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Short Communication

A Facile and Cost Effective Synthesis of Biomass-Supported Palladium Nanoparticles Using Sodium Hypophosphite for Catalytic Dechlorination of Chlorobenzene

Jacob B Omajali[1,2]* and Lynne E Macaskie[2]

[1]Department of Chemistry, Thompson Rivers University, Kamloops, Canada

[2]Unit of Functional Bio-nanomaterials, Institute of Microbiology and Infection, School of Biosciences, University of Birmingham, United Kingdom

***Corresponding author:** Jacob B Omajali, Department of Chemistry, Thompson Rivers University, Canada

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Abstract

Although molecular hydrogen is very useful in environmentally clean technology, its usage also comes with some associated hazards and hence the need to use hydrogen donor compounds such as sodium hypophosphite in the generation of hydrogen as electron donor. In this study, sodium hypophosphite was utilized as a source of hydrogen and as an electron donor in the biogenic reduction of palladium onto the surface of bacterial cells (aerobic and anaerobic bacteria) to produce bio-nanoparticles with potential in the dehalogenation of chlorinated pollutants like chlorobenzene. The purpose of this paper is to provide a facile and cost effective approach to the synthesis of biogenic nanoparticles using sodium hypophosphite as a hydrogen donor compound.

Introduction

Hydrogen is a source of environmentally clean and sustainable energy of the future. It has great potential in power generation e.g. in polymer electrolyte membrane (PEM) fuel cell technology [1,2]. For more details on polymer membrane (PEM) fuel cell technology and applications, the reader is referred to an extensive review by Wang Y, et al. [3]. However, molecular hydrogen has been described as a gas of low molecular weight, high diffusibility with ease of ignition resulting in hazards, especially in large scale production [4]. Despite extensive efforts there is still no hydrogen storage method with a sufficiently high H_2/weight ratio. Hence, hydrogen donor compounds are becoming increasingly viable alternatives for both storage and generation of hydrogen gas, requiring no hydrogen vessels for storage and major challenges of containment and transport are avoided. Examples of such alternative hydrogen donor compounds include $NaBH_4$, formic acid, formate and NaH_2PO_2 which are safer, environmentally greener alternatives and can be more easily handled than molecular hydrogen. The objective of this study was to investigate the use of sodium hypophosphite ($NaPO_2H_2$) as a simple and cost-effective alternative source of hydrogen for the catalytic synthesis of palladium (Pd) nano-catalysts supported on bacteria and the subsequent application in reductive dehalogenation of chlorobenzene.

Materials and Methods

Bacillus benzeovorans NCIMB 12555 and *Desulfovibrio desulfuricans* NCIMB 8307 were grown according to the method of Omajali JB, et al. [5,6]. Cells were harvested by centrifugation followed by sorption of Pd (II) (30 °C, 30min) in a given volume of Na_2PdCl_4 (pH2 adjusted with 0.01M HNO_3) to make a final 20wt % bio-Pd (0) on cells. Reduction to Pd (0) was done with a 20mM solution of sodium hypophosphite ($NaPO_2H_2$) from a 500mM stock without shaking the content. The reduction occurred immediately. Samples were washed with distilled water and prepared for various characterization techniques (TEM, XRD and XPS). The catalyst made by both *B. benzeovorans* and *D. desulfuricans* were compared in reductive dehalogenation of chlorobenzene as described by Omajali [6].

Results and Discussion

The reduction of palladium by both bacteria using sodium hypophosphite ($NaPO_2H_2$) occurred almost immediately with black deposits of Pd on and within cells. The black deposits were examined using TEM (Figure 1) on *D. desulfuricans* and *B. benzeovorans* respectively. More Pd was found localized on the periplasm and outer membrane of D. desulfuricans than inside the cells while intracellular deposition was more apparent in *B. benzeovorans*. Similar palladium nanoparticle (Pd-NP) formation was reported by Omajali JB, et al. [5] using both formate and hydrogen as electron donors. Some larger Pd-particles were visible on the outside of the cells (Figure 1) which were not seen in the previous work [5]. In this study the Pd-NPs were confirmed as palladium via XRD (X-ray powder diffraction) (Figure 1). However, the average Pd crystallite size made by *B. benzeovorans* was larger (10.7±069nm) than that made by *D. desulfuricans* (8.7 ± 0.94 nm) determined from the XRD data [6]. This difference is very clear when the XRD patterns from both cells were compared; with bio-Pd (0) of *D. desulfuricans* producing mostly broader Pd peaks (Figure 1) than that of *B. benzeovorans* (Figure 1). The peak broadening in both bio-Pd (0) may be due to interaction of phosphorus (P) from the reductant ($NaPO_2H_2$) with Pd, forming a PdP alloy on cells; using XRD a similar result was reported [7] in the synthesis of PdP/ on carbon by $NaPO_2H_2$ reduction, leading to peak broadening.

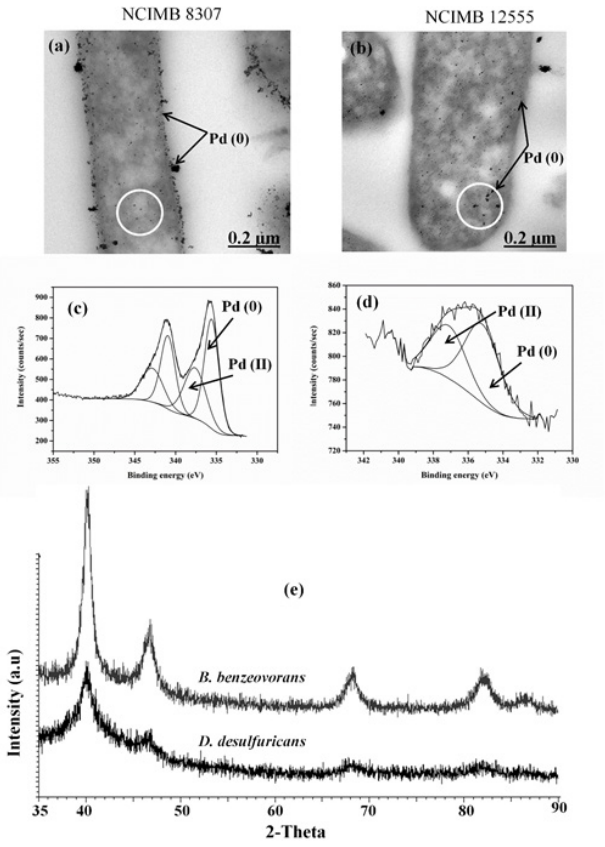

Figure 1: TEM images (a, b), XPS spectra of Pd 3d (c, d) and XRD (e) patterns of catalyst made via sodium hypophosphite mediated Pd (II) reduction on cells of *D. desulfuricans* (left) and *B. benzeovorans* (right). White circles highlight intracellular palladium nanoparticles.

X-ray photoelectron spectroscopy (XPS) provided information on the oxidation states and elemental composition of the surface of each catalyst made by both cells [8]. Both catalysts were reduced mostly to metallic palladium with corresponding binding energies at 335.6 eV and 335.2 eV for *D. desulfuricans* and *B. benzeovorans* respectively, with some residual palladium (II) occurring at binding energies of 337.6 eV and 337.1eV (Figure 1). However, differences were apparent in O1s (Figure 2) and P2p (Figure 2) surface elements. There were shifts to higher binding energies (531.9 eV and 533.2 eV) of the O1s in the catalyst made by bio-Pd of *D. desulfuricans* compared to lower binding energies (530.5 eV and 532.1 eV) seen in *B. benzeovorans*. A similar difference seen with P2p shows two key binding energies of 134.33 eV and 133.1 eV while three different peaks and binding energies at 132.5 eV, 133.81 eV and 135.1 eV were associated with *B. benzeovorans*. This difference in binding energy may be as a result of Pd interaction with phosphorus during Pd reduction with $NaPO_2H_2$. The differences in the surface elements are more prominent when the atomic concentrations were determined (Table 1). Reductive dehalogenation of chlorobenzene resulted in the removal of 82mg/L of chloride (46.2%) and 77.6mg/L (43.7%) by bio-Pd made by *D. desulfuricans* and *B. benzeovorans* after 24h (Figure 3). The rate of

removal after the first 30 min of reaction was faster (0.072mmol/min/mg Pd) for the catalyst made by *D. desulfuricans* than that made by *B. benzeovorans* (0.04mmol/min/mg Pd). This preliminary investigation has shown that sodium hypophosphite can potentially be used as an alternative electron donor to molecular hydrogen in the reduction of biogenic palladium during the synthesis of Pd bio-nanoparticles. These newly synthesized bio-nanoparticles have demonstrated the ability to dehalogenate aromatic chlorinated pollutant such as chlorobenzene.

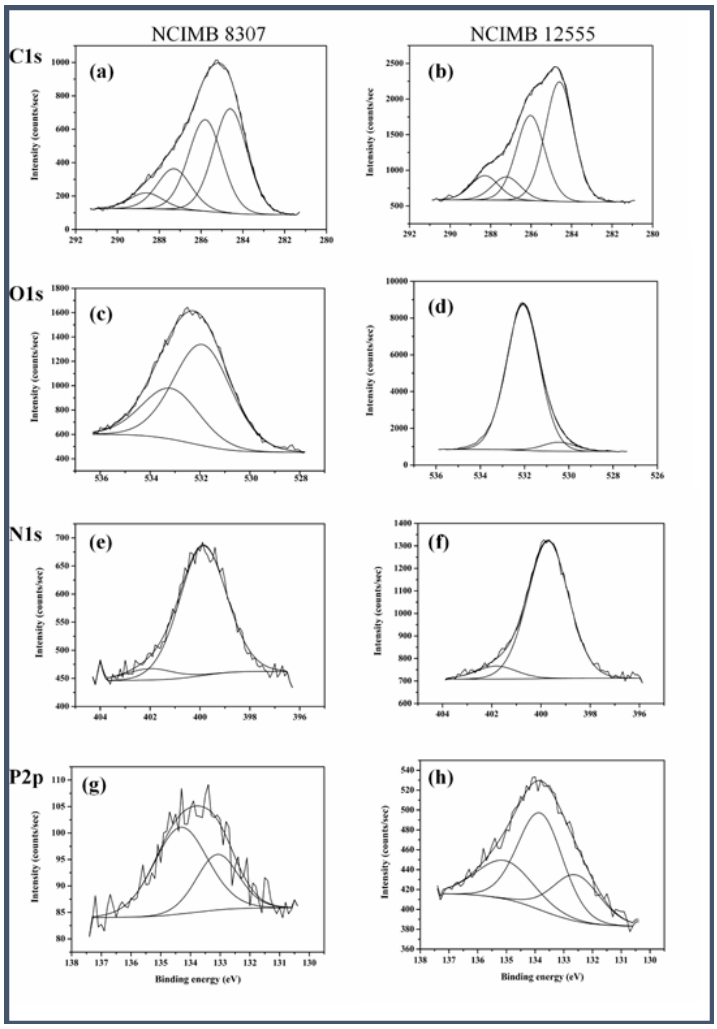

Figure 2: XPS spectra of surface composition of elements found on catalyst reduced via sodium hypophosphite by *D. desulfuricans* NCIMB 8307 (left) and *B. benzeovorans* NCIMB 12555 (right).

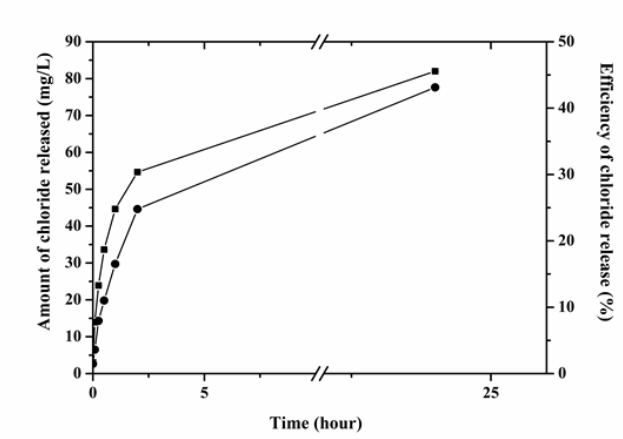

Figure 3: Efficiency and amount of chloride released by bio-Pd catalyst made by sodium hypophosphite reduction on cells of *D. desulfuricans* (■) *and B. benzeovorans* (●) after 24 h of reductive dechlorination of chlorobenzene.

Table 1: Atomic concentration of elements on catalyst surface made by bacteria after Pd (II) reduction with sodium hypophosphite analysed using XPS.

Element	Atomic Concentration (%)	
	NCIMB 8307	NCIMB 12555
C1s	62.1	48
N1s	6.7	6.1
O1s	25.9	43.3
P2p	0.95	2.43

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