

# Tetracycline Hydrochloride electro-oxidation: influence of the current density in degradation efficiency and byproduct formation

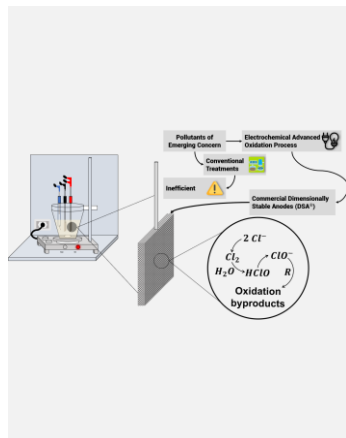
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Maria Thalia P. de Farias (PG)<sup>1</sup>, Evanny L. dos Santos (PG)<sup>1</sup>, Adeildo J. de Oliveira (PQ)<sup>2</sup>, João P. T. da S. Santos (PQ)<sup>1</sup>, Vinicius Del Colle (PQ)<sup>1,3</sup>  
[maria.thalia@arapiraca.ufal.br](mailto:maria.thalia@arapiraca.ufal.br), [delcolle@ita.br](mailto:delcolle@ita.br)\*

<sup>1</sup>Programa de Pós-graduação em Agricultura e Ambiente, Universidade Federal de Alagoas – Campus Arapiraca.

<sup>2</sup>Universidade Federal de Alagoas, Núcleo de Ciências Exatas (NCEX) – Campus de Arapiraca.

<sup>3</sup>Instituto Tecnológico de Aeronáutica, Departamento de Química.



In this was investigated the effect of the increase in current density ( $j$ ) for active-chlorine production using a commercial DSA® electrode (a material with good mechanical and chemical stability) for the electro-oxidation (EO) of tetracycline hydrochloride (TCH). A conventional electrochemical cell was used, and the experiment was performed for 7,200 seconds in a solution of TCH (20 mg L<sup>-1</sup>) with a mixture of Na<sub>2</sub>SO<sub>4</sub> (0.1 mol L<sup>-1</sup>) and NaCl (0.01 mol L<sup>-1</sup>) as a supporting electrolyte. Three different  $j$  (12.5, 25, 50, and 100 mA cm<sup>-2</sup>) were used. The TCH is electro-oxidized rapidly in all current densities. The  $j$  of 50 mA cm<sup>-2</sup> showed the best global efficiency with an apparent kinetic constant of 0.0188 s<sup>-1</sup> and TCH 100% in 300 s. Showed an energetic consumption of 2.57 × 10<sup>-3</sup> kWh(gTCH)<sup>-1</sup>. In the conditions investigated herein, a byproduct is formed, because the bands attributed to TCH disappeared and a band at ~290 nm rises with time, in 50 mA cm<sup>-2</sup> we observed the byproduct was formed in the smallest quantity with its subsequent electro-oxidation.

## Introduction

The electrochemical advanced oxidation process (EAOP) is versatile, environmentally compatible, has a good cost-benefit, and generates oxidative species in situ for antibiotic electro-oxidation [1]. The current density ( $j$ ) is an important key parameter since this parameter influences directly the formation of oxidative species [2]. The indirect electro-oxidation using DSA® in the chloride ions presence is very attractive, since this material is very efficient for chlorine evolution reaction (CER), consequently, in aqueous media produces the so-called active chlorine, a strong oxidative species [3, 4]. A disadvantage of this material is the possibility of organo-chloride byproducts, therefore, is important to explore conditions to modulate and avoid or degrade byproducts [2, 5]. This study aimed to investigate the effect of the increase in the current density applied to a commercial DSA® electrode in a supporting electrolyte containing chloride ions for tetracycline hydrochloride (TCH) electro-oxidation.

## Material and Methods

This study aimed to investigate the effect of the current density increase ( $j = 12.5, 25, 50,$  and  $100$  mA cm<sup>-2</sup>) applied to a commercial DSA® electrode (nominal composition: Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub>) for active-chlorine production to degrade tetracycline hydrochloride (TCH) in a concentration of 20 mg L<sup>-1</sup> in support electrolyte containing Na<sub>2</sub>SO<sub>4</sub> (0.1 mol L<sup>-1</sup>) and NaCl (0.01 mol L<sup>-1</sup>).

## Results and Discussion

The applied current density is very important for EAOP since this variable regulates the amount of oxidized species formed [6].

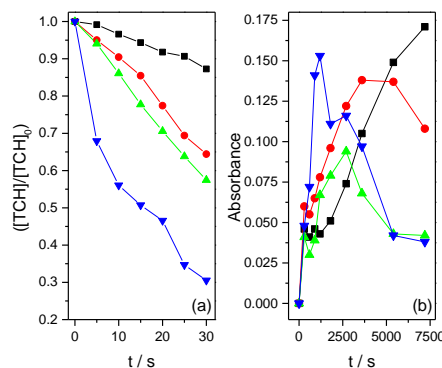


Fig. 1. (a) TCH ( $\lambda_{\max} = 358$  nm) electro-oxidation with different current densities. (b) Byproduct ( $\lambda_{\max} = 290$  nm) rate and degradation. (■) 12.5 mA cm<sup>-2</sup>; (●) 25 mA cm<sup>-2</sup>; (▲) 50 mA cm<sup>-2</sup> and (▼) 100 mA cm<sup>-2</sup>.

As observed in Fig. 1 the increase in the current density improves TCH electro-oxidation, Table 1 presents the apparent kinetic constants for each current density used.

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

$j$ (mA cm <sup>-2</sup> )	Abatement (%)	$k$ (s <sup>-1</sup> )	Energetic consumption (kWh(gTCH) <sup>-1</sup> )
12.5	12.75	0.0046	0.17 x 10 <sup>-3</sup>
25	35.60	0.0150	0.72 x 10 <sup>-3</sup>
50	42.55	0.0188	2.57 x 10 <sup>-3</sup>
100	70.00	0.0363	2.06 x 10 <sup>-2</sup>

The increase in current density improves the CER, consequently, TCH indirect electro-oxidation becomes more efficient, since DSA® is a great electrocatalytic material for active-chlorine species production. TCH degradation majority occurs in the first 30 s for the two highest current densities, while for the other one electro-oxidation occurs more slowly because the rate of CER diminishes, resulting in a soft initial pollutant electro-oxidation [6]. Current density cannot be increased arbitrarily because this parameter may turn the CER into a parasitic reaction, causing a diminution in the efficiency.

As shown in Table 1, the energetic consumption increases as the current density increases, although, the efficiency was maintained. We proceed with the electrolysis until 7,200 s to evaluate, beyond the TCH electro-oxidation as well as the byproduct formation. For all current densities, it was observed a complete TCH disappearance in 300 s and, above this time, a byproduct formation in ~290 nm (Fig. 1(b)), just in 25, 50, and 100 mA cm<sup>-2</sup> there was also degradation of it. This may be because there is the necessity of higher overpotential to also oxidize the byproduct.

### Conclusions

The use of the DSA® electrode is still very promising as combined with NaCl, results presented here showed that the control in current density applied to the anode is outstanding to modulate the formation and degradation of byproducts. Global parameters studied showed that 50 mA cm<sup>-2</sup> is the best current density for TCH electro-oxidation, with 100% TCH degradation after 7,200 s,  $k=0.0188$  s<sup>-1</sup>, and an energetic consumption of 2.57 x 10<sup>-3</sup> kWh(gTCH)<sup>-1</sup>.

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