ELSEVIER

Chemical Engineering Journal 105 (2005) 139–145

Chemical Engineering Journal

www.elsevier.com/locate/cej

Process analysis for treatment of industrial plating wastewater: simulation and control approach

R. Aguilar[*], S.A. Martínez, M.G. Rodríguez, G. Soto

Departamento de Energía, Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo No. 180, Reynosa-Tamaulipas,
Azcapotzalco, 02200 México, D.F., Mexico

Received 22 March 2004; received in revised form 30 September 2004; accepted 6 October 2004

Abstract

One of the better options to remove chromium VI (Cr(VI)) from wastewaters is the electrochemical continuous reactor. This process can be used to clean rinse waters from the plating industry. A mathematical model of the reactor is developed by classical application of mass balances for Cr(VI) and Fe, both corroborated in a bench scale electrochemical reactor. The reactor model is employed as the *real* process where the proposed controller is implemented. For the controller synthesis a reduced order uncertainty estimator is employed to infer the reaction rate, which is assumed unknown and an input/output linearising controller is designed, using the input flow to the reactor as control input and the Cr(VI) concentration in the wastewater as controlled variable. This procedure yields a nonlinear PI controller; where new tuning rules are given. Stability analysis of the closed loop behaviour of the reactor under the proposed methodology is done via mathematical analysis of the equations that describe the dynamic behaviour of the estimation and regulation errors. The performance of the controlled reactor is illustrated with numerical simulations.

Keywords: Electrochemical reactor; Hexavalent chromium reduction; Robust regulation; Wastewater

1. Introduction

Hexavalent chromium (Cr(VI)) is, perhaps, one of the most worrying pollutants from the plating industry. This metal, at this oxidation state, is generally presented in rinsing waters of many electroplating processes. Moreover, it is prohibited to discharge these waters into rivers or sewers if there is a certain amount of Cr(VI), which is too low to attempt recovery (as a metal) by electrochemical methods. Conventional treatment—such as ferrous sulphate reduction with lime precipitation—generates large amounts of sludge. In fact, the use of calcium hydroxide to precipitate reduced chromium could reach a sludge generation of up to 307 kg per 100 kg of chromium hexavalent reduced to its trivalent form.

In some countries such sludge is considered hazardous, there are limitations to its maximum concentration level (the Mexican norm is less than 0.5 mg/L) and, therefore it requires special handling [1]. Consequently, its final disposal is always expensive [2]. An electrochemical continuous reactor is proposed as an alternative to the chemical precipitation process. It is based on the reduction of hexavalent chromium to its trivalent chromium oxidation state (Cr^{3+}) due the presence of Fe^{2+}, which is liberated from the electrodes inside the reacting solution when an established direct current quantity is applied to the anode. In order to obtain satisfactory performance of the reactor and comply with environmental constrains, the necessity to regulate the operation of this kind of processes arises spontaneously.

Usually, regulative control of process is performed by linear proportional-integral-derivative (PID) controllers. The crude approach to this strategy has several drawbacks that lead to inadequate performance, such as poor robustness properties against sustained disturbances, high nonlinear behaviour and changes in operating conditions. This situation can be explained given that these controllers (PID) are designed via linear analysis and consequently only show satis-

---

[*] Corresponding author.
E-mail address: raguilar@correo.azc.uam.mx (R. Aguilar).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2004.10.004

Nomenclature

Cr(VI)	residual concentration of chromium(VI) in solution (mg/L)
F	volumetric reactor flow ($\mathrm{L\,min^{-1}}$)
F_a	Faraday's constant (96,500 C/mol)
g	control gain ($\mathrm{min^{-1}}$)
k_1	kinetic constant = 0.78 ($\mathrm{min^{-1}}$)
K_2	adsorption constant = 0.155 (L/mg)
l	current intensity ($\mathrm{A/m^2}$)
M	molar mass (mg/mol)
n	number of electrons
$r_{\mathrm{Cr(VI)}}$	kinetic term for Cr(IV) consumption ($\mathrm{mg\,L^{-1}\,min^{-1}}$)
r_{Fe}	kinetic term for Fe generation ($\mathrm{mg\,L^{-1}\,min^{-1}}$)
Theta	control input (=F/V) $\mathrm{min^{-1}}$
V	volume of reactor (L)

Greek letters

τ	observer gain ($\mathrm{min^{-1}}$)

factory performance in a small neighbourhood around the operating set-point chosen for its design [3]. Therefore, for processes with high nonlinear behaviour other kinds of control strategies are needed. The control of process with complex behaviour is a current challenge, due to the necessity of global efficiency in process performance which provokes processes to be operating under more demanding conditions. Despite the great interest in the study of processes with complex dynamic behaviour, the industrial application of the control developments for these kinds of systems is still limited. It seems that the industrial strategy is to avoid troublesome operating conditions and design parameters, which could produce instabilities, ignition, and other conditions of maloperation. This conservative philosophy was quite justifiable before the great advances achieved during the last few years in the development of rigorous models for chemical processes and the great advance in the computer hardware for data processing and control. Actually, the state of affairs suggests that the industrial view should change into the direction of exploring available opportunities with regard to higher conversion, yield and selectivity regions.

In this paper, a simplified mathematical model of the electrochemical reactor (under CSTR behaviour) experimentally corroborated is employed as the *real* process for the design of an input–output linearising controller based on a reduced order observer. The observer estimates on-line the reaction rate, which is assumed unknown, in order to regulate Cr(VI) concentration in the reactor, using the input reactor flow as the control input. This controller's structure is equivalent to a standard PI where new tuning rules for the control gains are giving in terms of process parameters; therefore control variables have strong physical meaning.

The paper has the following structure: Section 2 describes the experimental electrochemical reactor and presents the mathematical analysis of the process. Section 3 deals with the synthesis of an uncertainty observer and develops a non-ideal control law, which is equivalent to a PI controller; also the new tuning rules are proposed. Section 4 is related to the numerical simulations showing the open-loop dynamic behaviour, and the closed-loop performance of the reactor when the proposed controller is used.

2. Experimental

2.1. Reactor modelling and validation

Synthetic (prepared with potassium dichromate at 130 mg Cr(VI)/L) and industrial rinse water (at 273 mg Cr(VI)/L) were treated in a continuous electrochemical reactor with a volume of 16 L (Fig. 1). A rotating iron ring electrode was used during each electrochemical removal process. The rotating iron electrodes consists of 14 iron steel rings, 11.5 cm diameter, allocated as a sequence of one cathode and one anode. The gap between the ring electrodes was 1.0 cm. The superficial area of each iron ring was 75.0 $\mathrm{cm^2}$. Electrical current of 5.0 A and voltages between 2.75 and 4.5 V were applied during the process, using a direct current power supply. A shaft was used to support the ring arrangement and was connected to a variable speed motor. The pH in the reactor solution was maintained at 2.0 units during the electrochemical process by the addition of sulphuric acid. In order to evaluate chromium reduction, samples were taken out, from the electrochemical reactor at different times during the process. For each sample the pH was raised to 8.5 units (under this condition chromium hydroxide and ferric hydroxide are formed and precipitated) by the addition of sodium hydroxide. After precipitation, the concentration of Cr(VI) in the supernatant liquid was measured by the diphenylcarbazide method [4].

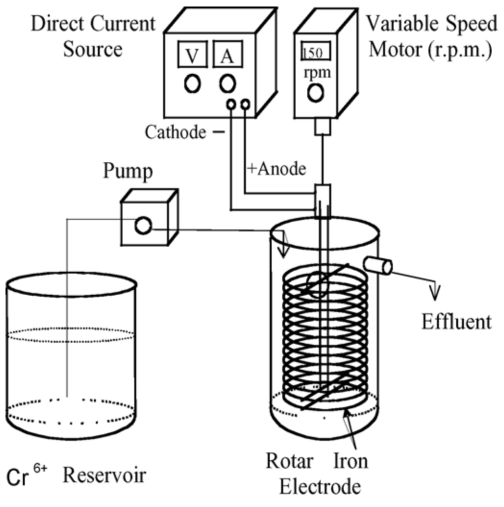

Fig. 1. Electrochemical reactor with rotating iron electrodes.

A classical mass balance was performed for the hexavalent chromium concentration in the solution. The following modelling assumptions were considered: (i) continuous stirred tank behaviour; (ii) non-steady state operation; (iii) constant reaction volume (adequate for liquid phase). Ferrous ions are released from the anode by electron transfer (Eq. (1)); meanwhile Cr(VI) is reduced in the solution (Eq. (2)).

$$\mathrm{Fe}^0 - 2\mathrm{e}^- \rightarrow \mathrm{Fe}^{2+} \tag{1}$$

$$6\mathrm{Fe}^{2+} + \mathrm{Cr_2O_7}^{2-} + 14\mathrm{H}^+ \rightarrow 6\mathrm{Fe}^{3+} + 2\mathrm{Cr}^{3+} + 7\mathrm{H_2O} \tag{2}$$

During the electrochemical process a Cr(VI) reduction on the cathode can occur, as shown in Eq. (3) [5]:

$$\mathrm{Cr_2O_7}^{2-} + 6\mathrm{H}^+ + 6\mathrm{e}^- \rightarrow \mathrm{Cr_2O_4}^{2-} + 3\mathrm{H_2O} \tag{3}$$

2.1.1. Chromium(VI) kinetic removal model

In order to determine the kinetic model in the process, a set of experiments was carried out in the batch reactor described.

Experimental data points are shown in Fig. 3. The Cr(VI) reduction as function of time is described by a kinetic model obtained that passes the goodness of fit Chi-square test at 0.01 significance level (a 99% confidence level). The experimental data were accurately fitted using a zero order reaction rate model at high Cr(VI) concentrations and by a first order reaction rate model at low concentrations. The overall rate equation ($r_{\mathrm{Cr(VI)}}$) with respect to the Cr(VI) (Eq. (4)), was obtained by applying the integral method [6]. See nomenclature section for variables definition:

$$r_{\mathrm{Cr(VI)}} = \frac{k_1\mathrm{Cr(VI)}}{1 + K_2\mathrm{Cr(VI)}} \tag{4}$$

The resulting expression for the mass balance of the chromium(VI) in the solution is the following:

$$\frac{\mathrm{dCr(VI)}}{\mathrm{d}t} = \frac{F}{V}(\mathrm{Cr(VI)_{in}} - \mathrm{Cr(VI)}) - r_{\mathrm{Cr(VI)}} \tag{5}$$

Naturally, the reaction rate has its own dynamic behaviour, which can be expressed as:

$$\frac{\mathrm{d}r_{\mathrm{Cr(VI)}}}{\mathrm{d}t} = h(\mathrm{Cr(VI)}, t) \tag{6}$$

The mass balance of the iron in the solution is as follows:

$$\frac{\mathrm{d}C_{\mathrm{Fe}}}{\mathrm{d}t} = -\frac{F}{V}C_{\mathrm{Fe}} + r_{\mathrm{Fe}} \tag{7}$$

$$r_{\mathrm{Fe}} = \frac{MI}{nF_{\mathrm{a}}V} \tag{8}$$

See notation section, for parameters description.

Note that this kind of system presents a complex behaviour and electrochemical reaction occurs in the aqueous media as well as on the corresponding electrodes. For dynamic analysis and control purposes the model developed was believed to be adequate.

3. Design of the control methodology

3.1. Control methodology

The control of nonlinear systems has been widely studied during the last 20 years, especially the characterization of input/output and exact linearisable systems. This corresponds to systems that can be fully or partially linearised by a change of coordinates and/or state feedback following differential-geometric concepts, e.g. [7]. Such class of nonlinear systems can be linearised by state feedback control which cancels all the nonlinearities assuming perfect knowledge of the mathematical model, producing global asymptotic stability [8]. A drawback of exact linearisation techniques is that they rely on exact cancellation of nonlinearities. In practice, exact knowledge of system dynamics is not possible. A more realistic situation is to know some nominal functions of the corresponding nonlinearities, which are employed in the control design. However, the use of nominal model nonlinearities can lead to performance degradation and even closed-loop instability. In fact, when the systems presents strong nonlinearities, the standard linearising controller cannot cancel completely such nonlinearities and instabilities can be induced. The worse case is when the knowledge of the nonlinearities is very poor or null, consequently conventional linearising techniques are inadequate.

Because of these events, the robust stability problem for uncertain systems arises as a necessary control design approach to supply the controller with the corresponding on-line information and try to realise a satisfactory closed-loop performance. Research on robust control design for linearisable nonlinear systems has be done considering observed-based controllers [9,10] where peaking phenomena, stability issues and robust performance are still topics that deserve further study.

Generally, nonlinear systems can be transformed into canonical controllable form via a nonlinear change of coordinates given by $L_{\mathrm{B}}\varsigma_i = 0$, $i = 1,2, \ldots, n - r$, where r is the relative degree of the system (4) and $L_{\mathrm{f}}h(x)$ are the Lie derivatives of the measured output $h(x)$ along the vector field of the system $f(x)$ [13].

The system under study can be transformed into the following canonical form (Eq. (9)):

$$\begin{aligned}
&\dot{\varepsilon}_i = \varepsilon_{i+1} \quad \text{for} \quad i = 1, 2, \ldots, r - 1,\\
&\dot{\varepsilon}_r = L_{\mathrm{f}}^r h(x) + L_{\mathrm{B}}L_{\mathrm{f}}^{r-1}h(x)u,\\
&\dot{\varsigma} = g(\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_r, \varsigma), \qquad y = \varepsilon_1
\end{aligned} \tag{9}$$

The conditions for the existence of this transformation are related to a well-defined relative-degree of the system [11].

The zero dynamics are given by the $(n - r)$-dynamic subsystem $\dot{\varsigma} = g(0, \varepsilon_2, \ldots, \varepsilon_r, \varsigma)$. For this process, zero dynamics are locally stable. Consequently, the static feedback controller for $L_{\mathrm{B}}L_{\mathrm{f}}^{r-1}h(x) \neq 0$ and some being external input ν related to u by the equality $u = \frac{\nu - L_{\mathrm{f}}^r h(x)}{L_{\mathrm{B}}L_{\mathrm{f}}^{r-1}h(x)}$, can linearise the input/output map of the system. In the case under study, the relative-degree of the system is $r = 1$.

The study of systems that exhibit relative-degree one is very important for many control applications, for example a wide class of chemical reactors show this characteristic. They are mathematically modelled as control affine systems where the control input is a linear term [12]. This kind of system displays some interesting features, such as the equivalent dissipativeness by means of a state or an output feedback. In general, it is easier to stabilize dissipative systems than non-dissipative ones [3].

The input–output linearising control law is related to the input volumetric flow as control input, which is employed to regulate the chromium(VI) concentration in the wastewater, considering this chemical reactive as measured reactor output (Eq. (10)):

$$F = \frac{1}{(\mathrm{Cr(VI)_{in}} - \mathrm{Cr(VI)})}[-ge_2 - r_{\mathrm{Cr(VI)}}]V \tag{10}$$

This ideal control law imposes a linear behaviour to the tracking error ($e_2 = \mathrm{Cr(VI)} - \mathrm{Cr(VI)}^{\mathrm{sp}}$); in this way, it is possible to guarantee that $\lim_{t\to\infty} \mathrm{Cr(VI)} \to \mathrm{Cr(VI)}^{\mathrm{sp}}$, considering the controller gain $g > 0$. However, as can be observed, this kind of control methodology is based on an ideal mathematical model of the process.

Nevertheless, it is well known that mathematical models have some uncertain terms related to non-modelled dynamics and/or unknown parameters. One of the most common uncertainties during the modelling of chemical reactors is the reaction rate. Evaluation of reaction rates generally is a difficult task in chemical processes, especially in the case of complex electrochemical reactions which take place in the reactor. This lead to construct an uncertain mathematical model of this process, introducing the problem of on-line estimation of reaction rates. Currently, estimation theory is one of the most active research areas due to the necessity of obtaining on-line estimates of unknown terms related to mathematical models for process identification and control purposes [13].

By taking the chromium(VI) concentration in the solution as the measured output variable, the system given by Eqs. (4) and (5) can be written in an observability form [14], so that it satisfies the observability condition. Hence, $r_{\mathrm{Cr(VI)}}$ can be reconstructed by means of a state observer. Such observer could be constructed as a copy of the system (Eqs. (4) and (5)) corrected by an observation error. However, this typical observer structure cannot be realized because the term $h(\mathrm{Cr(VI)}, t)$ is unknown. In the process considered, some of the state variables (chromium(VI) concentration) are directly the system output. Therefore, a reduced-order observer to estimate the unknown terms related to the reaction rate in the reactor is proposed (Eq. (11)):

$$\frac{\mathrm{d}\hat{r}_{\mathrm{Cr(VI)}}}{\mathrm{d}t} = \tau(r_{\mathrm{Cr(VI)\text{-}obs}} - \hat{r}_{\mathrm{Cr(VI)}}) \tag{11}$$

Here, the observed uncertainty $r_{\mathrm{Cr(VI)\text{-}obs}}$ is obtained by solving the mass balance equation (Eq. (12)):

$$r_{\mathrm{Cr(VI)\text{-}obs}}(\mathrm{Cr(VI)}, t) = -\frac{\mathrm{dCr(VI)}}{\mathrm{d}t} + \frac{F}{V}(\mathrm{Cr(VI)_{in}} - \mathrm{Cr(VI)}) \tag{12}$$

As it can be seen, the structure of the proposed observer includes the derivative of the chromium(VI) concentration, which must be calculated in order to obtain estimates of the reaction rate. However, the synthesis of derivators is a difficult task; moreover, if concentration measurements are noisy the synthesis could be impossible. In order to avoid this situation a change of variable is proposed (Eq. (13)). The new variables produce an uncertainty observer with the structure given in Eq. (14):

$$\Theta = \hat{r}_{\mathrm{Cr(VI)}} - \tau e_2 \tag{13}$$

$$\frac{\mathrm{d}\Theta}{\mathrm{d}t} = g\tau e_2 \tag{14}$$

Then the corresponding equation for the uncertainty estimator depends on the tracking error (Eq. (15)):

$$\hat{r}_{\mathrm{Cr}} = g\tau \int_0^t e_2(\sigma)\,\mathrm{d}\sigma + \tau e_2 \tag{15}$$

The non-ideal control law employs an estimate of the reaction rate, and its structure is given by Eq. (16):

$$F = \frac{1}{\mathrm{Cr(VI)_{in}} - \mathrm{Cr(VI)}}[-ge_2 - \hat{r}_{\mathrm{Cr(VI)}}]V \tag{16}$$

This controller is able to produce practical stability, which means that the controller can lead the trajectories of the reacting process into a neighbourhood around the set point when the uncertainty values converges adequately to the real values of the uncertainty, i.e. the estimation methodology converges asymptotically [10]. Now, including Eq. (11) in Eq. (12) it is possible to obtain a non-ideal controller (Eq. (17)):

$$F = \frac{V}{\mathrm{Cr(VI)_{in}} - \mathrm{Cr(VI)}}\left[(g+\tau)e_2 + g\tau\int_0^t e_2(\sigma)E\sigma\right] \tag{17}$$

As it can be seen, Eq. (17) follows a PI structure, where the controller's gains are related to the closed-loop characteristic time g^{-1} and the measurement characteristic time τ^{-1}. The classical structure of PI controllers is given by Ogunaike and Ray [15] (Eq. (18)):

$$F = K\left[e + \frac{1}{\tau_i}\int_0^t e_2(\sigma)\,\mathrm{d}\sigma\right] \tag{18}$$

By algebraic comparison of Eqs. (17) and (18), tuning rules for proportional gain (Eq. (19)) and the integral time (Eq. (20)) are given. These tuning rules avoid the identification steps of the process and the use of semi-empirical methods like root locus, Ziegler-Nichols, IMC, etc.

Therefore the proportional control gain is given by:

$$K = -\frac{g+\tau}{\mathrm{Cr(VI)_{in}} - \mathrm{Cr(VI)}} \tag{19}$$

And the corresponding integral control gain is:

$$\tau_i = -\frac{g+\tau}{g\tau} \tag{20}$$

3.2. Stability comments

First let us consider the convergence analysis of the proposed observer (Eq. (11)), which is an asymptotic proportional reduced observer for the system given by Eq. (6), where the observer gain $\tau > 0$, determines the desired convergence rate of the observer.

Now, consider that the following assumptions are satisfied. There exist $\tau \in \Re^+$ and $N \in \Re^+$ such that:

Assumption 1. $\|h(\mathrm{Cr(VI)}, t)\| \leq N$ and $\lim_{t\to t_0} \frac{N}{\tau} = 0$

Assumption 2. $\lim_{t\to t_0} \left\|\exp\left(-\int_0^t \tau \, \mathrm{d}\sigma\right)\right\| = 0$, where t_0 is large enough.

Then, estimation errors could be defined by Eq. (21), which, considering Eqs. (12) and (13), exhibits the dynamics of the estimation error as given by Eq. (22):

$$e_1 = r_{\mathrm{Cr(VI)\text{-}obs}} - \hat{r}_{\mathrm{Cr}} \tag{21}$$

$$\dot{e}_1 + \tau e_1 = h(\mathrm{Cr(VI)}, t) \tag{22}$$

Eq. (22) can be solved to obtain the error dynamics in the time domain (Eq. (23)):

$$e_1 = e_{10}\exp(-\tau t) + \int_0^t \exp(-\tau t) h(\mathrm{Cr(VI)}, s)\,\mathrm{d}s \tag{23}$$

where e_{10} is the corresponding initial condition of the estimation error. Now, taking norms of both sides of Eq. (23) yields an inequality (Eq. (24)), which is limited after Assumptions 1 and 2 (Eq. (25)):

$$0 \leq \lim_{t\to t_0} \|e_1\| \leq \|e_{10}\| \lim_{t\to t_0}\left[\left\|\exp\left(-\tau\int \tau\,\mathrm{d}t\right)\right\|\right] + \frac{\lim_{t\to t_0}\left[\int_0^t \|\exp(\tau\,\mathrm{d}t)h(\mathrm{Cr(VI)}, t)\,\mathrm{d}\sigma\|\right]}{\lim_{t\to t_0}\left\|\exp\left(\int\tau\,\mathrm{d}t\right)\right\|} \tag{24}$$

$$0 \leq \lim_{t\to t_0}\|e_1(t)\| \leq \frac{\lim_{t\to t_0}\left[N\int_0^t \left\|\exp\int\tau\,\mathrm{d}\sigma\right\|\right]}{\lim_{t\to t_0}\left\|\exp\left(\int\tau\,\mathrm{d}t\right)\right\|} \tag{25}$$

Eq. (25) is an example of the ∞/∞ case of uniform L'Hopital's rule, which can be applied to solve the undefined quotient (Eq. (26)). Now, taking the limit when $t \to t_0$ (remember that t_0 is large enough) it is possible to obtain a quota for the estimation error (Eq. (27)). This inequality implies that the estimation error can be as small as is desired, if the observer gain τ is chosen large enough:

$$0 \leq \lim_{t\to t_0}\|e_1(t)\| \leq \lim_{t\to t_0}\frac{N\left\|\exp\left(\int\tau\,\mathrm{d}t\right)\right\|}{\left\|\exp\left(\int\tau\,\mathrm{d}t\right)\right\|\,\|\tau\|} = \lim_{t\to t_0}\frac{N}{\|\tau\|} \tag{26}$$

$$|e_1| \leq \frac{N}{\|\tau\|} \to 0 \tag{27}$$

Note that if the system output is corrupted by additive noise, i.e. $Y = \mathrm{Cr(VI)} + \delta$ and the noise δ is considered bounded, i. e. $\|\delta\| \leq \Delta$, a similar methodology, used to analyze the estimation error e_1 can be applied in order to prove that the steady-state estimation error becomes $\frac{(N+\Delta)}{\tau}$, which proves robustness against noisy measurements.

In order to analyze the closed-loop stability of the Cr(VI) trajectories in the reactor, the closed-loop dynamic equation of the mass balance should be used (Eq. (28)):

$$\dot{e}_2 = ge_2 + (r_{\mathrm{Cr(VI)}} - \hat{r}_{\mathrm{Cr(VI)}}) \tag{28}$$

If $\hat{r}_{\mathrm{Cr(VI)}} \to r_{\mathrm{Cr(VI)}}$ then $r_{\mathrm{Cr}} - \hat{r}_{\mathrm{Cr}} \to 0$, the ideal control law is recovered together with its stability properties; otherwise, the estimation error is limited as $|r_{\mathrm{Cr(VI)}} - \hat{r}_{\mathrm{Cr(VI)}}| \leq \frac{N+\Delta}{\tau}$, accordingly with the above development.

Solving the linear ordinary differential equation (28) and applying the Gronwall inequality, it is possible to obtain a quota for the mass balance error (Eq. (29)); this quota can be evaluated when $t \to t_0$ with t_0 large enough (Eq. (30)):

$$|e_2| \leq \frac{N+\Delta}{g\tau} + e_{20}\exp(-gt) \tag{29}$$

$$|e_2| \leq \frac{(N+\Delta)}{g\tau} \tag{30}$$

It is important to note that tracking error e_2 can be made as small as desired in two ways. The first one is to consider a control gain g large enough; however this approach has several drawbacks such as great control effort, input saturation and so on. The second way is related to the estimation error: it tends asymptotically to zero rapidly increasing the estimator gain τ. This second way diminishes the tracking error value, avoiding the peaking phenomena and yielding good performance of the estimation methodology.

4. Results and discussion

Numerical simulations were carried out in order to valid the proposed mathematical model for Cr(VI) concentration. The corresponding nominal operating conditions are shown in Table 1.

Figs. 2 and 3 show the performance of the proposed model of the reactor compared with experimental data, as it can be seen the model has a good agreement with the experiments.

Table 1
Nominal operating conditions for the electrochemical reactor

Variable	Value	Units
F/V	0.052	min^{-1}
$\mathrm{Cr(VI)_{in}}$, case 1	130	mg/L
$\mathrm{Cr(VI)_{in}}$, case 2	273	mg/L

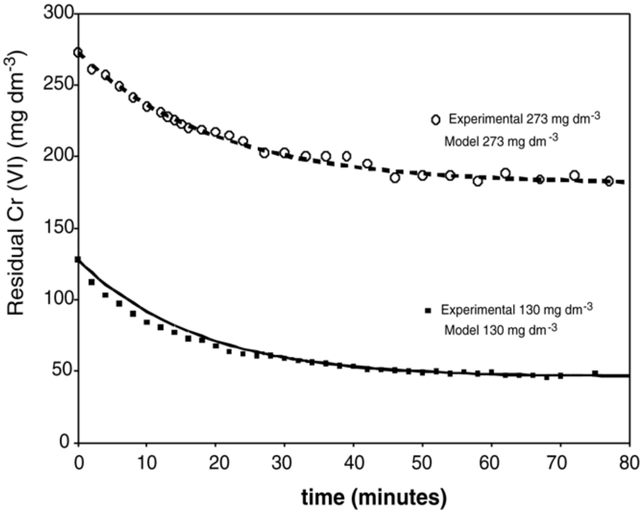

Fig. 2. Performance of the proposed model compared with experimental data.

In Fig. 3, the Faraday curve, obtained from Eq. (8), shows that the Fe(II) released rate by the electric current applied, which is actually lower than the experimental curve of ferrous ions released. It means that there is another mechanism where the Fe(II) is freed to reach the actual releasing rate. These Fe(II) ions are released by dissolution (corrosion) of the electrodes caused by acidic media as shown by the corrosion curve.

Furthermore, Fig. 4 is related to an open-loop bifurcation-like map, which shows the behaviour of the Cr(VI) concentration in steady state for the corresponding value of the inverse of the residence time (*F*/*V*). It can be observed that to reach the Cr(VI) concentration around the desired level (less than 0.5 mg/L) the volumetric flow of the reactor must to be near to zero. This means that batch regimen operation must be selected, which reduce highly the benefits of the continuous operation as large production.

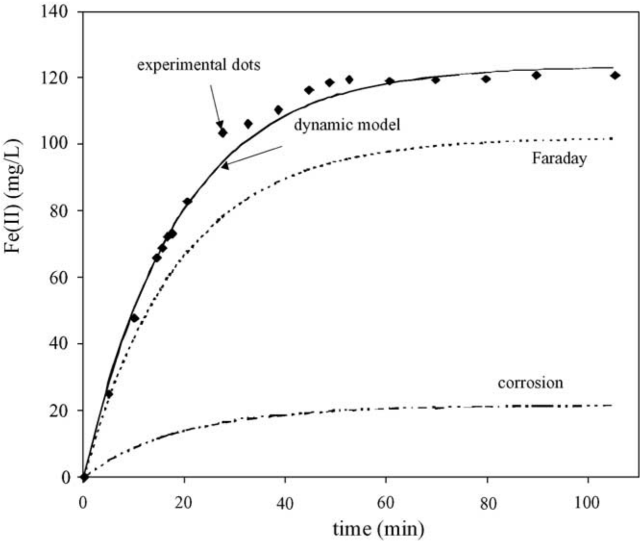

Fig. 3. Performance of the dynamic model proposed (dynamic model), corrosion effect (corrosion) and current applied effect (Faraday) to describe Fe(II) released in the continuous stirred flow reactor during the electrochemical process.

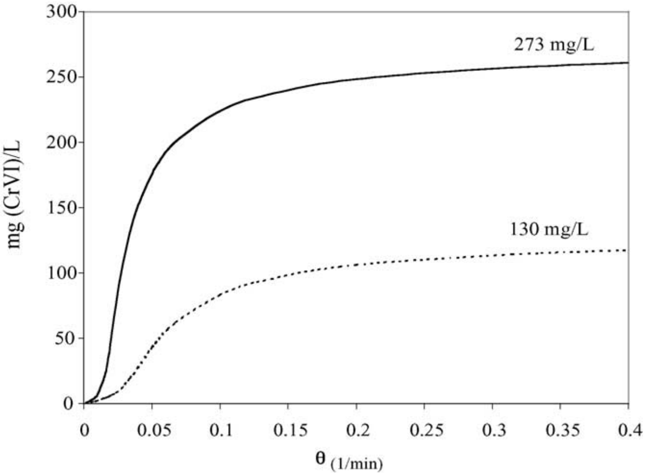

Fig. 4. Bifurcation map of Cr(VI) vs. control input for influent with 130 and 273 mg/L.

With the results shown in Fig. 4, the necessity to implement a control strategy arises spontaneously in order to maintain continuous operation. The performance of the on-line reaction rate observer is shown in Fig. 5; it is possible to note that the estimated values of the reaction rate converge adequately to the real values of the real kinetic term. Fig. 6 is related to the closed-loop performance of the Cr(VI) concentration, it presents a smooth behaviour to reach the set point needed, without overshoots and oscillations Finally the performance of the control input can be seen in Fig. 7, where the controller diminish to zero de volumetric flow of the reactor, in order to reach the reference required, considering the high concentrations of Cr(VI) in the inlet flow and the initial concentration in the reactor; remember that volumetric flows near to zero are needed to reach low Cr(VI) concentrations as is shown in Fig. 4. Considered the above mentioned the controller closes the volumetric input flow, to allow the Cr(VI)

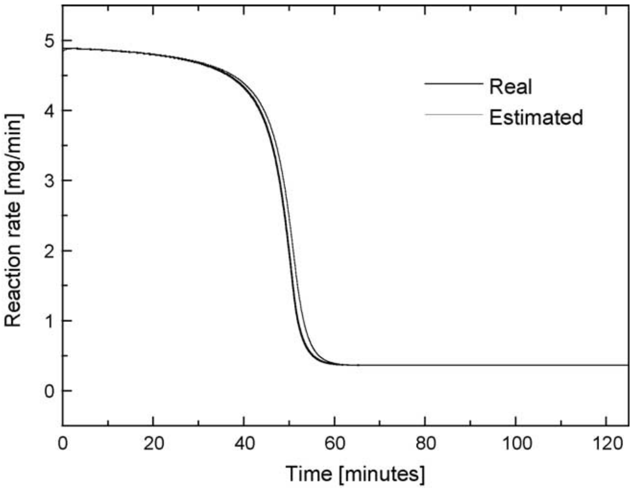

Fig. 5. Performance of the uncertainty observer.

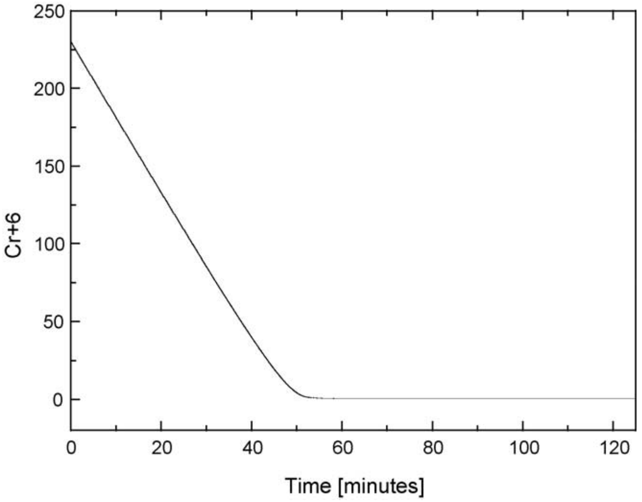

Fig. 6. Closed-loop behaviour of Cr(VI) concentration (mg/L).

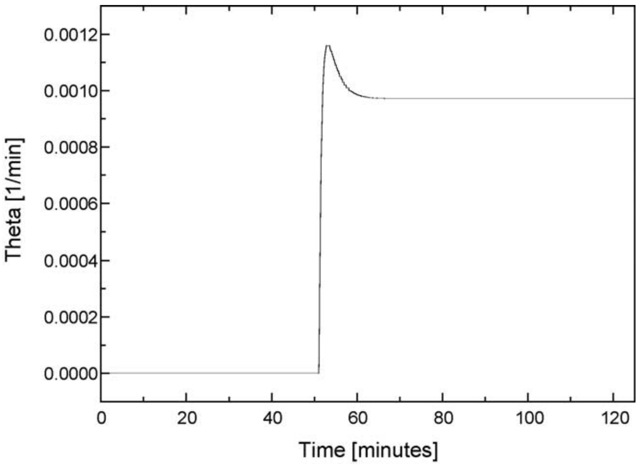

Fig. 7. Performance of the control input.

diminishes enough by electrochemical reduction. At 50 min the controller, in accordance with the structure of Eq. (17), increases the flow in order to keep the reference concentration value, without great effort.

5. Conclusions

In this paper a mathematical model for electrochemical continuous stirred reactor is presented, it is employed to analyze the open-loop behaviour of the process related with the Cr(VI) removal, simulation results shown that open-loop continuous operation is not factible to reach the output Cr(VI) concentration required (∼0.5 mg/L). Therefore control actions must be taken. The proposed controller is synthesized via a linearising input–output controller based of uncertainty (kinetic term) estimator. This structure is equivalent to PI controller with variable gains. Stability analysis of the proposed methodology is developing in order to show asymptotic convergence to a small neighbourhood of the set point required. Numerical simulations illustrate a satisfactory closed-loop performance of the electrochemical reactor.

References

[1] Ministry of the Environment, Natural Resources and Fisheries NOM-001-ECOL-1996, Ministry of the Environment, México, D.F., México, 1997.
[2] W. Eckenfelder, Industrial Water Pollution Control, McGraw-Hill, New York, 1989, pp. 87–123.
[3] R. Aguilar, R. Martínez-Guerra, A. Poznyak, Reaction heat estimation in continuous chemical reactors using high gain observers, Chem. Eng. J. 87 (3) (2002) 351–356.
[4] American Public Health Association/American Water Works Association/Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA, 1995.
[5] D. Goloub, Y. Oren, Removal of chromium from aqueous solutions by treatment with porous carbon electrodes: electrochemical principles, J. Appl. Electrochem. 19 (1988) 311–316.
[6] O. Levenspiel, Chemical Reaction Engineering, 3rd ed., Wiley, 1999.
[7] A. Isidori, Nonlinear Control Theory, Springer-Verlag, New York, 1995.
[8] J. Slotine, W. Li, Applied Nonlinear Control, Prentice-Hall, New Jersey, 1991.
[9] M. Jankovic, Adaptive nonlinear output feedback tracking with partial high gain observer and backstepping, IEEE Trans. Autom. Contr. 42 (1997) 106–117.
[10] R. Aguilar, J. González, M. Barrón, J. Alvarez-Ramirez, Control of a fluid catalytic cracking units based on proportional-integral reduced order observers, Chem. Eng. J. 75 (1999) 77–85.
[11] C. Kravaris, P. Doutiris, Nonlinear state feedback control of second-order nonminimum phase systems, Comput. Chem. Eng. 14 (1990) 439–449.
[12] J. Kolavennu, Semiglobal stabilization of a class of nonlinear systems using output feedback, IEEE Trans. Autom. Contr. 38 (1993) 1412–1415.
[13] N. Kazantis, C. Kravaris, Nonlinear observer design for process monitoring, Ind. Eng. Chem. Res. 39 (2000) 408–419.
[14] S. Diop, M. Fliess, Nonlinear observability, identifiability, and persistent trajectories, in: Proceedings of the 30th Conference on Dec. and Ctrl., Brighton, England, 1991, pp. 714–719.
[15] B.A. Ogunnaike, W.A. Ray, Process Dynamics, Modeling and Control, Oxford University Press, 1994.