Validation of a Three-parameters Hydrodynamic Model to Describe the non-ideal Flow in a Continuous Stirred Tank Reactor of the Electro-Fenton Oxidation of Organic Pollutants in Wastewater

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Abstract. This research deals with the effect of the electrolyte flow behavior on electrochemical continuous stirred tank reactor performance. The reactor was simulated to remove organic pollutants from the wastewater and to determine the conditions for removal that will examine the effect of the electrolyte flow through the reactor. The flow behavior has been investigated using the pulse tracer technique at selected operating conditions. A model comprises three hydrodynamic parameters (bypass, active volume, and recirculation fractions) that have been used to analyze the residence time distribution. The modeling results indicate that with the increasing of the space-time, the bypass and the active volume fractions were decreasing, while the active volume of the reactor was decreasing. The obtained non-ideal space-time of the reactor using the hydrodynamic parameters and the relationship of the tracer concentration with time was much less than the ideal space-time, because of the great effect of bypassing fraction. Finally, the experimental results for the organic removal were closeted to the results that simulated at non-ideal space-time. This comparison proving a significant impact of non-ideal flow on the reactor performance, and showing that the proposed model was well-describing the behavior of the electrolyte through the reactor.

1. Introduction
Traditional methods for treating industrial wastewater before disposal or reuse include biological and physicochemical methods [1]. The physicochemical methods have several drawbacks in terms of performance, expense, regeneration, and secondary contamination, although they may be successful and cost-effective in certain applications [2]. The newest, efficacious, and low-cost wastewater treatment technology is the electrochemical methods [3]. Among these, the advanced oxidation process is a promising alternate for pollutants elimination effluent where conventional wastewater treatment processes (biological, physical, and chemical) are inefficient or have poor removal ability [4].
Electrochemical technology is one of the most interesting methods of wastewater treatment and an ideal option for solving environmental problems related to various industries. Several electrochemical reactors are using in this technique, such as tank cells, plate frame filter press cells, mixed reactor, cylindrical and tubular electrochemical reactors, rotating cells, and three-dimensional electrode reactor systems including fluidized bed, packed bed cell or porous carbon packing cells [5].

Designing the chemical and electrochemical reactor is not a routine matter. The shape of the reactor and its mode of operation under certain operating conditions are the key factors that determine the size of the proposed reactor [6]. Also, the hydrodynamics, fluid flow behavior and mixing conditions in operating continuous reactors are important for achieving the planned requirements for a system and resolving problems that usually result in lower reactor performance [7].

Continuous flow reactors, such as plug flow reactors or continuous stirred tank reactors (CSTR), are used in most large-scale chemical processes. Practically, no system behaves perfectly in operation, and there is often a large deviation from the ideal theoretical state which is assuming a perfect mixing inside the reactor. The deviation in the real continuous reactors appears due to as feed stream bypassing, stagnant areas, channeling, and so on, cause non-ideality in reactors flow behavior [8], [9]. Nonideal flow patterns can cause significant deterioration in product quality and a loss of process efficiency, resulting in significant economic losses for the industry concerned [10], [11].

The causes of creating a full-velocity distribution map for the fluid flowing through the reactor, an investigation of deviation from the ideal reactor's model. As well as knowledge of what is going on within the reactor (i.e., how long individual molecules or fluid elements stay in the reactor) [6]. To define and model non-ideal reactors, three principles are used; the distribution of residence times in the system, mixing quality, and the model used to describe the system [12]. One of the major components in understanding the vessel hydrodynamics has been studying the flow behavior through reactors using residence time distribution (RTD) studies [13]. RTD is a property of chemical reactor mixing that measuring how long the reaction mixture has been in the reactor for. For a variety of purposes, including developing accurate kinetic modeling of the system and designing reactors with the desired flow pattern, quantitative knowledge of liquid RTD is critical. It's also a useful tool for scaling up operations successfully [14]. Therefore, the accurate continuous reactor design results must combine an appropriate mixing model for the tank with the kinetics of the reaction to be conducted in the tank [15].

The concept of using the distribution of residence times to analyze chemical reactor output was reportedly first proposed by MacMullin and Weber in a pioneering paper [16]. However, the term did not appear to be widely used until the early 1950s, when Danckwrt [17] organized RTD by identifying most of the relevant distributions. The RTD function alone is insufficient to predict or study reactor efficiency because it only tells how long different fluid elements have been in the reactor but not how much matter has exchanged between them (mixing). Consequently, must find a mathematical model and since it is the dead and active areas, and material exchange between them, are not considered in current models [18].

The aim of this research is determination of the three-parameter model for electrolyte residence distribution in an advanced oxidation electro-Fenton of phenol occurs in CSTR. After calculation of the volume of the dead and active regions and material exchange between them, a determination will be done of the real (non-ideal) reactor space-time and compare the obtained organic conversion (removal) from the simulation of the CSTR, the conversion obtained by the solved model and the real experiments.
2. Experimental
The experimental system of the continuous electro-Fenton oxidation of organic consists of a glass beaker of 2000 ml placed on heating-magnetic stirrer to keep the certain temperature (30 or 60 °C). There is an inlet pipe protruding into the beaker, carrying the phenolic stream to the reactor and the treated stream exited from the reactor via the outlet tube. The system consists of a rotating anode of MnO$_2$-graphite substrate rod. The rotating electrode of dimensions 1.5 cm in diameter and 6 cm mm length was rotated at 300 rpm via a mechanical stirrer. The cathode was a hollow graphite cylinder of dimensions 8 cm inside diameter, 10 cm outside diameter, and 15 cm length. The applied current density was 8 mA/cm$^2$. The inlet flow rate of the phenolic solution of 150 ppm of phenol solution was driven into the reactor by a pump and the required amount of flow was controlled by a flowmeter. The ionic strength of the feed was maintained constant by adding 0.055M Na$_2$SO$_3$ and 0.4 mM of FeSO$_4$.7H$_2$O. While the feed pH was kept in the range between 2.8 and 3 by adding H$_2$SO$_4$. Also, 1 l/min of air was bubbled into the reactor via Resun Electromagnetic Air Pump (type ACO-001), to provide oxygen needed for the electro-Fenton reaction. The method of total organic conversion was illustrated previously [19], [20] and used with no modification.

The measurement the RTD of the electro-Fenton reactor was achieved by using the pulse response tracer method, with water as test fluid. A volume of 30 ml of 500 ppm methylene blue was injected into the tank as a tracer at time zero. The outlet concentration versus time ($c(t)$) can be detected using the computer in-line photometer, by measuring the resistance of the outlet stream and read the concentration values based on calibration curve.

3. Results and Discussion
3.1. Simulation batch date to CSTR
The organic conversion via electro-Fenton oxidation with zero-order kinetics equation was simulated for ideal electrochemical CSTR, using the previously found kinetics model. [19] The space-time for CSTR ($\tau_{CSTR}$) was obtained from the performance equation (Eq. 1) for the CSTR. [21] The simulation results shown in Figure (1).

$$\tau_{CSTR} = \left( \frac{C_{org} V}{F_{org}} \right)_m = \frac{C_{org} x_{org}}{r_{org}}$$ (1)

The simulation results (Figure 1) shows that the conversion of the organic pollutants increases linearly with increasing with the space-time of the reactor. This linear behavior is because of the zero order of the electro-Fenton reaction. In zero-degree reactions the relationship between concentration (or conversion and removal) and the reaction time or reactor space-time linear. Zero-degree reactions are also characterized by the possibility of complete conversion of the reactant substrate (complete removal) since these reactions depend on the temperature of the reaction and do not depend on the concentration of the reactant. [21]

Table (1) summarizing CSTR space-time required for certain values of organic conversion at different temperatures. For the removal range between 80 to 100 %, the lowest required time was 155.3 minute for 80% removal at 60 °C and 8 mA/cm$^2$. While the highest required time was 286.8 minute at 30 minutes at 30 °C and for highest possible organic conversion for zero order reaction (complete removal) and 194.1 minute at 60 °C. These conditions were selected to obtain experimentally $E(t)$ and
$E(t/\tau)$, because it covers a wide range of reactor space-time and therefore will describe well the RTD in the CSTR through the hydrodynamic parameters’ values.

![Figure 1. Simulation results of the organic conversion by a CSTR via electro-Fenton reaction](image)

**Figure 1.** Simulation results of the organic conversion by a CSTR via electro-Fenton reaction

| Table 1. Simulated CSTR space-time results for certain values of organic conversion at different temperatures |
| --- |
| Temp., °C | Time required (min.) for conversion value of 80 % | 90 % | 100 % |
| 30 | 229.4 | 258.1 | 286.8 |
| 40 | 207.8 | 229.4 | 258.1 |
| 50 | 180.1 | 202.6 | 225.1 |
| 60 | **155.3** | 174.7 | **194.1** |

3.2. RTD model and solution

The determination of RTD experimentally was carried out by tracer technique. Methylene blue was used as tracer solution (500 ppm) and water as test fluid. The exit age distribution $E(t)$ calculated from the outlet concentration of the tracer $c(t)$ at different times $(t)$ by using the Eq. (2).

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

The experimentally obtained values of $E(t)$ versus time shown in Figure (2). Generally, the $E(t)$ at different ideal reactor space-time appears with multiple peaks which are indicated to strong internal recirculation. Also, the peaks intensity for certain ideal reactor space-time decreases with increasing time due to distribution of the trace concentration on longer operating time.
The importance of studying the hydrodynamic parameters (bypass, active and dead volume and recirculation) and calculating their values for a specific reactor appears to obtain a more accurate sight of what is happening to the flow of materials inside the reactor. Thus, it helps to modify the behavior of the reactor and obtain its higher efficiency after solving the flow problems in the reactor, whose values can be measured from the hydrodynamic parameters.

The three-parameters model [22] assuming that the total volume of the reactor (V) is divided into two zones names as active and dead zone, V(β) and V(1−β), respectively. Also, there is a fluid fractional recirculation (γ) between these two zones. The model supposes that the electrolyte flow to the reactor is divided into bypass flow and active flow, where α is the fraction of electrolyte bypass and Q represents the volumetric flow rate. Figure (3) present a schematic of the proposed three-parameters CSTR model.

Figure 2. Experimental $E(t)$ versus time at different ideal space-time

Figure 3. Schematic of the three-parameters model for electrochemical CSTR
The exit age distribution function of CSTR for pulse tracer input is determined by using equations (3) to (10) [22].

The mean residence time calculated by Eq. (3).

\[
\bar{t} = \int_0^\infty t E(t) dt
\]  
(3)

\[
\theta = \frac{t}{\tau}
\]  
(4)

The real reactor space-time was considered as Eq. (4).

\[
\tau = \frac{V}{Q}
\]  
(5)

\[
E_{(\theta)} = \frac{C_1}{C_0} = \frac{(1-\alpha)^2}{\beta(R_1 - R_2)}[(R_1 + B_2)e^{R_1\theta} - (R_2 + B_2)e^{R_2\theta}]
\]  
(6)

And,

\[
B_1 = \frac{(1-\alpha)\gamma}{1-\beta}; B_2 = \frac{(1-\alpha)(1+\gamma)}{\gamma}; B_3 = \frac{(1-\alpha)^2\gamma^2}{\beta(1-\beta)}
\]  
(7)

Where,

\[
R_1 = -\frac{1}{2} \left[ (B_1 + B_2) - \sqrt{(B_1 - B_2)^2 + 4B_3} \right]
\]  
(8)

A program written in Python [23] was used to solve the three-parameters model by minimization of the sum of squares of the difference between experimental and model values of \(E_{(\theta)}\) by prediction of the hydrodynamic parameters (\(\alpha, \beta, \gamma\)). The minimization solved by using a genetic algorithm with 0.075 mutation rate, 100 population size and 0.001 convergence.

The obtained values of \(E_{(\theta)}\) from model solution were plotted with the experimental \(E_{(\theta)}\) versus time for different ideal reactor space-time in Figure 4 (a, b and c). Generally, the found \(E_{(\theta)}\) from the model describes fairly the behavior of the experimental \(E_{(\theta)}\) for various ideal reactor space-time. The comparison showed a clear convergence between the \(E_{(\theta)}\) calculated by the model and those that obtained from experiments, as shown in Figure 4 (d). Some dispersed points were noticed because the model was not describing considerably the peaks of the experimental results of \(E_{(\theta)}\). The statistical analyses, summarized in the Table 2, appearing a clear convergence in the mean values obtained from experiments and the model. Also, the results showed a higher variance value for the experimental results due to the emergence of peaks that indicates to the strong high recirculation. While the total correlation coefficient was 0.9166 for 435 of observations.
Figure 4. Experimental and model $E(\theta)$ versus time (a: 155.3 min., b: 194.1 min., c: 286.8 min.), and model versus experimental $E(\theta)$ (d) for different ideal reactor space-time.

Table 2. Statistical comparison between experimental and model $E(\theta)$

|                      | Experimental $E(\theta)$ | Model $E(\theta)$ |
|----------------------|--------------------------|-------------------|
| Mean                 | 1.0273                   | 1.0726            |
| Variance             | 0.3004                   | 0.2103            |
| Correlation coefficient | 0.9166                  |                   |
| Total observations   | 435                      |                   |
3.3. Hydrodynamic parameters and organic removal

The results of the mathematical model gave the values of the hydrodynamic parameters of the reactor with ideal reactor space-time. The obtained values of the hydrodynamic parameters were tabulated in Table 3. As the ideal reactor space-time increased (feed flow rate decreased) from 155.3 to 286.8 minute, the probability of the feeding stream to mix with the reactor fluid increasing and thus the fraction of the bypass decreasing from 0.5410 to 0.3995, and the exchange fraction will increase, causing decreasing in reactor active volume and increasing the dead volume of the reactor from 9.69 to 14.81%.

| τ, min. (ideal) | Bypass fraction (α), - | Active volume fraction (β), - | Exchange flow fraction (γ), - | V dead, % |
|----------------|------------------------|-------------------------------|-----------------------------|---------|
| 155.3          | 0.5410                 | 0.9032                        | 0.3801                      | 9.69    |
| 194.1          | 0.4845                 | 0.8739                        | 0.4524                      | 12.65   |
| 286.8          | 0.3995                 | 0.8519                        | 0.5231                      | 14.81   |

Also, the mathematical model results also gave space-time values for the electrochemical CSTR in the non-ideal condition. It is noted from Table 4 that the calculated space-time of the reactor for the non-ideal reactor, based on the relationship of the tracer concentration and time, is much less than the space-time of the proposed reactor based on reactor idealism. The reason for this obvious difference is largely due to the amount of the bypass fraction, which ranges between 0.3995 and 0.5410. Although an amount of electrolyte fluid remains in the dead reactor part for a long time. The amount of the bypass portion is relatively large, which does not pass the reactor literally, and thus the retention time of the bypass fraction is zero, which causes the observed decrease in the space-time of the reactor.

| τ, min. (ideal) | τ, min. (non-ideal) | Removal, % (ideal-simulation) | Removal, % (non-ideal, simulation) | Removal, % (experimental) |
|----------------|---------------------|-------------------------------|------------------------------------|---------------------------|
| 155.3          | 59.1                | 80                            | 20.59                              | 16.91                     |
| 194.1          | 78.5                | 100                           | 40.43                              | 38.13                     |
| 286.8          | 110.9               | 100                           | 57.12                              | 55.48                     |

The removal (conversion) of the organic matter was simulated using non-ideal reactor space-time values. The results showed that the removal values ranged between 20.59 and 57.12 %. After that, experiments for the organic pollutant removal were conducted under the same conditions. The experimental results indicated that the organic removal values came close to and slightly less than the simulated values of the electrochemical CSTR with non-ideal flow. These results demonstrate that the electrochemical CSTR, with the current design, suffers from significant imperfection in flow due to a large bypass fraction and that the proposed three-parameters model perfectly describes the behavior of this type of reactor.

4. Conclusions

RTD behavior of the electrolyte flow through an electrochemical CSTR at various ideal reactor space-time was studied. A previous kinetics data of the electro-Fenton oxidation of organic removal from wastewater was used to predict the conversion (removal) of organics in CSTR. Selected operating
conditions were used to study the RTD of the electrolyte behavior using a pulse of methylene blue solution as a tracer and follow its exit concentration. Multiple peaks of the E(t) versus time were noticed, which indicated a strong internal recirculation of the electrolyte inside the reactor in all conditions, which agreed with the values of the exchange fraction obtained by the model later. Analysis of the exit age distribution was achieved by three hydrodynamic parameters' model and the values of bypass, active volume, and recirculation fractions were determined. The model results showing a decrease in bypass and active volume with increasing reactor space-time, while the exchange fraction was increased proportionally with the space-time. The real (non-ideal) reactor space-time was determined and was much less than the ideal space-time because of high values of bypass fraction which is the amount that not pass through the reactor. Therefore, the organs in the bypass fraction had not reacted nor converted, causing a lowering in the total removal in the electrochemical CSTR. Also, using the non-ideal space-time in the simulation gives a conversion of organic approximately equal to the experimental removal results via electro-Fenton reaction indicating bad electrolyte flow through the reactor. The convergence of the experimental phenol conversion values with the estimated from the model confirm the validity of the three-parameter model to describe non-ideal flow in the electrochemical reactors. Also, all results show that using the same batch reactor design as the mixing reactor is unwise as it will lead to a big decrease in the expected amount of organic removal via the electro-Fenton oxidation reaction. Therefore, a new design and configurations of the electro-Fenton reactor will be required to increase the mixing efficiency and reduce the values of the bypass fractions and the dead volume of the reactor.

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