The influence of different support electrolyte compositions for Tetracycline Hydrochloride electro-oxidation and byproduct formation

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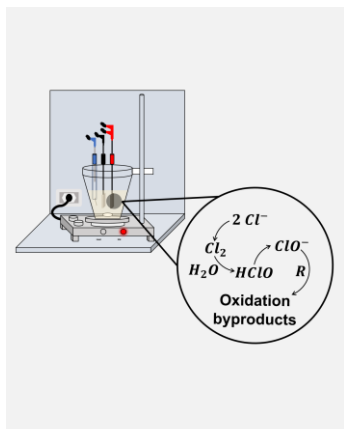
This study aimed to investigate the effect of the increase in NaCl concentration using a commercial DSA® electrode (a material with good mechanical and chemical stability) for the degradation of tetracycline hydrochloride (TCH) in a conventional electrochemical cell with a constant current density (100 mA cm^{-2}), during 7,200 seconds in a solution of TCH (20 mg L^{-1}) with a mixture of Na_2SO_4 (0.1 mol L^{-1}) and NaCl (0.01, 0.025 and 0.05 mol L^{-1}) as support electrolyte. The TCH is electro-oxidized rapidly and NaCl 0.01 mol L^{-1} showed the best global efficiency with an apparent kinetic constant of 0.036 s^{-1} and decrease of concentration over time of 100%, and energetic consumption of 0.05 kWh(gTCH)$^{-1}$. For different NaCl concentrations used herein, a stable subproduct is formed, because the bands attributed to TCH disappeared and a band at ~290 nm rises with time. The smallest quantity of byproduct was formed in 0.01 mol L^{-1}, consequently, showing the best electro-oxidation efficiency of it.

Introduction

The conventional treatments are not capable of the elimination of Pollutant of Emerging Concern. The electrochemical advanced oxidation process (EAOP) is an interesting method to generate oxidative species *in situ* [1, 2]. The so-called dimensionally stable anodes (DSA®) are widely used due to their mechanical and chemical stability, in addition, it has a high electrocatalytic surface area [3]. DSA® is extremely active for chlorine evolution reaction (CER), consequently, in aqueous media, produces the so-called active chlorine [2, 4]. A disadvantage of this material is the possibility of organo-chloride byproducts, therefore, is important to explore conditions to modulate and avoid byproducts [5, 6]. This study aimed to investigate the influence of a constant current density applied to a commercial DSA® electrode in a solution containing different chloride ion concentrations applied to the electro-oxidation of tetracycline hydrochloride (TCH).

Material and Methods

This study aimed to investigate the effect of the support electrolyte composition (Table 1) for TCH electro-oxidation in a constant current density (j = 100 mA cm^{-2}) applied to a commercial DSA® electrode (nominal composition: Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$) for active-chlorine production to degrade tetracycline hydrochloride (TCH) in a concentration of 20 mg L^{-1} during 7,200 s. The TCH degradation was determined by molecular spectroscopy in ultraviolet-visible.

Results and Discussion

The support electrolyte is very important for electrical current flow. Furthermore, ions addition to reactional media can provide the production of strong oxidation species, such as active chlorine [7]. As observed in Fig. 1a, the TCH concentration as a function of the time rapidly decays.
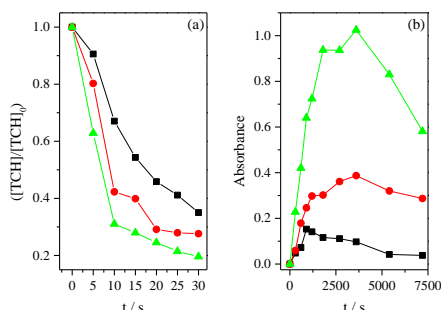

Fig. 1. (a) TCH (λ_{max} = 358 nm) electro-oxidation with different support electrolyte compositions. (b) Byproduct (λ_{max} = 290 nm) rate and degradation with different support electrolyte compositions. (■) [NaCl] = 0.01 mol L^{-1}; (●) [NaCl] = 0.025 mol L^{-1}; (▲) [NaCl] = 0.05 mol L^{-1}.

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The increase in NaCl concentration provides an increase in TCH abatement, causing TCH degradation in the first 30 s. The chloride ions availability improves the electro-oxidation because more active chlorine is disposable to degrade the pollutant. Table 1 shows kinetic and energetic information.

Table 1. TCH abatement, kinetic constants, and energetic consumption values for the different conditions evaluated.

Electrolyte composition		Abatement (%)	k (s^{-1})	Energetic consumption (kWh(gTCH)$^{-1}$)
[Na$_2$SO$_4$] (mol L^{-1})	[NaCl] (mol L^{-1})			
	0.010	64.97	0.036	0.005
0.100	0.025	72.37	0.045	0.004
	0.050	80.40	0.052	0.003

The electrooxidation reaction was kept for 7,200 s to evaluate the byproduct formation, and, as shown in Fig. 1(b), in all conditions, a byproduct is formed with a maximum absorbance of 290 nm, which appears above 300 s of electrolysis. The increase in NaCl concentration leads to an increase in the formation of the byproduct. The concentration of 0.01 mol L^{-1} presented a minimum byproduct formation and just that which also oxidizes it.

Conclusions
The use of dimensionally stable anodes is still very promising with NaCl, results presented here showed that the control in chloride ions available is very important to modulate the formation and degradation of byproducts. Global parameters studied showed that NaCl in 0.01 mol L^{-1} is the best concentration for TCH electro-oxidation, with 100% TCH degradation in 300 s, k = 0.036 s^{-1}, and an energetic consumption of 0.005 kWh(gTCH)$^{-1}$.

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