Int. J. Electrochem. Sci., 7 **(2012)** 1386 - 1401

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

CFD Modeling of Continuous Stirred Tank Electrochemical Reactor

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Received: 18 November 2011 / *Accepted:* 29 December 2011 / *Published:* 1 February 2012

Electrochemical reactors play an important role in electrochemical industries as they directly involve in achieving higher conversion and current efficiency for the desired reaction. The continuous stirred-tank electrochemical reactor (CSTER) is extensively used in electrochemical industries for various applications. The flow behavior of electrolyte in a continuous stirred tank electrochemical reactor [CSTER] has been experimented using Residence Time Distribution (RTD) studies. Experiments were carried out using pulse tracer technique and the exit age distribution curves for various operating conditions have been critically analyzed. A two-dimensional flow model was developed to visualize the electrolyte flow behavior inside the CSTER using Computational Fluid Dynamics (CFD). GAMBIT, Geometry and mesh generation software has been used as pre-processor and computational grid domain was generated with appropriate boundary conditions. Navier-Stoke's equations were used to estimate the electrolyte flow. The influence of electrolyte flow rate, stirrer speed on electrolyte flow behavior was critically examined.

Keywords: Continuous stirred tank electrochemical reactor, Modeling, Computational fluid dynamics, Residence Time Distribution

1. INTRODUCTION

In electrochemical technique, electron is used to degrade all the organics present in the effluent without generating any secondary pollutant or bi-product/sludge. The advantage of electrochemical technique is high removal efficiencies and has lower temperature requirements compared to non-

electrochemical treatment. In addition to the operating parameters, the pollutant degradation rate depends on the anode material. When electrochemical reactors operate at high cell potential, the anodic process occurs in the potential region of water discharge, hydroxyl radicals are generated. On the other hand, if chloride is present in the electrolyte, an indirect oxidation via active chlorine can be operative; this technique has been successfully adopted for treatment of several industrial effluents. In our earlier investigations electrooxidation has been tested for different industrial effluent using oxide coated electrodes [1-4]. Various electrochemical reactors used in electrochemical industries ranging from conventional plate to advanced electrodes three-dimensional electrodes. Since the reactor geometry plays an important role in the process yield, the design/selection becomes important in electrochemical process [5, 6]. Continuous Stirred Tank Electrochemical Reactor (CSTER) is one such reactor extensively used in electrochemical industries [Figure.1].

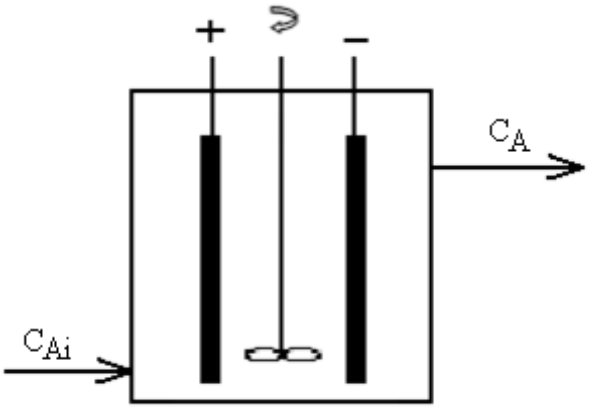


Figure 1. Representation of Continuous Stirred Tank Electrochemical Reactor [CSTER]

A CSTER consists of a reactor equipped with anode, cathode and a stirrer. The design and scale-up of continuous stirred tank electrochemical and the quantification of electrolyte flow in them have been traditionally tackled by developing empirical design equations mainly due to the complexity of the fluid dynamics of mixing [7]. Although this approach has proven to be satisfactory for many applications, it is rather limited because it neglects the complexity of flow in most mixing applications. Polcaro *et al.,* [8] experimented water disinfection in a stirred tank electrochemical reactor using boron doped diamond electrode and developed a model for E(t) distribution for a pulse input considering two CSTRs in parallel. In our earlier investigations [9-11], we have developed three parameter and three thanks series models to describe the flow characteristic in a continuous electrochemical reactor. In the present paper, it is attempted to extend our model with CFD simulations to gain better understanding of flow behavior, which is essential for equipment design and selection.

2. COMPUTATIONAL FLUID DYNAMICS

Computational fluid dynamics (CFD) provides a tool for determining detailed information on fluid flow (hydrodynamics), gives better understanding of flow behavior in the process, which is essential for equipment design and selection. Traditional restrictions in flow analysis and design limit the accuracy in solving and visualization of fluid-flow problems is particular three dimensional in nature involve turbulence, chemical reactions, and/or heat and mass transfer. All these can be considered together in the application of Computational Fluid Dynamics, a powerful technique that can help to overcome many of the restrictions influencing traditional analysis. CFD modeling provides a good description of flow field variables, velocities, temperatures, or a mass concentration anywhere in the region with details not usually available through physical modeling. CFD codes contain three main elements: (i) a pre-processor, (ii) a solver, (iii) a post-processor. Good amount of work has been reported on CFD based modeling continuous stirrer tank reactors. Spinla *et al.*, [7] studied solid particle distribution in a stirred vessel using conductivity measurements and results are validated with Computational Fluid Dynamics predictions and concluded a good agreement with simulations and experimental data. Alessandro Serra *et al.*, [12] studied turbulent flow in a CSTR using time-dependent finite-volume simulations and quantitatively compared the numerical results with experimental results and CFD predictions. *Alberto Brucato et al.,* [13] studied a mixing sensitive process consisting of two parallel reactions in stirred tank reactor using Computational Fluid Dynamics and validated with experimental results and found a good agreement between experimental and Computational Fluid Dynamics simulations. In the present study electrolyte flow behavior in a continuous stirred tank reactor is studied using CFD. Experiments were conducted using tracer technique. Experimental results are compared with Computational Fluid Dynamics simulations. The commercial CFD package, FLUENT 6.3 (FLUENT Inc., 2006) was used for all CFD modeling.

3. CONTINUOUS STIRRED TANK ELECTROCHEMICAL REACTOR

Let us consider a typical continuous stirred tank electrochemical reactor [CSTER] as shown in Figure 1. The material balance for CSTER can be written as

$$Q(C_{Ai} - C_A) = \frac{iA}{nF} \tag{1}$$

Where A is surface area of the electrode and C_{Ai}, C_A is the initial and final concentrations. The above equation can be written in term of residence time as

$$C_{Ai} - C_A = \frac{\sigma \tau i}{nF} \tag{2}$$

Where σ refers the interfacial area of the electrode and τ represents the residence time. It is defined a surface area of electrode per unit volume. The electrode kinetics is assumed to follow Butler-Volmer type equations, i.e.

$$\frac{i}{nF} = k_{f1}C_A^S - k_{b1}C_B^S \tag{3}$$

Where k_{f1} and k_{b1} represent the reaction rate constants for forward and reverse reactions respectively and C_A^S,C_B^S. The current density can be expressed in terms of the mass transport A for steady state operation as

$$\frac{i}{nF} = k_{LA}(C_A - C_A^S) \tag{4}$$

Where k_{LA} represents the mass transfer coefficient of A. Equation (3) can be written as for Tafel reaction is

$$\frac{i}{nF} = k_{f1}C_A^S \tag{5}$$

Combining the equation (4) and (5) the surface concentration can be eliminated resulting surface concentration in terms of bulk concentration, i.e.

$$\frac{i}{nF} = \frac{k_{f1}C_A}{1+\frac{k_{f1}}{k_{LA}}} \tag{6}$$

Substituting equation (6) in equation (2) and the rearranging the equation results

$$C_{Ai} - C_A = \sigma\tau \frac{k_{f1}C_A}{(1+D_{a1})} \tag{7}$$

The above equation can be rearranged as

$$\frac{C_A}{C_{Ai}} = \frac{1}{1+\frac{\sigma\tau k_{f1}}{1+D_{a1}}} \tag{8}$$

The equation (8) represents the conversion equation for a continuous stirred tank electrochemical reactor. The electrolyte residence time distribution can be represented by exit age distribution curve E(t). At any point of time, the electrolyte spent a time between t and (t + dt) in the reactor, represented by E(t)dt, i.e.

$$\int_0^\infty E(t)dt = 1.0 \tag{9}$$

The exit age distribution E(t) can be calculated for pulse tracer output using the following equation.

$$E(t) = \frac{c(t)}{\int_0^\infty c(t)dt} \tag{10}$$

Where c(t) represent the exit tracer concentration at time 't'. While the mean residence time can be calculated as

$$\tau = \int_0^\infty tE(t)dt \tag{11}$$

The integral under the denominator is the area under the C curve. For an ideal continuous stirred tank reactor, the exit age distribution for an ideal reactor can be given as

$$E(t) = \frac{e^{\frac{-t}{\tau}}}{\tau} \tag{12}$$

4. EXPERIMENTAL

The experimental consists of a glass beaker of 300 ml capacity with PVC lid having provision for anode and cathode. RuO_2/Ti and Stainless Steel sheet of 6.5x5cm^2 were used as anode and cathode respectively [14]. The uniform electrolyte concentration inside the reactor is maintained with the help of magnetic stirrer. Experiments were conducted to study the flow behavior of electrolyte in a continuous stirred tank electrochemical reactor without electrochemical reaction with water as electrolyte. Electrolyte flow rate was adjusted using a throat valve and the samples were collected for analysis of color removal at steady state. The RTD was determined experimentally by injecting a 10 ml

volume of 1000ppm Acid Red 88 dye solution into the tank at time zero. The samples were collected periodically at the outlet of the reactor and analyzed using colorimeter.

5. RESULTS AND DISCUSSION

5.1. CFD simulations

CFD simulations have been executed for the CSTER system using a commercial code FLUENT 6.3 by Fluent Inc. The main aim of the performed studies was an elaboration of robust and efficient CFD models and their verification with experimental data. A 2-Dimensional computational grid domain model has been generated for CSTER using Gambit software with appropriate boundary conditions. The computational grid domain model for CSTER is shown in Figure 2.

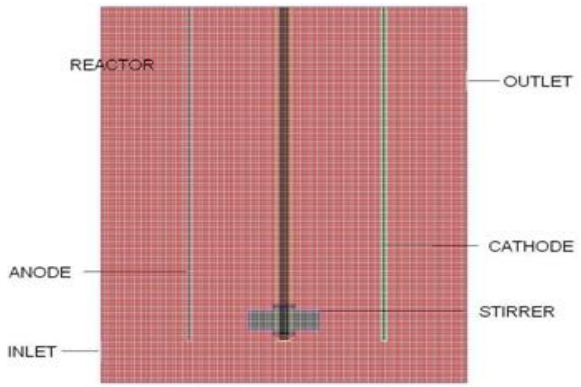


Figure 2. Computational grid domain generated for CSTER

Table 1. Dimensions of computational grid domain

S.No	dimension	Value (m)
1	Reactor diameter	0.075
2	Reactor height	0.09
3	Baffle length	0.07
4	Baffle width	0.03
5	Stirrer diameter	0.005
6	Stirrer height	0.08
7	Inlet/ outlet pipe diameter	0.005
8	Distance between baffles	0.04
9	Rotating blade width	0.015
10	Rotating blade height	0.005

The boundary conditions for shaft and rotating blades have considered as moving mesh and the reactor wall has been assumed to be fixed wall with no slip. A perfect mixing assumed i.e., a single point temperature measurement fully represents the state of reactor—this is a situation met in the used experimental set-up. The Table 1 shows the dimensions of computational grid domain. The governing equations are

Continuity equation

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0 \tag{13}$$

Momentum equation

$$\rho\frac{\partial u_x}{\partial t} + \rho\left[\frac{\partial (u_x^2)}{\partial x} + \frac{\partial (u_x u_y)}{\partial y}\right] = -\frac{\partial P}{\partial x} + \mu\left[\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2}\right] \tag{14}$$

$$\rho\frac{\partial u_y}{\partial t} + \rho\left[\frac{\partial (u_y^2)}{\partial y} + \frac{\partial (u_x u_y)}{\partial x}\right] = -\frac{\partial P}{\partial y} + \mu\left[\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2}\right] \tag{15}$$

Tracer transport equation

$$\frac{\partial C}{\partial t} + \frac{\partial (u_x C)}{\partial x} + \frac{\partial (u_y C)}{\partial y} = D\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right] + S(C) \tag{16}$$

Where:

S(C) = 0 (transport of tracer by convective diffusion without reaction)

S(C) = -KC (for first order irreversible reaction)

User Defined Functions (UDFs) have used for tracer which has similar properties as water and linked to the FLUENT. Flow characteristics are studied under various operating conditions [Table 2].

Table 2. The CSTER process conditions used in simulations

S.No	parameters	Value
1	Water flow rate ($mlmin^{-1}$)	35, 75,100
2	Stirrer speed (rpm)	0, 25, 50, 75,100
3	Tracer mass flow (mg/injection)	1

The reactor is assumed to be filled with water and the tracer is injected as pulse at time t = 0 after the reactor attaining steady state.

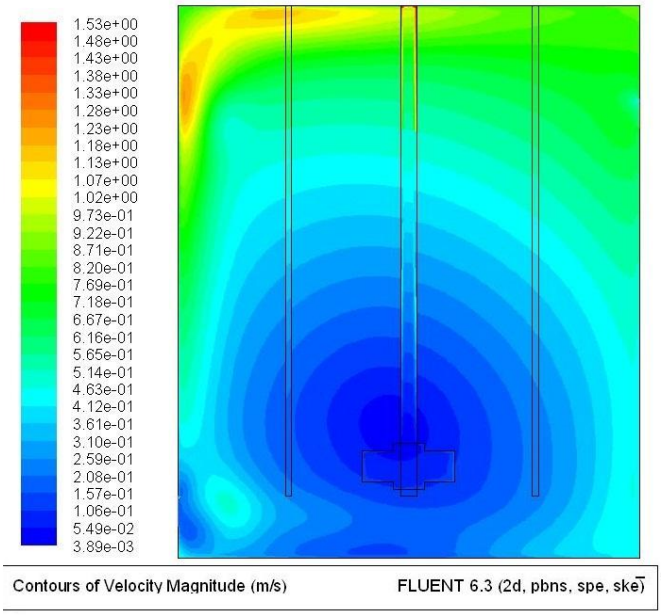


Figure 3. Contours of velocity magnitude of electrolyte in CSTER

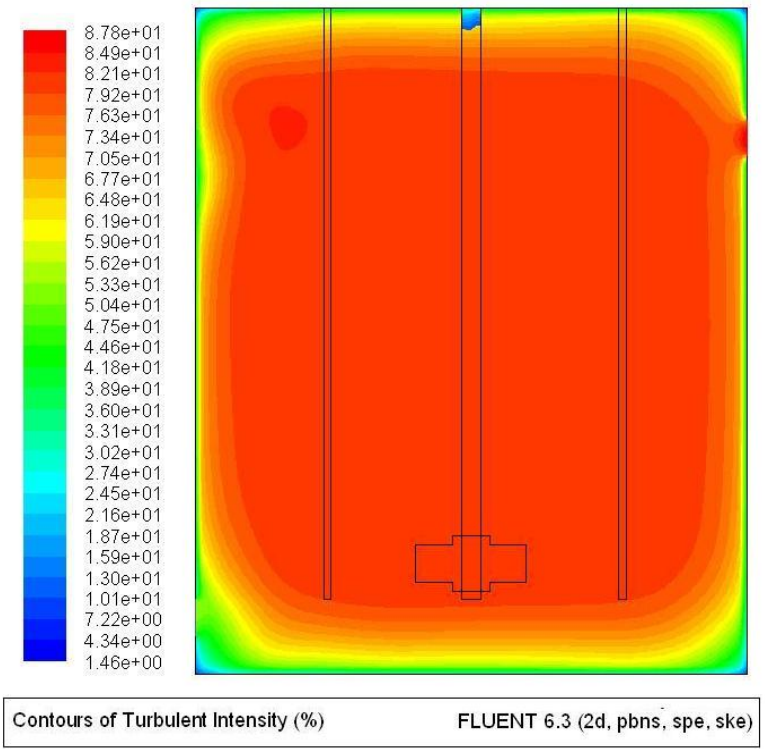
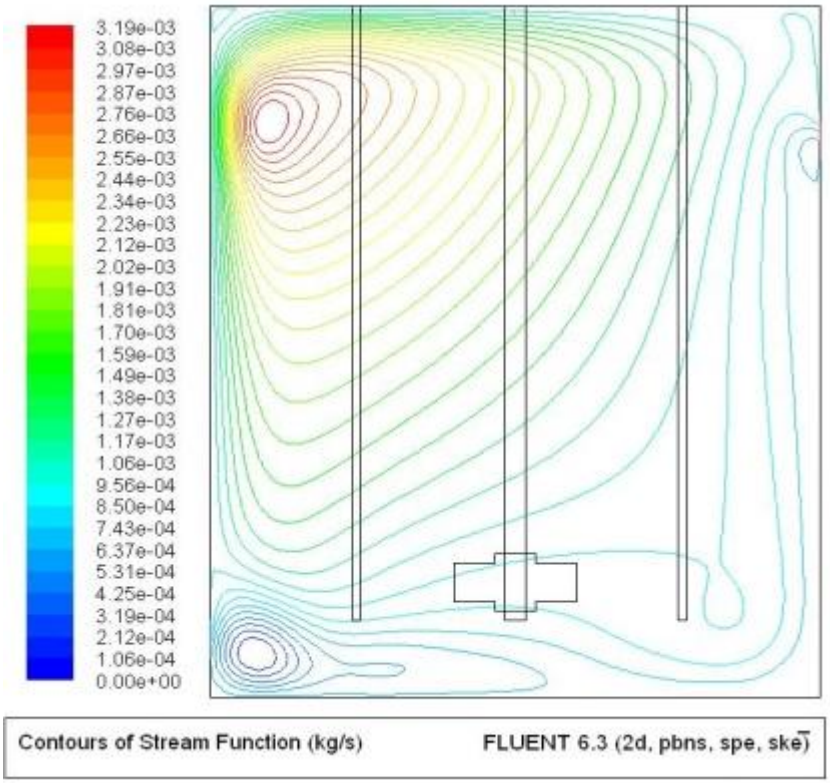


Figure 4. Contours of turbulent intensity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2.97e-03
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2.23e-03
2.12e-03
2.02e-03
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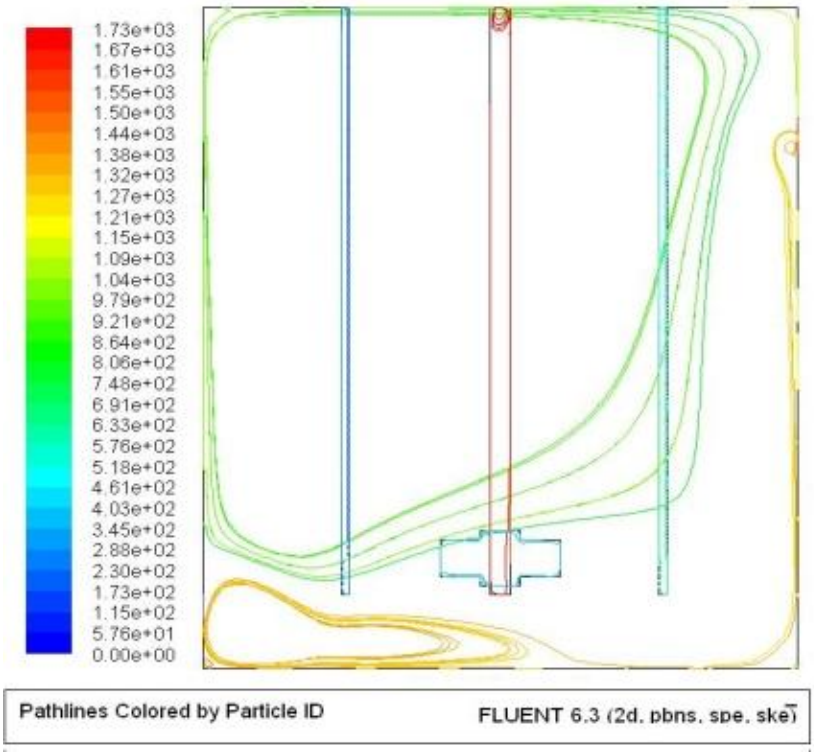
1.38e-03
1.27e-03
1.17e-03
1.06e-03
9.56e-04
8.50e-04
7.43e-04
6.37e-04
5.31e-04
4.25e-04
3.19e-04
2.12e-04
1.06e-04
0.00e+00
Contours of Stream Function (kg/s)
FLUENT 6.3 (2d, pbns, spe, ske)

A1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1.15e+03
1.09e+03
1.04e+03
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9.21e+02
8.64e+02
8.06e+02
7.48e+02
6.91e+02
6.33e+02
5.76e+02
5.18e+02
4.61e+02
4.03e+02
3.45e+02
2.88e+02
2.30e+02
1.73e+02
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5.76e+01
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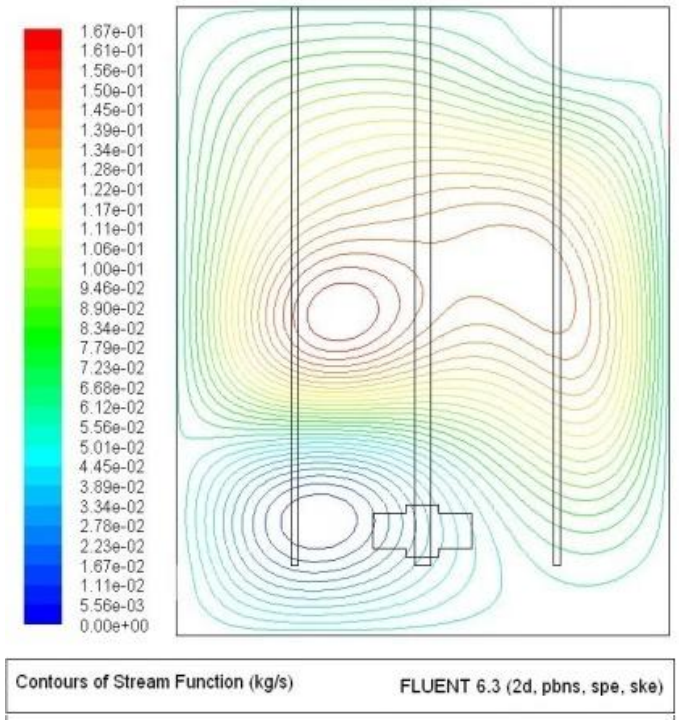
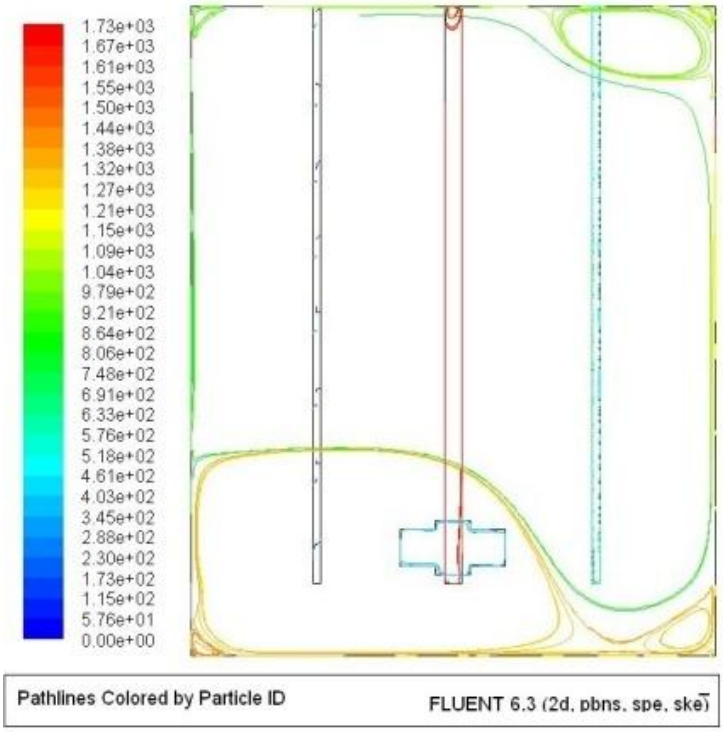
Pathlines Colored by Particle ID
FLUENT 6.3 (2d, pbns, spe, ske)

A2

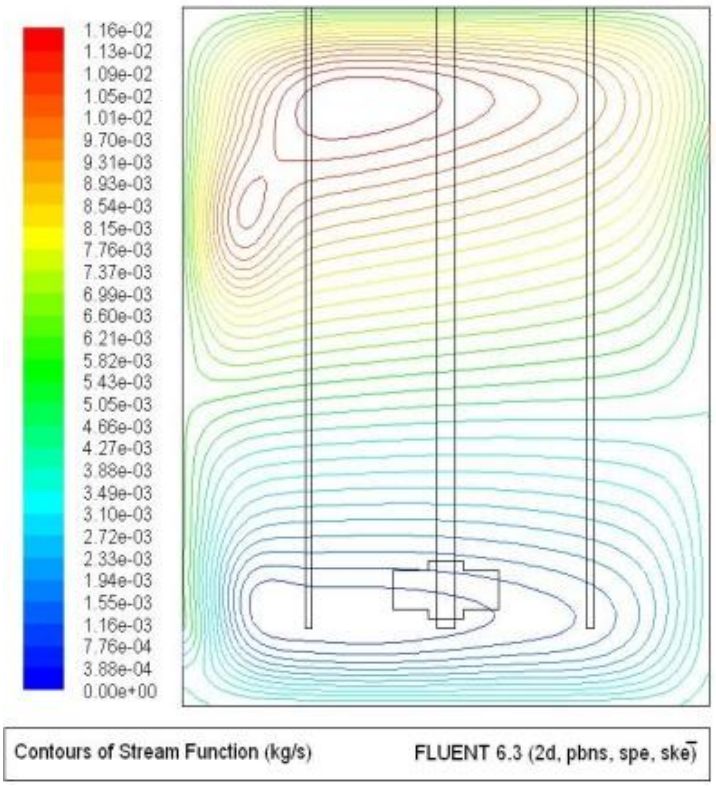


B1



B2

Figure 5. Steady state contours of stream function (A1, B1) and corresponding tracer (A2, B2) path lines in the CSTER: Stirrer speed: 100 rpm; Electrolyte flow rate: (A1,A2) 35 ml min^{-1}; (B1,B2) 75ml min^{-1}: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1.16e-03
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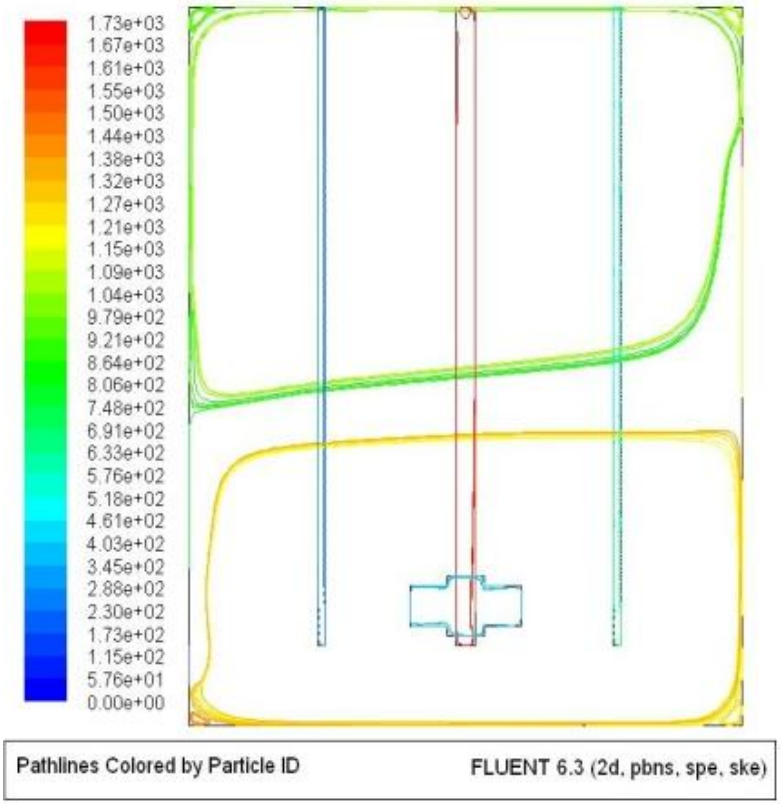
Contours of Stream Function (kg/s)
FLUENT 6.3 (2d, pbns, spe, ske)

A1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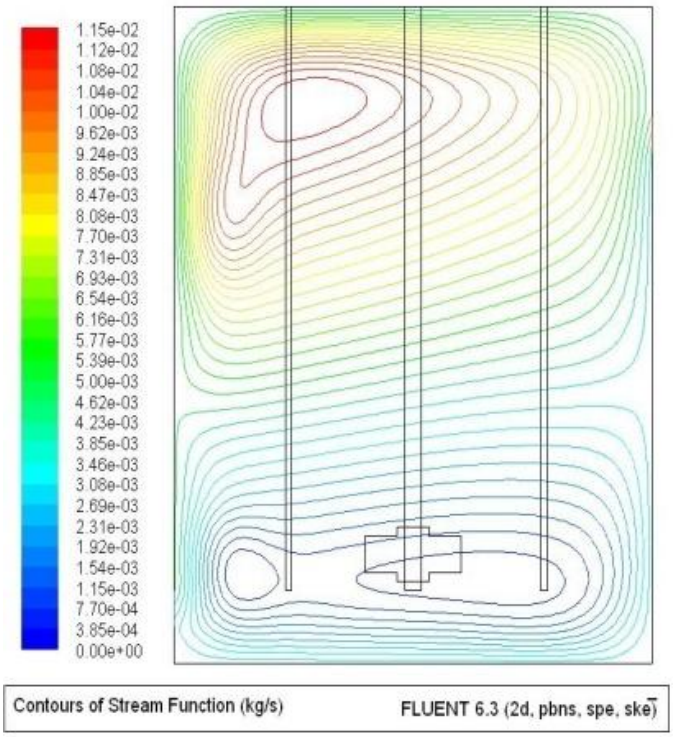
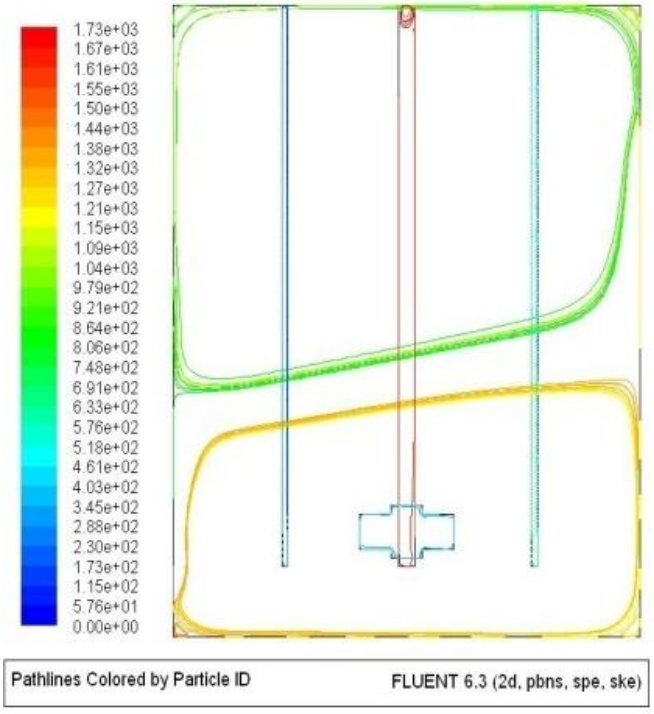
1.21e+03
1.15e+03
1.09e+03
1.04e+03
9.79e+02
9.21e+02
8.64e+02
8.06e+02
7.48e+02
6.91e+02
6.33e+02
5.76e+02
5.18e+02
4.61e+02
4.03e+02
3.45e+02
2.88e+02
2.30e+02
1.73e+02
1.15e+02
5.76e+01
0.00e+00
Pathlines Colored by Particle ID
FLUENT 6.3 (2d, pbns, spe, ske)

A2



B1



B2

Figure 6. Steady state contours of stream function (A1, B1) and corresponding tracer (B1,B2) path lines in CSTER; Electrolyte flow rate: 75 ml min^{-1}; stirrer speed (A1,A2): 50rpm, (B1,B2): 100rpm

A spatial distribution of the local liquid velocity obtained CFD hydrodynamic model is shown in Figure 3. It can be noticed from the figure that, at close vicinity of the stirrer shaft and at the upper part of the reactor vessel, zones of relatively poor mixing can be distinguished. As it has been mentioned above, local values of liquid velocity taken from a close neighborhood of the propeller stirrer have been implemented into the CFD model.

The Figure 4 shows the turbulent intensity inside the CSTER. It can be ascertained from the figure that a recirculation zone forms above the reactor inlet at low electrolyte flow rate which a stagnant zone. Noticed that this region increased with an increase in the electrolyte flow rate, lower the velocities smaller the stagnant region and more curved streamlines. The influence of electrolyte inlet flow rate on tracer path lines for different flow rates is shown in Figure 5. It can be noticed from the figure that an increase in the electrolyte flow rate decreases the path length of tracer and thus residence time.

The Figure 6 shows steady state plots of streamlines and tracer path lines in CSTER for various stirrer speeds. For a given stirrer speed, it is evident the formation of a recirculation zone above the entrance of the reactor, suggesting the formation of stagnant region. It can be ascertained from the figure that the importance of such regions increases with increase in stirrer speed. Lower the stirrer speeds leads to smaller stagnant regions and more curved streamlines. The tracer path lengths are decreasing with increase in stirrer speed.

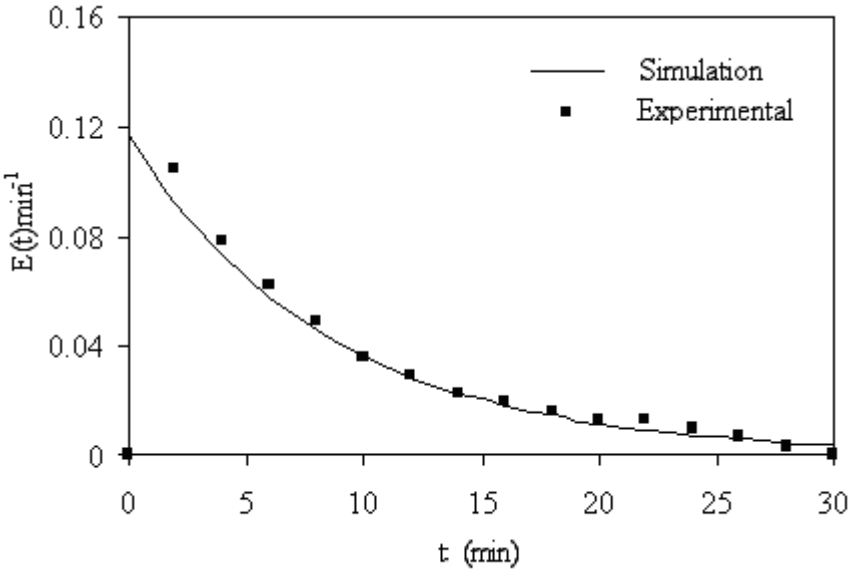
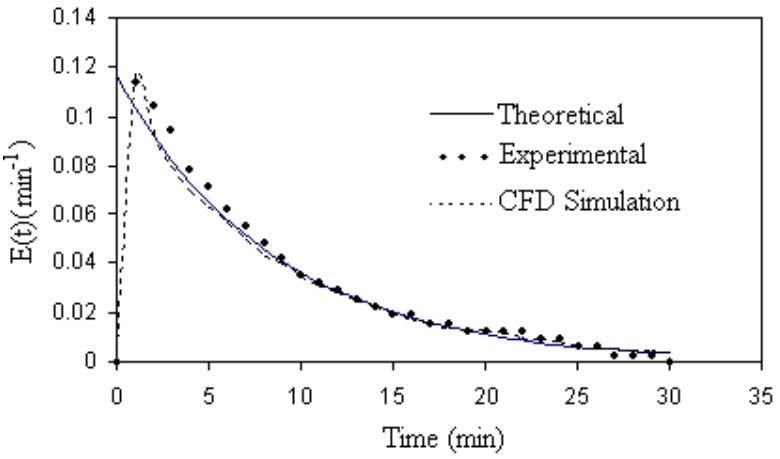


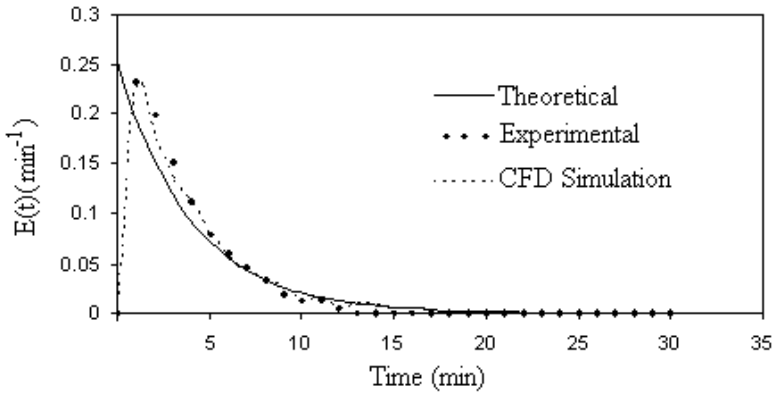
Figure 7. Comparison of model simulation of E(t) with experimental observations. Q: 35

As The electrolyte flow behavior in a continuous stirred tank electrochemical reactor has been simulated for pulse tracer input using the model equations developed in the previous section. The exit

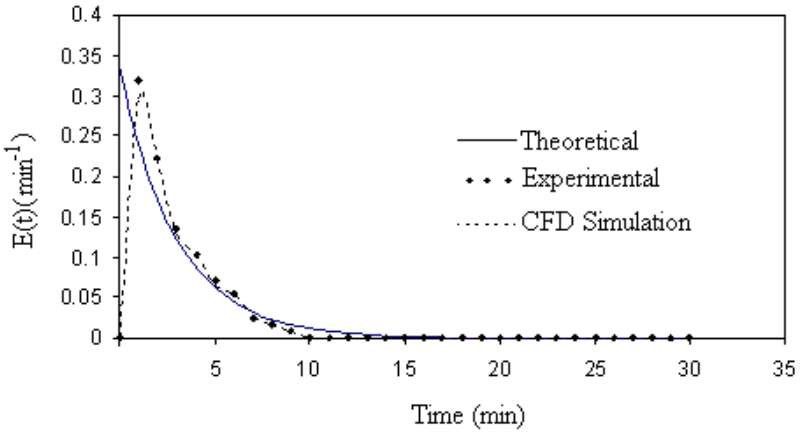
age distribution $E(t)$ can be calculated from the tracer output. The Figure 7 shows the simulation of model predictions for single CSTER along with experimental observation.



A



B



C

Figure 8. comparison of simulated residence time distribution with experimental observations. (a)35ml min^{-1} (b)75ml min^{-1} (c) 100ml min^{-1}

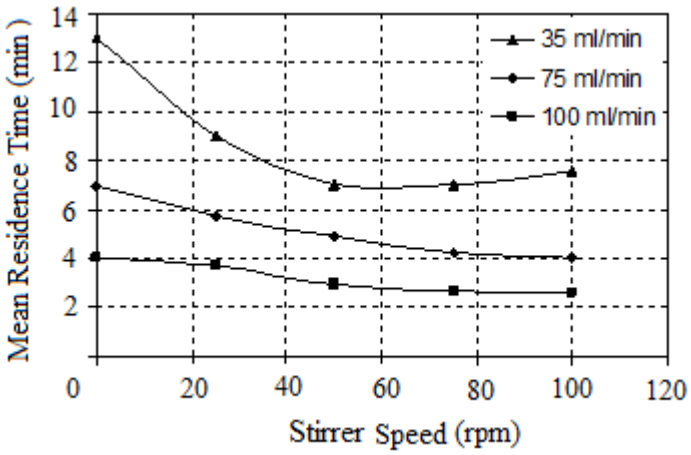


Figure 9. Effect of stirrer speed and electrolyte flow rate on mean residence time

The residence time has been calculated theoretically using equation (10) for various electrolyte flow rate.

The Figure 8 compares the simulated RTD by CFD and theoretical (equation 10) with experimental observations. It can be ascertained from the figure that the both CFD and theoretical simulation match well with the experimental results. The Figure 9 shows the influence of stirrer speed on the mean residence time distribution. It can be noticed from the figure that the stirrer speed has significant role in residence time of electrolyte at lower electrolyte flow rate and has very marginal effect at higher flow rate.

6. CONCLUSIONS

The electrolyte flow behavior in a continuous stirred tank electrochemical reactor has been described using commercial CFD. Experiments were carried out to predict RTD using pulse tracer technique. Experimental results and theoretical results are compared with simulation predictions. A good agreement is found between experimental results and simulation predictions. Further simulations are extended to study the effect of electrolyte flow rate and stirrer speed on mean residence time. Increasing electrolyte flow rate and stirrer speed the tracer mean residence time in continuous stirrer tank electrochemical reactor is decreasing.

Notations

A : surface area of the electrode (m^2)
C_{Ai} : initial concentration (ppm)
C_A : final concentration (ppm)

c(t) : exit tracer concentration
D_{a1} : reactor diameter (m)
E(t) : exit age distribution
F : Faraday's constant (96485 C)
i : current density (A m^{-2})
k_{f1} : reaction rate constant (min^{-1})
k_{b1} : reaction rate constant (min^{-1})
k_{LA} : mass transfer coefficient of A(m^2 s^{-1})
n : number of electrons
Q : electrolyte flowrate (ml min^{-1})
t : time (min)

Greek

σ : interfacial area of the electrode (m^2)
τ : residence time (min)
ρ : fliud density (kg m^{-3})
μ : fluid viscosity (kg m^{-1} s^{-1})

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