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Development of an innovative approach for low-impact wastewater treatment: A microfluidic flow-through electrochemical reactor

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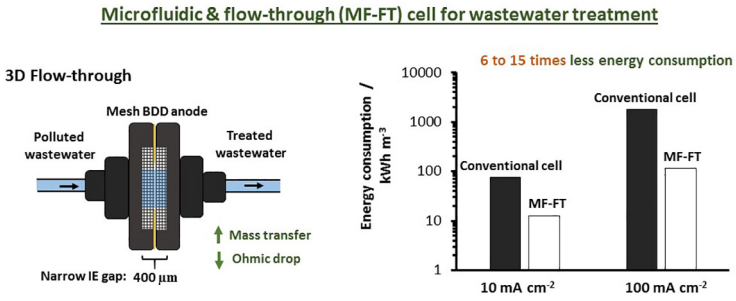
HIGHLIGHTS

- New concept of electrochemical cell combining low inter-electrode gap and flow-through electrodes.
- Low ohmic losses and high mass transfer in a flow-through electrochemical reactor.
- From 4 to 10 times reduction in applied electric charge for total mineralization.
- From 6 to 15 times cut in energy consumption for the same mineralization.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a novel approach for the development of fast and low-consuming electrochemical reactors for wastewater treatment is studied. It consists in the use of a microfluid flow-through cell with a very narrow inter-electrode gap (to minimize ohmic drops) and flow-through electrodes (to maximize mass transport towards the electrodes). The ohmic drop was studied for different inter-electrode gap and electrolyte conductivities. A low ohmic drop of 6 Ω was measured using an inter-electrode gap of 400 μm in a liquid electrolyte with 0.7 mS cm^{-1} of conductivity. The mass transfer coefficient (k_m) was evaluated at different inlet flow velocities, obtaining $1.45 \cdot 10^{-5}$ m s^{-1} at a velocity of $1.0 \cdot 10^{-2}$ m s^{-1}, considerably superior to the data reported for flow-by cells. Finally, the efficiency for wastewater treatment via anodic electro-oxidation with diamond anodes was evaluated. In this work, 100 ppm of clopyralid contained in a synthetic soil washing effluent were completely removed in this system using 2.71–8.54 Ah dm^{-3} and 12.5–115.0 kWh m^{-3} at 10 and 100 mA cm^{-2}, respectively. Comparison with a commercial flow-by (Diacell® 101) shows that the novel approach requires between 4 and 10 times less electric charge and from 6 to 15 times less energy consumption. The microfluidic flow-through configuration stand as a promising approach to reduce the environmental impact of electrochemical wastewater technologies.

1. Introduction

One of the reasons that impede the widespread application of electrochemical technologies for wastewater treatment is the high energy consumption (EC) when it comes to treat low-conductive affluents [1,2]. EC is directly proportional to the cell voltage (E_{cell}) which can be, in turn, subdivided into different contributing terms: reversible cell voltage ($E_e^c - E_e^a$), cathodic/anodic overpotential ($|\eta_c|$, $|\eta_a|$) and the sum of the different ohmic resistors of the electrical circuit ($\sum^I \cdot R$) [3–5].

The E_{cell} depends on the reaction taking place in the reactor while

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the over-potentials are mainly a function of the electrode materials and the current density. Hence, all the aforementioned parameters are largely independent from the electrode layout. Conversely, the term $\sum I{\cdot}R$ strongly depends on cell design. Ohmic drops represent an inefficiency and a loss of energy, being always detrimental for the performance of the cell. Therefore, they must be minimized to reduce EC [3,5].

Among the different ohmic resistors, the contribution of aqueous electrolytes is normally critical due to their low conductivity [3,5]. Electrolyte concentration can be strongly increased to minimize the ohmic drop in the inter-electrodic (IE) gap, such as in chloro-alkali industry or in water electrolyzers [6,7]. However, the addition of extra supporting electrolyte in the case of wastewater treatment leads to a secondary pollution since the inorganic compounds will persist in the effluent after the treatment [2,8,9]. Furthermore, it also increases the operating costs and compromises the viability of the electrochemical processes on an industrial scale.

A different approach to keep the IR drop using aqueous electrolytes low consists in reducing the distance between the electrodes (IE gap), such as in micro-fluidic (MF) reactors [8,10,11]. Those devices deal with fluids constrained in environments with internal dimensions in the order of micro-meters [12,13]. The main feature of MF electrochemical reactors is the small IE gap (normally < 1000 μm) [14,15]. In this context, Scialdone et al. reported the use of microfluidic flow-by (electrolyte passing between the parallel-plate electrodes) reactors for wastewater treatment by means of electroFenton and anodic oxidation with boron-doped diamond (AO-BDD) technologies, obtaining high abatements of organic pollutants and moderate E_{cell} even in the absence of supporting electrolyte [8,16–20].

Nevertheless, the reduction of the IE gap increases the pressure drop of the fluid passing by the reactor due to the higher surface area-to-volume ratio which implies a higher relative friction. This undesired characteristic of microfluidic flow-by reactors limit the flow rates and, thus, the treatment capacity of those devices, which are normally operated at mL min^{-1} in single-pass mode [17,19,21]. These reactors also suffers from partial clogging of the channel when gas-evolving electrodes are used and high current densities are applied, as previously reported by Bouzek et al. [22,23].

Another important aspect in the design of electro-chemical reactors is the evaluation of mass-transport conditions, since electro-chemical reactions are of a heterogeneous nature and the reactants have to be transported towards the electrode and the products transported away from it [3,24]. In the particular case of reactors for wastewater treatment, mass-transport is usually considered a bottleneck and its improvement is highly desirable to improve the efficiency and attractiveness of such technologies on an industrial scale [1,25,26]. Recently, different authors have proposed the use of three-dimensional (3D) electrodes (including meshes, foams or packed) in different flow-through reactor concepts to increase mass transport rate, achieving interesting results [27–35].

In a previous work [36], a novel microfluidic flow-through (MF-FT) cell was introduced. The objective of this geometry is not only the simultaneous minimization of ohmic drop and maximization of mass transfer but also avoid the operational problems of conventional MF reactors for wastewater treatment derived from the accumulation of gases within the IE gap. In a microfluidic flow-by geometry, the crossing area for the fluid is narrowed when the IE gap is reduced but, interestingly, this is not the case of the MF-FT configuration [36]. In this manner, the MF-FT proposed allows the electrodes to be placed as close as required while keeping constant the crossing area of the fluid and, thus, high circulation velocities can be used to strip the gases out of the IE gap.

In this work, the objective is to gain insight in the characteristics of the MF-FT cell. To do this, the ohmic resistance of the MF-FT is systematically evaluated at different IE gap and electrolyte concentrations. The performance is compared with a conventional stirred tank (ST) parallel-plate reactor. On the other hand, mass-transfer is evaluated at different inlet flow velocities and electrode layouts and is compared to previous studies in bibliography. Finally, the performance of the MF-FT reactor as an AO-BDD reactor to abate a model organochlorinated pollutant, clopyralid, is compared both to a state-of-the-art commercial FB reactor and to other previous studies to assess the potentiality of the system.

2. Materials and methods

2.1. Reagents

Sodium sulphate (Na_2SO_4), sodium carbonate (Na_2CO_3), Potassium Hexacyanoferrate (II) 3-hydrate ($K_4Fe(CN)_6{\cdot}3H_2O$) and Potassium Hexacyanoferrate (III) ($K_3[Fe(CN)_6]$) were provided by Panreac (Barcelona, Spain). The simulated soil washing effluent was prepared by dissolving 0.1 g of clopyralid, 0.67 g of $MgSO_4{\cdot}7H_2O$, 0.13 g of NaCl, 0.13 g of $NaNO_3$, 0.025 g of KI and 0.25 g of $CaCO_3$ per liter of Milli-Q water, according to bibliography [37] The rest of solutions were also prepared in Milli-Q water.

2.2. Experimental setup

A schematic representation of the experimental setup is shown in Fig. 1.

The core of the system is the electrochemical cell. It consists in a filter-press cell with electrodes separated by plastic spacers of different thicknesses. The geometric area of the electrodes (which corresponds to the diameter of the inlet/outlet pipe) is 33 cm^2. The wastewater is fed perpendicularly to the electrodes, flows through them and leaves the system at the opposite end, as can be found in Fig. 1b. More details about the MF-FT reactor and the experimental setup can be found elsewhere [36]. Details about the experimental setup and the commercial electrochemical cell (Diacell® 101) used to compare the performance of the MF-FT in Section 3.3 are available in this Ref. [9]. The ST reactor consisted in a thermostated glass beaker in which the electrodes, arranged in a parallel-plate configuration, were inserted into the electrolyte, being the latter mixed by means of a magnetic stirrer.

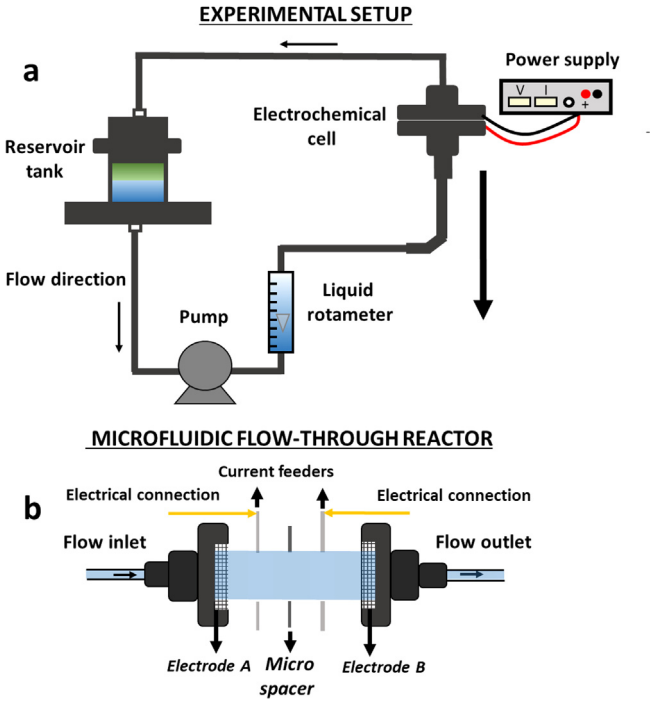

Fig. 1. Schematic representation of the experimental setup (a) and the MF-FT cell (b).