Application of Doehlert matrix to the study of electrochemical oxidation of Cr(III) to Cr(VI) in order to recover chromium from wastewater tanning baths

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Abstract

The aim of this study was to optimize simultaneously the chemical and faradic yields of electrochemical oxidation of chromium(III) to chromium(VI) over a titanium–platinum anode in order to recover trivalent chromium from aqueous and tanning baths effluent. A Doehlert design was used to optimize the significant experimental variables: concentration of chloride ions $[Cl^-]$ $(mol\,L^{-1})$; temperature of reactional media T (°C); pH of reactional media; intensity of electrolysis current I (A); time of electrolysis t (h). The quadratic models of second degree relate chemical (R_C) and faradic (R_F) yields to the different variables affecting the electrochemical reaction were determined by the NEMROD software program. Having to study simultaneously two responses, the Pareto graphic analysis of effects was used.

The results obtained in this study have shown that the current intensity and the electrolysis time were the main influent parameters on the removal ratio of chemical oxygen demand (COD), total organic carbon (TOC) and electrochemical oxidation of trivalent chromium.
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1. Introduction

Tannery wastewater is a complex mixture with toxic compounds such as Cr(III) and S(-II) and conventional pollutants: biological oxygen demand, chemical oxygen demand (COD), grease, total suspended solids, chloride, and total dissolved solids.

In order to preserve natural water resources, drastic constraints were imposed to leather industry to reduce pollutants in tannery effluents. Because of high toxicity, chromium was considered as one of the major pollutant in tannery effluents [1].

Many approaches were examined by several authors for removing chromium from residual water of tanneries: precipitation [2,3], ion-exchange [4], liquid–liquid extraction [5,6], membrane filtration [7,8] and electrocoagulation [9–10]. In spite of the efficiency of those methods for trace amounts of chromium (to the exception of the precipitation approach), they are not well suited to treat high amounts of wastewater of tanning baths.

One elegant way to achieve this purpose is electrochemical oxidation of chromium(III) to chromium(VI), which then, can be selectively extracted and recovered by tributylphosphate $PO(C_4H_9O)_3$ (TBP) in acidic chloride media [11]. This method has the advantage to destroy organic contaminants present at high levels in tannery effluents and to be easily used at industrial scale.

Since tannery effluent is a complex mixture of unknown compositions, the optimization of the electrochemical oxidation of

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trivalent chromium on such effluents is difficult. As a consequence, the optimization was first performed on an ideal solution model of chromium(III) sulphate basic like salt utilized in tannery and where the chromium concentration is of the order of magnitude of those generally found in real effluents. On the other hand, the electrochemical oxidation of chromium(III) depends on several variables, which may interact. Therefore, the only reasonable way to optimize this reaction is to use a multivariate method [12–15]. We have chosen an experimental matrix proposed by Doehlert [16–25].

Doehlert matrix has some interesting qualities; it presents a uniform distribution of the experimental points within the space of the coded variables. Uniform networks are especially useful if one seeks to cover an experimental field with a set of uniformly distributed points, and if one seeks to explore the whole field (limits and the interior) without proposing any prior model.

The "Doehlert uniform shell design" used in this study consists of a set points uniformly distributed in space filling. For two variables, the Doehlert design consists of one central point and six points forming a regular hexagon, and therefore situated on a circle. In three dimensions it can be viewed in is a cube-octahedron.

The total experimental domain is explored through a minimum number of experiments which depends on the number of factors studied: indeed, k factors will require a minimum of $k^2 + k + 1$ experiments. It allows an optimal organization of experiences and, consequently, a reduction of time and cost.

Different factors can influence the electrochemical oxidization of the Cr(III) in Cr(VI). Preliminary works using a fractional factorial design permitted us to define and to select the most influential experimental variables and to determine the level that must take every factor [26]. In the present paper, on the basis of the results given by a fractional factorial design [26], the considered factors affecting the responses are:

U_1: first factor representing the concentration of chloride ions in the media $\{[Cl^-] \,(mol\,L^{-1})\}$;
U_2: second factor representing the temperature of reactional medium $\{T\,(^\circ C)\}$;
U_3: third factor representing the pH of reactional medium;
U_4: fourth factor representing the intensity of electrolysis current $\{I\,(A)\}$;
U_5: fifth factor representing the time of electrolysis $\{t\,(h)\}$.

Other important property of Doehlert design regards the number of levels that each variable takes. With five variables (U_1, U_2, U_3, U_4 and U_5) the numbers of levels are 5, 7, 7, 7 and 3 respectively [27].

In order to compare the effects of the different factors in the experimental field concerned coded variables were used. The factors U_1, U_2, U_3, U_4 and U_5 can be transformed into coded variable X_1, X_2, X_3, X_4 and X_5 by the following relation:

$$X_i = \frac{U_i - \overline{U_i}}{\Delta U_i} \tag{1}$$

where X_i the value taken by the coded variable i; U_i the value taken by the factor i; $\overline{U_i}$ the value taken by the factor i in the

Table 1
Factors and experimental field

Coded variable (X_i)	Factor (U_i)	Experimental field		$\overline{U_i}$	ΔU_i
		Lower limit	Upper limit		
X_1	U_1: $[Cl^-]$ (mol L^{-1})	0.10	0.30	0.20	0.10
X_2	U_2: T (°C)	30.0	60.0	45.0	17.3
X_3	U_3: pH	2.00	4.00	3.00	1.22
X_4	U_4: I (A)	0.40	2.80	1.60	1.52
X_5	U_5: t (h)	0.20	1.80	1.00	1.03

centre of the experimental field concerned and ΔU_i the range of variation of the factor i.

$$\overline{U_i} = \frac{(\text{upper limit of }(U_i) + \text{lower limit of }(U_i))}{2} \tag{2}$$

$$\Delta U_i = \frac{(\text{upper limit of }(U_i) - \text{lower limit of }(U_i))}{2\gamma_i} \tag{3}$$

where γ_i is the coded value limit for each factor: $\gamma_1 = 1$; $\gamma_2 = 0.866$; $\gamma_3 = 0.816$; $\gamma_4 = 0.791$; $\gamma_5 = 0.775$.

The appropriate selection of experimental domain for each factor was made from prior experiences and knowledge's of the assay system [26]. The experimental levels chosen for the five studied factors are presented in Table 1.

In the present study, for the five-factor designs mentioned, a Dohlert matrix consisting of a set of 31 different experiments was used (see Table 2).

The experimental responses were the chemical yield R_C (to be maximized) and the faradic yield R_F (to be maximized) of the electrochemical oxidization reaction of Cr(III) in Cr(VI), defined by:

■ The chemical yield:

$$R_1 = R_C = \frac{n_{Cr(VI)_{formed}}}{n_{Cr(III)_{initial}}} \times 100 \tag{4}$$

$n_{Cr(VI)_{formed}}$ represents the number of mole of the Cr(VI) formed by electrochemical oxidation; $n_{Cr(III)_{initial}}$ represents the initial trivalent chromium number of mole before oxidation.

■ The faradic yield:

$$R_2 = R_F = \frac{Q_{calculated}\,(Ah)}{Q_{applied}\,(Ah)} \times 100 = \frac{n_e \times n_{Cr(VI)_{formed}} \times F}{Q_{applied} \times 3600}$$

$$\times 100 = \frac{n_e \times [Cr(VI)] \times V \times F}{M_{Cr} \times Q_{applied} \times 3600} \times 100 \tag{5}$$

where $Q_{calculated}$ is the calculated quantity of electricity necessary for Cr(VI) formed by electrochemical oxidation (Ah); $Q_{applied} = It$ is the quantity of electricity applied to the system (Ah); $[Cr(VI)]$ is the mass concentration of hexavalent chromium (g L^{-1}); M_{Cr} is the chromium molar mass (52 g mol^{-1}); V is the volume of the trivalent chromium solution (1 L); F is the number of Faraday (96485,4 C mol^{-1} = 26.80 Ah mol^{-1}) and n_e is the electrons number exchanged during the electrochemical oxidation of Cr(III) in Cr(VI).

Table 2
Doehlert matrix and experimental plan

Number	Doehlert matrix					Experimental plan				
	X_1	X_2	X_3	X_4	X_5	U_1 [Cl$^-$] (mol L^{-1})	U_2, T (°C)	U_3, pH	U_4, I (A)	U_5, t (h)
1	1.000	0.000	0.000	0.000	0.000	0.30	45	3.00	1.60	1.0
2	−1.000	0.000	0.000	0.000	0.000	0.10	45	3.00	1.60	1.0
3	0.500	0.866	0.000	0.000	0.000	0.25	60	3.00	1.60	1.0
4	−0.500	−0.866	0.000	0.000	0.000	0.15	30	3.00	1.60	1.0
5	0.500	−0.866	0.000	0.000	0.000	0.25	30	3.00	1.60	1.0
6	−0.500	0.866	0.000	0.000	0.000	0.15	60	3.00	1.60	1.0
7	0.500	0.289	0.816	0.000	0.000	0.25	50	4.00	1.60	1.0
8	−0.500	−0.289	−0.816	0.000	0.000	0.15	40	2.00	1.60	1.0
9	0.500	−0.289	−0.816	0.000	0.000	0.25	40	2.00	1.60	1.0
10	0.000	0.577	−0.816	0.000	0.000	0.20	55	2.00	1.60	1.0
11	−0.500	0.289	0.816	0.000	0.000	0.15	50	4.00	1.60	1.0
12	0.000	−0.577	0.816	0.000	0.000	0.20	35	4.00	1.60	1.0
13	0.500	0.289	0.204	0.791	0.000	0.25	50	3.25	2.80	1.0
14	−0.500	−0.289	−0.204	−0.791	0.000	0.15	40	2.75	0.40	1.0
15	0.500	−0.289	−0.204	−0.791	0.000	0.25	40	2.75	0.40	1.0
16	0.000	0.577	−0.204	−0.791	0.000	0.20	55	2.75	0.40	1.0
17	0.000	0.000	0.612	−0.791	0.000	0.20	45	3.75	0.40	1.0
18	−0.500	0.289	0.204	0.791	0.000	0.15	50	3.25	2.80	1.0
19	0.000	−0.577	0.204	0.791	0.000	0.20	35	3.25	2.80	1.0
20	0.000	0.000	−0.612	0.791	0.000	0.20	45	2.25	2.80	1.0
21	0.500	0.289	0.204	0.158	0.775	0.25	50	3.25	1.84	1.8
22	−0.500	−0.289	−0.204	−0.158	−0.775	0.15	40	2.75	1.36	0.2
23	0.500	−0.289	−0.204	−0.158	−0.775	0.25	40	2.75	1.36	0.2
24	0.000	0.577	−0.204	−0.158	−0.775	0.20	55	2.75	1.36	0.2
25	0.000	0.000	0.612	−0.158	−0.775	0.20	45	3.75	1.36	0.2
26	0.000	0.000	0.000	0.633	−0.775	0.20	45	3.00	2.56	0.2
27	−0.500	0.289	0.204	0.158	0.775	0.15	50	3.25	1.84	1.8
28	0.000	−0.577	0.204	0.158	0.775	0.20	35	3.25	1.84	1.8
29	0.000	0.000	−0.612	0.158	0.775	0.20	45	2.25	1.84	1.8
30	0.000	0.000	0.000	−0.633	0.775	0.20	45	3.00	0.64	1.8
31	0.000	0.000	0.000	0.000	0.000	0.20	45	3.00	1.60	1.0

The Dohlert matrix is the same for both responses ($R_1 = R_C$ and $R_2 = R_F$) and allowed the estimation of coefficients (b) of a second degree polynomial model as indicated by the following quadratic equation of the response surface:

$$R = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 +$$
$$b_5 X_5 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 +$$
$$b_{44} X_4^2 + b_{55} X_5^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 +$$
$$b_{14} X_1 X_4 + b_{15} X_1 X_5 + b_{23} X_2 X_3 + b_{24} X_2 X_4 +$$
$$b_{25} X_2 X_5 + b_{34} X_3 X_4 + b_{35} X_3 X_5 + b_{45} X_4 X_5. \qquad (6)$$

where R represent the experimental response; b_0 is an independent term; b_i represent the coefficients of the linear terms; b_{ii} the coefficients of the quadratic terms and b_{ij} ($i \neq j$) is the coefficient corresponding to the interaction term between the factor i and the factor j for example, b_{12} represents the estimation of the interaction between the concentration of chloride ions and temperature.

The calculation of coefficients is carried out through the least squares method by means of

$$B = (X^T X)^{-1} \cdot X^T \cdot Y \qquad (7)$$

where Y is the vector of measured response, X is the model matrix, X^T the transposed model matrix and B is the vector of estimates of the coefficients.

2. Materials

2.1. Reagents and standard

All chemicals used were of analytical-reagent grade of Merck, and double-distilled water was used throughout the experiments.

Aqueous solutions of trivalent chromium of concentration [Cr(III)]$_{initial}$ = 1 g L^{-1}, prepared from chromium(III) sulphate basic[1] (Cr$_4$H$_2$O$_{22}$S$_5$; 26% in Cr$_2$O$_3$, Merck, Germany) in double-distilled water, added of appropriate amounts of sodium chloride salt (purities: over 99.9%, NEN Tech. Ltd., UK). The pH of the solution was adjusted by a concentrated sodium hydroxide or nitric acid solutions

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[1] Chromium(III) sulphate basic: salt used for tanning and that contains a big variety of chrome(III) complex. The basicity term translates the replacement of partial fraction of sulphate ions by hydroxyls ions in the chromium sulphate molecules (Cr$_2$(SO$_4$)$_3$). For example (Cr$_2$(OH)$_2$ (SO$_4$)$_2$) is a salt to 33% of basicity.

Table 3
The used electrodes characteristics

Type	Nature	Form	Geometrical surface (dm^2)	Specific surface (dm^2)
Anode	Ti/Pt	Cylindrical	3.00	6.60
Cathode	Ti/Pt	Cylindrical	$\cong 0.30$	$\cong 0.42$

in order to not modify the concentration of trivalent chromium.

A certified atomic absorption standard solution containing $1.000 \pm 0.003\,g\,L^{-1}$ of Cr(III) (Merck, Germany), was used after appropriate dilution in doubly distilled water for calibration of the FAAS.

2.2. Apparatus

A flame atomic absorption spectrometry (PerkinElmer 3100 FSAA, USA) in an air–acetylene flame was used for determining the concentration of chromium in aqueous solutions after appropriate dilution with double-distilled water in the following conditions:

Lamp current: 25 mA; integration time: 0.5 s; wavelength: 357.9 nm; slit width: 0.7 mm; air–acetylene ratio: 4/3; linear calibration range: 0–$5\,mg\,L^{-1}$; replicates: 3; calibration by reference standard solutions.

The pH measurement was made on a control dynamics digital pH meter (Titrino 716 DMS Metrohm, Switzerland) with a combined glass electrode (Metrohm).

The chemical oxygen demand and the total organic carbon (TOC) of the initial and the electrolyzed real sample were determined respectively with a 45600 COD-HACH Reactor and a TOC 5050 Shimadzu Total Organic Carbon Analyzer.

2.3. Procedure

Aqueous solutions of trivalent chromium of concentration $[Cr(III)]_{initial} = 1\,g\,L^{-1}$, were electrolyzed at constant current imposed by a current generator "P. Fontaine MC 2030 C" in the electrolytic cell (see Fig. 1). The volume of electrolyzed solution during each experiment was 1 L.

The electrolytic cell is constituted by two coaxial cylindrical titanium–platinum electrodes [26] and a thermostatic reactor (1 L) equipped with a Teflon mechanical agitator "Heidolph RZR-200". The constants temperature of the reactional media to $\pm 0.5\,°C$ is assured by a water circulation thermostat bath.

The use of Ti/Pt electrode (anode) is interesting since it catalyses well the electrochemical reaction of oxidation trivalent chromium; offer a great resistance to corrosion therefore has a long lifespan. This electrode is insoluble, contrary to the chromium, nickel, steel and aluminium electrodes [28]. It is also stable contrary to the lead dioxide electrode (does not pose a problem of instability and insoluble's deposits) [29].

In order to favourite the electrochemical oxidation of Cr(III) into Cr(VI), we are chose to work with anodic activate specific surface higher than this of cathode. The characteristics of the used electrodes are reported in Table 3.
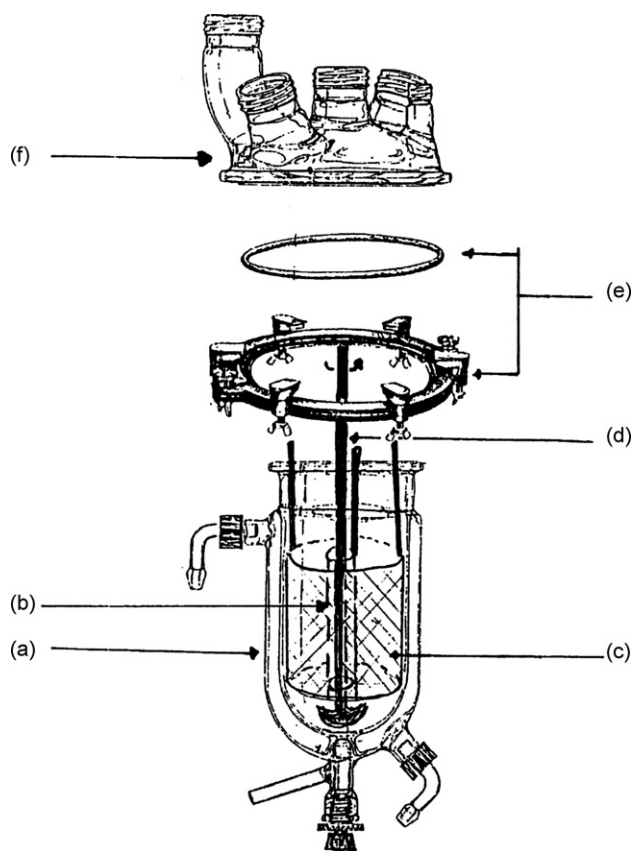

Fig. 1. Electrochemical reactor. (a) Thermostatic reactor; (b) cylindrical cathode; (c) cylindrical anode; (d) tree of agitation; (e) necklace of closing and tightness; (f) reactor cover.

2.4. Analysis of chromium and determination of chemical and faradic yields

The chemical and faradic yields of the electrochemical oxidation of Cr(III) in Cr(VI) according to relations (4) and (5) were determinate by measuring the chromium(III) and the chromium(VI) in the solution before and after electrolysis.

The hexavalent chromium concentration in solution after electrolysis, noted $[Cr(VI)]_{final}$ was determinate as following:

1. after oxidization, the total chromium concentration $[Cr]_{tf}$ in the solution was measured by a flame atomic absorption spectrometry FAAS;
2. the determination of the final trivalent chromium concentration in solution noted $[Cr(III)]_{final}$, was measured by FAAS after elimination of hexavalent chromium by precipitation in acetic tampon media (pH 4.65) with the $Pb(NO_3)_2$ and filtration across a 0.45 μm membrane porosity;
3. the final hexavalent chromium concentration in solution, noted $[Cr(VI)]_{final}$, was calculated by difference between the total chromium concentration $[Cr]_{tf}$ and the final trivalent chromium concentration $[Cr(III)]_{final}$.
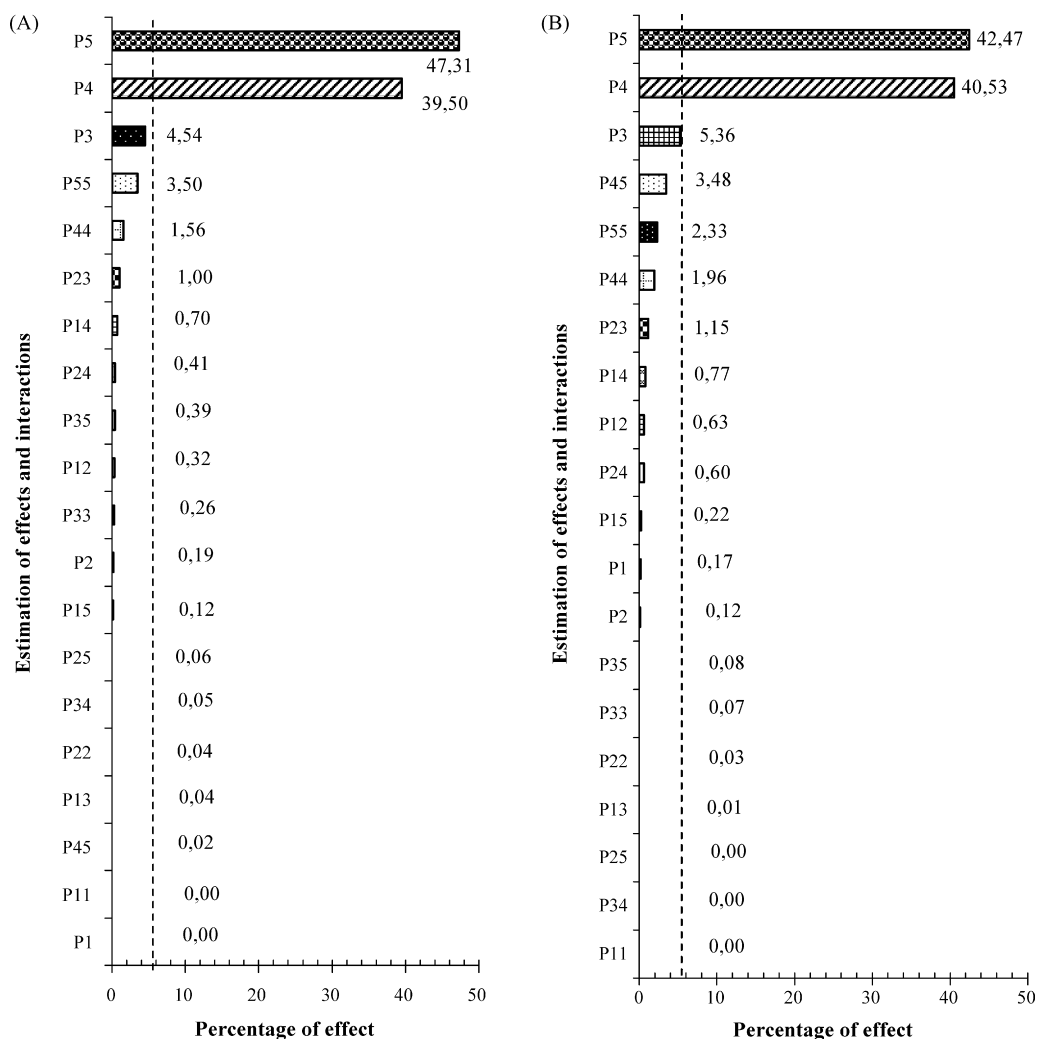
Fig. 2. Pareto graphic analysis of effects (the dashed lines define the 95% confidence interval). (A) Chemical yield; (B) faradic yield.

2.5. Analysis of the real tannery wastewater

The mineralization of real tannery wastewater was monitored by the abatement of the total organic carbon using a Shimadzu VCSH TOC analyzer. Samples were acidified with HCl (1% HCl 2 mM) before injection of 50 μL. TOC measurements were based on the combustion of organics and detection of CO_2 formed by infrared gas analysis method.

The chemical oxygen demand was measured according to standard method [30,31] with a COD-HACH reactor, model 45600.

The real tannery effluent samples were passed through 0.45 μm Whatman GF/C filters, diluted and analyzed for total dissolved chromium by FAAS after an acid decomposition of the leather samples, according to general AAS procedures [32,33].

The chemical and faradic yields for tannery wastewater samples were determinate by measuring the trivalent and hexavalent chromium in real tannery effluent solutions pre-treated by the same process as that of the synthetic ones.

3. Results an discussion

3.1. Doehlert optimization for synthetic solutions

Replicates at the central level of the variables are performed in order to validate the model by means of an estimate of experimental variance. The experiment at the centre (experiment number 31) was carried out three times (experiments 31–33) in order to obtain an estimation of the experimental error. The coefficient of variation (CV) also is known as the relative standard deviation (R.S.D.) calculated for R_C and R_F are 0.4 and 0.9 respectively.

The experimental results for the five selected variables are shown in Table 4. The responses (R_C and R_F) were analyzed by regression analysis according to the proposed model (Eq. (6)). According to these obtained results, the coefficients of the polynomial model (Eq. (6)) were calculated using the NEMROD software program (L.P.R.A.I., Marseille, France) [34]. The estimated model parameters for the chemical and faradic yields

Table 4
Experimental plan and results

Experiment number	$[Cl^-]$ (mol L^{-1})	T (°C)	pH	I (A)	t (h)	$R_1 = R_C$	$R_2 = R_F$
1	0.30	45	3.00	1.60	1.0	61.34	59.99
2	0.10	45	3.00	1.60	1.0	65.42	65.18
3	0.25	60	3.00	1.60	1.0	57.62	56.02
4	0.15	30	3.00	1.60	1.0	58.61	56.86
5	0.25	30	3.00	1.60	1.0	63.99	65.24
6	0.15	60	3.00	1.60	1.0	67.69	66.00
7	0.25	50	4.00	1.60	1.0	62.18	64.78
8	0.15	40	2.00	1.60	1.0	43.21	44.31
9	0.25	40	2.00	1.60	1.0	42.97	42.69
10	0.20	55	2.00	1.60	1.0	59.61	61.18
11	0.15	50	4.00	1.60	1.0	73.65	75.30
12	0.20	35	4.00	1.60	1.0	75.35	73.91
13	0.25	50	3.25	2.80	1.0	97.00	53.57
14	0.15	40	2.75	0.4	1.0	25.50	98.57
15	0.25	40	2.75	0.4	1.0	24.00	92.77
16	0.20	55	2.75	0.4	1.0	23.00	88.91
17	0.20	45	3.75	0.4	1.0	25.00	96.64
18	0.15	50	3.25	2.8	1.0	81.00	44.73
19	0.20	35	3.25	2.8	1.0	80.00	44.18
20	0.20	45	2.25	2.8	1.0	77.00	42.52
21	0.25	50	3.25	1.84	1.8	93.00	43.42
22	0.15	40	2.75	1.36	0.2	17.00	96.64
23	0.25	40	2.75	1.36	0.2	16.00	90.95
24	0.20	55	2.75	1.36	0.2	17.00	96.64
25	0.20	45	3.75	1.36	0.2	17.00	96.64
26	0.20	45	3.00	2.56	0.2	32.00	96.64
27	0.15	50	3.25	1.84	1.8	86.00	40.15
28	0.20	35	3.25	1.84	1.8	85.00	39.68
29	0.20	45	2.25	1.84	1.8	69.00	32.21
30	0.20	45	3.00	0.64	1.8	63.00	84.56
31	0.20	45	3.00	1.6	1.0	63.95	62.73
32	0.20	45	3.00	1.6	1.0	64.29	62.85
33	0.20	45	3.00	1.6	1.0	63.81	61.85

are:

$$R_1 = R_C = 64.017 - 0.338X_1 + 2.444X_2 + 11.875X_3 + 35.034X_4 + 38.344X_5 - 0.637X_1^2 - 2.507X_2^2 - 5.996X_3^2 - 14.097X_4^2 - 20.321X_5^2 - 8.920X_1 \cdot X_2 - 3.723X_1 \cdot X_3 + 15.286X_1 \cdot X_4 + 6.350X_1 \cdot X_5 - 17.599X_2 \cdot X_3 + 11.710X_2 \cdot X_4 + 4.531X_2 \cdot X_5 + 4.040X_3 \cdot X_4 + 11.600X_3 \cdot X_5 - 2.685X_4 \cdot X_5.$$
(8)

$$R_2 = R_F = 62.477 - 1.958X_1 + 1.621X_2 + 10.891X_3 - 29.949X_4 - 30.660X_5 + 0.108X_1^2 - 1.965X_2^2 - 2.708X_3^2 + 13.327X_4^2 + 13.999X_5^2 - 10.600X_1 \cdot X_2 - 1.702X_1 \cdot X_3 + 13.569X_1 \cdot X_4 + 7.413X_1 \cdot X_5 - 15.970X_2 \cdot X_3 + 11.931X_2 \cdot X_4 + 0.448X_2 \cdot X_5 + 0.436X_3 \cdot X_4 + 4.488X_3 \cdot X_5 - 29.375X_4 \cdot X_5.$$
(9)

To check the weight of the different coefficients, the Pareto graphic analysis of effects was used [35,36]. Plots of the contribution of every term are displayed in Fig. 2. The advantage of this plot is that the numerical values of the effects are displayed. The Pareto graphic analysis of effects (Fig. 2) indicate that the time and the intensity of electrolysis current were the most influential factors on the both responses R_C and R_F with a total contribution of the order of 60 and 46% respectively. On the other hand is noted the imported negative interaction between the time and the intensity of electrolysis current for the R_F with a contribution of 21.67% (see Fig. 2 and Eq (9)).

According to signs of values of b_i (see Eqs. (8) and (9)) and the Pareto graphic analysis of effects (Fig. 2), we can note that an extension of the time of electrolysis entails an increasing of the chemical yield (R_C) and a decreasing of the faradic yield (R_F). In the same way the increasing of the intensity of electrolysis current have as consequence an increasing of the chemical yield (R_C) and a decreasing of the faradic yield (R_F). On the other hand, an increase of the pH of the solution increases slightly the both responses.

The optimum is often chosen according to want them of the operator, so, the optimum is not necessarily the maximum. Having to study simultaneously two responses, it was necessary to find the best compromise between the responses. We
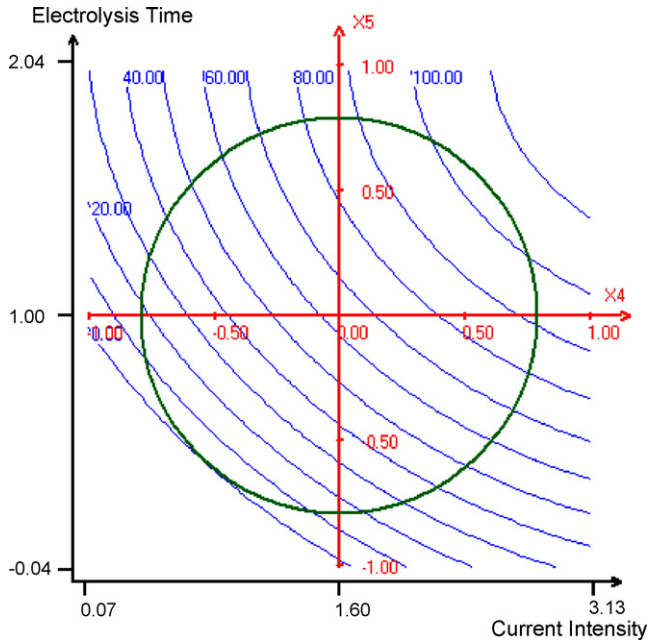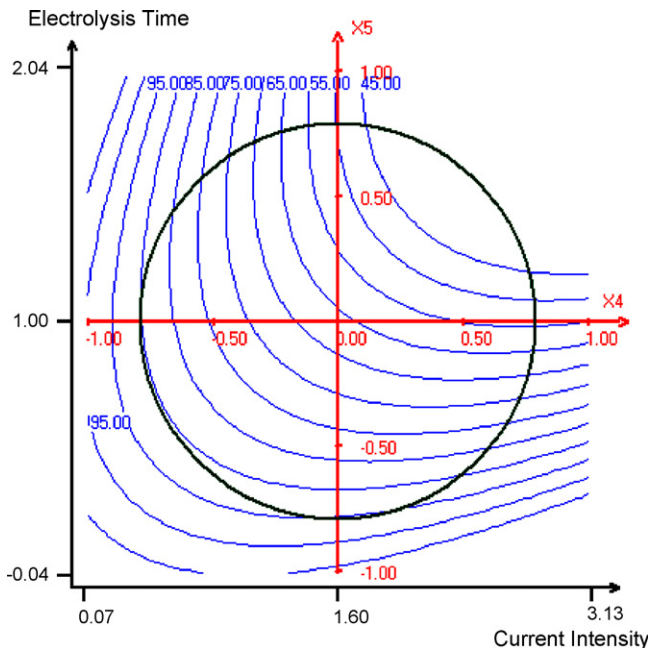
Fig. 3. Isoresponses curves in the plan (I,t) for chemical yield (R_C) at the fixed followings factors: $[Cl^-] = 0.25 \, \text{mol} \, L^{-1}$; $T = 50 \, ^\circ C$; pH 3.25.

have chosen to obtain $R_C \geq 90\%$ and $R_F \geq 50\%$. The followings operatives conditions: $[Cl^-] = 0.25 \, \text{mol} \, L^{-1}$; $T = 50 \, ^\circ C$; pH 3.25; $I = 2.8$ A and $t = 1$ h, permitting to obtain a $R_C = 97\%$ and a $R_F = 54\%$ with a good repeatability (R.S.D. < 1%).

3.2. Test with a real tannery effluent

From the conclusions of the experimental design, we carried out complementary test with a real wastewater of tanning bath. The results obtained show the existence of other concur-

Fig. 4. Isoresponses curves in the plan (I,t) for faradic yield (R_F) at the fixed followings factors: $[Cl^-] = 0.25 \, \text{mol} \, L^{-1}$; $T = 50 \, ^\circ C$; pH 3.25.
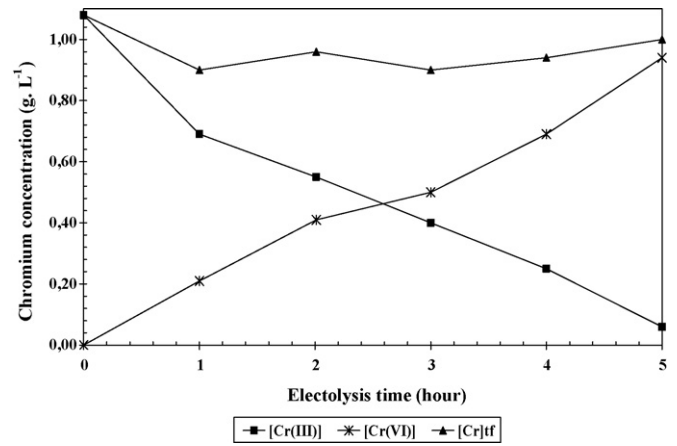

Fig. 5. Variation of trivalent, hexavalent and total chromium in solution during electrolysis time under the following conditions ($[Cl^-] = 0.25 \, \text{mol} \, L^{-1}$; $T = 50 \, ^\circ C$; pH 3.25).

rent reactions to the principal reaction of oxidation of trivalent chromium such as oxidation of tensioactive materials, organic and inorganic compound contrary to the case of the synthetic solutions. In fact, the baths of tanning was concentrated during the use by cations (Ca^{2+}, Mg^{2+}, Na^+, Fe^{2+}, . . .), anions (SO_4^{2-}, S^{2-}, Cl^-, . . .) and organic compounds such as protein molecules (coming from solubilisation of collagen by hydrolysis), sodium formate, organic sulphides, phthalates, sodium oxalate and salts of dicarboxylic acid . . .).

Based on the different experimental results of experimental design methodology and isoresponses curves in the plan (I,t) (Figs. 3 and 4) for the synthetic solution at the fixed followings factors: $[Cl^-] = 0.25 \, \text{mol} \, L^{-1}$; $T = 50 \, ^\circ C$; pH 3.25, we considered it useful to increase the electrolysis time and not the current density for the real effluents of tanning bath. Indeed, the increasing of the current density to cause the formation on the cathode of a trivalent chromium hydroxide film (greenish solid). This film, which adheres to the cathode, has for consequently the passivation of the electrode and the increase of the voltage between the electrodes.

The analysis shows that this solid contains hydrogen with a percentage of about 3% (3.13 and 2.87%) and of chromium
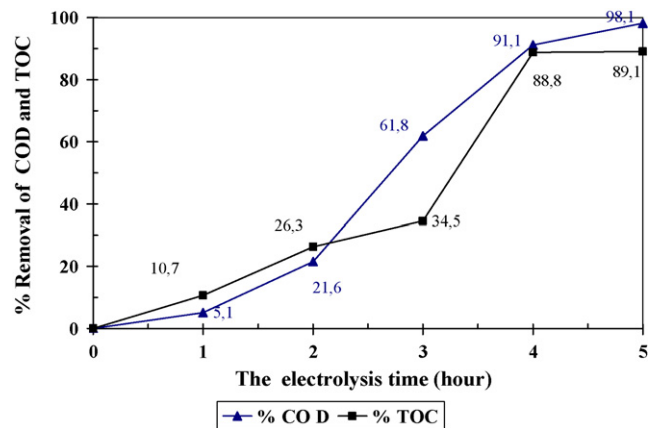

Fig. 6. Variation of COD and TOC removal during electrolysis time under the following conditions ($[Cl^-] = 0.25 \, \text{mol} \, L^{-1}$; $T = 50 \, ^\circ C$; pH 3.25).

with a percentage of 47%. the solid that adheres on cathode is probably the hydroxide of trivalent chromium. The comparison of the theoretical percentages calculated for Cr(OH)$_3$ (which are 2.91 and 50.48% respectively for hydrogen and chromium) and those found by elementary analysis confirms this result.

The study of the variation of the oxidation of trivalent chromium at the followings operatives conditions: $T = 50\,°C$; pH 3.25; $I = 2.8$ A shown that about 5 h of electrolysis, we transforms the quasi-total of Cr(III) into Cr(VI) (Fig. 5). During the test with a real wastewater of tanning bath, the oxidation of chromium was accompanied by removal of the chemical oxygen demand and of total organic carbon (sees Fig. 6). Moreover, it is noted that the rates of abatements of the COD and the TOC are 98.13 and 89.1% respectively about 5 h of electrolysis.

Once the quantitative oxidation of trivalent chromium was carried out, we were then interested to the selective extraction of hexavalent chromium by the (TBP) for its possible recycling [11].

4. Conclusion

In this study it has been shown that, the experimental results obtained by using the Doelhert's matrix, enabled us to establish a mathematical model, whose essential interest is to be able to predict in any point of the experimental field the values of the chemical and faradic yields of the electrochemical oxidation reaction of Cr(III) into Cr(VI). By using such a design we have been able to establish the optimum conditions for the simultaneous responses for synthetic solutions in the followings operatives conditions: $[Cl^-] = 0.25\,mol\,L^{-1}$; $T = 50\,°C$; pH 3.25; $I = 2.8$ A and $t = 1$ h.

The experimental results show well the effectiveness of the electrochemical process in the case of processing the liquid waste of tanning. Indeed, it allows the quantitative oxidation of trivalent chromium as well as the electrochemical incineration of the organic and mineral pollutants present in tanning wastewater.

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