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Letter to the Editor

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# Comment on "Extracellular Palladium Nanoparticle Production Using *Geobacter sulfurreducens*"

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Yates et al.[1] reported on the capacity of the dissimilatory metal-reducing bacterium (DMRB), *Geobacter sulfurreducens,* to reduce soluble Pd(II) to Pd(0) nanoparticles (NPs) with hydrogen as the electron donor. These authors claim this is the first report demonstrating the direct reduction of palladium by *Geobacter* sp. This correspondence aims to highlight and provide explanations for inconsistencies found between the report by Yates et al.[1] and our earlier publication[2] in which we demonstrated the capacity of *G. sulfurreducens* to produce Pd(0) NPs from soluble Pd(II) both with acetate and hydrogen as electron donors.

The main discrepancy between the paper by Yates et al.[1] and our study[2] is that they conclude acetate is not an effective electron donor for palladium reduction by *G. sulfurreducens*. In contrast, we have demonstrated that this strain reduces Pd(II) coupled to acetate oxidation. After comparing the experimental conditions of both studies, we noticed that Yates et al.[1] have supplied a much higher Pd(II) concentration (100 mg Pd(II)/L) than that prevailing in our experiments (25 mg Pd(II)/L).[2] Another important difference detected between the experimental conditions is the lower biomass:palladium ratio used by Yates et al.[1] as compared to our study.[2]

Unlike other DMRB, such as *Shewanella* species, which can secrete extracellular electron shuttles,[3] *G. sulfurreducens* depends on direct contact to Pd(II) (and other metals) to reduce it due to the location of cytochromes (extracellular space and outer membrane) necessary for electron transfer.[4] Thus, the mechanism of the direct (when an extracellular electron shuttle is not present) Pd(II) reduction can be described in two steps:[5,6] (1) adsorption or deposition of the metal on the cell and (2) enzymatic reduction and nucleation. Cells represent the surface area available for Pd(0) NPs deposition. Thus, by providing a higher cellular density in microbial incubations, a larger and faster reduction of Pd(II) and deposition of Pd(0) NPs is expected, a scenario which was shown to occur in our study.[2] Therefore, the lower cellular concentration, combined with a higher Pd(II) concentration applied by Yates et al.,[1] may explain the inconsistency detected between the two studies referred to here because less active sites are expected to promote Pd(II) reduction as compared to our experiments. The relatively high concentration of Pd(II) supplied by Yates et al.[1] might also have promoted inhibition of *G. sulfurreducens*, thus severely impacting its capacity to reduce this metal.

Another difference observed between the results reported by Yates et al.[1] and our findings[2] is that they did not observe abiotic reduction of Pd(II) in controls lacking cells provided with hydrogen as the electron donor after 6 h of incubation, whereas we observed complete reduction of Pd(II) within 1 h of incubation both in microbial and abiotic cultures. The reason to explain this inconsistency may be the higher concentration of hydrogen supplied in our experiments (80%, v/v)[2] as compared to those performed in the study by Yates et al. (1−2.5%, v/v).[1] Overall, the underlined differences observed in both studies should be considered when designing a microbial process to produce Pd(0) NPs with *G. sulfurreducens*.

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### Notes

The authors declare no competing financial interest.

## REFERENCES

(1) Yates, M. D.; Cusick, R. D.; Logan, B. E. Extracellular palladium production using *Geobacter sulfurreducens*. *ACS Sustainable Chem. Eng.* **2013**, *1* (9), 1165−1171.

(2) Pat-Espadas, A. M.; Razo-Flores, E.; Rangel-Mendez, J. R.; Cervantes, F. J. Reduction of palladium and production of nano-catalyst by *Geobacter sulfurreducens*. *Appl. Microbiol. Biotechnol.* **2012**, DOI: 10.1007/s00253-012-4640-9.

(3) Von Castein, H.; Ogawa, J.; Shimizu, S.; Lloyd, J. R. Secretion of flavins by *Shewanella* species and their role in extracellular electron transfer. *Appl. Environ. Microbiol.* **2008**, *74*, 615−623.

(4) Ding, Y. H.; Hixson, K. K.; Giometti, C. S.; Stanley, A.; Esteve-Nunez, A.; Khare, T.; Tollaksen, S. L.; Zhu, W.; Adkins, J. N.; Lipton, M. S.; Smith, R. D.; Mester, T.; Lovley, D. R. The proteome of dissimilatory metal-reducing microorganism *Geobacter sulfurreducens* under various growth conditions. *Biochim. Biophys. Acta* **2006**, *1764*, 1198−1206.

(5) Lloyd, J. R.; Yong, P.; Macaskie, L. E. Enzymatic recovery of elemental palladium by using sulfate-reducing bacteria. *Appl. Environ. Microbiol.* **1998**, *64*, 4607−4609.

(6) Rotaru, A. E.; Jiang, W.; Finster, K.; Skrydstrup, T.; Meyer, R. L. Non-enzymatic palladium recovery on microbial and synthetic surfaces. *Biotechnol. Bioeng.* **2012**, *109*, 1889−1897.

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