

# Environmental impact elimination of chrome tanning effluent using electrocoagulation process assisted by chemical oxidation

# M.A. El-Khateeb<sup>a,\*</sup>, El-Shahat H.A. Nashy<sup>b</sup>, N.A. Abdel Ghany<sup>c</sup>, Ahmed M. Awad<sup>d</sup>

<sup>a</sup>Water Pollution Control Department, National Research Centre, Dokki, Cairo, Egypt, Tel. +201003282503; email: elkhateebcairo@yahoo.com

<sup>b</sup>Chemistry of Tanning Materials and Leather Technology Department, National Research Centre, Dokki, Cairo, Egypt, Tel. +201018813557; email: nashy\_eha@yahoo.com

<sup>c</sup>Electrochemistry and Corrosion Department, National Research Centre, Dokki, Cairo, Egypt, Tel. +201004476238; email: na\_mamakhly@yahoo.co.uk

<sup>d</sup>Chemical Engineering and Pilot Plant Department, National Research Centre, Dokki, Cairo, Egypt, Tel. +201092002549; email: awadx1@yahoo.com

Received 2 April 2016; Accepted 2 October 2016

#### ABSTRACT

Chrome tanning operation is one of the most important processes in the leather industry. Chromium tannery wastes cause serious environmental threats. In the present study, an advanced oxidation technique based on electrocoagulation process was applied for the treatment of chrome tanning effluent as an alternative method for conventional chemical and biological processes. Reaction time and different current densities were investigated to determine the optimum operating conditions for the elimination of chrome and sulfide, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total Kjeldahl nitrogen (TKN) and total suspended solids (TSS). The results indicated a good quality of the treated effluent. The chromium concentration was reduced from 3,844 to 0.4 mg/l (99.99% removal), and the sulfide was eliminated from 1,450 to 0.45 mg/l (99.97% removal) as well. Due to the presence of organic materials, variable doses of  $H_2O_2$  were added to support oxidation process. The concentration of COD, BOD, TKN and TSS was reduced from 5,830, 140, 590 and 1,800 to 989, 110, 65 and 10 mg/l, respectively. The treated effluent could meet the national regulatory standard for discharge into the sewerage systems with respect to the studied parameters.

*Keywords:* Electrocoagulation; Chrome tanning effluent; Hazardous wastes; Chemical treatment; Environmental pollution

## 1. Introduction

Chrome tannage has been proven to be the efficient technique of tanning [1]. It is used for the production of various types of leathers such as light leathers and other garments. Chrome tan enhances the characteristics of leather (high thermal stability, lightweight and high strength properties) than other tanning agents [2]. Several by-products and effluents are produced during the production of leather, which may cause serious environmental problems. One ton of salted hides yield, an average, approximately 50 m<sup>3</sup> of liquid effluents, up to 600 kg solid wastes (0.25 ton of tanned and 0.35 ton of non-tanned wastes) and 240 kg leather [3–5].

Chromium salts are not completely taken up from the tanning bath under normal tanning conditions. Non-reacted chrome tan (about 40%) does not react with the hide proteins and discharged in the form of spent tanning solution as wastewater [6,7]. Chromium waste is considered as a source of pollution in tannery waste effluent. This attributed to the significant disposal problem of such wastes [4,8]. Hexavalent chromium is very toxic for both plant and animal life [9]. It was detected in a mixture of  $Cr^{(3+)}$  and  $Cr^{(6+)}$  in some Egyptian tanneries [10]. Wastewater is currently discharged directly into the domestic

<sup>\*</sup> Corresponding author.

<sup>1944-3994/1944-3986</sup> $\ensuremath{\mathbb{C}}$  2017 Desalination Publications. All rights reserved.

sewerage systems without any treatment. Consequently, the infrastructure utilities under this area are seriously damaged.

Treatment of tannery effluent using conventional methods represents a serious environmental and technological problem. According to the current legislation on the environment, it is necessary to eliminate the toxic pollutants by non-conventional technologies. Several techniques have been studied for the treatment of chrome tanning effluent, but many of the organic compounds applied in leather tanning processes have refractory nature and resist conventional biological and chemical wastewater treatment processes [11,12]. Additionally, conventional wastewater treatments do not meet the national regulatory standards and require a long period of time for removing the pollutants. Other technologies are studied as an alternative for biological physico-chemical treatment. Some attempts were carried out to overcome this problem. These technologies consist mainly of adsorption processes and micro-filtration, or chemical oxidation/reduction methods for destruction of the contaminants [13], or pretreatment followed by biological oxidation processes [14]. Electrochemical oxidation process is one of the promising techniques for the treatment of tannery wastewater. The rate of the electrochemical process is about hundredfold faster than biological oxidation process [15].

Advanced technique using electrochemical oxidation is one of the most efficient systems for the oxidation of pollutants in wastewater [16]. This reactivity is due to the in situ generation of hydroxyl radicals, which is attributed to the dissociation of the  $H_2O_2$  molecule. These radicals are extremely reactive oxidants for the disintegration and oxidation of organic matter in wastewater. Hydrogen peroxide is added to an aqueous system containing an organic substrate (wastewater) and ferrous sulfate in a strong acid [17]. Complex redox reactions can be represented as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$
(1)

$$^{\circ}OH + H_2O_2 \rightarrow HO_2^{\circ} + H_2O \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^-$$
(3)

$$2HO_2^{\phantom{1}} \rightarrow H_2O_2 + O_2 \tag{4}$$

Therefore, in this work, an advanced oxidation process based on electrochemical oxidation reactions was evaluated as one of electrochemical treatment, which includes the combined advantages of electrochemical and Fenton treatment methods, where each of them is a powerful treatment choice. The electrocoagulation was applied for treatment of chrome tanning effluent as an alternative process for conventional chemical and biological wastewater treatment processes.

Wastewater is characterized with high concentration of salts, suspended solids, unwanted skin proteins, colloidal, oil and grease, chromium species, biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The annual world production of fresh hides is 8–9 million tons, and the corresponding waste production is 1.4 million tons.

The main target of this study is the removal of chromium salts and remediation of wastewater, so electrocoagulation process was applied. In addition, the presence of organic materials of high level of COD 5,830 mg/l, which urgently require high oxidation, so  $H_2O_2$  was added to enhance the oxidation process.

### 2. Materials and methods

## 2.1. Sampling

The tanneries are located in an area called "Sour Al-Oiun" south of Cairo city. Samples under investigation were taken after the tanning operation. The samples were collected from three local tanneries. Tanneries effluent is currently discharged directly into the domestic sewer network without treatment. The schematic diagram of tanning operation, chemicals used and the associated pollution problems is illustrated in Fig. 1.

#### 2.2. Tannery effluent characteristics

The main characteristics of wastewater were shown in Table 1. The concentration of COD ranged from 8,960 to 3,580 mg/l with an average of 5,830 mg/l, while the average concentration of BOD was 140 mg/l. The average concentration of chromium species was 3,844 mg/l. Sulfides concentration ranged from 1,970 to 950 mg/l with an average of 1,450 mg/l. Also, the BOD/COD ratio was found to be 0.024. The high concentration of chromium and sulfide species affects the biodegradability of effluent. Consequently, chemical treatment is recommended to carry out by this study.

#### 2.3. Electrocoagulation process

The experimental parameters (e.g., current density,  $H_2O_2$  doses and reaction time) were examined to determine the



Fig. 1. Schematic diagram of the environmental impact associated with tanning process.

Table 1	
The mean characteristics of raw tan	nery effluent

Parameters	Tannery effluent
рН	$3.5 \pm 0.2$
COD (mg/l)	$5,830 \pm 2,005$
BOD (mg/l)	$140 \pm 60$
TKN (mg/l)	$590 \pm 200$
TSS (mg/l)	$1,800 \pm 850$
Sulfides (mg/l)	$1,450 \pm 520$
Chrome (mg/l)	$3,844 \pm 1,200$
Sludge volume (ml/l)	$600 \pm 150$
Sludge weight (mg/l)	$1,500 \pm 350$

optimum operating conditions for electrocoagulation. The experiments were carried out under continuous stirring and constant pH value. The pH was adjusted to  $3.0 \pm 0.2$  with 2 N H<sub>2</sub>SO<sub>4</sub> solutions according to the previous work [18,19]. The supernatant was withdrawn immediately for analysis. The experimental setup used in the present study is demonstrated in Fig. 2.

The reactor cell consisting of a 250-ml glass beaker equipped with the cathode and anode, both made of mild steel and installed in parallel under the ambient temperature. The composition of mild steel is shown in Table 2. The distance between the electrodes was kept constant at 2.5 cm (dimensions of exposed areas were  $2.5 \times 1.6 \times 0.2$  cm). The total effective electrode area was 8 cm<sup>2</sup>. Electrodes were inserted into the reaction vessel containing 100 ml of tannery wastewater. The process of electrochemical treatment was carried out at current densities ranging from 250 to 750 mA/area with 250 mA interval. Digital DC power supply was used as a power source (Fig. 2). Then different concentrations of H<sub>2</sub>O<sub>2</sub>



Fig. 2. Electrochemical cell.

#### Table 2 Composition of mild steel

Element	Amount (%)
С	0.047
Mn	0.289
Si	0.037
Р	0.017
S	0.013
Cu	0.054
Cr	0.049
Ni	0.057
Ti	0.02
Al	0.003
Мо	0.002
Sn	0.02
Fe	99.392

were added (0.25%, 0.5%, 1% and 2%) for each individual experiment. The current density was adjusted to the desired value, and electrolysis was started. After 1 h sedimentation, the supernatant of the treated samples were withdrawn for analysis.

## 2.4. Chemical and physical treatment

Chemical and physical treatment processes were carried out for comparison with the electrocoagulation process. Lime (CaO) was used for chemical coagulation and was added under continuous stirring for 5 min at 100 RPM, followed by 20 min of slow mixing (30–40 RPM) and 1 h of settling. Acids and alkalis (NaOH and/or  $H_2SO_4$ ) were added to adjust the pH if it was needed. On the other hand, physical treatment was performed using active charcoal.

## 2.5. Analytical measurements

The performance of the treatment process was evaluated by monitoring the quality of the raw wastewater and treated effluents. The physico-chemical analysis covered: pH, BOD, COD, total Kjeldahl nitrogen (TKN), total suspended solids (TSS), sulfides (S<sup>2–</sup>) and total chromium. The analysis followed the Standard Methods for the Examination of Water and Wastewater [20]. The total chromium was measured using atomic absorption spectrometer. Atomic absorption spectrometry measurements were carried out using Varian atomic absorption spectrometer model Specter AA 220.

#### 3. Results and discussion

### 3.1. Effect of reaction time

Different periods of reaction were applied at the obtained optimum dose of  $H_2O_2$  (1%) and at a current density of 66.6 mA/cm<sup>2</sup>. It is clear from Fig. 3 that chromium concentration was reduced from 3,844 to 0.6 mg/l at 1.5 h in the presence of 1%  $H_2O_2$ . As the reaction time increases, the degradation of sludge increases as shown in Fig. 4. The sludge volume and weight were greatly reduced at reaction time 1.5 h. However,



Fig. 3. Performance of the electrocoagulation process as a function of reaction time.



Fig. 4. Sludge characteristics as a function of reaction time during the electrocoagulation process.

when the reaction time increased much longer, the reverse effect was observed in increasing the weight of sludge. This referred to the release of excess iron (Eqs. (1) and (6)–(9)) in the reaction medium, which affects the sludge weight.

It is worth to mention that the pH value of the tanning effluent was raised after electrocoagulation treatment ranging from 3.4 to 5.5 (Table 3). This can be explained on the oxidation reaction that produces hydroxide ion during the treatment process according to Eqs. (1) and (7).

## 3.2. Effect of current density

The electrode (anode) material was dissolved and produced coagulants during the electrocoagulation process. The metal ion generation occurs at the anode, and chromium removal with the electrocoagulation process has been detected by electrodes of different metals. Anodic materials are soluble during the reaction. The current densities were applied (33.3, 66.6 and 100 mA/cm<sup>2</sup>) at the optimum peroxide (H<sub>2</sub>O<sub>2</sub>) dose (1%) and reaction time (1.5 h). The performance of the treatment process is shown in Fig. 5.

Ferrous (Fe<sup>2+</sup>) ions were liberated by anodic dissolution on the anode surface. Also, OH<sup>-</sup> groups were produced by electrolysis of H<sub>2</sub>O molecules in the bulk solution. Therefore, an excess amount of high Fe(OH)<sub>2</sub> molecules were formed as flocs suspended in water. These flocs are highly adsorbent and coagulant of dissolved chromium ions, which settle down by gravity as sludge, then it could be separated by appropriate filtration.

The concentration of chromium and COD were highly reduced at current density 66.6 mA/cm<sup>2</sup> (Fig. 5). While lower (33.3 mA/cm<sup>2</sup>) current density than 66.6 mA/cm<sup>2</sup> led to lower reduction of chromium concentration and COD. At a higher current density (100 mA/cm<sup>2</sup>), a little effect has occurred. Also, the same behavior was noticed with the produced sludge as demonstrated in Fig. 6. Therefore, the optimal current density 66.6 mA/cm<sup>2</sup> was chosen as the optimum

Table 3

Sample type	pH value
Raw	3
After 0.5 h	3.57
After 1 h	4.42
After 1.5 h	5.25
After 2 h	5.5



Fig. 5. Performance of the electrocoagulation process as a function of current densities.

applied current. Increasing the current density leads to a higher production of ferrous (Fe<sup>+2</sup>) ions, ferric (Fe<sup>3+</sup>) ions and OH<sup>-</sup> dosage over time. This leads to the reduction of Cr<sup>(6+)</sup> concentration; consequently, the electrocoagulation reaction time was increased. Hexavalent (Cr<sup>6+</sup>) was reduced and precipitated as Cr(OH)<sub>3</sub> with high current applied into the reactor. Moreover, it was found that the pH increased during the reaction time. The increase of current from 66.6 to 100 A/cm<sup>2</sup> did not lead to an enhancement of the speed of Cr<sup>6+</sup> removal. The corresponding reactions (water reduction and electrochemical metal reduction) in acidic solution are as follows:

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
 (5)

In acidic solution,  $Cr^{6+}$  ions are reduced to  $Cr^{3+}$  ions. Therefore, the removal efficiency of  $Cr^{6+}$  is considerable. It is clear that chromium exists as chromic acid  $Cr(OH)_3$  and other hydroxyl forms at conditions beyond pH 4 to alkaline (according to pE–pH relationships). On the other hand, chromium exists as  $Cr(OH)_2^{2+}$ ,  $Cr(OH)_2^+$  form at acidic medium (pH 4) [21,22]. The reduction rate demanded is so high that some  $Cr^{6+}$  is reduced to  $Cr^{3+}$  along with H<sub>2</sub> evolution, at higher current densities. Oxide reduction cannot meet the demanded reduction rate, and the system shifts through a limiting current to the evolution of hydrogen either from water when a current density is reached [23]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{6}$$

or from H<sup>+</sup> discharge during the electrochemical reactions:

$$2H^+ + 2e^- \rightarrow H_2 \tag{7}$$

The evolution of H<sub>2</sub> at cathodic surface reduces chromic to chromous species by the reaction given below:

$$Cr(OH)_3 + H^+ + e^- \rightarrow Cr(OH)_2 + H_2O$$
(8)

Hence at slightly acidic conditions of pH 4.5, chromium mostly occurs in chromous state of  $Cr(OH)_2^{2+}$ , which is more likely to reduce rapidly than  $Cr(OH)_3$ . The overall treatment process of the obtained optimum operating conditions is shown in Table 4.



Fig. 6. Performance of the electrocoagulation process as a function of  $\rm H_2O_2$  doses.

#### 3.3. Effect of H<sub>2</sub>O<sub>2</sub> concentration

The effect of variable doses of  $H_2O_2$  on the performance of treatment process at current density of 66.6 mA/cm<sup>2</sup> for 1 h reaction time is shown in Fig. 6. It is clear that the dose of 1%  $H_2O_2$  by volume is more efficient than the other doses for removal of organic contaminants and reduced COD value and chromium. The high reduction of COD and chrome was found to be at 1% more efficient than 2% dose of  $H_2O_2$ . This can be attributed to the residue of  $H_2O_2$  in the final effluent that leads to undesirable reactions as shown in Eqs. (3), (4) and (8), which decrease pollutant removal efficiency [22].

The sludge produced during the electrocoagulation process at different doses of  $H_2O_2$  is shown in Fig. 7. It was found that the increase in the addition of  $H_2O_2$  reduces the sludge volume and sludge weight. This could be referred to effective oxidation of organic matters in effluent. This reactivity is due to the in situ generation of highly oxidation species (hydroxyl radicals) as a result of the dissociation of  $H_2O_2$  molecule, which affect the degradation of the sludge. Also, it was noticed that the dose of 1% is parallel effective to 2%  $H_2O_2$  for the degradation of the sludge. Accordingly, for economic point of view, 1% dose of  $H_2O_2$  was chosen as an optimum dose for the subsequent experiments.

## 3.4. Chemical and physical treatment for tanning effluent

In order to valorize the performance of the electrocoagulation process, comparison between chemical and physical treatment were carried out. Calcium oxide and active charcoal were used for the treatment of effluent directly without primary treatment. Three different doses of calcium oxide were applied (i.e., 150, 300 and 600 mg/l). It is clear from Table 5 that the removal of COD and chromium at the dose of 600 mg/l calcium oxide is higher than that recorded in the case of 150 and 300 mg/l. However, the use of charcoal was found to be not efficient for the removal of COD and chromium [22].

#### 3.5. Comparison between treatment methods

Wastewater samples from the tannery industrial process could be treated till the level of the local sewerage system discharge limit (1,100 mg COD/l) using an electrochemical oxidation process. Electrocoagulation treatability studies gave the best results (over 83% COD, 99.99% chromium removal, 99.4% TSS and 89% TKN) at pH = 3, 1% ml  $H_2O_{2'}$ 500 mA for 1.5 h. In addition, the sulfide concentration in the tannery effluent was highly eliminated (99.97%). Conversely, the chemical coagulation treatment cannot meet the National Regulatory Standard for discharge into the sewerage systems with respect to COD, chromium and sulfide concentrations. The COD could meet the limits for the discharge into the



Fig. 7. Sludge characteristics as a function of  $H_2O_2$  doses during the electrocoagulation process.

#### Table 4

Collective parameters and efficiency of the treatment process at the optimum operating conditions

Parameter	Raw effluent	Treated effluent	Removal percentage (%)	National Regulatory Standards (Decree 44/2000)	
COD (mg/l)	5,830	989	83	1,100	
BOD (mg/l)	140	110	21.43	600	
BOD/COD ratio	0.024	0.111	-	0.6	
TSS (mg/l)	1,800	10	99.4	800	
TKN (mg/l)	590	65	89	100	
Total sulfide (mg/l)	1,450	0.45	99.97	10	
Total chromium (mg/l)	3,844	0.4	99.99	0.5 (Cr(VI))	
Sludge volume (ml/l)	600	132	78	-	
Sludge weight (mg/l)	1,500	181	88	-	

#### Table 5

Effect of chemical and physical treatment on COD and chromium concentration

Sample	COD (mg/l)	Removal	Cr (mg/l)	Removal	Sludge volume	Sludge
		percentage (%)		percentage (%)	(ml/l)	weight (mg/l)
Raw effluent	$5,830 \pm 2,005$		$3,844 \pm 352$		$600 \pm 150$	$1,500 \pm 350$
150 mg/l CaO	$4,\!580\pm450$	$21.4 \pm 2$	$1,980 \pm 180$	$48.5\pm5$	$250 \pm 95$	$1,670 \pm 280$
300 mg/l CaO	$3,950 \pm 415$	$32.2 \pm 3.5$	$178 \pm 35$	$95.4 \pm 7$	$270\pm110$	$1,830 \pm 300$
600 mg/l CaO	$990 \pm 150$	$83.0 \pm 6$	$108 \pm 21$	$97.2 \pm 7$	$310 \pm 105$	$2,120 \pm 450$
Active charcoal, 1 g/l	$3,\!985\pm400$	$31.6 \pm 4$	$1,\!830\pm174$	$52.4 \pm 4$	$515 \pm 200$	$2,510 \pm 550$

sewerage systems only at high dosage of chemical (CaO) as shown in Table 5. But, the concentration of chromium was not reduced to the limit. Consequently, electrocoagulation improves the biodegradability (indicated by BOD/COD ratio) and reduces the toxicity of the effluent.

The process under study provides a solution in 1.5 h instead of long periods of chemical and biological treatments. This means that the present work introduces the electrocoagulation as an effective treatment method for the non-biodegradable effluent than the classical chemical and physical treatment. The electrochemical oxidation treatment will increase since there are organic and toxic inorganic substances present in the tannery effluent (like Cr and S) and the substances that have high resistance to biological degradation were removed. These results are in a good accordance with the previous reported results [21–25].

## 4. Conclusions

The following conclusions are derived from the results gained in the endeavored work:

- The chromium tanning effluent causes serious environmental impacts if not properly treated before discharged in the raw state. Therefore, it must be treated separately before discharging the tannery into environment.
- Electrochemical oxidation is an effective treatment method for the chrome tannery effluent than the classical chemical and physical treatment.
- Electrocoagulation treatment not only eliminates the chromium salts and sulfide ions but also reduces the organic loads represented as COD, TSS, and TKN in wastewater.
- Electrocoagulation treatability studies gave the best results (over 83% COD, 99.99% chromium and 99.97% sulfide removal with corresponding concentration of 989, 0.4 and 0.45 mg/l, respectively) at pH = 3, 1% ml  $H_2O_{2'}$  500 mA, ambient temperature for 1.5 h.
- The electrocoagulation treatment reduces the environmental impact and at the same time saves energy and time.

## References

- H. Wachsmann, Retannage or Combination Process? World Leather, 2001, pp. 64–65.
- [2] F.-D. Michalina, Leather and Leather Products, Handbook of Material Biodegradation, Biodeterioration, and Biostablization, 2nd ed., ChemTec Publishing, Toronto, 2015, pp. 133–256.
- [3] S. Dixit, A. Yadav, P.D. Dwivedi, M. Das, Toxic hazards of leather industry and technologies to combat threat: a review, J. Clean. Prod., 87 (2015) 39–49.
- [4] K.J. Sreeram, T. Ramasami, Sustaining tanning process through conservation, recovery and better utilization of chromium, Resour. Conserv. Recycl., 38 (2003) 185–212.
- [5] M. Mwinyikione, Pollution control and remediation of the tanning effluent, Open Environ. Pollut. Toxicol. J., 3 (2012) 55–64.
- [6] G. Zhen-Ren, Z. Guangming, F. Jiande, D. Xiudong, Enhanced chromium recovery from tanning waste water, J. Clean. Prod., 14 (2006) 75–79.

- [7] Z. Gao, C. Su, Treatment of Tannery Waste Water, Beijing Chemical Engineering Publisher, 2001.
- [8] M.A. Baig, M. Mohsin, M. Shazad, Z. Bhatti, Laboratory scale studies on removal of chromium from industrial wastes, J. Environ. Sci., 15 (2003) 417–422.
- [9] P. Kavouras, E. Pantazopoulou, S. Varitis, G. Vourlias, K. Chrissafis, G.P. Dimitrakopulos, M. Mitrakas, A.I. Zouboulis, Th. Karakostas, A. Xenidis, Incineration of tannery sludge under oxic and anoxic conditions: study of chromium speciation, J. Hazard. Mater., 283 (2015) 672–679.
- [10] M.A. Eid, E.H.A. Nashy, K.A. Eid, E.A. El Ashkar, E. Borai, Speciation of chromium ions in tanning effluents and subsequent determination of Cr (VI) by ICP–AES, J. Am. Leather Chem. Assoc., 97 (2002) 451–455.
- [11] S.G. Schrank, H.J. Jose, R.F.P.M. Moreia, H.Fr. Schröder, Elucidation of the behavior of tannery wastewater under advanced oxidation conditions, Chemosphere, 56 (2004) 411–423.
- [12] S.G. Schrank, H.J. Jose, R.F.P.M. Moreia, H.Fr. Schröder, Applicability of Fenton and H<sub>2</sub>O<sub>2</sub>/UV reactions in the treatment of tannery wastewater, Chemosphere, 60 (2005) 644–655.
- [13] D.W. Ticiane, C. Leonardo, J.J. Humberto, P.M.M. Regina, L.B.O. Andrē, Advanced oxidation process applied to tannery wastewater containing Direct Black 38—elimination and degradation kinetics, J. Hazard. Mater., 135 (2006) 274–279.
- [14] R.G. Parag, B.P. Aniruddha, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, Adv. Environ. Res., 8 (2004) 501–551.
- [15] L. Szpyrkowicz, S.N. Kaul, R.N. Neti, Tannery wastewater treatment by electro-oxidation coupled with a biological process, J. Appl. Electrochem., 35 (2005) 381–390.
- [16] C.C.C. Regina, C.C.M. Flàva, E.F.O. Patricia, M. Fabiano, D.A. Jose, Controlled reduction of red mud waste to produce active systems for environmental applications: heterogeneous Fenton reaction and reduction of Cr(VI), Chemosphere, 78 (2010) 1116–1120.
- [17] J.J. Pignatello, E. Oliveros, A. Mackay, Advanced oxidation processes for organic contaminant destruction based on Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol., 36 (2006) 1–84.
- [18] F.A. El-Gohary, M.I. Badawy, M.A. El-Khateeb., A.S. El-Kalliny, Integrated treatment of olive mill wastewater (OMW) by the combination of Fenton's reaction and anaerobic treatment, J. Hazard. Mater., 162 (2009) 1536–1541.
- [19] S.I. Abou-Elela, M.A. El-Khateeb, Treatment of ink wastewater via heterogeneous photo catalytic oxidation, Desal. Wat. Treat., 7 (2009) 1–5.
- [20] APHA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), 2005.
- [21] U. Kurt, O. Apaydin, M.T. Gonullu, Reduction of COD in wastewater from an organized tannery industrial region by electro-Fenton process, J. Hazard. Mater., 143 (2007) 33–40.
  [22] M.M. Emamjomeh, M. Sivakumar, Review of pollutants
- [22] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage., 90 (2009) 1663–1679.
- [23] S. Aber, A.R. Amani-Ghadim, V. Mirzajani, Removal of Cr(VI) from polluted solutions by electrocoagulation: modeling of experimental results using artificial neural network, J. Hazard. Mater., 171 (2009) 484–490.
- [24] C. Franqoise, R. Bourg, A.C.M. Bourg, Aqueous geochemistry of chromium: a review, Water Res., 25 (1991) 807–816.
- [25] T. Srinath, T. Verma, P.W. Ramteke, S.K. Garg, Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria, Chemosphere, 48 (2002) 427–435.