A microfluidic flow-through electrochemical reactor for wastewater treatment: A proof-of-concept

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A B S T R A C T

In this work, a microfluidic flow-through electrochemical reactor for wastewater treatment is presented which simultaneously minimizes ohmic drop and mass transfer limitations, two of the most important bottlenecks in electrochemical wastewater treatment. A proof-of-concept comparison versus a state-of-the-art flow-by commercial reactor revealed that the proposed reactor greatly outperforms the commercial system. The novel system requires only 2.4 Ah dm^{-3} (vs. 11.4 Ah dm^{-3}) and 12.5 kWh m^{-3} (vs. 75.0 kWh m^{-3}) to completely mineralize 100 mg dm^{-3} of clopyralid spiked in a low-conductive (1 mS cm^{-1}) matrix with both systems using diamond anodes. The microfluidic flow-through configuration represents a promising approach to the development of cost-effective electrochemical technologies for wastewater treatment.

1. Introduction

Over recent decades, electrochemical advanced oxidation processes (EAOPs) have demonstrated great potential for the treatment of wastewater polluted with refractory organic compounds in laboratory studies [1,2]. However, they have not yet been implemented on a large scale and there is an urgent need to develop of EAOPs able to compete with current commercial technologies [3]. Two of the most important problems in scaling up EAOPs are energy consumption and mass transfer limitations [3].

Energy consumption is directly proportional to the cell voltage. Of the three terms contributing to the cell voltage (thermodynamic potential, overpotential and ohmic resistance) the last always represents a loss of efficiency and should therefore be minimized. Most of the electrical resistance (R_{ohm}) occurs in the electrolyte (i.e. the wastewater) since its conductivity is several orders of magnitude lower than that of the other components of the system [4]. The conductivity of the wastewater can be increased by the addition of salts (i.e. a background electrolyte), a common practice in laboratory studies [3,5]. However, this implies an increase in the operating costs and, more importantly, secondary pollution of the effluent with inorganic compounds [6], which may be more persistent although less hazardous than the original organic waste.

An interesting alternative is the reduction of the inter-electrode (IE) gap to the order of micro-meters, as in microfluidic (MF) reactors [7]. Scialdone et al. have reported the use of different EAOPs (anodic oxidation-BDD and electro-Fenton) in flow-by MF reactors, achieving interesting results even in the absence of supporting electrolyte [8–13]. As an example, the complete removal of 5 mM of chloroacetic acid at 5 mA cm^{-2} has been reported using a microfluidic reactor with BDD as the anode and compact graphite as the cathode, in a medium without supporting electrolyte containing 0.5 mM FeSO$_4$ at pH 3 [10]. However, we believe that this reactor design may suffer from important pressure drops due to the extremely narrow IE gap, although to the best of our knowledge this has not yet been systematically studied. Another important issue is the partial clogging of the channel when gas-evolving electrodes are used [14,15]. These drawbacks compromise the treatment capacity of MF reactors and limit their usefulness for large-scale applications.

Mass transport is a key aspect in electrochemical reactor design given that the charge transfer between the electrode and the species present in solution is, by definition, a heterogeneous process [16]. Thus the rate of EAOPs is often determined by the rate at which the electroactive species arrives at the electrode. An interesting alternative is the pre-concentration of the pollutant e.g. in a coupled electrodialysis/electro-oxidation reactor for soluble pollutants [17] or electrocoagulation/electro-oxidation reactor for colloids [18]. For a given concentration of pollutant, mass transfer can also be improved by increasing the mass transport coefficient (k_m) and electrode area (A).

It is known that k_m is strongly dependent on the fluid dynamics within the system. In particular, the special hydrodynamic conditions established in flow-through (FT) electrodes create favourable mass

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transport conditions and the resulting k_m may be around 5 to 6 times greater than for a flow-by parallel plate reactor at similar linear empty tube velocities [16]. In recent years, a number of authors have exploited the superior performance of this configuration for the design of efficient electrochemical reactors [19–21]. In a comparison of a flow-by vs. flow-through EF reactors for the degradation of methylene blue, Ma et al. obtained a considerably higher TOC removal efficiency (57.9% vs. 39.1%) in the flow-through system [19]. In addition, the 3D electrodes (porous, bed or mesh) required for the construction of FT reactors offer a considerable increase in specific surface area in comparison with plate electrodes [22].

With this background in mind, a design to combine the low ohmic resistance of MF reactors with the high mass transfer of FT systems is proposed in this work. The performance of the MF-FT reactor is compared with a commercial Diacell® 101 (WaterDiam, Switzerland) flow-by reactor for the treatment of a low-conductive soil-washing effluent polluted with clopyralid as the model refractory organic pollutant.

2. Materials and methods

2.1. Experimental set-up

Fig. 1 represents schematically the set-up used during this work. The tank, equipped with a cooling jacket to control the temperature, feeds a Heidolph KrP25/4 centrifugal pump which circulates the electrolyte through the electrochemical cell.

The electrochemical cell is a home-made filter press fabricated in optically-transparent and chemically-resistant polycarbonate plates. The inter-electrode spacer was a plastic film (300 μm) and current collectors were fabricated using aluminium thin foils (50 μm each), producing 400 μm of IE gap. The cross section of the fluid is 33 cm^2. The anode used in the degradation of clopyralid is a 3D-mesh Diachem® diamond electrode supported on niobium supplied by Condias GmbH (Germany) together with a home-made perforated-plate stainless steel cathode.

As mentioned in the introduction, the reduction of the IE gap is an interesting approach to reducing the IR drop. In the case of flow-by reactor geometries, the reduction of the IE gap also implies a reduction in the channel size, an increase in frictional forces and, concomitantly, a higher pressure drop. However, it is important to note that in the case of the FT configuration a reduction of the IE gap does not affect the cross section. In other words, if the electrolyte is fed perpendicularly, the electrodes can be placed as close as required while keeping the cross-sectional area of the fluid and, thus, the pressure drop, constant (see Fig. 1c). This design therefore allows the use of high flow rates and multi-pass configurations, in contrast with flow-by MF reactors (which are normally operated at mL min^{-1} in single pass [10,12,23]). The fast circulation of the fluid through the IE gap also promotes the stripping of evolved gases in such a way that it is no longer an operational problem. A detailed schematic picture of the reactor can be found in Fig. 1b.

2.2. Electroanalytical measurements

The electro-analytical techniques were carried out by means of a Potentiostat-Galvanostat Autolab 302N controlled with NOVA 2.1 software. The electrical resistance (R_{ohm}) was calculated by means of electrochemical impedance spectroscopy (EIS) using a sinusoidal perturbation with an amplitude of 0.01 V$_{RMS}$ – between $1 \cdot 10^5$ and 0.01 Hz and 0.5 g dm^{-3} Na$_2$SO$_4$ as electrolyte. The value of k_m was evaluated by means of the limiting-current technique using hexacyanoferrate (II)/(III) as redox pair according to a procedure described previously [24]. The external area of the mesh electrode was calculated using a Rexcon DS$_3$ silver 3D scanner equipped with EZScan 8 and the Geomagic Wrap 2015 software.

2.3. Electrooxidation test

Electrolysis was carried out at 10 mA cm^{-2} in a soil-washing effluent (SWE) prepared according to the literature [5, 25]. It contains

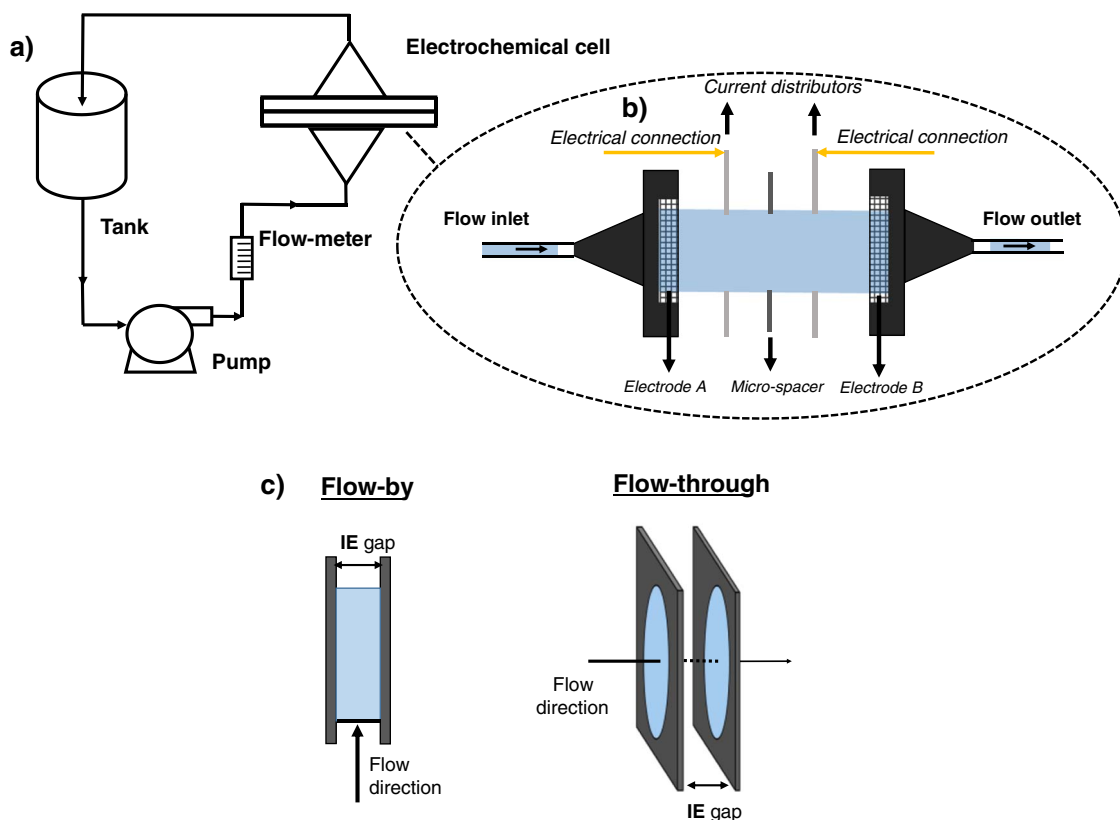**Fig. 1.** Experimental set up used in this work. (a) Flow diagram, (b) electrochemical cell (c) comparison of flow-by and flow-through configurations.