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Reactive diffusion migration layer and mass transfer wall function to model active chlorine generation in a filter press type electrochemical reactor for organic pollutant degradation

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ABSTRACT

Degradation of organic compounds by active chlorine is a feasible technology for elimination of recalcitrant pollutant discharge into the environment. However, the achievement of a highly efficient treatment system requires the development of well-founded reactor design and scale-up methods. Modeling and simulation can provide description of the complex interrelations of phenomena inside the reactor to analyze their behavior and thus help the development of the desired reactors and treatment systems. Thus, in this paper we propose a comprehensive model for active chlorine generation in a filter press type reactor focused on the mass transport coupled with the kinetics of electrochemical reactions and the electrical potential distribution. Two approaches are used: the reactive diffusion migration layer (RDML) model based on the Nernst-Planck equation in laminar regime and the mass transfer wall function (MTWF) model intended to account for the effect of turbulence induced by the inlet and outlet reactor distributors. It is aimed at acquiring detailed space and time information on relevant operating characteristics inside the reactor such as local efficiency, overpotential distribution along the electrode, zones of high current density, among others. The comparison of model results to experimental data show that the MTWF approach predicts better the behavior of chloride oxidation for active chlorine generation and efficiency at 100 and 200 A m⁻² and 0.8 and 1.6 L min⁻¹ than the RDML model. The predicted generation rate of oxidizing agents allows describing closely the degradation process of Reactive Black 5 as a test system.

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1. Introduction

Electrochemical oxidation is one of the most promising methods for treating effluents contaminated with refractory compounds (Martínez-Huitle and Ferro, 2006; Panizza and Cerisola, 2009; Sirés et al., 2014). In

particular organic pollutants in effluents containing chloride ions are appropriate for degradation by this type of technology since chloride can be used to electrochemically produce active chlorine. The capability of active chlorine to oxidize and degrade different organic compounds has been shown in a number of papers (García-Segura et al., 2018;

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Nomenclature

a_5, a_6, b_5, b_6	Kinetic constants of water reduction and oxidation
A	Empirical constant in wall function
A_λ	Absorbance
A_s	Area of the outlet boundary
C_i	Concentration
C_i^+	Dimensionless concentration
$C_{i,R}$	Concentration integrated over A_s
$C_{i,T}$	Concentration in the recirculation tank
$C_{i,w}$	Electrolyte concentration at the electrode interface
C_μ	Constant of turbulence model
D_i	Diffusion coefficient
$D_{i,T}$	Turbulent diffusion coefficient
E_a	Anodic potential
E_c	Cathodic potential
E_{eq}	Equilibrium potential
F	Faraday constant
J	Current density vector
J_a	Current density at the anode
J_c	Current density at the cathode
$J_{Cl^-,a}$	Current density for chloride oxidation
$J_{ClO_2^-,c}$	Current density for hypochlorite reduction
$J_{ClO_2^-,c,lim}$	Limiting current density for hypochlorite reduction
$J_{H_2O,a}$	Current density for water oxidation
$J_{H_2O,c}$	Current density for water reduction
$J_{i,0}$	Exchange current density
k	Eddy kinetic energy
k_{dye}	Kinetic constant of decolorization reaction
k_1	Kinetic constant of chlorate formation
k_{2f} and k_{2b}	Forward and backward constants for hypochlorous acid dissociation
k_{3f} and k_{3b}	Forward and backward constants for water dissociation
k_A	Decolorization rate constant
k_{COD}	Kinetic constant for oxidation of organics
k_f and k_b	Forward and backward constants for chlorine hydrolysis
N_i	Flux of component i
$N_{i,w}$	Mass transport flux at the electrode
Pc_i	Factor of mass transfer wall function (Eq. (33))
Q	Volumetric flow
R	Universal gas constant
R_{Cl_2}	Reaction rate of chlorine hydrolysis
$R_{ClO_3^-}$	Reaction rate of chlorate formation
R_{COD}	Oxidation rate of organics
R_{H_2O}	Reaction rate of water dissociation
R_{HClO}	Reaction rate of hypochlorous acid dissociation
Sc_i	Schmidt number ($=\mu/\rho D_i$)
Sc_T	Turbulent Schmidt number ($=\mu_T/\rho D_{iT}$)
T	Temperature
t	Time
u	Velocity vector
$u_{m,i}$	Ionic mobility ($=D_i/RT$)
V	Volume of recirculation tank
y^+	Dimensionless wall distance ($y(\tau_w/\rho)^{1/2}/\rho/\mu$)
y	Wall distance or y -coordinate
z_i	Charge on species i

Greek symbols

α_1, α_8	Transfer coefficient for reactions 1 and 8
ϕ	Electrical potential
ϕ_a	Potential at the anode interface
ϕ_c	Potential at the cathode interface
κ	Karman constant
μ	Viscosity
μ_T	Turbulent viscosity
$\nu_{i,j}$	Stoichiometric coefficient
ρ	Density
σ	Conductivity
τ_w	Wall shear stress

Martínez-Huitle and Ferro, 2006; Panizza and Cerisola, 2009; Rajkumar and Kim, 2006; Sirés et al., 2014). Active chlorine formation takes place by electrochemical oxidation of chloride to chlorine and the subsequent hydrolysis of chlorine to form hypochlorous acid, a weak acid that dissociates in water. Active chlorine generated *in situ* is not only composed of hypochlorite ion, chlorine and hypochlorous acid, but also of small amounts of other species produced in secondary reactions during electrolysis, such as: ClO_2 , ClO_2^- and minor amounts of ClO_3^- (Chianca de Moura et al., 2014).

The so-called DSA electrodes, originally developed in the environment of chlorine and caustic soda process, have been frequently used in organic compound degradation. These electrodes formed by a coating of noble metal oxides on a titanium substrate have proved to be adequate for the generation of active chlorine (Chen et al., 2011; Chianca de Moura et al., 2014). The oxidation reaction of chloride to chlorine on DSA electrodes is typically very efficient at high chloride concentrations, reaching efficiencies as high as 99% (Trasatti and Lodi, 1981). However, the decrease in chloride concentration causes the decrease in efficiency (Trasatti and Lodi, 1981) due to parallel competitive reactions, mainly due to the oxygen evolution reaction (OER). At low chloride concentrations, typically present in degradation processes, the effect of chloride concentration on the rate of degradation has been observed (Llanos et al., 2018; Malpass et al., 2007). Several studies have been carried out to prove the capability of active chlorine, generated *in situ* with DSA electrodes, to degrade different types of organic compounds at different conditions of current density, stirring velocity or flow rate, pH and temperature. However, most studies on recalcitrant compound degradation have been performed in laboratory cells under conditions that cannot be scaled up to pilot or industrial reactors. The very few studies reported on the use of reactors with well-defined flow configuration and geometric disposition show that performance parameters depend on the reactor design and operating conditions (Basha et al., 2012, 2010; Ltaïef et al., 2017; Mascia et al., 2012; Rodríguez et al., 2013; Scialdone et al., 2009; Szpyrkowicz and Radaelli, 2006).

Despite obvious advantages of degradation by active chlorine using DSA electrodes, it is still necessary to develop chemical reactor engineering in order to design efficient reactors with optimum energy consumption and high space-time yield that could make this technology feasible for practical application. In this sense, it is important to understand the effect of flow and flow pattern on mass transport of present species and their relation to the current and the potential as well as to main and side reactions. Modeling reactors for organic compound degradation by means of active chlorine is a convenient way to understand these complex relations, but unfortunately it has not been explored enough. In this regard, Mukherjee et al. (2010) reported a simplified model to calculate the potential of an electrochlorination cell with parallel electrodes in the absence of flow. Cheng and Kelsall (2007) developed a model of a plate electrode cell for hypochlorite production by solving Nernst-Planck equations in diffusion layers of both electrodes considering a 100 μm thickness; the components considered were: Na^+ , Cl^- , H^+ , OH^- , ClO^- , $Cl_2(aq)$, O_2 , H_2 and $HClO$. Recently, Spasojević et al. developed a model to predict efficiency in hypochlorite reactors. However, to our knowledge no model has yet been published

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