



Application of Doehlert matrix to determine the optimal conditions of electrochemical treatment of tannery effluents

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ABSTRACT

The oxidation of organic and inorganic pollutants present in tannery effluents has been realised by electrochemical way. The influence of the electrochemical reactor parameters was carried out by the use of Doehlert matrix. The obtained results 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), electrochemical oxidation of trivalent chromium and sulphite ions.

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1. Introduction

The tanning industry becomes one of the leading economic sectors in many countries. However, it generates large quantities of heavily polluted wastewater containing organic and inorganic substances. These substances are derived from hides and skins and from addition of reagents during various processes to obtain finished product.

Two operations are known as the most polluting: liming and tanning operations. The low efficiency of these two operations leads to large amounts of polluted effluents. Indeed, the effluent emanating from liming operations contains high concentration of sulphite ions due to the addition of a concentrated solution of sodium lime and sulphites.

In the other hand, chromium is extensively used in tanning operation to obtain leather of a desirable quality. Therefore, the resulting wastewater (effluent) is rich in chromium besides organic matter.

Consequently, in order to sustain our global water supply, many technological systems for the removal of organic and inorganic pollutants from tannery wastewater have been recently developed. Among them, the precipitation of trivalent chromium [1,2], elec-

tro coagulation [3–5], membrane filtration [6–8], ion exchange [9], electrochemical methods [10–14].

In the present work, an electrochemical reactor was applied to study the treatment of tannery wastewater whose characteristics are reported in Table 1. Thus, the planning of the experimental work for investigating the influence of the principal experimental parameters: current intensity (I), electrolysis time (t) and medium temperature (T) on the oxidation of trivalent chromium, sulphite ions and the removal of the chemical oxygen demand (COD) and the total organic carbon (TOC), was based on the experimental design methodology. Therefore, the optimal conditions for the degradation of the liming and the tanning beamhouse were studied by the use of Doehlert matrix [15–17].

Indeed, these designs are formed by uniformly distributed points that may be represented in normalized variables (X_i). These designs estimates the coefficients of a quadratic polynomial mathematical model, whose essential interest is to be able to predict in any point of the experimental region, the values of the response Y . The number of experiments for a Doehlert matrix for k factors is given by the relation: $N = k^2 + k + 1$. The experimental response of interest associated to a Doehlert matrix (for 3 variables) is represented by a quadratic polynomial model:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$$

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Table 1
Physico-chemical characteristics of tannery effluents

Parameters	Value	
	Liming effluent	Tanning effluent
pH	12.4	3.6
COD (mg/L)	14,540	7,814
BOD ₅ (mg/L)	1,300	164
TOC (mg/L)	3,255	832
Sulphite ions (mg/L)	640	–
Chloride ions (mg/L)	5,000	33,430
Chromium (mg/L)	–	3,920

where Y : experimental response; b_i : estimation of the principal effect of the factor i for the response Y ; b_{ii} : estimation of the second effect of the factor i for the response Y ; b_{ij} : estimation of the interaction effect between factor i and j for the response Y .

The coefficients of this model are calculated, in the experimental region (Table 3), using the least squares method:

$$B = (X^T X)^{-1} X^T Y$$

where B : the vector of estimates of the coefficients; X : the model matrix; Y : the vector of the experimental results.

The experimental (natural) values U_i are calculated from the coded variables X_i using the following formula [18]:

$$X_i = \frac{U_i - U_{i,0}}{\Delta U_i} \times \alpha$$

where

$$U_{i,0} = \frac{U_{i,\max} + U_{i,\min}}{2}$$

is the value of U_i at the centre of the experimental region;

$$\Delta U_i = \frac{U_{i,\max} - U_{i,\min}}{2}$$

is the step with $U_{i,\max}$ and $U_{i,\min}$ maximum and minimum values of the effective variable U_i , respectively.

α is the maximum coded value of X_i : $X_1 = 1$; $X_2 = 0.866$; $X_3 = 0.816$.

2. Experimental

2.1. Equipment

Electrolyses are carried out in an electrochemical cell (Fig. 1). This cell is consisted with two coaxial cylindrical electrodes and a thermostatic reactor (1 L) equipped with a Teflon mechanical agitator "Heidolph RZR – 200". The constants temperature of the reactional media to $\pm 0.5^\circ\text{C}$ is assured by a water circulation thermostat bath. The titanium platinum was been the most suitable metal to the anodic oxidation of trivalent chromium since it limits the water oxidation. This electrode is insoluble, contrary to the chromium, nickel, steel and aluminium electrodes. It is also stable unlike dioxide lead electrode [19]. Moreover, a significant removal of the COD was obtained with these electrodes [20]. 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 2.

Electrolyses were performed with a "P. Fontaine MC 2030 C" current generator. The temperature of the reactional medium is maintained constant (± 0.5) with a thermostated bath equipped with an internal water circulation.

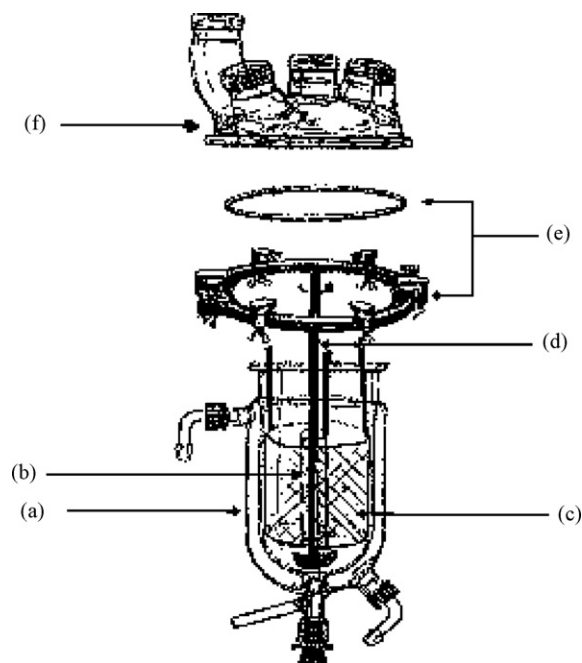


Fig. 1. The electrochemical reactor: (a) thermostatic reactor; (b) cylindrical cathode; (c) cylindrical anode; (d) tree of agitation; (e) necklace of closing and tightness; (f) reactor cover.

Table 2
The used electrodes characteristics

Type	Nature	Forme	Geometrical surface (dm ²)	Specific surface (dm ²)
Anode	Ti/Pt	Cylindrical	1.50	3.30
Cathode	Ti/Pt	Cylindrical	≈0.15	≈0.21

2.2. Analytical methods

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

1. after oxidization, the total chromium concentration $[\text{Cr}]_{\text{tf}}$ in the solution was measured by a flame atomic absorption spectrometry FAAS;
2. the determination of the final trivalent chromium concentration in solution noted $[\text{Cr(III)}]_{\text{final}}$, was measured by FAAS after elimination of hexavalent chromium by precipitation in acetic tampon media (pH 4.65) with the $\text{Pb}(\text{NO}_3)_2$ and filtration across a $0.45 \mu\text{m}$ membrane porosity;
3. the final hexavalent chromium concentration in solution, noted $[\text{Cr(VI)}]_{\text{final}}$, was calculated by difference between the total chromium concentration $[\text{Cr}]_{\text{tf}}$ and the final trivalent chromium concentration $[\text{Cr(III)}]_{\text{final}}$.

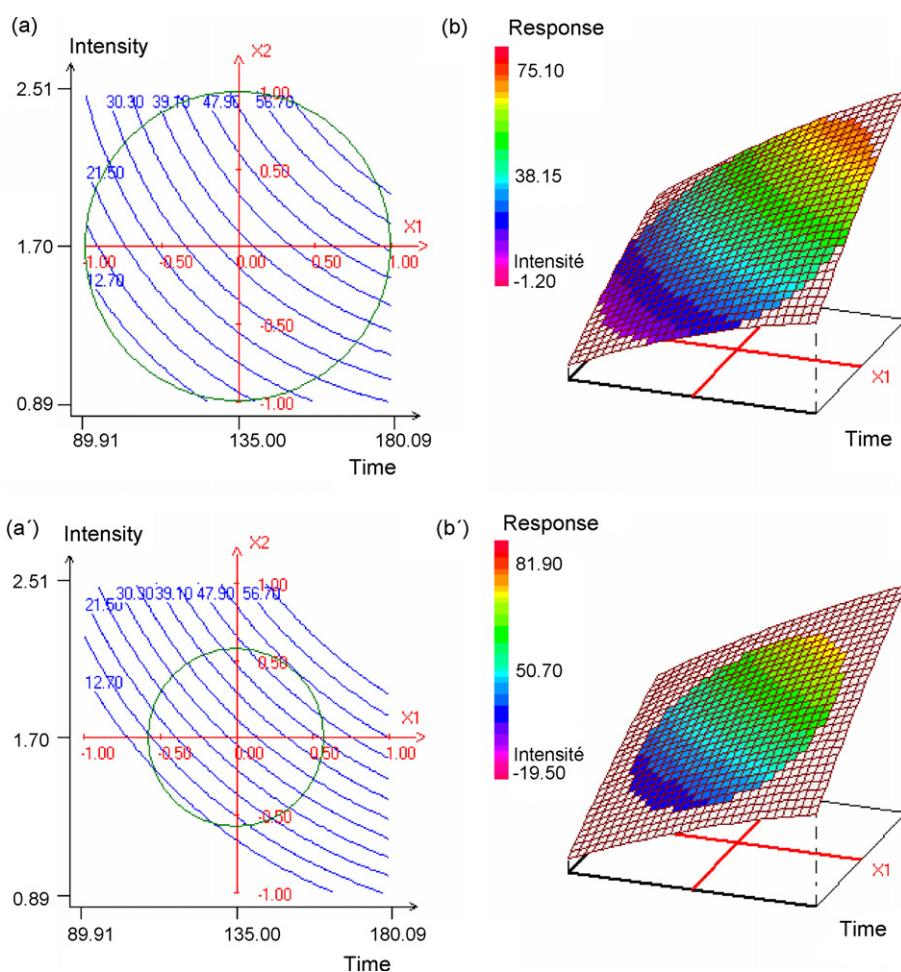
The chemical oxygen demand and the total organic carbon of the initial and the electrolysed samples were determined, respectively with a DCO – HACH reactor, model 45600 and a Shimadzu TOC – 500 analyzer.

Table 3
Experimental region investigated for the tannage effluent

Variables	Factors (U_i)	Unit	Experimental region	
			Minimum value	Maximum value
X_1	U_1 : time	min	90	180
X_2	U_2 : intensity	A	1	2.4
X_3	U_3 : temperature	$^\circ\text{C}$	30	50

Table 4
Experimental design and results of the tannage effluent

Experiment no.	Time (min)	Intensity (A)	Temperature (°C)	R _c (%)	COD (%)	TOC (%)
1	180	1.7	40	53.3	79.3	86.9
2	90	1.7	40	14.8	61.2	27.0
3	158	2.4	40	61.0	80.9	90.8
4	113	1.0	40	12.7	58.3	22.7
5	158	1.0	40	25.5	65.9	45.4
6	113	2.4	40	38.8	70.2	73.0
7	158	1.9	50	52.6	76.1	81.6
8	113	1.5	30	20.9	64.7	32.5
9	158	1.5	30	34.7	69.9	71.8
10	135	2.2	30	41.1	74.3	72.6
11	113	1.9	50	25.8	66.7	48.6
12	135	1.2	50	13.0	59.3	25.3
13	135	1.7	40	36.5	69.9	72.1

**Fig. 2.** (a) Contour plots of R_c yield of trivalent chromium oxidation versus the current intensity (A) and the electrolysis time (h) at a fixed temperature T=40°C; results obtained from Doehlert matrix (Table 5); (b) corresponding three-dimensional plot; (a') contour plots of R_c yield of trivalent chromium versus the current intensity (A) and the electrolysis time (h) at a fixed temperature T=50°C; (b') corresponding three-dimensional plot.

The sulphite ions were determined by a volumetric analysis with a ferricyanide potassium solution.

3. Results

3.1. Treatment of the tanning effluent

The optimal conditions of the current intensity (*I*), the electrolysis time (*t*) and the medium temperature (*T*) for the oxidation of the trivalent chromium (R_c) and the mineralization of the organic matter (the removal of the COD and the TOC) were studied.

Table 5
Repeated experiments in the centre of the investigated region (tannage effluent)

Time (min)	Intensity (A)	Temperature (°C)	R _c (%)	COD (%)	TOC (%)
135	1.7	40	38.1	70.3	72.4
135	1.7	40	37.8	69.7	72.7
135	1.7	40	36.5	69.9	71.1

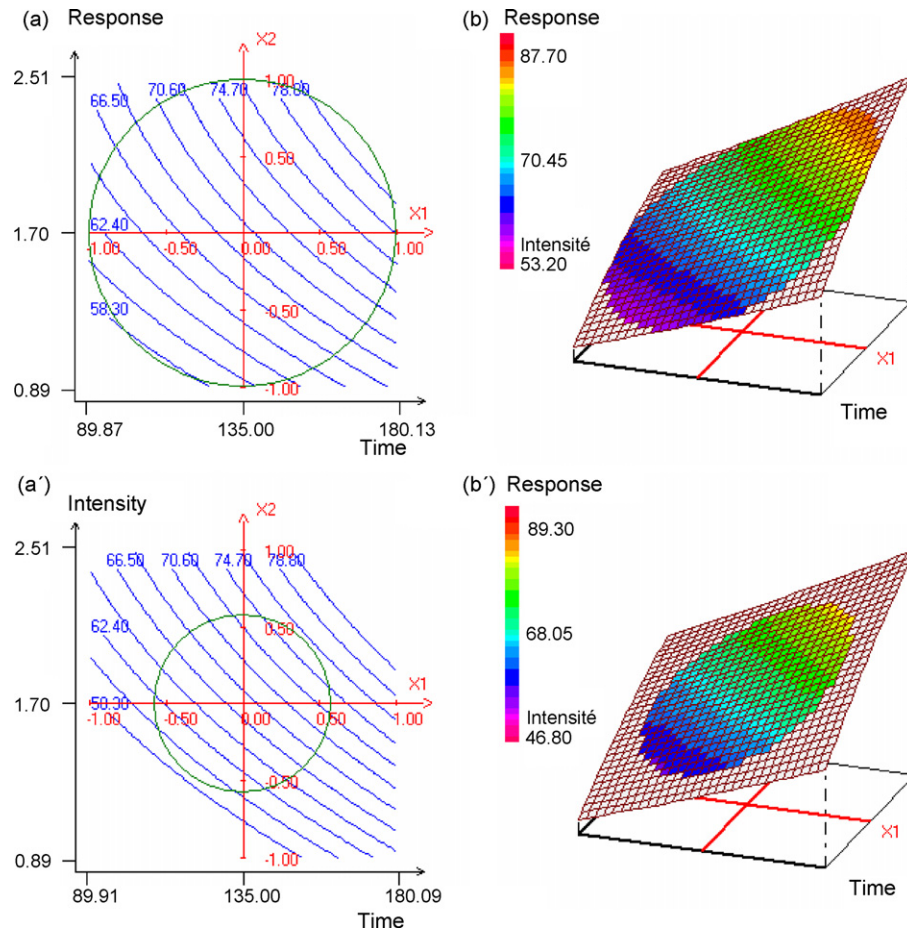


Fig. 3. (a) Contour plots of COD removal versus the current intensity (A) and the electrolysis time (h) at a fixed temperature $T = 40^\circ\text{C}$; results obtained from Doehlert matrix (Table 5); (b) corresponding three-dimensional plot; (a') contour plots of COD removal versus the current intensity (A) and the electrolysis time (h) at a fixed temperature $T = 50^\circ\text{C}$; (b') corresponding three-dimensional plot.

Referring to the previous work [11], the experimental region investigated is represented in Table 3. The Doehlert matrix for 3 factors is composed by 13 experiments as reported in Table 4. The levels of the independent variables (effective variables U_i) were calculated according to these following relations:

$$U_1 = 45X_1 + 135$$

$$U_2 = \frac{0.7}{0.866}X_2 + 1.7$$

$$U_3 = \frac{10}{0.816}X_3 + 40$$

The experimental design and results are represented in Table 5. 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 13) was carried out three times (Table 6) in order to obtain an estimation of the experimental error.

Table 6
Experimental region investigated for the liming effluent

Variables	Factors (U_i)	Unit	Experimental region	
			Minimum value	Maximum value
X_1	U_1 : time	h	1	3
X_2	U_2 : intensity	A	2	2.8

According to these obtained results, the coefficients of the polynomial model were calculated using the NEMROD Software [21]:

$$R_c = 36.480 + 19.077X_1 + 19.019X_2 - 1.092X_3 - 2.420X_1^2 - 1.857X_2^2 - 6.648X_3^2 + 5.398X_1X_2 + 6.058X_1X_3 + 9.309X_2X_3$$

$$\% \text{ COD removal} = 69.900 + 8.619X_1 + 8.582X_2 - 1.396X_3 + 0.325X_1^2 - 1.555X_2^2 - 1.810X_3^2 + 1.836X_1X_2 + 1.966X_1X_3 + 2.916X_2X_3$$

$$\% \text{ TOC removal} = 72.130 + 29.079X_1 + 29.415X_2 - 4.352X_3 - 15.190X_1^2 - 13.807X_2^2 - 17.855X_3^2 - 2.835X_1X_2 - 2.868X_1X_3 + 14.176X_2X_3$$

The chemical yield of the trivalent chromium oxidation, the COD and TOC removal ratio are defined as follows:

$$R_c = \frac{n_{\text{Cr(III)}}}{n_{\text{Cr(VI)}}} \times 100$$

$$\% \text{ COD removal} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100$$

$$\% \text{ TOC removal} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100$$

To interpret these results, the predicted contour plots (curve of constant response) and the three-dimensional representation of the same plots are given in Figs. 2–4. The graphic analysis of these figures shows that the medium temperature has a negligible effect on the oxidation of the trivalent chromium and the COD and TOC removal, in the investigated experimental region. Moreover, it is noted that the maximum of the three studied response (R_c , % COD removal, % TOC removal) would be obtained with increasing not

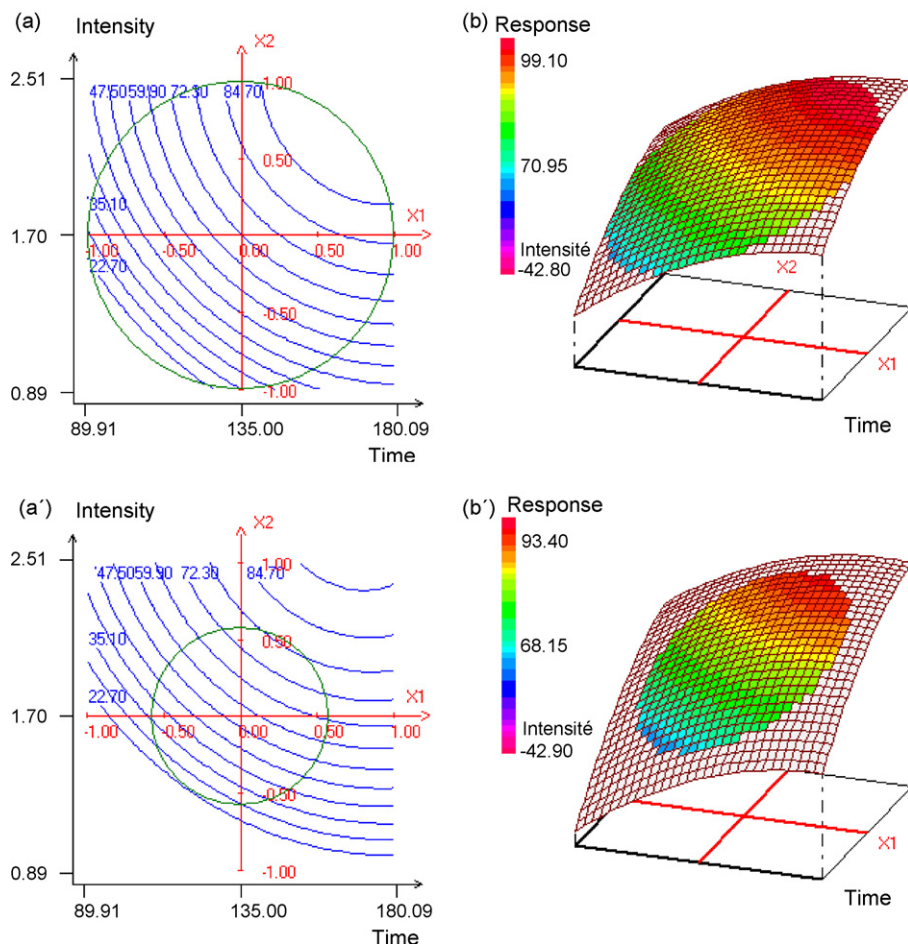


Fig. 4. (a) Contour plots of TOC removal versus the current intensity (A) and the electrolysis time (h) at a fixed temperature $T=40^{\circ}\text{C}$; results obtained from Doehlert matrix (Table 5); (b) corresponding three-dimensional plot; (a') contour plots of TOC removal versus the current intensity (A) and the electrolysis time (h) at a fixed temperature $T=50^{\circ}\text{C}$; (b') corresponding three-dimensional plot.

only the electrolysis time but also the current intensity. However, it is noted that the increase of the current intensity leads to the precipitation of the trivalent chromium (greenish solid) at the cathode surface [12,22]. This solid, which adheres to the cathode, causes the passivity of the electrode and increases the electrolysis voltage. Therefore, it would be better to increase the electrolysis time only.

On the basis of these various results, the variation of the electrochemical oxidation of Cr(III) and the removal of the organic matter were investigated during the electrolysis time. The current intensity and the medium temperature are fixed, respectively at the maximum and the centre value of the investigated experimental region.

The variation of the electrochemical oxidation of the trivalent chromium under these conditions was reported in Fig. 5. This figure shows that 94% of Cr(III) is oxidized into Cr(VI) after 4 h of electrolysis. Moreover, it is noted that under these conditions, the organic matter is nearly completely degraded: 92% and 95% of respectively COD and TOC removal (Fig. 6).

These results show the effectiveness of the electrochemical process in the treatment of the tannery wastewater. However, this process must be followed by an extraction of the hexavalent chromium which is more toxic than the trivalent chromium [10].

3.2. Treatment of the liming effluent

Based on the previous results for the tanning wastewater, the effect of the current intensity and the electrolysis time on

the oxidation of the organic and inorganic matter of the liming effluent was studied. We have chosen the approach of Doehlert to determine, in any point of the investigated region, the COD and TOC removal and the electrochemical oxidation of sulphide ions.

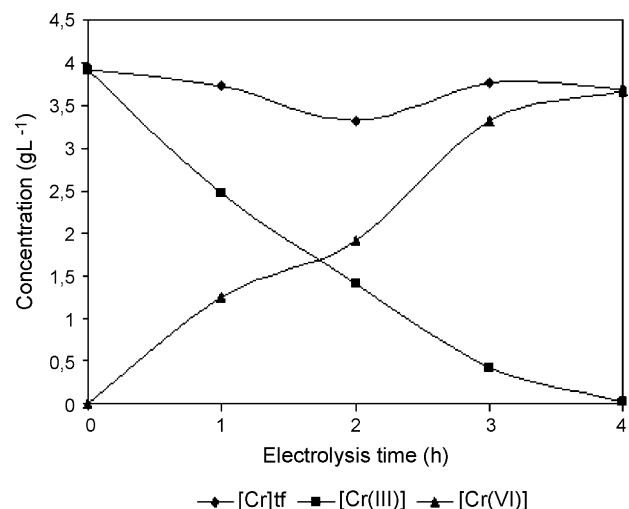


Fig. 5. Variation of trivalent; hexavalent and total chromium during time electrolysis under the following conditions ($I=2.4\text{ A}$; $T=40^{\circ}\text{C}$).

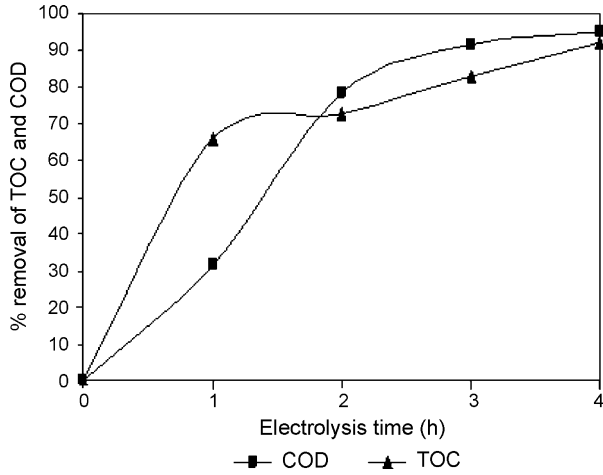


Fig. 6. Variation of COD and TOC removal during time electrolysis under the following conditions ($I=2.4\text{ A}$; $T=40^\circ\text{ C}$).

The experimental region investigated for this effluent is represented in Table 6. Indeed, a preliminary test under the following conditions: $I=2.4\text{ A}$; $T=30^\circ\text{ C}$; $t=2\text{ h}$ shows that 98% of sulphide ions are oxidized and more than 50% of the COD and the TOC are disappeared.

The Doehlert matrix for two factors is formed by 7 experiments as reported in Table 7. The levels of the independent variables U_i were calculated according to the following relations:

$$U_1 = X_1 + 2$$

$$U_2 = \frac{0.4}{0.866} X_2 + 2$$

The experimental design and the results are represented in Table 7.

According to these obtained results, the coefficients of the polynomial model were calculated using the NEMROD Software:

$$R_c = 98.430 + 0.282X_1 + 0.130X_2 - 0.005X_1^2 - 0.092X_2^2 + 0.087X_1X_2$$

$$\% \text{ COD} = 51.400 + 8.500X_1 + 7.893X_2 - 6.025X_1^2 - 7.792X_2^2 + 9.446X_1X_2$$

$$\% \text{ TOC} = 63.400 + 11.450X_1 + 9.094X_2 - 7.815X_1^2 - 10.862X_2^2 + 2.044X_1X_2$$

Therefore, the predicted contour plots and the three-dimensional representation of the same plots are given in Figs. 7–9. The graphic analysis of Figs. 7 and 8 show that the current intensity and the electrolysis time were very meaningful for the degradation of the liming effluent; their effect is positive. Thus, an increase of the electrolysis time and the current intensity increases the COD and TOC removal ratio. However, Fig. 9b presents a plan with a maximal yield in any point of the investigated region. This shows that the decrease

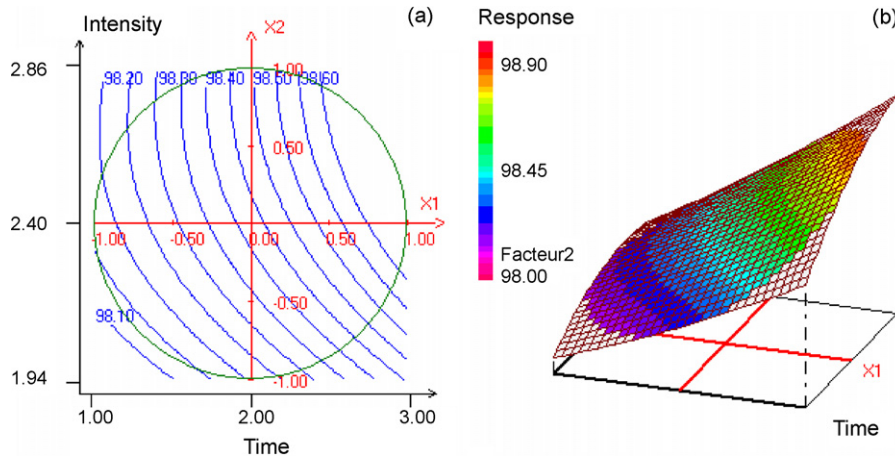


Fig. 7. (a) Contour plots of COD removal versus the current intensity (A) and the electrolysis time (h) at a fixed temperature $T=30^\circ\text{ C}$; results obtained from Doehlert matrix (Table 9); (b) corresponding three-dimensional plot.

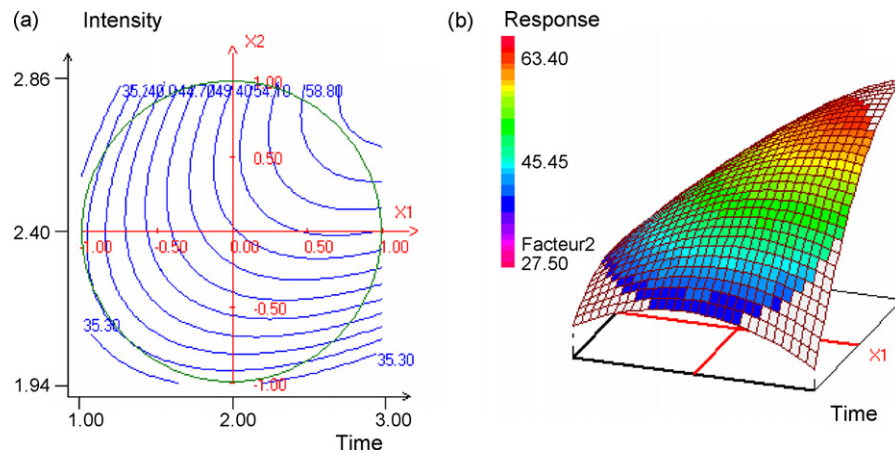


Fig. 8. (a) Contour plots of TOC removal versus the current intensity (A) and the electrolysis time (h) at a fixed temperature $T=30^\circ\text{ C}$; results obtained from Doehlert matrix (Table 9); (b) corresponding three-dimensional plot.

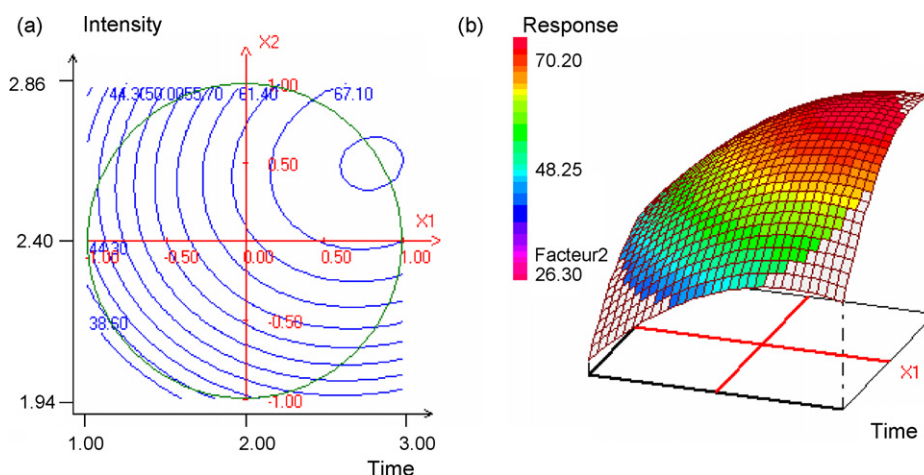


Fig. 9. (a) Contour plots of R_c of sulphite ions oxidation versus the current intensity (A) and the electrolysis time (h) at a fixed temperature $T=30^\circ\text{C}$; results obtained from Doehlert matrix (Table 9); (b) corresponding three-dimensional plot.

Table 7

Experimental design and results of the liming effluent

Experiment no.	Time (h)	Intensity (A)	R_c (%)	COD (%)	TOC (%)
1	3.0	2.4	98.7	52.1	65.0
2	1.0	2.4	98.2	38.7	46.3
3	2.5	2.8	98.7	61.0	69.9
4	1.5	2.0	98.1	35.3	38.6
5	2.5	2.0	98.4	39.2	52.4
6	1.5	2.8	98.3	40.8	52.5
7	2.0	2.4	98.4	51.4	63.4

of sulphide ions depends only on the current intensity. This result is reported by Bouzid [14] where he showed that the sulphide ions can be quickly oxidized with a minimum of energy. Moreover, he noted that this oxidation reaction generates besides sulphate ions, a quantity of elementary sulphur and thiosulphate ions that oxidized preferentially to sulphate ions. Therefore, the degradation of the organic matter of the liming effluent would require an important energy.

According to these obtained results, 2 experiments are considered in order to determine the optimal conditions; the results are summarized in Table 8. These two tests confirm the last results. Indeed, they show that there is not a lot of difference of a current intensity of 2.8 A or 3 A. This phenomenon is due to the formation of other products which consume oxygen and thus contribute to increase the COD.

In order to check the reproducibility of the studied process and to validate the model, the experiment at the centre is repeated three times and reported in Table 9. The following table shows a good reproducibility (R.S.D. < 1%).

The electrochemical oxidation process shows a complete oxidation of sulphide ions (99%), but the degradation of the organic matter of this effluent requires other conditions to improve the mineralization.

Table 8

Optimal conditions and results

Parameters	Experiment 1		Experiment 2	
	$I=2.8\text{ A}$	Time = 3 h	$I=3\text{ A}$	Time = 3 h
R_c (%)	98.8		99.0	
COD (%)	62.5		64.0	
TOC (%)	70.6		72.3	

Table 9

Repeated experiments in the centre of the investigated region (liming effluent)

Time (h)	Intensity (A)	R_c (%)	COD (%)	TOC (%)
2	2.4	98.5	51.4	61.8
2	2.4	98.4	51.7	64.8
2	2.4	98.4	51.3	63.8

4. Conclusion

The experimental design methodology was been adopted in this work. The Doehlert matrix demonstrated that the current intensity and the electrolysis time are the most influent parameters on the oxidation of the organic and the mineral matter of the tannery effluent.

By the use of Doehlert matrix, we have been able to define the optimum conditions for the two studied effluents: liming and tanning effluent. In deed, the following conditions: $I=2.4\text{ A}$, $t=4\text{ h}$, $T=40^\circ\text{C}$ lead to a complete oxidation of the trivalent chromium ($R_c=94\%$) and the organic matter contained in the tanning effluent: 92% and 95% of COD and TOC removal were respectively obtained. For the liming effluent, the optimum conditions are determined as follow: $I=3\text{ A}$, $t=3\text{ h}$, $T=30^\circ\text{C}$. In deed, under this conditions, the total oxidation of sulphite ions (99%) and an important degradation of the organic matter (COD = 64% and TOC = 72%).

The electrochemical oxidation was proved to be an effective process for the degradation of wastewater effluents containing a lot of toxic pollutants, organic and inorganic. However, the treated tanning wastewater must be followed with a selective extraction of the hexavalent chromium.

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