

# Bacteria, their precious metal armour, and a new weapon against waste

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Sulfate-reducing bacteria have exciting applications in the biorecovery of precious metals and in the bioremediation of toxic wastes.

The words 'bacteria' and 'palladium' rarely spring to mind together, but in fact they combine to produce a powerful way of dealing with toxic waste chemicals. Many types of wastes can be treated using sulfate-reducing bacteria (SRB) that as part of their normal cellular respiration process reduce sulfate to hydrogen sulfide, analogous to the way that mitochondria reduce oxygen to water. However, the SRBs are versatile bacteria, and some can use metallic ions or even chlorinated aromatic compounds in place of sulfate.

## ● Palladium

The price of palladium remains high, with the current annual demand exceeding production. The major palladium sources are Russia and South Africa, accounting for 90% of the world's platinum group metal (PGM) production. The largest current consumer of palladium worldwide is the automotive industry, where it is used with other PGMs in catalytic converters to control vehicle emission pollution. Palladium is also used in the electronic, chemical and dental industries. Due to the high demand for palladium and the increasing price, its recovery from scrap is becoming increasingly important. Techniques for recovery include pyrometallurgy, chemical treatment, electrochemical recovery and solvent extraction, but these are costly, time-consuming and not environmentally friendly. This means that a 'clean', effective, economical and simple method is needed.

**Biorecovery of palladium from waste.** Work at Birmingham University has shown that resting cells (growth-decoupled cells) of the SRB *Desulfovibrio desulfuricans* ATCC 29577 can recover palladium from solution, industrial waste and automotive catalyst waste leachates. The technique first uses biosorption of Pd(II) ions onto the biomass, followed by its reduction to minute crystals of metallic palladium [Pd(0)] using an appropriate electron donor. Thus, palladium can be recovered as a base metal 'overcoat' surrounding the biomass ['Bio-Pd(0)'] (see Fig. 1).

**'Bio-Pd(0)'** Palladium metal has many uses as an industrial catalyst. 'Bio-Pd(0)', similarly, has catalytic properties which are thought to be dependent upon the distribution and size of the nanocrystalline palladium metal deposits on the biomass surface. The cells can be loaded with palladium in different ways, varying from heavily loaded to almost bare (Fig. 2). The preparation of 'Bio-Pd(0)' using hydrogen as the electron donor can be seen in Fig. 3. The cells loaded with palladium form a black powder which is ground prior to its use as a catalyst.

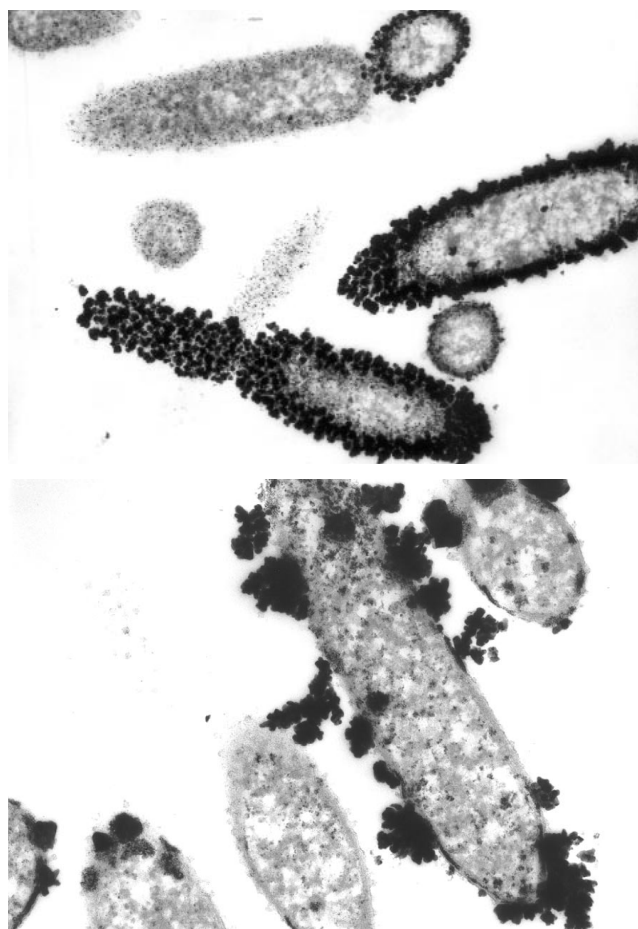
**Remediation of toxic wastes.** One possible use of the 'Bio-Pd(0)' catalyst is in the remediation of toxic waste.

Two examples have been highlighted below: chromium and polychlorinated biphenyls (PCBs).

## ● Chromium

Chromium is one of the most widely used metals in industry. In the form of Cr(VI) it is a known mutagen and carcinogen. Cr(VI) exists in solution as  $\text{CrO}_4^{2-}$  and, due to its structural similarity to  $\text{SO}_4^{2-}$ , it can overcome the cellular permeability barrier, entering via the transport pathway(s) for  $\text{SO}_4^{2-}$ . Once inside the cell it can oxidatively damage DNA via the production of the more oxidizing and reactive transient Cr(V) and Cr(IV) species that produce  $\text{RS}^-$  and  $\text{OH}^-$  simultaneously. The more inert Cr(III) cannot readily enter the cell and this reduced form, applied exocellularly, is not known to be carcinogenic and can precipitate as  $\text{Cr}(\text{OH})_3$ . Hence, the reduction of Cr(VI) to Cr(III) is an important step in the removal of Cr(VI) from solution.

Reduction of Cr(VI) using resting cells alone can be fairly slow. Furthermore, the cells have a low tolerance to Cr(VI), limiting the application to the 'polishing' of Cr(VI) wastes. Finely ground palladium metal on its own ['Chemical-Pd(0)'] cannot reduce Cr(VI). However 'Bio-



TOP RIGHT:  
Fig. 1. Palladium-coated biomass 'Bio-Pd(0)'  
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BOTTOM RIGHT:  
Fig. 2. Cells loaded with varying amounts of palladium.  
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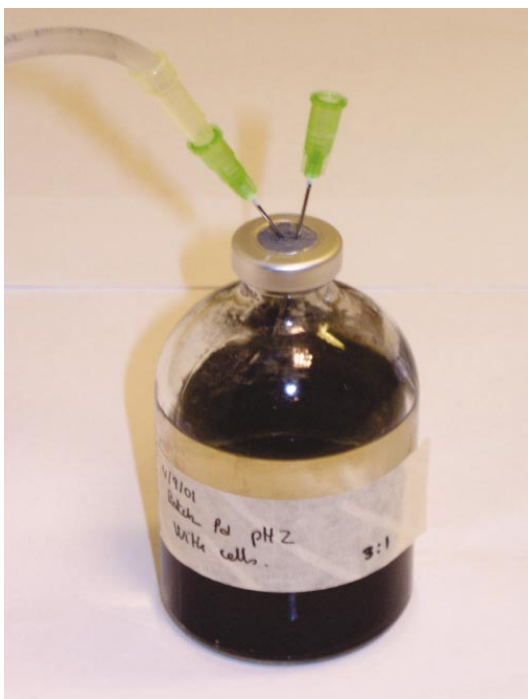
Pd(0)' can rapidly reduce high concentrations of Cr(VI). The solution changes from its characteristic yellow colour to colourless at neutral pH as Cr(VI) is removed, but without producing a precipitate. No residual chromium is left in solution either, and this indicates that the surface of the 'Bio-Pd(0)' is the 'resting place' for the Cr(III). Many industrial wastes are acidic and 'Bio-Pd(0)', held within a flow-through column, completely reduces Cr(VI) to Cr(III) at pH 3 over several weeks. The acid-soluble Cr(III) can easily be precipitated as Cr(OH)<sub>3</sub> downstream by adding a strong alkali like NaOH.

#### ● PCBs

Chlorinated aromatic compounds are another toxic waste and environmental pollutant that are difficult to treat. The polychlorinated biphenyls (PCBs) are composed of two linked benzene rings that can have multiple substitutions by chlorine (or other halogen groups) in a great variety of combinations. PCBs have been used extensively in industry due to their excellent physical and chemical properties, including low water solubility, relative inertness, flame resistance and superb dielectric properties. Approximately one-third of the total USA production of PCBs has been released into the environment via deliberate or accidental discharge. The production and release of PCBs in the USA has been banned since 1978, although contamination still occurs and the accumulation in the environment and potential toxicity to humans and wildlife is of great current concern. PCBs accumulate mainly in fish, meat and dairy produce, affecting the health of the individuals who consume these contaminated products. Skin irritations, respiratory tract symptoms, gastrointestinal effects and even possible liver cancer can result.

'Bio-Pd(0)' has been tested as a bioinorganic reductant for these wastes because of the ability of an iron surface coated in palladium to act as a chemical reductant for PCBs. The reductive dehalogenation of PCBs has proved to be possible using 'Bio-Pd(0)', as measured by the release of chloride ions. Significantly lower rates of reductive dehalogenation were obtained with the 'Chemical-Pd(0)' alone, and in the case of 2,2',4,4',6,6'-hexachlorobiphenyl, a compound which is not water-soluble, this was only attacked (from a hexane in water suspension) by the biologically derived material. The mechanism is thought to involve the Pd(0) loaded on the bacteria, which effects the homolytic fission of H<sub>2</sub> within the crystal matrix for delivery of H<sup>•</sup> to the target PCB.

Industrial Pd-based catalysts are usually supported on, for example, a carbon matrix and it is thought that the biomass acts as a template and support for the 'Bio-Pd(0)', enhancing the catalytic activity. Finally,



LEFT:  
Fig. 3. The preparation of 'Bio-Pd(0)' using hydrogen as the electron donor.  
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evaluation of the biomaterial against a commercial supported Pd-catalyst using a test reaction involving hydrogen addition across a C=C double bond showed that it performed comparably.

Thus, in addition to their potential as biorecovery agents for precious metals, SRBs can effect a one-pot conversion of waste to a valuable product, which cannot be achieved by the chemical industry alone, providing a new weapon in the armoury against waste.

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#### Further reading

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