Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1055811

57 (2016) 13056–13065
June

Taylor & Francis
Taylor & Francis Group

Reduction of Cr(VI) utilizing biogenic sulfide: an experimental and mathematical modeling approach

Vicente Peña-Caballero[a], Ricardo Aguilar-López[b], Pablo A. López-Pérez[c], M. Isabel Neria-González[d,*]

[a]*División de Ciencias de la Salud e Ingenierías, Departamento de Ingeniería Agroindustrial, Universidad de Guanajuato, Campus Celaya-Salvatierra, Av. Ing. Barros Sierra No. 201, Ejido de Santa María del Refugio, CP 38140, Celaya, Guanajuato, Mexico, Tel. +52 461 598 5922; email: vicente.caballero@ugto.mx*

[b]*Departamento de Biotecnología y Bioingeniería, CINVESTAV-IPN, Av. Instituto Politécnico Nacional, No. 2508, San Pedro Zacatenco, CP 07360 D.F. México, Mexico, Tel. +52 55 5747 3800; email: raguilar@cinvestav.mx*

[c]*Escuela Superior de Apan, Universidad Autónoma del Edo.de Hidalgo, Carretera Apan-Calpulalpan, Km 8, Chimalpa Tlalayote S/N, Chimalpa CP 43900, Hidalgo, Mexico, Tel. +52 771 7172000; email: save1991@yahoo.com.mx*

[d]*División de Ingeniería Química y Bioquímica, Tecnológico de Estudios Superiores de Ecatepec, Av. Tecnológico S/N, CP 55120, Ecatepec de Morelos, Edo. de México, Mexico, Tel. +52 55 5000 2300; emails: mineriag@tese.edu.mx, ibineria@hotmail.com*

Received 31 October 2014; Accepted 21 May 2015

ABSTRACT

The aim of this work was to analyze the performance of a wastewater system for Cr(VI) and sulfate compounds reduction via mathematical modeling. The considered process is coupled to chemical reactors to achieve its tasks. The first stage of the considered process is a biological sulfate-reducing reactor, by which sulfate compounds can be reduced to biogenic sulfide; then, in the second stage, the above-mentioned biogenic sulfide is fed to a second reactor in which the Cr(VI) is reduced, allowing high Cr(VI) concentration removal. The kinetic model of the biological sulfate-reducing process and the Cr(VI) reduction via biogenic sulfide reactions were experimentally corroborated and employed as a benchmarck for the wastewater process analysis via numerical simulations to achieve several feasible operation conditions, under the system's constraints. The mathematical model was extended to a continuous operation, where numerical experiments were carried out predicting an excellent removal of 99% of Cr(VI) and 75% of sulfate compounds.

Keywords: Sulfate-reducing process; Sulfide production; Chromium reduction; Mathematical model

1. Introduction

Increasing contamination of domestic and industrial wastewaters by toxic heavy metals (e.g. some heavy metals are of concern, including toxic metals [Hg, Cr, Pb, Zn, Cu, Ni, Cd, Co, As, Sn, etc.], precious metals [Pd, Pt, Ag, Au, Ru, etc.], and radionuclides [U, Th, Ra, Am, etc.]) have generated severe environmental pollutions problems [1]. These inorganic contaminants are a public health concern since they are not biodegradable and they are highly toxic. Besides, heavy metals mutagenic and carcinogenic features render them hazardous

*Corresponding author.

at very low concentrations [2,3]. Chromium is a pollutant of concern due to its widespread use in industrial applications, such as electroplating, metallurgy, and leather tanning, as well as its natural occurrence in ultramafic rocks and volcanic dusts. Chromium, used in iron, steel, and nonferrous alloys, enhances hardness and resistance to corrosion and oxidation. In the environment, chromium (Cr) exists as Cr(III) or Cr(VI). The concentration of naturally occurring chromium in US soil ranges from 1 to 2,000 mg kg^{-1}, with an average concentration of 54 ppm (Environmental Assessment Division, 2001). Among the heavy metal discharges into the environment, through different industrial effluents, chromium is one of the most toxic. In the environment, trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are the most stable oxidation states [4] and they are found in the wastewaters of different industrial processes, such as ore refining, electroplating, production of steel and alloys, metal plating, tannery, wood preservation, and pigmentation [5].

Conventional methods of Cr(VI) removal from industrial wastewaters are chemical reduction to Cr(III) followed by precipitation under alkaline conditions, as well as ion exchange, reverse osmosis, electrochemical treatment, and adsorption [6–8], which demand large amounts of chemicals and energy, generating toxic sludge or other residues that are difficult to manage and treat [9]. Therefore, an alternative method to treat Cr(VI) ions is using the natural ability of micro-organisms, e.g. biosorption, bioaccumulation, complexation, methylation, oxidation, dissimilatory reduction, precipitation by production and excretion of metabolites. Bacteria and fungi are the most important microbial agents for metallic detoxification of industrial effluents. In this context, sulfate-reducing bacteria (SRB) have been described as a potential bioremediation tool to remove metals from industrial wastewater [10–12]. In Table 1, some published results from the open literature show the ability of chromium removal by different bacteria, including SRB. It is noteworthy that this ability is evaluated as a function of removal percentage, as well as according to the operation time.

Moreover, in comparison with chemical precipitation of metals, such as hydroxides or oxyhydroxides, the use of hydrogen sulfide (H_2S) produced by anaerobic respiration of SRB generates metallic sulfide of lower solubility at acidic pH, less amounts of residual sludge, and is highly efficient, so this method can be considered as efficient and cost effective [21,22]. Reduction of Cr(VI) by H_2S has been demonstrated in different studies [23,24], and H_2S is considered a strong reducer agent capable of reducing Cr(VI) to Cr(III). Hexavalent chromium ion is highly soluble in aqueous solution, very toxic, and mutagenic, while trivalent chromium ion is water insoluble and significantly less toxic [25,26]. In addition, some SRB like *Desulfovibrio* spp. can reduce the Cr(VI) ion by metabolic processes involving hydrogenase and c_3 cytochrome [27,28].

In general, the sulfate-reducing processes (SRPs) are better metallic removal methods than chemical–physical systems. However, for Cr(VI) treatment, guidelines to select the most adequate process are missing. For this reason, different processes to remove Cr(VI) have been reported, i.e. Szpyrkowicz et al. [29] used a combination of electrochemical and biological processes to eliminate Cr(VI) in wastewater treatment, but these processes become expensive and ineffective when treating large volumes of wastewater. Farabegoli et al. [30] carried out experiments to determine the feasibility and efficiency of treating tannery wastewater containing chromium through sequencing batch reactors. Experimental results confirmed that the sequencing batch reactors allowed selecting a more resistant biomass, which was acclimated quickly to inhibitory conditions by chromium [180 mg L^{-1}]. Likewise, sludge with a large amount of chromium was generated, while the effluent was devoid of the metal. In this work, Cr(VI) and sulfate reduction via mathematical modeling based on experimental results was analyzed. The global process considered two coupled reactors: a biological reactor (BR) where sulfate is reduced to biogenic sulfide by *Desulfovibrio alaskensis* 6SR; and the reduction of Cr(VI) carried out in a chemical reactor (CR), which is fed by biogenic H_2S allowing for a high removal of Cr(VI). The mathematical model was extended to a continuous operation, where numerical experiments were conducted predicting an excellent removal of 99% of Cr(VI) and 75% of sulfate.

2. Materials and methods

The corresponding methodology was carried out in three steps: the first one was the synthesis of the kinetic model for the SRP (i.e. parametric identification process using SRB *D. alaskensis* 6SR); followed by the synthesis of the kinetic model for chromium reduction with biogenetic hydrogen sulfide; and finally, the proper numerical analysis of the proposed model for chromium reduction by biogenic sulfide under continuous operation conditions.

2.1. Sulfate-Reducing Process

D. alaskensis 6SR was used as biological model for this study. The strain 6SR was isolated from a biofilm

Table 1
Micro-organisms capable of removing hexavalent chromium

Micro-organism	Cr (mg L^{-1})	Removal (%)	Time (d)	References
Sulfate-reducing consortium	50	Not reported	Not reported	[13]
Bacillus sphaericus	20	62	2	[14]
Mixed sulfate reducers	5–50	85–95	90	[15]
Sulfate-reducing consortium	50	97	250	[15]
Bacillus sp.	15	84.4	15	[16]
Sulfate-reducing consortium	22.7–98.4	99	6	[17]
Caenorhabditis elegans	50	95	7.2	[18]
Sulfate-reducing consortium	10	65	7.5	[19]
Desulfovibrio vulgaris	15	15–24.7	11	[20]
Desulfovibrio sp.	15	15–25.5	11	[20]
D. alaskensis 6SR	50	96	16.6	In this work

developed inside an oil pipeline [31]. The strain was maintained routinely in Hungate tubes with 5 mL of Postgate's medium C at 37°C [32,33].

Experiments were carried out using modified Postgate's C medium, which contained (gL^{-1}): KH_2PO_4 (0.5), NH_4Cl (1.0), Na_2SO_4 (4.5), $MgSO_4{\cdot}7H_2O$ (0.06), sodium lactate (5.0), $CaCl_2{\cdot}H_2O$ (0.06), yeast extract (1.0), sodium citrate (0.3), and NaCl (30.0). The medium was adjusted to pH 7.0 and 90 mL of medium was placed into 160 mL serum bottles. These vessels were capped with crimped aluminum butyl rubber stoppers. Besides, 450 mL of medium was placed into 1,000 mL glass bottles (Schott Duran® bottles). The bottles were sealed placing a rubber stopper followed by a screw cap. Culture medium was prepared and dispensed in anaerobic conditions under a N_2 (99.998% purity) atmosphere, and the remnant oxygen in the bottles containing the medium was displaced by a N_2 flow for 3 min. Then, all bottles with culture medium were sterilized in an autoclave at 121°C. The reagents used in these experiments were analytical grade from J.T. Baker, Mexico.

The inoculum for the kinetic study was cultured in 90 mL of modified Postgate's C medium at 37°C until an OD_{580} between 0.35 and 0.4 was obtained. A 50 mL aliquot of cell suspension was taken to inoculate 450 mL of fresh medium. All cultures were incubated at 37°C for 8 d.

Bacterial growth, consumption of sulfate, and sulfide production were monitored each 3 or 4 h; samples were taken carefully with a sterile syringe, avoiding contact with oxygen. A 0.5 mL aliquot was taken anoxically and immediately analyzed for the content of hydrogen sulfide [34]. Then, another 5 mL of sample was taken from the BR. Bacterial growth was followed through optical density (OD) methodology; the OD reading for cell growth was transformed into dry mass (mg L^{-1}) through a standard growth curve. The consumed sulfate in the medium was measured by a turbidimetric method based on the precipitation of barium [35]. Consumption of lactate and acetate production were monitored at the same time through HPLC (Shimadzu LC10Ai) connected to a UV detector ($\lambda = 210$ nm), with a BioRad HPLC Organic Acid Analysis Column, a flow of 0.700 mL min^{-1}, mobile phase sulfuric acid/water (0.33/0.067). Samples were centrifuged at 15,600 × *g* for 5 min. The supernatant was transferred to a new tube, and 1 mL of supernatant was diluted to 1:10 with $ZnCl_2$ to remove sulfide, the dilution was filtered through 0.22 μm pore diameter filter and injected to the HPLC equipment to measure lactate and acetate concentrations. Lactic acid (60% v/v, HPLC grade, SIGMA) and anhydride sodium acetate (HPLC grade, SIGMA®) were used as standards.

2.2. Cr(VI)-reducing process

The experimental setup used in this study is shown in Fig. 1. A stock of $K_2Cr_2O_7$ solution was prepared at 1,000 mg L^{-1} with respect to the ion Cr(VI) All the experiments were performed in 1,000 mL glass bottles with modified screw caps (Schott Duran®) containing 0.5 mL synthetic wastewater. The synthetic wastewater contained Cr(VI) ion.

Experiments were performed under anaerobic conditions, the pH was controlled at 7.6 with phosphate buffer, and the temperature was maintained at 37 ± 0.1°C using a thermostatic water jacket. Kinetic experiments were conducted by monitoring the change of Cr(VI) concentration as a function of time using a UV–VIS Varian 50 Spectrophotometer (Fig. 1). The CR was fed with biogenic H_2S produced by anaerobic respiration of *D. alaskensis* 6SR; the H_2S is drawn from the bioreactor through a N_2 stream (see Fig. 1). The experimental development to reduce

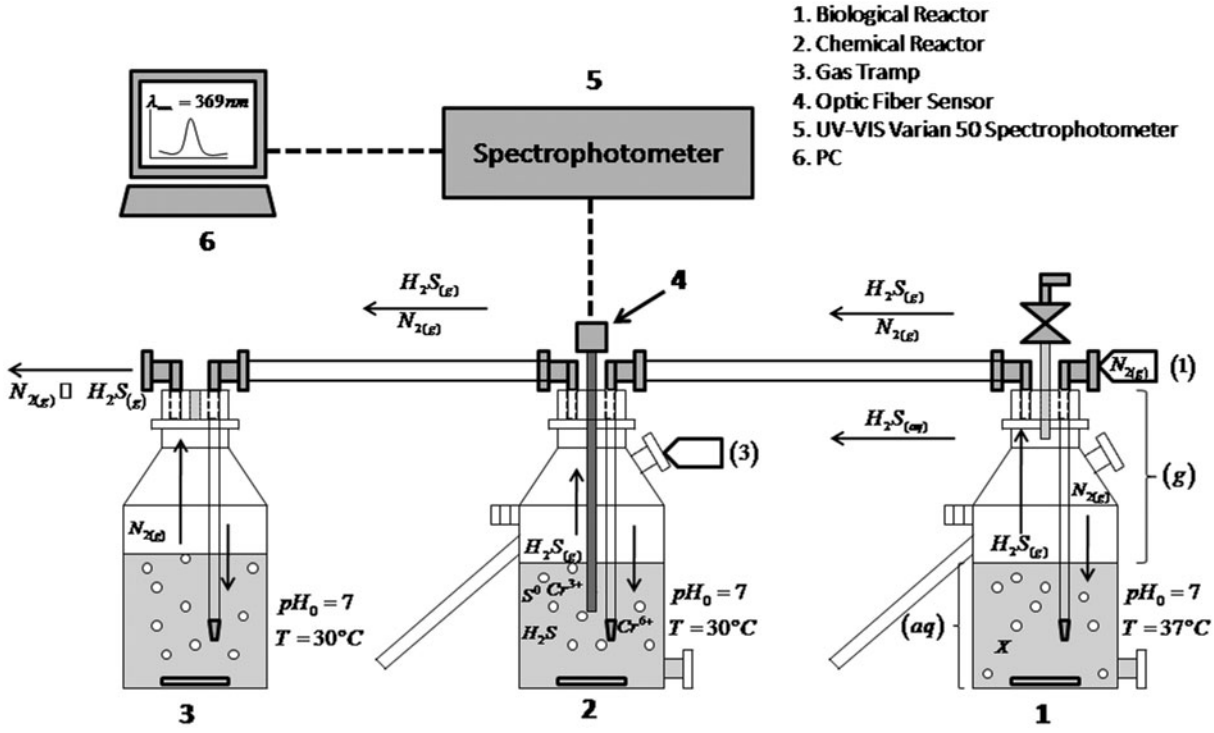

Fig. 1. Schematic diagram of treatment process, the process considered two coupled reactors: (1) BR where sulfate is reduced to biogenic sulfide by *Desulfovibrio alaskensis* 6SR; (2) CR where the reduction of Cr(VI) is carried out by feeding biogenic H_2S; and (3) experimental system considered a buffer tank.

chromium was done at 5, 12, and 25 mg L^{-1} initial concentrations of Cr(VI) in independent experiments; then, the sensor was immersed into the synthetic wastewater and the concentration of Cr(VI) was measured on-line each 0.5 s.

2.3. Mathematical modeling

As a first task, the kinetic models of the biological sulfate-reducing system and the Cr(VI) reduction via biogenic H_2S must be done. In general, the considered chemical reactions for both processes are the following:

$$2CH_3CHOHCOOH + 3SO_4^{2-} \rightarrow 3H_2S + 6HCO^- \quad (1)$$

$$H_2S + M^{2+} \rightarrow MS(s) + 2H^+ \quad (2)$$

where: M^{2+} = metallic ion

The production of biogenic H_2S generated by sulfate-reducing bacteria during anaerobic respiration (Eq. (1)) and the reaction of biogenic H_2S with metallic ions (Eq. (2)) produce insoluble metallic sulfide.

From Eq. (2), the reduction of Cr(VI) by action of biogenic H_2S is as follows:

$$3HS^- + 2Cr(VI) \rightarrow 3S^0 + 2Cr(III) \downarrow + 3H^+ \quad (3)$$

In general, unstructured kinetic models are widely employed to represent biological reaction systems; this is due to the simplicity of structured models [36]. The experimental data for the sulfate-reducing process were applied to the BR, and these were used to determine the kinetic parameters of the proposed unstructured kinetic model $\left(\frac{\mu(\cdot)}{\mu_{max}}\right)$ for the biological system. The experimental data obtained for Cr(VI) reduction via biogenic sulfide were used to propose a power law kinetic model. The kinetic models are included in a general form of the mass balances under the assumption of stirred tank reactors.

2.3.1. Mass balances

Biomass concentration in the BR (x_1)

$$\frac{d}{dt}x_1 = \mu_{max}\frac{x_3}{x_3 + k_{S_2}}\left[1 - \frac{x_4}{x_4^\circ}\right]^n x_1 - k_d x_1 - \frac{F_{10}}{V_{R_1}}x_1 \quad (4)$$

Lactate concentration in the BR (x_2)

$$\frac{\mathrm{d}}{\mathrm{d}t}x_2 = -Y_1\mu_{\max}\frac{x_3}{x_3+k_{S_2}}\left[1-\frac{x_4}{x_4^{\circ}}\right]^n x_1 + \frac{F_{10}}{V_{R_1}}\left[x_2^{\mathrm{in}}-x_2\right] \quad (5)$$

Sulfate concentration in the BR (x_3)

$$\frac{\mathrm{d}}{\mathrm{d}t}x_3 = -Y_2\mu_{\max}\frac{x_3}{x_3+k_{S_2}}\left[1-\frac{x_4}{x_4^{\circ}}\right]^n x_1 + \frac{F_{10}}{V_{R_1}}\left[x_3^{\mathrm{in}}-x_3\right] \quad (6)$$

Sulfide concentration in the BR (x_4)

$$\frac{\mathrm{d}}{\mathrm{d}t}x_4 = Y_3\mu_{\max}\frac{x_3}{x_3+k_{S_2}}\left[1-\frac{x_4}{x_4^{\circ}}\right]^n x_1 - k_{\mathrm{La}}\left(x_4^{*}-x_{4\mathrm{sat}}^{*}\right) - \frac{F_{10}}{V_{R_1}}x_4 \quad (7)$$

Acetate concentration in the BR (x_5)

$$\frac{\mathrm{d}}{\mathrm{d}t}x_5 = Y_4\mu_{\max}\frac{x_3}{x_3+k_{S_2}}\left[1-\frac{x_4}{x_4^{\circ}}\right]^n x_1 - \frac{F_{10}}{V_{R_1}}x_5 \quad (8)$$

Chromium concentration in the CR (x_6)

$$\frac{\mathrm{d}}{\mathrm{d}t}x_6 = -k_1[x_6]^{\alpha_1}[x_7]^{\beta_1} + \frac{F}{V_{R_2}}\left[x_6^{\mathrm{in}}-x_6\right] \quad (9)$$

Sulfide concentration in the CR (x_7)

$$\frac{\mathrm{d}}{\mathrm{d}t}x_7 = -k_2[x_6]^{\alpha_2}[x_7]^{\beta_2} + k_{\mathrm{La}}\left(x_4^{*}-x_{4\mathrm{sat}}^{*}\right) - \frac{F}{V_{R_2}}x_7 \quad (10)$$

where $\frac{\mathrm{d}}{\mathrm{d}t}x_i$ is the rate of concentration change of each x_i with $i = 1,2,\ldots,n$ with $n = 7$, x_1 is bacterial biomass concentration (mg L^{-1}), x_2 and x_3 are concentration of residual substrates, lactate and sulfate concentrations (mg L^{-1}), respectively, x_4 and x_5 are concentrations of products (mg L^{-1}), hydrogen sulfide and acetate concentrations in mg L^{-1}, Y_j ($j = 1,2,\ldots,m,$) with $m = 4$ is the yield coefficient for bacteria, and k_d is the constant cellular death (h^{-1}). The biomass kinetics is held by $\frac{\mu(\cdot)}{\mu_{\max}}$, where $\mu_{\max}$ is the maximum specific growth rate (h^{-1}). The specific growth rate valid for the kinetics of lactate oxidation by *D. alaskensis* 6SR is assumed as a Levenspiel's kinetic model $\frac{\mu(x_3,x_4)}{\mu_{\max}}$ [36]. Experimental findings suggest that high concentrations of hydrogen sulfide have an inhibitory effect on cell growth. The dependence of the specific growth rate on sulfate and sulfide concentrations was assumed to follow the Levenspiel's kinetic model that considers product limitation as follows:

$$\frac{\mu(x_3,x_4)}{\mu_{\max}} = \frac{x_3}{x_3+k_{S_2}}\left(1-\frac{x_4}{x_4^{\circ}}\right)^n \quad (11)$$

where x_4° is the sulfide inhibitory concentration for cellular growth (mg L^{-1}); k_{S_2} is the affinity constant (mg L^{-1}), and n is a constant of the model.

Considering that the biogenic sulfide concentration fed to the CR corresponds to the gas phase from the headspace phase of the bottle in the BR, a thermodynamic phase equilibrium in the BR is assumed, where the mass fraction of hydrogen sulfide is given by $y_{H_2s} = x_{H_2S}\frac{P_{H_2S}}{P}$, here y_{H2S} and x_{H2S} correspond to the molar fraction of the hydrogen sulfide in the gas and liquid phases, respectively, P is the total pressure in the gas phase and P_{H2S} is the partial pressure of the hydrogen sulfide. Besides, the real concentration of hydrogen sulfide in the second stage, corresponding to the CR, is related to the hydrogen sulfide solubilized in the liquid phase, it can be calculated via Henry's law, where $x_4^{*} = K_H P_{H_2S}, x_{4\mathrm{sat}}^{*}$ is the corresponding saturation concentration and k_{La} is the mass transfer coefficient. The thermodynamic parameters and transport coefficients for this system are reported in [37,38].

In the CR, x_6 and x_7 represent the chromium and sulfide concentrations (mg L^{-1}); V_{R1} and V_{R2} are the reaction volume (L) for BR and CR, respectively; F_{10} and F_{30} are the inlet flow rates (L h^{-1}) in BR and CR, respectively; F_1 and F_2 are out flow rates (L h^{-1}) for BR and CR, respectively; x_2^{in} and x_3^{in} are lactate and sulfate concentrations (mg L^{-1}) inlet flow in BR; x_6^{in} and x_4^{in} is chromium and sulfide concentrations (mg L^{-1}) in the inlet flow in CR; and is sulfide concentration in BR, see Fig. 2.

The estimated kinetic parameters for the biological sulfate-reducing system are presented in Table 2.

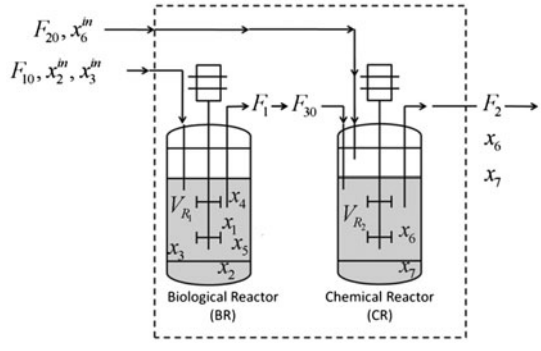

Fig. 2. Schematic diagram of Cr(VI)-reducing process. The BR is coupled to the CR.

Table 2
Kinetic parameters for the sulfate-reducing model

Kinetic parameters	Value
μ_{max} (h^{-1})	0.1633
K_d (mg L^{-1} h^{-1})	0.0031
Y_1	13.0408
Y_2	7.1324
Y_3	1.4074
Y_4	8.17194
x_4° (mg L^{-1})	509
N	0.83480
K (mg L^{-1})	1,500

Under the above set of parameters, the mathematical model of the SRP reveals the performance given in Fig. 3 with the corresponding correlation coefficients.

Model validation was done by simulations where the model-predicted values were compared with the experimental data. For model simulations, the initial concentration of biomass, lactate, sulfate, sulfide, and acetate was considered as 110, 4,500, 3,150, 24, and 300 mg L^{-1}, respectively.

The parameter identification for the CR was achieved by linearizing the proposed power law model, where the corresponding set of kinetic parameters is given in Table 3. The corresponding results can be observed in Fig. 4, where the model data versus experimental data are compared with their corresponding correlation coefficients.

Table 3
Kinetic parameters for the chromium reduction model

Kinetic parameters	Value
α_1	1
α_2	0.35
β_1	0.54
β_2	1
$k_1\left(\frac{L^{0.54}h^{0.54}}{mg^{0.54}}\right)$	1.64
$k_2\left(\frac{L^{0.35}h^{0.35}}{mg^{0.35}}\right)$	3.9

The methodology for the parametric identification is based on the least squares method implemented in the MATLAB 7.4 software and the mathematical model (Eqs. (4)–(11)) was solved using Solver ode45. The solver ode45 uses Runge–Kutta method for integration library of MATLAB 7.4 (The Math Works Inc., Natick, MA).

3. Results and discussion

This section presents the simulation results employing the model represented by Eqs. (4)–(11), where the operability analysis of the proposed system

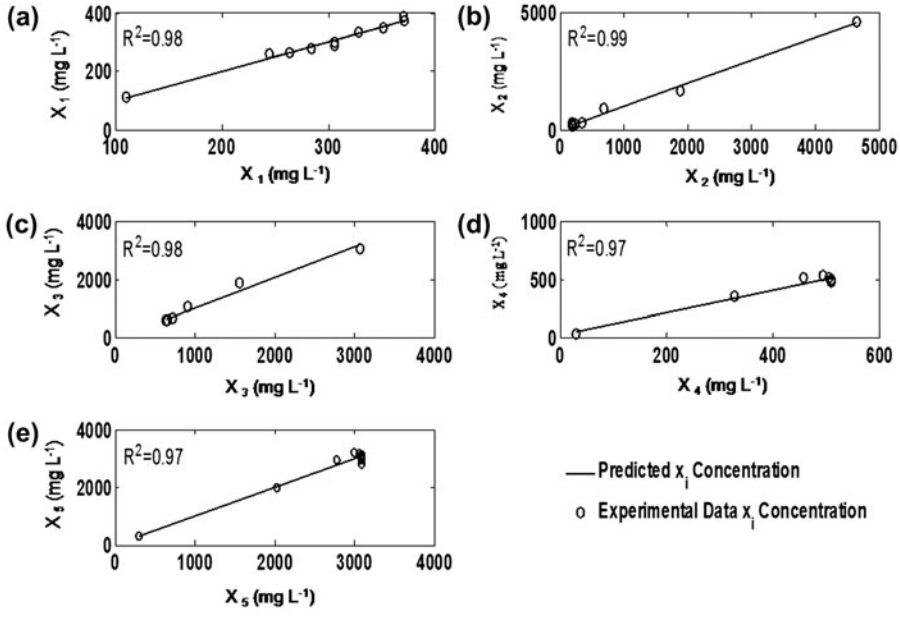

Fig. 3. Correlation coefficients of experimental and model predicted concentration profiles for lactate oxidation by *D. alaskenis* 6SR. (a) X_1 = biomass, (b) X_2 = lactate, (c) X_3 = sulfate, (d) X_4 = sulfide, and (e) X_5 = acetate concentrations. Predicted concentration vs. experimental concentration.

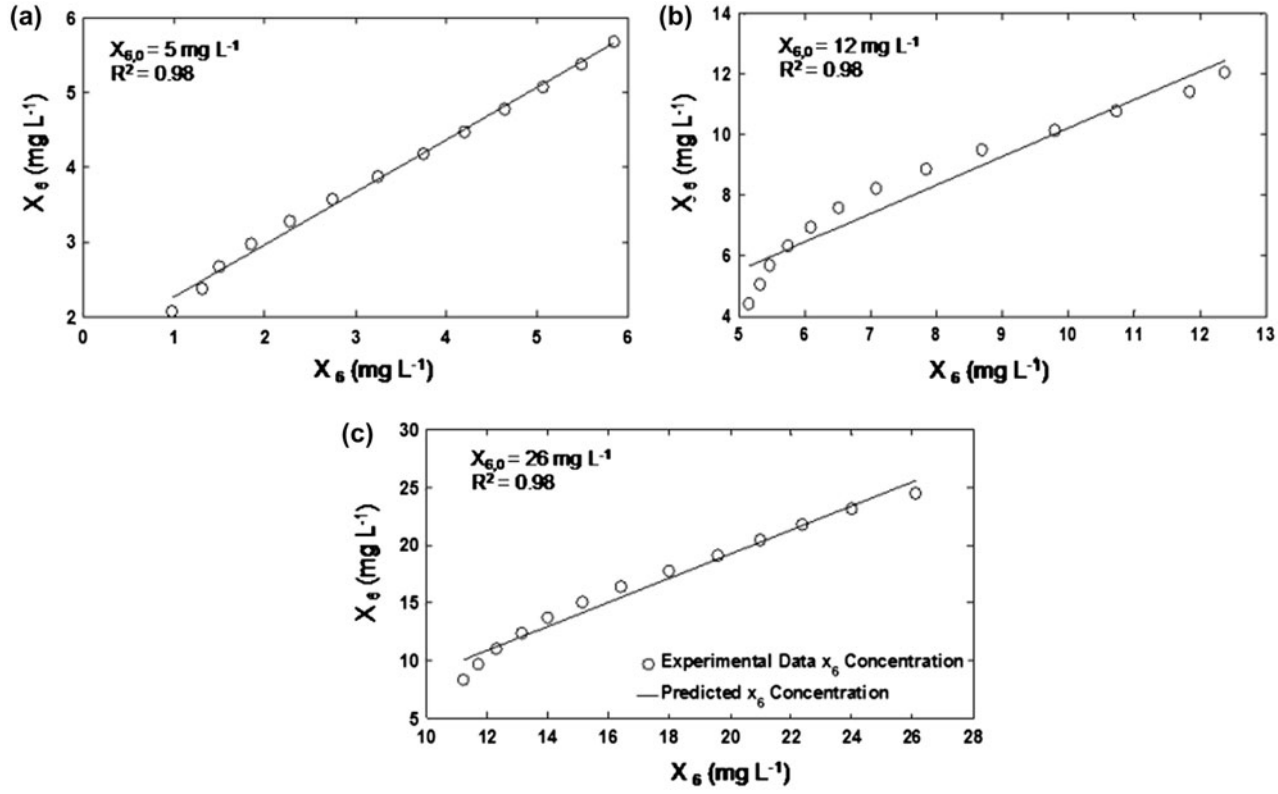

Fig. 4. Correlation coefficient between experimental data and model prediction for different concentrations of chromium (VI), $x_{6,0}$ (mg L^{-1}): (a) 5, (b) 12, and (c) 26. Predicted concentration vs. experimental concentration.

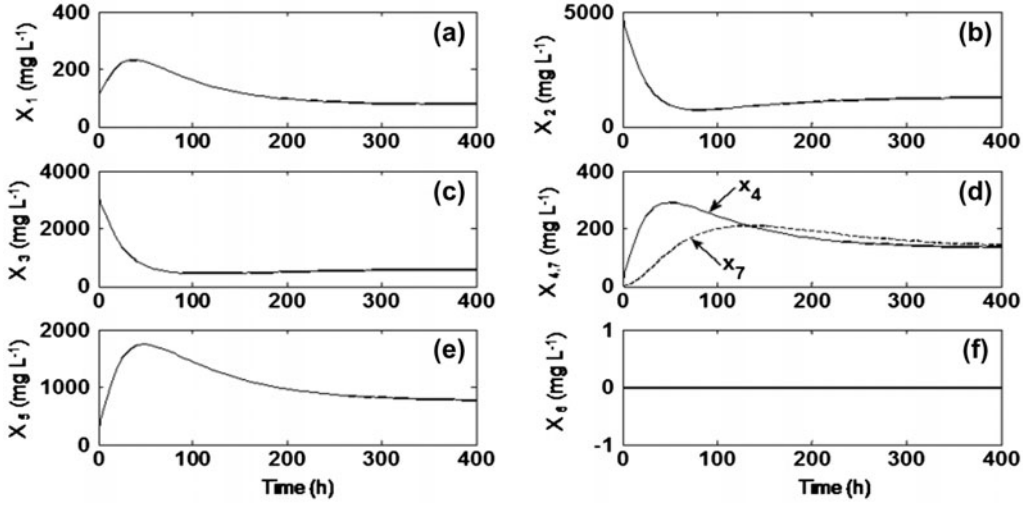

Fig. 5. Dynamic behavior of the proposed system with $D = 0.012\ h^{-1}$, $x_2^{in} = 2,500\ mg\ L^{-1}$ and $x_3^{in} = 1,250\ mg\ L^{-1}$ in the BR. $F_{20} = 0\ L\ h^{-1}$, i.e., $x_6^{in} = 0\ mg\ L^{-1}$, and $x_{6,in} = 0\ mg\ L^{-1}$ in the CR. (a) X_1 = biomass, (b) X_2 = lactate, (c) X_3 = sulfate, (d) X_4, X_7 = sulfide, and (e) X_5 = acetate, X_6 = Cr(VI) concentrations.

for chromium reduction using hydrogen sulfide produced by *D. alaskensis* 6SR is applied. This model is represented in Fig. 2.

To illustrate the influence of lactate $\left(x_2^{in}\right)$ and sulfate$\left(x_3^{in}\right)$ concentrations at inlet conditions on the production of hydrogen sulfide in the proposed

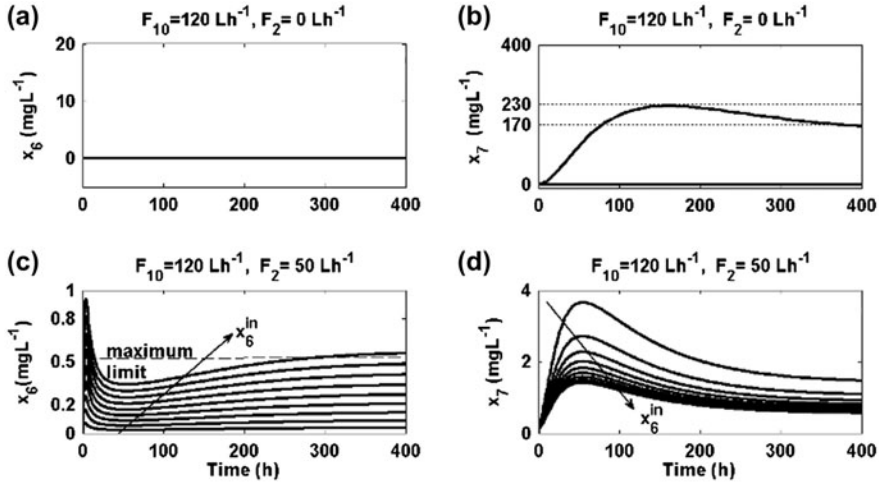

Fig. 6. Dynamic behavior in the proposed system with $D = 0.012\ \mathrm{h}^{-1}$, $x_2^{\mathrm{in}} = 2,500\ \mathrm{mg\ L}^{-1}$ and $x_3^{\mathrm{in}} = 1,250\ \mathrm{mg\ L}^{-1}$ in the BR. (a) and (b) $F_{20} = 0\ \mathrm{L\ h}^{-1}$ with $x_6^{\mathrm{in}} \in 0(15-90)\ \mathrm{mg\ L}^{-1}$ in the CR, and (c) and (d) $F_{20} = 100\ \mathrm{L\ h}^{-1}$ with $x_6^{\mathrm{in}} \in (15-90)\ \mathrm{mg\ L}^{-1}$.

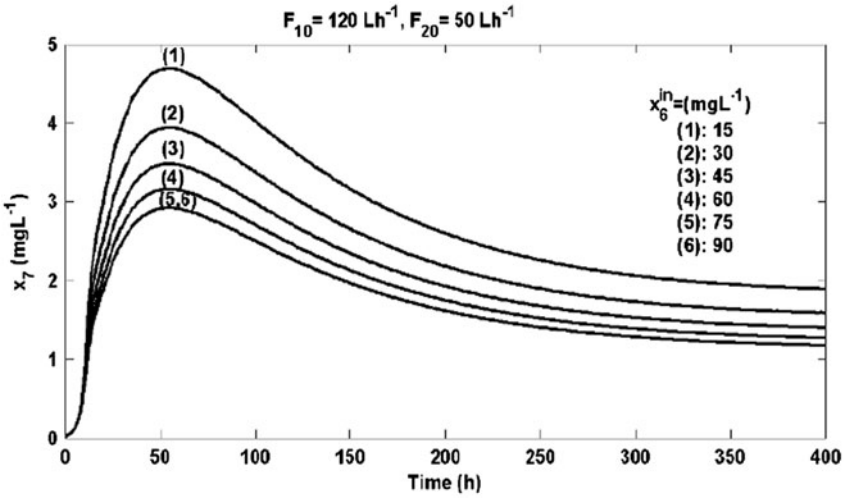

Fig. 7. Dynamic simulation of residual concentration of hydrogen sulfide, x_7, in the CR with $F_{20} = 50\ \mathrm{L\ h}^{-1}$.

system, different ratios $\left(\frac{x_2^{\mathrm{in}}}{x_3^{\mathrm{in}}}\right)$ were analyzed numerically for different dilution rates, $D = \frac{F_{10}}{V_R}$, in the BR (data not shown here). For $\left(\frac{x_2^{\mathrm{in}}}{x_3^{\mathrm{in}}}\right) = 2$, the bioreactor reached a maximum concentration of hydrogen sulfide of $x_4 = 154\ \mathrm{mg\ L}^{-1}$ with $D = 0.012\ \mathrm{mg\ L}^{-1}$ (Fig. 5(d)); this concentration was fed into the CR considering zero Cr(VI) concentration at the inlet condition, i.e. $x_6^{\mathrm{in}} = 0$, as a result, the biogenic sulfide in the CR (x_7) reaches also $154\ \mathrm{mg\ L}^{-1}$ at time $t = 400$ h (see Fig. 5(d)). Residual concentration of sulfate in the BR (x_3) is less than $500\ \mathrm{mg\ L}^{-1}$ (Fig. 5(c)); this is important, because the maximum permissible limit for sulfate concentration in wastewaters is $500\ \mathrm{mg\ L}^{-1}$ according to environmental regulations. The rest of the state's variables such as biomass (x_1), lactate (x_2), acetate (x_5), and chromium (x_6) concentrations are shown in Fig. 5(a), (b), (e), and (f), respectively.

In the CR, operating under the conditions mentioned for the BR, Cr(VI) reduction can be achieved for a wide range of chromium concentrations up to $90\ \mathrm{mg\ L}^{-1}$. Fig. 6 shows chromium reduction during the continuous operation of the proposed reactors system fed different chromium concentrations in the range of 15–90 $\mathrm{mg\ L}^{-1}$.

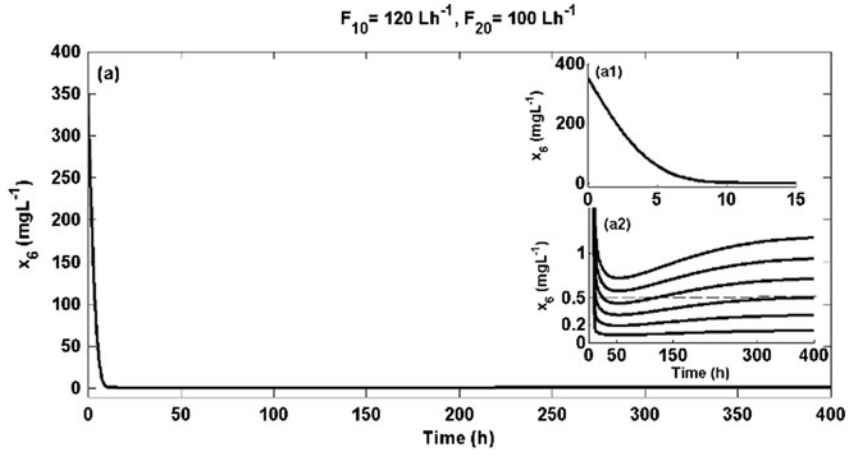

Fig. 8. Dynamic behavior of Cr(VI) concentration in the proposed system with $D = 0.012\ h^{-1}$, x_2^{in}=2,500 mg L^{-1} and x_3^{in}=1,250 mg L^{-1} in the BR. $F_{20} = 50\ L\ h^{-1}$ with $x_6^{in} \in 0$(15–90) mg L^{-1} in the CR (a_1) and $F_{20} = 100\ L\ h^{-1}$ with $x_6^{in} \in$ (15–90) mg L^{-1} (a_2).

The inlet chromium concentration $\left(x_6^{in}\right)$ was increased from 15 to 90 mg L^{-1}, it was observed that, in steady state, the residual chromium concentration is less than 0.5 mg L^{-1} in the effluent F_2 for all cases (see Fig. 6(c)), indicating that the chromium reduction efficiency was higher than 99%, independently from the inlet concentration. In the effluent of the CR, the H_2S concentration decreased, as expected (Figs. 6(b) and (d) and 7), due to the reduction reaction of H_2S with chromium, according to Eq. (3).

Other simulation results are shown in Fig. 8, when F_{20} was varied to 100 L h^{-1} with the same concentrations of x_6^{in} (15–90 mg L^{-1}).

4. Conclusion

In this study, a mathematical model of coupled reactors is proposed, where the first, BR, produces enough sulfide concentration that is fed into a second, CR, for Cr(VI) reduction purposes. The kinetics of sulfate reduction to sulfide in Postgate's medium using a sulfate-reducing bacterium, *D. alaskensis* 6SR, was analyzed. In addition, we investigated the kinetics of chromate (Cr(VI)) reduction in aqueous phase using biogenic sulfide. The model presented in this work provides a good mathematical tool to predict the performance of the SRP, in terms of cell mass production, substrates consumption, products formation, and Cr(VI) reduction by biogenic sulfide in the aqueous phase. Satisfactory conformity between the predictions of state variables and experimental data was demonstrated. The mathematical model was extended to a continuous operation, where numerical experiments were carried out predicting an excellent removal of 99% of Cr(VI) and 75% of sulfate compounds.

References

[1] X. Wang, T. Sato, B. Xing, S. Tao, Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish, Sci. Total Environ. 350 (2005) 28–37.
[2] Environmental Protection Agency (EPA), Toxicological Review of Hexavalent Chromium, US Environmental Protection Agency, Washington DC, 1998.
[3] K.H. Cheung, J.-D. Gu, Bacterial color response to hexavalent chromium, Cr^{6+}, J. Microbiol. 40 (2002) 234–236.
[4] N.Y. Tsibakhashvili, L.M. Mosulishvili, T.L. Kalabegishvili, E.I. Kirkesali, M.V. Frontasyeva, E.V. Pomyakushina, S.S. Pavlov, H.-Y.N. Holman, ENAA studies of chromium uptake by *Arthrobacter oxydans*, J. Radioanal. Nucl. Ch. 259 (2004) 527–531.
[5] A. Wójtowicz, A. Stokłosa, Removal of heavy metal ions on smectite ion-exchange column, Pol. J. Environ. Stud. 11 (2002) 97–101.
[6] M. Owlad, M.K. Aroua, W.W. Daud, S. Baroutian, Removal of hexavalent chromium-contaminated water and wastewater: A review, Water Air Soil Pollut. 200 (2009) 59–77.
[7] V. Orescanin, R. Kollar, I.L. Mikelic, K. Nad, Electroplating wastewater treatment by the combined electrochemical and ozonation methods, J. Environ. Sci. Health Part A Toxic/Hazard. Subst. Environ. Eng. 48 (2013) 1450–1455.
[8] A. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere 56 (2004) 91–106.
[9] G. Hu, J. Li, G. Zeng, Recent development in the treatment of oily sludge from petroleum industry: A review, J. Hazard. Mater. 261 (2013) 470–490.

[10] P.A. López-Pérez, M.I. Neria-González, L.B. Flores-Cotera, R. Aguilar-López, Mathematical model for cadmium removal using a sulfate reducing bacterium: *Desulfovibrio alaskensis* 6SR, Int. J. Environ. Res. 7 (2013) 501–512.
[11] M.C. Costa, M. Martins, C. Jesus, J.C. Duarte, Treatment of acid mine drainage by sulphate-reducing bacteria using low cost matrices, Water Air Soil Pollut. 189 (2008) 149–162.
[12] M. Bhagat, J.E. Burgess, A.P.M. Antunes, C.G. Whiteley, J.R. Duncan, Precipitation of mixed metal residues from wastewater utilising biogenic sulphide, Miner. Eng. 17 (2004) 925–932.
[13] R. Singh, A. Kumar, A. Kirrolia, R. Kumar, N. Yadav, N.R. Bishnoi, R.K. Lohchab, Removal of sulphate COD and Cr(VI) in simulated and real wastewater by sulphate reducing bacteria enrichment in small bioreactor and FTIR study, Bioresour. Technol. 102 (2011) 677–682.
[14] A. Pal, A.K. Paul, Aerobic chromate reduction by chromium-resistant bacteria isolated from serpentine soil, Microbiol. Res. 159 (2004) 347–354.
[15] E. Sahinkaya, A. Kilic, M. Altun, K. Komnitsas, P.N.L. Lens, Hexavalent chromium reduction in a sulfur reducing packed-bed bioreactor, J. Hazard. Mater. 219–220 (2012) 253–259.
[16] Y. Liu, C. Pan, W. Xia, G. Zeng, M. Zhou, Y.L. Liu, J. Ke, Simultaneous removal of Cr(VI) and phenol in consortium culture of *Bacillus* sp. and *Pseudomonas putida* Migula (CCTCC AB92019), Trans. Nonferrous Met. Soc. China. 18 (2008) 1014–1020.
[17] D. Çetin, S. Dönmez, G. Dönmez, The treatment of textile wastewater including chromium(VI) and reactive dye by sulfate-reducing bacterial enrichment, J. Environ. Manage. 88 (2008) 76–82.
[18] F. Pagnanelli, C.C. Viggi, A. Cibati, D. Uccelletti, L. Toro, C. Palleschi, Biotreatment of Cr(VI) contaminated waters by sulphate reducing bacteria fed with ethanol, J. Hazard. Mater. 199–200 (2012) 186–192.
[19] J.M. Márquez-Reyes, U.J. López-Chuken, A. Valdez-González, H.A. Luna-Olvera, Removal of chromium and lead by a sulfate-reducing consortium using peat moss as carbon source, Bioresour. Technol. 144 (2013) 128–134.
[20] G. Cabrera, R. Pérez, J.M. Gómez, A. Ábalos, D. Cantero, Toxic effects of dissolved heavy metals on *Desulfovibrio vulgaris* and *Desulfovibrio* sp. strains, J. Hazard. Mater. 135 (2006) 40–46.
[21] T.K. Tsukamoto, H.A. Killion, G.C. Miller, Column experiments for microbiological treatment of acid mine drainage: Low-temperature, low-pH and matrix investigations, Water Res. 38 (2004) 1405–1418.
[22] M. Gallegos-Garcia, L.B. Celis, R. Rangel-Méndez, E. Razo-Flores, Precipitation and recovery of metal sulfides from metal containing acidic wastewater in a sulfidogenic down-flow fluidized bed reactor, Biotechnol. Bioeng. 102 (2009) 91–99.
[23] P.N.L. Lens, A. Visser, A.J.H. Janssen, L.W. Hulshoff Pol, G. Lettinga, Biotechnological treatment of sulfate-rich wastewaters, Crit. Rev. Environ. Sci. Technol. 28 (1998) 41–88.
[24] I.I. Volkov, N.N. Zhabina, Determination of free sulphur by reduction to hydrogen sulphide with metallic chromium, J. Anal. Chem. 26 (1971) 359.
[25] C.-M. Neculita, G.J. Zagury, B. Bussière, Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: Critical review and research needs, J. Environ. Qual. 36 (2007) 1–16.
[26] M. Pettine, F.J. Millero, R. Passino, Reduction of chromium (VI) with hydrogen sulfide in NaCl media, Mar. Chem. 46 (1994) 335–344.
[27] I.S. Chang, B.H. Kim, Effect of sulfate reduction activity on biological treatment of hexavalent chromium [Cr(VI)] contaminated electroplating wastewater under sulfate-rich condition, Chemosphere 68 (2007) 218–226.
[28] D.R. Lovley and E.J. Phillips, Reduction of chromate by *Desulfovibrio vulgaris* and its c_3 cytochrome, Appl. Environ. Microbiol. 60 (1994) 726–738.
[29] L. Szpyrkowicz, S. Kaul, R. Neti, Tannery wastewater treatment by electro-oxidation coupled with a biological process, J. Appl. Electrochem. 35 (2005) 381–390.
[30] G. Farabegoli, A. Carucci, M. Majone, E. Rolle, Biological treatment of tannery wastewater in the presence of chromium, J. Environ. Manage. 71 (2004) 345–349.
[31] I. Neria-González, E.T. Wang, F. Ramírez, J.M. Romero, C. Hernández-Rodríguez, Characterization of bacterial community associated to biofilms of corroded oil pipelines from the southeast of Mexico, Anaerobe 12 (2006) 122–133.
[32] J.R. Postgate, The Sulfate-reducing Bacteria, second ed., Cambridge University Press, Cambridge, 1984.
[33] R.E. Hungate, A roll tube method for cultivation of strict anaerobes, in: J.R. Norris, D.W. Ribbons (Eds.), Methods in Microbiology, vol. 3B, Academic Press, London, 1969, pp. 117–132.
[34] R. Cord-Ruwisch, A quick method for the determination of dissolved and precipitated sulfides in cultures of sulfate-reducing bacteria, J. Microbiol. Methods 4 (1985) 33–36.
[35] Å. Kolmert, P. Wikström, K. Hallberg, A fast and simple turbidimetric method for the determination of sulfate in sulfate-reducing bacterial cultures, J. Microbiol. Methods 41 (2000) 179–184.
[36] K. Han, O. Levenspiel, Extended monod kinetics for substrate, product, and cell inhibition, Biotechnol. Bioeng. 32 (1988) 430–447.
[37] J.M. Odom, R. Singleton, The sulfate-reducing bacteria: Contemporary perspectives, Springer-Verlag, New York, NY, 1993.
[38] W. Sun, S. Nešić, S. Papavinasam, Kinetics of corrosion layer formation. Part 2—Iron sulfide and mixed iron sulfide/carbonate layers in carbon dioxide/hydrogen sulfide corrosion, Corrosion 64 (2008) 586–599.