Performance of a tubular electrochemical reactor, operated with different inlets, to remove Cr(VI) from wastewater

S.A. Martínez-Delgadillo, H.R. Mollinedo P., M.A. Gutiérrez, I.D. Barceló, J.M. Méndez

1. Introduction

In Mexico, most of the electroplating, leather tanning, and textile industries are small facilities, which release relatively large amounts of chromium in surface waters. In addition, solid wastes from chromate-processing facilities have been disposed of improperly in landfills, being sources of contamination for groundwater. The removal of Cr(VI) from metal-finishing liquors and wastewaters is necessary due to its toxicity. Certain compounds of Cr(VI) are carcinogenic, and the health effects of the chromium are closely related to its valence state and time of exposure. Conventional processes to remove Cr(VI) from wastewater are based on the reduction–precipitation process (e.g. reduction of Cr(VI) to Cr(III) with FeSO4 and Cr(III) hydroxide precipitation with lime), where it is necessary to add 2.5 times more ferrous sulfate than the stoichiometric requirements

which is always expensive. Electrochemical Cr(VI) reduction, with iron electrodes, is an alternative process, which has been studied and applied with success to remove Cr(VI) from wastewater. Several mechanisms are involved in the electrochemical reduction of Cr(VI) to Cr(III), such as the primary reduction through formation of ferrous ions Fe(II) liberated from the electrodes into the solution when an established quantity of direct current is applied to the anode. Additionally, there are two important reactions during the process: Cr(VI) reduction at the cathode and Fe(III) reduction to Fe(II) at the same electrode, while in the conventional process do not. Both reactions, reduce the Fe(II) stoichiometrically required to reduce the Cr(VI) therefore, the amount of sludge generated is lower than conventional process. Moreover, during the electrochemical treatment sludge with Chromite (FeCr2O4) is formed, and it is possible to reuse treated waters in the rinsing stages of the plating industry reducing wastes and costs.

Electrochemical Cr(VI) reduction, with iron electrodes, is an alternative process, which has been studied and applied with success to remove Cr(VI) from wastewaters. Different kind of electrochemical reactors has been used, but their performance has been evaluated as they were a “black box”. In this work, the performance of a novel tubular electrochemical continuous reactor (Martínez & Rodríguez, 2007), in laminar flow using state-of-the-art CFD tools (Atilano, Meier, Iess, & Mori, 2008; Kulkarni & Ranade, 2008; Schonfeld & Hardt, 2004; Zalc, Szlai, Alvarez, & Muzzio, 2002) was evaluated. This powerful tool allows knowing...
2. Materials and methods

The electrochemical tubular reactor of carbon steel material, shown in Fig. 1a, was used during the experiments. The operation volume was 2.289 L and its dimensions were 1.05 m long and 0.054 m internal diameter (ID). Three reactor inlets were tested; lateral (L), central (C) and tangential (T), as shown in Fig. 1b.

A central polished carbon steel rod measuring 1.05 m served as the anode with the same material and ID, which served as the cathode by rubber gaskets.

2.1. Mathematical model

The flow through the reactor is governed by mass and momentum conservation laws. These are generally expressed in terms of partial differential equations in a continuum domain, and then by numerical methods transformed into discrete domain (cells) using a computational grid. The integration of the governing equations on these individual control volumes leads to an algebraic system of equations for the discrete dependent variables, where the field variables are basically our problem unknowns: velocity and pressure. The steady state continuity equation (mass conservation) is given by:

\[ \nabla \cdot \bar{v} = 0 \]  

where \( \bar{v} \) = velocity vector.

The conservation of momentum in an inertial reference frame is given by:

\[ \frac{\partial}{\partial t} \left( \rho \bar{v} \right) + \nabla \cdot (\rho \bar{v} \bar{v}) = - \nabla p + \nabla \cdot (\bar{T}) + \rho \bar{g} + \bar{F} \]  

where \( p \) = density; \( \bar{T} \) = stress tensor; \( \rho \bar{g} \) = gravitational body force; \( \bar{F} \) = external force vector.

Fluent® uses a control-volume-based technique to convert a general scalar transport equation to an algebraic equation that can be solved numerically. This control volume technique consists of integrating the transport equation about each control volume, yielding a discrete equation that express the conservation law on a control-volume basis. Discretization of the governing equations can be illustrated most easily by considering the unsteady conservation equation for transport of a scalar quantity \( \phi \). This is demonstrated by the following equation written in integral form for an arbitrary control volume \( V \) as follows:

\[ \int_V \frac{\partial \rho \phi}{\partial t} dV + \oint_{\partial V} \rho \phi \bar{v} \cdot d\bar{A} = \oint_{\partial V} \Gamma_\phi \nabla \phi \cdot d\bar{A} + \int_V S_\phi dV \]  

where \( \rho \) = density; \( \bar{v} \) = velocity vector; \( \bar{A} \) = area vector; \( \Gamma_\phi \) = diffusion coefficient for \( \phi \); \( S_\phi \) = source per unit volume.

2.2. Numerical simulation

Fluent version 6.3 has been used to simulate the steady (fully developed flow) and unsteady state fluid flow (species transport); a pressure-based segregated algorithm solver has been used, where the governing equations are solved sequentially.

For the pressure-velocity coupling a non-linear procedure called Semi-implicit pressure-linked equation (SIMPLe) algorithm was used, for pressure discretization the Standard scheme was selected, and for the momentum discretization, the Second Order Upwind scheme was used.

2.2.1. Model formulation for tracer injection

To simulate the tracer injection, a tracer with the same material properties as working fluid and a concentration of unity is applied at the inlet surface, then the conservation equations for species transport equations is solved. Fluent predicts the local mass fraction of each species, the concentration of the tracer was monitored at the outlet surface to obtain the residence time distribution RTD curve. The nonreactive tracer, had the same physicochemical properties as the fluid in the reactor.

To evaluate the effect on the dispersion in the reactor, the exit age distribution function \( E \) was obtained and the dispersion \( (Nd = D/ul) \) was evaluated. It was considered the tubular electrochemical reactor was a closed vessel and Eq. (4) was used to evaluate the \( Nd \) (Levenspiel, 1999). This method is reliable to use when \( D/ul < 1 \).

\[ \sigma^2 = \frac{D}{ul} \left( \frac{D}{ul} \right)^2 \left( 1 - e^{(ul/D)} \right) \]  

where \( \sigma^2 \) = variance (min\(^2\)); \( \bar{T} \) = mean residence time (min); \( D \) = dispersion coefficient (m\(^2\) s\(^{-1}\)); \( ul \) = flow velocity (m/s); \( L \) = reactor length (m); \( \theta = t/\bar{T} \) (dimensionless).

The conservation equation takes the following general form:

\[ \frac{\partial}{\partial t} (\rho Y_i) + \nabla \cdot (\rho \bar{v} Y_i) = - \nabla \cdot \bar{j}_i \]  

where \( Y_i \) = local mass fraction; \( \bar{j}_i \) = diffusion flux of the species \( i \).

The diffusion flux can be written as:

\[ \bar{j}_i = -D_{i,m} \nabla Y_i \]  

where \( D_{i,m} \) = is the diffusion coefficient for species \( i \) in the mixture.
Fig. 1. The schematic diagram of the electrochemical tubular reactor.

Fig. 2. Electrochemical reactor grid with the three inlets.
Once the steady state was obtained, the tracer injection was modeled (transient simulation), defining a unit mass fraction for tracer species introduced at the inlet for a short lapse of time (5 s) and then concentration is return to zero again to simulate a pulse injection (Levenspiel, 1999; Sandesh et al., 2009). The concentration of the tracer is monitored at the outlet, to obtain the RTD curve. For the time step discretization, a second order discretization scheme was used because it was observed a better convergence per time step. The time step used, was 5 s, with 20 iterations per time step.

2.2.2. Boundary conditions
At the inlet reactor (Type Velocity Inlet boundary condition), the velocity was 0.0481 m/s.
For interior and exterior walls (including the electrodes) the Type Wall boundary condition was assumed.
For the outlet of reactor, the zero normal gradient for all variables was assumed (Type Outflow boundary condition).

2.2.3. Material properties
The working fluid and tracer are modeled with liquid water properties: density = 1000 kg/m³ and viscosity = 0.0008 kg/m s.
Laminar flow was considered at the inlet, this option is appropriate only when the turbulence levels at the inlet boundary are negligible or does not have importance in the accuracy of the overall solution. In our case, the dimensions of the inlet pipe are negligible compared to the entire body of the reactor.

2.2.4. Computational model
The complete 3D grid model of the electrochemical reactor with the three different inlets was prepared with Gambit® software. The numerical simulation was performed using the single-precision that produces sufficient accuracy for the problem. The maximum residual tolerance was 10^{-5} for the continuity equation. The solution for the steady state problem has required an average of 285 iterations to solve the problems. The fluid domain was meshed using Tet/Hybrid type TGrid four nodes tetrahedral elements, using: 1251285 tetrahedral cells and 243514 nodes (model with lateral inlet), 1258034 tetrahedral cells and 244626 nodes (model with central inlet), 1256861 tetrahedral cells and 244669 nodes (model with tangential inlet).

The numerical simulation was performed using the single-precision that produces sufficient accuracy for the problem. The maximum residual tolerance was 10^{-5} for the continuity equation.

2.2.5. Electrochemical chromium hexavalent (Cr(VI)) removal model
After obtaining the dispersion and the residence times for each type of inlet, simulations were performed with the electrochemical chromium hexavalent (Cr(VI)) removal model (Martinez & Rodriguez, 2007) to evaluate the electrochemical reactor performance operating with each inlet. The model applied to describe the increase in pH due to the OH⁻ production during the electrochemical process and the Cr(VI) removal in the tubular reactor at the non-steady was validated experimentally (Martinez & Rodriguez, 2007). In spite of fact that the model was validated with the electrochemical reactor with lateral inlet, the electrochemical reactions are the same, and then it was used in this work because the effect on its performance is mainly due to the hydrodynamic behavior of the reactor due to the different inlets. The simulations were performed until the reactor reached the steady state, then the Cr(VI) concentration and pH in the effluent (reactor outlet) obtained for each inlet were compared. The pH variation model is shown in

Fig. 3. The exit age distribution curve $E$ for fluid flowing through the electrochemical reactor for each inlet.

Fig. 4. Contours of axial velocity ($\geq 0$).
Fig. 5. Contours of axial velocity ($\leq 0$).

Fig. 6. Contours of axial velocity for each inlet.
Eq. (7) and the most largely used boundary conditions (Danckwerts, 1953), are shown in Eqs. (8)-(9).

\[
\frac{\partial \text{pH}}{\partial t} = \frac{D}{u_L} \frac{\partial^2 \text{pH}}{\partial z^2} - \frac{\partial \text{pH}}{\partial z} + th \frac{k_{1pH} \cdot \text{pH}}{1 + k_{2pH} \cdot \text{pH}}
\]

\[
\text{pH} = \frac{D}{u_L} \frac{\partial \text{pH}}{\partial z} - \text{pH}_i = 0 \quad \text{at} \quad z = 0
\]

\[
\frac{\partial \text{pH}}{\partial z} = 0 \quad \text{at} \quad z = 1
\]

The Cr(VI) removal in the tubular reactor is described by Eq. (10) (Martínez & Rodríguez, 2007).

\[
\frac{\partial \text{Cr}}{\partial t} = \frac{D}{u_L} \frac{\partial^2 \text{Cr}}{\partial z^2} - \frac{\partial \text{Cr}}{\partial z} - th \frac{k_1 \cdot \text{Cr}}{1 + k_2 \cdot \text{Cr}}
\]

And the boundary conditions (Danckwerts, 1953), are shown in Eqs. (11) and (12).

\[
\text{Cr} = \frac{D}{u_L} \frac{\partial \text{Cr}}{\partial z} - \text{Cr}_i = 0 \quad \text{at} \quad z = 0
\]

\[
\frac{\partial \text{Cr}}{\partial z} = 0 \quad \text{at} \quad z = 1
\]

where \( \text{pH}_i \) = influent pH; \( k_{1pH} \) = constant rate of pH variation (min\(^{-1}\)); \( k_{2pH} \) = constant rate of pH variation (dimensionless); \( \text{Cr} = \text{Cr} \) (VI) concentration in the reactor (mg dm\(^{-3}\)); \( \text{Cr}_i \) = influent Cr(IV) concentration (mg dm\(^{-3}\)); \( k_1 \) = constant rate of Cr(IV) removal (min\(^{-1}\)); \( k_2 \) = constant rate of Cr(VI) removal (dm\(^3\) mg\(^{-1}\)); \( x \) = across position in the reactor (m); \( t \) = time (min); \( th \) = hydraulic residence time (min); \( z = x/L \) (dimensionless).

### 3. Results and discussion

The complete 3D model grid of the electrochemical with the three different inlets was obtained with Gambit® and it is shown in Fig. 2. As seen, the reactor length was 1.05 m as the experimental electrochemical reactor (Martínez & Rodríguez, 2007). The fluid domain was meshed with Tet/Hybrid type TGrid four nodes tetrahedral elements, using 1251285 tetrahedral cells and 243514 nodes. Tracer injection simulations were performed to obtain the RTD. The results of the exit age distribution curves (E), for fluid flowing through the electrochemical reactor for each inlet, as a function of \( \theta \), are shown in Fig. 3.

As seen, the distributions for central and lateral are very close. It can be explained because the axial velocity distributions along the reactor are similar (as seen in Fig. 7). It is important to realize that although close the inlet the axial velocity distributions are different, after a position in the reactor of about 0.1 m (central inlet) and 0.15 m (lateral inlet), the axial velocity distribution in both cases trend to be similar, however the reactor with the central inlet, presented a higher dispersion and the highest dispersion number (0.057). On the other hand, the Nd = 0.041 in the reactor with the tangential inlet was lowest of the three reactors inlets. The Nd values obtained with the model agree with the experimental values, about 0.066 (Martínez & Rodríguez, 2007). As shown, flow in the electrochemical reactor in the three cases have large deviation from plug flow (Nd = 0) because in all the cases the Nd > 0.01 (Levenspiel, 1999). Based on the RTD, the mean residence time of the fluid in the flow electrochemical reactor with each inlet were evaluated and compared with the residence time (1654.7 s) of the reactor operating as an ideal plug flow reactor, that was calculated with the experimental operation conditions; flowrate of 1.38 × 10\(^{-3}\) L/s and operation volume of 2.289 L. The residence time in the reactor with central (1631.7 s) and lateral (1641.9 s) are shorter than that value of the ideal plug flow reactor.

On the other hand, the residence time obtained for the reactor with tangential inlet, was 1855.2 s, this is longer than in the ideal plug flow reactor and the reactors with the other inlets. Both, the dispersion and the residence time will affect the performance in the electrochemical reactor. To understand the different performances of the reactor and to characterize the degree of backmixing during flow due to the different inlets, the axial velocities within the reactor were evaluated for each case. Figs. 4 and 5, show the contours of axial velocities ranging from 0.0 to 5.0 × 10\(^{-3}\) m/s and 0.0 to −3.82 × 10\(^{-3}\) m/s, respectively. As seen, the distribution of axial velocities <0 is different in each kind of inlet (showed in yellow in Fig. 4). It was obtained that the % of elements that are into the range of negative axial velocities is the following: 4.33% in the case of the central inlet, 9.01% with the lateral inlet and 0.075 m with the central zone. It was obtained that the lowest dispersion number or lower tendency to be similar, however the reactor with the central inlet, presented a higher dispersion and the highest dispersion number (0.057). On the other hand, the Nd = 0.041 in the reactor with the tangential inlet was lowest of the three reactors inlets. The Nd values obtained with the model agree with the experimental values, about 0.066 (Martínez & Rodríguez, 2007). As shown, flow in the electrochemical reactor in the three cases have large deviation from plug flow (Nd = 0) because in all the cases the Nd > 0.01 (Levenspiel, 1999). Based on the RTD, the mean residence time of the fluid in the flow electrochemical reactor with each inlet were evaluated and compared with the residence time (1654.7 s) of the reactor operating as an ideal plug flow reactor, that was calculated with the experimental operation conditions; flowrate of 1.38 × 10\(^{-3}\) L/s and operation volume of 2.289 L. The residence time in the reactor with central (1631.7 s) and lateral (1641.9 s) are shorter than that value of the ideal plug flow reactor.

This zone of negative axial velocities reaches until 0.15 m in the first part of the reactor, when was operated with lateral inlet, 0.11 m with the tangential inlet and 0.075 m with the central zone.

While the electrochemical reactor is operated with the central inlet, more negative axial velocities are achieved, as shown in Fig. 5d, while the electrochemical reactor is operated with the central inlet, more negative axial velocities are achieved, as shown in Fig. 5d, with the tangential inlet and 0.075 m with the central zone.
Fig. 6 shows the contours of axial velocity along the reactor with the three inlets to know what is happening within the reactor. As shown, it is possible to identify clearly the zones with different velocity into the reactor and see the behavior of the liquid around the electrodes, from the inlet to the reactor exit. When the reactor is operated with central inlet, the axial velocities are not evenly distributed along the electrochemical reactor. In different positions, specifically in 0.3 m, 0.4 m, and between 0.65 m, 0.8 m and 0.95 m there are large zones of low axial velocity (cyan zones) in one side, while in the other, streams with high velocities (in yellow) emerge. It must be mentioned that the zones of higher velocities (in yellow), along the central electrode are not homogeneously distributed. Additionally, the axial velocity distribution profiles as a function of the position, after 0.2 m from the inlet until the outlet of the reactor, for the three reactor inlets were obtained and they are shown in Fig. 7. As seen, for the central inlet, it is possible to see that there are several peaks of high and low velocity along the reactor, which are the most unequally distributed of the three inlets. In the case of the lateral inlet (Fig. 6), the contours of the axial velocities show that the fluid behavior was slightly more homogeneous than when the reactor was fed by the central inlet and the higher axial velocities (in yellow,) were fairly better distributed.

However, zones with low and high velocity at the same position, still come out in different positions along the reactor; namely in 0.2 m and 0.3 m. In Fig. 7, the axial velocity along the reactor with lateral inlet show that the high velocities were reduced, consequently the peaks are slightly shorter than the reactor with central position.

Fig. 8. Axial velocity profiles and contours at the exit of the reactor operated with different inlets.
inlet. On the other hand, the contours of the reactor with tangential inlet (Fig. 6) show that the velocities are distributed more homogeneously than with the reactor operating with central or lateral inlets. The low velocity zones are reduced. The % of low axial velocity (from 0 to 0.0002 m/s) was obtained based on the number of elements of the grid and it was found out the following: central 15.01%, lateral, 14.4% and tangential 10.20%. As seen, with tangential inlet the low axial velocity zones are drastically reduced. However, the axial velocity increases slowly along the position in the reactor, and at the last part, next to the exit, it shows an important increase, as shown for the last velocity peak. It must be noticed that the zones of higher velocities (in yellow), are distributed much more homogeneously along the central electrode, than with the lateral or central inlets. This is an advantage because the high velocity near the electrodes increases the mass transfer between the electrode and the solution. The results of the axial distribution for the tangential inlet, shown in Fig. 7, reveal that the axial velocity peaks were reduced and are the most homogeneous of the three cases. The mean velocity was evaluated for the three cases and the mean velocities reached with the central and lateral inlet (5.8508 × 10⁻⁴ m/s and 5.8555 × 10⁻⁴ m/s), are very similar, but the mean velocity with the tangential inlet is lower than the other inlets, 5.733 × 10⁻⁴ m/s. As shown before, the distribution of the axial velocity along the reactor depends on the reactor inlet that affects the axial velocity profile at the reactor outlet. In Fig. 8, shows the axial velocity profiles and contours at different positions of the reactor outlet, for each type of inlet. In the three cases, there is a zone of high axial velocity. The axial velocities distributions for central and lateral inlets are similar, but nevertheless in the case of the tangential inlet, higher velocities are reached at the last part of the reactor, as shown in Figs. 6 and 7, that produces the higher velocity peak at the reactor outlet, as seen in the contours an profiles of the tangential inlet in Fig. 8.

Based on the dispersion and the residence times obtained, simulations were carried out to evaluate the electrochemical reactor performance to reduce the hexavalent chromium (Cr(VI)) from a wastewater. The conditions used to carry out the simulations were: Cr(VI) concentration in the influent of 890 mg/L and the influent pH = 0.5. The simulations were performed to reach a concentration of Cr(VI) < 0.5 mg/L in the effluent that it is the maximum concentration permitted by the environmental Mexican regulations (SEMARNAP, 1997). The results for each reactor inlet and an ideal plug flow reactor (PFR) are shown in Table 1.

The result in Table 1, show that the type of inlet affects the performance of the reactor. The residence time for the central and lateral inlets, is shorter than both, the ideal plug flow reactor and the reactor operated with tangential inlet. As seen before, this can be explained because when the reactor operates with the tangential inlet, the zones of lower velocity (dead zones) are lessened. Consequently, this effect causes a better use of the reactor volume because when the reactor is operated with the other inlets, the operation volume is lessened (about 11% less than the reactor with the tangential inlet) due to there are more zones with low velocity than with the tangential inlet. Additionally, with the tangential inlet, the backmixing is reduced and consequently cause a lower dispersion (the lowest Nd of the three inlets) in the reactor.

Those effects make that the Cr(VI) concentration in the effluent from the reactor operated with the tangential inlet is the lowest of the three and complies with the Mexican environmental regulations (0.5 mg/L). On the other hand, with the other inlets, it is not possible to reduce Cr(VI) to the level permitted by the environmental regulations and it would be necessary increase the residence time from 27.19 min to 33.3 min for central inlet and from 27.37 min to 32.8 min for lateral inlet, which means that to reach the Cr(VI) concentration (<0.5 mg/L), it would be necessary, for example, to increase reactor volume in about 22.5% and 19.8%, respectively. Comparing the performance of the PFR with the reactor with tangential inlet, it can be noticed that the residence time in the PFR is shorter than the one of the reactor with the tangential inlet, agree with other studies (Martínez & Rodriguez, 2007). This can be explained because the spiral electrode obligates the fluid particles within the reactor to have a spiral trajectory (green contours in Fig. 6) that is longer than the linear trajectory of the fluid particles considered to evaluate the residence time in the PFR. During the electrochemical Cr(VI) reduction, hydroxide ions are generated (Pletcher & Walsh, 1993; Rodriguez, Mendoza, Puebla, & Martinez, 2009), due to the reaction, 2H₂O+2 e⁻ → H₂ + 2OH⁻, hence the pH in the reactor trends to increase. As seen, slightly higher pH values are reached with the tangential inlet, because the residence time and reduction of Cr(VI) to Cr(III) are higher. Note that to precipitate the Cr(III) to remove it and to comply with the pH parameter established by the Mexican environmental regulations, it is necessary to increase the pH to values about 8.0.

4. Conclusions

The type of electrochemical reactor inlet clearly affects its performance. By CFD simulation, it was possible to obtain the axial velocity profiles within the reactor at different operation inlets. The axial velocity profile is specific for each inlet, which is as its footprint. The electrochemical reactor operated with tangential inlet gives the best performance of the three types of inlets tested. The lowest Cr(VI) in the electrochemical reactor effluent was obtained when it was operated with the Tangential inlet. This type of inlet produces a more homogeneous axial velocity distribution within the reactor that reduces the backmixing, hence the dispersion in the reactor. The fluid particles in the reactor follow spiral trajectories that increase the path length and the residence time. Moreover, by CFD simulations, is possible to find out and estimate the fluid behavior within the electrochemical reactor to evaluate and correct its operation.

References


<table>
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<tr>
<th>Table 1</th>
<th>Results for each reactor inlet and an ideal plug flow reactor.</th>
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<tbody>
<tr>
<td>Parameter</td>
<td>PFR (no dispersion)</td>
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<tr>
<td>Residence time (s/min)</td>
<td>1654.7/27.578</td>
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<tr>
<td>Nd = D/UL</td>
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<tr>
<td>Effluent Cr(VI) (mg/L)</td>
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</tr>
<tr>
<td>Effluent pH</td>
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