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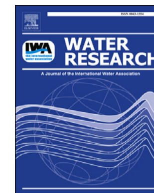

Biogenic platinum and palladium nanoparticles as new catalysts for the removal of pharmaceutical compounds

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ABSTRACT

Pharmaceutical products (PhP) are one of the most alarming emergent pollutants in the environment. Therefore, it is of extreme importance to investigate efficient PhP removal processes. Biologic synthesis of platinum nanoparticles (Bio-Pt) has been reported, but their catalytic activity was never investigated. In this work, we explored the potential of cell-supported platinum (Bio-Pt) and palladium (Bio-Pd) nanoparticles synthesized with *Desulfovibrio vulgaris* as biocatalysts for removal of four PhP: ciprofloxacin, sulfamethoxazole, ibuprofen and 17β-estradiol. The catalytic activity of the biological nanoparticles was compared with the PhP removal efficiency of *D. vulgaris* whole-cells. In contrast with Bio-Pd, Bio-Pt has a high catalytic activity in PhP removal, with 94, 85 and 70% removal of 17β-estradiol, sulfamethoxazole and ciprofloxacin, respectively. In addition, the estrogenic activity of 17β-estradiol was strongly reduced after the reaction with Bio-Pt, showing that this biocatalyst produces less toxic effluents. Bio-Pt or Bio-Pd did not act on ibuprofen, but this could be completely removed by *D. vulgaris* whole-cells, demonstrating that sulfate-reducing bacteria are among the microorganisms capable of biotransformation of ibuprofen in anaerobic environments. This study demonstrates for the first time that Bio-Pt has a high catalytic activity, and is a promising catalyst to be used in water treatment processes for the removal of antibiotics and endocrine disrupting compounds, the most problematic PhP.

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1. Introduction

The widespread occurrence of pharmaceutical products (PhP) in the environment has become a worldwide issue (Gavrilescu et al., 2015; Luo et al., 2014; Stuart et al., 2012). Globally, thousands of different active compounds are used in human and veterinary medicine and most of them are excreted in unaltered form or as active metabolites (Petrie et al., 2015). Due to their inefficient removal in wastewater treatment plants (WWTP) and improper disposal of industrial wastewaters, PhP are continuously introduced in the environment (Gavrilescu et al., 2015; Petrie et al., 2015). These pollutants are not only detected in wastewaters but also in surface waters, in sea and groundwater and even in drinking water in several countries (Gavrilescu et al., 2015; Luo et al., 2014; Stuart et al., 2012). Despite the low concentrations in which they are usually detected, their accumulation and persistence in the environment can lead to harmful effects on human and animal health and on the ecosystems (Gavrilescu et al., 2015; Luo et al., 2014; Stuart et al., 2012).

The most problematic PhP are non-steroidal anti-inflammatory drugs, estrogens and antibiotics (Fischer et al., 2012; Santos et al., 2010). Estrogens are commonly found in aquatic systems, and there is strong evidence that they affect the fertility and development of fish, reptiles and aquatic vertebrates (Boxall, 2004; Santos et al., 2010). Antibiotics are also a severe environmental problem because even at vestigial levels they can induce resistance in bacterial populations (Gavrilescu et al., 2015).

To prevent environmental contamination by PhP and their possible adverse effects, it is essential to develop new strategies to remove these pollutants from wastewaters. Advanced oxidation processes, such as UV/H_2O_2, UV/O_3, and UV/TiO_2, have been the most studied processes for PhP degradation (Homem and Santos,

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2011; Liu et al., 2009; Watkinson et al., 2007). However, these technologies require high investment and high operational costs and in some cases produce a variety of mutagenic and toxic compounds, thus aggravating the problem (Du et al., 2014; Homem and Santos, 2011; Quero-Pastor et al., 2014).

Remediation processes based on the use of metal nanoparticles as catalysts are a very promising approach for wastewater treatment (Jiang and Pinchuk, 2015; Trujillo-Reyes et al., 2014). Compared to bulk catalysts, nano-sized catalysts exhibit greatly enhanced activity due to their large surface-to-volume ratios (Jiang and Pinchuk, 2015). Moreover, the use of biologically synthetized nanomaterials is a clean, nontoxic and environmentally-friendly approach (Hulkoti and Taranath, 2014; Schrofel et al., 2014). Among metal nanoparticles, biogenic palladium nanoparticles (Bio-Pd) have emerged as efficient catalysts for the reductive removal of several environmental contaminants, namely Cr(VI), polychlorobifenyls, trichloroethylene and azo dyes (Hennebel et al., 2012, 2009; Quan et al., 2015; Schrofel et al., 2014; Suja et al., 2014). However, their application in the removal of PhP has been poorly explored. So far, only the dechlorination of diclofenac, a non-steroidal anti-inflammatory drug, using Bio-Pd and mixed Bio-Pd-Au has been reported (De Corte et al., 2012b, 2011; Gusseme et al., 2012). On the other hand, the synthesis of biogenic platinum nanoparticles (Bio-Pt) is much less studied than Bio-Pd (Capeness et al., 2015; Konishi et al., 2007; Rashamuse and Whiteley, 2007) and their catalytic potential was never investigated.

In this work we evaluated for the first time the potential of two biogenic metallic nanoparticles (Bio-Pd and Bio-Pt) as catalysts for removal of four PhP belonging to the most problematic classes: one non-steroidal anti-inflammatory drug (ibuprofen), one estrogen (17β-estradiol) and two antibiotics (sulfamethoxazole and ciprofloxacin). The Bio-metals were synthesized using the microorganism *Desulfovibrio vulgaris* and their catalytic activity was compared with the PhP removal efficiency of *D. vulgaris* whole-cells in sulfate reducing conditions.

2. Materials and methods

2.1. Chemicals

Ibuprofen and 17β-estradiol were purchased from Sigma-Aldrich, while sulfamethoxazole and ciprofloxacin were purchased from Fluka. Stock solutions (3 g L^{-1}) of ibuprofen, 17β-estradiol and sulfamethoxazole were prepared by dissolution of each compound in acetonitrile, while ciprofloxacin was dissolved in distilled water acidified with glacial acetic acid (5 mL L^{-1}). All PhP stock solutions were stored at −20 °C. Pd (II) and Pt (IV) stock solutions (1 g L^{-1}) were prepared by dissolving sodium tetrachloropalladate (II) and platinum (IV) chloride (both from Sigma-Aldrich), respectively, in distilled water acidified with HCl (pH 2.5). The chemical structure of the four pharmaceutical compounds is shown in Fig. S1 in Supplementary Information Section.

2.2. Microorganism and growth conditions

The present work was performed using *D. vulgaris* Hildenborough (DSM 644). This strain was grown in modified Postgate medium C (pH 7.2) containing 0.5 g L^{-1} KH_2PO_4, 1 g L^{-1} NH_4Cl, 2.5 g L^{-1} Na_2SO_4, 0.06 g L^{-1} $CaCl_2.2H_2O$, 0.06 g L^{-1} $MgSO_4.7H_2O$, 1 g L^{-1} yeast extract, 0.0071 g L^{-1} $FeSO_4.7H_2O$, 0.3 g L^{-1} sodium citrate tribasic dihydrate, 0.1 g L^{-1} ascorbic acid, 0.1 g L^{-1} sodium thioglycolate, 4.5 g L^{-1} sodium lactate and 0.3 g L^{-1} resazurin. Bacterial growth was carried out at 37 °C using 120 mL serum bottles with a working volume of 50 mL and N_2 as gas headspace.

2.3. Synthesis of Bio-Pt and Bio-Pd nanoparticles

The preparation of Bio-Pt and Bio-Pd was performed according to Humphries et al. (2006). *D. vulgaris* cells were collected the end of log phase, harvested by centrifugation (2500×g, 10 min), washed twice with anaerobic MOPS/NaOH buffer (pH 6.8, 20 mM) and resuspended in the same buffer. A known volume of the concentrated cell suspension was transferred using a syringe to the anaerobic bottles containing the metal solution (pH 2.5, 100 mg L^{-1} of metal). The metal solution was prepared anaerobically: a known volume of metal stock solution was added to serum bottles containing boiled and degassed water. The solution was again flushed with N_2 during 1 h and then the bottles were sealed with butyl rubber stoppers and aluminum crimp seals. After the addition of concentrated cells, the solution was flushed with N_2 during 5 min. Cells were added in order to give a final ratio of dry cells:metal of 3:1 (w/w). After 1 h of incubation at 37 °C to allow for metal biosorption, the metal-loaded cells were flushed with H_2 and left overnight at 37 °C under a headspace overpressure of H_2 (0.8 bar). After confirmation that the metal was completely precipitated (the amount of metal in solution was determined spectrophotometrically as described in Section 2.9), the cell-bound nanoparticles were recovery by centrifugation (3000×g, 10 min), washed twice with distilled water, once with acetone and left overnight to dry at room temperature. The dried solid was ground to a fine powder and used in the catalytic assays.

2.4. Transmission electron microscopy (TEM) of metal-loaded bacterial cells

After overnight incubation with H_2, the metal-loaded bacterial cells were collected, harvested by centrifugation (2500×g, 10 min), washed twice with distilled water and fixed in 2.5% (w/v) glutaraldehyde. The pellet was centrifuged (3000×*g*, 10 min), resuspended in 2% (w/v) low melting point agarose and washed with 0.1 M phosphate buffer (pH 7.4). Unstained metal-loaded cells were dehydrated through a graded ethanol series (30, 50, 75, 90 and 100%) and embedded in EPON resin. Thin sections were cut, placed onto a copper grid and viewed with a Hitachi H-7650 TEM.

2.5. Evaluation of catalytic activity of Bio-Pd and Bio-Pt in PhP removal

Batch experiments were performed during 25 h in anaerobic conditions using 15 mL serum bottles with 1 mg of the metallic cell-bound nanoparticles (25% of total mass composed by metal) and 5 mL of solution containing the pharmaceutical compound (1 mg L^{-1}). The pH of all PhP solutions was adjusted to 3.2 except for ibuprofen, which was adjusted to 5.3 since we observed its chemical degradation at low pH. The solutions were flushed with N_2 during 20 min and then with H_2 during 10 min in order to activate the biocatalysts. The assays were conducted with a serum headspace overpressure of 0.8 bar H_2. Two control assays were performed: i) PhP and bio-catalyst not activated with H_2 and ii) PhP under H_2 but without bio-catalyst. All assays were conducted in triplicate, in the dark at 25 °C with rotation of 150 rpm. The reusability of the biocatalysts in the removal of PhP was also investigated. At the end of each experiment cycle, the catalyst was recovered by centrifugation (3000×g, 10 min), washed twice with distilled water, once with acetone and dried overnight at room temperature. The washing was performed to eliminate eventual PhP and other compounds originating from the previous catalytic reaction that could be adsorbed to the catalysts. The recovered dried solid was reused in catalytic assays as previously described. Periodically, liquid samples were collected and filtered through a

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