MODELING OF TUBULAR ELECTROCHEMICAL REACTOR FOR DYE REMOVAL

V. VIJAYAKUMAR, R. SARAVANATHAMIZHAN*, N. BALASUBRAMANIAN

Department of Chemical Engineering, A.C. Tech Campus,
Anna University, Chennai-600025, India
*Corresponding Author: thamizhan79@rediffmail.com

Abstract

The aim of the present investigation is to model a tubular electrochemical reactor for the treatment of synthetic dye wastewater. The tubular reactor was modeled and solved by finite difference method. For the model solution, the column was divided into 11 nodes in the axial direction and the variation in the radial direction has been neglected. An initial dye concentration of 200 mg L\(^{-1}\) was taken in the reservoir. The reactor was operated in a batch with recirculation operation. Based on preliminary experiments all parameters have been optimized. The model simulation is compared with the experimental value and it is observed that the model fairly matches well with the experiment. The modeling of tubular electrochemical reactors for dye waste water treatment could be useful in the design and scale up of electrochemical process.

Keywords: Tubular electrochemical reactor, Dye waste water, Finite difference, Modeling.

1. Introduction

Electrochemical techniques have been receiving greater attention in recent years due to the distinctive advantages of environmental compatibility, versatility and safety. Electrochemical methods compete with other conventional technologies including evaporation, precipitation, ion exchange and solvent extraction to offer solutions to the needs of the many industries [1].

In industry level various electrochemical reactors are used for the waste water treatment applications such as tank cells, plate and frame cells, tubular electrochemical reactor, rotating cells, to complicated three-dimensional electrode reactor systems like fluidized bed, packed bed cell, or porous carbon packing cells.
The materials for waste water treatment are dimensionally stable anodes (DSA) made of titanium substrate coated with thin layer of noble metal oxides, which have been used extensively in electrochemical industry. The electro-oxidation of different kinds of wastewater had been investigated by numerous researchers using different types of the electrochemical reactors [3 - 5].

Modeling of electrochemical reactor is important for the scale up and design to industrial level. In industrial scale one of the most common types of the electrochemical reactor is tubular reactor. Tubular reactor is widely studied by the researchers for the wastewater treatment and modeling [6, 7]. Tubular reactor is frequently assumed as dispersed plug flow of fluid inside the reactor. There is a gradual reduction of dye concentration in the reservoir of batch operation with recirculation system. In order to design and model the plant process, the development of a model is essential which permits the prediction of the variation of dye concentration with time in the reservoir of batch with recirculation operation. The flow in the tubular electrochemical reactor is considered as plug flow model and dispersed plug flow (one parameter) model [3].

Many researchers have modeled the tubular electrochemical reactor for the waste water treatment. Mustoe and Wragg [8] developed a model to obtain concentration as a function of time in an electrochemical tubular reactor for a batch with recirculation operation using dispersed plug-flow model. The author reported that the experimental data obtained for the electrodeposition of copper and silver from dilute solutions matches well with dispersed plug-flow model. Korbathi and Tanyolac [9] modeled tubular electrochemical reactor for phenol removal. The author included the weight ratio function in the dispersed plug flow equation and used finite difference method to solve the model equation. The authors observed that the experimental results matches well with the model simulations. Maria Georgiadou used a finite-difference method for predicting the current-density distribution in electrochemical systems. The results were compared to experimental measurements for the copper ion and the ferricyanide ion reduction [10]. Martinez and Rodriguez [11] experimented Cr(VI) removal as a function of pH and residence time, in a plug flow reactor with a spiral carbon steel as anode. The author observed that the dynamical model of process for the chromium removal satisfactorily matches well with the experimental chromium removal.

In the present study, the treatment of dye waste water in a tubular electrochemical reactor was considered and the governing equation was solved by means of finite difference method. The finite difference method is a frequently-used and more applicable method than any other numerical methods available for simple as well as complex problems [9]. Batch with recirculation operation were also performed in a tubular electrochemical reactor to find the optimum conditions of the operational parameters and reaction kinetics.

2. Model development

Axial dispersion model is used to represent the tubular electrochemical reactor for the present investigation. To determine the exit concentration of the pollutant in the z-direction for unsteady state condition, a differential elemental length ‘\( \partial z' \) along the length of reactor was chosen and writing the mass balance over the differential element of length ‘\( \partial z' \) gives [12]:
\[ D_s \frac{\partial^2 C_A}{\partial z^2} - \theta \frac{\partial C_A}{\partial z} - [kC_A^2] = \frac{\partial C_A}{\partial t} \]  
(1)

where, \( C_A \) is the concentration of dye (mg L\(^{-1}\)), \( \theta \) is axial flow velocity (m s\(^{-1}\)) \( D_s \) is diffusivity of dye (m\(^2\) s\(^{-1}\)), \( k \) is rate constant (s\(^{-1}\)), \( \alpha \) is order of the reaction. The diffusivity is calculated using Nernst-Heckel equation [13]:

\[ D_s = (8.928 \times 10^{-10}) \cdot T \cdot \left( \frac{s + t}{n + s} \right) \]  
(2)

where, \( T \) is Temperature (K), \( n_s \), \( n \) is valence of the cation and valence of the anion respectively, \( \lambda_s \), \( \lambda \) is the limiting ionic conductance of the cation and of the anion respectively \((\text{A/m}^2) \cdot (\text{V/m}) \cdot (\text{g.equiv.}/\text{m}^3)\). \( D_s \) is calculated for the present work to be 5.25\( \times \)10\(^{-9}\) m\(^2\)s\(^{-1}\) at 298 K.

The tubular electrochemical reactor was divided into 11 nodes in \( z \)-direction. Mass balance equation, Eq. (1), is written using finite difference method. The first and second order spatial partial derivatives in the partial differential equation were written using central difference formulation at any node in \( z \) direction, except boundary node along the height of reactor. Time derivative term is written using backward difference formulation. The finite difference formulation for the individual node can be written as:

\[ D_s \left( \frac{C_{A,z+1}^t - C_{A,z}^t - (C_{A,z-1}^t - C_{A,z}^t)}{(2 \Delta z)} \right) - \theta \cdot \left( \frac{C_{A,z+1}^t - C_{A,z-1}^t}{(2 \Delta z)} \right) - kC_A^t = \frac{C_{A,z}^{t-\Delta t} - C_{A,z}^t}{\Delta t} \]  
(3)

The partial derivative for the boundary node using backward difference formulation is written as:

\[ D_s \left( \frac{C_{A,z}^t - (C_{A,z-1}^t + C_{A,z+1}^t)}{(2 \Delta z)} \right) - \theta \cdot \left( \frac{C_{A,z+1}^t - C_{A,z-1}^t}{(2 \Delta z)} \right) - kC_A^t = \frac{C_{A,z}^{t-\Delta t} - C_{A,z}^t}{\Delta t} \]  
(4)

Equations (3) and (4) are simplified and can be written as:

\[ C_{A,z}^t - \left[ \frac{(b-a)C_{A,z+1}^t + (a+b)C_{A,z-1}^t + C_{A,z}^{t-\Delta t}}{(1+2b+m)} \right] = 0 \]  
(5)

\[ C_{A,z}^t - \left[ \frac{(2a-2b)C_{A,z-1}^t + (b)C_{A,z+1}^t + C_{A,z}^{t-\Delta t}}{(1+2a-b+m)} \right] = 0 \]  
(6)

where

\[ \alpha = \frac{\theta \Delta t}{2 \Delta z^2} ; \quad b = \frac{D_s \Delta t}{\Delta z^2} ; \quad m = k \cdot \Delta t \]  
(7)

Concentration of the pollutant at any node along the length of the reactor has been obtained from Eqs. (5) and (6). The above equations have been solved for \( C_{A,z}^t \) using Microsoft Excel SOLVER function to obtain the concentration of the pollutant at any node ‘\( z \)’ and at time ‘\( t \)’.

3. Experimental

The schematic diagram of the Tubular electrochemical reactor is shown in Fig. 1. The tubular reactor consists of a tubular electrode, electrolyte reservoir, centrifugal pump, flow meter and a power supply with necessary fittings.

The cathode is made of stainless steel with a diameter of 0.07 m and a height of 1.1 m. The thickness of the tube is 0.002 m. The anode is made of RuO$_2$ coated Ti mesh, perforated (60%) and tubular of diameter 0.05 m and height 1.0 m which resulted in an effective anode area of 0.0628 m$^2$. The anode is inserted inside the cathode, and is sealed with the end frames. In the cylindrical electrolytic cell, a batch recirculation operation was performed. Electrodes are fixed in the cylindrical cell frame with a spacing of 0.02 m. The tubular electrochemical cell volume is measured as 0.0038 m$^3$. The cylindrical electrolytic cell is fixed with a rigid frame, and the electrodes are connected to a power supply made of AE Rectifier (230 V input, 0 - 50 V output, 100 A). DC power is supplied to the electrodes according to the required current density and the experiments are carried out under constant current conditions.

Synthetically prepared dye solution of 200 mg L$^{-1}$ was taken in the reservoir. The pump inlet is connected to the reservoir and the outlet of the pump was connected to the cylindrical reactor inlet. The flow rate of dye solution has been measured using a flow meter connected to the inlet line of the reactor. The cylindrical reactor outlet was recirculated to the reservoir for the batch with recirculation operation. The samples collected at equal time interval were analyzed for COD using Uniphos®COD digester. The COD reduction measured as:

$$\frac{C}{C_i} = \frac{(\text{COD after electrolysis})}{(\text{COD before electrolysis})}$$

(8)
4. Results and Discussion

The model simulation of the tubular electrochemical reactor using central difference formulation, Eqs. (5) and (6) for different time interval is shown in Fig. 2. For the model solution, the column was divided into 11 nodes in the axial direction and the variation in the radial direction has been neglected. Model parameter such as rate constant \( (8.3 \times 10^{-5} \text{ s}^{-1}) \), diffusion coefficient \( (5.25 \times 10^{-6} \text{ m}^2 \text{s}^{-1}) \) has been chosen from the experiment and the equation has been solved using Microsoft® Excel SOLVER function for the time interval of 10 seconds with \( 10^{-6} \) accuracy. The model simulation has been done for the dye concentration of 200 mg\( \text{L}^{-1} \) and the result at each node along the length of the reactor \((z = 0 \text{ m})\), and the concentration of pollutant in the reaction medium remains constant. At length \( z = 0.1 \text{ m}, z = 0.2 \text{ m}, z = 0.3 \text{ m}, z = 0.4 \text{ m}, z = 0.5 \text{ m}, z = 0.6 \text{ m}, z = 0.7 \text{ m}, z = 0.8 \text{ m}, z = 0.9 \text{ m} \), and \( z = 1 \text{ m} \) (outlet), the degradation of the pollutant reaches its steady state at 90 min, 100 min, 100 min, 105 min, 110 min, 115 min, 120 min, 130 min, 145 min, 150 min respectively.

![Fig. 2. Variation of concentration of Evan’s blue dye along the length of tubular electrochemical reactor with respect to time current density: 90 Am\(^{-2}\); pH : 7; flow rate: 100 L h\(^{-1}\); initial concentration: 200 mg L\(^{-1}\) ; NaCl concentration: 1 g L\(^{-1}\); rate constant \( k \): 8.3\( \times 10^{-5} \) s\(^{-1}\).](image-url)

The effect of flow rate on COD reduction is shown in Fig. 3. It is observed from this figure that the COD reduction increases with increase in flow rate. At higher flow rates the destruction of organic content is more due to increased production of oxidants in the process and the transfer coefficient increases with increase in flow rate [14, 15]. This type of oxidation is indirect electro oxidation happening in the presence of chloride. The hypochlorite ions are the main reagent for the organic degradation in the indirect oxidation. In this case, as the electrolyte circulation rate increases, the transport of the \( Cl^- \) ion from the bulk to the electrode surfaces increases. This would facilitate \( Cl_2 \) generation, as well as the dissolution of \( Cl_2 \) to form \( OCl^- \) for reaction with the organic contaminant, which tern increases the rate of degradation.
Modeling of Tubular Electrochemical Reactor for Dye Removal

The comparison of model simulation for the 200 mg L\(^{-1}\) dye concentration for the flow rate of 100 L h\(^{-1}\) is shown in Fig. 4. It is observed form this figure that the model satisfactorily matches with the experimental result. Similar results were observed for the other flow rates also.

5. Conclusion

Continuous tubular electrochemical reactor has been modeled using finite difference method for the treatment of dye waste water. In this work the Evans blue dye effluent has been treated using tubular electrochemical reactor using this
DSA electrode. The simulation has been carried out using Microsoft Excel Solver function. It has been concluded from the present investigation that the developed model satisfactorily matches with the experimental value. Modeling of a tubular electrochemical reactor could provide important information for the design, operation and scaling up of pilot reactors for wastewater treatment.

References
