

Contribution to the study of electrocoagulation mechanism in basic textile effluent

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Abstract

Electrocoagulation method with iron electrode is used to treat the industrial textile wastewater in batch reactor. The effects of operating parameters such as time and potential electrolysis on the decolourization and COD removal efficiency have been investigated. The results indicate that electrocoagulation is very efficient and able to achieve 100% colour and 84% COD removal in 3 min at potential 600 mV. The effluent wastewater is very clear and its quality exceed the direct discharge standard. Furthermore, the mechanism of electrocoagulation is elucidated by zeta potential measurement.

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1. Introduction

Textile industries are one of the most polluting industries in terms of the volume and complexity of its effluents discharge. The dyeing and finishing operations in textile industries contribute a major share to wastewater generation. Dye bath effluents, in particular, are not only aesthetic pollutants by nature of their colour, but may interfere with light penetration in the receiving bodies of water, thereby disturbing biological processes. Furthermore, dye effluent may contain chemicals, which are toxic and carcinogenic. Moreover, textile wastewater are known to have various pH solution (either alkaline or acidic, depending on the process used), high temperature, high biological oxygen demand (BOD), high chemical demand (COD) and high concentrations of suspended solids (SS). Textile mill effluents are also characterised by high levels of colour caused by residual dyes.

Conventionally textile wastewater is treated through biological, physical and chemical methods [1,2]. Biological treatment processes are often ineffective in removing dyes which are highly structured polymers with low biodegradability

[3]. However, various physical–chemical techniques, such as chemical coagulation, adsorption on activated carbon, reverse osmosis and ultrafiltration [1,2], are also available for the treatment of aqueous streams to eliminate dyes. But those later are limited by the low concentration ranges that can be treated coupled with the high concentrations in reject streams. Further, the main drawbacks of chemical coagulation are the addition of further chemicals. In recent years, ozonation [3,4] and photooxidation [4–6] have been proposed as alternatives because they were qualified to be very effective. But the high cost of these methods leads to further consideration. Indeed, electrochemical method has been successfully tested [1,7] to deal with dyeing wastewater. But as for some dyes, which have good water solubility and small molecule weight, traditional electrochemical ways do not work effectively [3].

Electrocoagulation is a process consisting of creating metallic hydroxide flocs within the wastewater by electrodisolution of soluble anodes, usually constituted by iron or aluminium. This method has been practiced for most of the 20th century with limited success. Recently, there has been renewed interest in the use of electrocoagulation owing to the increase in environmental restrictions on effluent wastewater. Indeed, electrocoagulation has been tested successfully to treat urban wastewater [8], restaurant wastewater [9,10] and oil–water emulsion [9–11]. It has also

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been used to remove clay suspension [12,13] and heavy metal [14–16].

The objective of the present study is to examine the feasibility of electrocoagulation in treating textile wastewater, to determine the optimal operational conditions and to establish which iron hydroxide, formed during electrolysis, is responsible of electrocoagulation process.

2. Materials and methods

In our investigation, we use a sample of textile wastewater, which is taken from a textile-dyeing operation from commercial textile industry located in Casablanca, Morocco. Table 1 summarises the characteristics of the raw textile effluents.

Experiments were carried out, at a laboratory scale, in cell equipped with two iron electrodes (anode and cathode with 6.4 cm^2 area) and saturated Ag/AgCl as reference electrode. A potentiostat (VoltaLab, PGZ 100) is used to apply the desired potential (Fig. 1). In each run, 100 cm^3 wastewater is placed into electrolytic cell. At the end of the experiment, the solution is filtered before analysis. Chemical oxygen demand (COD) is measured using COD reactor with direct reading spectrophotometer (AL 32, Aqualitic). Iron concentration is determined by atomic absorption spectroscopy (AAS, Varian model AA-20). Apparent colour of samples is determined by measuring the average absorbance at 436, 525 and 620 nm [17] by using Helios γ UV–vis spectrometer. A Malvern zeta potential analyzer (model zetasizer 3000 HS, Malvern Instrument) is used to determine zeta potential of flocs formed during electrolysis.

3. Experimental results

3.1. Effect of electrocoagulation time

3.1.1. Effect of electrocoagulation time on COD removal

Electrocoagulation test was first performed at fixed potential of 600 mV and at different electrolysis times. The variation of COD with electrolysis time is shown in Fig. 2. COD decreases

Table 1
Characterisation of the textile wastewater

Parameter	Value
pH	10.6
Temperature ($^{\circ}\text{C}$)	100
Conductivity (ms/cm)	42.6
COD (mg/l)	485
BOD ₅ (mg/l)	80
Chloride (mg/l)	27069
Sulfate (mg/l)	2161
Turbidity (NTU)	1.45
Sodium (mg/l)	5965
Calcium (mg/l)	260
Suspended solids (mg/l)	70
A _{436 nm}	0.663
A _{525 nm}	0.415
A _{620 nm}	0.286
Fe (mg/l)	0.92

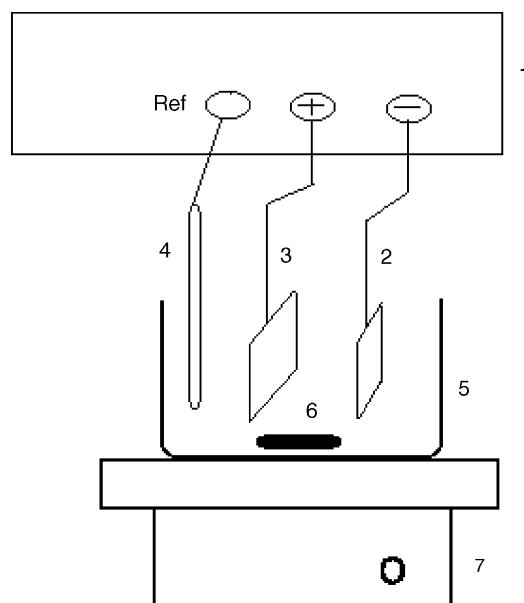


Fig. 1. Electrocoagulation set-up. 1: Potentiostat, 2: Anode, 3: Cathode, 4: Reference electrode, 5: Batch reactor, 6: Magnetic stir bar, 7: Magnetic stirrer.

with increasing electrolysis time and starts to increase after 3 min. At this time COD decreases from 485 to 78.5 mg/l with a removal efficiency of 84%. The same trend of evolution of COD with electrolysis time is reported by Diaz et al. [16].

3.1.2. Effect of electrocoagulation time on absorbance

In Fig. 3, we represent the absorbance at 436, 525 and 620 nm. As shown in this figure, the absorbance decreases with increasing electrolysis time, which is good agreement with literature [18,19]. After 3 min, the absorbance is very low and the decolourization efficiency of effluent reaches 100%.

3.1.3. Effect of electrolysis time on pH and residual iron

The variation of pH and the iron generated concentration in solution during electrolysis are given in Fig. 4. From this figure, it can be seen that the pH of the effluent does not change with electrolysis time. This result was found by Kobya et al. [20] for initial pH > 8. However, the iron in solution presents a peak of 10 mg/l at lower time. But at long time the solution becomes practically exempt from iron.

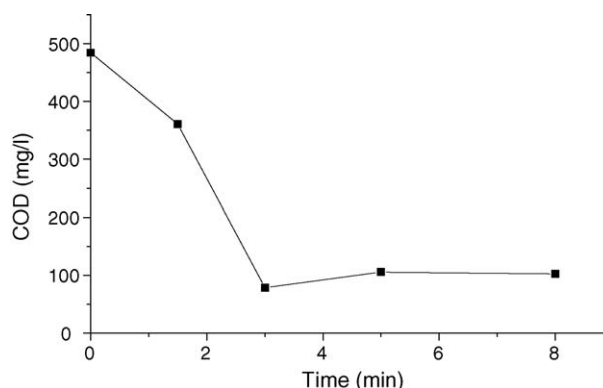


Fig. 2. Evolution of COD with electrolysis time at $E = 600 \text{ mV}$.

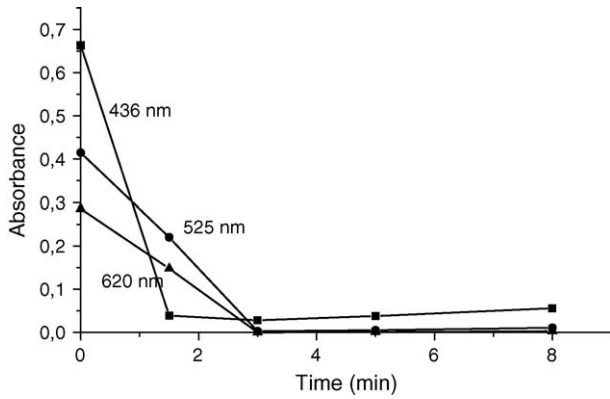


Fig. 3. Evolution of the absorbance at 436, 525 and 620 nm with electrolysis time at $E = 600$ mV.

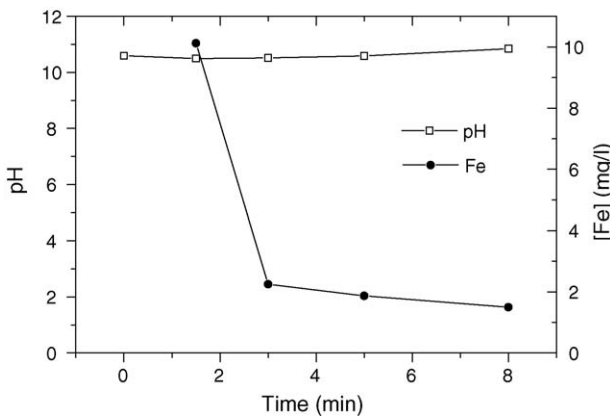


Fig. 4. Evolution of pH and residual iron concentration in solution with electrolysis time at $E = 600$ mV.

3.2. Effect of electrolysis potential

3.2.1. Effect of electrolysis potential on COD removal

The investigation of the effect of electrolysis potential on treatment efficiency was conducted under a fixed electrocoagulation time of 3 min. Evolution of COD with electrolysis potential is presented in Fig. 5. The COD decreases with increasing potential. This behaviour is similar to those founded in literature [5,19].

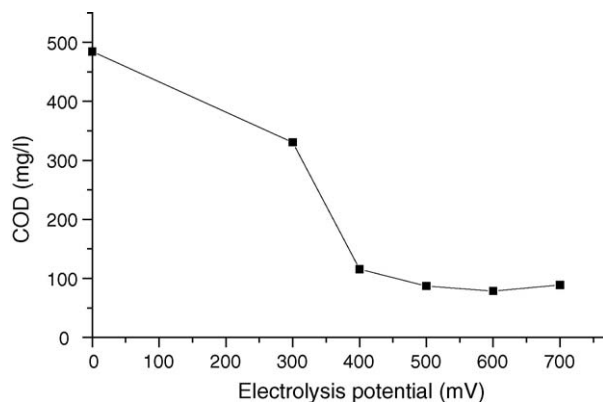


Fig. 5. Evolution of COD with electrolysis potential (electrolysis time = 3 min).

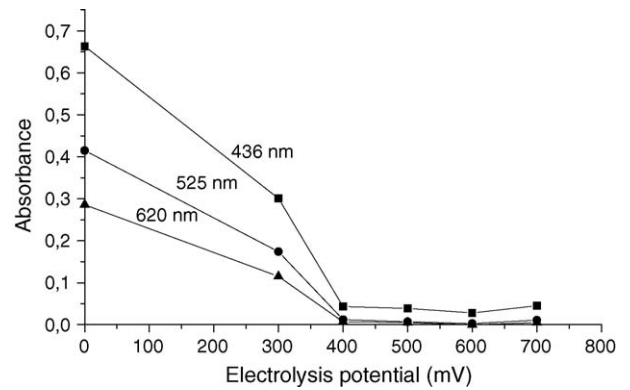


Fig. 6. Evolution of the absorbance at 436, 525 and 620 nm with electrolysis potential (electrolysis time = 3 min).

At $E = 600$ mV, the COD decreases from 485 to 78.5 mg/l, which correspond to 84% removal efficiency.

3.2.2. Effect of electrolysis potential on absorbance

The evolution of absorbance at 436, 525 and 620 nm with electrolysis potential is represented in Fig. 6. It shows that the decolourization of effluent increases rapidly with increasing electrolysis potential. The same trend is found in previous works [5,19]. Then, at potential of 400 mV, the decolourization efficiency is 100%. Furthermore, from Figs. 5 and 6, we can consider $E = 600$ mV as an optimum electrolysis potential.

3.2.3. Effect of electrolysis potential on pH solution and dissolved iron

Fig. 7 shows clearly that the pH solution is independent from electrolysis potential. However, the load of iron in solution after treatment is high at lower potential and becomes practically zero at high potential.

3.3. Determination of zeta potential

The stability of a pollutant is determined by its physico-chemical properties. Many pollutants are composed of similarly charged particles that repel each other, with the repulsive forces creating a stable, colloidal system. In order to maintain

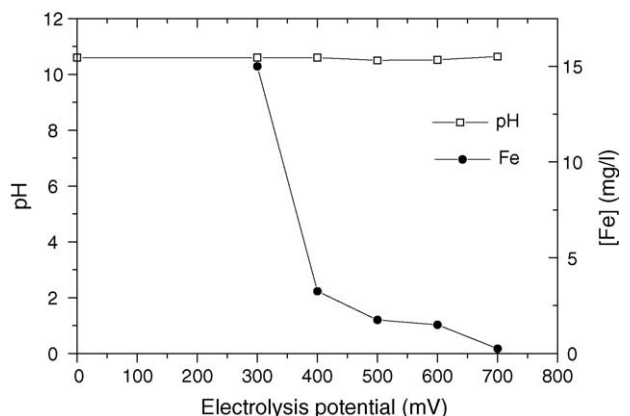


Fig. 7. Variation of pH and residual iron generated in solution with electrolysis potential (electrolysis time = 3 min).

electroneutrality, oppositely charged ions are attracted to the (charged) pollutant particles. The attraction of counter ions to a negatively charged pollutant forms an electric double layer divided into a Stern and diffuse layer. It is difficult to measure the charge at the colloid surface, due to the charge concentrations in the Stern and diffuse layers. Consequently, the zeta potential is used as an experimental measure of the effective charge of the particle as it moves through the solution, providing a direct indicator of solution stability [21].

The role of the iron matrix generated during electrolysis is to destabilise the colloidal suspension by reducing the attractive forces, thereby lowering the energy barrier and enabling particles to aggregate. A number of electrocoagulation mechanisms including charge neutralisation, double layer compression, bridging and adsorption, have been postulated dependent on the physical and chemical properties of the solution, pollutant and coagulant.

The measure of zeta potential evolution with time (for an applied potential of 600 mV) and with potential (at fixed time of 3 min) were executed in objective to determine the charge of particle formed during the electrocoagulation. The obtained results are plotted in Fig. 8. It shows that zeta potential of formed flocs is negative and constant in all conditions.

3.4. Current efficiency

The current efficiency is defined as the ratio of the actual electrode consumption to the theoretical value. It is an important

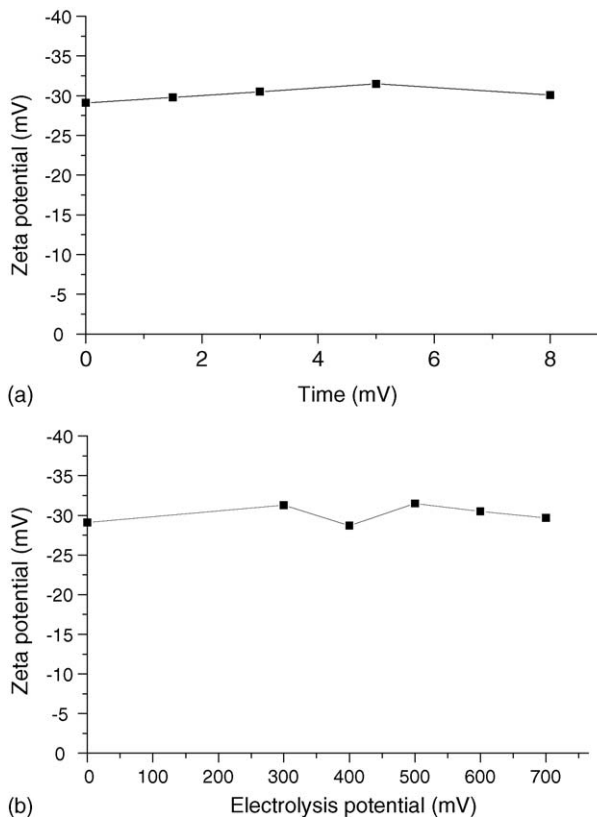


Fig. 8. (a) Evolution of zeta potential with time at $E = 600$ mV, (b) evolution of zeta potential with electrolysis potential (electrolysis time = 3 min, pH 10.6, pH of wastewater).

parameter for the electrocoagulation process because it affects the lifetime of the electrode. So, the both values, theoretical and experimental, consumed electrode are determined. The first one is calculated using Faraday's law:

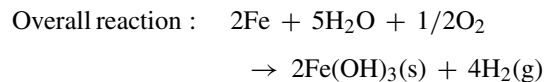
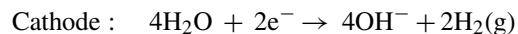
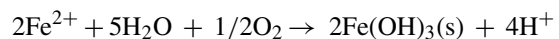
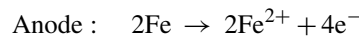
$$m = ItM/ZF$$

$Z = 2$ is the number of electrons corresponding to iron oxidation, M the molecular weight (g/mol) and F is Faraday's constant (96 500 C) and the second value is determined by weighing the electrode before and after experiment. Results show that the both values are similar and increase with electrolysis time and potential. Then, the current efficiency is 100%.

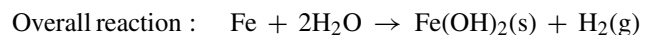
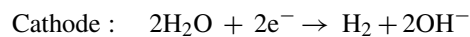
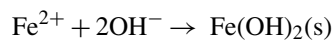
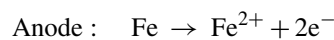
4. Discussion

In the case of electrocoagulation process using iron anode, two mechanisms for the production of metal hydroxide have been proposed [19,22]:

- Mechanism I:



- Mechanism II:



In all our experiments and during electrolysis, the solution becomes green and bubbles of gas are seen at cathode. After few times, the effluent becomes clear and a green and yellow sludge is formed. The green and yellow colours can probably be attributed to Fe(II) and Fe(III) hydroxide. Metal hydroxides formation occurs following mechanisms I and II cited above. These hydroxide flocs have a large specific surface area that can remove pollutants by adsorption, surface complexation or electrostatic attraction.

The removal efficiency of COD and colour depends on the quantity of iron generated, which is bound with time and potential electrolysis. Then, when one of two parameters increases, the distribution of the coagulation agent density is more effective. This can produce the related coagulation and completes the removal of pollutants. Consequently, high removal efficiency of COD and colour are observed at high time and high potential. Indeed, at a time of 3 min and a potential of 400 mV a quantity of iron hydroxide is sufficient to have 100% of decolourization efficiency but COD removal is low. On the other hand, the maximal elimination of the COD (84%) is reached at a potential of 600 mV. Consequently, 3 min of electrolysis time and 600 mV of electrolysis potential are optimum conditions for treatment. According to Muruganathan et al. [23], at high potential, formation of Fe (III) ions is favour. In a basic environment, simultaneous formations of ferric hydroxide/oxides are also expected. Precipitates of Fe(III) hydroxides thus formed have a coagulating character better than Fe(II) hydroxide, because Fe(OH)₃ is more stable than Fe(OH)₂. Then, the removal efficiency is good.

Generally, the mechanism of electrocoagulation for wastewater treatment is very complex. The COD removal process may involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment. However, the colour removal may involve, besides adsorption, complexation with the iron hydroxide forming ionic bonds. Colour removal can also take place if some of the substituents, which determine the colour, are altered.

In order to understand the mechanism of removal of pollutants and explain more the obtained results, zeta potential measurements were carried out at potential of 600 mV under different electrolysis time, and at 3 min under different potentials. The value of zeta potential of the formed flocs is -30 mV and solution pH = 10.6 remains stable.

In Fig. 9, we represents the evolution with pH of zeta potential of Fe(II) and Fe(III) hydroxide resulting from iron ions synthetic solutions.

The obtained result shows that:

- The zeta potential of Fe(III) hydroxide is stable at pH value $2 < \text{pH} < 10$ and its value is -4 mV.

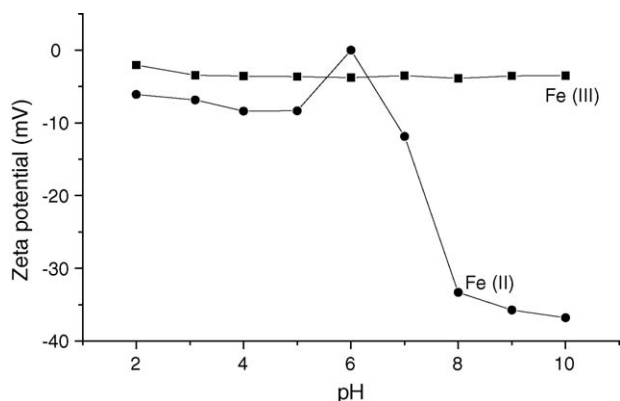


Fig. 9. Evolution of zeta potential of iron hydroxide II and III with pH (in synthetic solution).

- The zeta potential of Fe(II) hydroxide is more negative in basic middle than in acidic one and the iso-electric point is observed at a pH 6.

As given in this figure, at pH 10 (pH of wastewater) the zeta potential of Fe(OH)₃ is -4 mV and the one of Fe(OH)₂ is -37 mV. This later value is comparable with the one of electrocoagulation tests (-30 mV). Then, the probable formed flocs are Fe(II) hydroxide. Since the zeta potential of this precipitate remains the same at all experiments. So, there isn't any chemical interaction between the pollutants and iron hydroxide precipitate. But, the pollutants can probably removed by hydrogen bonding and the van der Waals interaction. This type of attraction does not require any change of zeta potential. Also, the pollutants are possibly enmeshed in the pore of porous iron hydroxide precipitate. And if it is the case, zeta potential will have the same value in all run. Another more probable mechanism can be consider for electrocoagulation, consist in ferrous hydroxide formation. It's about sweep flocculation. The precipitate can physically sweep the pollutants from the suspension. This mechanism does not involve any change in charge. Furthermore, the lower removal efficiency at low time and potential can be explained by the fact that the amount of precipitate formed is not enough.

The pH solution does not change during all experiences because the electrocoagulation exhibits some pH buffering capacity, especially in alkaline medium [20]. Also, this result permits us to conclude that all hydroxyl ions (OH⁻) generated during reduction of water to the cathode lead to the formation of the iron hydroxide. However, the residual iron in solution at lower potential and time (15 mg/l) can be explained by the fact that, this potential or this time, is insufficient to enhance to the complete precipitation of iron. At pH 10.6 (pH of the solution treated), the dominant specie of dissolved iron is Fe(OH)₄⁻ [16]. But, when we enhance the electrolysis time or when the electrolysis potential increases, the solution practically becomes exempt of the iron because the middle grow more rich by hydroxyl ions (OH⁻). Generally, the quantity of dissolved iron found in all tests is very weak, which can be attributed to alkaline pH of wastewater, because the iron precipitates totally in this range of pH.

5. Conclusion

Electrocoagulation is an efficient process to treat textile wastewater characterised by high dyes content and high COD content. The time and potential are the most important operation variable for treatment efficiency. The results showed that (3 min, 600 mV) are optimum conditions. The removal efficiency of colour and COD of the effluent is 100 and 84%, respectively. Zeta potential measurement demonstrate that iron hydroxide Fe(OH)₂ is probably responsible of electrocoagulation process.

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