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Strategy for the online monitoring of the Cr(VI) reduction

In this contribution, we describe an algorithm for the continuous monitoring of Cr(VI) occurring during a wastewater treatment. This approach performs its task having available only the online measurements of the redox potential. The results show that the redox potential is a valuable indicator of the process time evolution. The strategy here presented is based on the development of a mathematical model that includes online measurable states, with the property of being observable. Then, a sliding observer is designed for the estimation of Cr(VI). The paper includes the detailed design of the monitoring scheme as well as its experimental application at the laboratory level.

Key words: Hexavalent chromium, ORP electrode, mathematical model, online monitoring.

1. INTRODUCTION

Nature has an intrinsic capacity to remove contaminants. Unfortunately, since man has begun the production on a massive scale, nature's capacity has been exceeded. Chromium compounds are an example of such problems. Different compounds of chromium have been in widespread commercial use for over the last century. Early applications include chrome pigments and tanning liquors, and lately, in electroplating, wood preservation, among many others [1]. As it is well known, chromium chemical characteristics and degree of toxicity depend upon its oxidation state, which is dominated by the trivalent (Cr(III)) or hexavalent forms [2]. Cr(VI) residues are considered dangerous, whereas trivalent chromium is substantially harmless. Therefore, the Cr(VI) reduction through an oxidation-reduction process is environmentally beneficial since a hazardous species is transformed into a nonhazardous one.

Many reactor configurations for the reduction of Cr(VI) have been extensively studied [3-6]. However, none of them have included online measurable variables. In other words, the monitoring process in those works happens offline, occurring an important delay between the sample time and the moment in which the results are available. Such delay makes difficult or even impossible to take any corrective action in the reactor. In general, the best approach for monitoring and control at any time a varying process is to have online measurable states.

Taking into account the fact that rarely one can have a sensor on every state variable, and some form

of reconstruction from the available measured output data is needed, an algorithm (observer) can be constructed using the mathematical model of the process to obtain an estimate, say $\hat{x}_1(t)$ of the true state $x_1(t)$. This estimate can then be used as a substitute for the unknown state. The usage of state observers has proven useful in process monitoring and in many other tasks. The engineering concept of observer means an algorithm capable of giving a reasonable estimation of the unmeasured variables of a process using only the measurable output. In order to be able to rebuild the nonmeasured states from the system output, the mathematical models should have a mathematical property called observability. Dynamical systems observability (DSO henceforth) is a rigorous mathematical concept used to investigate if it is possible to know the internal functioning of a given dynamical system. More precisely, one says that a dynamical system is *observable* if it allows the usage of the available information about the output $y(t)$ of the system to estimate the states $x(t)$ of the system, assuming that $x(t) \in \mathbb{R}^n$. Thus, the main idea behind observability is to find the dynamical states of a system based on the knowledge of its output.

Since the redox reaction involves an exchange of electrons, it can be used to generate measurable electrical current as occurs with the Oxidation-Reduction Potential sensors (ORP probe or Redox electrode). Thus, ORP is a measure, in millivolts of the tendency of a chemical substance to oxidize or reduce another chemical substance. Hence, the ORP could be included as one of the states of the model. Then, for the monitoring purpose, a sliding observer can be developed to provide a real-time measurement of the Cr(VI) concentration. Sliding observers are widely used in monitoring non-linear systems and their advantages and disadvantages have been thoroughly described [7].

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Therefore, the aim of the present work is modeling and monitoring the Cr(VI) reduction process, in a batch reactor. We perform our task, building a mathematical model and designing a software sensor to infer the Cr(VI) from an online measurable ORP signal.

2. MATERIALS AND METHODS

An electrochemical glass batch reactor, shown in Figure 1, was used to reduce the concentration of hexavalent chromium, having 1 L operation volume. The reactor was equipped with two iron plates with an area of 30 cm² and with no current source. A synthetic wastewater solution, contaminated with Cr(VI), was used. The solution was prepared with potassium dichromate (K₂Cr₂O₇) and potassium sulfate 0.05 M (K₂SO₄) in distilled water given a final Cr(VI) concentration of 75 ppm. The pH in the solution was fixed at 2.0 through the addition of sulfuric acid, this is an experimental condition, necessary to avoid interference in the ORP lectures due to pH variation. Additionally, the effect of the oxidation of Fe(II) over the total ORP signal was analyzed by using a blank solution over the Fe(II) plates. The blank solution was prepared with potassium sulfate 0.05 M (K₂SO₄) in distilled water and adjusting the pH at 2.0. To minimize the effect of the O₂ and CO₂ in the ORP lectures, N₂ was added to the solution to bubble and drag out these gases from the reactor.

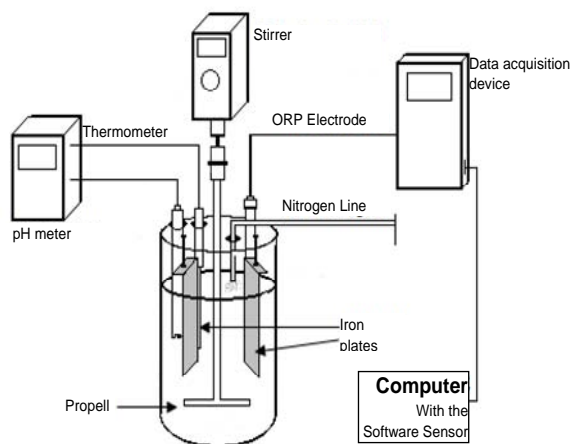


Figure 1. The schematic representation of the experimental setup used for the experiment

The batch processes was monitored for 2 h through sampling. At the same time, the redox potential measurements were acquired periodically each 2 seconds, and the data were stored and computed online in a PC. The redox potential was acquired with Orion® potentiometer with a Calomel ORP electrode

saturated with Hg₂Cl₂-Hg. The collected samples were analyzed, for Fe determination, with a Varian® atomic absorption spectrophotometer using a multielement lamp Cu/Fe/Mn/Cr/Co. Whereas, the Cr(VI) determination was performed by the diphenylcarbazide method [3,6].

3. RESULTS AND DISCUSSION

Since the ORP signal is the results of all the Oxidation-Reduction reactions occurring during the process, the difference between ORP signal in the blank solution (ORP_{Fe(II)}), and the ORP signal in the synthetic wastewater (ORP_{Global}), is Cr(VI) contribution to the ORP signal (ORP_{Cr(VI)}). In other words, the signal ORP_{Cr(VI)}, can be rebuilt by the following subtraction: ORP_{Cr(VI)} = ORP_{Global} - ORP_{Fe(II)}. The results of this idea are presented in the Figure 2, where it is possible to appreciate the rebuilt ORP_{Cr(VI)} signal. This idea is based on the fact that the time evolution of the Fe(II) concentrations is equal in the blank solution and in the synthetic wastewater (see Figure 3).

3.1. The Dynamic Model

The differential mass balance model was created for the adjustment of experimental data and predicts the dynamic behavior of the Cr(VI) reduction process. The model is based on the following hypothesis: (i) there are no spatial gradients, (ii) isothermal operation, (iii) constant pH and volume, (vi) the ORP signal is the results of the additive contribution associated to the Cr(VI) reduction and the oxidation of Fe(II). The resulting dynamical model is described by the following set of ordinary differential equations:

$$\frac{d}{dt}X_1 = K_1X_1$$

$$\frac{d}{dt}X_2 = K_2$$

$$\frac{d}{dt}X_3 = K_1X_1(\alpha_1 + 2\alpha_2X_1 + 3\alpha_3X_1^2 + 4\alpha_4X_1^3 + 5\alpha_5X_1^4)$$

$$\frac{d}{dt}X_4 = \frac{\beta_1K_2(-1 + \beta_2X_2^2)}{(1 + \beta_2X_2 + \beta_3X_2^2)^2}$$

where the value and meaning of the parameters are given in Table 1. The experimental data and the model dynamics are shown in Figure 4 and 5.

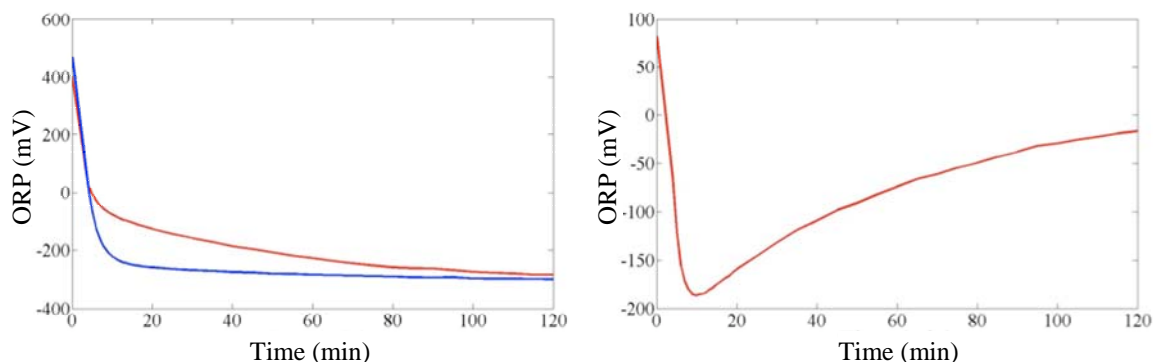


Figure 2.

In the left-hand side, the comparison between ORP_{GLOBAL} signal obtained during the Cr(VI) reduction (blue), and the $ORP_{Fe(II)}$ signal obtained during Fe(II) oxidation in the blank solution (red). While the right-hand side, $ORP_{Cr(VI)}$ signal obtained from the algebraic subtraction of the experimental ORP_{GLOBAL} and $ORP_{Fe(II)}$.

reduction processes. The red circles line experimental data of Cr(VI) and Fe(II) concentration and the dynamic model. The blue solid line represents Fe(II) concentration calculated by eq. 6; Fe(II) concentration. The red solid line represents Cr(VI) calculated by eq. 5; the red circles line represents Cr(VI) experimental data.

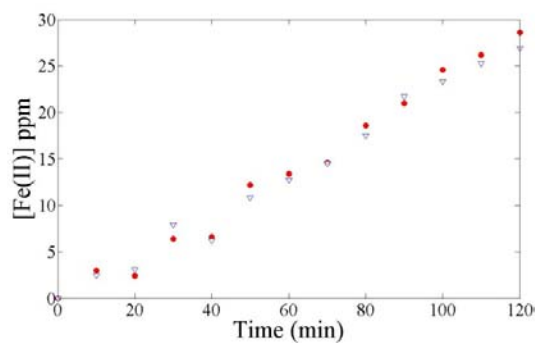


Figure 3.

The figure shows that the difference between the concentration time evolution of Fe(II) during the experiment with the blank solution and the experiment with the solution with Cr(VI) concentration.

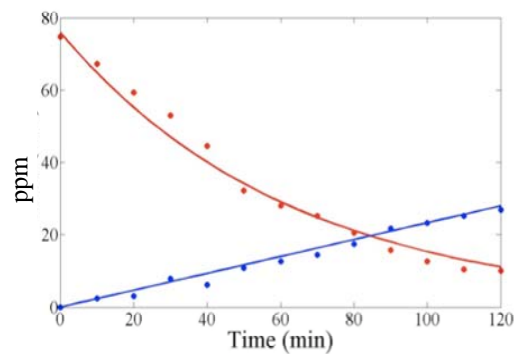


Figure 4.

The figure shows the ability of mathematical model to describe the dynamic behaviour of the chemical

Table 1 - Process model parameters and values used in the simulations

Symbol	Meaning	Value	Units
X_1	Cr(VI) Concentration	-	g/L
X_2	Fe(II) Concentration	-	g/L
X_3	$ORP_{Cr(VI)}$	-	mV
X_4	$ORP_{Fe(II)}$	-	mV
$y(t)$	System Output	-	mV
K_1	Cr(VI) Reaction Rate Constant	-0.016	min^{-1}
K_2	Fe(II) Reaction Rate Constant	0.2332	g/L min
α_1	$ORP_{Cr(VI)}$ Rate Constant	2.3	(mV L)/g
α_2	$ORP_{Cr(VI)}$ Rate Constant	-0.664	(mV L ²)/g ²
α_3	$ORP_{Cr(VI)}$ Rate Constant	0.0304	(mV L ³)/g ³
α_4	$ORP_{Cr(VI)}$ Rate Constant	-0.00057	(mV L ⁴)/g ⁴
α_5	$ORP_{Cr(VI)}$ Rate Constant	0.00000371	(mV L ⁵)/g ⁵
β_1	$ORP_{Fe(II)}$ Rate Constant	981.3	(mV L)/g
β_2	$ORP_{Fe(II)}$ Rate Constant	1.6	L/g
β_3	$ORP_{Fe(II)}$ Rate Constant	-0.01	L ² /g ²

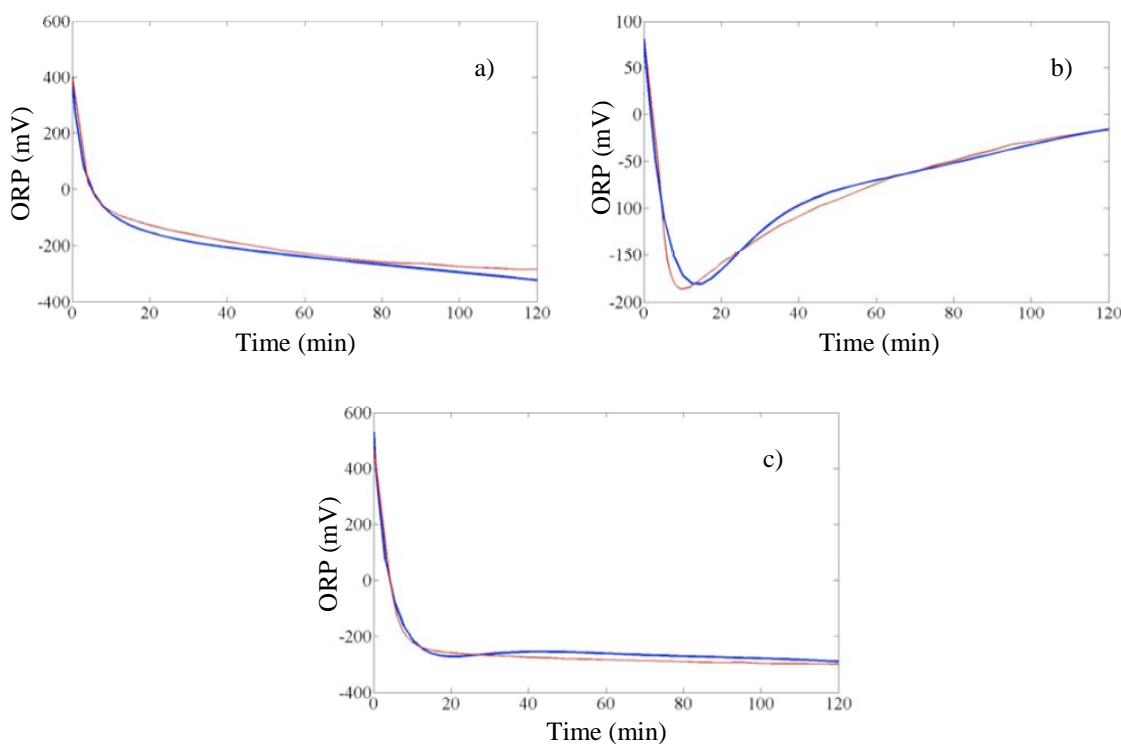


Figure 5.

Model ORPs signals vs. experimental data: a) Fe(II) ORP calculated from blank solution (red thin line) vs. model ORP (eq. 8), b) Cr(VI) ORP calculated from the subtraction of Fe(II)ORP -Total ORP (red thin line) vs. Model ORP of (VI), (eq. 7), c) Total ORP obtained from electrode (red thin line) vs. dynamic Model Total ORP (eq. 7+ eq. 8)

Since the dynamical behavior of the Fe(II) is independent of the presence of the Cr(VI) it is possible to obviate its contribution to the Global ORP, thus allowing the construction of a reduced observer.

3.2. The Sliding Sensor

To create an observer the model was analyzed with an observability test, using Isidori's algorithm [8], proving the model was indeed observable, and therefore susceptible to online monitoring.

Using this dynamic model, a nonlinear software sensor has been created based on a sliding observer structure described by [7].

Though the measured redox potential is given by the reduction of Cr(VI) and the oxidation of Fe(II), it has been proved that $ORP_{Fe(II)}$ is independent of Cr(VI) concentration, therefore we can assume $ORP_{Fe(II)}$ is known and concentrate on recreating the $ORP_{Cr(VI)}$, thus, the resulting system is a reduced sliding observer that follows both, the $ORP_{Cr(VI)}$ dy-

namic and the concentration of the reduced element Cr(VI) despite the differences between the initial conditions on either the ORP or the chromium concentration.

It is worth noting that the real output of the systems is $y(t) = X_3 + X_4$, but since X_4 is an independent value of X_1 , and as it can be seen by the Fe(II) dynamic equation (2), the $ORP_{Fe(II)}$ will depend only of Fe(II) concentration initial condition. Since it can be assumed that this value is known, the output can become:

$$y(t) - X_4 = X_3$$

From this output the reduced sliding sensor can be obtained.

The sliding sensor is given by the estimated state system \hat{X} and the estimated state equations:

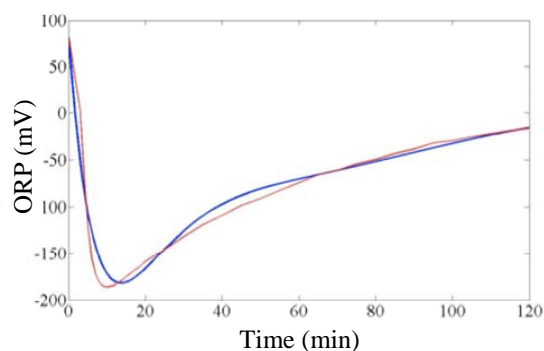
$$\begin{aligned} \frac{d}{dt} \hat{X}_1 &= K_1 \hat{X}_1 + k_1 \text{sat}(\hat{X}_3 - X_3) \\ \frac{d}{dt} \hat{X}_2 &= K_1 \hat{X}_1 (\alpha_1 + 2\alpha_2 \hat{X}_1 + 3\alpha_3 \hat{X}_1^2 + \\ &+ 4\alpha_4 \hat{X}_1^3 + 5\alpha_5 \hat{X}_1^4) + k_2 \text{sat}(\hat{X}_3 - X_3) \end{aligned}$$

where the signal $\mathbf{h}(X) = \bar{X}_s$ and the values of k_1 and k_2 are constants for their respective equations.

The saturation function $\left(\text{sat}\left(\frac{\bar{X}}{\phi}\right)\right)$ will determine the sliding surface and is defined by [7] as follows:

$$\bar{X}_n = X_n - \hat{X}_n$$

$$\text{sat}(\bar{X}_s) = \begin{cases} \bar{X}_n & \text{if } |\bar{X}_n| \leq \phi \\ \text{sgn}(\bar{X}_n) & \text{if } |\bar{X}_n| > \phi \end{cases}$$



Where ϕ is the thickness of the sliding surface, and the sign function $\left(\text{sgn}\left(\frac{\bar{X}_n}{\phi}\right)\right)$

The performance of this model was tested during another run of the experiment mentioned above, under the same conditions. The performance of the observer to rebuilt the Cr(VI) concentration and the $\text{ORP}_{\text{Cr(VI)}}$ along the reaction is shown in Figures 6.

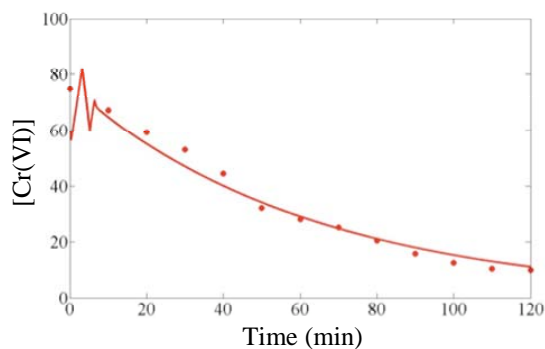


Figure 6.

In the left-hand side, the blue line represent the estimated ORP given by the software sensor and the thin red line stand for experimental measurements. In the right-hand side, the red dots represents the Cr(VI) concentration obtained experimentally, while the red circles line represents the Cr(VI) concentration estimated by the software sensor.

4. CONCLUSIONS

Experimental data shows a steady dynamic of the reaction $\text{Cr(VI)} \rightarrow \text{Cr(III)}$ and a close relation to the ORP signal. This information has allowed the construction of a dynamic model that has an online measurable state (the ORP) within its structure; furthermore, this model has proven to be observable, which has permitted the creation of non-linear sensor based on a sliding observer structure. The sensor was proved in a second run of the experiment, showing it can easily follow the dynamic and providing accurate data of the $\text{Cr(VI)} \rightarrow \text{Cr(III)}$ reduction process.

These developments (both the dynamic model and software sensor) form an efficient tool for monitoring this process and can be used in any wastewater treatment plant that might desire control its process of Cr(VI) elimination in real-time and without the use of an atomic absorption spectrophotometer, thus, saving money and time.

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