

## Electrocoagulation treatment of black liquor from paper industry

M. Zaied<sup>a</sup>, N. Bellakhal<sup>a,b,\*</sup>

<sup>a</sup> Laboratoire de Chimie Analytique et Électrochimie, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, 2092 Tunis El Manar, Tunisia

<sup>b</sup> Département de Chimie et de Biologie Appliquées, Institut National des Sciences Appliquées et de Technologie (INSAT), B.P. No. 676, 1080 Tunis Cedex, Tunisia

### ARTICLE INFO

#### Article history:

Received 14 December 2007

Received in revised form 13 July 2008

Accepted 14 July 2008

Available online 5 August 2008

#### Keywords:

Black liquor

Electrocoagulation

Electrode of aluminum

Water treatment

### ABSTRACT

The procedure of electrocoagulation is an effective, fast and economic technique for treatment of black liquor resulting from paper industry. The effect of electrolysis time, current density, type of electrode material and initial pH were studied in an attempt to achieve a higher removal capacity. Under the optimal experimental conditions (initial pH 7,  $t=50$  min and  $J=14$  mA cm<sup>-2</sup>), the treatment of black liquor by electrocoagulation has led to a removal capacity of 98% of COD, 92% of polyphenols and 99% of color intensity with a good repeatability (R.S.D. < 3%) making it possible to highlight the industrial interest of this electrochemical process.

© 2008 Published by Elsevier B.V.

### 1. Introduction

Black liquor is one of the main by-product of pulp paper industry, which is considered as pollutant because it contains about 50% of lignin. In order to manufacture good quality paper, the pulp and paper industry discards lignin as an unwanted constituent of wood and raw materials [1]. Lignin is a mixture of polyphenolic compounds with a rather complex chemical structure that resists to traditional biological treatment processes due to their non-biodegradable nature. The presence of lignin in the wastewater involves a strong increase in the chemical oxygen demand (COD) and biological oxygen demand (BOD). In addition to lignin the black liquor contains aliphatic acids, acid greases, resins and polysaccharides. This organic matter, mainly dissolved, creates a chemical and biological oxygen demands some relatively high [2]. The rejection of this effluent in nature without any treatment is responsible of serious damage for the environment and constitutes a threat for human health [3].

The literature gives a report on many works relating to the treatment of black liquor and more particularly of lignin. Ksibi et al. [1] showed that photocatalytic oxidation in the presence of TiO<sub>2</sub> (UV/TiO<sub>2</sub>) can improve the biodegradability of the lignin extracted from black liquor. Torrades et al. [4] explored the treatment of an effluent of bleaching from paper industry, by means of the oxidizing

action of the Fenton reagent in the presence of a solar irradiation UV (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV). The Fenton's reagent under solar irradiation UV is proven effective for the treatment of these types of wastewater. Indeed, a clear reduction of total organic carbon (TOC) was obtained after treatment. Several other methods were developed to the treatment of the wastewater paper industries. Wallberg et al. [5–7] applied the technique of ultra-filtration for the recovery of lignin starting from black liquor resulting from a Kraft process. They showed that this method makes it possible to retain 30–40% of lignin and 10% of total dry matter under the optimum conditions such as temperature, flow rate and transmembrane pressure. In addition to the weak rates of retention of lignin, these processes of treatment are very restricted because the high cost of the membranes and their maintains. On the other hand, Zhang and Chuang [8] explored the adsorption of organic pollutants from effluents of a Kraft pulp mill on activated carbon and polymer resin (polystyrene divinylbenzenecopolymer).

Although these methods of treatment seem effective for the liquid waste processing of paper industry, they present the disadvantage of being expensive because of their operating cost and/or the relatively high cost for the chemical reagents used.

It is in this context that we present the technique of electrocoagulation to overcome the disadvantages of conventional technologies for the treatment of black liquor from paper industries.

Electrocoagulation is a simple and efficient method where the flocculating agent is generated in situ by electro-oxidation of a sacrificial anode, generally made of iron or aluminum that leads, at appropriate pH, to insoluble metal hydroxide able to remove pollutants by surface complexation or electrostatic attraction. In this

\* Corresponding author at: Département de Chimie et de Biologie Appliquées, Institut National des Sciences Appliquées et de Technologie (INSAT), B.P. No. 676, 1080 Tunis Cedex, Tunisia. Tel.: +216 1 703627; fax: +216 1 704329.

E-mail address: [Nizar.Bellakhal@insat.rnu.tn](mailto:Nizar.Bellakhal@insat.rnu.tn) (N. Bellakhal).

process, the treatment is done without adding any chemical coagulant or flocculant, thus reducing the amount of sludge, which must be disposed [9].

The electrocoagulation has been successfully used to treat oil wastes, with removal efficiencies as high as 99% [10]. A similar success was obtained when treating dye containing solutions [11–13], urban and restaurant wastewater [14], nitrate [15], arsenic [16] and fluoride [17] containing waters. In addition, a great deal of work performed in the last decades [18–20] has proved that electrocoagulation is an effective technology for the treatment of heavy metal containing solutions.

In this study, electrocoagulation was conducted to investigate the treatment of black liquor from paper industry. The effect of operational variables, such as treatment time, current density, type of electrode material and initial pH, on the removal efficiency is explored and discussed to determine the optimum operational conditions. The removal efficiency of the treatment was determined by monitoring the decrease of total phenol, COD and color intensity.

## 2. Experimental details

### 2.1. Reagents and analytical procedures

All used chemicals were of analytical grade. Folin–Ciocalteu reagent (FCR) (Fluka, U.K.) was used at 1:10 dilution in distilled water. Determination of total polyphenols index was carried out with the official spectrophotometric procedure [21]. Analysis of COD was determined by the procedure described in the standard method [22]. The total suspended solids (TSS), was obtained by centrifugation then drying at 105 °C [23]. The chlorides were proportioned in neutral medium by a silver AgNO<sub>3</sub> solution according to the Mohr method [23]. The color intensity was determined by measuring the sample absorbance at 450 nm (UV–vis spectrophotometer, Beckman, DU 530). A digital calibrated pH-meter (Metrohm, 744) was used to measure the pH of the black liquor wastewater samples.

### 2.2. Characterisation of the black liquor

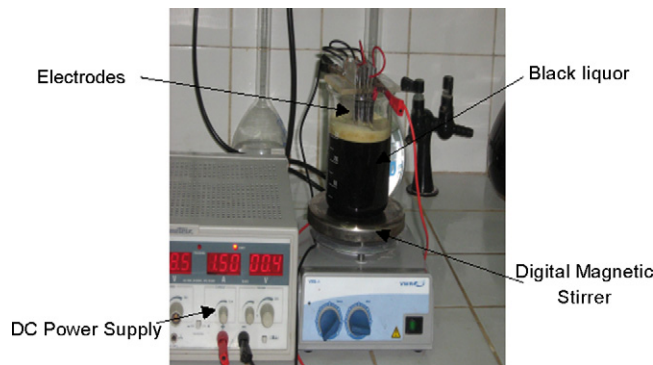
Black liquor utilised for this study was supplied by pulp and paper firm located in south Tunisia, collected in a closed container and stored in obscurity at 4 °C. The main characteristic of this effluent before treatment is presented in Table 1.

### 2.3. Electrocoagulation procedure

The experimental setup is shown in Fig. 1. The electrocoagulator was made of Plexiglas cell, with a special cover supporting a series of parallel aluminum or iron sheets used as sacrificial electrodes. Three electrodes were connected as anodes and three as cathodes (active surface = 50 cm<sup>2</sup>), and the spacing between electrodes was 5 mm. A small hole was drilled into the cover to serve as sampling port. All the runs were performed at room temperature and at a constant magnetic stirring speed of 200 rpm.

**Table 1**  
Physico-chemical characteristic of black liquor from paper industry

Parameters	Concentration
TSS (mg L <sup>-1</sup> )	1160
COD (mg L <sup>-1</sup> )	7960
Polyphenol (mg L <sup>-1</sup> )	3220
DO (450 nm)	0.39
Chloride (mg L <sup>-1</sup> )	1207
pH	12
Conductivity (mS cm <sup>-1</sup> )	42.72



**Fig. 1.** The electrocoagulation reactor in the laboratory experiments.

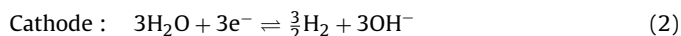
In each run, 300 cm<sup>3</sup> of the black liquor solution was placed into the electrolytic cell. The electrodes were connected to a DC power supply (Metrix, model AX 322) with galvanostatic operational options for controlling the current density. To follow the progress of the treatment, samples were periodically taken from the reactor then filtered to eliminate sludge formed during electrolysis.

In preliminary tests, the effects of working parameters such as treatment time, current density, electrode material and initial pH were studied in an attempt to achieve a more efficient treatment of black liquor. The optimised parameters were then applied for the treatment of black liquor to validate the treatment efficiency.

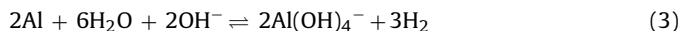
## 3. Description of electrocoagulation process

Electrocoagulation is a complex process occurring via electrolytic reactions at electrode surfaces and formation of coagulants in the aqueous phase. Coagulant species is believed to be the responsible in aggregation as well as precipitation of suspended particles and simultaneously adsorption of dissolved contaminants [11,20].

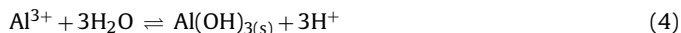
The most widely used electrode materials in EC process are aluminum and iron. In the case of aluminum, main reactions are as [11,13]:



On the other hand, at high pH values, the cathode may be chemically attacked by OH<sup>-</sup> ions generated during H<sub>2</sub> evolution [11]:



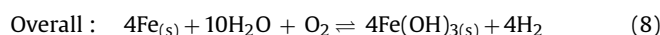
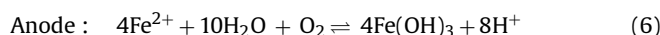
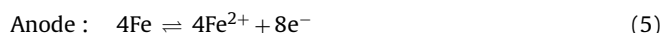
Al<sup>3+</sup> and OH<sup>-</sup> ions generated by electrode reactions (1) and (2) react to form various monomeric species such as Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub><sup>+</sup>, Al<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, Al(OH)<sub>4</sub><sup>-</sup>, and polymeric species such as Al<sub>6</sub>(OH)<sub>15</sub><sup>3+</sup>, Al<sub>7</sub>(OH)<sub>17</sub><sup>4+</sup>, Al<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup>, Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub><sup>7+</sup>, Al<sub>13</sub>(OH)<sub>34</sub><sup>5+</sup>, which finally transform into Al(OH)<sub>3(s)</sub> according to complex precipitation kinetics [13,24,25].



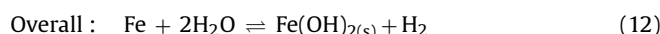
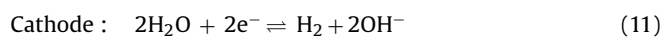
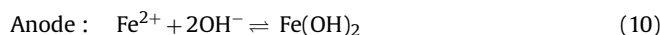
Freshly formed amorphous Al(OH)<sub>3(s)</sub> “sweep flocks” have large surface areas, which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocks are removed easily from aqueous medium by sedimentation or H<sub>2</sub> flotation [11,24].

When iron is used as anodes, upon oxidation in an electrolytic system, it produces iron hydroxide, Fe(OH)<sub>n</sub> where n = 2 or 3. Two mechanisms for the production of the metal hydroxide have been proposed [13]:

• Mechanism 1:



• Mechanism 2:



Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, and polymeric hydroxy complexes, namely:  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ ,  $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$ ,  $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$  and  $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$  depending on the pH of the aqueous medium [2,24,25].

The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials. The EC process is intrinsically associated with electroflotation since bubbles of hydrogen and oxygen are produced at the cathode and anode, respectively. The success of an EC process and for that matter EF process is determined by the size of the bubbles as well as by the proper mixing of the bubbles with wastewater. It is generally believed that the smaller bubbles provide more surface area for attachment of the particles in aqueous stream, resulting in better separation efficiency of the EF process [11,24].

#### 4. Results and discussion

The electrocoagulation process is quite complex and may be affected by several operating parameters, such as treatment time, current density, electrode material and initial pH. In order to enhance the process performance, the effects of those parameters have been investigated.

##### 4.1. Repeatability tests

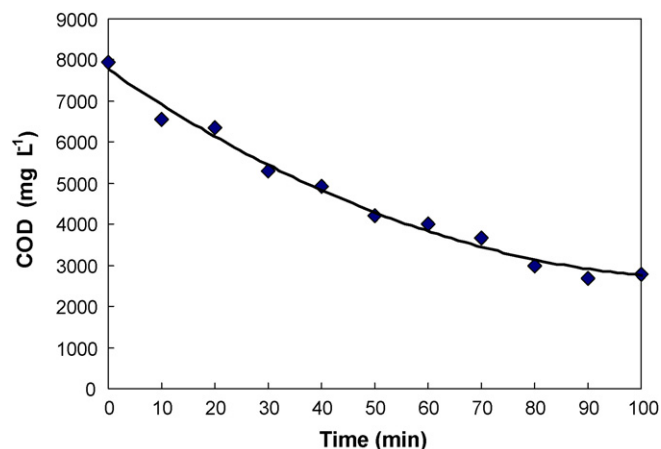
To estimate the relative standard deviation [26], during the treatment of black liquor by electrocoagulation, a series of four experiments was carried out with aluminum electrodes under the same experimental conditions ( $J = 10 \text{ mA cm}^{-2}$ ,  $t = 30 \text{ min}$ , initial pH 12).

From the results presented in Table 2, we can conclude that electrocoagulation makes it possible to carry out an electrochemical treatment of the black liquor with a good repeatability (R.S.D. < 3%).

**Table 2**  
Results of repeatability tests

	COD removal (%)	Polyphenols removal (%)	Color removal (%)
Test 1	34.9	44.4	18.2
Test 2	36.1	45.7	18.0
Test 3	33.9	45.8	18.4
Test 4	35.1	46.3	19.0
$\bar{x}$	35.0	45.5	18.4
$S_F^2$	0.8	0.7	0.2
R.S.D. (%)	2.5	1.8	2.2

R.S.D. =  $(S_F/\bar{x}) \times 100$ : relative standard deviation.  $S_F(x) = \sqrt{\sum_{i=1}^{n_i} (x_i - \bar{x})^2 / n - 1}$ : standard deviation of repeatability.  $\bar{x} = \sum_{i=1}^{n_i} x_i / n$ : arithmetic mean.  $n = 4$ : number of measurements carried out.



**Fig. 2.** Effect of the treatment time on the residual fraction of COD ( $J = 10 \text{ mA cm}^{-2}$ , initial pH 12,  $V = 300 \text{ cm}^3$ ).

The variation with the average being weak, it is considered in the points represented on the curves.

##### 4.2. Chemical oxygen demand reduction

The black liquor samples were treated in the electrocoagulation glass cell at fixed current density  $J = 10 \text{ mA cm}^{-2}$ .

In this section, the elimination of organic compound is determined by monitoring the decrease of COD. Fig. 2 shows that the COD decreased with increasing treatment time. For example, after 60 min of treatment, 50% of the initial chemical oxygen demand ( $7960 \text{ mg L}^{-1}$ ) is reduced, so that it reaches 66% after 90 min. This decrease of COD with increasing electrolysis time caused by the adsorption of organic matter on the  $\text{Al}(\text{OH})_3$  flocks formed in situ. In addition, when anode potential is sufficiently high, secondary reactions may occur also, such as direct oxidation of organic compounds and of  $\text{Cl}^-$  ions present in paper mill effluents [10,11]. The chlorine produced is a strong oxidant that can oxidize same organic compounds and promote electrode reactions.



This result shows that the electrocoagulation technique can be successfully used for the treatment of paper industry effluent.

##### 4.3. Effect of electrode material

Electrode assembly is the heart of the present treatment facility. Therefore, the appropriate selection of its materials is very important. The most common electrode materials for electrocoagulation are aluminum and iron [2,10,25]. They are cheap, readily available, and proven effective. Thus both were tested in this study under similar experimental conditions. Result obtained for COD, polyphenol and color removal for these two kinds of electrodes using the same current density ( $J = 10 \text{ mA cm}^{-2}$ ) are shown in Fig. 3.

As can be seen from Fig. 3(a) and (b) that both materials showed similar efficacy in reducing COD and polyphenol index. Nevertheless, with increasing time, rates of COD and polyphenols removal, obtained with Al electrode, were slightly higher than these with Fe electrode. In addition, aluminum is more effective in removing the color of black liquor than iron (Fig. 3(c)). The resulting effluent treated with aluminum electrodes was found very clear and stable, whereas that treated with iron electrodes appeared greenish first,

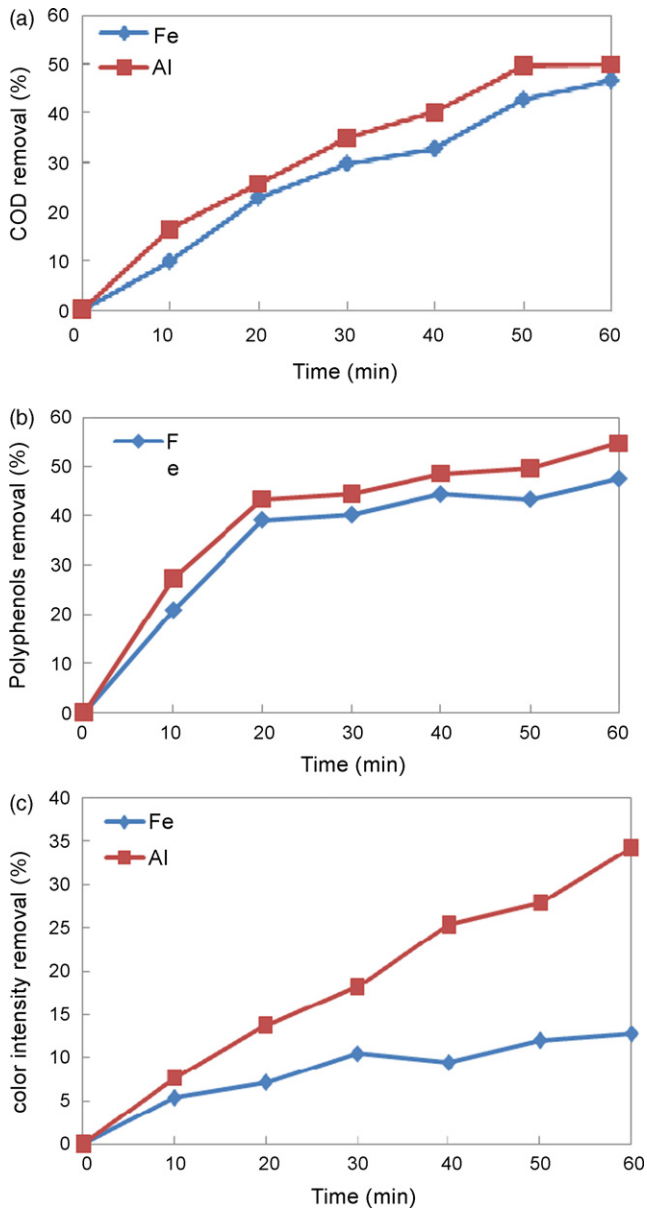


Fig. 3. Effect of electrode material on the removal efficiency of COD (a), polyphenols (b) and color intensity (c), as a function of time (initial pH 12,  $J = 10 \text{ mA cm}^{-2}$ ,  $V = 300 \text{ cm}^3$ ).

and then turned yellow and turbid. The green and yellow colors could be resulted from Fe(II) and Fe(III) species generated during the electrolysis and characterised by their yellow-brown color [10]. Another possible explanation is the occurrence of complexing reaction between  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and polyphenol molecules leading to brown soluble compounds [10,25].

In order to check the initial pH effect on the behaviour of each material, the same comparative study was carried out in slightly acid medium (pH 5). The results of this comparison with the same current density ( $J = 10 \text{ mA cm}^{-2}$ ) and operating time of 60 min are presented in Fig. 4. These results show that in two different pH media (alkaline and slightly acidic); aluminum is more effective for treatment of black liquor.

On the other hand, the cost of the process depends mainly of the consumption of the sacrificial electrode and the electrical energy, which economically are the advantages of this method.

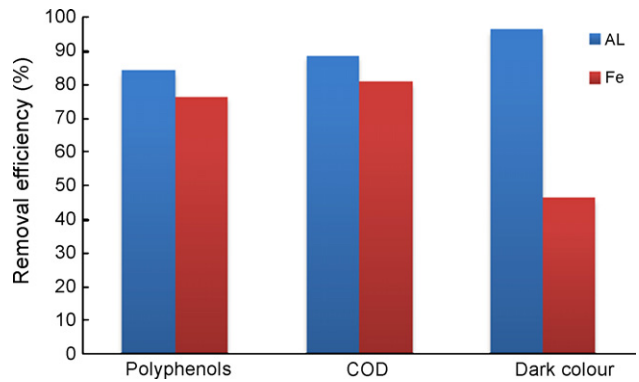


Fig. 4. Effect of electrode material on the treatment efficiency of polyphenols, COD, and color intensity (initial pH 5,  $t = 60 \text{ min}$ ,  $J = 10 \text{ mA cm}^{-2}$ ,  $V = 300 \text{ cm}^3$ ).

As seen from Fig. 5, it is clear that aluminum electrodes are more energetically efficient than iron. The energy consumed to remove 1 kg of each compound (COD and polyphenols) during the electrocoagulation was calculated with the following equation [25]:

$$EE \text{ (kWh/kg of compound)} = \frac{VIt}{60 \times 0.3 \times (C_0 - C_t)} \quad (16)$$

where  $V$  is the applied voltage (V),  $I$  the current amount (A),  $t$  the electrolysis time (min),  $C_0$  the initial concentrations ( $\text{g L}^{-1}$ ),  $C_t$  the concentration value of compounds ( $\text{g L}^{-1}$ ) at time  $t$  and 0.3 is the volume of black liquor (L).

Fig. 6 shows that, for both electrodes, the amount consumption per cubic meter of black liquor treated increase with increasing

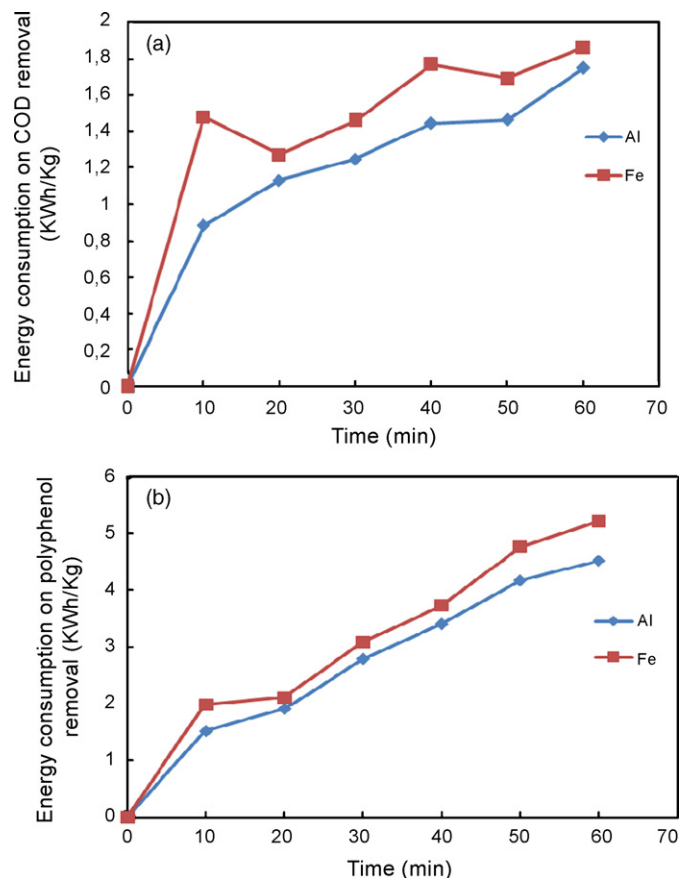


Fig. 5. Energy consumption on COD (a) and polyphenols (b) removal as a function of time ( $J = 10 \text{ mA cm}^{-2}$ , initial pH 12,  $V = 300 \text{ cm}^3$ ).

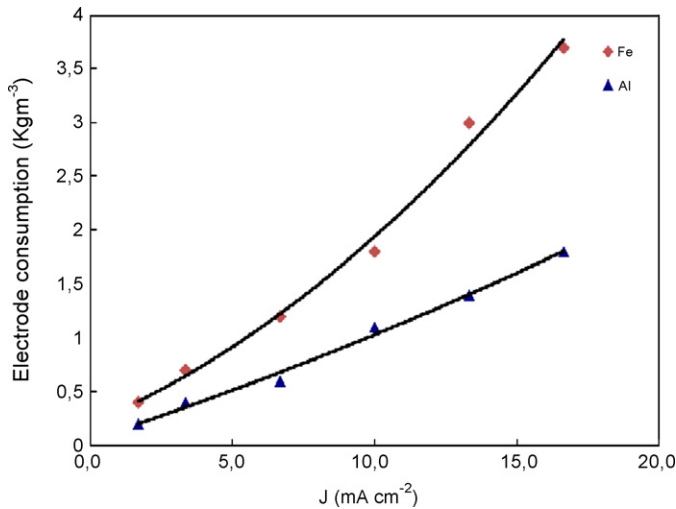


Fig. 6. Electrode consumption as a function of current density ( $t = 60$  min, initial pH 12,  $V = 300$  cm<sup>3</sup>).

current density. However, this economically important process parameter is higher for the iron than the aluminum electrode.

Thus, it is obvious that aluminum is a better electrode material than iron for the present application. Consequently, all subsequent experiments were carried out with aluminum electrodes.

#### 4.4. Effect of initial pH

It has been established that the influent pH is an important operating factor influencing the performance of electrocoagulation process [2,10,14]. To examine its effect on the treatment of black liquor, the pH was varied in the range 2–12 using low volume of sulphuric acid  $10^{-2}$  M.

Fig. 7 illustrates the removal efficiencies of COD and a change in the pH of the black liquor after electrocoagulation, as a function of the influent pH. All controlled parameters showed similar behaviour as expected, the treatment efficiency was very poor either at low (<2) or high pH (>8). This behaviour was observed by many investigators and was attributed to an amphoteric behaviour of  $\text{Al}(\text{OH})_3$  that does not precipitate at pH less than 2 [10,17]. In addition, it was demonstrated that high pH values will increase  $\text{Al}(\text{OH})_3$  solubility and lead to the formation of soluble  $\text{Al}(\text{OH})_4^-$ , which is useless for water treatment [18,27].

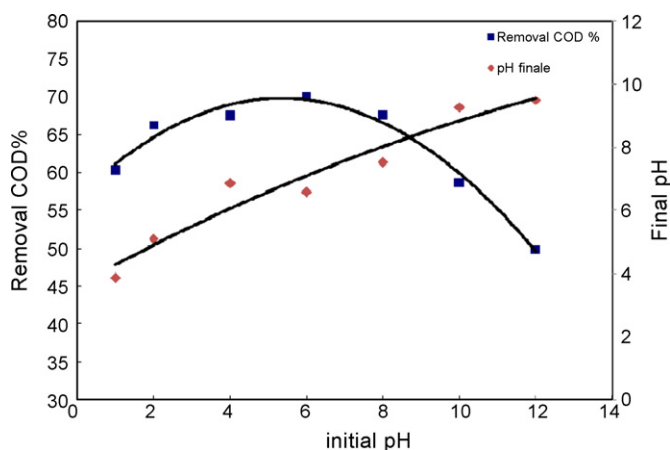


Fig. 7. The removal efficiency of COD and the pH change of black liquor after electrocoagulation as a function of initial pH ( $J = 10$  mA cm<sup>-2</sup>,  $t = 60$  min,  $V = 300$  cm<sup>3</sup>).

When initial pH was adjusted in the range 4–8, all aluminum cations produced at the anode formed polymeric species  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  [18,27] and precipitated  $\text{Al}(\text{OH})_3$  leading to a more effective treatment and high removal capacities of COD (70%). The highest removal efficiencies have been obtained in acidic medium, at pH values in the range 5–7.

As observed by other investigators [10,11,14], a final pH increase occurs when the influent pH is low. However, it is also found that when the influent pH is above 9, a pH drop occurs. In other words, the electrocoagulation can act as a pH neutralization. This newly found characteristic of the electrocoagulation is quite meaningful in its application to wastewater treatment. The pH increase is due to hydrogen evolution at cathodes [10]. However, this was contested by Chen et al. [14] who explained this increase by the release of  $\text{CO}_2$  from wastewater owing to  $\text{H}_2$  bubble disturbance. Indeed, at low pH,  $\text{CO}_2$  is over saturated in wastewater and can release during  $\text{H}_2$  evolution, causing a pH increase. In alkaline medium (pH > 8), the final pH does not vary very much and a slight drop was recorded. This result is in accord with previously published works [11,14] and suggests that electrocoagulation can act as pH buffer and is particularly interesting, since the black liquor is a strongly alkaline effluent (initial pH 12). In addition, when the optimum initial pH required to achieve high removal yield was adjusted to 5–7, the final pH after electrocoagulation treatment reached 6.6–7.6 allowing the effluent to be directly discharged into natural aquatic streams without pH adjustment.

#### 4.5. Effect of current density and charge loading

Many study reported that current density can influence the treatment efficiency of the electrochemical process [10,14]. Fig. 8 shows COD removal upon electrolysis time, when current density was varied from 1.7 to 16.7 mA cm<sup>-2</sup>. As expected, it appears that for a given time, the removal efficiency increased significantly with increase of current density. The highest current (16.7 mA cm<sup>-2</sup>) produced the quickest treatment with 80% COD reduction occurring after only 30 min. This is ascribed to the fact that at high current, the amount of aluminum oxidized increased, resulting in a greater amount of precipitate for the removal of pollutants. It is well known that current not only determines the coagulant dosage rate but also the bubble production rate, size and the flocks growth [18], which can influence the treatment efficiency of the electrocoagulation. In addition, it was demonstrated that bubbles density increases and their size decreases with increasing current density [27,28], resulting in a greater upwards flux and a faster removal of pollutants and sludge flotation.

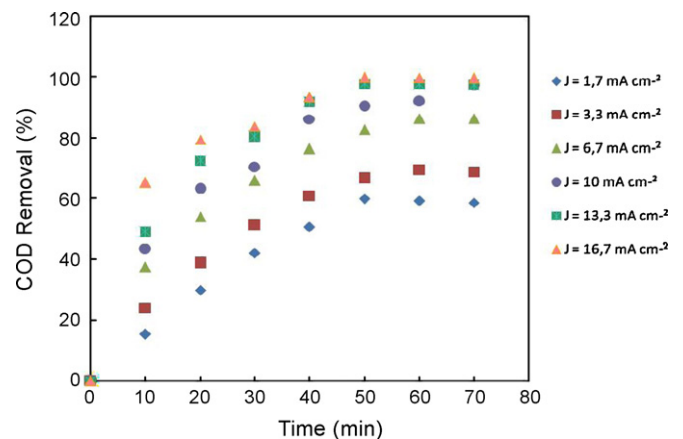


Fig. 8. Effect of current density on the COD removal (initial pH 7,  $V = 300$  cm<sup>3</sup>).

**Table 3**  
Effect of current density on the COD removal at a fixed charge loading  $Q = 1500$  C

$J$ (mA cm <sup>-2</sup> )	$t$ (s)	COD removal (%)
16.7	600	65.2
13.3	750	64.5
10	1000	66.3
6.7	1500	65.0
3.3	3000	66.6

The results presented in Table 3 show that the current density had no significant effect on the COD removal in the large range from 3.3 to 16.7 mA cm<sup>-2</sup> at a fixed charge loading ( $Q = It$ ) of 1500 C. Nevertheless, as the current decreased, the time needed to achieve similar efficiencies increased. This indicates that it is not the current density but the charge loading that really affects the treatment efficiency [10,15].

Indeed, the amounts of aluminum and hydroxide ions generated at a given time, within the electrocoagulation cell are related to the current flow, using Faraday's law:

$$m = \frac{ItM}{zF} \quad (17)$$

where  $I$  is the current intensity,  $t$  is the time,  $M$  is the molecular weight of aluminum or hydroxide ion (g mol<sup>-1</sup>),  $Z$  is the number of electrons transferred in the reaction (3 for aluminum and 1 for hydroxide) and  $F$  is the Faraday's constant (96486 C mol<sup>-1</sup>).

However, these parameters should be kept at low level to achieve a low-cost treatment. For that a compromise of the current density and electrolysis time is necessary to optimise the treatment efficiency with the lowest cost.

Two comparative tests were carried out at  $J = 16$  and  $14$  mA cm<sup>-2</sup> shown that the optimum value of current density, allowing fast removal (50 min) of pollutants with low electrode consumption, was found to be 14 mA cm<sup>-2</sup>.

## 5. Conclusion

The present study has shown the applicability of electrocoagulation method in the treatment of black liquor from paper industry. The influence of variables such as electrolysis time, current density, type of electrode material and initial pH on the removal of polyphenols, COD and color intensity has been determined.

Aluminum electrodes are preferred for this application. Under optimal value of process parameters (initial pH 7,  $t = 50$  min and  $J = 14$  mA cm<sup>-2</sup>), COD and polyphenol removal reached 98% and 92%, respectively. In addition, high color removal (>99%) was obtained and the effluent became visually very clear following electrocoagulation treatment. The final pH of treated black liquor was nearly neutral, which allows it to be directly discharged in natural aquatic streams.

Consequently, electrocoagulation can be considered as a suitable alternative to existing methods or applied as pre-treatment step of biological process used for the treatment of black liquor.

## Acknowledgements

The authors would like to express their gratitude to Prof. J.L. Brisset (Laboratoire de Chimie Analytique Interfaciale et d'Electrochimie de l'Université de Rouen) for his available advices.

## References

- [1] M. Ksibi, S. Ben Amor, S. Cherif, E. Elaloui, Photodegradation of lignin from black liquor using a UV/TiO<sub>2</sub> system, *J. Photochem. Photobiol. A* 154 (2003) 211–218.
- [2] S. Mahesh, B. Prasad, I.D. Mall, I.M. Mishra, Electrochemical degradation of pulp and paper mill wastewater. Part 1. COD and color removal, *Ind. Eng. Chem. Res.* 45 (2006) 2830–2839.
- [3] M.A. Lara, A.J. Rodriguez-Malaver, O.J. Rojas, O. Holmquist, A.M. Gonzalez, J. Bullon, N. Penaloza, E. Araujo, Black liquor lignin biodegradation by *Trametes elegans*, *Int. Biodeterior. Biodegr.* 52 (2003) 167–173.
- [4] F. Torrades, M. Pérez, H.D. Mansilla, J. Peral, Experimental design of Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents, *Chemosphere* 53 (2003) 1211–1220.
- [5] O. Wallberg, A.S. Jönsson, R. Wimmerstedt, Ultrafiltration of kraft black liquor with a ceramic membrane, *Desalination* 156 (2003) 145–153.
- [6] O. Wallberg, A. Holmqvist, A.S. Jönsson, Ultrafiltration of kraft cooking liquors from a continuous cooking process, *Desalination* 180 (2005) 109–118.
- [7] O. Wallberg, A.S. Jönsson, Separation of lignin in kraft cooking liquor from a continuous digester by ultrafiltration at temperatures above 100 °C, *Desalination* 195 (2006) 187–200.
- [8] Q. Zhang, K.T. Chuang, Adsorption of organic pollutants from effluents of a Kraft pulp mill on activated carbon and polymer resin, *Adv. Environ. Res.* 3 (2001) 251–258.
- [9] V.E. Cenk, A.N. Belevstev, Electrochemical treatment of industrial wastewater, *Effluent Water Treat. J.* 25 (7) (1985) 243–249.
- [10] N. Adhoum, L. Monser, Decolorization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, *Chem. Eng. Process.* 43 (2004) 1281–1287.
- [11] M. Koby, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J. Hazard. Mater. B* 100 (2003) 163–178.
- [12] O.T. Can, M. Koby, E. Demirbas, M. Bayramoglu, Treatment of the textile wastewater by combined electrocoagulation, *Chemosphere* 62 (2006) 181–187.
- [13] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, *J. Hazard. Mater. B* 129 (2006) 116–122.
- [14] X. Chen, G. Chen, P.L. Yue, Electrocoagulation and electroflotation of restaurant wastewater, *J. Environ. Eng-ASCE* 126 (9) (2000) 858–863.
- [15] A.S. Kopal, U.B. Ogutveren, Removal of nitrate from water by electroreduction and electrocoagulation, *J. Hazard. Mater. B* 89 (2002) 83–94.
- [16] J.A.G. Gomes, P. Daida, M. Kesmez, M. Weir, H. Moreno, J.R. Parga, G. Irwin, H. McWhinney, T. Grady, E. Peterson, D.L. Cocke, Arsenic removal by electrocoagulation using combined Al-Fe electrode system and characterization of products, *J. Hazard. Mater.* 139 (2007) 220–223.
- [17] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewaters, *Chem. Eng. Sci.* 58 (2003) 987–993.
- [18] N. Adhoum, L. Monser, N. Bellakhal, J.E. Belgaied, Treatment of electroplating wastewater containing Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cr(VI) by electrocoagulation, *J. Hazard. Mater. B* 112 (2004) 207–213.
- [19] N. Bellakhal, J.L. Brisset, M. Dachraoui, Electrocoagulation treatment of tannery wastewater, *J. Soc. Chim. Tunisie* 6 (2004) 61–66.
- [20] D. Ghosh, H. Solanki, M.K. Purkait, Removal of Fe(II) from tap water by electrocoagulation technique, *J. Hazard. Mater.* 155 (2008) 135–143.
- [21] V.L. Singleton, J.A. Rossi, Colorimetry of total phenolics with phosphomolybdic phosphotungstic acid reagents, *Am. J. Enol. Viticult.* 16 (1965) 144–158.
- [22] R. Knechtel, A more economical method for determination of chemical oxygen demand, *J. Water Pollut. Contr.* 166 (1978) 25–29.
- [23] J. Rodier, *L'analyse de l'eau*, Dunod, Paris, 1996.
- [24] M. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, *J. Hazard. Mater. B* 114 (2004) 199–210.
- [25] M. Uğurlu, A. Gürses, Ç. Doğan, M. Yalçın, The removal of lignin and phenol from paper mill effluents by electrocoagulation, *J. Environ. Manage.* 87 (2008) 420–428.
- [26] Norme XP T 90-210, Qualité de l'eau: Protocole d'évaluation d'une méthode alternative d'analyse physicochimique quantitative par rapport à une méthode de référence, 1999.
- [27] P.H. Holt, G.W. Barton, M. Wark, A.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, *Colloids Surf. A: Physicochem. Eng. Aspects* 211 (2002) 233–248.
- [28] N.K. Khosla, S. Venkatchalam, P. Sonrasundaram, Pulsed electrogeneration of bubbles for electroflotation, *J. Appl. Electrochem.* 21 (1991) 986–990.