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BASIC RED DYE REMOVAL BY COUPLING ELECTROCOAGULATION PROCESS WITH BIOLOGICAL TREATMENT

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Abstract

The applicability of an electrocoagulation process with the biological treatment for the color removal of C.I. Basic Red 46 (BR46) dye was studied. It was shown that decolorization efficiency increased by increasing current density (j), pH, temperature (T) and agitation speed (ω) and decreased with the initial dye concentration $[BR46]_0$. The optimal conditions in presence of a grid electrode (waste) used as cathode were found to be $j=9 \text{ mA cm}^{-2}$, pH 8, $T=35^\circ\text{C}$, $[BR46]_0=30 \text{ mg L}^{-1}$ and $\omega=120 \text{ rpm}$. Under these conditions, the electrocoagulation process was able to achieve 100% color removal efficiency in 5 min. The kinetics study showed that the apparent rate constants increased with increasing current density and the results suggest also a zero-order kinetic model. In addition, the plot of $[BR46]_t/[BR46]_0$ ratio vs time presents two steps. The first step, named latency period (t_{latency}) is current-dependent, but depended only slightly on the initial BR46 dye concentration. The latency period obtained varies roughly as $1/I$ and a minimal iron concentration was required before electrocoagulation started (0.083 mg L^{-1}). The C.I. Basic Red 46 dye did not adsorb onto the flocs in its molecular form. The biodegradability of the solution treated by electrocoagulation process under the optimal conditions was examined and the increase of the BOD₅/COD ratio from 0.05 to 0.35 showed the enhancement of the biodegradability of the pretreated solution. The electrocoagulation coupled to 16 days biological treatment leads to almost 65% of the dissolved organic carbon mineralized by the hybrid process.

Keywords: activated sludge process, biological treatment, C.I. Basic Red 46 dye, electrocoagulation, textile effluent

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1. Introduction

Wastewaters generated by textile industries are known to contain considerable amounts of toxic aromatic dyes, especially azo dyes. It is well known that some azo dyes and their degradation products, such as aromatic amines, are highly carcinogenic. The colored and pesticides wastewater released into the ecosystem is a dramatic source of esthetic pollution and perturbation in the aquatic life (Daneshvar et al., 2007; Yola et al., 2014).

Conventionally, textile wastewater is treated through biological, physical and chemical methods (Mohan et al., 2001; Sevimli and Sarikaya, 2002; Zaroual et al., 2006; Tawfik et al., 2017). Biological treatment processes are often ineffective for removing dyes which are highly structured polymers with low biodegradability (Can et al., 2003). However, various physical–chemical techniques, such as chemical coagulation, adsorption on activated carbon, reverse osmosis and ultrafiltration (Atar et al., 2011; Janoš et al., 2016; He and Yan, 2009; Mohan et al., 2001;

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Olgun and Atar, 2009; Sevimli and Sarikaya, 2002; Zaroual et al., 2006), are also available for the treatment of aqueous streams to eliminate dyes. But the former methods are limited by the low concentration range that can be treated, coupled to high concentration in reject streams. Further, the main drawback of chemical coagulation is the addition of chemicals. In recent years, ozonation (Can et al., 2003; Zaroual et al., 2006) and photo-oxidation (Chu and Ma, 1998; Montazerzohori and Hoseinipour, 2017) have been proposed as alternatives because they were shown to be very effective but the high cost of these methods limits their practical use. Similarly, electrochemical methods have been successfully tested (Mohan et al., 2001; Szpyrkowicz et al., 2000) to deal with dyeing wastewater. But as for some dyes which exhibit high water solubility and have a low molecule weight, traditional electrochemical methods are inefficient (Can et al., 2003).

Electrocoagulation (EC) is an attractive method for the treatment of various kinds of wastewater, by virtue of various benefits including environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness. This process is characterized by simple equipment, easy operation, a shortened reactive retention period, a reduction or absence of equipment for adding chemicals and a decreased amount of precipitate or sludge which sediments rapidly (Bayramoglu et al., 2007; Yousuf et al., 2009; Szykh et al., 2018).

The process of electrocoagulation is based on the principle of sacrificial anodes. When a potential or a current is applied from an external power source, the anode material undergoes oxidation, while the cathode is subjected to reduction or reductive deposition of elemental metals. In electrocoagulation in the galvanostatic mode, current is imposed between two electrodes (usually in iron or aluminium) immersed in an electrochemical cell containing an electrolyte to release, in situ, metal ions (Fe^{2+} and Fe^{3+} , or Al^{3+}). The metal ions are formed at the anode and hydrogen gas is released from the cathode, which would also help to float the flocculated particles out of water. The electrochemical reactions with metal as the anode may be generally summarized in six main processes that may affect pollutants during electrocoagulation (Andrade-Cerqueira and da Costa, 2012; Daneshvar et al., 2006; Marques, 2012; Yousuf et al., 2009):

1. Migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralization of particles, droplets or colloids.

2. The cation or the hydroxyl ion (OH^-) forms a precipitate with the pollutant, which mainly occurs for the removal of heavy metals.

3. The metal cations interact with OH^- to form hydroxides, which have high adsorption properties, thus bonding the pollutant (bridge coagulation).

4. The hydroxides form larger lattice-like structures and sweep through the water (sweep coagulation).

5. The pollutants are subjected to electrochemical oxidation or reduction and converted into less toxic species.

6. They are removed by electroflotation and adhesion to bubbles, or sedimentation.

The main electrochemical reactions at the electrodes can be described as follows (Daneshvar et al., 2006):

- At the anode, there may be a competition between the electrodisolution of the metal M and water oxidation into O_2 :



- At the cathode, water reduction into H_2 differs as a function of pH:

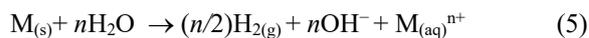
- in alkaline solutions:



- in acid solutions:



The objective is to achieve the following overall reaction by minimizing water oxidation on the anode:



When Fe metal is used as the anode, iron oxidation in an electrolytic system produces $\text{Fe}(\text{OH})_2^+$, $[\text{Fe}(\text{OH})_2]^+$, $[\text{Fe}(\text{OH})_2]^{4+}$, $[\text{Fe}(\text{OH})_4]^+$, $[\text{Fe}(\text{H}_2\text{O})_2]^+$, $[\text{Fe}(\text{H}_2\text{O})_3\text{OH}]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, $[\text{Fe}(\text{H}_2\text{O})_8(\text{OH})_2]^{4+}$, $[\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4]^{2+}$, which transform finally into insoluble $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OH})_2$ forms (Daneshvar et al., 2006).

The very high energy cost is the major obstacle for the electrochemical technology development on an industrial scale. Many coupled and hybrid electrochemical processes have been proposed aiming developing more powerful process for dye removal (Brillas et al., 2015).

However, no studies have investigated the use of the electrocoagulation process coupled to the biological treatment with activated sludge in order to reduce the cost of the EC treatment. Then, the main objective of this work is to investigate electrocoagulation as a pretreatment step of the activated sludge process to enhance the degradability of a biorefractory dye using synthetic wastewater. The respective effects of the operating parameters of electrocoagulation on the color removal efficiency have been studied, such as current density, temperature, agitation speed, initial dye concentration and electrode geometry. Finally, the optimum conditions of electrocoagulation have been applied to assess the feasibility of the coupling of electrocoagulation process with the biological treatment.

2. Material and methods

2.1. Reagents

The dye used in this study is C.I. Basic Red 46 (Asucryl GRL 300%, CA 12221-69-1), denoted BR46, obtained from the Textile Algerian Company (Alfaditex Bejaia, 300 km east Algiers). The main characteristics and chemical structure of dye are reported in Table 1.

2.2. Experimental set-up and procedure

The experimental set-up is schematically shown in Fig. 1. The electrocoagulation unit consisted of a 1L electrochemical reactor with three iron electrodes (two anodes and one cathode). The anodes (55 mm×50 mm×1 mm) were cut from an iron plate and the cathode (55 mm×50 mm×0.2 mm) is a grid obtained from a discharge of a sieve manufacturing company (Fig. 1). The electrodes were arranged vertically and the distance between the electrodes was 10 mm which is a typical value reported in the literature (Aleboyeh et al., 2008; Can et al., 2006; Feng et al., 2007; Merzouk et al., 2009); pH, water

conductivity and volume were fixed to 8.11, 744 $\mu\text{S cm}^{-2}$ and 750 mL, respectively. The electrodes were connected to a precision DC power supply (GPS-3030D, Gw INSTEK, China). Mixing was carried out by a magnetic stirring bar. Before each run, electrodes were treated with an HCl (0.2 mol L⁻¹) aqueous solution and rinsed again with tap water for cleaning prior use to avoid passivation.

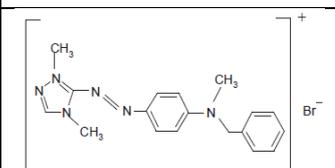
The experimental parameter ranges were selected as follows: initial BR46 concentration (30-200 mg L⁻¹), temperature (20-65°C), agitation speed (0-600 rpm) and current density (5-15 mA cm⁻²). Synthetic wastewater was prepared by dissolving 1 g L⁻¹ dye into tap water; the characteristics of the tap water are summarized in Table 2. After each electrocoagulation run, the liquid samples were centrifuged (6000 rpm, 4 min) for solid-liquid separation.

2.3. Analytical methods

2.3.1. Color removal efficiency measurements

In order to estimate the color removal efficiency, samples were collected periodically every minute during the experiments.

Table 1. Physico-chemical characteristics and chemical structure of BR46

Name	Chemical formula	Molecular Weight (g mol ⁻¹)	λ_{max} (nm)	Chemical structure
Asucryl GRL 300% (C.I. Basic Red 46)	C ₁₈ H ₂₁ N ₆ Br	400.9	531	

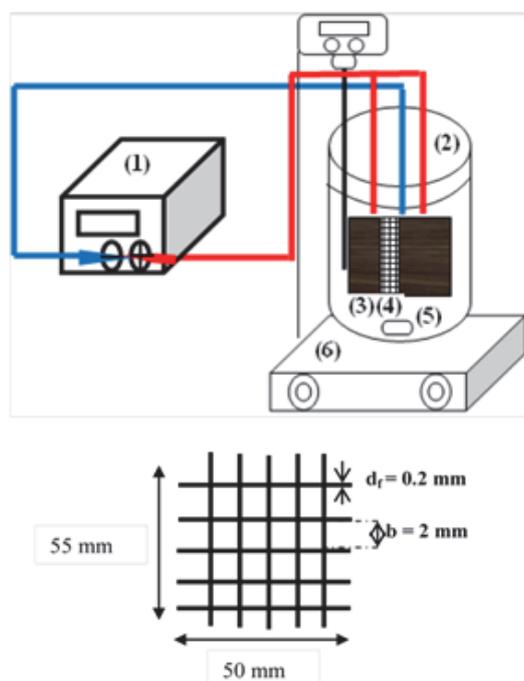


Fig. 1. Electrocoagulation set-up: (1) DC power supply; (2) Batch cell; (3) Anodes; (4) Cathode; (5) Magnetic stir bar; (6) Magnetic stirrer

Table 2. Physicochemical analysis of water

Parameter	Value	Unit	Guideline	Method
pH at 20°C	8.3		Guide: 6.5-8.5	NF T09-008
Conductivity at 20°C	637	$\mu\text{S cm}^{-1}$	2800	NA 749
Total hardness	1.7	$^{\circ}\text{C}$	10-50	NA 752
TA	00	mEq L^{-1}	/	NET 90 036
TAC	-2.2	$^{\circ}\text{C}$	/	NET 90 036
Calcium	84	mg L^{-1}	200	NF T 90-003
Chlorides	49.7	mg L^{-1}	500	NF T 90-014
Magnesium	34.1	mg L^{-1}	150	NF T 90-003
Nitrates	2.3	mg L^{-1}	50	NF T 90-045
Sulfates	108.8	mg L^{-1}	400	NF T 90-009

The residual concentration of dye (BR46) in the synthetic wastewater was determined spectrophotometrically at the maximum absorption wavelength, 531 nm, of the dye using an ultraviolet-visible light (UV-vis) system (Nanocolor UV/VIS, Macherey-Nagel, Hoerd, France) and calibration curves. All measurements were duplicated. The percentage of color removal ($R\%$) (Brillas et al., 2015) is determined from the relation given below (Eq. 6):

$$R(\%) = ((ABS_0 - ABS_t) / ABS_0) \times 100 \quad (6)$$

where: ABS_0 and ABS_t were the initial absorbance and at a given time t absorbance of RB46, respectively.

2.3.2. COD and BOD₅ measurements

Chemical oxygen demand (COD) and five-day biological oxygen demand (BOD₅) were measured using a Nanocolor 500D photometer (Macherey-Nagel, Hoerd, France); all COD and BOD₅ measurements were duplicated for statistical purpose. The determination of BOD₅ was carried out in test tubes in the presence of added nutrients according to EN 1899-1-H51. N-allylthiourea was also added as a nitrification inhibitor. The incubation of the samples was directly carried out in the test tubes and the determination of the amount of oxygen dissolved in water was measured after 5 days in accordance to the Winkler method (EN25813-G21) by photometric evaluation of iodine-color. The COD was measured using Kits Nanocolor® 15-160 mg L^{-1} COD according to DIN ISO 15705 at 148°C. The amount of oxygen required for the oxidation of the organic and mineral matter at 148°C for 2 h was quantified after oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ at acidic pH and under heating (Yahiaoui et al., 2013a, 2013b, 2014).

2.3.3. Dissolved organic carbon measurements

Dissolved organic carbon (DOC) was measured by TOC-V_{CPH/CPN} Total Organic Analyzer (Shimadzu, Japan). Samples taken were filtered through a 0.45 μm membrane syringe filter (Sartorius Stedim Biotech GmbH, Germany) for the measurement of dissolved organic carbon (Yahiaoui et al., 2013a, 2013b, 2014).

2.4. Biological treatment

Activated sludge was collected from a local wastewater treatment system (Sidi Ali Labhar, Bejaia, Algeria). It was first washed thoroughly at least five times with distilled water and centrifuged at 2500 rpm for 5 min to remove any residual carbon and mineral sources.

2.4.1. Media and culture conditions

Biological treatments of non-treated and electrolyzed solutions were carried out at 25°C in shake flasks (250 mL) for 16 days containing 0.5 g L^{-1} of activated sludge and the following mineral supplementation was added in the flasks: 0.5 mL of KH_2PO_4 : 43.8 mg L^{-1} , and Na_2HPO_4 : 33.4 mg L^{-1} , 0.150 mL of CaCl_2 : 27.5 g L^{-1} , ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$: 22.5 g L^{-1}) and of (NH_4NO_3 : 3 g L^{-1}). 0.5 mL of the following trace elements solution was also added in the medium ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 1.36 g L^{-1} , $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$: 0.24 g L^{-1} , $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$: 0.25 g L^{-1} , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$: 0.11 g L^{-1} , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$: 1.01 g L^{-1} , H_3BO_3 : 0.1 g L^{-1}). The pH was adjusted to 7.0 with 1 mol L^{-1} NaOH solution (Yahiaoui et al., 2013a, 2013b, 2014).

3. Results and discussion

3.1. Effect of the geometry of the cathode

The shape of the electrodes may affect the pollutant removal efficiency in the electrocoagulation process because it modifies the equipotential surfaces, the current lines and, finally, the cell potential. Figure 2 illustrates the color removal efficiency using different cathode geometries and surface area (perforated electrode, grid electrode and not perforated electrode). In Fig. 2, experiments were conducted under the following conditions: $[\text{BR46}]_0 = 30 \text{ mg L}^{-1}$, $j = 9 \text{ mA cm}^{-2}$, $\omega = 120 \text{ rpm}$, $T = 35^{\circ}\text{C}$ and initial pH 8. The plots in Figure 2 were similar with the three electrodes and they clearly demonstrate that 99% of the color was removed when using the three different shapes of the electrodes in less than 7 min. This constitutes a very interesting result, especially with the grid electrode which is a waste.

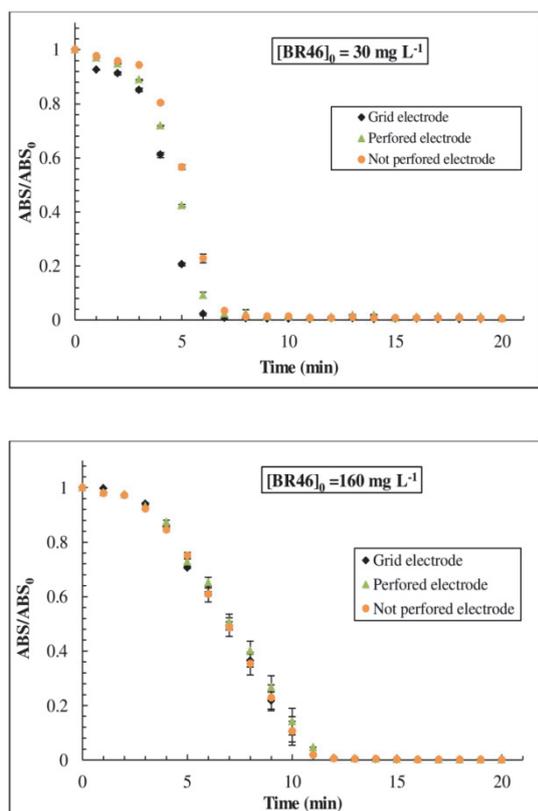


Fig. 2. Effect of the geometry of the cathode. Conditions: $[\text{BR46}]_0 = 30 \text{ mg L}^{-1}$, $j = 9 \text{ mA cm}^{-2}$, $\omega = 120 \text{ rpm}$, $T = 35^\circ\text{C}$ and initial pH 8

3.2. Effect of agitation speed

Agitation speed plays on mixing, which helps to maintain uniform conditions and avoid the formation of concentration gradient in the electrolysis cell. Furthermore, the agitation in the cell imparts local velocity, which is necessary for the dispersion of the generated ions; it also enhances mass transfer on the surface of particles when adsorption is the prevailing mechanism, or at the surface of the electrodes when electrooxidation or electroreduction take part in color removal efficiency.

In this work, experiments were performed at different agitation speed of 120, 360 and 600 rpm to evaluate its effect on color removal efficiency. The experiments were conducted, keeping the electrode distance (1 cm) and geometry constant, the temperature (35°C), current density (9 mA cm^{-2}) for two initial BR46 concentrations ($[\text{BR46}]_0$ at 30 and 160 mg L^{-1}) and initial pH about 8. The plot of $[\text{BR46}]_t/[\text{BR46}]_0$ vs. time in Fig. 3 shows that the curves obtained for 120, 360 and 600 rpm were similar for the two tested initial BR46 dye concentrations. The same experiments performed without agitation speed (0 rpm) displayed a large experimental error, since the analysis could be strongly affected by the sampling point. This result highlights the presence of concentration gradients in the electrolysis cell and therefore a non-homogeneous solution without magnetic stirring.

An optimum agitation speed can therefore be fixed to 120 rpm. As a result, no mass transfer limitation prevailed at 120 rpm or above, and perfect mixing could be assumed in these conditions in the electrocoagulation cell. Fig. 3 also highlights that color removal strongly depended on the initial concentration of the dye: color removal was complete in both cases, but complete removal required 7 min when $[\text{BR46}]_0$ was 30 mg L^{-1} , while it was delayed to 12 min when $[\text{BR46}]_0$ was 160 mg L^{-1} .

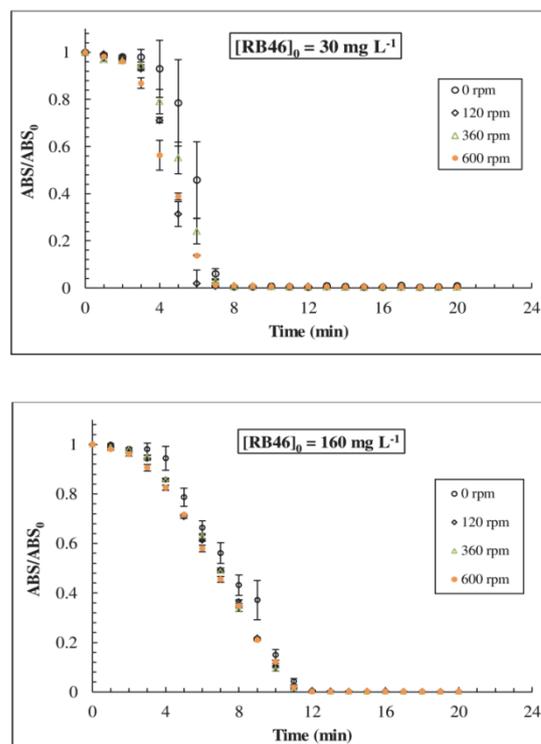


Fig. 3. Effect of agitation speed on color removal efficiency. Conditions: $j = 9 \text{ mA cm}^{-2}$, $T = 35^\circ\text{C}$ and initial pH 8

3.3. Effect of temperature

The influence of temperature was observed by studying color removal at different temperatures (20 , 35 and 65°C) with an initial dye concentration of either 30 or 160 mg L^{-1} . Figure 4 shows the evolution of the color removal at a function of the reaction temperature with 9 mA cm^{-2} current density, 120 rpm agitation speed and initial pH 8. It can be seen that the color removal efficiency was temperature- and concentration-dependent. The color removal efficiency increased with raising temperature, and the effect of this parameter was similar for both initial dye contents. Complete color removal was obtained after 9, 7 and 5 min for 30 mg L^{-1} initial dye concentration, and 12, 11 and 9 min for 160 mg L^{-1} initial dye concentration at temperature 20, 35 and 65°C , respectively. This means that increasing the temperature from 20 to 65°C decreased the time needed for complete decolorization from about 3 to 4 min, regardless of $[\text{BR46}]_0$.

In Fig. 4, all the curves exhibited the same shape: a plateau region in which color remained constant or decreased slightly (i.e. a latency period), followed by a linear decrease that can be fitted using a zero-order mechanism and is typical of an adsorption mechanism limited by the amount of adsorbent. In order to compare the evolution of the color removal efficiency of BR46 dye at different temperatures, the apparent rate constant (k_{app}) of the zero-order mechanism was estimated using the slope of the linear part of the curves obtained by plotting $[BR46]_t/[BR46]_0$ vs. time. The apparent rate constant for decolorization of BR46 increased with temperature and initial dye concentration. Indeed, for 20, 35 and 65°C, k_{app} values were 6.28, 9.40 and 9.43 mg L⁻¹ min⁻¹ for 30 mg L⁻¹ and 17.49, 19.12 and 22.86 mg L⁻¹ min⁻¹ for 160 mg L⁻¹, respectively.

Several mechanisms can explain the effect of temperature. The increase of temperature improves the destruction of the iron oxide film on the electrode surface (Chen, 2004), facilitates the mass transfer of different species which may lead to an enhancement of the rate of reaction of the coagulant species with the pollutant, but it may also enhance the kinetic rate of electrochemical reactions involving the dye. Due to the small difference between the k_{app} values obtained at 35 and 65°C at the same $[BR46]_0$, and considering the economic factor, a reasonable temperature was 35°C for electrocoagulation. This temperature will be used in the subsequent experiments of this study (Kobya et al., 2011).

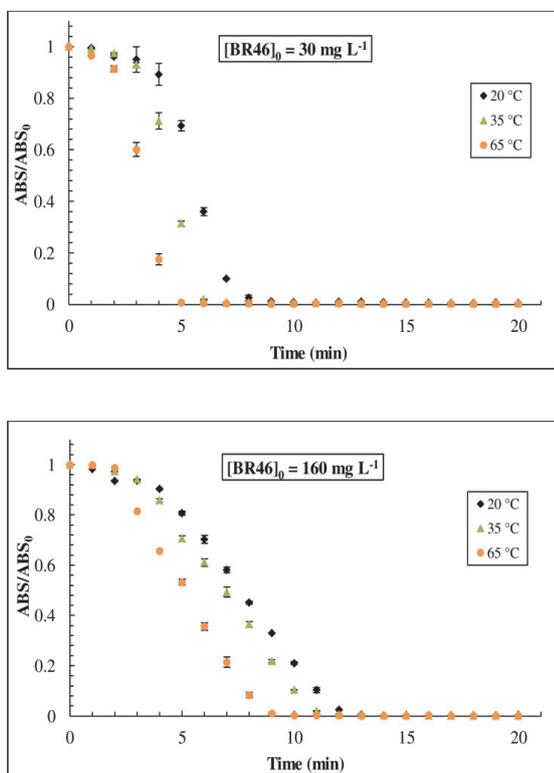


Fig. 4. Effect of temperature on the efficiency of color removal efficiency. Conditions: $j=9$ mA cm⁻², $\omega=120$ rpm and initial pH 8

3.4. Effect of the initial pH

It has often been reported that the pH is one of the most important parameter affecting the performance of the electrocoagulation process. Its effect on the pollutant removal efficiency has been described in the literature (Daneshvar et al., 2006). To evaluate the pH effect in the electrocoagulation of BR46 dye, a series of experiments were performed at 9 mA cm⁻² current density, 120 rpm agitation speed, 30 mg L⁻¹ initial dye concentration and 35°C. The solutions used were adjusted to the desired pH by adding sodium hydroxide or sulfuric acid solution. The color removal as a function of time for different pH in the range 2–11 and the evolution of the pH of the solution during the electrocoagulation process as a function of time are shown in Fig. 5. It can be seen that the initial pH has a significant effect, especially at low value. Color removal increased with increasing initial pH from 2 to 8 and remained practically unchanged between 8 and 11.

Measurement of pH as a function of time during electrocoagulation treatment showed that the pH value increased when the initial pH value of the solution was acidic and then stabilized around 5. When the initial pH value of the solution was alkaline, a decrease in solution pH was observed and it stabilized about 9. The maximum pH change observed was lower than 4. It can be concluded that at low initial pH, between 2 and 3, a sufficient amount of iron hydroxide complexes was not formed because hydroxide ions generated at the cathode were neutralized by H⁺ and, then, minimum removal efficiency was observed. The same results were reported by Daneshvar (2006). Conversely, the maximum color removal efficiency was the highest at initial pH equal to 8, although the difference with other initial alkaline conditions was slighter. Finally, this indicates that pollution removal can be driven by adsorption on the iron hydroxides, or by an electrochemical degradation enhanced under alkaline conditions.

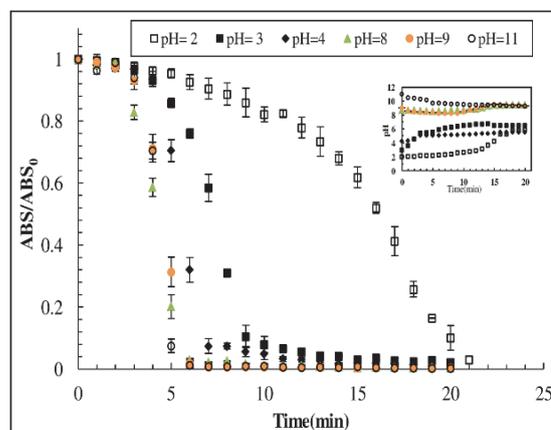


Fig. 5. Effect of the initial pH on the evolution of the pH and color removal vs. time. Conditions: $j=9$ mA cm⁻², $\omega=120$ rpm, T=35°C

3.4. Effect of current density

Current density is the key parameter of electrocoagulation process, as it determines the coagulant dosage rate, bubble production rate, and the size and growth rate of the flocs, which can affect the efficiency of the electrocoagulation (Daneshvar et al., 2004; Merzouk et al., 2009). To study the effect of current density on the C.I. Basic Red 46 decolorization, the experiments were conducted by varying the current density in the range 5-15 mA cm⁻², for 30, 80, 160 and 200 mg L⁻¹ initial BR46 dye concentrations (Fig. 6). As expected for this major parameter, a significant effect was observed. The plots of figure 6 present two steps. The duration of the first stage, named latency period and denoted $t_{Latency}$, is current (I) dependent, but depended only slightly on the initial BR46 dye concentration (Table 3); the highest current density used, the shortest duration of the latency period obtained. In Table 3, $t_{Latency}$ varies roughly as $1/I$. This result could be attributed to the need for a minimum concentration of coagulant species and of pollutant by-products formed by the electrochemical degradation of the dye before the pollutant starts to be removed by electrocoagulation. In order to confirm the degradation of the dye molecule before adsorption on flocs, an adsorption test of BR46 was conducted on iron hydroxides formed by electrocoagulation without the dye. In this test, the initial dye concentration decreased from 30 to 27 mg L⁻¹ after 60 min of contact time. This decrease could be attributed to the adsorption of the BR46 dye on the membrane syringe filter rather than to the adsorption of the BR46 dye molecules on the flocs. On the other hand, electrocoagulation experiments performed at 5, 3 and 2 min electrolysis time for 5, 9 and 15 mA cm⁻², respectively, showed that the mass of iron dissolved at the end of the first step was always nearly the same (0.083 mg L⁻¹). As a conclusion, this value corresponds to the minimal iron concentration

required before the zero-order mechanism of the electrocoagulation process may start.

The second part of the curves corresponds to the removal of pollutants (dye and by-products) by the electrocoagulation process. In this step, it can be noted that the color removal efficiency increased by increasing the current density from 5 to 15 mA cm⁻². The plots obtained in Fig. 6, with high correlation coefficients in Table 3, confirm the zero-order model already described in Fig. 6.

In order to compare the evolution of the color removal efficiency at different current density and initial dye concentration, k_{app} values were estimated and reported in Table 3. In this table, the apparent rate constants were shown to increase with increasing current density and initial BR46 dye concentration. The increase of k_{app} with current was expected, as it affects both the kinetics of floc formation and the electrochemical degradation of the dye. In addition, the increase of k_{app} vs. $[BR46]_0$ highlights a non-linear dependence of the removal kinetics as a function of dye concentration. Faradic yield (Eq. 7) and energy consumption were studied at various current density using Faraday's law (Eq. 8) (Daneshvar et al., 2007) and Eq. (9) to estimate energy consumption (Sengil and Ozacar, 2009).

$$\varphi = \Delta M / \Delta M' \quad (7)$$

$$\Delta M = MI t_{EC} / nF \quad (8)$$

$$E = UI t_{EC} \quad (9)$$

where ΔM is the mass of dissolved iron estimated by Faraday's law (in g), $\Delta M'$ is the real mass of dissolved iron (g), φ is the Faradic yield, M the molecular weight of iron (g mol⁻¹), n the number of electrons, U is the cell potential measured between the electrodes, I is the current, t_{EC} is the electrolysis time and F is Faraday's constant ($F=96487$ C mol⁻¹).

Table 3. Apparent zero-order rate constant (k_{app}) and determination correlation (R^2) of the fitting of BR46 dye decolorization at different temperatures and initial dye concentrations ($\omega=120$ rpm, initial pH 8)

$j= 5 \text{ mA cm}^{-2}$			
[BR46] ₀ (mg L ⁻¹)	$t_{Latency}$ (min)	k_{app} (mg L ⁻¹ min ⁻¹)	R^2
30	5	5.86	0.988
80	5	9.06	0.993
160	5	11.70	0.998
200	5	13.20	0.997
$j= 9 \text{ mA cm}^{-2}$			
[BR46] ₀ (mg L ⁻¹)	$t_{Latency}$ (min)	k_{app} (mg L ⁻¹ min ⁻¹)	R^2
30	3	9.40	0.989
80	3	14.98	0.990
160	3	19.12	0.997
200	3	19.70	0.994
$j= 15 \text{ mA cm}^{-2}$			
[BR46] ₀ (mg L ⁻¹)	$t_{Latency}$ (min)	k_{app} (mg L ⁻¹ min ⁻¹)	R^2
30	2	9.79	0.972
80	2	19.40	0.973
160	2	27.20	0.990
200	2	30.52	0.990

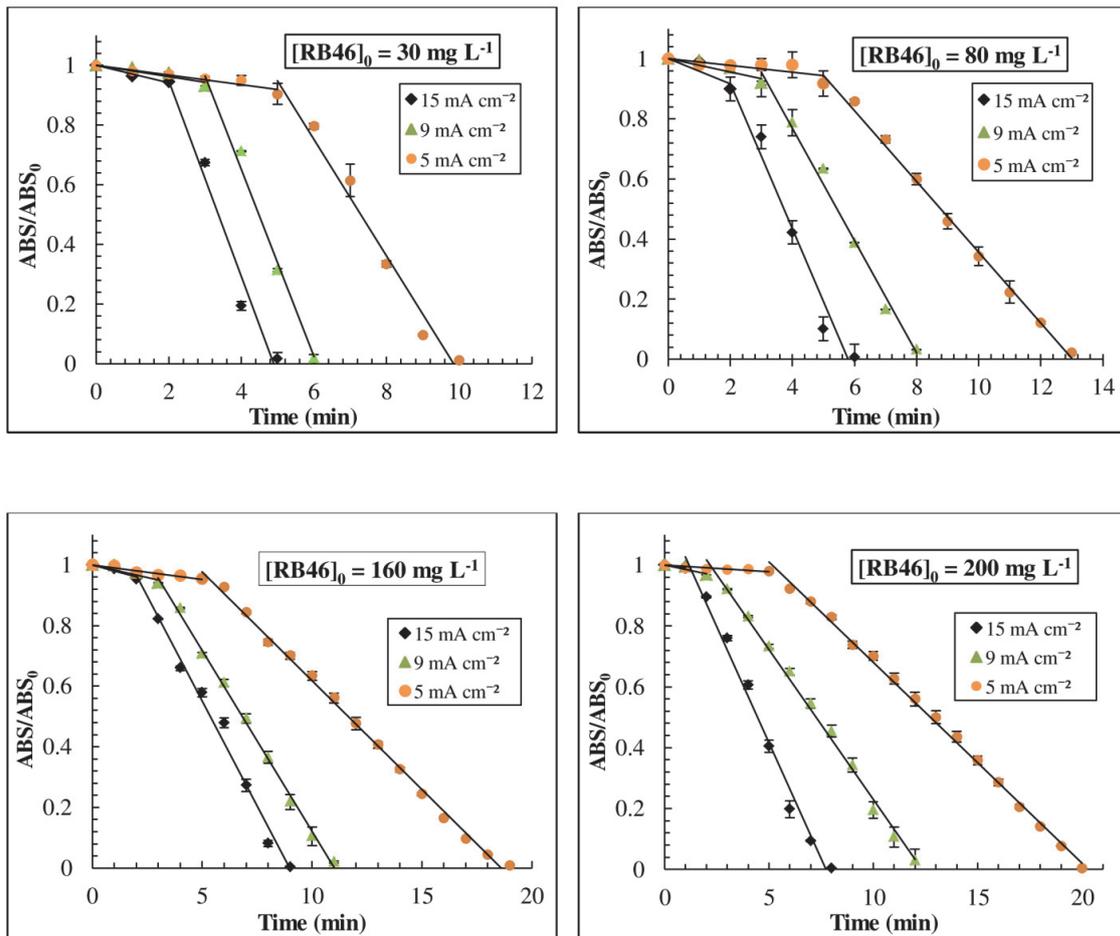


Fig. 6. Effect of current density (j) on the color removal efficiency. Conditions: $\omega=120$ rpm; $T=35^{\circ}\text{C}$ and initial pH 8

After 8 min electrolysis, experimental results showed that current density did not have a significant effect on the Faradic yield in the studied range, 5 – 15 mA cm^{-2} and the value is close about 100%, which highlights that oxygen release at the anode was minimized. However, energy consumption increased with increasing current density, from 0.56 to 3.07 kWh kg^{-1} colour removed when the current density increased from 5 to 15 mA cm^{-2} . On the other hand, the same yield of color removal efficiency (99%) was obtained for an initial dye content of 200 mg L^{-1} with 5, 9 and 15 mA cm^{-2} at 21, 13 and 5 min electrolysis time, respectively. As a result, in order to reduce the energy cost, working at 9 mA cm^{-2} appeared as an acceptable compromise.

3.5. Effect of the initial dye concentration

To investigate the effect of initial BR46 concentration on its color removal, electrocoagulation process was carried out at 9 mA cm^{-2} , 120 rpm and initial pH8 using various initial dye concentrations in the range 30–200 mg L^{-1} . The temperature of the BR46 solution was maintained at 35°C and the electrolysis time was fixed to 20 min (Fig. 7). It can be seen that the residual concentration decreased linearly with time after a low period of latency that increased slightly with $[\text{BR46}]_0$, and that when the initial dye

concentration increased, the operating time needed to remove the color increased significantly. For example, when the initial BR46 dye concentration increased from 30 to 200 mg L^{-1} in Fig. 7, complete decolorization was obtained after 6 and 13 min, respectively. This means that at constant electrolysis time, the color removal efficiency decreased gradually with an increase in the initial dye concentration. For example, after 6 min electrocoagulation time, the color removal was 29.36, 52.40, 62.30 and 72.19 mg L^{-1} , which corresponds to color removal percentage of 98, 61, 39 and 35% at initial BR46 dye concentrations of 30, 86, 160 and 200 mg L^{-1} , respectively. The presumed reason can be deduced from Faraday's law (Eq. 8) which provides the same amount of iron dissolved at the same current density and time for all dye concentrations. Consequently, the same amount of coagulant species would be produced in the liquid phase, which justifies the lower color removal efficiency obtained at higher BR46 dye concentrations. Indeed, the flocs produced at high dye concentration were insufficient to complete color removal. Similar results are reported by Daneshvar (2007). Ait Ouaisa (2014) also reported that the lower removal efficiency of tetracycline by electrocoagulation process was caused by a lower amount of coagulant $\text{Al}(\text{OH})_3$ species, which became therefore limiting. However, it must be noted that the

increase of the electrolysis time required to achieve complete decolorization, even in the second period, is not proportional to the initial dye concentration, which is in accordance with the fact that the dye does not adsorb directly on the flocs. As highlighted in Table 3 by the increase of k_{app} values with initial dye content, a degradation mechanism involving the production of secondary species that could adsorb more easily, probably constitutes a preliminary step in the mechanism of color removal. This step seems to be faster than adsorption and enhanced by an increase of $[BR46]_0$.

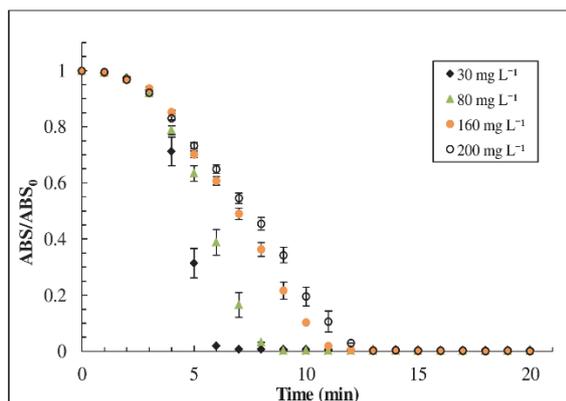


Fig. 7. Effect of initial concentration of BR46 dye on the color removal efficiency. Conditions: $j=9 \text{ mA cm}^{-2}$, $T=35^\circ\text{C}$, $\omega=120 \text{ rpm}$ and initial pH 8

3.6. Biodegradability tests and biological treatment

The solution treated by electrocoagulation under the optimal conditions: ($[BR46]_0=30 \text{ mg L}^{-1}$, $j=9 \text{ mA cm}^{-2}$, $\omega=120 \text{ rpm}$ and $T=35^\circ\text{C}$) allowed to reach 99% color removal efficiency for the BR46 dye, while the chemical oxygen demand (COD) reduction in the treated water was above 53%. This relatively low oxidation level, if compared to target compound removal, was in favor of the implementation of a biological treatment for BR46 dye degradation, downstream to electrocoagulation process (Yahiaoui et al., 2012).

3.6.1. Biodegradability tests

The biodegradability tests were conducted on the effluents of the electrocoagulation step using its optimal conditions described above. The BOD_5/COD ratio increased from 0.05 initially to 0.35 after 20 min pretreatment. Even though the limit of biodegradability (0.4) was not achieved, an activated sludge process could be promisingly considered as the adequate downstream treatment following an electrocoagulation step (Yahiaoui et al., 2012, 2013a, 2013b, 2014).

3.6.2. Biological treatment

The absence of biodegradation by activated sludge for non-pretreated water (30 mg L^{-1}), which was illustrated by the constant values of the dissolved organic carbon ratio $[DOC]_t/[DOC]_0$ observed

throughout the culture (16 days). This result confirms the biorefractory character of the BR46 dye. The evolution of the $[DOC]_t/[DOC]_0$ values as a function of time during activated sludge culture on BR46 dye solution pretreated by electrocoagulation under the optimal condition. A rapid decrease of this ratio to 71% was observed at the beginning of the culture. However, this cannot be attributed to dye biodegradation, as this decrease seems to be related to the biosorption of intermediate compounds formed on activated sludge, which corresponds to about 18-22% of the DOC decrease (Fig.8). Then, the degradation of organic compounds by activated sludge could be observed. At the end of the culture (16 days), 65% of the overall DOC decrease was achieved if the hybrid process was considered, namely by coupling the electrocoagulation pretreatment and the biological treatment.

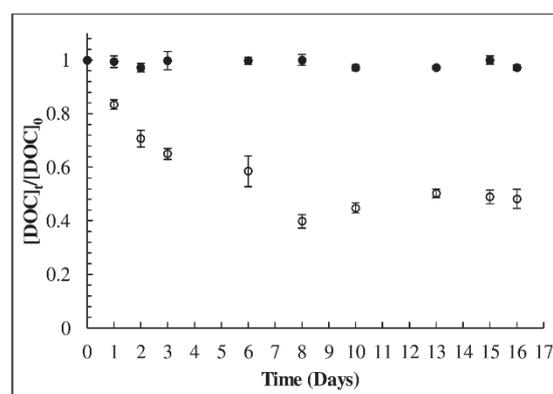


Fig. 8. Evolution of $[DOC]_t/[DOC]_0$ values during activated sludge cultures on non-treated BR46 dye solution (●) and after 20 min electrocoagulation pretreatment (○), respectively

4. Conclusions

In this work, the feasibility of an electrocoagulation-activated sludge hybrid process was investigated on the removal of C.I. Basic Red 46 dye. In the first part of this study, the effect of the operating parameters on the color removal efficiency by the electrocoagulation process was examined. From the experimental data, the following conclusions can be drawn:

- The color removal efficiency was enhanced by increasing current density and temperature, whereas the opposite emerged for the initial dye concentrations.
- The optimization of the operating parameters led to the following optimal values for BR46 dye decolorization: 30 mg L^{-1} , $j=9 \text{ mA cm}^{-2}$, $T=35^\circ\text{C}$, $t=20 \text{ min}$, initial pH 8 and $\omega=120 \text{ rpm}$. Under these conditions, electrocoagulation is a very efficient pretreatment and is able to achieve 99% color removal efficiency in 5 min and 53% COD removal.
- The shape of the cathode does not affect the color removal efficiency.

- The obtained results suggest that a zero-order model describes the kinetic behavior. The apparent rate constant (k_{app}) of this step increases with increasing current density and initial BR46 dye concentration. BR46 dye was not adsorbed in its molecular form on the flocs, and electrocoagulation removed about 50% of the initial COD. This highlights a complex mechanism of dye removal that combines electrochemical degradation and adsorption of by-products. The minimal iron concentration required before color removal by electrocoagulation started was 0.083 mg L⁻¹.

In the second part, the effect of the coupling between electrocoagulation process and the biological treatment for the degradation of BR46 dye was analyzed and the increase of the BOD₅/COD ratio from 0.05 initially to 0.35 after 20 min of electrocoagulation pretreatment was observed. This enhancement of biodegradability was confirmed during biological treatment, since 65% of the dissolved organic carbon (DOC) was removed by means of the combined process after 16 days of biological treatment.

As a conclusion, this work demonstrates that a textile wastewater treatment based on the integration of electrocoagulation and biological oxidation processes is may be an efficient alternative method that allows satisfactory treatment of wastewater effluents in accordance with environmental requirements.

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