

# Using the Membrane Biofilm Reactor (MBfR) to Recover Platinum Group Metals (PGMs) as Nanoparticles from Wastewater

B.G. Lusk<sup>1,2</sup>, C. Zhou<sup>1,3</sup>, A. Tomaswick<sup>1</sup>, and B. Rittmann<sup>1,3</sup>

<sup>1</sup>Precient Technologies, LLC, Scottsdale, AZ, andy.tomaswick@gmail.com

<sup>2</sup>Science The Earth, Mesa, AZ, bradley.lusk@gmail.com

<sup>3</sup>Swette Center for Environmental Biotechnology, Biodesign Institute, Arizona State University, Tempe, Arizona 85287, United States, aspen.zhou@gmail.com, Rittmann@asu.edu

## ABSTRACT

Platinum group metal (PGM) miners and recycling facilities are losing ~\$2 billion (~10% of the total market value) of PGM annually in wastewater and tailing. The membrane biofilm reactor (MBfR) is a modular biotechnology which contains a microbial community that can reduce and recover PGMs and potentially precious metals including gold (Au) at mining, refining, or manufacturing sites at concentrations between 0.04 and ~500 ppm. The biofilm employed in the MBfR naturally accumulates PGMs, particularly palladium (Pd) and platinum (Pt), as nanoparticles that have high economic value due to their high specific surface area and superior catalytic capability. In addition, when recovered as nanoparticles using an MBfR, PGMs have ~6x more value than bulk PGMs. In contrast, conventional physical and chemical processes for PGM recovery are costly and introduce contamination into the environment. Thus, MBfR technology is a relatively low-cost and benign alternative to conventional PGM recovery techniques.

**Keywords:** Bioremediation, Platinum group metals, precious metal recovery, wastewater treatment, biofilm

## 1 INTRODUCTION

Platinum Group Metals (PGMs) are widely applied in industry, especially in automotive catalytic converters (~65% of its consumption) [1,2]. The global demand for Pd has increased and continues to increase, as gasoline-powered vehicles must be manufactured to meet stricter emissions standards. Efficient recovery of PGMs from their major waste streams -- mining, metal refining, waste electrical and electronic equipment (WEEE), and catalytic-converter industries -- is needed for a sustainable means to recycle them in order to meet market demand, maintain an affordable market price, and reduce their environmental impacts [3].

Conventional physical and chemical processes for PGM recovery are costly and introduce contamination into the environment [4-6]. Alternatively, microorganisms [7] can biologically recover soluble PGMs as metallic nanoparticles: e.g., Pd(II) to Pd(0) (i.e., metallic palladium). Microbial reduction of Pd(II) is advantageous

because it yields controllable nanoparticulate Pd(0) with large specific surface area and, therefore, high catalytic activity [7,8].

The Membrane Biofilm Reactor (MBfR) is a technology that enables microbial reduction of PGMs with in situ recovery of Pd(0) nanoparticles. MBfRs are modular, which means that they can be scaled to meet the recovery needs of individual sites. MBfRs also are efficient, simple to operate, and cost-effective. MBfRs make recovery of PGMs feasible and highly profitable: conservative estimates predict at least a 10-to-1 return in value for PGM nanoparticles recovered from metal contaminated waters when compared to the price of operating an MBfR.

## 2 MARKET VALUE FOR PRECIOUS METAL RECOVERY

Low-cost recovery of platinum group metals (PGMs) using MBfRs has enormous market potential, since PGMs are used in growing economic sectors and have high unit prices. According to the US Geological Survey, the largest demand for PGMs is as catalysts in automobile catalytic converters, but PGMs also are widely used in many other sectors: e.g., as catalysts for manufacturing bulk chemicals, in petroleum refining, and in laboratory equipment [9].

The current market for PGMs worldwide is ~ \$18.5 billion annually, and ~ \$5 billion comes from PGM recovered from existing sources. However, PGM miners are losing an estimated \$1.7 billion annually in PGMs that are lost in water: almost 10% of the total market value. Considering that these PGMs can be recovered as nanoparticles using an MBfR, the PGMs lost in mining waste streams have a potential market value of \$10.2 billion. This value is a consequence of PGM nanoparticles being worth about six times more than the bulk PGMs due to their unique physical properties and the high costs associated with producing nanoparticles from bulk PGMs.

Although it is possible that recovery of PGMs using the MBfR could reduce their value by adding to the market supply, the growing global demand for PGM materials in several industries has left many mining operations struggling to keep up with demand. Precient's MBfR technology enables PGM miners and refiners to recover that lost potential while mitigating environmental impacts and

without requiring additional mining infrastructure, permits, or reserves.

Conventional PGM recovery techniques produce less valuable metal aggregates unless special steps are taken to prevent aggregation of PGMs into large particles that have poor catalytic properties. Examples include stabilizers (e.g., polyvinylpyrrolidone) and carrier materials (e.g.,  $\text{Al}_2\text{O}_3$ ). These materials may have deleterious effects on the environment and human health, have low selectivity, and add to the already high operational costs [10].

### 3 THE MBfR, A BENIGN BIOTECHNOLOGY FOR PGM RECOVERY

A promising alternative to chemically synthesizing palladium nanoparticles is exploiting microorganisms' ability to reduce metals. Waste palladium is palladium (II) (i.e., Pd(II) or  $\text{Pd}^{2+}$ ), which microorganisms can reduce to the desirable palladium nanoparticle palladium (0) ( $\text{Pd}(0)$  or  $\text{Pd}^0$ ), as shown in equation 1:

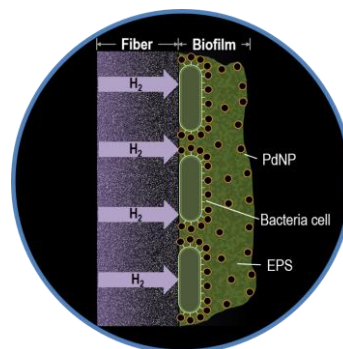


The MBfR is a system for reducing, removing, and harvesting PGMs from a fluid that contains Pd(II). The system is comprised of a set of hollow-fiber membranes, an inoculant comprising a biofilm-forming population of PGM reducing microorganisms, and a  $\text{H}_2$ -gas source. The biofilm-forming population of microorganisms contains a  $\text{H}_2$  oxidizer that reduces PGMs. The microorganisms naturally form a biofilm that is anchored to the outer surface of a hollow-fiber membrane.

$\text{H}_2$ -gas is supplied from a compressed-gas container and a gas-pressure regulator. The gas pressure regulator manages the pressure of the  $\text{H}_2$  gas in the interior of the membrane (usually between 18.0-28.0 psia), and the  $\text{H}_2$  gas diffuses through the membrane wall and into the biofilm at a rate determined by the availability of oxidized PGM in the liquid on the outside of the membranes. The microorganisms of the biofilm oxidize  $\text{H}_2$  gas as their electron donor, and they transfer the electrons to reduce the PGMs. Upon microbial reduction, the reduced PGM spontaneously precipitates as a nanoparticle that is captured and retained in the biofilm. Biofilm can be collected, and the nanoparticulate PGMs are harvested by separation from the biomass. Figure 1 shows an overview of this process.

The components of the MBfR are presented in Figure 2. During MBfR operation, wastewater containing PGM(s) (4) flow(s) into the chamber containing the biofilm grown on fibers (7) and (8), where the biofilm reduces PGMs to solid nanoparticles using  $\text{H}_2$  gas as the electron donor (2). The resulting solid PGM nanoparticles are captured by the biofilm where they are stored within the microorganisms of the biofilm and/or trapped within the matrix of extracellular polymeric substances (EPS: biomass attached to the outside of microbial cells) of the biofilm. Accordingly, the reduced

PGM contaminant may be collected by harvesting the biomass within the aqueous system, which comprises the biofilm (7) and (8). Operating parameters of the MBfR can be adjusted to accommodate specific sites by altering: the feeding rate of PGM containing wastewater into the MBfR using the feeding pump (5), the recirculation rate of PGM containing wastewater in the MBfR via the recirculation pump (9), the amount of  $\text{H}_2$  or  $\text{CO}_2$  gas delivered by volume by using different gas mixtures (2), the rate at which  $\text{H}_2$  or  $\text{CO}_2$  gas is delivered by manipulating the gas pressure regulator (3).



**Figure 1** – Overview of process occurring in MBfR at the fiber-biofilm interface.  $\text{H}_2$  gas is delivered via porous membranes to bacteria growing in a biofilm. The biofilm oxidizes  $\text{H}_2$  gas and reduces PGM, using it as the terminal electron acceptor. As a result, insoluble nanoparticulates (NPs) accumulate in the extracellular polymeric substances (EPS) of the biofilm which can be harvested.

$\text{H}_2$ -induced bio-reduction was reliable for PGM concentrations greater than 100 mg/L and with concomitant organics contamination of less than 10 mg/L as dissolved organic carbon [11-13]. The microbial community employed with the MBfR system was highly robust over an industrially relevant pH range, with an ideal operational pH range of 2-8. Pd reduction and recovery was almost 100% whether the pH was near 7 or near 4.5, and the average Pd-removal rate was 1.3 g/m<sup>2</sup> membrane/day at steady state.

Pd(II)-containing water was provided at a flow rate of 1.0-3.0 mL/min, giving surface-loading ranges from 1.4 to 14 g Pd/m<sup>2</sup>-day. For example, Pd-recovery capacities were sustained at > 95% at surface loading rates lower than 3.4 g/m<sup>2</sup>-day (hydraulic retention time (HRT) larger than 8 hours) and were sustained at 80% at a maximum surface loading of 14 g/m<sup>2</sup>-day.

Recovered metallic Pd(0) was maintained in nanoparticle sizes and retained in the biofilm. In the outside layer of the biofilm, the Pd(0) was predominantly trapped and dispersed in EPS. The nanoparticles did not agglomerate, and remained at an average size of < 10 nm. In addition, the MBfR maintained its ability to capture PGMs in the presence of concomitant oxidized nitrogen species, including nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ), which were simultaneously denitrified (> 99%) to  $\text{N}_2$  gas [13].

## 5 CONCLUSIONS

The MBfR is a robust, low-cost, and benign technology for the recovery of PGM. Instead of requiring expensive and hazardous chemicals, the MBfR takes advantage of the ability of microorganisms to reduce the polluting form of the PGMs in waste streams to highly valuable nanoparticles. The only added material is hydrogen gas ( $H_2$ ), which is non-toxic and readily produced by reforming natural gas.  $H_2$  gas is delivered by its diffusion through the wall of non-porous gas-transfer membranes, and a biofilm of  $H_2$ -oxidizing and PGM-reducing bacteria naturally grown as a biofilm on the exterior surface of the membranes. The water flowing past the membranes contains the oxidized form of the PGM, which is reduced to the elemental form by the bacteria, and the elemental PGM forms nanoparticles that are retained and stabilized by the biofilm.

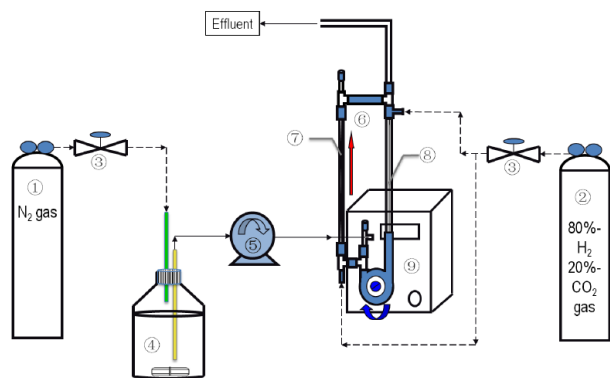
The MBfR has been developed to the commercial level for treating other kinds of wastewater. The commercial scale units are modular, allowing for several units to be assembled and operated in parallel. The same kind of modular approach is appropriate in this instance, where the primary goal is PGM recovery. This enables installation of devices in situ at diverse mining and PGM contaminated sites.

MBfR biofilms are a simple, efficient, low-cost, and sustainable means to capture PGMs as highly valuable nanoparticles [1,11,12]. In addition to PGM recovery, the MBfR technology improves the quality of wastewater by simultaneously treating other contaminants that may be present along with the PGMs, including nitrate ( $NO_3^-$ ) and nitrite ( $NO_2^-$ ) [13]. The MBfR's biofilm, being a living biocatalyst, is adaptable to the PGMs at a given site and is capable of self-selection, regeneration, and self-stabilization.

Based on known costs for treating nitrate-contaminated water with the MBfR, the cost of PGM recovery with the MBfR will be a tiny fraction of the value of the recovered PGM. Waste streams from mines and processing facilities typically contain ~ 5-10 mg/L of PGM. Precient plans to price their modular bioreactors such that a system that can recover at least 10 times its cost at typical concentration levels. In addition, the MBfR can manage higher than typical concentrations levels (> 100 mg/L) and will have increased rates of return as PGM contamination levels increase [11-13].

## 6 ACKNOWLEDGEMENTS

The authors would like to acknowledge the Biodesign Swette Center for Environmental Biotechnology for its administrative and financial support. In addition, the authors thank Brent Sebold and Charlie Lewis at Skysong Innovations and Stephanie Sims at Venture Devils for their advice and guidance.



**Figure 2** - Schematic of the bench-scale MBfR system used for Pd recovery. The major components include: ① pure  $N_2$  gas to feed the headspace of the medium bottle; ② mixed gas tank with 80%  $H_2$  and 20%  $CO_2$  gas tank to feed the fiber bundles of the MBfR; ③ gas pressure regulators; ④ Pd medium bottle with a stir bar; ⑤ feeding pump; ⑥ MBfR configuration (the red arrow indicates the flow direction); ⑦ main bundle with 50 fibers; ⑧ additional bundle with 10 coupon fibers; ⑨ recirculation pump. The black solid arrows indicate the liquid flow, and the black dashed arrows indicate the gas flow.

## 4 TOWARDS COMMERCIALIZATION OF MBfR FOR PGM RECOVERY

The MBfR has been developed to the commercial level for applications in which oxidized-contaminant removal is the sole goal, including: nitrate/nitrite [14,15], perchlorate/chlorate [16], bromate [17], chromate [18], selenate [19], arsenate [20], trichloroethylene (TCE) [21], and benzene [22]. The commercial-scale units are modular, allowing for several units to be assembled and operated in parallel, series, or both. In addition, the MBfR was approved for the purpose of drinking water treatment by the California Dept. of Public Health in 2013.

MBfRs are effective at PGM recovery from water containing a variety of dissolved PGM content, which is common at PGM mines, refineries, and recycling plants [23]. In addition, the MBfR also removes harmful contaminants that are commonly associated with PGM containing water, thus reducing the cost of down-stream processing.

The next steps for commercializing the MBfR for PGM recovery require the acquisition of metal-containing wastewater or tailings from a commercial PGM recycling plant or mining operation. After metal-containing water is acquired, custom parameters will be used to address the specific concentration of PGMs and other materials in the acquired water. In addition, MBfRs will be operated in parallel to ensure that the modular reactors can be scaled to treat all the water coming from a mine or recycling plant while maintaining the ability to recover a significant amount of the PGM.

## REFERENCES

- [1] De Corte, S.; Hennebel, T.; De Gusseme, B.; Verstraete, W.; Boon, N. Bio-palladium: from metal recovery to catalytic applications. *Microb. Biotechnol.* 2012, 5 (1), 5–17.
- [2] McGlone, M. Precious Metals, Gold, and Emerging Markets. *J. Investing* 2015, 24 (1), 124–131.
- [3] Hoque, M. E.; Philip, O. J. Biotechnological recovery of heavy metals from secondary sources: An overview. *Mater. Sci. Eng., C* 2011, 31 (2), 57–66.
- [4] Böck, R. Use and demand of palladium for the industry. In *Palladium Emissions in the Environment*; Springer: New York, 2006; pp 39–51.
- [5] Demopoulos, G. Refining of platinum-group metals. *Can. Min. Metall. Bull.* 1989, 82 (923), 165–171.
- [6] Hennebel, T.; De Gusseme, B.; Boon, N.; Verstraete, W. Biogenic metals in advanced water treatment. *Trends Biotechnol.* 2009, 27 (2), 90–98.
- [7] 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 (8), 1889–1897.
- [8] De Windt, W.; Boon, N.; Van den Bulcke, J.; Rubberecht, L.; Prata, F.; Mast, J.; Hennebel, T.; Verstraete, W. Biological control of the size and reactivity of catalytic Pd (0) produced by *Shewanella oneidensis*. *Antonie van Leeuwenhoek* 2006, 90 (4), 377–389.
- [9] U.S. Geological Survey. Mineral Commodity Summaries on PLATINUM-GROUP METALS. 2014.
- [10] Godlewska-Żyłkiewicz, B. and Malejko, J. Appraisal of Biosorption for Recovery, Separation and Determination of Platinum, Palladium and Rhodium in Environmental Samples. Springer-Verlag Berlin Heidelberg. *Platinum Metals in the Environment, Environmental Science and Engineering*, 2015.
- [11] Zhou, C.; Ontiveros-Valencia, A.; Wang, Z.; Maldonado, J.; Zhao, H.; Krajmalnik-Brown, R.; Rittmann, B. Palladium Recovery in a H<sub>2</sub>-Based Membrane Biofilm Reactor: Formation of Pd(0) Nanoparticles through Enzymatic and Autocatalytic Reductions. *Environmental Science & Technology*, 2016a, 50(5), 2546-55.
- [12] Zhou, C.; Wang, Z.; Marcus, A.K.; Rittmann, B.E. Biofilm-enhanced continuous synthesis and stabilization of palladium nanoparticles (PdNPs). *Environ. Sci.: Nano*, 2016b, 3, 1396
- [13] Zhou, C.; Wang, Z.; Ontiveros-Valencia, A.; Longd, M.; Laie, C.; Zhao, H.; Xiad, S.; Rittmann, B.E. Coupling of Pd nanoparticles and denitrifying biofilm promotes H<sub>2</sub>-based nitrate removal with greater selectivity towards N<sub>2</sub>. *Applied Catalysis B: Environmental* 206, 2017, 461–470.
- [14] Rittmann, B.E.; Lee, K.C. U.S. patent 6,387,262. Washington, DC: U.S. Patent and Trademark Office. 2002.
- [15] Rittmann, B.E.; Torres, C.; Cowman, J. U.S. Patent No. 7,491,331. Washington, DC: U.S. Patent and Trademark Office. 2009.
- [16] Rittmann, B.E.; Nerenberg, R. U.S. Patent No. 7,186,340. Washington, DC: U.S. Patent and Trademark Office. 2007.
- [17] Chung, J.; Rittmann, B.E.; Wright, W.F.; Bowman, R.H. Simultaneous bio-reduction of nitrate, perchlorate, selenate, chromate, arsenate, and dibromochloropropane using a hydrogen-based membrane biofilm reactor. *Biodegradation*. 2007, 18: 199-209.
- [18] Chung, J.; Nerenberg, R.; Torres, C.; Rittmann, B.E. Bio-reduction of soluble chromate using a hydrogen-based membrane biofilm reactor. *Water Res.* 2006a, 40: 1634-1642.
- [19] Ontiveros-Valencia, A.; Krajmalnik-Brown, R.; Rittmann, B.E. Hydrogen-fed biofilm reactors reducing selenate and sulfate: community structure and location of elemental selenium with the biofilm. *Biotechnol. Bioengr.* 2016, 113: 1736-1734.
- [20] Chung, J.; Li, X.; Rittmann, B.E. Bio-reduction of arsenate using a hydrogen-based membrane biofilm reactor. *Chemosphere*. 2006b, 40: 24-34.
- [21] Chung, J.; Krajmalnik-Brown, R.; Rittmann, B.E.; Bio-reduction of trichloroethene using a hydrogen-based Membrane biofilm reactor. *Environ. Sci. Technol.* 2008, 42(2): 477-483.
- [22] Liu, Z.; Ontiveros-Valencia, A.; Luo, Y.H.; Long, M.; Xu, H.; Li, A.; Zhou, C.; Rittmann, B.E. Continuous Benzene Removal through Aerobic Benzene Activation Followed by Denitrification-Coupled Degradation in a O<sub>2</sub>-based Membrane Biofilm Reactor. 2017, Manuscript submitted for publication.
- [23] Livingstone, S.E. *The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum: Pergamon Texts in Inorganic Chemistry*. 2017, Elsevier.