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Original Research

Removal of Chromium (Cr) and Formaldehyde [CH_2O (H−CHO)] from Leather Tannery Effluents Using Electrocoagulation Treatment Process

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Abstract

Pollution with contaminants from effluents of industrial units constitutes a danger to health and environment. This is the case of chromium (Cr) and formaldehyde [CH_2O (H−CHO)] contained in leather tannery effluents, identified and characterized by ICP-OES (Inductively coupled plasma - optical emission spectrometry) and HPLC (High Performance Liquid Chromatography). The levels recorded for these two contaminants in wastewater constitute an environmental risk of average degree. The treatment of this wastewater by electrocoagulation completely eliminates chromium and reduces organic pollution by 65%. We applied an electric current (I) of variable intensity (1 to 2.5 Ampere). The best results were obtained with the highest current intensity.

Keywords: chromium, electrocoagulation, formaldehyde, pollution, wastewater

Introduction

Chromium is a chemical element with the symbol (Cr) and atomic number 24. It is a blue-white metallic element found naturally only in combination and used especially in alloys and in electroplating. It is used in combination with other metals to make chrome and to cover other metals with a shiny surface. Chromium is a hard, steel-gray metallic element, resistant to tarnish and corrosion and found primarily in chromite [1]. It is a metallic element with oxidation states ranging from chromium (-II) to chromium (+VI) with the trivalent (III) and hexavalent (VI) states being the most predominant. Elemental chromium, chromium (0), does not occur naturally. Although there is a divalent state, chromium II (chromous), it is relatively unstable under environmental conditions and is readily oxidized to the trivalent (III or chromic) state. Chromium compounds are most stable in the trivalent state under environmental conditions and occur in nature in ores, such as ferrochromite (FeCr2O4). The hexavalent (VI or chromate) is the second most stable state; however, it only occurs naturally in rare minerals such as crocoite (PbCrO4) [2]. There is good evidence from the clinic and the laboratory that Cr(VI) is the ion responsible for most of the toxic actions, although much of the underlying molecular damage may be due to its intracellular reduction to the even more highly reactive and short-lived chemical species Cr(III) and Cr(V). Exposure to Cr(VI) can result in various point mutations

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in DNA and to chromosomal damage, as well as to oxidative changes in proteins and to adduct formation [3, 4]. The National Toxicology Program (NTP) released a 2-year study demonstrating that ingested Cr(VI) was carcinogenic in rats and mice. Hexavalent chromium compounds primarily arise from anthropogenic sources [5]. According to the Toxics Release Inventory, in 1997, the estimated releases of chromium were 320328 Kg to the air, 50522 Kg to water and 13998874 Kg to soil [6].

Formaldehyde is a chemical commonly used to kill germs and to preserve laboratory specimens and tissues. It is also used to make building materials (such as wood), glue, fabric, paint, fertilizers, pesticides, and other substances. Formaldehyde is also found in tobacco smoke and in the vapor made from burning fuel, such as the exhaust from cars or household stoves and heaters. It has a strong odor and catches fire easily. Formaldehyde is known to cause cancer. Being exposed to formaldehyde increases the risk of developing myeloid leukemia and cancers of the paranasal sinuses, nasal cavity, and nasopharynx. A colorless, toxic, potentially carcinogenic, water-soluble gas, with the formula CH_2O, having a suffocating odor, usually derived from methyl alcohol by oxidation: used chiefly in aqueous solution, as a disinfectant and preservative, and in the manufacture of various resins and plastics. The toxic effects of formaldehyde and formalin were described in literature such as bronchitis, pneumonia, gastritis, myositis [7-21]. The concept of health security corresponds to the control of risks that can alter the state of human health. The purpose is to monitor incidents, adverse effects, or risks of incidents or adverse effects that may result from the use of chromium and formaldehyde. The control of the environmental contamination is maintained by specific standards that determine the maximum concentration of these elements in the environment (water, soil, air).

Several treatment procedures such as adsorption, chemical precipitation, ion exchange, electrodialysis, and membrane separation are available for removal of Cr from wastewater [22]. Different methods have been established to remove formaldehyde from effluents [23]. It is mainly removed by adsorption, biodegradation and advanced oxidation. Electrocoagulation (EC) is a technique for applying direct current to sacrificial electrodes that are submerged in an aqueous solution. It determines the rate of collision of coagulated particles during floc formation. The process of bubble formation elicits predominant impact on mass transfer between pollutants, coagulant, and gas microbubbles that eventually govern the electrocoagulation of ions and charged colloidal particles. Generally, current density affects the rate of hydrolysis of metal species due to variation in pH during electrocoagulation process. According to Alemu [24], the variation in current density is strongly depends upon the specification of contaminants but the range between 0.01 and 880 A/m^2 has been recommended by researchers. However, very high current might downregulate the efficiency of electrocoagulation (EC) process as it could initiate secondary reaction and might provoke particle retabilization as well [25]. A combined electrocoagulation and electroflotation process was designed to reduce Cr^{6+} to Cr^{3+} first and then to remove the total Cr from wastewater to a value below 0.5 mg/L. When aluminum ions are either added or produced in situ in the coagulation unit, the treated wastewater can be discharged without any filtration [24]. The effect of different parameters affecting the electrocoagulation process, such as initial hexavalent chromium concentration, applied current, electrolyte type concentration and initial pH of the solution was documented. The performance of electrocoagulation using iron electrodes for the treatment of aqueous solutions containing chromium hexavalent ions using fixed bed electrochemical batch reactor was studied [26]. The optimum conditions for the EC process by using the present cell based on minimum initial hexavalent chromium concentration, energy consumption and operating cost were 100 mg of Cr(VI)/l, 0.55 A, 1.5 g of sodium chloride/land pH of 1. Electrocoagulation of chromium in tannery wastewater by a composite anode modified with titanium was realized by Li et al. [27] using parametric and kinetic study. The optimal EC conditions were the pH value of 6 and a voltage of 5 V that contributed to the around 100% current efficiency.

There are many methods used for formaldehyde removal from wastewater: biological method, evaporation, membrane separation and adsorption method [28]. The combination of thermochemistry and electrochemistry makes the STEP-formaldehyde treatment highly efficient with rapid kinetics [29]. The removal of total organic carbon (TOC) from wastewater generated from phenolformaldehyde resin manufacturing industry using the electrocoagulation process was studied. Electrocoagulation is a treatment process that is capable of being an effective treatment process as conventional methods such as chemical coagulation. It has been noted that electrocoagulation had high removal efficiencies of color, chemical oxygen demand (COD), biochemical oxygen demand (BOD), and achieving a more efficient treatment processes quicker than traditional coagulation and inexpensive than other methods of treatment such as ultraviolet (UV) and ozone [30].

The purpose of this work is the depollution of the wastewater from the tanneries using electrocoagulation process (current: 1, 1.5, 2 and 2.5 A). The present study was designed to test the following hypotheses (1) The risks resulting from the leather tannery effluents show a degree of pollution by chromium and formaldehyde, (2) Treatment method by electrocoagulation has reliability and efficiency in depolluting organic and mineral contaminants.

Material and Methods

Chemical determination of trace element contents by ICP-OES was performed according to the international standard ISO 17072-2 2015. Digestion of the ground leather is performed using a ternary acid mixture or microwave digestion until complete mineralization. The residue is again dissolved with water and analyzed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry, Perkin Elmer Optima 8000). The filtrate was analyzed against reference solutions of metals whose concentration is known at a specific wavelength for each of the different elements (International Standard ISO 17072-2 2015).

Chemical determination of chromium (VI) content was performed by colorimetric method according to the international standard ISO 17075-1. The extractable chromium VI is leached out in a phosphate buffer pH 7.5 and the co-extracted colored substances affecting the detection are removed by solid phase extraction. The chromium VI solution causes oxidation of 1,5-diphenylcarbazide to give a red/violet chromium-containing complex which can be quantified photometrically at 540 nm using a Specord 210 Plus Analytik Jena double beam UV-Visible Spectrophotometer (International Standard ISO 17075-1). The chromium content was calculated from the formula:

$$\mathrm{W(CrIV)(mg/kg)} = \frac{(\mathrm{A_1}-\mathrm{A_2})\times\mathrm{V_0}\times\mathrm{V_4}\times\mathrm{V_2}}{\mathrm{V_1}\times\mathrm{V_3}\times\mathrm{m}\times\mathrm{F}} \quad (1)$$

Where:

$W_{Cr(VI)}$ (mg/kg): The weight fraction of extractable chromium VI from leather.

A_1: Absorbance of the sample solution containing diphenylcarbazide.

A_2: Absorbance of the sample solution without diphenylcarbazide.

F: The slope of the calibration curve.

m (g): The weight of the leather sample.

V_0 (mL): The volume of extraction of the initial sample.

V_1 (mL): The aliquot of the initial sample extraction volume.

V_2 (mL): The total volume of eluate (S_1), after passage through the column of the acid phase extraction system to which V_1 was supplemented.

V_3 (mL): Aliquot of the solution S_1.

V_4 (mL): Final volume, adjusted to the gauge line, of the aliquot of the S_1 solution.

The recovery rate of chromium was determined by the following formula:

$$\eta\ (\%) = \frac{(A_1S-A_2S)-(A_1-A_2)}{\rho * F}\times 100 \quad (2)$$

Where:

η (%): The recovery rate of chromium

(µg/mL): The concentration of the added chromium (VI) solution.

F: the slope of the calibration curve.

A_1S: The absorbance of the solution after the addition of chromium (VI) and diphenylcarbazide.

A_2S: The absorbance of the solution after the addition of chromium (VI), but without the addition of diphenylcarbazide.

A_1: The absorbance of the sample solution with diphenylcarbazide.

A_2: The absorbance of the sample solution without diphenylcarbazide.

The rate must be higher than 80% to ensure that the maximum amount of chromium VI.

Detection of formaldehyde was performed by ultra performance liquid chromatography according to the international standard ISO17226-1/2008. The formaldehyde content was determined using the EN ISO 17226 Standard method. Formaldehyde-based resin was extracted with sodium dodecyl sulphate solution. Once extracted and after filtration, an aliquot of the filtrate was reacted with dinitrophenylhidrazine and, afterwards, the formaldehyde was determined by HPLC (Agilent Waters ACQUITY UPLC H-Class System).

Content of chromium was calculated by the formula below:

$$\mathrm{WF\ (mg/kg)} = \frac{\rho\times\mathrm{F}}{\mathrm{m}} \quad (3)$$

Where:

WF (mg/kg): The formaldehyde concentration in the sample.

ρ (µg/mL): The concentration of formaldehyde obtained from the calibration curve.

m (g): The weight of leather.

The recovery rate of formaldehyde was determined by the following formula:

$$\mathrm{Rr\ (\%)} = \frac{(\rho s_2-0.5\rho)\times 100}{\rho\times\mathrm{F}\times\mathrm{A1}} \quad (4)$$

Where:

RR (%): The recovery rate of formaldehyde in percent rounded to 0.1

ρs_2 (µg/ 10 ml): The concentration of formaldehyde obtained from the calibration curve.

ρs (µg/10 mL): The concentration of formaldehyde in the unspiked sample.

ρFA1 (µg/10 mL): The spiked amount of formaldehyde.

Determination of formaldehyde in leather was performed by colorimetric method according to standard 17226-2. The formaldehyde content was determined in accordance with the EN ISO 17226 Standard (International Agency for Research on Cancer 2012). Formaldehyde was extracted from leather with sodium dodecyl sulphonate. For the extraction, reciprocal linear shaker at 40 strikes per minute (Selecta, Unitronic OR) was used. Once extracted and after filtration, the formaldehyde present in the filtrate was colorimetrically determined by measuring the absorbance at 412 nm after reaction with acetylacetone solution in ammonium acetate and glacial acetic acid medium. The concentration of formaldehyde in the sample was evaluated by the formula below:

$$Wp = \frac{(Ep+Ee)\times V_0\times Vf}{F\times m\times Va} \tag{5}$$

Where:
Wp (mg/kg): The concentration of formaldehyde in the sample.
Ep: The absorbance of the filtrate after reaction with acetylacetone.
Ee: The absorbance of the filtrate.
V_0 (mL): The volume of the elution (standard conditions: 50 mL).
Va (mL): The aliquot part taken from the filtrate (standard conditions 5 mL).
Vf (mL): the volume obtained with the reaction with acetylacetone (standard conditions 10 mL).
F: the slope of the calibration curve.
m (g): the weight of leather.

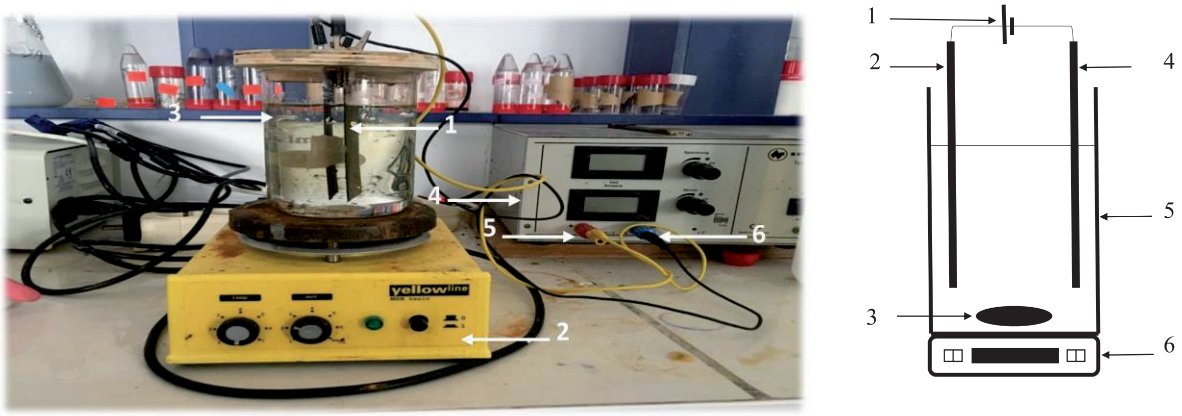
If the recovery rate of formaldehyde is not between 80% and 100%, the analysis should be repeated. The recovery rate of formaldehyde was determined by the following formula:

$$Rr\ (\%) = \frac{(Ea-Ep)\times 100}{Ezu} \tag{6}$$

Where:
Rr (%): the recovery rate in percentage.
Ea: The absorbance of the spiked sample.
Ep: The absorbance of the unspiked sample.
Ezu: The expected absorbance for formaldehyde that has been added (from the calibration curve).

Wastewater purification was performed by electrocoagulation method (Fig. 1). The wastewater was collected and stored at 4ºC. Several tests are carried out to determine the optimal conditions of time (20 min) and intensity (1, 1.5, 2 and 2.5 A) for the removal of traces elements. A current is imposed between two aluminum electrodes immersed in the wastewater to be treated. The ions (Al^{3+}) caused a coagulation- flocculation of the pollutants. Electrolysis can also coagulate the soluble oxidizable or reducible compounds contained in the effluent. The electric field creates a movement of ions and charged particles. This action allows gathering the suspended matters in the form of flocs, which are then eliminated by a classic physical process (decantation, flotation, and filtration). Wastewater samples were filtered and acid stabilized after collection from leather tannery effluents. A 200 mL aliquot of a well-mixed, acid preserved sample was transferred to a beaker. 20 mL of concentrated HCl was added to the sample. The sample was heated (not boiled) on a steam bath until it was evaporated to near dryness. The beaker was rinsed thoroughly with 10% v/v HCl solution and the contents were transferred to a 20 mL volumetric flask, and made up to the mark with 10% v/v HCl solution. All standard solutions were prepared from high purity ICP 10000 ppm stock standards. The samples were filtered and kept for analysis by ICP-OES [31].

Measurement of chemical oxygen demand was performed using the bichromate method. Chemical oxygen demand (COD) is an indirect measure of the total organic matter widely used for wastewater monitoring, design and operation of STPs. It consists of the amount of oxygen required for the organic



Electrocoagulation device
1: Aluminium electrodes; 2: Magnetic stirrer; 3: Beaker; 4: Generator; 5: Anode; 6: cathode

Electrocoagulation device
1. DC power supply
2. Anode
3. Bar magnet
4. Cathode
5. Electrocoagulation cell
6. Magnetic stirrer

Fig. 1. Wastewater purification by electrocoagulation method. A current was imposed between two aluminum electrodes immersed in the wastewater during 20 min with intensity of 1, 1.5, 2 and 2.5 Amperes.

Table 1. Contents of chrome and formaldehyde in leather samples analyzed by ICP OES.

	Content in leather samples (mg/Kg)	The recovery rate (%)	Norms	Conformity
Chrome	0.68±0.1 mg/Kg	≥80%	≤3 mg/Kg	Conform
Formaldehyde	0.45±0.1 mg/Kg	≥80%	≤15 mg/Kg	Conform

matter to be oxidized by a chemical oxidant (potassium dichromate in acid medium). The sample is mineralized for 2 h at 150ºC. COD is indirectly measured through Cr(VI) or Cr(III) contents by titration or UV–vis spectrophotometry. COD is a critical parameter of determining water quality, which represents the degree of organic contamination in water bodies. The concentration of COD was measured following the procedure of American Public Health Association (1995) according to the following formula:

$$\mathrm{COD\ (mg\ O_2/L)} = \frac{\mathrm{M}}{\mathrm{V}} \tag{7}$$

Where:
M (mg): the amount of substance.
V (L): Water volume at the inlet.

COD removal rate was determined using the following formula:

$$\mathrm{COD\ removal\ (\%)} = \frac{\mathrm{COD\ (mg\ O_2/L)In} - \mathrm{COD\ (mg\ O_2/L)Out}}{\mathrm{COD\ (mg\ O_2/L)In}} \times 100 \tag{8}$$

Where:
COD (mg O_2/L)In: Measured concentration of COD from photometer (mg/L) of inflow
COD (mg O_2/L)Out: Measured concentration of COD from photometer (mg/L) of outflow

COD load was calculated from equation:

$$\mathrm{COD\ Load\ (kg/day)} = \frac{\mathrm{Concentration\ (mg/L)} \times \mathrm{Flow\ (m^3/day)}}{1000} \tag{9}$$

Statistical analyses was also conducted. Differences in the variables among control and treatments were tested using parametric one-way ANOVA tests. A posteriori paired multiple-comparisons were performed using Tukey HSD test when significant differences were $p<0.05$.

Results and Discussion

To analyze the degrees of contamination of the leather sample and the health risks that can cause serious illnesses, we determined the chromium and formaldehyde contents in leather samples. As presented in Table 1, the results show levels of chromium and formaldehyde contamination of leather significantly lower than the threshold values of the international standards accepted by the authorities. The chromium content represents 23% of that of the accepted threshold value. The formaldehyde content represents 3% of the accepted threshold value, which shows low contamination by this product.

The risks and dangers associated with the use of various products in the leather industry could cause

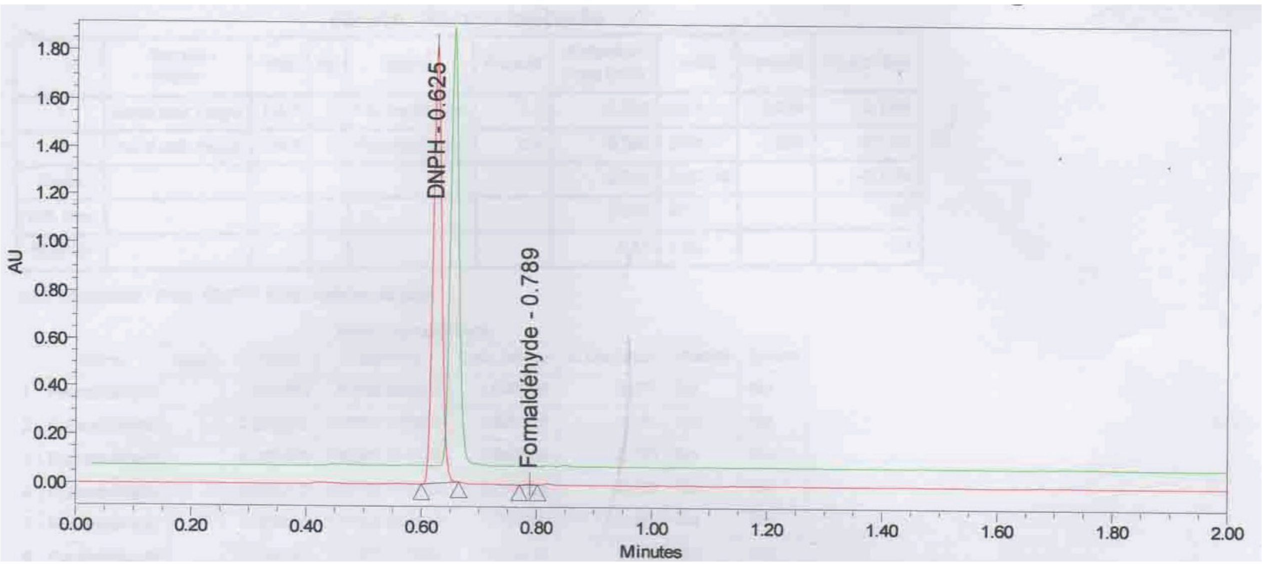


Fig. 2. Peaks of formaldehyde in leather sample analyzed by HPLC.

Table 2. Trace element contents in tannery wastewater before and after electrocoagulation treatment.

Trace elements	Wastewater without treatment	Wastewater after electrocoagulation treatment			
		E1 (1 A)	E2 (1.5 A)	E3 (2 A)	E4 (2.5 A)
Hg (mg/Kg)	ND	ND	ND	ND	ND
Pb (mg/Kg)	ND	ND	ND	ND	ND
Co (mg/Kg)	ND	ND	ND	ND	ND
Cu (mg/Kg)	0.239 ±0.01	0.153±0.01	0.153±0.01	0.144±0.01	0.131±0.01
Cr (mg/Kg)	0.063±0.01	0.030±0.01	0.020±0.01	ND	ND
Ni (mg/Kg)	0.030±0.01	0.020±0.01	ND	ND	ND
As (mg/Kg)	ND	ND	ND	ND	ND
Mn (mg/Kg)	ND	ND	ND	ND	ND
Li (mg/Kg)	0.163±0.01	0.154±0.01	0.148±0.01	0.137±0.01	0.122±0.01
Fe (mg/Kg)	ND	ND	ND	ND	ND
Zn (mg/Kg)	ND	ND	ND	ND	ND

damage to public health and the environment. For the cases of chromium and formaldehyde, the levels accepted for leather-based garments are of the order of 0-15 mg/kg. For shoes, the values of these two products vary from 3-152 ppm [32]. The majority of products are contaminated but with low doses. The presence of formaldehyde in products can be identified by the use of HPLC. The results show peaks around 0.80 (Fig. 2).

Despite the low levels of chromium and formaldehyde detected in the samples analyzed, this prompted us to look for effective solutions to minimize or eliminate contamination of the environment by these types of pollutants, especially in effluents of treatment plants from industrial leather sites. In particular, studies focus on the degree of pollution of this industry and evolution of the involvement of this industry on a global scale in the contamination of the environment, the risks resulting from these types of pollutants and the latest health reports.

Among the purification solutions, we have proposed electrocoagulation. Wastewater samples were purified. The results in Table 2 show the presence of metallic trace elements in the wastewater such as Cu, Cr, Ni and Li. After treatment by electrocoagulation, we recorded a total elimination of contamination by Cr and Ni. The contents of other elements are reduced

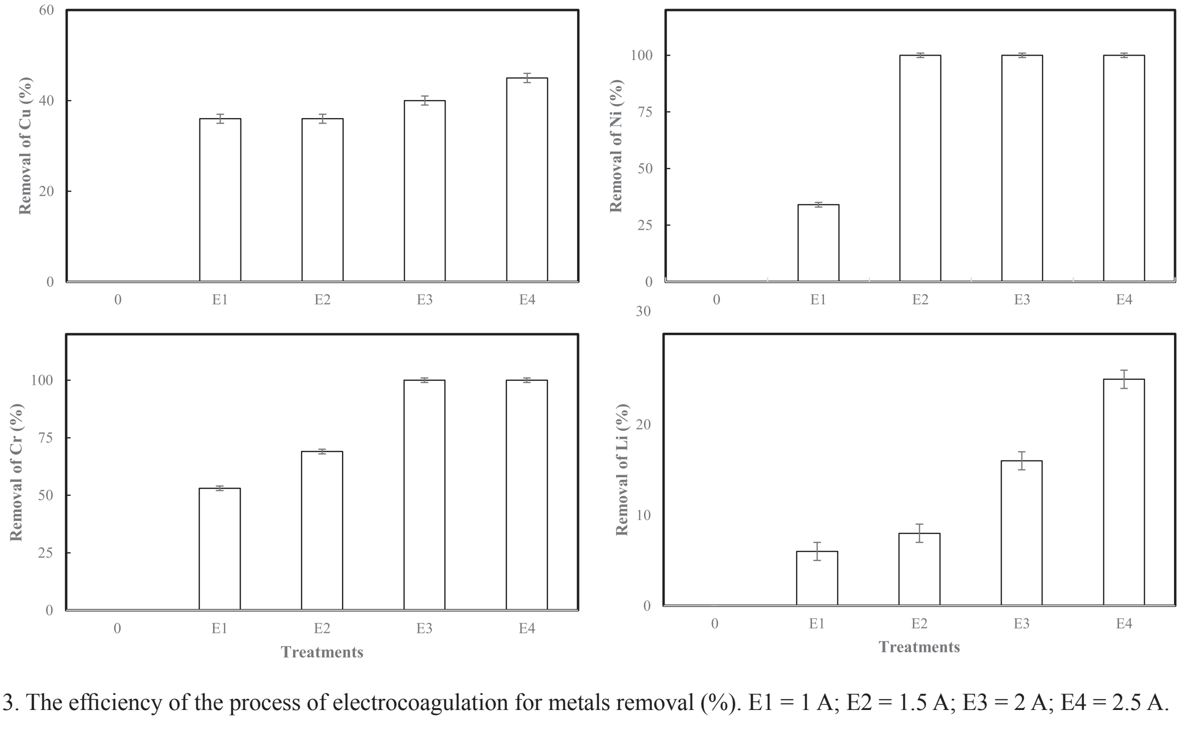


Fig. 3. The efficiency of the process of electrocoagulation for metals removal (%). E1 = 1 A; E2 = 1.5 A; E3 = 2 A; E4 = 2.5 A.

Table 3. The amount of oxygen required for the organic matter removal in tannery wastewater before and after electrocoagulation treatment.

		COD concentration (mg/L)	Load (Kg/day)
Wastewater without treatment		0.220±0.01	11
Wastewater after electrocoagulation treatment	E1 (1 A)	0.090±0.01	4.490±0.54
	E2 (1.5 A)	0.100±0.01	4.980±0.81
	E3 (2 A)	0.113±0.01	5.625±0.98
	E4 (2.5 A)	0.078±0.01	3.920±0.51

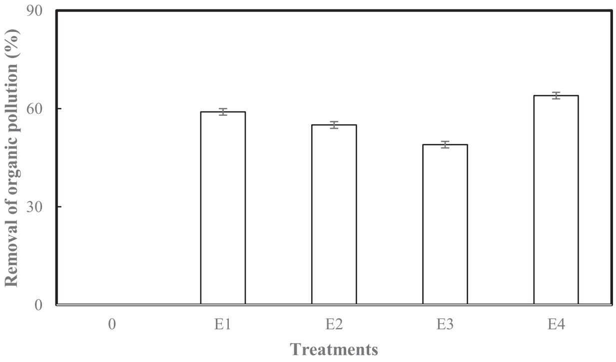


Fig. 4. The efficiency of the process of electrocoagulation for organic pollution removal (%). E1 = 1 A; E2 = 1.5 A; E3 = 2 A; E4 = 2.5 A.

by more than 25% and 45% for the cases of Cu and Li, respectively. These results vary significantly with increasing current intensity (Fig. 3). Similarly, we have reported a significant reduction in organic pollution with depollution rates varying from 59% for an intensity of one ampere to a depollution of 64% for an intensity of 2.5 amperes (Table 3, Fig. 4). This technique can be used for other categories of pollutants such as detergents [33], pesticides [34], oils [35] and drugs [36]. The effectiveness of the treatment method varies considerably with several factors such as the concentration of the pollutant current intensity and pH [37], type of pollutant [38], and wastewater flow [39]. Several techniques were used today to solve problems related to environmental pollution. The choice of the appropriate method is a challenge that arises in view of the variations in the application conditions. For this present study, it seems that the electrocoagulation method could be a solution to deal with environmental problems related to organic and mineral pollution. However, this could be effective for low to medium pollution degrees. To confirm this choice, it is necessary to apply the method on a large scale, in the wastewater treatment plant of a tannery while controlling the conditions and especially the beginnings, and the reduction rate of the station. This technique has already been used before at the station level in a study published by Feng et al. [40]. The degree of sulfur pollution is low with high current intensity [41]. Other techniques show metal treatment efficiency such as membrane technology [42]. The benefits of using electrocoagulation method are low costs [43], little energy [44] and the possibility of eliminating a wide range of pollutants [45]. Biological treatment, fenton oxidation, membrane separation and physiochemical treatment have some major disadvantages, such as their high operational costs, higher sludge formation, long retention time and production of toxic by-products [46-48]. The costs of fenton oxidation method is \$1.46 m^{-3}. The operating cost concerning only electrical cost is \$0.52 m^{-3}. The reagent cost was estimate to be \$0.01 m^{-3} and \$0.93 m^{-3} for $FeSO_4 \cdot 7H_2O$ and H_2O_2, respectively [49]. A cost of 0.92 \$ m^{-3} was estimated for the membrane separation process [50]. Using electrocoagulation process, Fe (99.17%), Mn (99.97%), TSS (99.35%) and other metals such as Cu, Zn and Cd were removed in more than 99%, and removal of 45.14% COD, with an energy consumption of 3.30 kwh/m^3 at a cost of 0.29\$ m^{-3} [51].

Conclusion

We have analyzed in this work the risks resulting from the leather tannery effluents of an industrial unit.

- The results of analyzes show a degree of pollution by chromium and formaldehyde of medium degree. The levels obtained do not exceed the accepted limit thresholds (Table 1).
- We have proposed a treatment technique by electrocoagulation of pollutants. This technique has shown high efficiency in depolluting organic and mineral contaminants. It eliminates up to 100% of metallic trace elements such as chromium, and has reduced the organic pollution of effluents by 65% (Figs 3 and 4; Tables 2 and 3).
- These results are very encouraging in the case of treatment of this type of contaminants by electrocoagulation process because the method is inexpensive and does not consume much energy compared to other techniques currently applied. It can be concluded that effluents from industrial units are a major source of environmental pollution. They present a hazard whose severity and frequency of risks may vary depending on the types of pollutants in these effluents. The health and environmental hazards could be of low, medium or high degree.

- We recommended the execution of *In situ* research works in leather tannery treatment plants while controlling the parameters, which can influence this treatment process.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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