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

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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 PGM at mining, refining, or manufacturing sites at concentrations between 0.04 and ~500 ppm. The biofilm employed in the MBfR naturally accumulates PGM, including elemental palladium (Pd^0), as nanoparticles that have high economic value due to their high specific surface area and superior catalytic capability. In contrast, conventional physical and chemical processes for PGM recovery are costly, often inefficient, 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) [1,2,3]. 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 [4,5].

Conventional physical and chemical processes for PGM recovery are costly and introduce contamination into the environment [6-8]. Alternatively, microorganisms [9] can biologically recover soluble PGM 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 [9,10].

The Membrane Biofilm Reactor (MBfR) is a technology that enables microbial reduction of PGM with in situ recovery of elemental PGM 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 PGM 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 PGM using MBfRs has enormous market potential, since PGM are used in growing economic sectors and have high unit prices. According to the US Geological Survey, PGM are a critical resource for economic prosperity in the USA. The largest demand for PGM is as catalysts in automobile catalytic converters, but PGM also are widely used in many other sectors: e.g., as catalysts for manufacturing bulk chemicals, in petroleum refining, jewelry, and in laboratory equipment [3].

The market for PGM worldwide is ~$20 billion USD annually and is increasing at a 6.8% compound annual growth rate (CAGR), with the exception of 2020, which saw an ~20% decrease in demand due to the impact of Covid-19 on the automobile and jewelry markets [11,12]. Over 25% of the world's PGM demand is supplied by recovered materials from existing sources. However, PGM miners and refiners are losing an estimated ~$2 billion USD annually in PGM that are lost in water, oftentimes at concentrations greater than 100 ppm, representing almost 10% of the total market value.

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. Preicent'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 have poor capture efficiencies for PGM including Rhodium (Rh) and Ruthenium (Ru), and produce less valuable metal aggregates unless special steps are taken to prevent aggregation of PGM into large particles that have poor catalytic properties. Examples include ion exchange membranes, stabilizers (e.g., polyvinylpyrrolidone), and carrier materials (e.g., Al_2O_3). These materials may have

 TechConnect Briefs 2021, TechConnect.org, ISBN 978-0-578-99550-2

deleterious effects on the environment and human health, have low selectivity, and add to the already high operational costs [13].

3 THE MBfR, A BENIGN BIOTECHNOLOGY FOR PGM RECOVERY

A promising alternative to chemically synthesizing palladium nanoparticles is exploiting microorganisms' ability to reduce metals. Environmental benefits include the elmination of chemical additives, including resins, a significant reduction in waste and carbon footprint, and the persistance of the microbial catalyst with minimal intervention. An outstanding example is waste palladium (II) (i.e., Pd(II) or Pd^{2+}), which microorganisms can reduce to the desirable palladium nanoparticle palladium (0) (Pd^0), as shown in equation 1:

$$Pd^{2+} + H_2 = Pd^0 + 2H^+ \quad (1)$$

The MBfR is a system for reducing, removing, and harvesting PGM from a fluid that contains soluble PGM. The system is comprised of a set of hollow-fiber membranes, an inoculant comprising a biofilm-forming population of PGM reducing microorganisms, and a H_2-gas source. The biofilm-forming population of microorganisms contains a H_2 oxidizer that reduces PGMs. The microorganisms naturally form a biofilm that is anchored to the outer surface of a hollow-fiber membrane.

H_2-gas is supplied from a compressed-gas container and a gas-pressure regulator. The gas pressure regulator manages the pressure of the H_2 gas in the interior of the membrane (usually between 18.0-28.0 psia), and the 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 H_2 gas as their electron donor, and they transfer the electrons to reduce the PGM. 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 PGM 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 flows into the chamber containing the biofilm grown on fibers, where the biofilm reduces PGM to solid nanoparticles using H_2 gas as the electron donor. (CO_2 gas can also be delivered to regulate pH.) 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 may be collected by harvesting the biomass within the aqueous system, which comprises the biofilm. 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 a feeding pump, the recirculation rate of PGM containing wastewater in the MBfR via a recirculation pump, the amount of H_2 or CO_2 gas delivered by volume by using different gas mixtures, and the rate at which H_2 or CO_2 gas is delivered by manipulating the gas pressure regulator.

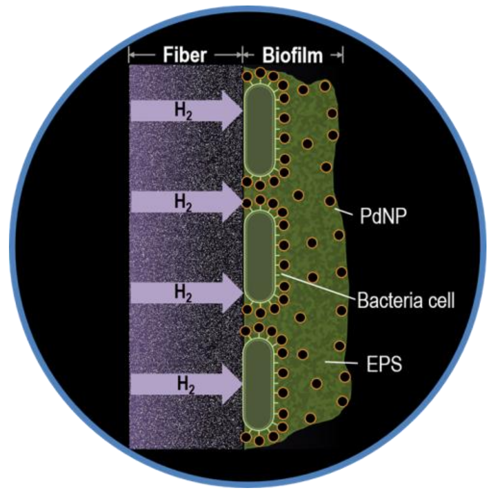

Figure 1 – Overview of process occuring in MBfR at the fiber-biofilm interface. H_2 gas is delivered via porous membranes to bacteria growing in a biofilm. The biofilm oxidizes H_2 gas and reduces PGM, in this case palladium (Pd), using it as the terminal electron acceptor. As a result, insoluble nanoparticulates (PdNP) accumulate in the extracellular polymeric substances (EPS) of the biofilm which can be harvested.

H_2-induced bio-reduction was proven reliable for PGM concentrations greater than 100 mg/L and with concomitant organics contamination of less than 10 mg/L as dissolved organic carbon [14-16]. The microbial community employed with the MBfR system was highly robust over an industrially relevant pH range, with an ideal operational pH range of 3-9. Pd reduction and recovery is almost 100% whether the pH was near 7 or near 4.5, and the average Pd-removal rate was 1.3 g/m^2 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^2-day. For example, Pd-recovery capacities were sustained at > 95% at surface loading rates lower than 3.4 g/m^2-day (or hydraulic retention time (HRT) larger than 8 hours) and were sustained at 80% at a maximum surface loading of 14 g/m^2-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 PGM in the presence of concomitant oxidized nitrogen species, including nitrate (NO_3^-) and nitrite (NO_2^-), which were simultaneously denitrified (> 99%) to N_2 gas [16].

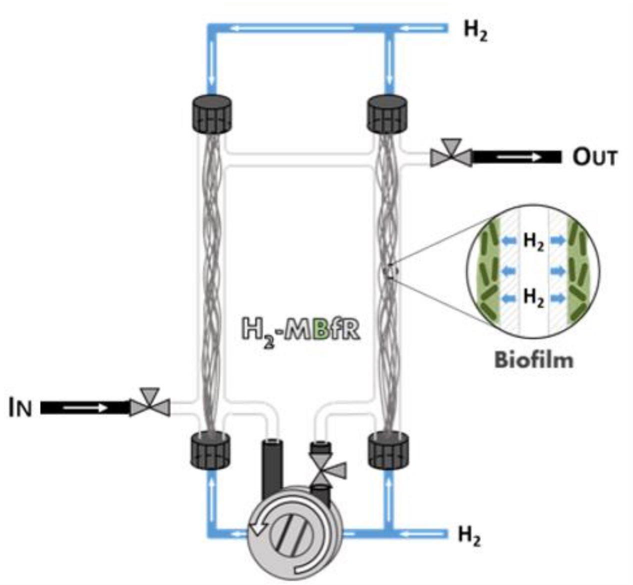

Figure 2 - Schematic of the bench-scale MBfR system used for Pd recovery.

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 [17,18], perchlorate/chlorate [19], bromate [20], chromate [21], selenate [22], arsenate [23], trichloroethylene (TCE) [24], and benzene [25]. 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 Department of Public Health in 2013.

MBfRs are effective at PGM recovery from water containing a variety of dissolved PGM that are common at PGM mines, refineries, and recycling plants [26]. In addition, the MBfR also removes harmful contaminants that are commonly associated with PGM containing water, thus reducing the cost of down-stream processing. As a consequence, the MBfR is able to recover PGM from processing water at a 20:1 annual return on investment (ROI)

Precient Technologies has received water samples from major PGM recyclers and refiners and is currently in the process of recovering PGM from their process streams. Precient is currently manufacturing pilot and fullscale MBfRs via a systems integrator. Precient has US and international patents pending for the recovery of PGM that are expected to be issued in Q1 2021 and has filed provisional patents for gold, silver, and Rare Earth Element (REE) recovery. Precient is seeking investors to finance onsite pilot MBfRs.

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 [1,14,15]. 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^-) [16]. 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 its modular bioreactors such that a system can recover at least 10 times its cost at typical concentration levels in one year. 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 [14-16].

6 ACKNOWLEDGEMENTS

The authors would like to acknowledge the Biodesign Swette Center for Environmental Biotechnology for its administrative and financial support and Skysong Innovations- Arizona State University's technology transfer office. This article contains excerpts from [27].

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