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Catalytic dechlorination of diclofenac by biogenic palladium in a microbial electrolysis cell

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Summary

Diclofenac is one of the most commonly detected pharmaceuticals in wastewater treatment plant (WWTP) effluents and the receiving water bodies. In this study, biogenic Pd nanoparticles ('bio-Pd') were successfully applied in a microbial electrolysis cell (MEC) for the catalytic reduction of diclofenac. Hydrogen gas was produced in the cathodic compartment, and consumed as a hydrogen donor by the bio-Pd on the graphite electrodes. In this way, complete dechlorination of 1 mg diclofenac l^{-1} was achieved during batch recirculation experiments, whereas no significant removal was observed in the absence of the biocatalyst. The complete dechlorination of diclofenac was demonstrated by the concomitant production of 2-anilinophenylacetate (APA). Through the addition of –0.8 V to the circuit, continuous and complete removal of diclofenac was achieved in synthetic medium at a minimal HRT of 2 h. Continuous treatment of hospital WWTP effluent containing 1.28 μg diclofenac l^{-1} resulted in a lower removal efficiency of 57%, which can probably be attributed to the affinity of other environmental constituents for the bio-Pd catalyst. Nevertheless, reductive catalysis coupled to sustainable hydrogen production in a MEC offers potential to lower the release of micropollutants from point-sources such as hospital WWTPs.

Introduction

Diclofenac [2-(2,6-dichloranilino)phenylacetic acid] is a widely utilized non-steroidal and anti-inflammatory drug, used as an analgesic (Zhang *et al*., 2008). After human consumption, diclofenac is almost completely excreted in urine. Because of its limited sorption and its low biodegradability, the removal of diclofenac in conventional wastewater treatment plants (WWTPs) is generally limited to 30% and thus diclofenac enters the environment through WWTP discharges (Ternes *et al*., 2004; Joss *et al*., 2006). As a consequence, diclofenac is very often detected in WWTP effluents (in μg l^{-1}), the receiving surface waters and even in tap water (in ng l^{-1}) (Ternes, 1998; Heberer, 2002). Since it has been shown to interfere with the biochemical functions of fish and causes tissue damage at environmentally relevant concentrations (Mehinto *et al*., 2010), diclofenac may be considered as one of the most relevant compounds with respect to the persistence of pharmaceuticals in the environment. According to the precautionary principle, the environmental input of such persistent and long-living, mobile compounds should be limited.

Advanced oxidation processes (AOP) such as UV/H_2O_2 and O_3 have been demonstrated to effectively remove diclofenac from WWTP effluents (Ternes *et al*., 2003). However, an increase in toxic and mutagenic compounds after ozonation has been shown, probably related to the production of intermediates such as *N*-nitrosodimethylamine (NDMA), hydroxylamines or aldehydes (Guzzella *et al*., 2002; Schmidt and Brauch, 2008; Benner and Ternes, 2009). As an alternative to AOP, reductive treatment using metal catalysts is currently under investigation. Biogenic Pd nanoparticles ('bio-Pd') have been demonstrated to be potent catalysts for the dechlorination of chlorinated solvents and PCBs (Hennebel *et al*., 2009a), but the use of bio-Pd catalysis for the dechlorination of diclofenac has not been explored yet. To support the catalytic hydrodehalogenation reaction, an external hydrogen donor is required. Hydrogen gas (H_2) was shown to be the most effective reactant (Hennebel *et al*., 2009b), because Pd catalysts are able to convert H_2 to adsorbed atomic hydrogen, which is a powerful reducing agent (Mackenzie *et al*., 2006).

Because the external supply of H_2 can give rise to technical difficulties, it is still the limiting factor for continuous treatment of chlorinated pollutants by bio-Pd catalysis. Recently, microbial electrolysis cells (MECs) have been developed as a safe route for H_2 production and

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supply (Rozendal *et al.*, 2006; Huang *et al.*, 2011). This technique provides *in situ* produced H_2-gas, which can immediately be used as hydrogen donor to activate the bio-Pd. This elegant solution allows continuous dosage of hydrogen, which was one of the major challenges for the implementation of bio-Pd technology until now (Hennebel *et al.*, 2009b; 2011). In the anodic compartment of such a MEC, organic substrates are oxidized by electrochemically active bacteria that pass the electrons to the anode. These electrons are transported through an external circuit to the cathode, where they can be consumed for H_2 production (Rozendal *et al.*, 2006). To force the electrons to migrate to the cathodic compartment, a supplemental voltage needs to be supplied to the electrical circuit.

The aim of this study was to examine the applicability of bio-Pd to catalyse the dechlorination of diclofenac. In order to supply H_2 as hydrogen donor to the biocatalysts, a MEC was used and recirculation experiments were conducted at different cell voltages, aiming at complete dehalogenation of the model compound. The latter has been investigated by monitoring of the fully dechlorinated transformation product 2-anilinophenylacetate (APA). Furthermore, the use of the MEC system for the continuous removal of diclofenac was examined in both synthetic medium and hospital WWTP effluent, an important point-source of absorbable organic halogens (AOX).

Results and discussion

H_2 production by a MEC supports the bio-Pd catalysis of diclofenac

Batch recirculation experiments were conducted with the MEC to treat synthetic medium with 1 mg diclofenac l^{-1}. The graphite electrodes in the cathodic compartment were coated with 5 mg bio-Pd g^{-1} graphite. When a voltage of –0.4 V was applied to the MEC, 92 ± 10% removal was achieved after 24 h of recirculation (Fig. 1). The mean cathode potential was –570 ± 63 mV versus SHE (Table 1), and at that potential H_2 production was detected at the cathode (data not shown). No significant removal was achieved with the bio-Pd MEC in open circuit and no gas production could be observed in that case.

Our results demonstrate the importance of sufficient H_2 supply to the bio-Pd catalysts, and the necessity of applying an external potential to the MEC to facilitate H_2 production at the cathode. Rozendal and colleagues (2006) already reported on the production of H_2 at an applied voltage of –0.5 V, and they expected a decrease to –0.4 V or –0.3 V by an improvement of the MEC design. In the present study, a packed bed with graphite granules was applied as electrodes, which offers a high surface area (1.3 m^2 g^{-1}) to electrochemically active microorganisms, and increases the electricity output and conversion of acetate to hydrogen gas (Wang *et al.*, 2010). Furthermore, the presence of the Pd nanoparticles themselves in the cathode are known to facilitate hydrogen production by a MEC by lowering of the cathode overpotential (Huang *et al.*, 2011). Because of various electrochemical losses, the required voltage was higher than the theoretically –0.14 V but lower than the minimally required –1.6 V for direct electrolysis of water (Rasten *et al.*, 2003), which is the major advantage of a MEC system.

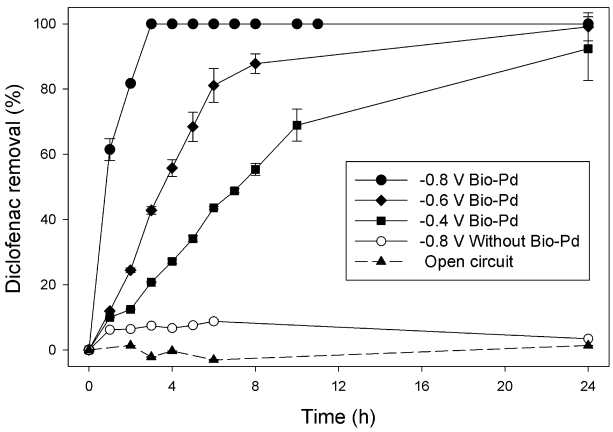

Fig. 1. Percentage of diclofenac removal from synthetic medium as a function of time, during the batch recirculation experiments using the MEC with bio-Pd coated graphite granules in the cathode. The MEC runs were performed at different applied voltages (–0.4, –0.6 and –0.8 V) and in open circuit. A control experiment at an applied voltage of –0.8 V using non-coated graphite granules in the cathode is included as well. Error bars represent the standard deviation of triplicate measurements (sometimes smaller than symbols).

The sustainable production of H_2 at the cathode supports the catalytic removal of diclofenac by bio-Pd. The use of a MEC to supply H_2 to bio-Pd has been successfully demonstrated for the dehalogenation of the chlorinated solvent trichloroethylene and the iodinated contrast medium diatrizoate as well (De Gusseme *et al.*, 2011; Hennebel *et al.*, 2011). In these reports and in this study, no removal of the model compounds was observed in the open circuit experiment. Moreover, applying higher voltages resulted in increasing removal rates: application of –0.6 V and –0.8 V resulted in a complete removal of diclofenac after 24 h and 3 h respectively (Fig. 1). This is probably related to the higher production of H_2 and thus the faster supply of the reactant to the bio-Pd catalyst. Higher H_2 production rates with higher applied voltages were previously described for other MEC configurations as well (Cheng and Logan, 2007).

Complete dechlorination of diclofenac by bio-Pd catalysis

In contrast to the high removal efficiency obtained in the MEC with bio-Pd coated graphite, the diclofenac removal

Table 1. Overview of the cell voltage, the cathodic potential and the current production during the different MEC experiments.

MEC experiment	Cell voltage (mV)	Cathodic potential (mV versus SHE)	Current production (A m^{-3} NCC)
Batch run synthetic medium at –0.4 V	–452 ± 4	–570 ± 63	308 ± 53
Batch run synthetic medium at –0.6 V	–599 ± 6	–621 ± 81	411 ± 78
Batch run synthetic medium at –0.8 V	–837 ± 10	–743 ± 42	428 ± 58
Batch run synthetic medium at –0.8 V without bio-Pd	–847 ± 45	–800 ± 25	454 ± 93
Continuous run synthetic medium at –0.8 V, HRT = 0.5 h	–787 ± 2	–773 ± 17	451 ± 22
Continuous run synthetic medium at –0.8 V, HRT = 2 h	–825 ± 39	–849 ± 23	434 ± 10
Continuous run synthetic medium at –0.8 V, HRT = 4 h	–827 ± 36	–852 ± 26	405 ± 41
Continuous run synthetic medium at –0.8 V, HRT = 8 h	–813 ± 2	–883 ± 74	481 ± 17
Continuous run hospital WWTP effluent at –0.8 V, HRT = 8 h	–808 ± 4	–923 ± 2	588 ± 34

NCC, net cathodic compartment.

was only 3.5 ± 0.2% after 24 h of recirculation in the MEC with non-coated graphite electrodes, even when an external voltage of –0.8 V was applied (Fig. 1). However, the current production was comparable with the batch recirculation experiment in the MEC with bio-Pd coated graphite (Table 1), and gas production was observed in the cathode compartment, also at –0.4 V and at –0.6 V (data not shown). This shows that the presence of the bio-Pd catalyst was necessary for diclofenac removal, and that the removal is not the result of straightforward electrochemical reduction in the MEC, as was the case for trichloroethylene (Hennebel *et al*., 2011). Apparently, dechlorination of diclofenac by direct electrochemical reduction at bare graphite electrodes is not possible at a cathode potential of –800 ± 25 mV (Table 1). The importance of the presence of Pd for diclofenac removal has been shown before under anoxic conditions. Ghauch and colleagues (2010) could significantly improve the diclofenac removal efficiency of an iron catalyst by coating the surface of the Fe(0) particles with Pd.

By means of chromatographic analyses, we were able to identify APA as the main transformation end-product and the monodechlorinated diclofenac as intermediate. However, the latter could not be quantified due to a lack of a commercially available standard. From the structural formula, it is clear that APA formation is the result of straightforward reduction of the carbon atoms, eliminating the two chloride substituents (Fig. 2). When a voltage of –0.4 V was applied to the MEC, 2.6 ± 0.1 μM diclofenac (= 0.77 ± 0.03 mg l^{-1}) was removed after 24 h, corresponding to a removal efficiency of 92 ± 12% (initially 0.85 ± 0.01 mg l^{-1} present). Concomitantly, 2.4 ± 0.1 μM APA (= 0.55 ± 0.02 mg l^{-1}) was detected, which means that the mass balance could be closed for 92% (Fig. 2). In case of an applied voltage of –0.6 or –0.8 V, all diclofenac was transformed into APA after 24 and 3 h respectively.

The occurrence of the fully dechlorinated APA was previously reported by Ghauch and colleagues (2010) as well. Using PdFe catalysts under anoxic conditions, they could detect APA during diclofenac removal, whereas no dechlorinated products were discernible under oxic conditions. Reductive catalysis thus offers the advantage of complete dechlorination and the production of a single product, while AOP may result in a wide variety of degradation products and by-products, which can increase the mutagenicity and toxicity of the wastewaters. This is in contrast with the dechlorinated end-product APA. Indeed, batch incubation tests using a nitrifying culture proved the biodegradability (Material S2), which implies that APA cannot (bio)accumulate and exert toxic or mutagenic effects. During this experiment (Fig. S1), it was observed that almost all APA was removed after 7 days of incubation, while the biomass-free and heat-inactivated controls gave no degradation at all. Conclusively, dehalogenation of micropollutants can significantly lower the AOX content of WWTP effluents, rendering transformation products that may be more biodegradable.

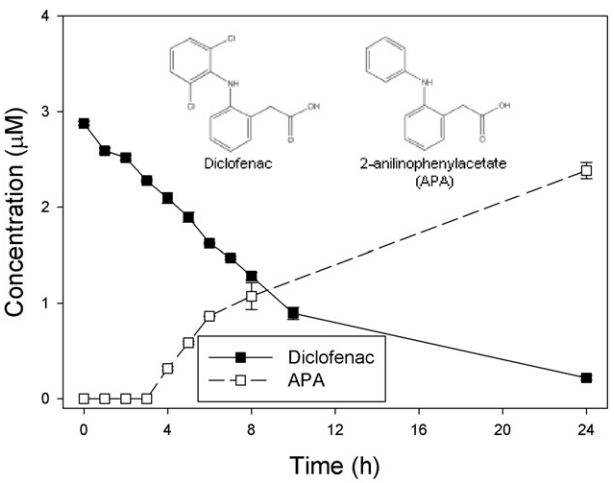

Fig. 2. Removal of diclofenac from synthetic medium and formation of APA as a function of time in the batch recirculation experiment using the MEC with bio-Pd coated graphite granules in the cathode. A voltage of –0.4 V was applied and the error bars represent the standard deviation of triplicate measurements (sometimes smaller than symbols).

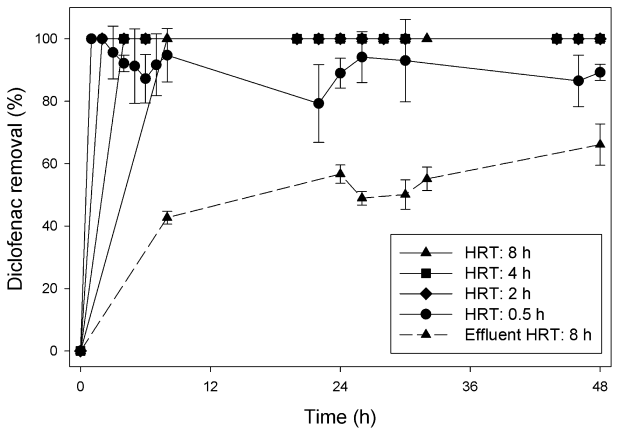

Fig. 3. Continuous MEC experiments for the treatment of synthetic medium and hospital WWTP effluent at an applied voltage of –0.8 V. Different hydraulic retention times (HRT) in the cathodic compartment were used for the treatment of the synthetic medium: 0.5, 2, 4 and 8 h, while for the hospital WWTP effluent only a HRT of 8 h was provided. Error bars represent the standard deviation of triplicate measurements (sometimes smaller than symbols).

Continuous dechlorination in synthetic medium and hospital WWTP effluent

To examine the use of the MEC system for continuous treatment of diclofenac, the synthetic medium was fed continuously to the cathode compartment at different HRT (Fig. 3). Applying a cell voltage of –0.8 V, a HRT of 0.5 h was clearly too low to allow complete removal of diclofenac. Between 3 and 48 h after start-up, an average removal efficiency of 90 ± 4% could be achieved. When a HRT of minimally 2 h or a volumetric loading rate of 3 g diclofenac m^{-3} TCC day^{-1} was provided, all diclofenac was removed. Moreover, APA was detected and at a HRT of 2 h, the mass balance with diclofenac could be closed for 96% after 48 h of operation.

At a longer HRT of 4 h, 95% of diclofenac could still be recovered as APA but other transformation products were detected by chromatographic analyses. The latter was also the case at a HRT of 8 h and APA seemed to be subjected to further reduction since the mass balance with diclofenac could be closed for only 78% after 48 h. It should be noted that no significant pH changes were observed during the 48 h test runs, which may most probably be explained by the use of an anion exchange membrane in the MEC. In contrast to a cation exchange membrane, anion exchange membranes enhance proton conduction by carrying protons by negatively charged phosphate anions through the membrane (Cheng and Logan, 2007). In this way, elevation of the pH at the cathode and subsequent limiting of the hydrogen evolution reaction was prevented.

To lower the pharmaceutical load into the environment, separate decentralized treatment at point-sources such as hospitals has been suggested (Heinzmann *et al.*, 2008), especially because of the problems with AOP described above. In order to examine the performance of the MEC for the treatment of diclofenac in such an environmental matrix, a continuous experiment was performed with a hospital WWTP effluent containing 1.28 μg diclofenac l^{-1} (Fig. 3). Applying a voltage of –0.8 V and a HRT of 8 h, an average removal of 57 ± 9% was achieved between 24 and 48 h after start-up. This removal efficiency is lower than what was achieved by treatment of a spiked synthetic medium, which is most probably related to the lower diclofenac concentrations and the influence of interfering matrix compounds and other reducible compounds such as nitrate (28.85 ± 0.02 mg NO_3^--N l^{-1} present in the hospital WWTP effluent) (Shuai *et al.*, 2010). Moreover, the effluent contained 30.50 ± 0.04 mg SO_4^{2-}-S l^{-1}, which can influence the catalyst performance as well. Indeed, reduction of the latter might have resulted in the formation of sulfide, which is known to poison Pd catalysts (Angeles-Wedler *et al.*, 2008).

Hospital WWTP effluents often contain a mixture of recalcitrant and/or halogenated organics, and in this particular effluent, also diatrizoate (292 ± 17 μg l^{-1}) and other iodocompounds were detected (total iodine concentration of 2.7 mg I l^{-1}). These iodocompounds are known to compete with chlorocompounds for the catalytic sites at the Pd surface (Mackenzie *et al.*, 2006). Whereas diatrizoate was completely removed from this particular effluent using the MEC with bio-Pd (De Gusseme *et al.*, 2011), it is our hypothesis that the simultaneous hydrodechlorination of diclofenac was (partially) inhibited by the presence of iodocompounds. Furthermore, the release of halogenide ions might cause self-poisoning of the Pd catalyst and hamper its long-term performance.

Before the bio-Pd based MEC system can be applied for separate treatment of hospital effluents, future research dealing with mixtures of halogenated micropollutants is necessary to examine the lifetime of the catalyst, and to further investigate how the different affinity of these compounds for the catalyst influences their removal rates. In addition, higher removal efficiencies in the environmental matrix need to be achieved, for example by application of other catalysts to improve the hydrogen production (e.g. a Ni foam cathode) or by bimetallic catalysts, such as Pd plated on a zerovalent Fe support (Ghauch *et al.*, 2010; Jeremiasse *et al.*, 2010).

Experimental procedures

Tested media and diclofenac stock solution

A synthetic electrolyte medium was prepared for the MEC experiments containing 6 g $Na_2HPO_4.2H_2O$ l^{-1}, 3 g KH_2PO_4 l^{-1}, 0.1 g $(NH_4)_2HPO_4$ l^{-1}, 0.1 g $Ca_3(PO_4)_2$ l^{-1} and 0.5 ml l^{-1} of a trace metal solution previously described by

Rabaey and colleagues (2005). For the treatment of diclofenac in this medium, 1 mg l^{-1} was supplemented to the synthetic medium using a 5 g l^{-1} stock solution (Sigma-Aldrich, Germany) in deionized water. The pH and the conductivity of the effluent were 7.1 and 28.43 ± 0.08 mS cm^{-1} respectively.

To examine the diclofenac removal in an environmental matrix, the effluent of a hospital WWTP was sampled in dry weather conditions on 8 December 2010. The WWTP exclusively treats hospital wastewater by means of a conventional activated sludge system and the final effluent is discharged into a nearby surface water. The effluent sample contained 1.28 ± 0.04 μg diclofenac l^{-1} (and 292 ± 17 μg diatrizoate l^{-1} and a total iodine concentration of 2.7 mg I l^{-1}). The pH and the conductivity of the effluent were 7.2 and 2.30 ± 0.02 mS cm^{-1} respectively.

Microbial electrolysis cell

The MEC was constructed with two Plexiglass frames (12.5 × 8 × 1.5 cm per frame), which resulted in a total anodic and cathodic compartment (TCC) of 0.150 l. Both compartments were packed with 160 g of graphite granules (type 00514, ϕ: 1.5–5 mm, Mersen, France), and in each of them, a graphite rod current collector (ϕ: 5 mm, Morgan, Belgium) was provided to connect them with the external electrical circuitry. Between the anodic and cathodic frames, a cation exchange membrane was installed (Ultrex CMI7000, Membranes International, NJ, USA) during the batch recirculation experiments. A power source was used to supply an external voltage between anode and cathode. The voltage difference between both compartments, the voltage drop over a 1 Ω resistor in circuitry and the cathode potential were registered by a 34970A Data Acquisition Switch unit (Agilent, Belgium). The cathode potential was measured by monitoring the voltage difference between the cathode and an Ag/AgCl reference electrode (+0.197 V versus SHE).

Batch recirculation experiments

The synthetic medium was sparged with N_2, brought into 2 l vessels, and separately recirculated through the anodic and cathodic compartment at 17 ml min^{-1} or 6.67 l l^{-1} TCC h^{-1}. Sodium acetate (2 g l^{-1}) was added to the anode medium as feed, and the cathodic medium was spiked with 1 mg diclofenac l^{-1}. A batch recirculation experiment with non-coated graphite granules was performed during 24 h at an applied voltage of –0.8 V. Subsequently, the graphite granules in the cathode were replaced by graphite granules, coated with bio-Pd (5 mg Pd g^{-1} graphite) as previously described (Hennebel *et al.*, 2011). Batch MEC runs were performed in open circuit, and in closed circuit at various applied voltages: –0.4, –0.6 and –0.8 V. Before every test run, the MEC was conditioned overnight to the applied voltage. After each experiment, the anode and cathode medium were replenished. Samples for analysis of H_2, diclofenac and its transformation product APA were taken at regular intervals.

Continuous experiments

For the continuous experiments, the cation exchange membrane between the anodic and cathodic compartments was replaced by an anion exchange membrane (AMI-7001, Membranes International). Synthetic medium with 1 mg diclofenac l^{-1} was continuously pumped through the cathodic compartment with a net volume of 0.070 l. During operation, the active volume was measured to be 0.035 l due to gas accumulation. Different continuous experiments were performed during 48 h, with a HRT of 0.5, 2, 4 and 8 h in the cathodic compartment respectively. In the anodic compartment, synthetic medium with 2 g l^{-1} sodium acetate was recirculated. The voltage supplied to the MEC was –0.8 V. In addition, a hospital WWTP effluent was continuously pumped through the cathodic compartment with a HRT of 8 h. Samples were regularly taken for analysis of diclofenac and APA.

Chromatographic analyses

For chromatographic analysis of diclofenac and the complete dechlorinated compound APA in synthetic medium, 2 ml samples were filtered over 0.22 μm filters (Millipore, MA, USA) in a glass HPLC vial and stored at 4°C in the dark prior to analysis. Both compounds were analysed on a Dionex (CA, USA) HPLC system with a P580 pump, TCC-100 column oven, UV-DAD detector (UVD340S) and Chromeleon 6.8 software. Separation was performed on a Genesis C_{18} column (150 × 4.6 mm, 4 μm, Alltech, Belgium) with a guard column. The elution programme was isocratic at a flow rate of 1 ml min^{-1}, using 80% methanol and 20% deionized water + 0.1% formic acid. The injection volume was 50 μl, the column temperature was fixed at 40°C, and the detection wavelengths for diclofenac and APA were 203 and 275 nm respectively. The limit of detection (LOD) was determined at 100 μg l^{-1} for both compounds, based on the criterion that the signal to noise ratio (S/N) had to be at least 3.

For the detection of diclofenac and APA at lower concentrations, ultra-high performance liquid chromatography coupled to tandem mass spectrometry (U-HPLC-MS/MS) was used. Chromatography was carried out on a Thermo Scientific (CA, USA) Accela U-HPLC system comprising of a quaternary pump and autosampler, equipped with a Nucleodur C_{18} Pyramid column (100 × 2 mm, 1.8 μm, Macherey-Nagel, PA, USA). The details of the elution program and the specific MS parameters are given in the Supporting Information (Material S1.1 and Table S1). The limit of quantification (LOQ) was determined at 10 μg l^{-1} as the lowest point of the calibration curve.

The samples of hospital WWTP effluent were filtered and stored as described above. For the detection of diclofenac in this matrix, U-HPLC-MS/MS was performed as described above. However, other SRM transitions and other specific MS parameters were used, which are given in the Supporting Information (Material S1.2 and Table S2). The LOQ was determined at 50 ng l^{-1} as the lowest point of the calibration curve.

Chemical analyses

The presence of H_2 in the gas phase of the cathodic compartment was qualitatively analysed by a Compact GC with a thermal conductivity detector (Global Analyser Solutions, The Netherlands), equipped with a PoraBOND Q pre-column and a Molsieve 5A column (Varian). Because the cathodic

medium was extensively sparged with N_2 prior to the experiments, N_2 release from the medium significantly diluted the gas samples. Conductivity was measured using a Consort C833 multi-channel analyser with EC-electrode (Consort, Belgium).

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Supporting information

Additional Supporting Information may be found in the online version of this article:

Fig. S1. APA removal as a function of time during 7 days incubation of ABIL biomass (0.75 g VSS l^{-1}) in minimal medium supplemented with 1 mg APA l^{-1}. To examine sorption of APA to the biomass, heat-inactivated biomass was incubated in a control experiment (0.75 g VSS l^{-1}). Results from a biomass-free control in the minimal medium are also shown.
Table S1. Collected SRM transitions and compound specific MS parameters.
Table S2. Collected SRM transitions and compound specific MS parameters for the detection in the samples of the hospital WWTP effluent.
Material S1. Details of U-HPLC-MS/MS analyses.
Material S2. Biodegradability of APA.

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