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Electrochemical incineration of *p*-cresol and *o*-cresol in the filter-press-type FM01-LC electrochemical cell using BDD electrodes in sulfate media at pH 0

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Abstract

This work shows a comparative study of the incineration of 2-mM *p*-cresol and *o*-cresol in 1 M-H_2SO_4 in aqueous media. Microelectrolysis studies indicated that both the *p*-cresol and *o*-cresol oxidation were carried out *via* hydroxyl radicals ($OH^\bullet$) formed by water oxidation in the boron-doped diamonds (BDD)-H_2O-H_2SO_4-*p*-cresol and *o*-cresol interface. In both cases, the potential and current density ranges, where great amounts of $OH^\bullet$ are formed, were between $2.3\text{ V} \le E \le 2.75\text{ V}$ *versus* SHE and $J = 10\text{ mA cm}^{-2}$. Electrolyses in an undivided FM01-LC reactor were performed at different Reynolds values $27{,}129 \le Re \le 42{,}631$, and at $J = 10\text{ mA cm}^{-2}$. For *p*-cresol and *o*-cresol, the rate of degradation was slow, however it increases slightly as a function of the *Re*, indicating that the oxidation involves a complex pathway; current efficiency also rises as a function of the *Re*. For *p*-cresol, the mineralization at $Re = 42{,}631$ reached 90%, with 71% current efficiency and an energy consumption of 7.84 kWh m^{-3}; whereas *o*-cresol was mineralized to 84%, with 67% current efficiency and an energy consumption of 6.56 kWh m^{-3}. The results obtained in this work demonstrated that *o*-cresol is more recalcitrant than *p*-cresol.

Keywords: Degradation of organics; BDD electrodes; FM01-LC reactor; *p*-cresol; *o*-cresol

1. Introduction

Oil refineries as well as chemical, plastics and other industries generate effluent fluids with high concentrations of organic compounds, among which the most present are cresols that are recalcitrant to mineralization by traditional biological and physicochemical methods.

Incineration of cresols requires very strong oxidants, such as hydroxyl radicals ($OH^\bullet$). The generation of $OH^\bullet$ can be induced using two routes, either by irradiation onto TiO_2, which oxidizes to water forming $OH^\bullet$ [1,2], or by its generation on an electrode surface [3].

The selection of a treatment looks for the economically optimal method option that will depend on the control, cost-effectiveness and efficiency of treatment. Lately, electrochemical techniques have been considered as an alternative for the treatment of sewage [4].

Many investigations have been carried out on materials, such as RuO_2, PbO_2 and SnO_2, employed as anodes, for the degradation of organic pollutants [5–9]. At the surface of these materials, water oxidation products, such as $OH^\bullet$, H_2O_2, O_2 and O_3, are generated indirectly oxidizing organic pollutants. However, these anodes corrode and tend to become deactivated, diminishing their efficiency and useful life [8].

Recently, synthetic electrodes of boron-doped diamonds (BDD), manufactured by chemical vapor deposition (CVD), have been used for degradation of recalcitrant organic compounds. This degradation can take place through either direct oxidation at the surface of the electrode, or indirect oxidation using oxidants formed on the anode. These are mainly composed of hydroxyl radicals whose unique properties allow oxidizing to CO_2 compounds such as phenols, chlorophenols, methoxyphenol, hydroquinone, cresols, naphtols, to mention some of them [10–14].

The works reported in the literature on incineration in reactors employing BDD electrodes, have been carried out in flow-by cells, whose working (BDD) and auxiliary electrodes have circular geometry [10,15–18] and in an impinging jet cell [19,20].

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Panizza et al. [18] and Polcaro et al. [19] include the study on hydrodynamic conditions in incineration, indicating that incineration is increased as a function of flow rate. These authors conclude that total incineration of organics is due to the formation of hydroxyl radicals from the water discharge and that the oxidation was under mass-transport control.

There are different types of flow reactors classified according to the type of electrode, such as rotatory cylinder, parallel plate or three-dimensional electrodes [4]. Among these, the FM01-LC filter press electrolyzer stands out.

The FM01-LC reactor is well suited to laboratory feasibility studies in subject areas, such as electrosynthesis [21], redox flow cells [22] and environmental treatment, as well as for the investigation of the effect of process variables on electrochemical reactions. The FM01-LC is a laboratory-scale (projected area 64 cm^2) electrochemical cell, based on a larger (2100 cm^2) FM21-SP electrolyzer (INEOS Chlor-Chemicals), the latter having been originally designed with a plate-and-frame filter-press configuration. The FM01-LC is abundantly described in literature [23], where global and mass transport to electrodes [24–26], pressure drop [24] and hydrodynamics [27,28] have been studied. However, no electrochemical incineration with BDD electrodes has been performed in such cell.

The objective of this work is focused on the characterization of an FM01-LC electrochemical reactor, with two-dimensional BDD electrodes for electrochemical incineration of two model molecules, *p*-cresol and *o*-cresol.

2. Mass transfer in the FM01-LC

Under mass transport controlled conditions, that is, in the limiting current plateau region, the current is related to the global mass-transport coefficient, k_m [26]:

$$k_\mathrm{m} = \frac{I_\mathrm{L}}{AzFC} \tag{1}$$

where I_L is the limiting current for the electrochemical reaction, A the electrode area, z the number of electrons transferred, F the Faraday constant (96,485 C mol^{-1}) and C is the concentration of the electroactive species in the bulk electrolyte.

Mass transport in practice is usually characterized by measuring the limiting current over a range of electrolyte velocities. The mass transport dependence relative to convection is described by a dimensionless group correlation of the form [25,26,29]:

$$Sh = aRe^{b}Sc^{0.33} \tag{2}$$

The Reynolds number (*Re*) is defined as follows:

$$Re = \frac{ud_\mathrm{e}}{\upsilon} \tag{3}$$

where u is the mean linear flow velocity of the fluid through the cell, d_e the equivalent diameter of the flow channel and υ is the kinematic viscosity. On the other hand, the Sherwood number (*Sh*) is described as

$$Sh = \frac{k_\mathrm{m}d_\mathrm{e}}{D} \tag{4}$$

where D is the diffusion coefficient of the electroactive species. The Schmidt number correlates the fluid transport properties

$$Sc = \frac{\upsilon}{D} \tag{5}$$

Table 1
BDD electrode dimensions, experimental details on the FM01-LC electrolyzer

Electrode length, L	16 cm
Electrode height, B	4 cm
Electrode spacing, S	0.55 cm
Electrode area, A	64 cm^2
Hydraulic (equivalent) diameter, $d_e = 2BS/(B+S)$	0.97 cm
Mean fluid velocity, u	From cm s^{-1}
Turbulence promoter	Plastic mesh type D [a]CD and [b]LD = 11 mm
Overall voidage, ε	0.83
Electrolyte volume within the FM01-LC (=$BS\varepsilon L$)	29.22 cm^3
Temperature	298 K

Overall voidage is the ratio of the free space in the channel to overall channel volume.

[a] CD, internal dimension of shorter mesh diagonal.

[b] LD, internal dimension of longer mesh diagonal.

The exact form of the mass transport correlation is best evaluated though an analysis of experimental data and will depend on the electrode geometry, electrochemical cell geometry, and types of fluid flows. For the purpose of this paper, the mass transport correlation was taken as [26]:

$$Sh = 0.56Re^{0.62}Sc^{0.33} \tag{6}$$

This was obtained by Griffiths et al. [26] for the reduction process of ferricyanide to ferrocyanide ion. This correlation was obtained in presence of a type D turbulence promoter that increases mass transport. The dimensions of the FM01-LC employed in this paper (showed in Table 1) are the same to that presented in literature [26]. The electrolyte properties used for the evaluation of Eq. (6) were $D = 6.4 \times 10^{-6}$ cm^2 s^{-1} and $\upsilon = 9.56 \times 10^{-3}$ cm^2 s^{-1} [26].

3. Experimental details

All solutions were prepared with analytical grade reagents and deionised water with 18 mΩ^{-1} cm^{-1} resistivity from a Mill-Q^{TM} system. The concentrations of *p*-cresol and *o*-cresol were varied from 0.5, 2, 5 and 7 mM in 1.0 M H_2SO_4 maintained at 298 K. The solution was deoxygenated with nitrogen for about 10 min before each experiment.

3.1. Equipment

A potentiostat-galvanostat EG&G model PAR 273 and M270 software were used for all voltammetric experiments.

Chemical oxygen demand (COD) analyses were performed using a dry-bath Lab Line Model 2008, and a spectrophotometer Genesys 20.