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Mass transfer modeling and simulation at a rotating cylinder electrode (RCE) reactor under turbulent flow for copper recovery

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ABSTRACT

This work presents the numerical simulation of a laboratory reactor with rotating cylinder electrode (RCE) and a six-plate counter electrode that is used in studies on heavy metal recovery. The rate of electrode rotation and the potential applied are of such magnitude that the electrochemical reactor works in conditions of mass transport control under turbulent flow to obtain high recovery rates and formation of dendritic metal deposits. For hydrodynamics, the Reynolds averaged Navier–Stokes (RANS) equations were solved using the standard k–ε turbulence model, as well as wall functions based on the universal velocity distribution in the near-wall region. Results of 3-D simulations of the velocity field show clearly the formation of the turbulence Taylor vortex flow. For mass transfer, convection–diffusion equation was solved using the Kays–Crawford model for turbulent Schmidt number and Launder–Spalding wall functions adapted for mass transfer. Kinetics of copper recovery from aqueous solutions containing 0.019 M $CuSO_4$ and 1 M H_2SO_4, in the range of rotation speed of 400–1100 rpm, was adequately fit (error $<8\%$) during the electrolysis time to achieve a final recovery of 85% for potentiostatic and 60% for galvanostatic experiments. The fitting parameter of the concentration wall function used in all experiments was A=2.9.

1. Introduction

Electrochemical recovery of heavy metals from wastewaters is a very attractive way to treat polluted effluents (Bazan and Bisang, 2004; Giannopoulou and Panias, 2008; Grau and Bisang, 2007; Hunson et al., 2005; Koene and Janssen, 2001; Rivera et al., 2008). In particular, rinse bath waters of electroplating industry are adequate for this treatment (Rivera et al., 2008). The advantage of this technology is that it cleans waters, recovers metals and recirculates part of the water to the process without requiring the addition of chemicals or generating solid residues, as occurs with other methods, e.g., flocculation that forms hydroxides of the corresponding metals. The reactor with rotating cylinder electrode (RCE) has proved to be an efficient device for this task (Gabe et al., 1998; Rivera et al., 2008). One very important, distinctive characteristic of RCE is homogeneity of the shear stress and current density at the electrode surface, which allows the control over the mass transfer rate and the type of deposit formed. Any small variation of current density – caused, for example, by the use of plate counter electrodes placed around RCE as in the reactor studied herein – is averaged out by the fast movement of the electrode.

In metal recovery, it is very important to be able to form deposits with dendrite-like pattern loosely adhered to the electrode surface that make metal removal easier either by the movement of the electrode itself or with a help of a scraper. This is achieved by maintaining a high deposition velocity under conditions of potential, where the process is controlled by the mass transfer rate. Dendrite-like deposit has an additional advantage in that it improves mass transfer by increasing the effective area and by promoting greater turbulence due to higher roughness of the cathode surface (Barkey et al., 1989; Kappesser et al., 1971). Under practical operating conditions of the reactor, with electrolysis controlled by mass transfer in turbulent flow, the electrodeposition rate is directly related to the reactor hydrodynamics.

Although the RCE has been broadly investigated and there is a considerable amount of published papers and different reviews (Gabe et al., 1998; Low et al., 2005) that give an account of it, the mechanism of mass transfer under turbulent flow has not been studied enough. Since Eisenberg et al. (1954) published their recognized study on mass transfer at rotating cylinders, this issue has been approached by using overall mass transfer coefficients with empirical correlations of the type: $Sh=f(Re,Sc,Le)$. However,

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when transport mechanisms occurring along the mass transfer path from the bulk to the electrode surface (i.e., in the turbulent region, buffer zone and the so-called viscous sublayer) are taken into account, the approach based on overall coefficients is no longer sufficient since it only represents the mass transport phenomenon averaged in the whole reactor.

With regard to modeling and simulation works on mass transfer at RCE reactors, these have been performed in 2-D under laminar flow (Mandin et al., 2006) or using either overall mass transfer coefficient approach or its equivalent diffusion layer thickness ($=D_i/k_m$) (Lee and Talbot, 2007; Low et al., 2007) in the case of turbulent flow. In these studies, the effect of hydrodynamics (for instance, Taylor vortices) on the mass transfer rate cannot be observed, except the overall effect of the rotation speed of the cylinder. So, it is strongly necessary to investigate by simulation the mechanism of mass transport under turbulent flow and the effects of hydrodynamics on it. Therefore, the aim of the present work is to perform a more realistic 3-D simulation of the RCE reactor under turbulent flow in order to establish the relationship between hydrodynamics and the mass transport rate.

2. Experimental

Galvanostatic and potentiostatic electrolysis of Cu(II) were carried out at a laboratory RCE reactor shown in Fig. 1. The 0.085 m diameter reactor consists of an inner rotating cylinder of 0.038 m diameter and six 0.02 m × 0.13 m plates anchored to the inner wall of the reactor. The inner cylinder, 0.11 m high and built of stainless steel 316 was used as cathode and the RuO_2/TiO_2 DSA plates were employed as anode. The area of electrodes in contact with solution was 0.008 m^2 for the cathode and 0.0084 m^2 for the anode. A Caframo model BDC3030 motor of variable velocity was used to propel the RCE. A potentiostat–galvanostat EG&G model PAR 273 coupled to a Kepco^{TM} power supply of 10 A and 20 V capacity, with M270 software, was used. The Cu(II) concentrations were determined employing a Varian^{TM} Atomic Absorption Spectrophotometer Model 220FS. In the case of electrolysis with galvanostatic control, current density was set at the limit current density value (J_L) calculated with Eq. (1), which was previously obtained from experimental mass transfer coefficients (Rivera et al., 2008; Rivera and Nava, 2007):

$$J_L = 0.014\frac{z_i F D_i C_{i,0}}{d} Re^{0.91}\, Sc^{0.356} \tag{1}$$

where z_i is the number of electrons exchanged in the electrochemical reaction, F the Faraday constant (96,485 C mol^{-1}), D_i the diffusion coefficient, $C_{i,0}$ the initial concentration of the electroactive species in the bulk fluid in mol m^{-3}, d the cylinder diameter, Re the Reynolds number ($dv\rho/\mu$) and Sc is the Schmidt number ($\mu/(\rho D_i)$). Eq. (1) was obtained in the same RCE reactor with six plate anodes used in this paper.

Electrolyte solution was prepared with Milli-Q deionized water and analytical reagents at a concentration of 18.8 mM $CuSO_4$ and 1 M H_2SO_4.

3. Mathematical model and simulation

After increasing the Taylor number ($\upsilon^2(d_o-d)^3\rho^2/(4\mu^2 d)$) (Newman, 1991), hydrodynamic behavior occurring between an inner rotating cylinder and a fixed external cylinder passes through the following flow stages: simple laminar Couette flow, formation of Taylor vortices under laminar flow and turbulent Taylor vortex flow. In this latter case, the contribution of vortices to the velocity field decreases as the velocity increases. For simple laminar Couette flow, there is a known analytical solution for tangential velocity. For Taylor vortices under laminar flow, hydrodynamic behavior has been simulated by solving Navier–Stokes equations using finite elements (Granados et al., 2009). In the case of interest in this work, the hydrodynamics in turbulent flow can be simulated using different techniques (Bernard and Wallace, 2002), although the use of turbulence models is still an effective and practical tool to approach this kind of problems (Bernard and Wallace, 2002; Eça and Hoekstra, 2009; Lacasse et al., 2004; Trujillo et al., 2009). One of the difficulties of using this approach is the presence of solid walls, since turbulence models are not applicable in the proximity of the wall. One way to solve this problem is by using the so-called wall functions (Bernard and Wallace, 2002; Eça and Hoekstra, 2009; Lacasse et al., 2004). These functions are based on the universal velocity distribution in the boundary layer for flow inside tubes and over flat plates. In the case of curved surfaces such as RCE, where the

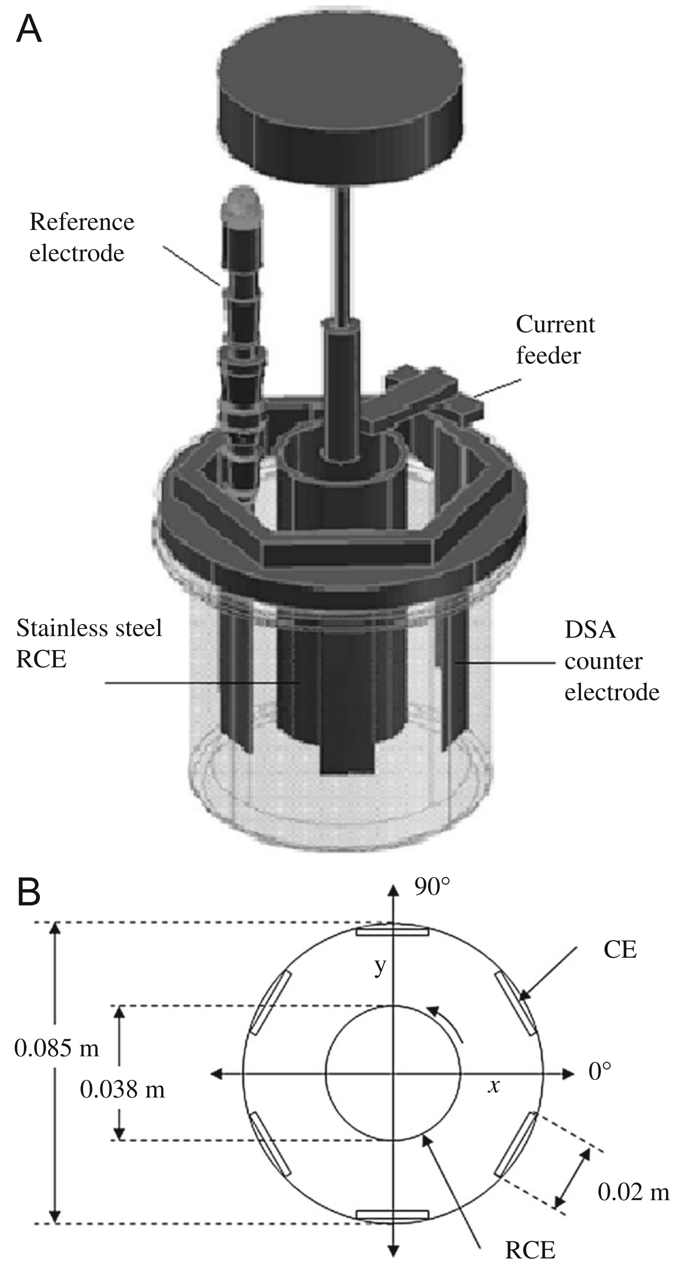

Fig. 1. (A) Rotating cylinder electrode reactor. (B) Dimensions of the reactor and distribution of electrodes.