₂O 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 micron sieve to obtain a fine powder catalyst.

2.4. Catalytic evaluation via reduction of Cr(VI) to Cr(III)

Catalyst prepared as described above (10 mg powder) was added to a 12 ml serum bottle and 5
ml 0.5 mM Na$_2$Cr$_2$O$_7$·4H$_2$O in 20 mM MOPS-NaOH buffer pH 7.0 was then added. The bottle was sealed with a butyl rubber stopper, degassed under vacuum (via a needle) and sparged with oxygen free nitrogen. It was then placed onto a rotary shaker (180 rpm; 10 min, room temperature) to ensure mixing and distribution of catalyst. Sodium formate (1 ml of a 25 mM solution) was added. The bottle (still under N$_2$) was returned to the shaker and sampled at 30 minute intervals. Sample supernatants were analysed for residual Cr(VI) using diphenylcarbazide (Mabbett et al., 2004).

2.5. Catalytic evaluation via hydrogenation of 2-pentyne

2-pentyne hydrogenation experiments were carried out in a three-phase 500 ml stainless steel autoclave reactor (Baskerville, Manchester, U.K.) To this, 150 ml solvent (2-propanol) and a weighed mass (usually 0.056 mmol Pd(Pt) unless stated otherwise) of ground catalyst were added. The comparator was 2wt% mass of Pd on Al$_2$O$_3$ (‘Pural SB’: Condea). The mixture was heated to 40˚C, nitrogen was purged in order to remove residual oxygen, and the catalyst was pre-reduced by bubbling a flow of hydrogen (0.5 L/min) through the system for 20 min with gentle stirring (500 rpm). 4 ml of 2-pentyne (98+%, Alfa Aesar UK) was then added. The reactions were stirred (1000 rpm) at 40 C under a constant 2 bar of hydrogen pressure. Liquid samples were withdrawn periodically. The composition of the reaction mixture was determined by gas chromatographic (GC) analysis using a Varian CP-3380 with a flame ionisation detector (FiD) and a 30 m Gamma DEX™ 225 capillary column (Thermo Electron Corporation UK) at 40C after equilibration for 10 min.
The major products from 2-pentyne hydrogenation are partially hydrogenated cis/trans-pentene and fully hydrogenated pentane. The performance of the catalyst was assessed in terms of selectivity toward cis-pentene; selectivity was calculated as the number of moles of cis-pentene divided by the total number of moles of all products detected.

Hydrogenation experiments were done twice, independently, with a difference between them of within 10% throughout and pooled data are shown.

2.6. Metal recovery from spent automotive catalyst by leaching and preparation of catalyst from leachate

Preparation of catalyst leachate was developed from methods described by Yong et al. (2003) as detailed by Murray (2011). A used ‘three way’ car catalyst (Peugeot 106 aftermarket catalyst provided by Humphries Garage, Bearwood, Birmingham) was stripped of its outer cladding to expose the cordierite and washcoat monolith, the latter containing the PGMs. The monolith was processed by jaw crushing to $d < 3.5$ mm (Sturtevant 150 mm jaw crusher with corrugated jaw plates), ground using a roll crusher (Sturtevant 150 mm Roll Crusher) and then passed through a 1 mm screen. Any oversize material was reground in the Roll crusher so that all test material was of diameter $d \leq 1$ mm. 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 1 mm was reground in order to avoid over-crushing but to facilitate maximum acid-washcoat interaction.

For leaching *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 (106°C in one min using a
power of 600W). That temperature was maintained (15 min) followed by a cooling cycle (5 min). The contents of the vessel were transferred with washings (half the volume of distilled water to *aqua regia*; final *aqua regia* concentration 67% vol/vol aq.), centrifuged (4000 rpm; 10 min) and the supernatant was retained for biomass metallisation tests. Commercial analysis of leachate was done by Engelhard Corporation (ICP-MS) with a stated ICP limit of detection of 0.1ppm for PGMs.

The procedure for making the catalyst from leachate was as follows. Due to the low level of Pd(II) (see Results and Discussion) the leachate used in this study was ‘spiked’ to 400 ppm with Pd(II). The leachate was diluted ten-fold in distilled water to reduce the concentration of acids to 6.7% (to avoid destruction of the biomass support) and it was brought to pH 2.2 with 6 M NaOH. Pre-palladised (‘seeded’) cells of *E. coli* (1 ml, 5 wt% initial Pd loading) were added to 77 ml of leachate (and model solution in parallel to a comparable metal loading; see 2.3) and H₂ was bubbled through this mixture (2 h) and then left to stand until the PGMs were removed (by assay of spent solution using SnCl₂). The other components of the catalyst, and their extraction by this method, were not analysed.

In order to implicate compound(s) responsible for the slower PGM deposition from the waste (see Results and Discussion) a simple test was carried out. Model leachates (Pd(II) and Pt(IV)) were prepared as above using fresh *aqua regia* and aliquots were spiked with Pd(II) (to 400 ppm final concentration), neutralised and diluted as before. The pH was adjusted to 2.0. Aliquots of the model leachates were spiked with silica (SiO₂ (to 173 ppm)) and Al₂O₃ (to 173 ppm) final concentrations) and also a mixture of both. The Pd- ‘seeded’ bioinorganic catalyst was added in each reactor and PGM removal was followed as before.
Results and Discussion

3.1. Analysis of leachates and leaching of PGMs from wastes

Commercial analysis of the leachate gave 24ppm Pd, and 4ppm Rh but no detectable Pt (although this method was confirmed to give effective leaching of Pt from solid scraps: (Murray, 2011)). 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. A comparison of the catalyst used in this work against other typical spent automotive catalysts showed that PGM levels were unusually low (probably due to losses onto roads during use), with the Pd content being approximately 10% of the value of another catalyst processed under the same conditions (this catalyst was retained for testing in another study). Hence the leachate of the catalyst used in this study was ‘spiked’ with additional Pd(II) (see Materials and Methods).

Optimal leaching conditions were initially developed as described by Murray (2011) to give the procedure described in Materials and Methods. Two solid samples were treated and analysed in order to determine the initial PGM content of both crushed catalysts (i.e. the catalyst providing material as used in this study and for a parallel catalyst which was used in other tests which will form the basis for a future publication). Since Yong et al., (2003) had reported relatively high PGM recoveries (>80% of maximum of Pd and Pt) using 50% aqua regia tests were conducted using both 50% and 100% aqua regia as shown in Table 1. The results (Fig. 1) show that for each condition approximately 90% of the Pd was recovered but 100% aqua regia was required for the highest recovery of Rh (>80%). For Rh no clear conclusion could be drawn regarding the advantage of using
a solid:liquid ratio of 10:1 as compared to 5:1 but use of 100% *aqua regia* gave enhanced extraction over 50% *aqua regia* at both liquid:solid ratios (Fig. 1). Use of a finely ground sample did not improve the extraction efficiency of Rh at a liquid:solid ratio of 5:1 (Fig. 1). The conclusion from this study is that effective metal recovery is only achieved using 100% *aqua regia* but that 50% *aqua regia* is sufficient for Pd recovery. The possibility to develop a selective method to separate Pd and Rh (i.e. concentration of Rh into the unextracted fraction) was not explored, while the occurrence of Rh in the final catalyst sample was not measured, and hence the ‘finished’ neo-catalyst was probably a mixture of Pd and a small amount of Rh which was not tested. However use of 50% *aqua regia* would represent a distinct advantage with respect to savings in acid costs as well as minimising the potential damage to the biomass support. Hence, subsequent tests used 50% *aqua regia* with microwave processing at 106°C for 15 minutes (see Materials and Methods). The advantage of microwave processing has been described elsewhere (Jafarifar et al., 2005) and the conditions were optimized for these samples previously (Murray 2011).

3.2. Hydrogenation of 2-pentyne using the model system with cells pre-seeded at 2 wt% Pd

A full description of the data with respect to catalytic activity of bio-catalyst made on cells that were ‘seeded’ to 1 wt%, 2 wt% and 5 wt% Pd was given by Taylor (2012). Cells seeded using 1 wt% Pd gave an inferior catalyst and hence in this study a pre-loading of 2 wt% was used in the hydrogenation tests.

Bennett et al. (2009) showed that bioPd functioned in the hydrogenation of 2-pentyne but a different reactor system and catalyst loading was used in the earlier work as compared to this study so direct comparisons are not possible. Fig. 2 shows that the slowest conversion rate was
seen using 2wt% bioPd alone but by supplementing with the additional metals the rates for the commercial and biocatalyst became comparable. Other tests (not shown) revealed that 5wt% pre-palladised cells (i.e. Pd alone) had a similar activity to the commercial catalyst shown in Fig. 2 and hence no further enhancement occurred by augmenting with additional Pd/Pt.

It is concluded that supplementing the initial Pd ‘seeds’ with additional Pt and Pd from the model mixture produced a catalyst comparable to a commercial catalyst. Bennett et al. (2010) noted that (under their conditions) the bioPd had only ~30% of the activity of its commercial counterpart but it showed a higher selectivity to the cis-ene product. Hence, the present study also examined the ability of the biomaterial to promote reaction specificity since production of the cis alkene over trans is highly desirable industrially. The results (Table 2) show that, with respect to the cis/trans products, the bio-catalyst gave much lower selectivity to trans-pentene (below 20 mol%; i.e. a higher selectivity to the cis-product), while commercial 2 wt% and 5 wt% Pd/Al₂O₃ gave above 35 mol% selectivity to undesirable trans. Using commercial catalyst the cis/trans-pentene ratio was 0.71 for 2 wt% Pd/Al₂O₃ and 0.68 for 5 wt% Pd/Al₂O₃. Hence, using bio-catalyst gave a 3-4 fold higher selectivity (data are averaged for the two loadings). However, Table 2 shows that, overall, there was no advantage (or disadvantage) in using the catalyst made from the mixture as compared to the ‘seeded’ cells alone. Hence, the advantage of providing additional catalyst from the mixture was that the activity of 2%wt bioPd was enhanced by approximately two-fold to become slightly better than the commercial comparator (Fig. 2) without loss of selectivity (Table 2). However such assessments are subject to a number of variables (e.g., solvent, reactor etc) and a more detailed investigation is warranted.
3.3. Recovery of PGMs from waste using ‘seeded’ cells

Due to the high acidity of the leachate native cells were not used to make catalyst from waste leachate, as the low pH was not physiologically compatible. Instead, recovery of PGMs from the waste leachate used ‘seeded’ cells (5 wt% Pd) as shown in Fig.3. Note that, whereas PGM recovery from model solutions was complete within five minutes (Taylor, 2012), the reaction took ~60 h to proceed to completion in a real waste (Fig. 3). The observed slow PGM reduction from the catalyst leachate by the pre-palladised E. coli cells proceeded in three distinct phases (Fig. 3). An initially rapid rate of metal removal (0-12 h) was followed by a ~ halving of the rate between 12-35 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 PGM species from solution was achieved after ~60 hours of contact.

In order to implicate the compound responsible for the inhibition of PGM reduction. Model leachates were spiked with Pd(II) as before, and were also spiked with silica (SiO$_2$ (to 173 ppm) and Al$_2$O$_3$ (to 173 ppm) final concentrations) and also a mixture of both. The addition of Pd-‘seeded’ bioinorganic catalyst and then addition of either Al or Si inhibited PGM reduction: Pd(II)/Pt(IV) disappearance from the supplemented model solution was observed only after 6 and 14 hours of contact with the bioinorganic catalyst with SiO$_2$ or Al$_2$O$_3$ respectively. Complete PGM removal was not observed from the model solution supplemented with both Si and Al even after 48 h. In contrast metal was removed from the unsupplemented control (model leachate + distilled water) within 5 mins (i.e. as seen with the model solutions). These results suggest that
the presence of Al and Si inhibit PGM recovery and are responsible for a more than 30-fold increase in reduction time observed with the spent car catalyst leachate.

These preliminary tests suggest that, since the actual composition of a waste is likely to vary according to source of the material (and any upstream processing) there is little to be gained by an in depth model study of critical inhibitory concentrations. This is because the potency of the inhibitory agent(s) may be synergistic (or moderated) by other agents present in the waste. Such studies are beyond the scope of this work but the preliminary results we describe suggest that wastes would need to be evaluated on a case by case basis for their amenability to ‘biorefining’.

Despite this, this combined biochemical and chemical approach shows potential for recovery of PGMs from leachates, albeit with longer contact periods. Although samples in this study were diluted (precluding re-use of the acid in this case) a previous study (Yong et al., 2003) showed metal recovery from 50% *aqua regia* which is suitable for Pd leaching with the application of microwave energy (Fig. 1). Hence, although acid re-use was not tested in subsequent leaching cycles, there is clear scope for a continuous metal recovery process (e.g. as described by Yong et al., 2003) with acid recycle, which is an important economic consideration for further development.

### 3.4. Catalytic activity of the PGM recovered from waste leachate

Cells pre-palladised with 5 wt% Pd(0) were used in the reduction and removal of Pd and Pt from the model solution and from the catalyst leachates prepared as described above. Both catalysts were active in Cr(VI) reduction (Fig. 4), with 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 ~ 2-fold 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 (above). Nevertheless, more than 90% of the Cr(VI) was reduced after 180 min by the biorecovered material. A similar conclusion was reached by Yong et al (2015) who showed, using immobilised neo-catalyst, that the slower rate was easily compensated by increasing the flow residence time in a continuous flow column system.

4.0. Conclusions and future scope

This study shows that via use of microwave assisted leaching Pd is recovered with high efficiency from spent car catalyst using 50% aqua regia. The biorecovered material reduced Cr(VI) at approximately half the rate as a similar biocatalyst prepared from model solution. Si and Al were shown to reduce the rate of removal of PGMs and were implicated in a reduced catalytic activity of the biorefined material, with the reaction requiring 180 min as compared to 120 min in the model system. Potential application to commercially-relevant industrial reactions is also indicated. Bio-reprocessing of waste PGMs into neo-catalysts is a key development towards realising added value from wastes. Future supplies of PGMs would be safeguarded as well as reducing the environmental burden of PGM primary processing from ores (comminution of ore is highly energy-expensive, e.g. overall, over 14 tonnes of CO₂ are generated per kilo of Pt produced (Anon 2008). On the other hand, recycling processes also carry impacts and consequences. Towards reducing these, waste E. coli bacteria left over from other processes have been used to make Pd bio-catalyst for use in hydrogenation (Zhu et al., 2016). However the true
impact of the ‘double benefit’ can only be assessed by a side by side comparison via a full life cycle analysis which is currently in progress incorporating both economic and environmental factors, which is not trivial. This considers ‘second life catalyst from waste’ against use of primary resources and also loss of catalyst in ‘once through’ systems as compared to metal recovery and re-use. With respect to the latter the use of immobilised bacteria brings the additional benefit of continuous catalyst use (Yong et al., 2015).

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References
Pd/Al$_2$O$_3$ and bio-Pd in the hydrogenation of 2-pentyne. *Chemical Engineering Science* 65: 282-290


Table 1. Leaching conditions applied to the spent automotive catalyst as used in this study

<table>
<thead>
<tr>
<th>Leaching Scheme</th>
<th>Aqua Regia Concentration</th>
<th>Liquid to Solid Ratio (ml/g)</th>
<th>Coarse(^{(a)}) or Fine(^{(b)}) material</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50%</td>
<td>5:1</td>
<td>Coarse</td>
</tr>
<tr>
<td>B</td>
<td>50%</td>
<td>10:1</td>
<td>Coarse</td>
</tr>
<tr>
<td>C</td>
<td>100%</td>
<td>5:1</td>
<td>Coarse</td>
</tr>
<tr>
<td>D</td>
<td>100%</td>
<td>10:1</td>
<td>Coarse</td>
</tr>
<tr>
<td>E</td>
<td>50%</td>
<td>5:1</td>
<td>Fine</td>
</tr>
</tbody>
</table>

Scheme A and E are similar experiments but one uses coarsely ground catalyst (with a particle size range of 1000µm ≥ d ≤ 45µm)\(^{(a)}\) and the other uses fine material (ground in a tema mill for 30 seconds so that d ≤ 38µm)\(^{(b)}\) in order to test the hypothesis that fine grinding does not increase leaching efficiency i.e. that gentle crushing to open the channels is sufficient for complete extraction of the PGM/washcoat layer.
Table 2. Comparison of selectivity between commercial catalyst and bio-catalyst in 2-pentyne hydrogenation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>commercial catalyst</th>
<th>bio-catalyst on <em>E. coli</em></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd/Al₂O₃</td>
<td>pre-palladised bio-Pd</td>
</tr>
<tr>
<td>loading (wt%)</td>
<td>2 5</td>
<td>2 5</td>
</tr>
<tr>
<td>selectivity to trans-pentene (mol%)</td>
<td>37.63 35.1</td>
<td>19.65 19.91</td>
</tr>
<tr>
<td>cis/trans-pentene ratio</td>
<td>0.71 0.68</td>
<td>2.82 2.58</td>
</tr>
</tbody>
</table>

| Average | 0.7       | 2.7       | 2.5       |

* Values of selectivity and cis/trans ratio obtained after achieving 100% 2-pentyne conversion.

* Average is obtained from the 2wt% and 5wt% samples in each case. Each datum is the mean of two experiments with a variation between them of less than 10%.
Highlights

- Bacteria recover precious metals from automotive catalyst leachate
- Metal recovery is slower the from pure solution but is eventually complete
- Neo-catalyst from waste reduces Cr(VI) comparably to purpose-made catalyst

Legends to Figures.

Figure 1. PGM recovery in leachate from spent automotive catalyst used in this study. A: concentrations of Pd and Rh recovered under various leaching conditions as shown in Table 1. B: Pd extraction (%). C: Rh extraction (%). C: coarse sample; F: fine sample. % is aqua regia concentration. Ratio is liquid to solid ratio. Error bars are ± 3.6% for Pd and ± 7.7% for Rh.

Figure 2. Activity of 2 wt% bioPd in the hydrogenation of 2-pentyne and supplemented with additional metals from the model solution. For comparison results using commercial 2 wt%Pd/Al₂O₃ (□) are also shown. The biocatalyst samples were as follows: ■, 2wt% Pd/E. coli; ▲, 16 wt%Pd/Pt/E. coli (starting material 2wt% bioPd). The conditions were 4 ml of 2-pentyne in 150 ml of isopropanol; T = 40 °C; pH₂ = 2 bar; Stirring = 1000 rpm. The data are averaged from two experiments with a reproducibility between them of within 10%.

Figure 3. PGM Recovery from leachate using 5% pre-palladised cells. Data are the average from two independent preparations with a reproducibility between them of within 10%.
Figure 4. Catalytic activity of biorecovered catalyst using 5% pre-palladised cells as shown in Fig. 2. Open circles: catalyst made from model mix (see Materials and Methods) Closed circles: catalyst made from real waste leachate (see text). Data are means ± standard error of the mean from three experiments.
Comparison of Pd and Rh Concentration in Leachates Produced under Different Leaching Conditions

% Pd Extraction from Catalyst Solids

% Rhodium Extraction from Catalyst Solids
Fig. 2

2-pentyne conversion (%)

Time (min)

- 2 wt% Pd/Al₂O₃
- 2 wt% Pd/E. coli
- 16 wt% PdPt/E. coli

2-pentyne concentration (%)

Time (min)
Fig. 3

[Graph showing the percentage of PGM reduced over time]