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Influence of operating parameters on electrocoagulation of C.I. disperse yellow 3

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Abstract

This work deals with the electrocoagulation (EC) process for an organic dye removal. The chosen organic dye is C.I. disperse yellow 3 (DY) which is used in textile industry. Experiments were performed in batch mode using Al electrodes and for comparison purposes Fe electrodes. The experimental set-up was composed of 1 L beaker, two identical electrodes which are separated 2 cm from each other. The main operating parameters influencing EC process were examined such as pH, supporting electrolyte concentration C_{NaCl} , current density i , and DY concentration. High performance EC process was shown during 45 min for 200 mg/L dye concentration at $i = 350 \text{ A m}^{-2}$ (applied voltage 12 V) and $C_{NaCl} = 1 \text{ g L}^{-1}$ reaching 98 % for pHs 3 and 10 and 99 % for pH 6. After 10 min, DY was also efficiently removed (86 %) showing that EC process may be conveniently applied for textile industry wastewater treatment. EC using Fe electrodes exhibited slightly lower performance comparing EC using Al electrodes.

Keywords:

Dye removal; aluminium; iron; current density; mechanism.

Introduction

The main problem of access to safe drinking water is continuous pollution of water resources by agriculture, urban waste and industry. In countries where water resources are relatively limited, treated wastewater reuse in agriculture has become an urgent necessity. The textile industry consumes considerable amounts of water in the dyeing and finishing. Effluents containing dyes

can be toxic to the environment [1-4]. In addition, their presence in aquatic systems, even at low concentrations, is very visible. It reduces the penetration of light and has a detrimental effect on photosynthesis [5-7].

Therefore, the remediation of water contaminated by these chemicals is necessary both to protect the environment and for future reuse [8-12]. Therefore, several biological, physical and chemical methods are used for the treatment of industrial effluents with different efficiencies [13-15]. Electrochemical technologies, such as electrocoagulation technique (EC), seem to be well adapted to the textile industry wastewaters treatment [16-22].

This work is devoted to the study of the EC process for bleaching synthetic water containing an azo dye, C.I. disperse yellow 3 (DY), used in the Algerian textile industry and the assessment of its performance versus certain operating parameters.

Experimental

Experimental set-up

The EC tests were performed using an experimental set-up shown in Figure 1. In a 1000 mL beaker, filled with 500 mL synthetic dye solution (distilled water + DY + NaCl), two Al (or Fe in some experiments) 4×20 cm electrodes were immersed (active surface $S = 4 \times 10.5 = 42 \text{ cm}^2$). The anode is connected to the positive pole and the cathode to the negative pole of the direct current power supply. The interelectrode distance is fixed at 2 cm. When the electric current is applied, the magnetic stirrer is started at an average velocity agitation.

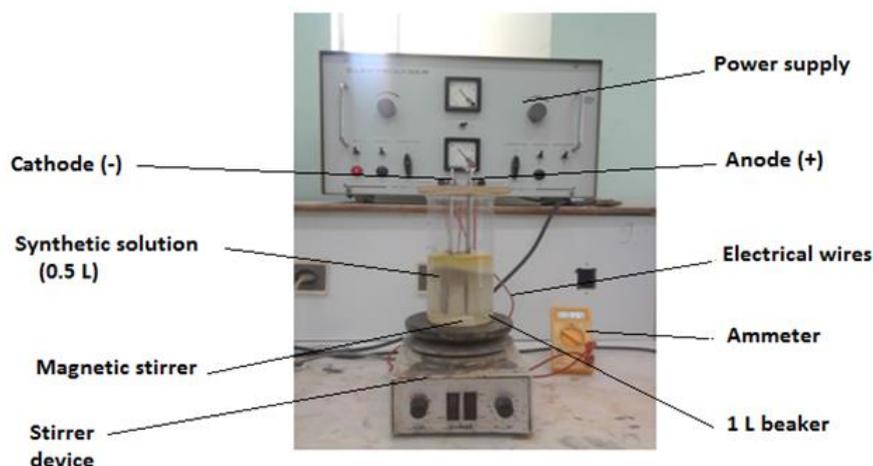


Figure 1. Photo of the EC experimental set-up.

Electrodes cleaning

Before experiments, the Fe electrodes were prepared to avoid the presence of any impurity as follows: (1) polishing with abrasive paper; (2) rinsing with distilled water; (3) degreasing by means of a solution composed of: NaOH (25 g), Na_2CO_3 (25 g), K_2CO_3 (25 g) and distilled water (q.s.p. 1,000 mL); (4) rinsing with distilled water; (5) pickling in a solution of sulphuric acid H_2SO_4 at 20 % for 20 min at room temperature; and again (6) rinsing with distilled water. For Al electrodes: (1) rinse with distilled water and polish using abrasive paper, (2) clean in hydrochloric acid solution (HCl at 20 %) during 10 min, and (4) rinse with distilled water.

Prepared solutions

To prepare a solution of 200 mg L⁻¹ dye, 0.2 g of the latter was poured into a 1 L flask and distilled water was added during stirring for better solubilisation. The initial pH was varied using a solution of 0.1 M HCl (acidic conditions) or NaOH (alkaline medium). The solution conductivity was increased by sodium chloride addition. All chemicals used were of analytical grade.

Methods

Once the EC test ends, the treated solutions were left to settle for 30 min in order to sediment the flocs formed. After decantation, and using a pipette, 25 mL of the solution were carefully collected for analysis.

The analyses done before and after treatment were as follows: pH, conductivity and ultraviolet (UV) absorbance (Shimadzu 1601, dual beam with 1 cm quartz vessel). The best UV absorbance long wave was found at 346 nm (*UV*₃₄₆). The DY removal was calculated using the relation (1):

$$R / \% = \frac{Ab_i - Ab_f}{Ab_i} \times 100 \quad (1)$$

where *Ab*_i and *Ab*_f were initial and final UV absorbances, respectively. All the tests were conducted at ambient temperature (20 °C).

Results and discussion

The aim of this work was to perform bleaching EC tests on dye synthetic solutions (distilled water+dye+NaCl) using EC process and evaluate its performance based on certain key parameters.

Influencing parameters on EC process

Common remarks

During EC tests, some common observations were:

- Aluminium dissolution according to Reaction (2):



- Production of H₂ gas bubbles at the cathode according to Reaction (3):



- Production of O₂ gas bubbles at the anode according to Reaction (4):



- Flocs formation and their fixation on the H₂(g) bubbles during their ascension to the solution surface as a white foam (Figure 2a and b). Indeed, anode dissolution generates coagulant species which destabilise the dye molecules forming flocs.



Figure 2. Foam formation: (a) face view, (b) top view. (c) Initial and final state of a 200 mg L⁻¹ DY solution treated by EC during 1 h: from right to left, initial solution, treated solution at 12, 8 and 4 V, respectively.

EC time

The EC efficiency is strongly influenced by the time residence in the electrochemical device. To study its effect, the EC period was varied from 5 to 75 min and the other parameters were kept constant. The results obtained are illustrated in Figure 3. The H₂ and O₂ release and flocs formation increased over time and the foam became thicker. From 30 min, the flocs settled and the solution became clearer.

As seen in Figure 3, the dye removal efficiency increased with electrolysis time until 45 min. After this time, EC performance decreased. Moreover, the good EC efficiencies were reached between 15 and 45 min.

The removal efficiency was directly dependent upon the metal concentration in solution [23-25]. The positive metallic species were produced by the Al anode neutralising the negative charges on the polluting molecules [26-30]. When the electrolysis duration was increased, the cationic species as well as metal hydroxide (Al(OH)_{3(s)}) concentrations increased [30-32]. Consequently, the pollutant removal increased [33-36].

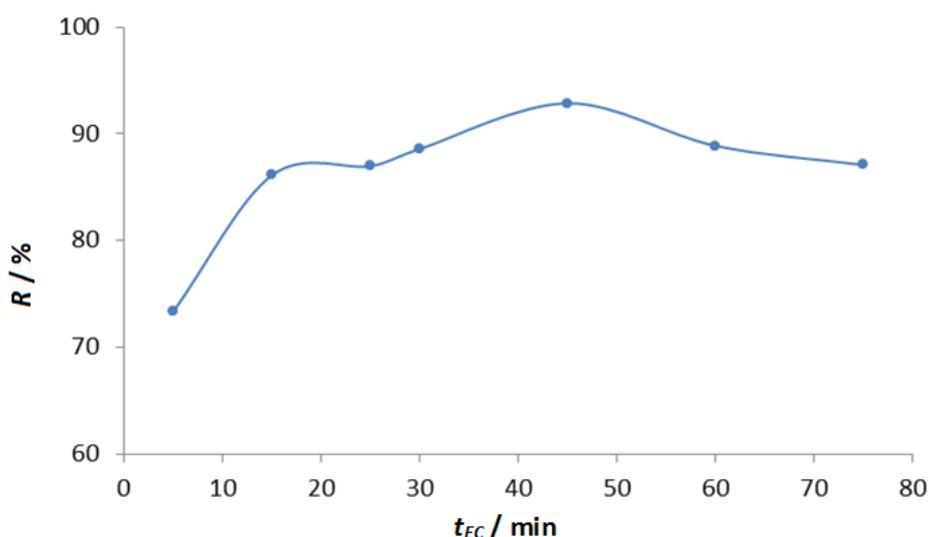


Figure 3. Dye removal as a function of EC time ($\text{pH } 6.5$; $C_{\text{NaCl}} = 1 \text{ g L}^{-1}$; $C_{\text{DY}} = 20 \text{ mg L}^{-1}$; $d = 2 \text{ cm}$).

Electric current density

The electric current density is the most important parameter of the electrochemical process [37]. The electric current density effect on the dye removal was studied. The current intensities were 120, 250 and 350 mA corresponding to the applied voltages of 4, 8 and 12 V, respectively. The dye concentration was fixed at 20 and 200 mg/L. The other parameters were maintained constant ($\text{pH } 6.5$; $C_{\text{NaCl}} = 1 \text{ g/L}$; $d = 2 \text{ cm}$). The obtained results are shown in Figure 4.

For $I = 120 \text{ mA}$ ($i = 29 \text{ A/m}^2$), the produced gas bubbles were small and the formed froth was thin. For $I = 250 \text{ mA}$ ($i = 60 \text{ A/m}^2$), the gas emanation was medium and the formed froth became important. For $I = 350 \text{ mA}$ ($i = 83 \text{ A/m}^2$), flocs settling became significant, the gas emanation became intense and the solution was transformed clear.

As seen in Figure 4, the electric current had a great effect on the dye removal especially for the first ten minutes. After 20 min, the electric current had a small effect. This is explained by the fact that the negative charge on the organic dye is neutralised after the Al³⁺ action on the dye molecules.

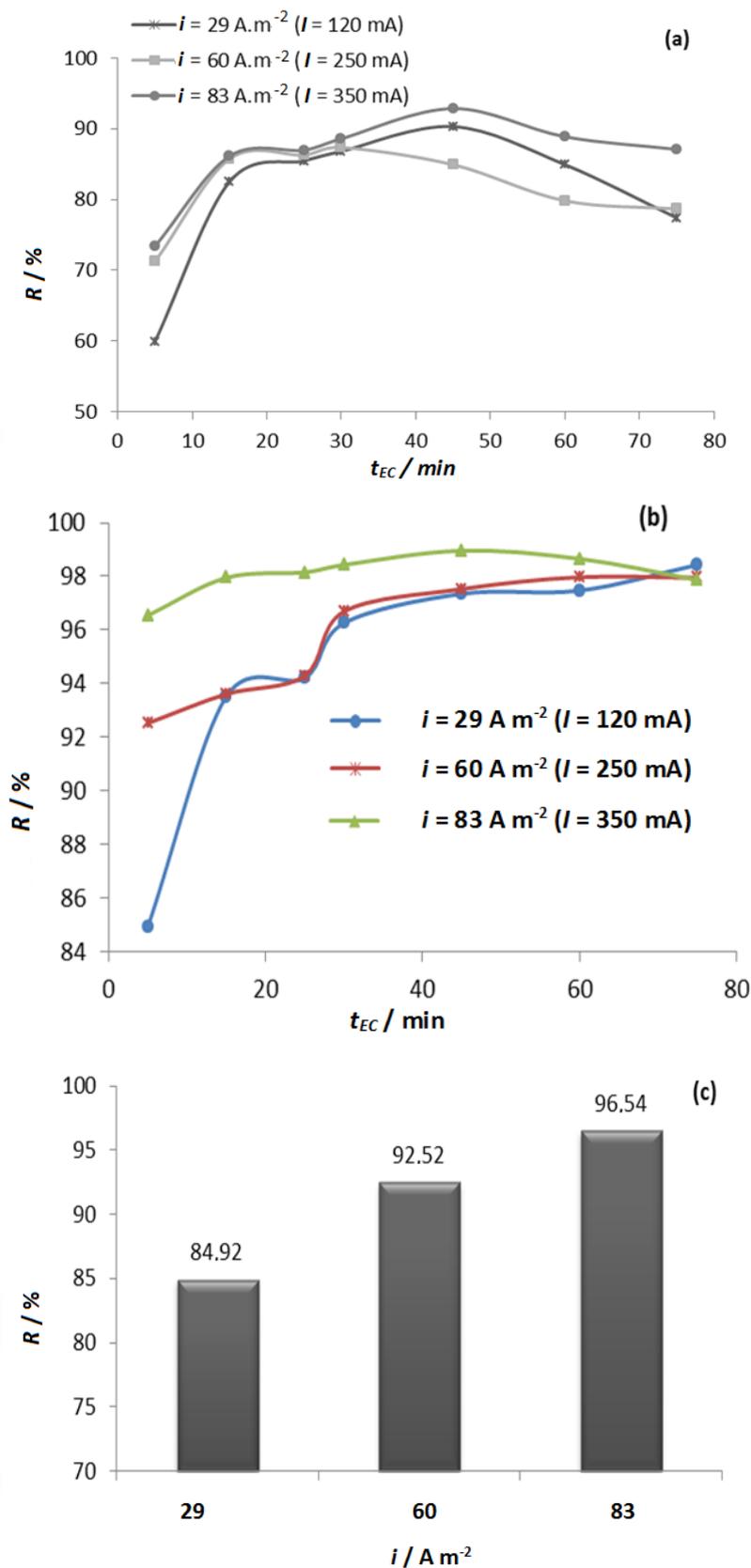


Figure 4. Effect of the electric current i on the EC efficiency for DY removal ($\text{pH } 6.5$, $d = 2 \text{ cm}$, $C_{\text{NaCl}} = 1 \text{ g L}^{-1}$)
 (a): $C_{DY} = 20 \text{ mg L}^{-1}$; (b): $C_{DY} = 200 \text{ mg L}^{-1}$; (c): $C_{DY} = 200 \text{ mg L}^{-1}$; $t_{EC} = 5 \text{ min}$

Initial pH

The solution pH is an important factor influencing the EC performance [37]. This is due to the fact that pH determinates the metallic ions speciation, the chemical state of other species in the

solution, and the formed products solubility. In order to examine the pH effect, the solution pH was adjusted to the values from 3 to 12 maintaining other parameters constant: $U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$), $C_{\text{NaCl}} = 1 \text{ g L}^{-1}$, $d = 2 \text{ cm}$, $t_{\text{EC}} = 30 \text{ min}$). The obtained results are shown in Figure 5.

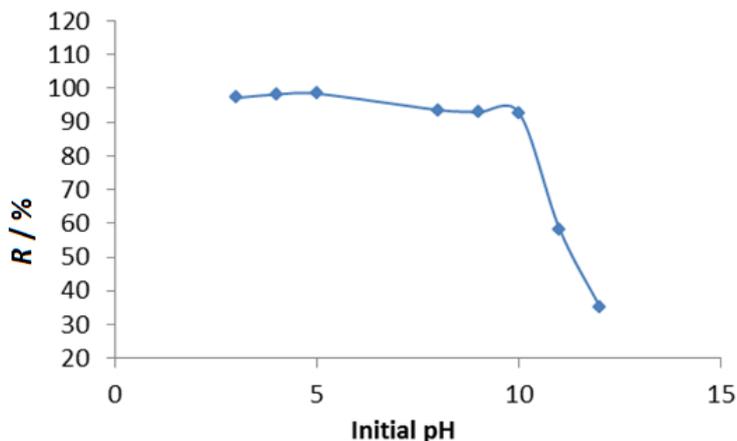


Figure 5. Effect of the pH on the EC efficiency for DY removal ($C_{\text{DY}} = 200 \text{ mg L}^{-1}$, $U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$); $t_{\text{EC}} = 30 \text{ min}$; $d = 2 \text{ cm}$).

For the acidic medium, the solution colour became orange after the addition of HCl. From the cathode, there is an intense emanation of H_2 bubbles. From the anode, there is an important formation of O_2 bubbles. The foam and sediment formed are denser at the anode.

For the alkaline medium, there was formation of white sediment at the bottom of the beaker, and its volume increased with time in comparison with the acidic medium.

As seen in Figure 5, we noted that the dye removal was well performed between pH 3 and 10. Several researchers found that the best removal efficiency with aluminum electrodes was reached in the pH range between 3 and 9 [19,34-36].

In Figure 6, we chose four pH values: 3, 4, 6.5 and 10 with other parameters fixed in order to illustrate the pH effect.

We also followed the change in pH as a function of time; Figure 7 shows the obtained results.

The medium pH changed during the EC process. This change depended on the type of electrode material and the initial pH of the treated solution.

We note from Figure 7 an increase in pH in the case of solutions with $\text{pH} < 7$. This increase was probably due to the release of H_2 from the cathode and the formation of OH^- according to the Reaction (3). Moreover, a decrease in pH in the case of solutions with $\text{pH} > 7$ was also noticed. This decrease was affected to the hydroxyl (OH^-) consumption according to Reaction (5):



Initial conductivity

Conductivity promotes the performance of electrochemical processes [26]. We chose NaCl as a supporting electrolyte. In order to determine its effect on the efficiency of bleaching of the synthetic solutions, we varied the concentration (0.25, 0.5, 1 and 1.5 g L^{-1}) while keeping the other parameters constant. The results are shown in Figure 8.

We have observed that (1) the gas production becomes higher with the increase in salt concentration, (2) the conductivity decreases during EC treatment and, (3) the formation of a small deposit on the anode.

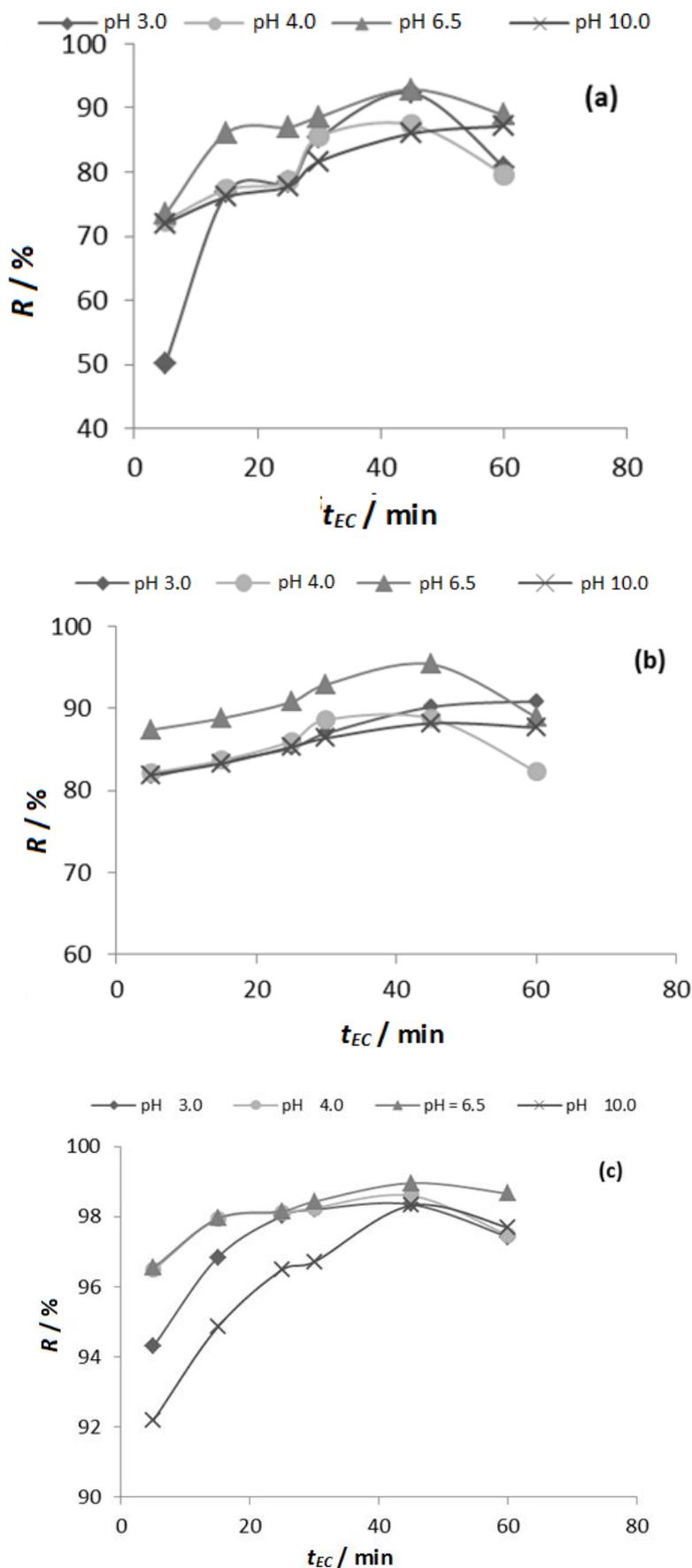


Figure 6. DY removal as a function of pH ($U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$), $t_{EC} = 30 \text{ min}$; $C_{NaCl} = 1 \text{ g L}^{-1}$; $d = 2 \text{ cm}$)
 (a) $C_{DY} = 20 \text{ mg L}^{-1}$; (b) $C_{DY} = 40 \text{ mg L}^{-1}$; (c) $C_{DY} = 200 \text{ mg L}^{-1}$

Figure 9 shows the solution conductivity as a function of time during EC process. We note that the conductivity decreased over time and the difference in the changes in pH was different due to the HCl and NaOH added during the pH adjustment before EC treatment.

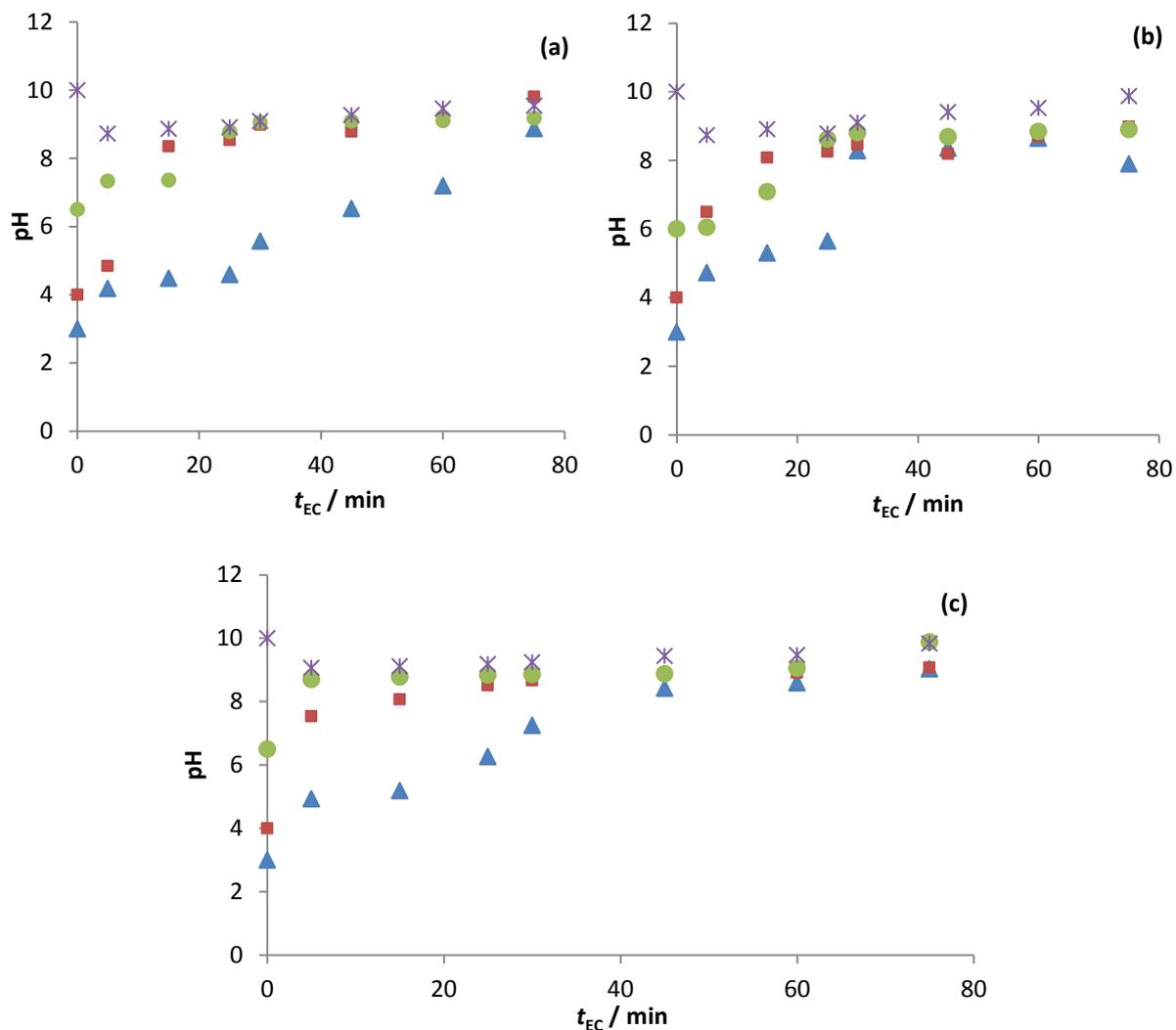


Figure 7. Evolution of pH during EC treatment (same conditions as for Figure 6).
 (a) $C_{DY} = 20 \text{ mg L}^{-1}$; (b) $C_{DY} = 40 \text{ mg L}^{-1}$; (c) $C_{DY} = 200 \text{ mg L}^{-1}$

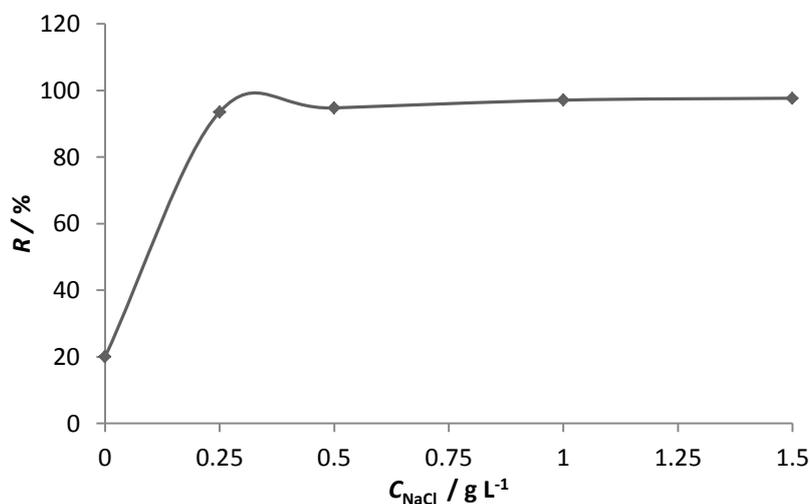


Figure 8. Effect of the NaCl concentration on the EC efficiency
 $U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$); $t_{EC} = 30 \text{ min}$; $d = 2 \text{ cm}$; $C_{DY} = 200 \text{ mg L}^{-1}$

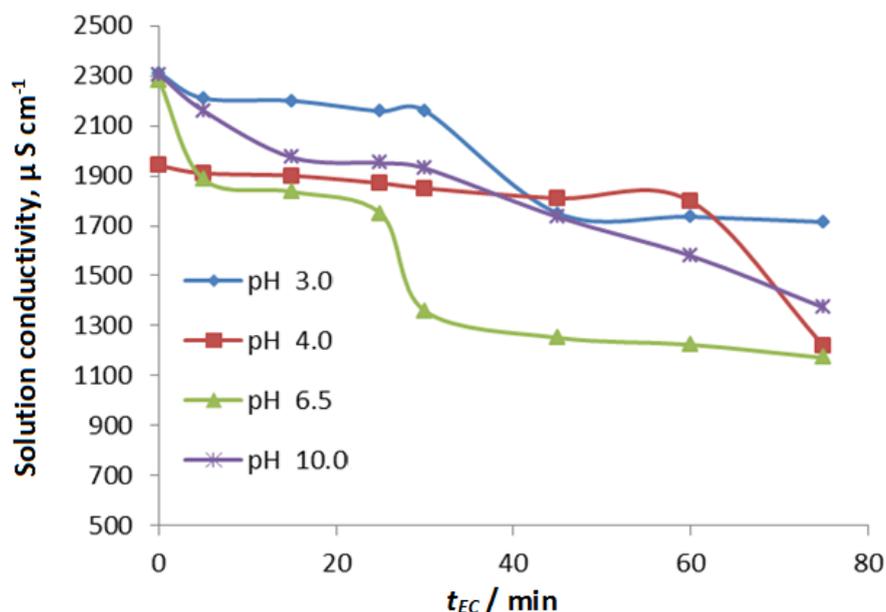


Figure 9. Solution conductivity as a function of time during EC process ($C_{NaCl} = 1 \text{ g L}^{-1}$; $C_{DY} = 200 \text{ mg L}^{-1}$; $d = 2 \text{ cm}$; $U = 12 \text{ V}$ ($i = 83 \text{ A}^2$))

Inter-electrode distance

We varied the distance between the electrodes $d = 0.8$; 1; 1.5 and 2 cm while fixing the other factors. The results are shown in Figure 10. When increasing the inter-electrode distance, the EC efficiency also increased. This can be explained as follows: for $d = 2 \text{ cm}$, there would be more probabilities to generate global flocs that are able to adsorb more dye molecules.

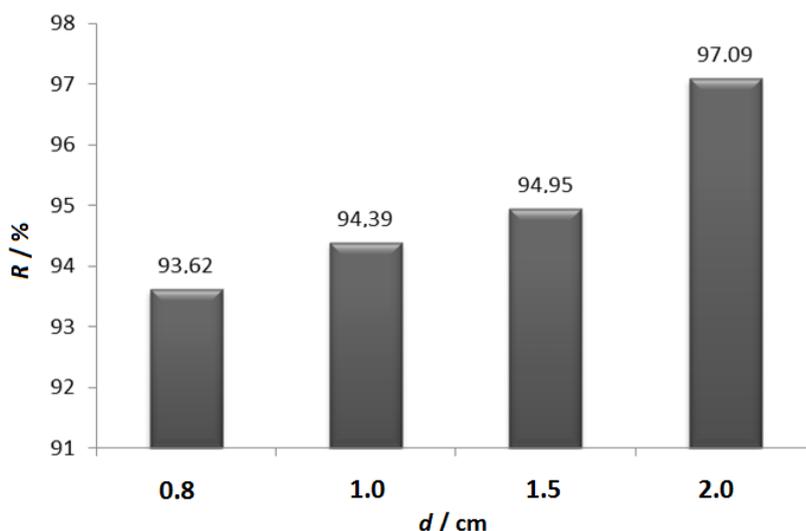


Figure 10. Effect of the inter-electrode distance on the EC performance ($C_{NaCl} = 1 \text{ g L}^{-1}$, $C_{DY} = 200 \text{ mg L}^{-1}$, $\text{pH} = 6.5$, $U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$)).

DY concentration

The aim of this part is to determine whether the EC method was applicable to solutions with a range of concentrations from 20 to 500 mg L^{-1} . The solutions were electrolysed, for a treatment time of 45 min, at a fixed voltage $U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$) and an inter-electrode distance of 2 cm. The results obtained are shown in Fig. 11.

Figure 11 shows that the EC method is effective in the range of selected concentrations. A yield of 97 % is reached at a dye concentration of 200 mg L^{-1} . The results obtained can be justified by

the increased probability of contact with the dye molecules to aluminum hydroxide $Al(OH)_3$ to form flocs of large sizes; thereby facilitating their separation by their attachment to the bubbles of released gases at the electrodes.

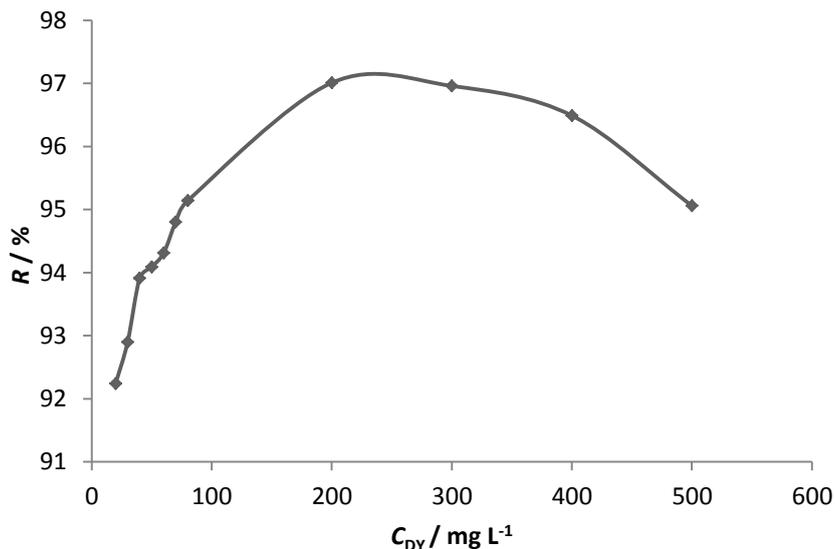


Figure 11. EC performance as a function of DY concentration
 $C_{NaCl} = 1 \text{ g L}^{-1}$; $pH \ 6.5$; $d = 2 \text{ cm}$, $U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$)

EC using Fe electrodes

To check if DY can be removed by EC using iron electrodes, some tests using the Al optimum conditions are performed. The results obtained are compared with those obtained with aluminum electrodes (Figure 12).

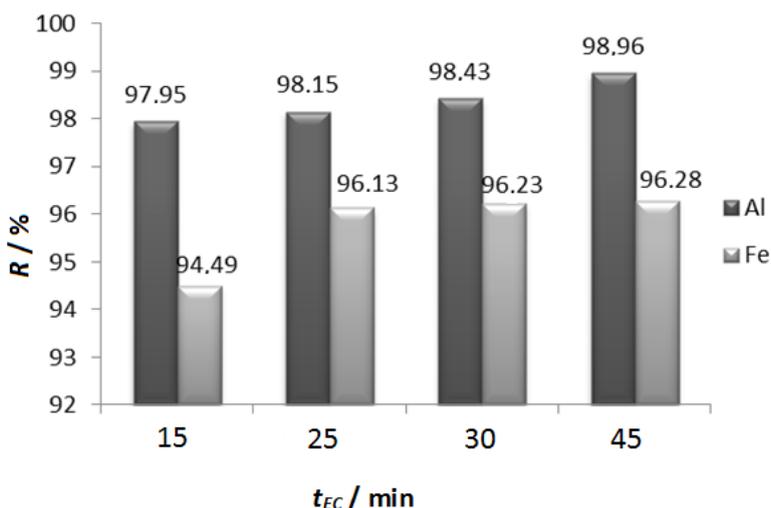


Figure 12. EC using Al and Fe electrodes: $C_{DY} = 200 \text{ mg L}^{-1}$; $C_{NaCl} = 1 \text{ g L}^{-1}$; $pH \ 6.5$; $d = 2 \text{ cm}$, $U = 12 \text{ V}$ ($i = 83 \text{ A m}^{-2}$)

During EC treatment using Fe electrodes, (1) clouds of green flocs came from the anode surface and settled to the beaker bottom and, (2) on the solution surface, two layers of foam were observed: the first a red-brown color, and below, the second green.

We find that the rate of reduction of the dye increased with time until a yield of 96.28 % in the case of iron electrodes (Figure 12). Comparing the test results with aluminum electrodes ($R = 98.96 \%$), we can say that iron is also effective in removing DY.

The reactions involved in the EC using iron electrodes are as follows: The iron, after oxidation in the electrolytic system, produces iron hydroxide $\text{Fe(OH)}_n(\text{s})$, with $n = 2$ or 3 ; and two mechanisms have been proposed [6,12,14,15,24,38]:

- Mechanism 1 (green coloration, $\text{Fe(OH)}_2(\text{s})$):



- Mechanism 2 (brown coloration, $\text{Fe(OH)}_3(\text{s})$):



The species $\text{Fe(OH)}_n(\text{s})$ formed (by the two mechanisms) remained in the aqueous phase in the form of gelatinous suspension which can then remove the pollutants from the water (Figure 13), either by complexation, or by electrostatic attraction, followed by coagulation and flotation or sedimentation [24,25,27,28].

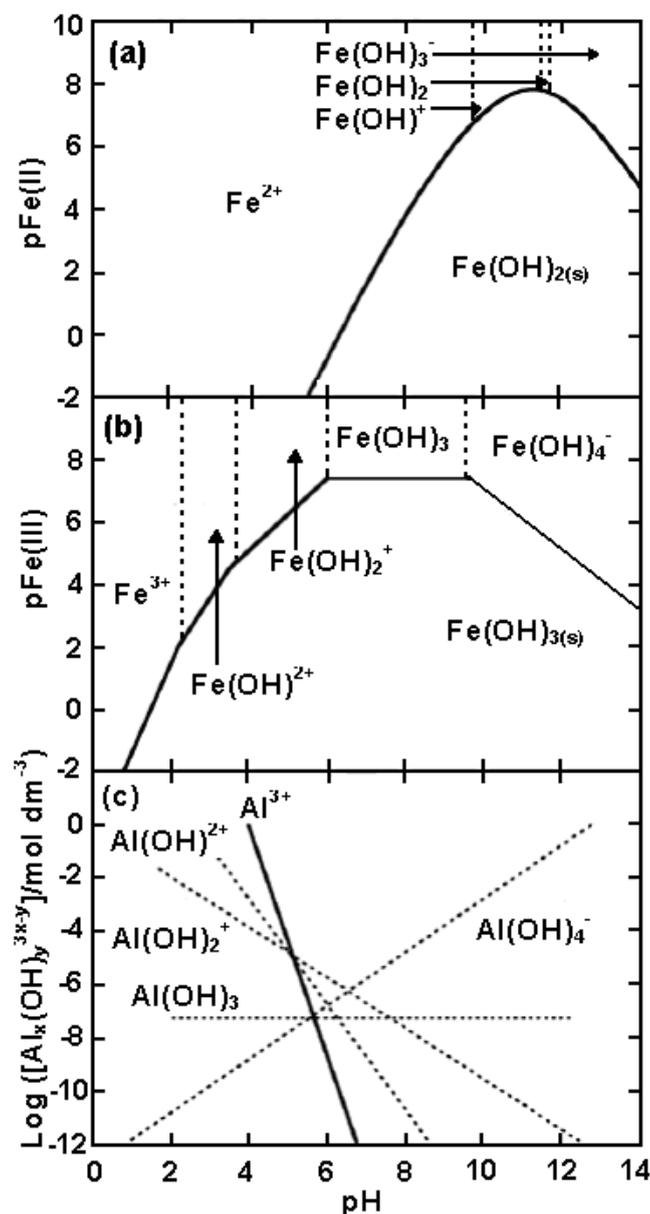


Figure 13. Predominance-zone diagrams for (a) Fe(II) and (b) Fe(III) chemical species in aqueous solution. The straight lines represent the solubility equilibrium for insoluble Fe(OH)_2 and Fe(OH)_3 , respectively, and the dotted lines represent the predominance limits between soluble chemical species. (c) Diagram of solubility of Al(III) species as a function of pH [27,28].

Conclusions

Highly performant EC process is shown in dye removal during 45 min for 200 mg/L dye concentration at $i = 350 \text{ A/m}^2$ (applied voltage 12 V) and $C_{\text{NaCl}} = 1 \text{ g/L}$ reaching 98 % for pH 3 and 10 and 99 % for pH 6. For 10 min, DY is also efficiently removed (86 %) showing that EC process may be well convenient for textile industry wastewater treatment. EC using Fe electrodes is slightly less performant than EC using Al electrodes.

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References

- [1] A. R. Amani-Ghadim, S. Aber, A. Olad, H. Ashassi-Sorkhabi, *Chemical Engineering and Processing* **64** (2013) 68-78.
- [2] W. Lemlikchi, S. Khaldi, M.O. Mecherri, H. Lounici, N. Drouiche, *Separation Science and Technology* **47** (2012) 1682-1688.
- [3] M. S. Secula, B. Cagnon, T. F. de Oliveira, O. Chedeville, H. Fauduet, *Journal of the Taiwan Institute of Chemical Engineers* **43** (2012) 767-775.
- [4] B. Merzouk, B. Gourich, K. Madani, Ch. Vial, A. Sekki, *Desalination* **272** (2011) 246-253.
- [5] M. Kobya, E. Demirbas, O. T. Can, M. Bayramoglu, *Journal of Hazardous Materials* **B132** (2006) 183-188.
- [6] A. Aleboye, N. Daneshvar, M. B. Kasiri, *Chemical Engineering and Processing* **47** (2008) 827-832.
- [7] S. Zodi, B. Merzouk, O. Potier, F. Lopicque, J.-P. Leclerc, *Separation and Purification Technology* **108** (2013) 215-222.
- [8] M. Eyvaz, M. Kirlaroglu, T. S. Aktas, E. Yuksel, *Chemical Engineering Journal* **153** (2009) 16-22.
- [9] E. Pajootan, M. Arami, N. M. Mahmoodi, *Journal of the Taiwan Institute of Chemical Engineers* **43** (2012) 282-290.
- [10] M.-C. Wei, K.-S. Wang, C.-L. Huang, C.-W. Chiang, T.-J. Chang, S.-S. Lee, S.-H. Chang, *Chemical Engineering Journal* **192** (2012) 37-44.
- [11] C. Phalakornkule, P. Sukkasem, C. Mutchimsattha, *International Journal of Hydrogen Energy* **35** (2010) 10934-10943.
- [12] M. Chafi, B. Gourich, A. H. Essadki, C. Vial, A. Fabregat, *Desalination* **281** (2011) 285-292.
- [13] P. Cañizares, F. Martínez, M.A. Rodrigo, C. Jiménez, C. Sáez, J. Lobato, *Separation and Purification Technology* **60** (2008) 147-154.
- [14] C. Gong, Z. Zhang, H. Li, D. Li, B. Wu, Y. Sun, Y. Cheng, *Journal of Hazardous Materials* **274** (2014) 465-472.
- [15] J. Llanos, S. Cotillas, P. Cañizares, M.A. Rodrigo, *Water Research* **53** (2014) 329-338.
- [16] S. Pulkka, M. Martikainen, A. Bhatnagar, M. Sillanpää, *Separation and Purification Technology* **132** (2014) 252-271.
- [17] E-S. Z. El-Ashtoukhy, N.K. Amin, *Journal of Hazardous Materials* **179** (2010) 113-119.
- [18] A. K. Golder, N. Hridaya, A. N. Samanta, S. Ray, *Journal of Hazardous Materials* **B127** (2005) 134-140.
- [19] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, H. Hamitouche, *Chemical Engineering and Processing* **49** (2010) 1176-1182.
- [20] Y. Ş Yildiz, *Journal of Hazardous Materials* **153** (2008) 194-200.

- [21] C.-L. Yang, J. McGarrah, *Journal of Hazardous Materials* **B127** (2005) 40-47.
- [22] J. G. Ibanez, M. M. Singh, Z. Szafran, *Journal of Chemical Education* **75** (1998) 1040-1041.
- [23] D. Ghernaout, S. Irki, A. Boucherit, *Desalination and Water Treatment* **52** (2014) 3256-3270.
- [24] D. Ghernaout, *Desalination and Water Treatment* **51** (2013) 7536-7554.
- [25] D. Ghernaout, M. W. Naceur, B. Ghernaout, *Desalination and Water Treatment* **28** (2011) 287-320.
- [26] D. Ghernaout, B. Ghernaout, *Desalination and Water Treatment* **27** (2011) 243-254.
- [27] D. Ghernaout, M.W. Naceur, A. Aouabed, *Desalination* **270** (2011) 9-22.
- [28] C. A. Martínez-Huitle, E. Brillas, *Applied Catalysis B: Environmental* **87** (2009) 105-145.
- [29] D. Ghernaout, A. Mariche, B. Ghernaout, A. Kellil, *Desalination and Water Treatment* **22** (2010) 311-329.
- [30] A. Saiba, S. Kourdali, B. Ghernaout, D. Ghernaout, *Desalination and Water Treatment* **16** (2010) 201-217.
- [31] D. Ghernaout, B. Ghernaout, *Desalination and Water Treatment* **16** (2010) 156-175.
- [32] D. Belhout, D. Ghernaout, S. Djezzar-Douakh, A. Kellil, *Desalination and Water Treatment* **16** (2010) 1-9.
- [33] D. Ghernaout, B. Ghernaout, A. Boucherit, M.W. Naceur, A. Khelifa, A. Kellil, *Desalination and Water Treatment* **8** (2009) 91-99.
- [34] D. Ghernaout, A. Badis, A. Kellil, B. Ghernaout, *Desalination* **219** (2008) 118-125.
- [35] D. Ghernaout, B. Ghernaout, A. Saiba, A. Boucherit, A. Kellil, *Desalination* **239** (2009) 295-308.
- [36] D. Ghernaout, B. Ghernaout, A. Boucherit, *Journal of Dispersion Science and Technology* **29** (2008) 1272-1275.
- [37] M. Muthukumar, M. Govindaraj, A. Muthusamy, G. Bhaskar Raju, *Separation Science and Technology* **46** (2011) 272-282.
- [38] C. Barrera-Díaz, B. Bilyeu, G. Roa, L. Bernal-Martinez, *Separation and Purification Reviews* **40** (2011) 1-24.