

## Response to “Comment on Extracellular Palladium Nanoparticle Production Using *Geobacter sulfurreducens*”

Matthew D. Yates, Roland D. Cusick, and Bruce E. Logan\*

Department of Civil and Environmental Engineering, 212 Sackett Building, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

ACS Sustainable Chem. Eng. 2013, 1 (9), 1165–1171. DOI: 10.1021/sc4000785

ACS Sustainable Chem. Eng. 2013, 1 (9). 10.1021/sc400309q

We thank Pat-Espadas et al.<sup>1</sup> for their comments on our publication<sup>2</sup> and especially for bringing to our attention their publication<sup>3</sup> on the effect of biomass concentration on the reduction of Pd by *Geobacter sulfurreducens* in the presence and absence of an exogenous redox mediator. We were not previously aware of their study, and therefore, we did not mention it in our paper. We find their results quite interesting and complementary to our own work on understanding nanoparticle production by *G. sulfurreducens*. While acetate and hydrogen were examined as electron donors in both studies, Pat-Espadas et al.<sup>3</sup> primarily conducted tests with high biomass concentrations and investigated the effect of a mediator, while we focused on the utility of hydrogen gas as an electron donor at low headspace concentrations over a range of Pd(II) concentrations.

Pat-Espadas et al.<sup>1</sup> suggest there are apparent discrepancies between reported findings in the two studies in two situations: (1) when acetate is used as the electron donor at a low Pd(II) concentration and (2) when hydrogen gas is the electron donor. Their conclusion is that acetate could be an effective electron donor for Pd(II) reduction based on experiments using higher biomass concentrations than we used and only at a low Pd(II) concentration. However, we do not agree that there is a discrepancy between our two studies on the effect of acetate. While we did not examine the impact of higher biomass concentrations, we did examine a wide range of Pd concentrations [10 to 200 mg/L Pd(II)] with acetate or hydrogen gas as electron donors. At a low concentration of Pd(II) and with acetate as an electron donor, we found that *G. sulfurreducens* effectively formed Pd nanoparticles<sup>2</sup> with 99% Pd(II) removal at 10 mg/L of Pd(II) and 30% removal at 50 mg/L of Pd(II) with a cell dry weight (CDW) of ~195 mg/L (based on an OD<sub>600</sub> of 1 ≈ 390 mg/L<sup>4</sup>). These results are quite similar to those of Pat-Espadas<sup>3</sup> showing 88% (800 mg/L CDW) and 62% (400 mg/L CDW) removal of a 25 mg/L solution of Pd(II). However, they did not examine higher Pd concentrations with *G. sulfurreducens* and acetate.

Pat-Espadas et al.<sup>3</sup> also indicated that they could not distinguish between abiotic and biotic hydrogen using a headspace containing 20<sup>3</sup>–25<sup>1</sup>% hydrogen. We reported similar findings, as we stated that a hydrogen concentration of 5% or greater in the headspace produced the same results with either biotic samples or abiotic controls.<sup>2</sup> However, we also examined lower levels of H<sub>2</sub> and found that the use of headspace concentrations <5% reduced abiotic Pd reduction over a range of Pd concentrations. Thus, we were able to distinguish biotic

Pd(II) reduction with hydrogen gas as an electron donor at these lower H<sub>2</sub> concentrations. We also found that high H<sub>2</sub> concentrations produced much larger Pd particles (1–10 μm) than those primarily resulting from biotic nanoparticle generation at lower H<sub>2</sub> concentrations (15–30 nm).<sup>2</sup> It is not possible to compare results on particle sizes in the two studies as their study does not report any data or provide figures on the size or location of the particles produced with hydrogen as the electron donor.

There are other notable differences between the two studies, as we studied fumarate as an alternative electron acceptor to Pd,<sup>2</sup> examined the reuse of the bacterial catalysts over multiple cycles,<sup>2</sup> and did not consider the use of redox mediators as they are not needed by *G. sulfurreducens* for metal reduction.<sup>3</sup> We also note that in their study the Pd nanoparticles that formed using acetate (no mediators) appeared to be highly associated with the cell surface (their Figure 3A), while in our study with hydrogen as the electron donor, a larger fraction of the particles were found unassociated with the cell surface. Therefore, although we were not aware of their previous report, each study stands on its own regarding the ability of *G. sulfurreducens* to reduce Pd(II) and form nanoparticles under both similar and different conditions. The findings reported in both papers will enable a better understanding of Pd nanoparticle synthesis by dissimilatory metal-reducing bacteria.

### ■ AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: blogan@psu.edu.

### ■ REFERENCES

- (1) Pat-Espadas, A. M.; Razo-Flores, E.; Rangel-Mendez, J. R.; Cervantes, F. J. Comment on “Extracellular palladium nanoparticle production using *Geobacter sulfurreducens*. ACS Sustainable Chem. Eng. 2013, DOI: 10.1021/sc400309q.
- (2) Yates, M. D.; Cusick, R. D.; Logan, B. E. Extracellular palladium nanoparticle production using *Geobacter sulfurreducens*. ACS Sustainable Chem. Eng. 2013, 1 (9), 1165–1171.
- (3) Pat-Espadas, A. M.; Razo-Flores, E.; Rangel-Mendez, J. R.; Cervantes, F. J. Reduction of palladium and production of nanocatalyst by *Geobacter sulfurreducens*. Appl. Microbiol. Biotechnol. 2012, DOI: 10.1007/s00253-012-4640-9.
- (4) Mabbett, A. N.; Sanyahumbi, D.; Yong, P.; Macaskie, L. E. Biorecovered precious metals from industrial wastes: Single-step

Received: September 18, 2013

Published: October 4, 2013

conversion of a mixed metal liquid waste to a bioinorganic catalyst with environmental application. *Environ. Sci. Technol.* **2005**, *40* (3), 1015–1021.