Detoxification and decolorization of Moroccan textile wastewater by electrocoagulation: energetic and toxicological evaluation

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Abstract

In Morocco the textile industry, representing 31% of all Moroccan industries, is accompanied by high water consumption and important wastewater discharges rejected without any treatment. The focus of this study was to characterize the effluent from the local textile industry and to carry out the treatment by electrocoagulation (EC). The effect of electrode materials, pH, applied current density and treatment time on decolorization, COD removal and toxicity aspect of the effluent. Results have indicated that the treatment efficiency was significantly improved by varying the current density, pH and operating time when Al and Fe electrodes were used for EC. The appropriate electrode type search for EC provided that aluminium supplies more COD removal (78%) than iron electrode (56%) at the end of the 25 min operating time and increased BOD5/COD index from 0.29 to 0.50. Whereas EC with iron electrodes was more beneficial for color removal 91% after 25 min of EC. The evaluation of toxicity by Daphnia magna test has shown that the effluent have a high toxicity. However electrocoagulation significantly reduced the toxicity of the effluent.

Keywords: daphnia test; toxicity; operating cost; decolorization.

1. Introduction

Textiles are one of the important sectors in Morocco and are the leading sector for producing excessive waste (R.Choukr-Allah 2005). The pollutants in textile wastewater are, especially, organics followed by color, toxic materials, inhibitor compounds, active substances, chlorine compounds (AOX), pH, salt and dyeing substances (Mountassir et al. 2013). These pollutants are carcinogenic, mutagenic and resistant to biodegradation (Jain et al. 2007). Added to this, the toxicity of these effluents has been confirmed by many studies (Gebrati et al. 2010). The most commonly used method for the treatment of textile wastewater is the combination of biological oxidation and physico-chemical treatment. However, these processes are quite ineffective in color removal of wastewater as most commercial dyes are toxic to organisms used in the biological process while the physico-chemical treatment provides only a phase transfer of dyes and generates huge volumes of hazardous sludge. Therefore, color removal remains the major problem in the treatment of textile effluents. Recently, electrochemical methods have attracted significant attention for treating recalcitrant toxic wastes (Martínez-Huitle and Brillas 2009). The main advantage of this technology is its environmental compatibility, versatility, high-energy efficiency, amenability to automation, and safety because it is operated at mild conditions (Mountassir et al. 2012). The main goal of this study is to compare the effectiveness of each electrode material in pollutant removal from real wastewater. Once the optimal conditions have been identified, we examine the decontamination efficacy in terms of organic loads, toxicity, and we estimate the energy consumption and operating cost.

2. Materials and methods

The pH values were adjusted by 0.1M sulfuric acid (H₂SO₄) and 0.1M sodium hydroxide (NaOH) as required. UV–vis spectra were obtained from samples of raw and treated wastewater using ANTHELIE Data SECOMAM, by measuring the absorbance at three wavelength (436, 540 and 660 nm) and taking the sum of these absorbance. The samples were scanned in glass cells with a 1cm optical path. The electrodes were weighed (AB107-S balance) before and after the experiments to determine the mass loss during the experiment. The experiment was conducted using wastewater from a large textile industrial "Tenmar" located in south of Morocco (Marrakech city) (Mountassir et al. 2013). These waters were stored in refrigerator at 4°C then transported to the laboratory for analysis and electrochemical treatment. The experiment was performed in Pyrex reactor that consisted of a 0.3 L capacity, equipped with a cathode and an anode. The distance between the electrodes was 1cm, and the total...
effective electrode area is calculated to be 25 cm$^2$. The selected anodes are aluminum and iron. The electrodes were dipped into the beaker containing wastewater with a 0.2 L working volume. Electrochemical cell is shown in figure 1.

**Figure 1.** Schematic view of the electrochemical set up: 1: DC power source, 2: ampermeter, 3: voltmeter, 4: electrodes, 5: magnetic stirring controller, 6: thermostatic bath, 7: thermometer.

All electrochemical experiments, were performed in the electrolytic cell, under fixed temperature 25°C and under agitation speed of 200 rpm (Can et al. 2003). After each test, the electrodes are cleaned daily with 0.1 M hydrochloric acid and immersed in a solution of KCl 3M and several times with deionized water. The electrodes were connected to a DC Power Supply 0-40V, $I_{\text{max}} = 0.9 \, A$. At the end of treatment; all samples were centrifugated 3000 rpm before any analysis.

2.1. **Analytical Procedures**

The samples were analyzed for various physicochemical parameters like $pH$, color, electrical conductivity (EC) and chemical oxygen demand (COD), according to standard methods (AFNOR.1999). Metal measurement (Al, Fe, Mn, Cu, Zn, Pb and Cd) was carried out by a flame Atomic Absorption Spectrophotometer (UNICAM 929). Table 1, shows the results obtained from the characterization of the real textile wastewater.

2.2. **Toxicity test**

The toxicity test was conducted in accordance with the method adopted by the AFNOR (AFNOR.1983), it is to bring together in test tubes the *Daphnia* selected with different dilutions of the effluent tested. In each test tube, we introduced five *Daphnia* in a volume of 10 ml. For each dilution; we performed four repetitions. The tubes are then placed in the dark in thermostated aquaria at 20 °C. For each test, we conducted a preliminary test before the final test in order to determine the LC$_{50}$ value of 24h (lethal concentration). Specimens of *Daphnia magna* used in the test were obtained from a farm where animals are fed with algae (*Chlorella vulgaris*). In parallel, a control test in the dilution water was conducted in four replicates. The test is to control the mobility of *Daphnia* after 24 h, 48 h, 72h and 96h of incubation, by counting the immobile *Daphnia* in each tube within 15 seconds after moderate agitation of the test tube. The results were processed by the statistical test "Probit EPA" to determine the LC$_{50}$ 24h and LC$_{50}$ 48h. The term toxic unit ($TU$) is introduced to compare the relative toxicity (Eq.1).

$$\text{Toxic unit} : TU = \frac{100\%}{LC_{50}} \quad (1)$$
### Table 1. Physicochemical characterization of raw wastewater

<table>
<thead>
<tr>
<th>Elements</th>
<th>Values</th>
<th>EU Limit&lt;sup&gt;a&lt;/sup&gt; (EU 1992)</th>
<th>Moroccan&lt;sup&gt;a&lt;/sup&gt; Limit (CNS 2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9 ±0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity (ms/cm)</td>
<td>3 ±0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total suspended solids (mg/L)</td>
<td>556±10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCO (mg O&lt;sub&gt;2&lt;/sub&gt;/L)</td>
<td>1730±300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DBO&lt;sub&gt;5&lt;/sub&gt; (mg O&lt;sub&gt;2&lt;/sub&gt;/L)</td>
<td>325±15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTK (mg/L)</td>
<td>126±50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P. total</td>
<td>200±30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color (absorbance)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>530 nm</td>
<td>2.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 nm</td>
<td>1.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>720 nm</td>
<td>0.230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>0.32±0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>4.20±1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>3.6±1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>1.4±0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>0.66±0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>1.40±0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0.05±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toxic unit (TU)</td>
<td>22.41</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Indirect discharge limits (discharge in the sewer).

EU: European Union.

### 3. Results and Discussion

#### 3.1. Characteristics of textile wastewater

The results showed that the effluent from the local textile unit was alkaline and presented a high salt concentration. The amount of nitrogen, phosphorus, and metals presented in the effluent were significantly higher (Table 1). The concentrations of solids and the oxygen demands were quite high. The analyzed samples demonstrate that 100% of them support the conclusion that textile discharges are serious potential pollution sources and are very important sources of toxic discharges. The treatment of all effluents generated by the textile factories in Morocco before their discharge is recommended.

#### 3.2. Electrocoagulation

The study tests show that there are several parameters that influence more or less the efficiency of treatment. The main parameters investigated in our study were: pH, current density and operation time.

##### 3.2.1. Influence of initial pH

The efficiency and nature of coagulant are profoundly dependent on the initial pH of the effluent (Cañizares et al. 2009). To examine its effect, several samples with pH between 2 and 12 were treated using Fe and Al electrodes under similar operational conditions (i= 100 A/m² and t=20 min).

As seen in figure 2, Fe electrodes showed higher treatment efficiency than Al. The rates of color removals for Fe and Al electrodes obtained were 60% and 46% in 20 min contact time and current density of 100 A/m² in the pH rang of 7-9 and 4-8, and above pH 9, they drop to 40% and 15%, respectively.
Figure 2. Evolution of color removal efficiencies as a function of initial pH for both electrodes, with $i= 100 \text{ Am}^2$, $t = 20 \text{ min}$.

Figure 3. COD removal efficiencies as a function of initial pH for both electrodes, with $i= 100 \text{ Am}^2$, $t = 20 \text{ min}$.

Figure 3, show the COD removal as a function of different initial wastewater pH, using Al and Fe electrodes under similar condition. As shown, the maximum COD reduction occurs in the pH range of 4-8 (54-56%) and pH range of 7-9 (32-36 %) respectively for Al and Fe electrodes. However, poor removal are found either at low (<4) or high (>9) pH. The possible explanation of these results was given from the observation of the solubility diagram of iron and aluminium hydroxide.

In contrast, at pH $< 3.0$ soluble Fe$^{3+}$ is the dominant species and Fe(OH)$_3$, flocs which has high adsorption propriety thus bonding to pollutant (coagulation) are quite poorly produced (<21% of color and COD removal ), whereas at pH $> 10$ Fe(OH)$_3$ is solubilized as Fe(OH)$_4$ (see figure 4), and lower amount of color and COD can be removed (40.8 % and 10 % ), causing the dissolution of the flocs formed. In the Al case, at pH 5-8 the solid precipitate of Al hydroxide is formed (maximum COD 55% and color removal 56 % ). However, it is interesting to note that at pH greater than 10 a new aluminium complex forms: Al(OH)$_4^-$. This ion is soluble and directly affects the color and COD removal (Mountassir et al. 2012).
3.2.2. Influence of current density and operation time

In any electrochemical process operating time and current density (A/m²) are important operational parameters setting the treatment efficiency and determine the ultimate operating cost for the process. When the current density increases, the rate of formation of hydroxides of iron and aluminium attains a significant increase in flocs formed, resulting in a greater amount of precipitate for the removal of pollutants, also the production rate of hydrogen bubbles increases and their size decreases when the current density increases. All these effects are beneficial for efficient removal of pollutants. In figure (4 and 5), the dependency of color and COD removals % vs time is given for different current densities. It is apparent that with the time increase up to a certain level, there is ions accumulation and step-by-step formation of corresponding hydroxides. Therefore, increased percentage of COD and color removal.

As seen from figure 5, color removal increases with time during the first 15 min, but between 25 and 35 min it does not demonstrate any substantial increase. With current density 75 A/m², color removal efficiency reaches a limit value of 63.5% for iron and 26% for aluminium during 25 min of treatment. The results of current density increase (i = 100 A/m²) better with Fe electrodes. For example, the 25 min processing with Fe electrodes results in 91% of color removal, while with Al electrodes we have only 55.6 %. However, it can be noticed that increasing the current density beyond 150A/m² would not show any significant improvement in the percentage color removal.

![Figure 4: Solubility diagram of iron and aluminium hydroxide (Mountassir et al. 2012).](image1)

![Figure 5: Color removal efficiencies observed during EC at varying electrical current densities for iron and aluminium electrodes.](image2)
Figure 6. COD removal efficiencies observed during EC at varying electrical current densities for iron and aluminium electrode.

Figure 6, represents the effects of operating time and current density on COD removal efficiencies for iron and aluminium electrode, the pH of the wastewater is adjusted to 7 in the case of aluminium. It can be noticed from the Figure 5, that for the given experimental conditions Aluminium shows better performance than iron electrode. Say for example, at a given electrolysis time of 25 min and 125 A/m², Aluminium anode shows more than 70% COD reduction, a significant part of the initial COD in solution persists in the case of iron with 56% of reduction. For the same current density (i=75 A/m²), iron anode show 32%, while aluminium anode show more than 50% COD reduction for a operating times of 25 min.

The experiments show that operating time and current density exhibit similar effects on the process performances, When the treatment time was quick, the charge loading (Q=It) was low as reported by Chen (Chen 2004). In such conditions, the metal ion (Fe³⁺, Al³⁺) dosage was not sufficient to destabilize all colloidal and finely suspended particles. Thus the COD removal efficiency was not high (t<25 min). Further electrogeneation of coagulant flocs has no positive effect on COD removal (t>25 min).

The efficiency of electrocoagulation with iron electrodes does not find the same trends for the color removal (91%) and the reduction of COD (56%) for the same current density (i=100 A/m²). However aluminium electrodes show nearly the same efficiency for color (72%) and COD (78%) removals with current density i=125 A/m²; since the wastewater not only comprised of dyes but also of a variety of sequestering, surface active and other dye auxiliary agents (dispersing agents, anti-creasing agents, sequestering agents, etc.) that significantly contributed to the effluent’s COD.

The plausible reason for lower COD removal efficiency by iron in comparison with aluminium could be explained considering the insufficient ability of hydrous iron oxide to adsorb the material contributed to effluent’s COD. Moreno-Casillas et al [18] have reported that aluminium has only one oxidation state, so when an organic compound reacts with aluminium to form an insoluble compound it will react almost completely, and when using aluminium electrodes there is oxygen evolution at the cathode which may promotes the elimination of COD. Arslan-Alton (Arslan-Alaton et al. 2008) have reported that EC with aluminium electrodes was better than stainless steel electrodes in terms of COD removal, as also reported in other studies using aluminium and iron electrodes (Mountassir et al. 2012). Moreover, it is noted that differences in COD and color removal are due to the characteristics of the studied wastewaters (complex components, several recalcitrant, and other undesirable impurities etc.)

3.2.3. Electric energy consumption

The electrical energy consumed (C_{energy}) was calculated in terms of kWh/m³ of treated effluent against time for the current densities corresponding to a maximal efficiency in terms of color and COD removals for iron (i=100 A/m²) and aluminium (i=125 A/m²) according to Eq.(2).

\[ E \ (kWh/m^3) = \frac{U \times I \times t}{V_r} \]  

Where U is the voltage measured during the reaction (in V), t is the time needed for the removal of a given pollutant (h); I is the total current applied (A) and V_r the reactor volume (in m³). The applied voltage and electrical current were continuously followed during EC. Figure 5 shows percent color and COD removal
efficiencies as a function of time in relation with energy consumption for EC with Fe (Figure.7) and Al (Figure.8) electrodes.

As shown, the minimum energy consumption was 1.75 kWh/m$^3$ and 2.18 kWh/m$^3$, respectively for Fe (90% color and 56% COD removal) and Al electrodes (color 71% and COD 78% removal). On the other hand, the energy consumption decreases with the degree of pre-treatment, due to the progressive lowering of the quantity of pollutants present, and consequently diminishing the necessary time for treatment, and it can be seen that 25 min, EC is almost sufficient to satisfy our color and COD removal for both electrodes. These electrical energy requirements for aluminium and iron electrodes are appreciably lower than those reported for degradation of pollutants with electrooxydation and advanced oxidation processes, and are still below the upper feasibility limit being set as 10 kWh/m$^3$ for the applicability of an industrial wastewater treatment technology as reported by Kabdash (Kabdash et al. 2008) Hence, the optimum operating conditions were established as (table 2).
3.2.4. Evaluation of toxicity after treatment

The toxicity study was carried out with the purpose of evaluating the toxicity of the treated wastewater. The samples analyzed were the raw effluent (solution without treatment) and the effluent after electrocoagulation process, in the optimum condition of color removal respectively. The response established for the acute toxicity test with D. magna was the average lethal concentration ($LC_{50}$) at which 50% of the species were killed during 24 h of exposure to the effluent.

Immobilization toxicity of wastewater for D. magna is summarized in Table 3. The results show that wastewater generated have important toxicity as classified by Vasseur et al (Vasseur et al. 1986) with a $CL_{50}$ value of 24 h of 4,462%. This high toxicity could be explained by the load of this effluent on organic dye and other chemicals. After treatment by electrocoagulation, $CL_{50}$ had a significant increase. It rose from 4,462% to 19,069% and 9.5% to 20,556% respectively for Al and Fe. Therefore, the treated effluent can be classified as slightly toxic. This decrease in toxicity is mainly due to the reduction of COD and color (Sponza and Demirden 2010). Treatment with Fe electrode recorded improved results in terms of detoxification of treated water than Al electrode. This toxicity behavior between Fe and Al electrode can be attributed to an increased ability of Fe for reduction of COD, because the electrocoagulation with aluminum electrode so greatly increased the concentration of aluminum in the treated effluent and the low color reduction (70%), it is possible that this affected the D magna metabolism.

Table 3. Toxicity of treated wastewater by electrocoagulation

<table>
<thead>
<tr>
<th>Raw wastewater</th>
<th>After treatment (Al)</th>
<th>After treatment (Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$LC_{50}$-24h</td>
<td>4,462</td>
<td>19,069</td>
</tr>
<tr>
<td>$LC_{50}$-48h</td>
<td>1,592</td>
<td>11,841</td>
</tr>
<tr>
<td>UT-24 (100/$LC_{50}$-24h)</td>
<td><strong>22.41</strong></td>
<td><strong>5.24</strong></td>
</tr>
</tbody>
</table>

Finally, a toxic unit (TU) was employed to numerically compare the relative toxicity of the effluents from each process. The TU value of the raw textile wastewater was 22.41%; the sample affects the mortality of D. magna due to its toxicity. Conversely, the TU of effluent treated by the electrochemical method was 4.86 % and 5.24 %, respectively for iron and Aluminium electrodes, implying that the toxic compounds in the real wastewater were detoxified by the electrocoagulation process.

$$UT = \frac{100}{LC_{50}} \quad (3)$$

3.1.2. Operating Cost

In the final step of the study, the operational costs can be calculated by considering (Bayramoglu 2004): the electrical operational cost and the amount of electrode material. The electrical operational cost (EOC) is
mainly composed of the electrical energy consumed as kWh/m$^3$ of the treated effluent and the electrical energy price as Dhs/kWh (US $= 8.63$ Dhs (Morocco Dirham’s)). On the other hand, the amount of electrode material (m) having a unit of kg Al or Fe/m$^3$ wastewater treated is determined experimentally.

$$\text{Operating Cost (Dhs/m}^3) = E \times \text{Energy price} + m \times \text{Electrode price} \quad (4)$$

These calculations were carried out after optimizing the operational parameters. The calculated values (Eq.4) are shown in Figure 9. According to the results obtained in this work and the economic data from Moroccan market in January 2013, as follows: electrical energy price 0.907 Dhs/kWh (NEO), electrodes materials prices 7.34 Dhs/kg for aluminum and 5 Dhs/kg in the case of iron electrodes. Cost calculations show that, in the case of aluminum electrodes, operating cost is approximately 3.45 Dhs/m$^3$, and for iron, it was 3.32 Dhs/m$^3$, nearly the same operating cost is obtained.

To conclude, the use of iron electrode in the treatment is more effective at color removal, but aluminium shows interesting effectiveness for COD removal. Given that the costs of both types of electrodes are almost the same and that each compound contribution to the COD in wastewater is different. It is convenient to try both electrodes and even a combined system to get best results.

4. Conclusion

The results obtained in this work can be concluded that electrocoagulation is a very interesting way to allow significant reduction of color and the value of COD and the toxicity of wastewater treated in this study. The effects of several parameters on the decolouration, reduction of COD and operating costs have been determined. This study aimed to show:

- Electrocoagulation is already known as an efficient removal of color and pollutants contained in discharges from the textile industry, as well as for the removal of soluble pollutants and colloid content in drinking water.
The effectiveness of treatment is strongly influenced by current density and duration of electrolysis. Comparing treatments using anodes aluminium and iron in optimum conditions, shows that the effectiveness of iron is more interesting than that of aluminium in terms of color removal (91% Fe and 70% for Al) during 25 min and with current density \( i =100 \text{ A/m}^2 \) corresponding to an electrical energy consumption of 1.75 kWh/m\(^3\) and without initial pH adjustment. However, COD abatement was significantly slower than EC with Al electrodes. EC with Al electrodes should be preferred in terms of COD abatement (78 %) obtained at a current density of 125A/m\(^2\) after 25 min and at pH 7 corresponding to 2.18 kWh/m\(^3\).

- The operating cost during EC was calculated based on Dhs/m\(^3\) of wastewater treated; nearly the same operating cost for aluminium and iron electrodes is obtained.
- Treatment of effluents from textile industries by electrochemical voice significantly reduced toxicity and reduces the mortality of Daphnia exposed to treated effluent.

Reference


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