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MICROBIAL RECOVERY OF PALLADIUM AND ITS CATALYTIC ROLE IN THE BIODEGRADATION OF RECALCITRANT POLLUTANTS IN ANAEROBIC REACTORS

Francisco J. Cervantes
División de Ciencias Ambientales, Instituto Potosino de Investigación Científica y Tecnológica A. C. (IPICYT)
fjcervantes@ipicyt.edu.mx

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Palladium (Pd) is a precious metal, which is widely used for different purposes, such as automobile catalysts, electronics, industrial catalysts, circuitry, dental alloys, jewelry and lately in the treatment of cancer (Kielhorn et al., 2002; Melber et al., 2002). In recent years, demand and production of Pd has increased rapidly, although a decreasing tendency was noticed since 2000 and it was due to increased market price (Ek et al., 2004; Matthey, 1996; Palacios et al., 2000). Under this scenario the recovery of this metal from Pd containing-streams has turned into an important issue since this would translate into a solution for its increasing demand, it would help to decrease capital cost and reduce environmental impact. Different methods to recover precious metals from aqueous solutions are currently used: solvent extraction, ion exchange, evaporation, cementation and chemical precipitation. Disadvantages regarding these methods are incomplete metal removal, high reagent and/or energy requirements and limited applicability when treating diluted effluents. Biological techniques have emerged to offer a new and efficient alternative for metal recovery and many reports have focused on Pd(II) reduction to Pd(0) by using pure cultures with concomitant production of valuable Pd(0) nanoparticles (De Windt et al., 2005; Lloyd et al., 1998; Pat-Espadas et al., 2013). More recently sulfate-reducing consortia (Martins et al., 2013) have also been explored. Most of these studies have been performed in batch mode under anaerobic conditions, and until now, palladium recovery using a continuous reactor has not been reported. For this reason, the aim of this study was to evaluate, in a continuous process, the capability of a methanogenic granular sludge to reduce Pd(II) to Pd(0) in an UASB reactor and evaluate the capacity of the Pd-enriched sludge to degrade two model recalcitrant pollutants: 3-chloro-nitrobenzene and iopromide in batch and continuous operation.

Two UASB reactors were inoculated with methanogenic granular sludge and were operated at a hydraulic residence time of 8 h with ethanol as electron donor. One of the reactors was tested for its capacity to achieve the reduction of Pd(II), while the other UASB reactor remained as control not exposed to Pd(II). Complete removal of Pd(II) (3 mg/L) was achieved during two weeks of operation and characterization (by XRD analysis) of Pd NP accumulated in the granular sludge confirmed that Pd(0) was produced and immobilized during the reduction of Pd(II). High removal efficiency (>95%) of 3CNB was achieved in the UASB reactors regardless the presence or absence of Pd(0) NP. However, further studies in batch incubations revealed that Pd-enriched sludge was able to completely convert 3CNB to aniline, which implies reduction of the nitro group and dehalogenation. In contrast, the control sludge incubated in the absence of Pd(0) NP only reduce the nitro group yielding 3-chloro-aniline as the only product. The UASB reactors were also tested for their capacity to degrade iopromide, a iodinated X-ray contrast medium. Complete removal of iopromide was achieved by the Pd-enriched sludge after 150 h of incubation, whereas sludge incubations without Pd(0) NP needed 300 h to completely remove this contaminant. During continuous operation of the UASB reactors (HRT = 8 h), more than 80% removal of iopromide was accomplished in the Pd(0)-enriched consortium and only 55% removal occurred in the control UASB reactor not supplied with Pd. Further analysis conducted by HPLC-MS elucidated the biodegradation pathway of iopromide by the anaerobic consortia evaluated.

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