Electrochemical treatment of tannery effluents and chrome recovery

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ABSTRACT: In most developing countries, the tanneries discharge their waste into the sewer systems, which in turn   poured into the waters of continental surface, or used for irrigation of the land.

The high concentrations of chromium and hydrogen sulphide present in residual waters of the tanneries have a bearing on the quality of the water and may give him unpleasant tastes and odors.

The suspended solids such as lime, hairs, the pieces of fat and flesh, etc., disturb surface water and settle to the bottom, which harmfully affect fish.

In our study, we used an original method of electrochemical treatment of tannery effluents in order to quantitatively oxidize the trivalent chromium to hexavalent chromium and simultaneously destroy oxidizable organic compounds.

After the electrochemical treatment is complete. The hexavalent chromium is recovered by selective extraction and the organic phase obtained brought into contact with formic acid to reduce the hexavalent chromium to trivalent chromium.

The solution obtained can be used as such in chromium plating bath or converted to trivalent chromium derivatives used in the tanning industry.

KEYWORDS: electrochemical treatment, tannery effluents, trivalent chromium, hexavalent chromium.

1   INTRODUCTION

Leather is a byproduct of slaughterhouse activities. It comes from the tanning of hides and skins of slaughtered animals and can be transformed into very different finished products. For each finished product, the process of tanning may be different and the type and quantity of waste products can vary widely.

Two processes of tanning are used, the chrome tanning and vegetable tanning.

At present, worldwide, between 70 and 80 % of the leather is produced by chrome tanning process [1].

Moreover, under the complexity of the transformation of the animal skin leather, the tannery industries use a large number of chemical agents and produce enormous volumes of wastewater and solid waste [2].Approximately 35 - 40 liters of water consumed per kg of treated skin [3].

With the annual worldwide capacity of 9 .106 tons of treated hides and skins, it is estimated that 30 – 40.107 m3 of liquid effluents are generated. These are consisting essentially of mixture of biogenic materials skins (hair, lipids, proteins …) and chemicals.

The tanning process is the transformation of skins and hides of animals into leather. Animal skin is subject to different processes to eliminate the meat, the lipids and the hairs.This step uses different chemicals (including: sodium hydroxide, sodium hypochlorite, potassium dichromate, lime, chloride, sulfuric acid, formic acid, surfactants, sodium sulphide, sodium salts and ammonium, etc.).

The skin obtained is then processed by Cr3+ or by the tannins plants, the mineral salts and dyes to produce leather (Figure 1).

The products used end up in the wastewaters with a net inflow of pollution load [4].
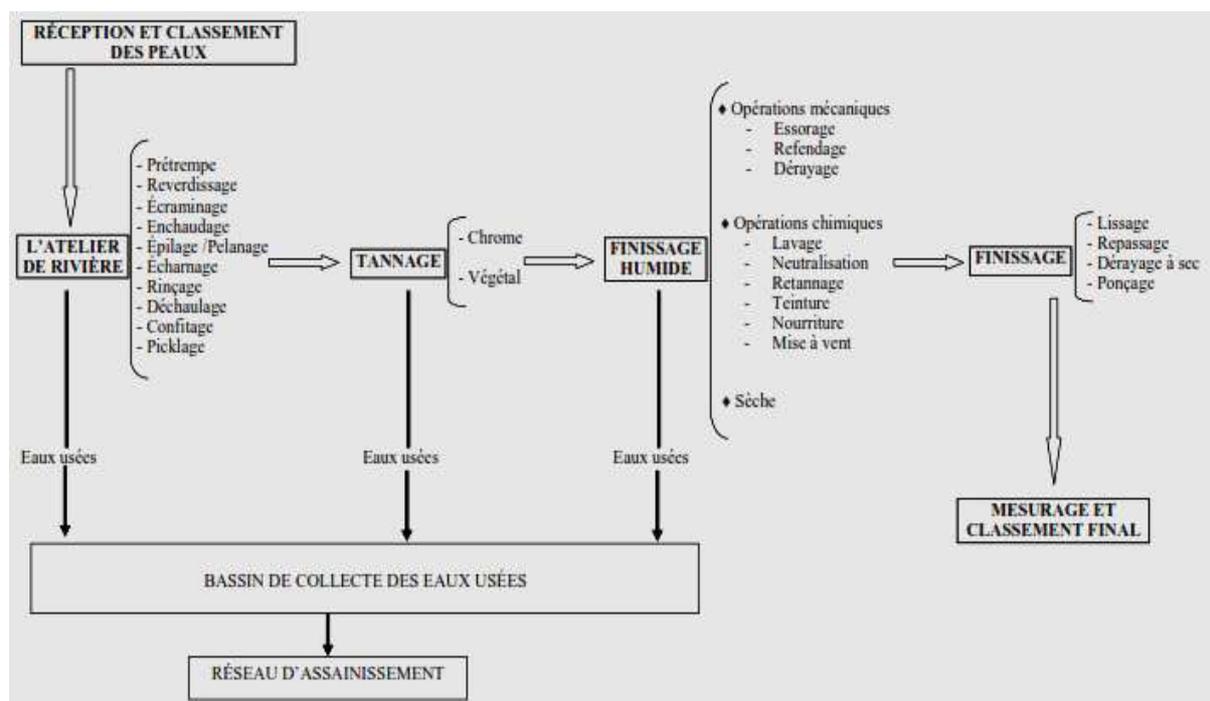
Fig. 1. Diagram of the leather manufacturing process and wastewater flow. [4]

2 MATERIALS AND METHODS

2.1 INDUSTRIAL DISCHARGE INVESTIGATED

We have chosen in our study an effluent chromium taken from a semi modern chrome-tanning unit. This effluent is very rich in chromium trivalent.

2.2 EXPERIMENTAL TECHNIQUES

The electrochemical process is based on the phenomenon of electrolysis, such that the electrolysis is an electrochemical reaction based on the passage of current between 2 electrodes which cause an oxidation of trivalent chromium in hexavalent chromium, therefore the organic matter in the effluent is automatically degraded. This is due tothe cathode and anode of a cell immersed in the reaction mixture.

The oxidation reaction of trivalent chromium to hexavalent chromium occurs according to the following reaction:

$$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H_2 + 6 e^- \qquad (2)$$
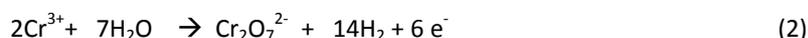
The normal potential of oxydation:

$$E° = - 1,333 + 0, 1379pH - 0,00981Log ([Cr_2O_7^{2-}] / [Cr^{3+}]^2) \qquad (3)$$

At the time of powering the electrodes (the anode is connected with the positive pole of the generator and the cathode with the negative pole), the reaction is activated spontaneously. We note the formation of a foam on the surface of the solution and the inner wall of the reactor, this foam is due to the oxidation of fat-containing products and impurities of organic nature.

The reaction is also accompanied by an off-gas, the main gas formed are the Cl_2, O_2, and H_2, this is due to the oxidation of ions Cl^-, OH^- at the cathode, and the reduction of ions H^+ at the anode.

The equations involved are as follows:

At the cathode: (Reduction) $2 H^+ + 2e^- \rightarrow H_2$ (4)

At the anode (oxidation): $2Cl^- \rightarrow Cl_2 + 2e^-$ (5)
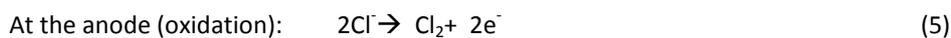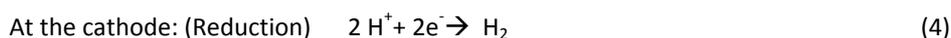
In light of this this release, provision must be made for a gas-bleeding system.

In this project, we have used a filter pump to remove gases formed; the gas (chlorine) will be absorbed in a vial guard containing the sodium hydroxide NaOH. As a result, the bleach will form when sodium hydroxide and chlorine react together.

Chemical reaction can be described by the following chemical equation:

$Cl_2 + 2(H^+, OH^-) \rightarrow 2HOCl^- + 2H^+$ (6)
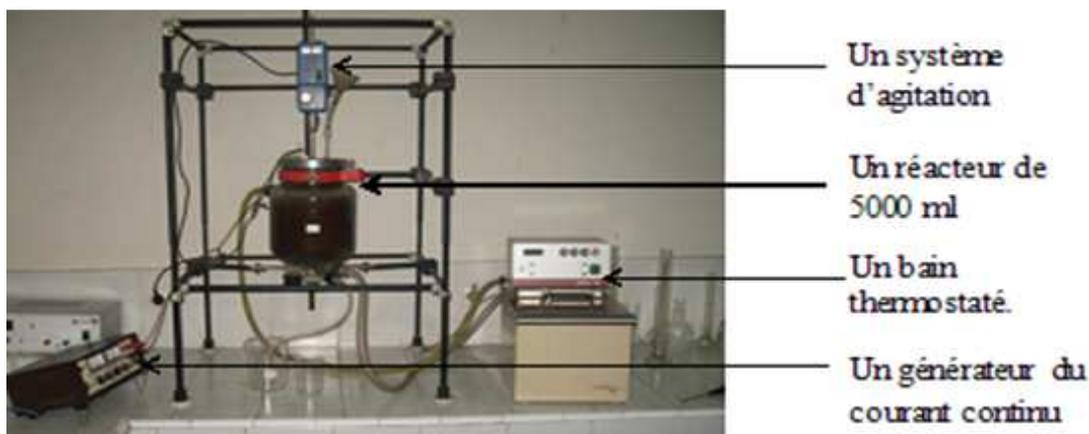
Fig. 2. The electrochemical processing unit used

This unit carried out in the laboratory, it is limited to the oxidation of trivalent chromium and the oxidation of organic matter, and it is constituted of:

Reactor: This is a reactor comprising a double glass envelope (to ensure that no oxidation of the reaction chamber) with a maximum capacity of 5 L. The power supply is done from the top, as well as the bleeding of gas. The cover is made of Plexiglas. The discharging of products is performed through a lower portion of a reactor.

Electrodes: The cathode is formed of felt and a grid of same materials that constitute the anode. The felt and the grid are arranged vertically in the center of the reactor, and between which the effluent to be treated circulates.

The design of the electrode is carried out in an appropriate way; to promote the reaction of oxidation of the Chromium (III) on the reaction of deposition of the Chromium under its metallic form. In our case, there will be at the level of the cathode a preferential reaction of the water.

Agitator: The solutions to be treated are homogenized by an agitator (BIOBLOCK SCIENTIFIC) turning at a speed (300 tr.min^{-1}). The stirring mobile body is made of an oxidation-resistant material, in our case; we used a stirrer in ebonite, whose movement is assured by a motor placed above the reactor.

The role of the agitator is to homogenize the concentration and the temperature of the reaction mass.

Electrical generator: it is a direct current generator device (EA-7015-050).). The intensity and voltage of thisgenerator, which supplies the electrochemical cell with electrical power, 5A and 15V respectively.

Thermostatic bath: to increase the kinetics of the reaction, we must adjust the temperature. Therefore, we use a Thermostatic bath (heat-transfer fluid) type (ULTRATEMPS 2000, julabo F30).

Filter pump: allows the extraction of gases and avoid accumulation that slowed the rate of oxidation.

2.3 PHYSICOCHEMICAL ANALYSES

The oxidation reaction was monitored by taking samples at regular time intervals, these samples once cooled to ambient temperature were analyzed: pH by a pH-meter (HACH -Model Sension 7) , the conductivity using a conductivity meter (HACH -Model Sension 7) and the absorbance using a spectrophotometer (SHIMADZU (UV-1201 V)).

The intensity of color was determined by the measure of the absorbance at a maximum wavelength of 540 nm. This value is identical to that found by [5]. The concentration of the chromium hexa was monitored by molecular absorption spectrophotometry after reaction with 1,5-diphenylcarbazide (Colorimetry). [6,7,8,9].

The suspended material (filtered through a membrane filter with a 0,45 μm pore diameter) [10].Dissolved oxygen levels (measured by anoximetry (HQ MODEL 40 d multi)).The alkalinity, the oxidizability and the chlorides have been determined according to the standard methods for examination of water and wastewater (11).The turbidity (measured by a turbidity meter (HACH Type -2100 N-)).

Trace elements (Fe, Al, ..) determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) at the laboratory of the Innovation Center of the University Sidi Mohamed Ben Abdellah- Fez.

The efficiency of the process is calculated according to the following expression:

$$\text{Amount of residual Cr (III)} = \frac{[Cr(III)]^o - [Cr(VI)]_f}{[Cr(III)]^o} * 100 \qquad (7)$$

knowing that:

$Cr(III)^o$= Concentration of trivalent Chromium in the untreated effluent

$Cr(VI)_f$= Concentration of hexavalent Chromium formed after treatment

The yield of the reaction (the rate of conversion of Cr (III)to Cr (VI))

The efficiency = 100 - Amount of residual Cr (III) $\qquad (8)$

2.4 RECOVERY OF CHROMIUM

In literature, several techniques were used for elimination and recovery of chromium. We develop main techniques below:

- The membrane process (reverse osmosis, electrodialysis, nanofiltration, ultrafiltration). [12.13]
- Chemical processes (coagulation, precipitation, complexation, solvent extraction). (14)
- Biological processes (bio-reduction, bio-remediation). [15,16,17]
- The processes of adsorption (ion exchange, specific resin) (18).

In our study we used an original method for the recovery of chromium which is performed in two steps:

- The first is to achieve a selective extraction of the chromic acid H2CrO4 by one of the extractants (of organic solvents) such as: the trioctylamine, the diethyl ether, isobutyl ketone, tri-n-butylphosphate(TBP) , the ethyl acetate[19], the amine tertaire Alamine [20] , quaternary amine (Aliquat) and the oxide phosphine (Cyanex) [21]) , in acid medium (pH= 1).

- The second corresponds to the reduction of the hexavalent chromium to trivalent chromium by a reducer organic either formic acid or methanol.

According to a practical embodiment, the solution of electrolysis acidified at the appropriate pH by sulfuric acid and placed in the presence of ethyl acetate, which allows an almost complete extraction of the chromic acid in the organic phase. Then the organic phase obtained is contacted with formic acid with an adjustment of pH to achieve the best reduction.

$$HCO^{2-} + 2CrO_4^{2-} + 5H^+ \xrightarrow{\hspace{1cm}} 2Cr^{3+} + 3CO_2 + 8H_2O \qquad (9)$$
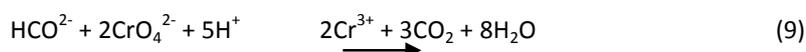
3 RESULTS AND DISCUSSION

3.1 PHYSICOCHEMICAL CHARACTERISTICS OF THE RAW EFFLUENT

The effluent used come from a semi modern chrome-tanning unit located in the region of Fez (AIN NOKBI). The wastewaters of this unit are very rich in trivalent chromium. The samples were taken from the December 29, 2014 from the chromium water storage and transported in bottles of 5 liters for the physicochemical assays and the treatment, and then were kept at 4°C for later use. Before treatment, the samples are filtered by a vacuum disk filterswith a 2,7 μm pore size.

As can be seen in the table 1 that the effluent is slightly acid and its pH is approximately 4.64 , and also rich in mineral salts.

The electrical conductivity that reflects ionic concentration of the medium shows average results of the order of 47.80 ms.cm^{-1}. These high levels are due in particular, use of large quantity of salts during the manufacturing process.

The size of suspended solids in raw effluent analyzed was 35 g L^{-1}. In addition, there are significant fluctuations in the amount of turbidity (91.80 NTU). This is in relation with the quality of effluents that are rich in suspended solids.

The high concentrations of chlorides (1.5 g /l) (table 1) are mainly due to the use of sodium chloride as agent of conservation of skins during thebeam house processes especially during the stages of soaking and during the pickling processes. Larger values, in the order of 8,4 g /l, have been reported by [22].

From the Table 1 it can be seen that the effluent contains chromium, magnesium, calcium, Ammonium. That may be one result of the products used in the transformation of the skin leather. In effect the tanning use:

- Barychrom A: mixture of sulphate of Cr and magnesia. The magnesia is used to increase the pH and to improve the fixation of chrome. This reagent justifies the presence of Cr and Mg and sulphate in the effluent.
- Salchromo: chromium sulphate
- Tansel: mixture of acid and salt. The salt limits the swelling.
- Citric acid: used in the step of deliming and bating, it allows to solubilize the Ca.
- Ammonium chloride: used also in the step of deliming and bating. It justifies the presence of Ammonium.

Table 1. Characteristics of effluents used

Parameters	Effluent
pH	4.64
MES (g/l)	35
Conductivity (mS/cm)	47.80
O$_2$dissolved (mg/l)	9,90
TA (meq/l)	0
TAC (meq/l)	10,10
Oxidability (mg/l)	100,80
Turbidity (NTU)	91,80
Chlorure (g/l)	1,5
Ammonium (mg/l)	12,80
Nitrite (mg/l)	0
Calcuim(mg/l)	459,93
Chrome(mg/l)	524,54
Magnisuim(mg/l)	99,87
Soduim(mg/l)	> 1000 ppm

3.2 TREATMENT OF CHROMIUM IN WATER BY ELECTROCHEMICAL PROCESS

3.2.1 EVOLUTION OF PH AND CONDUCTIVITY AS A FUNCTION OF TIME

As can be seen in the figure 3, after 6 hours of treatment, the pH decreases suddenly and then continues to decrease gradually during the treatment to reach a minimum value of the order of 1,42 after 10 hours of treatment.

This decrease in pH is probably due to the reactions of oxidation of trivalent chromium to hexavalent chrome (which produce ions H +) of the reaction medium (where there is a large quantity of Cr(VI) ions in the form of bichromate). After 14 hours, pH returns to the neutrality.

The electrical conductivity of the effluent, representing their degree of ionization, is experiencing a significant increase after 2 hour of treatment. To reach a maximum value of the order of 19 ,76mS/cm, and then slightly decreased. After 12h of treatment, the electrical conductivity achieves a maximum value 20.2 ms/cm).
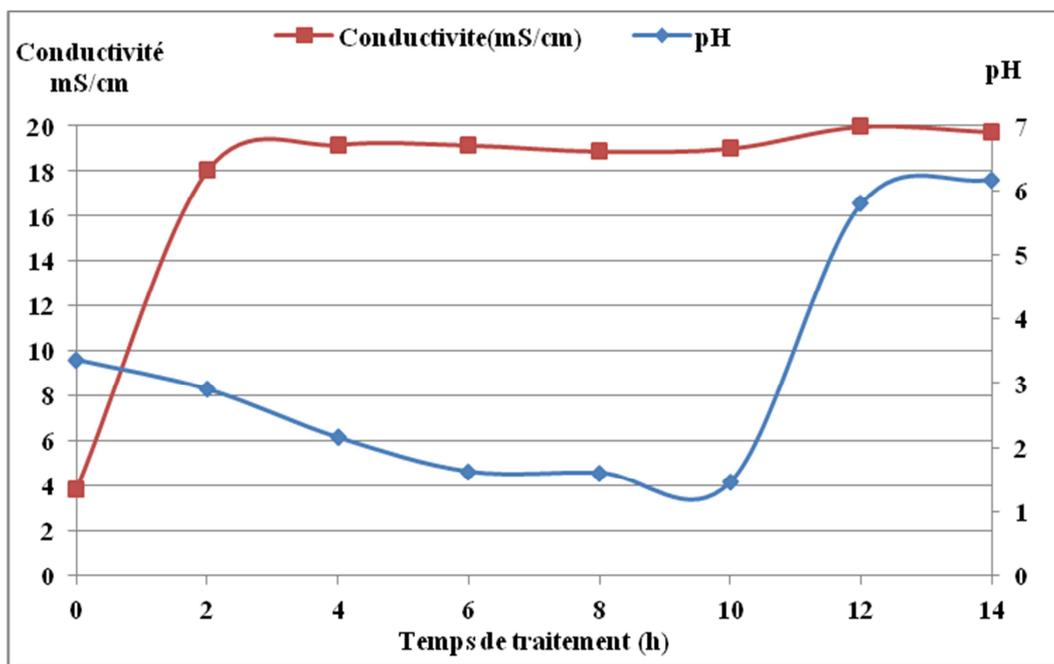

Fig.3.   Evolution of pH and Conductivity as a function of time

3.2.2   THE PERCENTAGE OF COLOR REDUCTION DURING THE TREATMENT

At the beginning we have seen the formation of a foam on the surface of the reactor (figure A- 4) which is probably due to the oxidation of organic matter.

In the figure 3, it can be shown a significant change in the color of the sample (color changed from blue to yellow orange as a function of time). Which may be an effect of the oxidation reaction of trivalent chromium to hexavalent chromium.
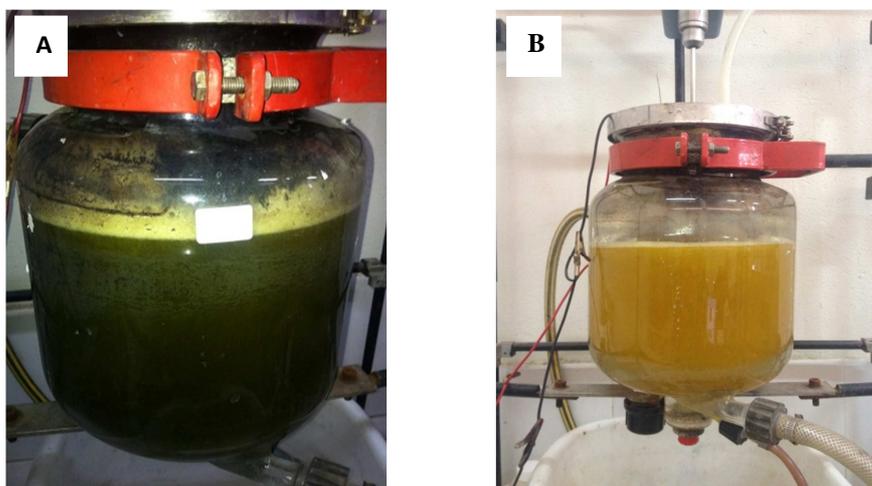

Fig. 4.   The aspect of the sample during treatment

The absorbance makes it possible to estimate the coloration of the effluent in an indirect way. We have proceeded to the scanning of the raw samples in order to find the wavelength more representative of the absorbance of the chromium plating effluent. This wavelength is 540 nm.

Figure 5 shows that the percentage of color reduction increase during the treatment to achieve a limit of 98% after 14 hours of treatment.
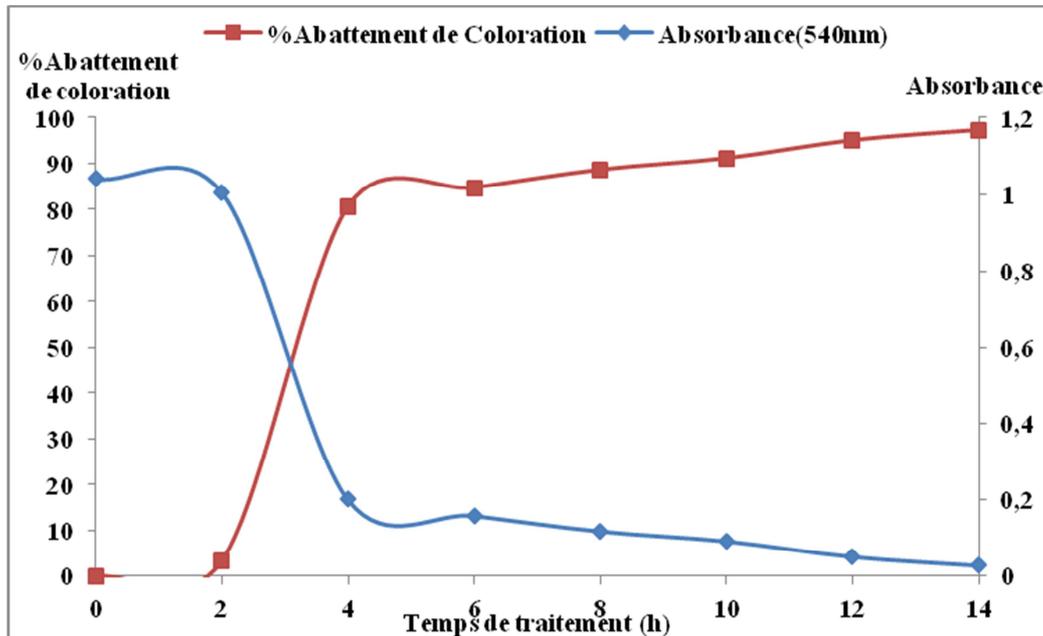
Fig.5 . the percentage of color reduction a function of time of treatment

The electrolysis of the chromium using a electrochemical reactor is a treatment process efficient and compact for the reduction of the color (97 %), of the MY (96.4 %), the oxidizability 15.6 %), chloride (46 %), ammonium (100 %), and of (51 %) of turbidity for a time of electrolysis of 14 hours.

The effectiveness of the treatment is represented in the following table:

Table 2. Characteristics Physico chemical of the effluent before and after electrochemical treatment

Paramètres	Effluent diluted 3 times before treatment	Effluent diluted 3 times after treatment
MES (g/l)	11	0,4
O$_2$ dissolved (mg/l)	9,90	9,67
pH	3,47	6 ,62
Conductivity (mS/cm)	13,80	19,65
Absorbance (540nm)	1,039	0,028
TA (meq/l)	0	0
TAC (meq/l)	9,80	7,80
Oxydability (mg/l)	92,80	78,40
Turbidity (NTU)	74,2	32,60
Chlorure (g /l)	1,04	0,56
Ammonium (mg/l)	9,8	0
Nitrite (mg/l)	0	0

3.3   THE RATE OF THE CONVERSION OF CR(III) TO CR(VI) AND THE YIELD OF THE OXIDATION REACTION.

The concentration of Cr(VI) formed increased in a significant way during the first 8 hours of treatment and began to stabilize after to reach a value almost fixed to the end of the rest of the treatment time.

The treatment time may be estimated at 10h, and the hexavalent chromium increased from 0 mg/l to 7.973 mg/l.
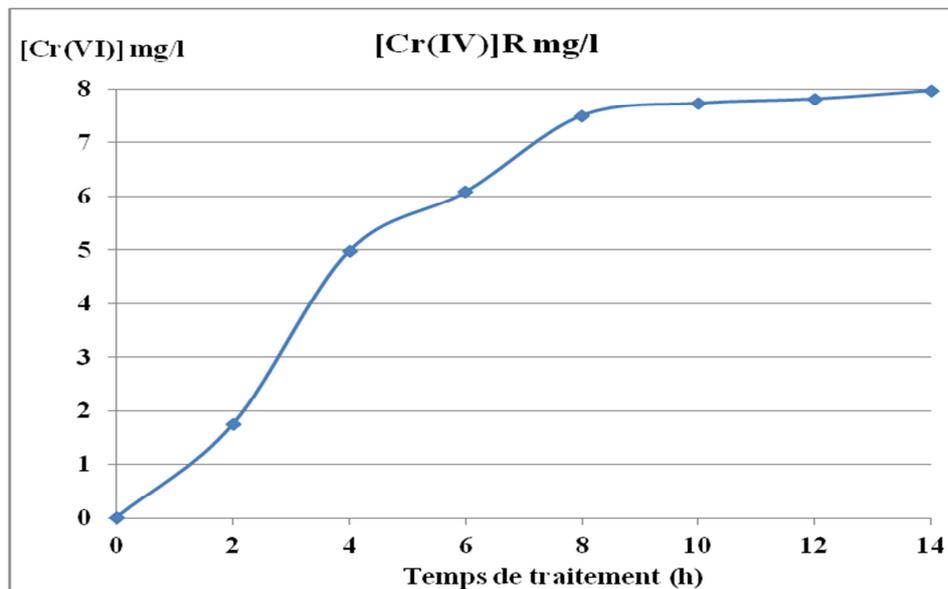
Fig.6. Variation of the concentration of hexavalent chromium in function of time

The concentration of trivalent chromium in the untreated effluent is in the order of 524.54 mg/l. After 14 hours of treatment, the hexavalent chromium formed was determined by colorimetry.

This value has been multiplied by 50 because the sample has been diluted in the order to evaluated it by UV-Visible, otherwise the law of Beer-Lambert will not be respected. Then the concentration of hexavalent chromium formed after treatment of the order of 398.65 mg/l.

The rate of remaining Cr (III) 24% and the yield of the reaction (the rate conversion of Cr (III) to Cr (VI)) is 76 %.

3.4   THE RECOVERY OF THE CHROME

The acidified electrolyte, which contains hexavalent chromium, is placed in contact with the ethyl acetate for the selective extraction. The organic phase obtained brought in contact with formic acid to reduce the hexavalent chromium to trivalent chromium. At the same time, pH has been adjusted by adding sulfuric acid (4N) or sodium hydroxide (5N).

The best-realized reduction has a pH between 2 and 3, which reaches a maximum value of the remaining hexavalent chromium concentration 1.5 mg/l. In practical terms that means that, the rate of reduction of hexavalent chromium to trivalent chromium was in the order of 80 %.
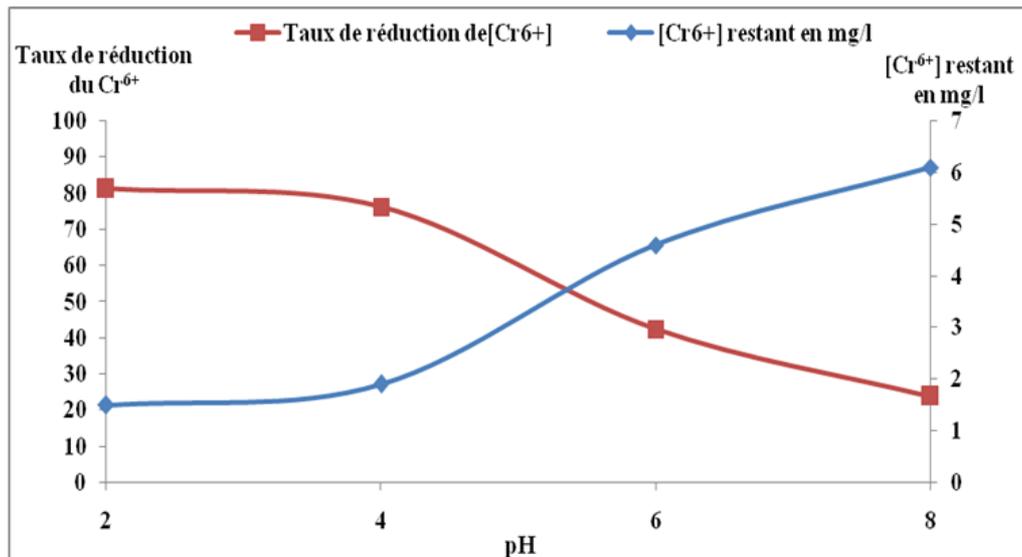
Fig.7. Variation of the concentration and the rate of reduction of hexavalent chromium in function of pH

4   CONCLUSION

The chemical analysis has been carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES).

The results of these analyzes show that the chrome is the predominant element as well as the sodium.

During the treatment the pH decreased substantially while the conductivity increases slightly.

The analysis of the concentration of chromium (IV) shows that at the end of a 10h any chromium (III) has been transformed into chromium (VI) with efficiencies in the range of 76 %.

The absorbance of the sample decreases and the percentage of color reduction increases which shows a dispersing decrease does not allow to see an obvious limit absorbance.

After the electrochemical treatment, the hexavalent chromium present in the electrolyte undergoes a selective extraction. The hexavalent chromium is recovered in the organic phase. It remains a solution including only ions minerals compatible with industrial discharges.

Then there is a reduction of hexavalent chromium present in the organic phase to trivalent chromium that can be directly used in chromium plating bath.

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