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Cost optimization of the current density for electroxidation wastewater processes

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ABSTRACT

The evaluation of treatment costs is one of the aspects which need more attention for the complete introduction of electrochemical reactors as an attractive alternative in the field of advanced oxidation processes. This paper presents the derivation and application of an expression to determine the optimal current density in order to carry out the direct electroxidation process of two pharmaceutical-compound-containing aqueous solutions ($50\,\mathrm{mg\,dm^{-3}}$) in a parallel plate divided cell using platinized titanium as the anode. The calculi are based on the classical definition of the total cost of electrolyzers, including the electrode service life and completed by one experimental value (obtaining a semi-empirical equation) related to the relationship between the abatement kinetics and the applied current density.

The determined value of the optimal current density resulted to be far from the diffusion-limiting current density, consequently, far from the maximum current efficiency, since the experimental parameter includes all other phenomenologies associated with rising in the electrical field across the cell.

The methodology could be useful to compare, in terms of cost, different electrochemical reactors and electrode materials for the treatment of a specific organic pollutant.

1. Introduction

The electrochemical oxidation process offers versatility, environmental compatibility, and potential cost-effectiveness for the degradation of different organic pollutants [1]. Accordingly, this method has been considered to be of practical interest, particularly for wastewaters containing biorefractory organic pollutants or microtoxic substances, which are not suitable for conventional biological abatement. The evaluation of treatment costs is one of the aspects which needs more attention for the full introduction of electrochemical reactors as an attractive alternative in the field of advanced oxidation processes (AOPs), considering that the technical feasibility of the electroxidative treatment has been proved on a myriad of organics structures and using different anode materials [2–19].

The overall cost evaluations so far available indicate that AOP systems are not more expensive than well established chemical or physical technologies for pollutant abatement [20] and among these AOPs, electrochemical oxidation has proved to be cost competitive and of simple implementation [21,22]. For a full-scale electrochemical oxidation system, these costs depend to a great extent on the nature and the concentration of the pollutants, the flow rate of the effluent and the configuration of the reactor (at fixed electrode performance).

Galvanostatic conditions are preferred due to the simplicity of the power supply and the operations. Conversely, optimization on the applied current density seems to be the most relevant tool to enhance the economy of the process. For a constant controlled current, and in the case of direct electroxidation, first-order reactions are considered and, for a batch purification operation, the efficiency tends to substantially decrease as the impurity is removed.

Efficiency could be improved if the currents were not kept constant and were instead programmed to decrease as impurity removal progresses, theoretically keeping the imposed current just close to or a little above the mass transfer limiting current value, thus minimizing the amount of current used to electrolyze water to oxygen. A validated oxidative abatement model, considering the performance of the reactor at a fixed current density, should be sufficient to programme a modulation of the applied current density, but this implies a loss of the characteristic ease of the electrochemical cell operation. As an alternative, a modular system can be adopted, where the applied current density (constant) can be changed for each step, considering the introduced organic pollutant concentration.

The purpose of this paper is to present the application of an optimization procedure for the direct organic pollutant electroxidation process, with the aim of determining the optimal current density necessary to perform each of the previously considered oxidative treatment steps, keeping fixed the other main design factors of the electrochemical system: temperature, fluodinamic regime and cell geometry.

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Nomenclature

a	electrode price
A_e	electrode area
b	cost of electrical energy
C_b	bulk concentration of organic pollutant
C_t	overall costs
F	Faraday constant
i	applied current density
i_{opt}	optimum current density
k_M	electrochemical mass transport coefficient
m	mass of the organic molecule
M	molecular weight
[R]	organic concentrations during the electrolysis time
$[R]_0$	starting organic concentrations
R_{eff}	effective electrical resistance
SL	electrode service life
t	electrolysis time
v_M	recirculation tank volume
z	number of electrons involved in the electrochemical reaction per mole of organic molecule
ΔV_{tot}	cell voltage
ϕ	current efficiency of the oxidative process

The calculi are based on the classical definition of the total cost of electrolyzers, that is the extended Ibl formula [23], and include the electrode service life and are completed by an experimental value (resulting in a semi-empirical equation) that is related to the relationship between the abatement kinetics, of an specific target compound, and the applied current density, while all the other operative parameters of the electrochemical system are kept invariable.

2. Total cost estimation model

The overall costs (C_t) are represented by the sum of the capital costs, the operating costs and the maintenance of the electrochemical cell (pumping and cooling costs must be considered in a parallel optimization in order to complete the optimization of the whole electrochemical system). In order to simplify the analysis, the capital costs are considered to be directly related to the price of the electrodes area and their replacement, in other words the price of anode area includes the membrane and the cell costs. On the other hand, the operative costs are attributed to the cost of the electrical energy [24]; (the electrolyte cost is considered as constant input), according to Eq. (1):

$$C_t = \Delta V_{tot} i A_e t b + a' A_e t \tag{1}$$

where ΔV_{tot} corresponds to the cell voltage, i to the applied current density, A_e to the electrode area, t to the electrolysis time, b to the cost of electrical energy and a' to the ratio between the electrode price (a) and it's service life (SL).

Let us consider the service life of the electrode related to the applied current density in the form of Eq. (2) [25]:

$$SL = \frac{c}{i^w} \tag{2}$$

$$a' = \frac{a}{SL} = \frac{a i^w}{c} \tag{3}$$

The a' parameter is then calculated from Eq. (3), where c and w are experimental constants.

The cell voltage contains the three terms of Eq. (4) [26,27]:

$$\Delta V_{tot} = V_0 + \sum_j \eta_j + R_{eff} i A_e \tag{4}$$

The first two terms, concerning the minimum tension necessary to generate a net Faradic current and the summation of the kinetics overpotential, can be grouped together, resulting in Eq. (5):

$$\Delta V_{tot} = V^* + R_{eff} i A_e \tag{5}$$

where R_{eff} is the effective electrical resistance of the electrochemical cell, which depends mainly on the electrolyte nature and concentration, temperature and on the inter-electrode gap. Eq. (1) can then be rewritten in the form of Eq. (6):

$$C_t = t\left[(V^* + R_{eff} i A_e) i A_e b + \left(\frac{a}{c}\right) A_e i^w\right] \tag{6}$$

The constants C_e and C_m in Eq. (10) are defined as:

$$C_e = R_{eff} A_e b \tag{7}$$

$$C_m = \left(\frac{a}{c}\right) \tag{8}$$

and the electrolysis time is considered according to the Faraday law:

$$t = \frac{zFm}{M\,3600\, i A_e \phi} = \frac{K}{i A_e \phi} \tag{9}$$

where z is the number of electrons involved in the electrochemical reaction per mole of original organic molecule, F is the Faraday constant, M the molecular weight, m the mass of the original organic molecule oxidized in the time t and ϕ is the current efficiency of the oxidative process.

After considering the value of V^* to be negligible, with reference to the term $R_{eff} i A_e$, Eq. (6) can be written in the form of Eq. (10):

$$C_t = \frac{K}{\phi}\left(C_e i + C_m \frac{i^w}{i}\right) \tag{10}$$

In order to determine an expression for the optimal current density, in terms of cost, expression (10) is derived, with reference to i, and equalled to zero:

$$\frac{\partial C_t}{\partial i} = 0 = \frac{K}{\phi}\left(C_e + C_m (w-1)\frac{i^w}{i^2}\right) + K\left(C_e i + C_m \frac{i^w}{i}\right)\frac{-1}{\phi^2}\frac{\partial \phi}{\partial i} \tag{11}$$

Eq. (13) is obtained after regrouping and considering the mathematical identity in Eq. (12):

$$\frac{\partial x}{x} = \partial\,\mathrm{Ln}\,(x) \tag{12}$$

$$\frac{C_e i_{opt}^2 + C_m (w-1) i_{opt}^w}{C_e i_{opt}^2 + C_m i_{opt}^w} = \frac{\partial \phi}{\phi}\frac{i}{\partial i} = \frac{\partial\,\mathrm{Ln}\,(\phi)}{\partial\,\mathrm{Ln}\,(i)} \tag{13}$$

where i_{opt} represents the optimum current density. This last equation underlines the relationship between the optimum value and the current efficiency to current density ratio. Conversely, this last ratio was evaluated considering that the direct electroxidation of low concentration organic pollutants is generally a limited mass transport process and the current efficiency has the form of Eq. (14):

$$\phi = \frac{zFk_M C_b}{i} \tag{14}$$

where k_M is the mass transport coefficient of the electrochemical reactor, C_b is the bulk concentration of the organic pollutant, and

$$\phi \propto \frac{k_M}{i} \quad \text{implying that} \quad \mathrm{Ln}(\phi) \propto \mathrm{Ln}\left(\frac{k_M}{i}\right)$$

The term on the right of Eq. (13) must correspond to the slope of the relationship between the mass transport coefficient-current density ratio and the applied current density:

$$\frac{\partial \mathrm{Ln}(\phi)}{\partial \mathrm{Ln}(i)} = \frac{\partial \mathrm{Ln}(k_M/i)}{\partial \mathrm{Ln}(i)} = \Delta \tag{15}$$

This slope is hypothesed to be a constant value and denoted with the symbol Δ which gives Eq. (16) from which an expression for the optimal current density is obtained (Eq. (17)):

$$\frac{C_e i_{opt}^2 + C_m(w-1)i_{opt}^w}{C_e i_{opt}^2 + C_m i_{opt}^w} = \Delta \tag{16}$$

$$i_{opt} = \left[\frac{a(1+\Delta-w)}{cR_{eff}A_e b(1-\Delta)}\right]^{1/(2-w)} \tag{17}$$

3. Experimental

The above derived expression (17) was used to determine the optimal current density in order to carry out the direct electroxidation process for a series of low concentration organics containing solutions. In order to obtain the experimental parameter Δ, a set of electroxidative runs were conducted (varying the applied current density).

Electrochemical oxidation experiments were carried out in a parallel plate divided cell (using an anionic Neosepta membrane—Ameridia) employing stainless steel as the cathode and platinized titanium as the anode.

The electrode surface area to anodic compartment volume ratio was equal to $1 \times 10^{-2}\,\mathrm{m}^{-1}$; the surface of the electrodes was $2 \times 10^{-2}\,\mathrm{m}^2$, the distance between the electrodes was 2 cm and the Reynolds number, in the anodic compartment, was above 5700; more cell details are given elsewhere [28,29]. The cell was connected by a simple current rectifier. The applied current was varied in the range 1.5–400 $\mathrm{A\,m^{-2}}$, at a controlled operating temperature of 30 ± 2 °C. The conversion of the original molecules was monitored by means of UV spectrophotometry (CARY 500 Scan single ray spectrophotometer).

The organic molecules here considered were pharmaceutical substances, Ofloxacin (9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7-oxo-7H-pyrido[1,2,3-de]-1,4-benzoxazine-6-carboxylic acid hemihydrate) for which electrochemical test was already reported in a previous work [28] and Ranitidine hydrochloride (N-(2-[(5-[(dimethylamino) methyl]furan-2-yl)methylthio]ethyl)-N-methyl-2-nitroethene-1, 1-diamine), hard to biodegrade, which were used as received from Sigma–Aldrich in a concentration of 50 $\mathrm{mg\,dm^{-3}}$ in distillated water and with 0.02 N Na_2SO_4. The used supporting electrolyte, ensured a minimum electro-generation of the bulk oxidants, and allowed pure heterogeneous direct electroxidation at the anode.

4. Results and discussion

Before the organic electroxidation runs, the electrochemical reactor was operated with different salt concentrations in order to determine the extent of validation of the linear relationship between the applied current density and the cell potential, which was assumed for the total cost expression in the model. The experimental values, for different concentrations of Na_2SO_4 (in grams per liter), are presented in Fig. 1. In this figure it is possible to denote a limit of applicability (in terms of current density) of Eq. (1) and also calculate the value of the R_{eff} and V^* parameters, the first corresponding to the slope of the linear segment of the relationship and the last corresponding to the limit, for i tends to zero.

A series of electroxidative runs was performed for both organic compounds varying only the applied current density. A pseudo-first-order kinetics constant and the mass transport coefficient (k_M) was calculated for each runs modeling the electrochemical system for the recirculation tank (perfectly mixed) and the anodic compartment of the cell as the plug-flow-reactor, consequently using Eq. (18):

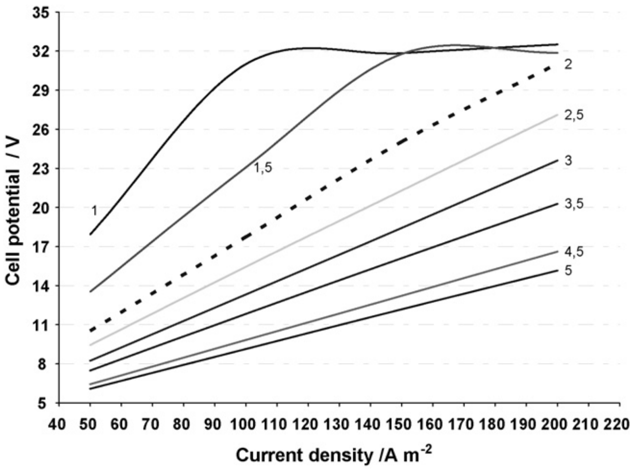

Fig. 1. Experimental relationship between the applied current density and the cell potential. The numbers indicate the concentration in grams per liters of Na_2SO_4 supporting the electrolyte.

$$-\mathrm{Ln}\left(\frac{[\mathrm{R}]}{[\mathrm{R}]_0}\right) = k_M \frac{A_e}{v_M \alpha} t \tag{18}$$

where [R] and $[\mathrm{R}]_0$ are the concentrations of the original organic molecule during the electrolysis time and at the beginning of the runs, respectively; v_M is the volume of the recirculation tank and α is defined as:

$$\alpha \equiv 1 - \frac{k_M A_e}{Q}$$

where Q is the cell-to-tank recirculation flow value.

The experimental values of k_M for both organic molecules are presented in Fig. 2. The values from Fig. 2 were used to build the relationship between k_M/i concerning i in logarithmic scale as shown in Fig. 3, from which it is possible to confirm the linear relationship considered in the derivation of Eq. (15). It is possible to distinguish two zones in Fig. 3; the first, at low applied current densities, presents a positive slope indicating that as the current

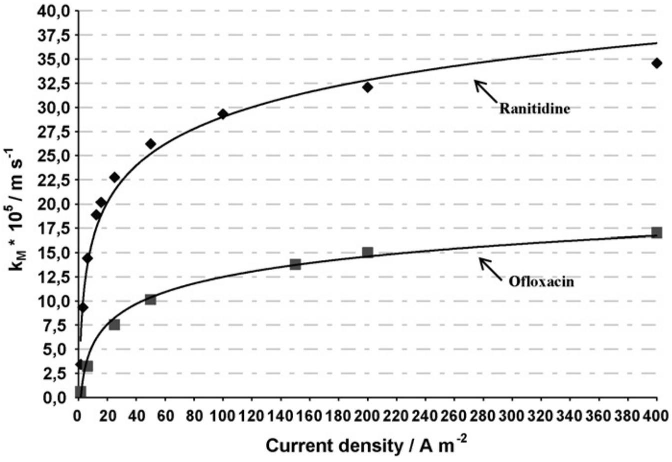

Fig. 2. Experimental relationship between the mass transport coefficient and the applied current density for the Ranitidine solution (upper curve) and the Ofloxacin solution (lower curve). Starting concentration of 50 $\mathrm{mg\,dm^{-3}}$; electrolyte Na_2SO_4 0.02 N.

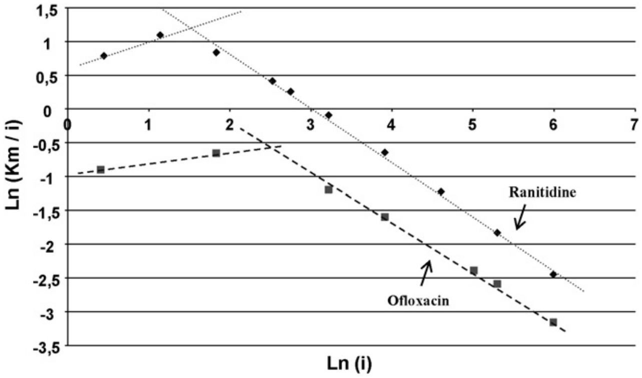

Fig. 3. Experimental relationship, in logarithmic scale, between the mass transport coefficient—applied current density ratio and applied current density for the Ranitidine solution (upper lines) and the Ofloxacin solution (lower lines). For data see Fig. 2.

density rises, the electroxidation kinetics rises linearly (kinetic control of the electroxidation reaction) while in the second zone the slope is negative, denoting a decrease in current efficiency, mainly due to the promotion of a parallel reaction (oxygen evolution) and Joule effect dissipation. Therefore, for each molecule it is possible to have two slopes and therefore two values for the parameter Δ, however, the first slope corresponds to a very low applied current density range to which a very low value of the kinetic constant is associated, consequently, the values of interest for the current density optimization were the negative slopes, which are -0.706 for the Ofloxacin treatment and the -0.825 for Ranitidine treatment.

From Eq. (15), and with the known value of Δ (which varies between 0 and -1), it is possible to establish an analytical expression to calculate k_M as function of the applied current density in the form of Eq. (19).

$$k_M = k_{M,0}\, i^{(1+\Delta)} \tag{19}$$

$k_{M,0}$ can be obtained graphically from Fig. 3 and it corresponds to the interception of the positive and negative slopes (a point from which the current efficiency starts to decay by 100%); in this case, the values for $k_{M,0}$ are $3.16 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ for Ofloxacin and $16.6 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ for Ranitidine.

The parameters related to the service life of the electrode (c and w) can be estimated from an accelerated service life test, which consists in applying a high current density to a studied electrode until a time at which the electrode potential increases to a defined value [30,31] at which it is known that either passivation or corrosion occurs and the electrode performance is lost.

Considering a couple of accelerated service life data i^* (current density used in the test) and SL^* (electrode service life determined in the test), and supposing a logarithmic relationship between these two values, Eq. (20) has been proposed to calculate the w value (i^* in $\mathrm{A\,m^{-2}}$ and SL^* in hours), while the c value has been proposed to calculate, from Eq. (21), where the f factor (calculate by Eq. (22)) adjusts Eq. (22) with Eq. (2).

$$w = [(\mathrm{Ln}(i^*))(\mathrm{Ln}(SL^*))]^{-1} \tag{20}$$

$$c = SL^* f \tag{21}$$

$$f = e^{1/(\mathrm{Ln}(SL^*))} \tag{22}$$

The electrode service life calculated with Eq. (2) and using Eqs. (20)–(22) is presented. In Fig. 4 it is possible to distinguish that as the w value decreases the electrode stability raises.

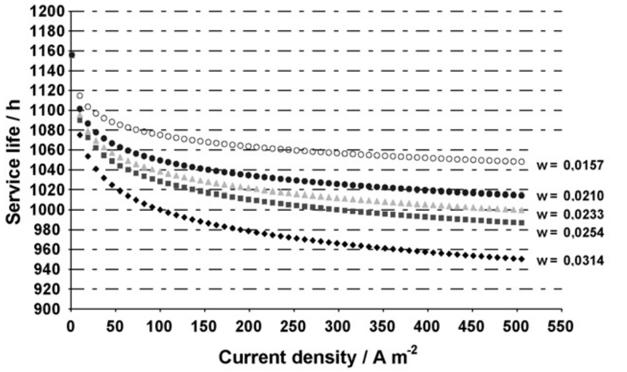

Fig. 4. Electrode service life calculated from Eq. (2), considering a standard electrode service life (SL^*) of 1000 h when the current density for the test (i^* in $\mathrm{A\,m^{-2}}$) was: 100 ($w = 0.0314$); 300 ($w = 0.0254$); 5000 ($w = 0.0233$); 1000 ($w = 0.0210$) and 10 000 ($w = 0.0157$).

Table 1
Estimated parameter values for the optimal current density calculation. The electrode cost (a) was estimated on the basis of a 2 mm thick titanium substrate [32] with a surface load of $20\,\mathrm{g\,m^{-2}}$ Pt [33].

Parameter	Value
SL^* (h)	1000
i^* ($\mathrm{A\,m^{-2}}$)	500
a (€ $\mathrm{m^{-2}}$)	1000
V^* (V)	2
R_{eff} (Ω)	7.2
b (€ $\mathrm{W\,h^{-1}}$)	0.0001

Table 2
Experimental parameter values for the oxidative treatment of Ofloxacin and Ranitidine using a platinized titanium anode.

Dimensionless constant	
Δ (Ofloxacin)	−0.706
Δ (Ranitidine)	−0.825
w	0.0233

The optimal current density was calculated for the two organic containing solutions with the values estimated in Table 1 and the experimental parameters summarized in Table 2. A value of $103\,\mathrm{A\,m^{-2}}$ was obtained for the Ofloxacin solution and $74.3\,\mathrm{A\,m^{-2}}$ for the Ranitidine solution. These results can also be obtained graphically analyzing the total cost curve in Fig. 5, which was build according to the following sequences:

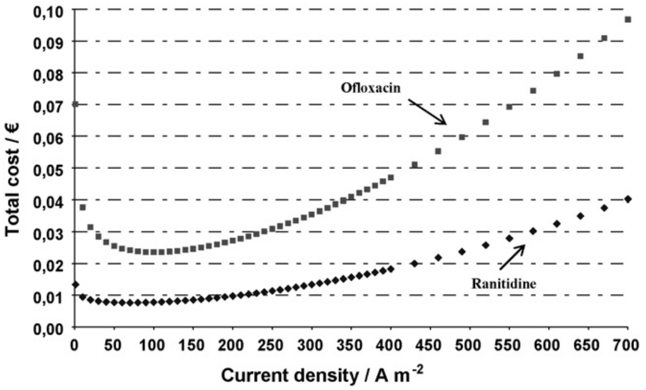

Fig. 5. Total cost for a 90% molar abatement of a $50\,\mathrm{mg\,dm^{-3}}$ Ranitidine solution (lower curve) and Ofloxacin solution (upper curve). The parameter values are shown in Tables 1 and 2 and the operative data are in Table 3.

Table 3
Operative parameters of the electrochemical reactor.

Parameter	Value
$Q\,(\mathrm{m^3\,h^{-1}})$	3.6
$A_e\,(\mathrm{m^2})$	0.02
$v_M\,(\mathrm{m^3})$	0.004

1. a molar percentage of abatement is given and the C/C_0 molar ratio is calculated;
2. a current density is given and the k_M value from Eq. (19) is calculated;
3. the electrolysis time needed is calculated from Eq. (18) with the parameters of the electrochemical system (in Table 3, for this case);
4. the total cost is calculated from Eq. (6) and the point (C_t, i) is plotted;
5. a new current density is given and the calculation procedure is repeated.

The total cost for the 90% molar abatement, in the electrochemical cell (4 l of starting concentration of $50\,\mathrm{mg\,dm^{-3}}$), applying the optimal current density, was estimated to be about 0.01€ for the Ranitidine solution and 0.022€ for the Ofloxacin solution.

The data in Fig. 3 shown that the loss in current efficiency starts at a lower value of applied current density for the Ranitidine treatment than for the Ofloxacin treatment; however the higher kinetics of the Ranitidine electroxidation has a strong impact on the total costs as shown in Fig. 5.

The resulting optimal current density, in both cases, is in a zone where the current efficiency is far from the highest values. This is mainly due to the fact that a rise in the current density implies an enhancement of all the on other factors, apart from the anodic reaction rate:

- the rise in the rate of molecule hydrolysis or homogeneous deprotonation as a result of the electrical field enhancement and faster pH gradient generation;
- the possible improvement of the turbulence in the cell, deriving from gas generation;
- the increase in electrode temperature, which increases the kinetics and the thermal gradient from the electrode to the bulk solution, and enhances the diffusion.

The optimal current density regarding the electrode cost, electrical energy cost and electrode stability parameters is presented in Fig. 6 for the Ofloxacin molecule case. In this figure it is possible to see that a value of w (corresponding to a highly unstable anode) exists after from which the process become no longer economically feasible, regardless of the electrode cost.

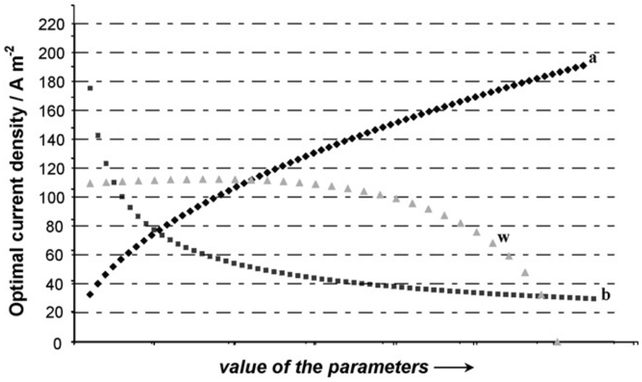

Fig. 6. Variation of the optimal current density with the parameters being varied one at time: electrode cost (a); electrical energy price (b) and electrode stability (w). The data are from the Ofloxacin solution treatment.

The assumption of V^* as negligible value with reference to the term $R_{eff}iA_e$, in Eq. (10) was validated by comparing the value of optimal current density computed in Eq. (17) (that no consider V^*) and the value obtained by the five step procedure described above (that use the value of V^*), the differences found between both methodologies were marginal.

Increasing in the applied current density implies a modification in variables that involves other cost variation, as example the cooling cost, this associated variation of costs must be considered for a overall cost optimization of the electrochemical treatment, that could be accomplished by a statistical methodology like response surface [34], that is out of the aim of this work.

5. Conclusions

In the present work, the optimal current density, in terms of total cost, to apply in a direct Ofloxacin or Ranitidine ($50\,\mathrm{mg\,dm^{-3}}$) solution electroxidation process has been established using semi-empirical formula that need only one operative parameter which is determined from the analysis of the electroxidation performance regarding the applied current density, the operative data, the cost and the stability of the electrode material.

This optimal value directly depends on the electrode cost and its service life and inversely on the electric current price. The values of the determined optimal current densities were far from the diffusion-limiting current density and far from the maximum current efficiency, since included all the phenomenology associated with rises in the electrical field across the cell and the thermal and fluodinamic effects associated with current increments.

The extension of the current density field on which parameter Δ is positive or negative, mainly depends on in the starting organic concentration of the solution that has to be treated, together with the mass transport limitation inside the electrochemical reactor. The methodology can also be extended to estimate the optimal current density cost for indirect or coupled indirect/direct electrochemical treatments and could be useful to compare, in terms of cost, different electrochemical reactors and electrode materials (with know relative reactivity, costs and service life) for the treatment of a specific organic pollutant.

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