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Electrochemical processes in macro and microfluidic cells for the abatement of chloroacetic acid from water

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ABSTRACT

The remediation of solutions contaminated with monochloroacetic acid (CAA), which is one of the most resistant haloacetic acids (HAAs) to chemical degradation, dramatically depends on the adopted electrochemical approach: (i) CAA is only poorly oxidized either by homogeneous hydroxyl radical in electro-Fenton (EF), electrogenerated active chlorine or electro-oxidation on Pt anode; (ii) it is moderately abated by direct reduction on silver or compact graphite cathodes (from 30% in macro cells to 60% in the microfluidic devices); (iii) it is quantitatively removed by direct electro-oxidation on a boron-doped diamond (BDD) anode. The use of a microreactor enables operation in the absence of supporting electrolyte and drastically enhances the performance of the cathodic process. Simultaneously performing direct oxidation on BDD and reduction on graphite in a microfluidic cell yields the fastest CAA removal with 100% abatement at low current densities (~5 mA cm^{-2}).

1. Introduction

Haloacetic acids (HAAs) are ubiquitous, toxic and persistent contaminants introduced into the environment through water chlorination, organochlorinated pesticide degradation, herbicide utilization, atmospheric cleavage of refrigerants and even by natural formation [1–3]. A number of techniques has been proposed for the treatment of water containing HAAs, including biodegradation [4,5], ultrasound- or microwave-assisted photolysis [6,7] and reduction and adsorption processes [8,9], most of them exhibiting relevant drawbacks such as poor abatements, long reaction times, high costs or production of hazardous wastes. Some electrochemical methods have also been proposed for the treatment of organic halocompounds [10–28]. Reduction processes were used for the efficient dehalogenation of a large number of light halocompounds either in water [10–15,21–26] or aprotic solvents [17,20]. Silver and copper have proven the most promising cathodes for such processes. Recently, it has been shown that aliphatic chlorides can also be treated by direct electro-oxidation [24,29–32] or electro-Fenton (EF) process [33]. In addition, coupled processes were also proposed for the treatment of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane, thus yielding a higher abatement after a given charge passage and entailing a lower accumulation of byproducts compared to single routes [24,33]. It is worth noting that the electrochemical oxidation of both chloroethanes results in the formation of chloroacetic acids that are more resistant to degradation than the parent compound [33].

The electrochemical removal of HAAs by electrochemical reduction at gold and copper cathodes was evaluated in detail by Korshin and Jensen [34]. Copper was found to be more effective than gold, leading to almost complete dehalogenation of brominated HAAs. The reduction of chlorinated acetic acids gave rise to the formation of monochloroacetic acid (CAA), whose reduction was more difficult than that of parent compounds. Recently, it has been shown that chloroacetic acids can be effectively reduced at activated silver plate or silver nanoparticles-modified cathodes [35,36] and Ag-Pd foam [37] or by sonoelectrochemical methods [38].

This paper reports the treatment of CAA, one of the more resistant HAAs to chemical and electrochemical processes [8,33]. It may appear as an ultimate intermediate in the degradation pathway of other halo-derivatives, but it is also a typical byproduct formed during disinfection of waters by chlorination, and its control is mandatory due to its potential carcinogenic and mutagenic effects [1,39]. Different electrochemical approaches, including direct cathode and anode processes, mediated oxidation by means of electrogenerated active chlorine, EF process and

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coupled systems have been investigated in order to compare the performance of each route and finally propose the most suitable one.

One of the main drawbacks that are inherent to the electrochemical technologies operated in conventional cells arises from the need of a high conductivity in order to minimize the ohmic drop in the aqueous solution and the overall potential difference between the anode and cathode. Consequently, the addition of a certain amount of supporting electrolyte is usually a must. This is certainly an important obstacle for the widespread introduction of many electrochemical technologies in the market, as in the case of water decontamination. Indeed, the addition of chemicals to polluted water streams is often a problematic issue, being contrary to general administrative regulations because this may lead to the formation of secondary pollutants during the electrochemical degradation of initial contaminants. Furthermore, it increases the operation costs. Recently, different research groups have demonstrated the successful application of microfluidic electrochemical reactors (i.e., cells with a distance of tens or hundreds of micrometers between the anode and cathode) to both, the electrochemical treatment of aqueous solutions of organic pollutants [40–44] and the synthesis of fine chemicals [45–48], in the absence of supporting electrolytes with a small potential difference between both electrodes. Therefore, the drastic reduction of distances between electrodes leads to a major reduction of the ohmic resistance. Furthermore, higher current efficiencies were achieved in microreactors for the electrochemical abatement of organic pollutants performed by both direct anodic oxidation and EF processes caused by an intensification of mass transport phenomena [41–44]. Hence, the treatment of aqueous solutions of CAA has been carried out in macro and microfluidic devices equipped with different anode and cathode materials in order to improve the performance of the electrochemical processes under study in terms of CAA and chemical oxygen demand (COD) abatement.

2. Experimental

Two macrofluidic cells, namely system I and system II, and a microfluidic cell were used to carry out galvanostatic electrolyses by employing an Amel 2053 potentiostat-galvanostat and a 3300 current integrator. Macro-scale electrolyses were performed in batch mode. System I was a bench, open, undivided, cylindrical glass cell of 150 mL capacity with a double jacket for circulation of external thermostated water to regulate the solution temperature at 25 °C. The anode was either a 3 cm^2 Pt sheet (SEMPSA) or a 3 cm^2 BDD thin-film electrode (Condias). The cathode was a 3 cm^2 carbon-PTFE air-diffusion electrode (ADE) from E-TEK, which was fed with air at 1.0 L min^{-1} for ensuring continuous H_2O_2 electrogeneration from the two-electron reduction of O_2. The interelectrode gap was about 1 cm. The solutions were always vigorously stirred with a magnetic bar at 800 rpm to enable mixing and transport of reactants. Comparative experiments were performed with 100 mL of solution. For the photoelectro-Fenton (PEF) process, a Philips TL/6 W/08 fluorescent black light blue tube (320-400 nm with λ_{max} = 360 nm) was placed above the solution. System II was equipped with an undivided filter-press reactor (ElectroCell AB) to work in a flow configuration. This reactor was composed of a BDD (Condias) or Ti/IrO_2-Ta_2O_5 (ElectroCell AB) anode and a cathode made of either compact graphite (Carbone Lorraine), Ag (ElectroCell AB), Cu or AISI 304 stainless steel plate. The exposed surface area of the plates was 10 cm^2 and the interelectrode gap was 4 mm. Comparative experiments were performed with 200 or 300 mL of solutions, which were placed in a jacketed glass reservoir of 350 mL and sparged with nitrogen or compressed air. The solutions were continuously recirculated at 1 L min^{-1} by a centrifugal pump.

The experiments in the microreactor were performed in flow mode with a single passage of the solution through the cell, which was enabled by a syringe pump (New Era Pump Systems, Inc.) that fed the solutions at a flow rate between 0.05 and 0.6 mL min^{-1}. The microreactor consisted in the abovementioned commercial undivided filter-press flow cell from ElectroCell AB, now equipped with one or two PTFE spacers (thickness of the spacer in the micrometer range, i.e., 50 or 100 μm) placed between the electrodes, which were selected among those used in system II (see references [41,48] for a more detailed description of the micro device). Thus, BDD or Ti/IrO_2-Ta_2O_5 and compact graphite or stainless steel, were employed as anode and cathode, respectively. The spacers were cut so as to expose a working area of 5 cm^2. For each tested operating condition, at least 2 samples of 1 mL were analyzed.

The concentrations of CAA and acetic acid were evaluated by high-performance liquid chromatography (HPLC) using an HP 1100 LC fitted with a Prevail Organic Acid 5 μ column (Grace Davison Discovery Sciences) at 25 °C and coupled with a UV detector selected at λ = 210 nm. A 25 mM KH_2PO_4 aqueous solution at pH 2.0 (H_3PO_4) was eluted at 1.0 mL min^{-1} as the mobile phase. The concentration of accumulated H_2O_2 was determined spectrophotometrically from the light absorption of the Ti(IV)–H_2O_2 colored complex at λ = 409 nm, by using titanium(IV) oxysulfate ($TiOSO_4{\cdot}H2O$) from Fluka. The COD was determined by using commercial Merck cell tests. The total organic carbon (TOC) abatement was evaluated by using a Shimadzu VCSN TOC analyzer. The oxychlorine ions (chlorate and perchlorate) were quantified by ion chromatography (IC) using a Shimadzu 10 Avp HPLC fitted with a Shim-Pack IC-A1S (100 mm × 4.6 mm (i.d.)) anion column at 40 °C and coupled with a Shimadzu CDD 10 Avp conductivity detector. The mobile phase was a solution with 2.4 mM tris(hydroxymethyl)aminomethane and 2.5 mM phthalic acid at pH 4.0 eluted at 1.0 mL min^{-1}. All the species were identified by comparison of their retention times with those of pure standards.

The electrolyses were performed using bidistilled water to prepare solutions of 5 mM CAA (Merck), which usually contained 0.035 M Na_2SO_4 (Janssen Chimica) as supporting electrolyte for macro-scale experiments. For the study of electrochemical Fenton processes, 0.25-1.0 mM $FeSO_4$ (Fluka) was added as catalyst. Sulfuric acid (Aldrich) was used to adjust the pH of the solution when necessary. Prior to each experiment with the BDD anodes, an anodic polarization was carried out at 3.0 V vs. SCE for 5 min. In the case of silver, the surface was polished with alumina powder and then activated by means of either an oxidation–reduction cycle process, at 10 mV s^{-1} in the range from -0.4 to 0.4 V (4 cycles, at 298 K) or amperostatic pulses in Na_2SO_4 or NaCl. Compact graphite and copper cathodes were mechanically polished with alumina powder.

The percentage of abatement (i.e., the CAA conversion and the COD removal) was defined by Eq. (1), while the current efficiency (*CE*, %) for the conversion of the pollutant was defined by Eqs. (2) and (3) for macro and a microfluidic cells, respectively.

$$X = 100\frac{\left(C^0 - C^f\right)}{C^0} \tag{1}$$

$$CE = 100\frac{nFVC^0X}{i_{app}At} \tag{2}$$

$$CE = 100\frac{nFC^0\varphi_V X}{i_{app}A} \tag{3}$$

where C^0 and C^f are the initial and final CAA concentrations or COD values, n is the number of required electrons for the conversion of the pollutant to carbon dioxide for oxidation processes (6) and to acetic acid for the reduction route (2), F the Faraday constant (96487 C mol^{-1}), i_{app} the applied current density, A the exposed