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Phenomenological behavior coupling hydrodynamics and electrode kinetics in a flow electrochemical reactor. Numerical analysis and experimental validation

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HIGHLIGHTS

- Flow distribution was analyzed by image processing techniques.
- Theoretical model of tertiary current-potential distribution was proposed.
- Methodologies employed evidenced importance of geometric configuration.
- Potential distribution is related intimately with concentration fields.
- Model proposed describe polarization curves within 7%.

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ABSTRACT

Parallel plate electrochemical reactors are frequently used in industry because its high range of applications in several electrochemical processes related with electrosynthesis, environment electrochemistry and energy storage systems. In such sense, the aim of this work is deal with the reaction environment characterization of a parallel plate flow reactor having a net-like spacer, by the employment of original experimental and theoretical techniques in order to evaluate the influence of transport phenomena on overall reactor performance. Flow distribution is analyzed by the use of automatic measurement of flow paths using image processing techniques, based on mathematical morphology theory. On the other hand, a theoretical model of current-potential distribution under intermediate kinetics control (tertiary current-potential distribution) based on numerical solution of turbulent diffusion-convection and binary electrolyte theory is proposed. In this case, concentration at electrode surface was determined in terms of dimensionless Damkhöler number, obtained from a mass balance at electrode-electrolyte interface in steady state. RTD curves obtained by image processing techniques describes correctly the fluid dynamics behavior in electrochemical reactor. Meanwhile, correspondence between calculated and experimental polarization curves using the oxidation of chloride ions to chlorine as model electrochemical reaction was made with an error values lesser than 7%, indicating a good agreement between theoretical model and experimental tests. Results founded in the parallel plate flow electrochemical reactor used here, evidenced that the methodology proposed to analyze the hydrodynamic and electrochemical behavior are adequate to its use in other electrochemical devices, particularly, when they work under intermediate kinetic and limiting current conditions.

1. Introduction

Electrochemical reactors have gained relevance since these kind of units are useful in the field of specialized chemicals electrosynthesis [1], energy sources like electrolyzers for hydrogen production, fuel cells [2,3], waste treatment of several industries [4] and even in the novel energy production process as the design of microbial electrolytic cell for biofuels production and redox flow cell for energy storage [5–7].

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In this way, parallel plate electrochemical reactors configurations are frequently used in industry because of its high range of applications in several electrochemical processes considering operation under undivided and membrane divided mode. Examples of some commercial multipurpose flow electrochemical reactors designs are Electrosyn AB [8], FM01-LC [9], Diacell [10], Asahi Glass CH-0 [11] among others.

Since the reactor performance depends on geometry of electrode, nature of electrochemical reactions and flow channel design, the influence of such aspects in phenomenological behavior must be studied deeply. For accomplish this task, the use experimental characterization techniques and computational analysis are needed in order to understand the effect of several design parameters. It is an important issue of study on electrochemical engineering, since these techniques allow evaluating the influence of several design parameters on hydrodynamics, mass transport and potential distributions inside the electrochemical reactor (known as electrochemical reaction environment characterization) [12].

Generally, reaction environment characterization is a sequential study. In first instance, characterization of flow distribution inside of reactor are carried out by means of residence time distribution tests using impulse-response techniques and it can be accompanied with the use computational fluid dynamics (CFD). Calculations obtained considering CFD techniques allow us to predict residence time distribution of a particular tracer, based in numerical solution of Navier-Stokes (NS) equations for laminar flow or Reynolds Average Navier Stokes (RANS) based in two equation models for turbulent flow [13].

Once hydrodynamic studies have been accomplished, experimental and theoretical studies of mass transport rate can be performed in order to elucidate the overall reactor behavior. This could be realized by means of local and global mass transport coefficients calculation and the determination of current-potential distributions under intermediate kinetic and fully limited by mass transport (limiting current density conditions).

The reaction environment characterization studies, generally are focused to obtain best design and operational conditions during an electrolytic process. For example, it is well known that the performance of these kind of electrochemical reactors strongly depends on the uniformity of their fluid distribution and its mass transport [14,15]. In this way, some experimental and theoretical studies have been conducted, in order to design specialized inlet geometries at flow channels to obtain a homogenous flow distribution [16,17] with different performance results. In addition, one of the most used experimental approaches for homogenizing flow pattern during electrochemical reactor studies at laboratory and pre-pilot scale, is the attachment of plastic net-like meshes as spacers inside of reactor flow channels, producing an enhancement of mass transport rate [18] due to an increment of contact between electrolytic fluid phase and electrode area.

Most of experimental and theoretical studies have been conducted on the hydrodynamic pattern determination inside of electrochemical reactors, using typical stimulus-response (Residence time distribution, RTD) technique. For construction of this plots, indirect concentration measurements achievements are needed, hereafter, such measurements techniques involving the propagation of experimental error. For this reasons, original methods for obtaining direct measurements of stimulus-response experiments must be developed.

On the other hand, examples of experimental mass transport studies are ample [15,16,19] since mass transport coefficients and dimensionless correlations with characteristic fluid velocity are important parameters for scale-up studies. In the field of mass transport calculations by computational techniques, some works have been focused to compare successfully the mass transport flux distribution with dimensionless correlations [16].

Additionally, reports concern to the study of potential and current distribution under intermediate kinetics control are scarce [20], since such study require numerical solutions of complex mathematical expressions associated with impossibility, at first instance, to the knowing of interfacial concentration at electrode surface. In order to overcome this challenge, some methodologies have been proposed. For example, Rivero et al. [20] recently suggest a simultaneous solution of algebraic and differential partial equations system generated from mathematical approaching of tertiary current distribution during Cu(II) ions electrochemical reduction at cathode of a flow electrochemical reactor. Boovaragavan et al. [21] proposed a semi-analytical method for 1D electrochemical systems to solve tertiary current distribution assuming that surface concentration can be written in terms of a power series and its coefficients are calculated by means of an iterative process. On the other hand, Low et al. [22] have been solve this problem using an initial guess value of concentration at electrode surface to implement a successive substitution process in order to find consistent surface concentration values during numerical solution of differential partial equations.

In such sense, the aim of this work is deal with the reaction environment characterization of a parallel plate flow reactor (based in prototype used in reference [18]) employing a net-like spacer, by means of novel theoretical and experimental analysis techniques in order to evaluate the influence of transport phenomena in overall reactor performance. Flow distribution is analyzed by the use of automatic measurement of flow paths using image processing techniques, based on mathematical morphology theory.

On the other hand, a theoretical model of current-potential distribution under intermediate kinetics control (tertiary current-potential distribution) based on numerical solution of turbulent mass transport equations and binary electrolyte theory is proposed. In this case, concentration at electrode surface is calculated in terms of dimensionless Damkhöler number and effectiveness factor, obtained from a mass balance at electrode-electrolyte interface in steady state. Numerical solution of this model, allowed calculation of theoretical polarization curves (current-overpotential relationship) and it was compared with experimental ones obtained during anodic chlorine electrogeneration from a sodium chloride electrolytic solution, operating at moderate cell potentials (low anodic overpotentials).

2. Experimental

2.1. Description of parallel plate reactor

Fig. 1 shows a scheme of the parallel plate reactor, used in this work. A plastic spacer mesh made of polypropylene are showed as inset in Fig. 1. Detailed of general and dimensional characteristics of parallel plate reactor prototype and net-like spacer used in this work are available in [18]. It is important to point out that only one piece of plastic mesh was employed to fill the flow channel and it occupied the available space avoiding bulk flow bypassing.

Experimental tracer tests were filmed by a high-resolution camera and were used to construct RTD curves by means of an image processing code designed to capture differences of tracer color intensity as a function of local velocity through reactor. These tests were compared with theoretical tracer experiments obtained by means of numerical simulation.

For experimental polarization curves in chloride solution, a DSA anode based on RuO_2/TiO_2 formulation was implemented, meanwhile a stainless steel sheet was used as cathodic material.

2.2. Tracer visualization (TV)

In order to visualize and process the experimental flow patterns inside the parallel plate reactor by means of mathematical morphology techniques, 1 mL of colored tracer (food grade colorant Carmine 50 at a concentration of 1 g L^{-1}) was injected at 1.5 cm before the reactor inlet. To visualize the flow inside the channel of the filter press electrolyzer, a transparent frame was constructed from polycarbonate sheet. The inner frame and spacers were clamped between two windows or outer frames.