# Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A comparative study

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## ARTICLE INFO

## ABSTRACT

The effectiveness of chemical coagulation (CC) was compared to electrocoagulation (EC) with aluminium electrodes for decolourization purpose of a synthetic textile wastewater containing a disperse red dye. For CC, ferric chloride $FeCl_3$ and aluminium sulphate $Al_2(SO_4)_3$ as the coagulant were compared: the respective effects of initial pH, coagulant dosage, initial dye concentration, ionic strength and mixing conditions were investigated in order to maximize decolourization yield. The comparison between CC and EC is based on recently published data on EC by the same authors. Experimental results showed first that $Al_2(SO_4)_3$ was far more effective than $FeCl_3$ for colour removal using CC, regardless of operating conditions. A removal yield higher than 90% could be achieved with a 40 mg/L dose of $Al_2(SO_4)_3$ $18H_2O$ in a large range of pH from 4 to 8 and for a dye concentration up to 235 mg/L. The removal yield could however be enhanced up to 95% using EC for pH values between 6 and 9 at the expense of higher operating costs. Nevertheless, EC presented the additional advantages to be more robust against pH change and to reduce simultaneously equipment costs in comparison to CC.

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## 1. Introduction

The textile industry is known as a water-intensive sector which involves a wide variety of wet processing operations and employs many toxic substances. In the textile production, the dyeing step presents the highest environmental risk, as it requires high concentrations of not only organic dyes, but also additives and salts [1]. Most of the time, this step consumes much more water than the others and, therefore, generates large throughputs of wastewaters characterized not only by high concentrations of biodegradable and non-biodegradable organic compounds, dissolved salt and suspended solids, but also by strong colour, various pH from 2 to 12 and sometimes high temperatures [2]. Dyes are usually used in excess, especially when they belong to the disperse dye class: this class groups, indeed, organic non-ionic compounds nearly insoluble, applied in aqueous solution using a simple immersion technique, which induces large water consumption [3]. Consequently, up to 40% of the amount of dyes is not fixed to textile fibres [4]. Residual dyestuffs in textile wastewaters present the disadvantage to exhibit simultaneously a high toxicity level and a poor biodegradability with an aesthetic pollution which has a strong psychological effect [5]. As dyestuffs are visible at low concentrations, aesthetic standards are often more difficult to meet than legal standards. Now, some dyestuffs are also suspected of carcinogenicity [6]. As these dyes are also toxic for microorganisms, they often inhibit bacterial growth. Consequently, conventional biological treatments cannot be directly applied to textile wastewater and a preliminary decolourization step based on physicochemical treatments is compulsory before biochemical oxygen demand ($BOD_5$) abatement [7]. Otherwise, dyestuffs could accumulate in water and soils, and even contaminate groundwaters. This is the reason why the removal of dyes from wastewater effluents constitutes a major problem for textile industries.

Many methods have been described in the literature for colour removal from dye-containing wastewater. These include adsorption (e.g. on active carbon), coagulation–flocculation, chemical oxidation (chlorination, ozonization, etc.) and photodegradation ($UV/H_2O_2$, $UV/TiO_2$, etc.) [8–21]. Actually, chemical coagulation is one of the most common and practical methods for removing the colloidal forms of pollution from wastewater and for chemical oxygen demand (COD) abatement. This consists in destabilizing colloids, aggregating and binding them together into flocculates; the resulting flocs can finally be removed either by settling or by flotation. Destabilization involves first an increase of ionic strength which promotes double-layer compression, and/or the neutralization of the particle surface charge by adsorbing counteranions, using the addition of chemicals called

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coagulants and flocculants, usually combined with pH adjustment [22]. In water treatment, the commonly used coagulants are hydrolysable metal salts that are effective for the destabilization of colloidal particles, as most colloids are negatively charged in natural waters and industrial effluents: these mostly correspond to aluminium(III) or iron(III) salts, such as aluminium sulphate $Al_2(SO_4)_3$ and ferric chloride $FeCl_3$ that are readily soluble in water [23,24]. Alum remains therefore the most widely used coagulant, although recent research turns towards the use of not only inorganic–organic composite coagulants [22], but also organic biodegradable coagulants from sustainable sources [25–27].

Coagulants are added directly in wastewater in conventional chemical coagulation (CC), but they can be delivered in situ by electrolysis in the alternative electrocoagulation process (EC): in EC, the coagulant results from the electrolytic oxidation of a sacrificial anode, usually in aluminium or iron, which leads to the electro-dissolution of metallic cations, such as $Al^{3+}$ or $Fe^{3+}$ as in CC [28–30]. Both in CC and in EC, these cations contribute to reduce the stability of suspended entities, first by reducing their zeta potential, but they can also precipitate in the form of polymerized amorphous hydroxides that promote pollution removal through a non-specific mechanism which is usually denoted *sweep coagulation* or *sweep flocculation* [22]. For example, the main precipitation reaction for aluminium Al(III) cations about neutral pH is summarized as follows

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \tag{1}$$

although this equation hinders a complex precipitation kinetics that involves various monomeric and oligomeric soluble and insoluble species which finally transform into insoluble $Al(OH)_{3(s)}$ [31]. As these sweep flocs exhibit a large interfacial area, they can favour first the rapid adsorption of soluble and insoluble pollutants, but colloids or suspended solids may also be simply embedded into the growing precipitate. Although efficient for pollution abatement, sweep flocculation usually presents the disadvantage to form voluminous flocs, easily removed by settling in CC, but leading to large amounts of sludge that must be subjected to downstream treatments.

In EC, the metal electrolytic oxidation is also coupled to water reduction into hydroxide anions at the cathode: for example, in the case of aluminium, the main reactions are as follows:

$$\text{Anode}: Al_{(s)} \rightarrow Al^{3+} + 3e^- \tag{2}$$

$$\text{Cathode}: 3H_2O + 3e^- \rightarrow \frac{3}{2}H_{2(g)} + 3OH^- \tag{3}$$
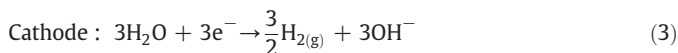
Even though the flocs can be easily removed from the aqueous medium by settling, flotation is naturally induced in EC by the $H_2$ bubbles generated at the cathode, and it can be considered that this phenomenon is one of the advantages in EC, as flocs can be removed either by combining flotation and decantation, or even uniquely by flotation (which is referred to as *electroflotation*). As the pH of the medium changes during CC and EC due to Eq. (1), another key advantage of EC is that this method exhibits a buffering capacity due to OH⁻ formation in Eq. (3), which prevents high changes of pH.

Despite the abundant literature on wastewater decolourization using EC or CC, this still remains poorly understood. For example, disperse dyes are known to be nearly insoluble, contrary to reactive dyes which are ionic and soluble. The consequence is that the removal of disperse dyes from synthetic wastewater using EC was reported to be easier than for reactive dyes [5], and similar results were observed for CC with $FeCl_3$ [32] because disperse dyes behave roughly as suspended solids. However, opposite results emerged between CC and EC on COD abatement: using EC, COD removal could be higher for reactive than for disperse dyes because reactive dyes include easily oxidizable azo or anthraquinone structures [5], whereas COD abatement remained weaker for reactive dyes using CC [32]. This analysis must however be moderated, as the comparison between CC and EC does not follow the same trends when applied to real wastewater from a textile factory. For example, EC was usually reported to be cheaper than CC for the decolourization and turbidity removal of real textile dye wastewater, despite a similar or even a slightly lower removal effectiveness [33,34]. Actually, operating costs were strongly reduced only when iron electrodes were used due to the higher price of aluminium metal. As a rule of thumb, EC and CC were always more effective for treatment of synthetic wastewaters than for real dyeing wastewater [35]. For real textile wastewater, experimental data followed usually the trends observed for disperse dyes in synthetic wastewater, i.e. EC promoted the highest COD abatement whereas CC maximized turbidity removal [33,34], probably because dyeing wastewaters usually contain large amounts of suspended solids. Finally, it can be concluded that despite the increased interest for EC in the last decade [33], the comparison between CC and EC for wastewater decolourization is not yet clearly established and may significantly vary with the properties and characteristics of the textile effluents.

In this study, the removal of a disperse red dye from a synthetic wastewater was therefore investigated using CC and compared with available data from a previous work of the same authors on EC. This comparison covers not only the key operating parameters common to EC and CC, such as the red dye concentration in wastewater before treatment, pH, water conductivity/ionic strength and retention/residence time, but also the specific parameters of each technique, such as coagulant dosage for CC and current density for EC. The optimum values of these parameters were primarily determined on the basis of the yield of decolourization, but operating costs based on coagulant dosage for CC and on electrode consumption and energy requirements for EC were also estimated for comparison purpose.

## 2. Materials and methods

### 2.1. Chemicals and methods

Experiments were carried out using a synthetic wastewater containing a red dye which consists of a mixture of 2-naphthoic acid and 2-naphtol (*Sigma-Aldrich Co.*, USA) with a total concentration ($C_i$) that could be varied between 25 and 380 mg/L. These non-ionic inorganic compounds are nearly insoluble in water, exhibit a colloidal stability, and belong therefore to the disperse dye class [36]. This dye and its concentration are typical of wastewaters from a Moroccan textile factory. Synthetic solutions were prepared by mixing the dye in tap water (Table 1) in a mechanically stirred tank. Solution conductivity ($\kappa$) and pH were measured using a CD810 conductimeter (*Radiometer Analytical*, France) and a ProfiLine pH197i pH meter (*WTW*, Germany). The initial pH of the synthetic wastewater was varied between 2.6 and 9.1 using the minute addition of 0.1 M $H_2SO_4$ or NaOH solutions (*Sigma-Aldrich Co.*, USA). The ionic strength, and consequently the conductivity of wastewater, were adjusted using the addition of sodium chloride (NaCl) in the following range, 0–6.0 g/L, which covers the values usually explored in the literature [36,37]. NaCl is, indeed, a salt exhibiting low toxicity at moderate level, reasonable cost, high conductivity and high solubility. This addition was always shown to have negligible effect on the initial pH of the synthetic wastewater.

**Table 1**
Summary of wastewater properties and characteristics.

| | |
|---|---|
| pH | 7.85 |
| Alkalinity (mg/L $CaCO_3$) | 150 |
| Total hardness (mg/L $CaCO_3$) | 350 |
| Turbidity (NTU) | 0.15 |
| Chloride (mg/L) | 392 |

Dye concentration ($C$) could be estimated from its absorbance characteristics in the UV–Vis range (200–800 nm), using a UV–Vis spectrophotometer (*Pye Unicam*, SP 8-400, UK) at the wavelength that provided the maximum intensity, i.e. about 450 nm. Measurements were carried out in triplicate. Samples were collected and filtered using 0.45 μm membrane filters before the measurement of residual dye contents. The colour removal yield ($Y_{COL}$) could therefore be defined as follows:

$$Y_{COL} = \frac{C_i - C}{C_i} \times 100 \qquad (4)$$

in which $C_i$ is the dye concentration in the synthetic wastewater. Statistical analysis on replicated measurements gave access to $Y_{COL}$ values with $\pm 0.2\%$ accuracy. COD was followed using the standard closed reflux colorimetric method. However, as the disperse dye constituted the main source of oxidizable material in this work, COD and colour usually varied in a similar proportion, as they provide redundant information; consequently, the evolution of the COD removal yield will not be reported.

## 2.2. Coagulation experiments

CC was investigated in the batch mode by running a series of six experiments in parallel in a multiple jar-test apparatus (i.e. a six spindle mixing device), with either aluminium sulphate octodecahydrate (Al$_2$(SO$_4$)$_3$ 18H$_2$O or alum) or ferric chloride hexahydrate (FeCl$_3$ 6H$_2$O) from *Sigma-Aldrich Co.* (USA) as the chemical coagulant. The experiments were carried out at room temperature ($24 \pm 2$ °C), using 1000 mL wastewater samples, by applying six different coagulant concentrations ranging from 20 mg/L to 120 mg/L. During the tests, coagulant was first rapidly dispersed using mechanical stirring at a rotation speed of 180 rpm for 3 min; these values were kept constant for all the experiments. Then, CC was studied at a slower stirring speed (30 rpm, 40 rpm and 60 rpm, respectively) for two mixing time values (20 min and 30 min, respectively). Once stirring was stopped, settling started. The settling time was varied between 10 min and 60 min. During the coagulation step, absorbance at 450 nm was measured every 10 min in order to follow the evolution of colour removal vs. time.

## 2.3. Electrocoagulation experiments

The electrocoagulation–electroflotation cell was the same as that already used by Merzouk et al. [37], which is described in detail in this previous work. This consists of a rectangular tank with a total volume of 8.6 L divided into two compartments. Aluminium electrodes of rectangular shape ($240 \times 20 \times 1$ mm, i.e. with 48 cm² electrode surface area) were used both as the anode and the cathode in the first compartment. The distance between the two electrodes was 10 mm, which is a typical value in EC cells [34,35,38]. Prior to use, these were treated with an HCl aqueous solution for cleaning to avoid passivation.

EC experiments were carried out in the continuous mode under steady state conditions at room temperature ($24 \pm 2$ °C). The first compartment of the EC cell was fed continuously with a peristaltic pump using the effluents from a wastewater tank. This was designed in order to maximize the formation of H$_2$ microbubbles at the cathode, which promoted a homogenous dispersion of the gas phase in the co-current upward flow, and also favoured floc removal by electroflotation in the second compartment [38]. As a result, the sludge was essentially recovered by flotation and removed continuously by overflow, while the more dense materials could settle in the second compartment. Finally, decolourized wastewater in which most of the suspended solids had been eliminated was recovered at mid-height in the second compartment [38].

During EC process, absorbance was measured over time on samples of treated wastewater recovered from the exit stream of the second compartment. Absorbance at 450 nm was measured every 2 min for EC in order to follow how the steady state conditions were achieved and at least three times when these were established.

Residence time ($\tau$) could be varied by adjusting the liquid flow rate ($Q$) between 25 and 78 L/h. EC was always conducted in the intensiostat mode, using a digital DC power supply (Didalab, France) and recording cell potential ($U$) during the experiments. Current density ($j$) was varied between 20.8 and 62.5 mA/cm², which corresponded to current values ($I$) between 1 and 3 A. The specific electrical energy consumption per kg dye removed ($E_{dye}$) and the specific electrode consumption per kg dye ($\mu_{Al}$) were calculated as follows

$$E_{dye}\left(\frac{kWh}{kg\,dye}\right) = \frac{UI}{1000\,Q(C_i\,Y_{COL})} \qquad (5)$$

$$\mu_{Al}\left(\frac{kg\,Al}{kg\,dye}\right) = \frac{3600\,M_{Al}\,I\,\Phi_{Al}}{3F}\frac{1}{Q(C_i\,Y_{COL})} \qquad (6)$$

using the dye concentration of wastewater in the inlet stream $C_i$ (kg/m³), current intensity $I$ (A), cell voltage $U$ (V), the molar weight of aluminium $M_{Al} = 0.02698$ kg/mol, Faraday's constant $F$ (96,487 C/mol) and the faradic yield $\Phi_{Al}$ of Al dissolution. $\Phi_{Al}$ was estimated as the ratio of the weight loss of the aluminium electrodes during the experiments $\Delta m_{exp}$ and the amount of aluminium consumed theoretically at the anode $\Delta m_{th}$:

$$\Phi_{Al} = \frac{\Delta m_{exp}}{\Delta m_{th}} = \Delta m_{exp} \cdot \frac{3F}{I \cdot M_{Al}} \cdot \frac{1}{t} \qquad (7)$$

in which $t$ (h) is the electrolysis time.

## 3. Results and discussion

### 3.1. Chemical coagulation

#### 3.1.1. Effects of mixing speed, mixing time and settling time

Fig. 1 illustrates the influence of mixing speed in the range 30–60 rpm as a function of settling time for 20 and 30 min mixing time, respectively. This figure presents the particular case of Al$_2$(SO$_4$)$_3$ 18H$_2$O as the coagulant at a 20 mg/L concentration with a 100 mg/L initial dye content at pH 6.4 and for $\kappa = 2.4$ mS/cm, but it is also representative of the trends observed for other dye and coagulant concentrations. Experimental data show that the colour removal yield $Y_{COL}$ increased both with mixing time and settling time, and with
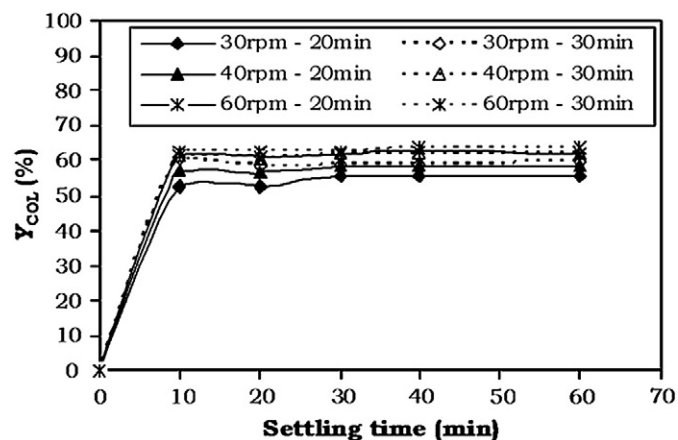


**Fig. 1.** Effects of mixing speed, mixing time and settling time on the colour removal yield using CC: $C_i$ 100 mg/L, initial pH 6.4, $\kappa = 2.4$ mS/cm (coagulant: Al$_2$(SO$_4$)$_3$ 18H$_2$O, 20 mg/L).

mixing speed in the range studied, as only moderate rotation speed values were studied to avoid breaking the flocs during their formation in this work. The increase of $Y_{COL}$ with rotation speed above 40 rpm became however insignificant when mixing time was 30 min. Similarly, at 60 rpm, $Y_{COL}$ improvement using mixing time was limited to about 2%. Finally, settling time is the parameter that presents the weakest effect after only a few minutes: only an insignificant evolution of $Y_{COL}$ was observed beyond a 10 min operation.

In Fig. 1, optimum operating parameters correspond, therefore, to 40 rpm rotation speed for 30 min mixing time and 10 min settling time. The maximum colour removal yield is only 63.8%, which has been observed when rotation speed was 60 rpm, mixing time was 30 min and settling time was 40 min. This value constitutes, however, a poor result that can still be improved, for example by changing coagulant type and dosage. For this reason, only the 30 min mixing time value will be systematically used in the subsequent experiments with a 60 rpm rotation speed, varying settling time: rotation speed and settling time have, indeed, only a poor influence on operating costs in comparison to coagulant dosage.

### 3.1.2. Effect of coagulant dosing

For $Al_2(SO4)_3$, experimental results are illustrated by Fig. 2. All the parameters, except coagulant dosage, were kept constant. It can be clearly seen that colour removal increased with the increase of alum content up to a plateau value. In detail, for an initial pH value of 6.4, the colour removal yield rose steeply when the coagulant content was increased from 20 mg/L to 40 mg/L, giving $Y_{COL}$ values about 94% at 40 min settling time, whereas a further addition of alum resulted only in small variations of removal yield. It is worthy to note that settling time had nearly no influence on colour removal, as in Fig. 1, regardless of coagulant dose. In Fig. 2, colour removal seemed to pass through a weak maximum as a function of coagulant dose between 20 and 60 mg/L, especially when settling time was 30 min. The highest efficiency at pH 6.4 was therefore achieved when alum dose was about 40 mg/L. This behaviour is not surprising, as coagulation occurs primarily when the zeta potential (usually negative for disperse dyes) tends to zero; overdosing coagulant dosage should therefore have adverse effects on colour removal. However, at the pH of Fig. 2, this trend is probably counterbalanced by the extensive precipitation of aluminium hydroxide in excess, which also promotes decolourization and COD abatement [22]; this explains why the $Y_{COL}$ curve presents apparently a plateau region when coagulant dose is between 60 and 120 mg/L, regardless of settling time.

### 3.1.3. Effect of coagulant type

The values of colour removal yield obtained with $Al_2(SO_4)_3$ have been compared to those achieved with $FeCl_3$. The effect of the $FeCl_3$

dosage on $Y_{COL}$ is illustrated by Fig. 2 in conditions similar to those of $Al_2(SO_4)_3$ for comparison purpose. Again, settling time exhibited no significant effect on $Y_{COL}$. For $FeCl_3$, the $Y_{COL}$ curves of Fig. 2 presented first a rapid increase of $Y_{COL}$ up to 60 mg/L $FeCl_3$ $6H_2O$, followed by a plateau region characterized by a lower $Y_{COL}$ value than for $Al_2(SO_4)_3$, about 75%. However, this plateau was followed by another region in which $Y_{COL}$ increased again, above 100 mg/L coagulant dose. As a result, a 90% removal yield was achieved, but only at 120 mg/L coagulant dose under the experimental conditions of Fig. 2, while the same result was achieved with 40 mg/L $Al_2(SO_4)_3$ $18H_2O$. From an economic point of view, alum is only slightly more expensive than $FeCl_3$ [33,34], which confirms the superiority of $Al_2(SO_4)_3$ as a coagulant. In practice, this means that 3.2 mg/L aluminium metal in $Al_2(SO_4)_3$ $18H_2O$ yielded a $Y_{COL}$ value similar to 24.6 mg/L iron metal in $FeCl_3$ $6H_2O$. Even though the quantitative comparison between $FeCl_3$ and $Al_2(SO_4)_3$ changed slightly with operating conditions, such as pH, experimental data highlighted that decolourization was always more effective and also cheaper with $Al_2(SO_4)_3$ $18H_2O$. As a result, only data obtained with alum will be reported in the following sections.

### 3.1.4. Effect of initial pH

The initial pH of wastewater is a key parameter in the coagulation process [22,39]. Only the use of a coagulant at its optimum pH displays maximum pollutant removal. In order to determine the optimum pH of the coagulation process, 40 mg/L $Al_2(SO_4)_3$ $18H_2O$ was added to each sample of 1000 mL synthetic wastewater on the basis of Fig. 2, at different pH values, adjusted using $H_2SO_4$ or NaOH solutions. The effect of initial pH on colour removal is shown in Fig. 3. It can be noticed that decolourization was the most effective in a pH range between 4.0 and 7.8 and that $Y_{COL}$ reached values between 86.0 and 93.6% in this pH region. This corresponds to the region where positively charged $Al(OH)^{2+}$ and $Al_2(OH)_2^{4+}$, and insoluble $Al(OH)_3$ species prevailed [22]: cations are able to conduct primarily charge neutralization, as colloidal particles are usually negatively charged, while insoluble species favour coagulation by sweep precipitation. Conversely, $Y_{COL}$ fell when soluble $Al(OH)_4^-$ anions become predominant at high pH. Finally, Fig. 3 also confirms that $Y_{COL}$ values higher than 90% can be achieved using CC with alum, as already seen in Fig. 2.

In Fig. 3, the maximum colour removal yield was observed for an initial pH around 5.5. However, the pH changed during coagulation process due to the formation of $Al(OH)_3$, as already described in Section 1, which appears clearly in Fig. 4. This evolution depends however on the initial pH, as $Al(OH)_3$ precipitation is possible only when the initial pH is higher than 4, which prevents a high change of pH below this value (Fig. 4). Above 4, the decrease of pH remains
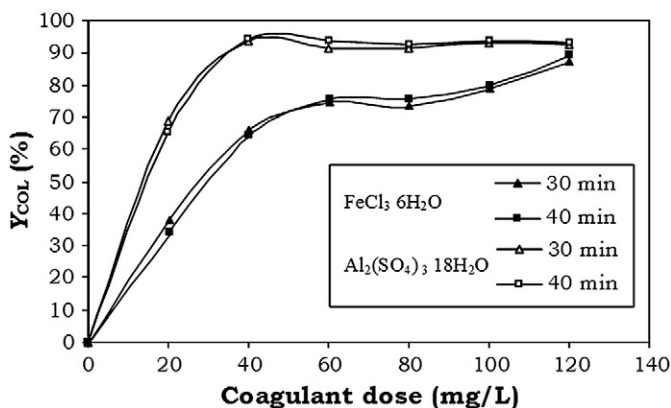
**Fig. 2.** Effect of coagulant dosage and settling time on the colour removal yield using CC ($C_i$ 100 mg/L, initial pH 6.4, $\kappa = 2.4$ mS/cm, mixing speed 60 rpm, mixing time 30 min): comparison between $FeCl_3$ $6H_2O$ and $Al_2(SO_4)_3$ $18H_2O$.
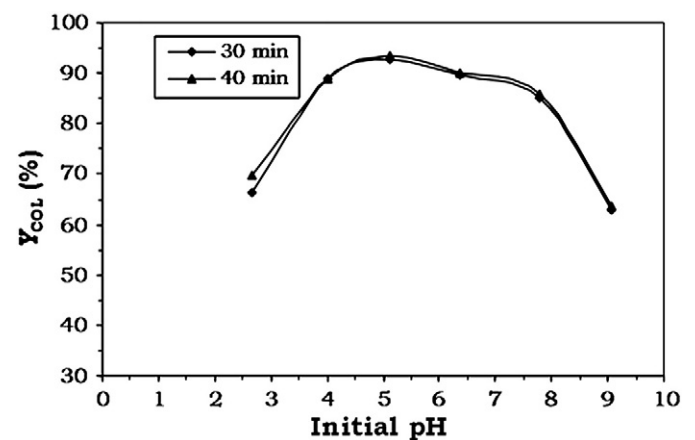
**Fig. 3.** Effect of initial pH and settling time on the colour removal yield using CC: $C_i$ 100 mg/L, mixing speed 60 rpm, mixing time 30 min, $\kappa = 2.4$ mS/cm (coagulant: $Al_2(SO_4)_3$ $18H_2O$, 40 mg/L).
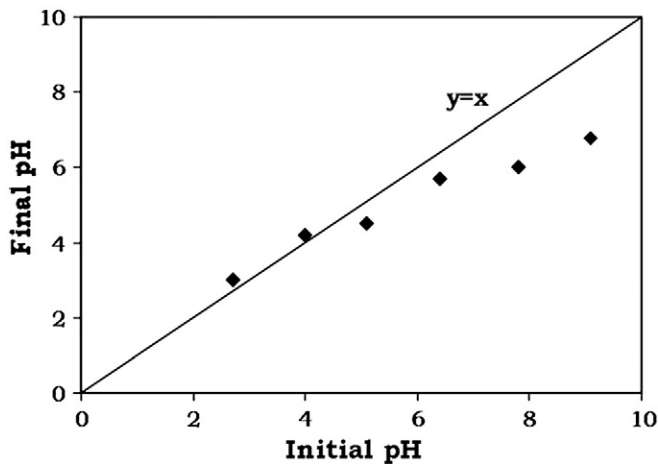
**Fig. 4.** Evolution of pH values due to CC after 40 min settling time for different values of initial pH: $C_i$ 100 mg/L, mixing speed 60 rpm, mixing time 30 min, $\kappa = 2.4$ mS/cm (coagulant: $Al_2(SO_4)_3$ $18H_2O$, 40 mg/L).

small due to the limited addition of alum (40 mg/L), which maintains the effectiveness of the coagulant in the optimum pH range even when the initial pH approaches 8.

### 3.1.5. Effect of initial dye concentration

Fig. 5 illustrates the evolution of the colour removal yield as a function of the initial dye concentration ($C_i$), using the optimum conditions obtained previously for mixing speed, mixing time, coagulant dose, settling time and pH. In this figure, dye solutions with different concentrations between 25 and 380 mg/L were treated by CC. Experimental data show that CC gave satisfactory results, i.e. $Y_{COL}$ values higher than 80%, for dye concentrations higher than 50 mg/L. In Fig. 5, the $Y_{COL}$ curve increased rapidly as a function of $C_i$ up to 60 mg/L, and then exhibited a plateau region above 90% for $C_i$ between 60 and 230 mg/L. Finally, $Y_{COL}$ decreased slightly, from 91% to 82%, for higher $C_i$ values between 230 and 380 mg/L, probably because the dye content becomes too high in comparison to the amount of coagulant added. Again, the effect of the settling time remained negligible, particularly when the plateau region was reached.

The most striking point, however, is the poor efficiency of CC at low $C_i$ values; contrary to expectations, $Y_{COL}$ does not tend to 100% when $C_i$ tends to 0. As already mentioned, overdosing coagulant (which occurs when $C_i$ is reduced) is known to have an adverse effect on CC by increasing colloidal stability, while underdosing reduces yield, as shown above. It seems therefore that there is an optimum
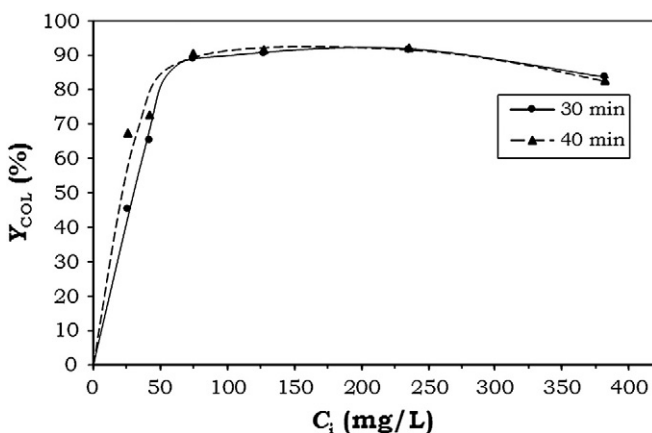
ratio between dye and coagulant concentrations that promotes sweep coagulation: for 40 mg/L alum, this lies between 1.5 and 6 for the red disperse dye of this work. As a conclusion, the coagulation process based on $Al_2(SO_4)_3$ seems robust because it can achieve more than 80% yield for $C_i$ between 60 and 380 mg/L with 40 mg/L coagulant; the removal yield also remains higher than 90% when $C_i$ is between 60 and 230 mg/L, but it must be pointed out that $Y_{COL}$ declines more rapidly in the presence of low initial dye concentrations than when these are high.

### 3.1.6. Effect of salt addition

NaCl may be added in wastewater before coagulation in order to increase the ionic strength of the water to be treated, especially when non-ionic pollutants prevail. Indeed, ionic strength reduces the zeta potential due to its screening effect on the electrical charges, which makes coagulation easier. Increasing water conductivity using NaCl also has other advantages: e.g., chloride anions could significantly reduce the adverse effects of other anions on coagulation, such as sulphate or bicarbonate anions [22]. However, such an addition is more common in EC processes because the added salt also increases water conductivity and, consequently, decreases simultaneously the ohmic loss between electrodes and power requirements (Eq. (5)). In this section, the conductivity and the ionic strength of the synthetic wastewater were adjusted, using the addition of NaCl in the range 0–6 g/L in deionized water instead of tap water to enlarge the range of $\kappa$ values.

The effect of NaCl on the effectiveness of CC is shown in Fig. 6 in which salt addition is expressed in terms of water conductivity. Experimental results illustrate the slight evolution of the colour removal yield with time as a function of $\kappa$. This figure shows that $Y_{COL}$ was only slightly improved at low $\kappa$ and, then, slightly decreased when conductivity was increased by NaCl addition. For example, when $\kappa$ was increased from 830 to 2620 μS/cm, $Y_{COL}$ was slightly reduced, from 91.8% to 88.1%. This result, contrary to expectations, results partly from the absence of bicarbonate anions in the synthetic wastewater, while chloride anions cannot reduce the role of sulphate anions from alum as interface co-ordinator with aluminium [22]. As a conclusion, NaCl addition cannot be used to improve $Y_{COL}$ using CC.

### 3.2. Comparison with electrocoagulation

In a previous work [37], Merzouk et al. had shown that a continuous EC process using Al electrodes could remove effectively the disperse red dye used in work. A colour removal yield between 85% and 95% could be achieved using EC in the same range of pH in
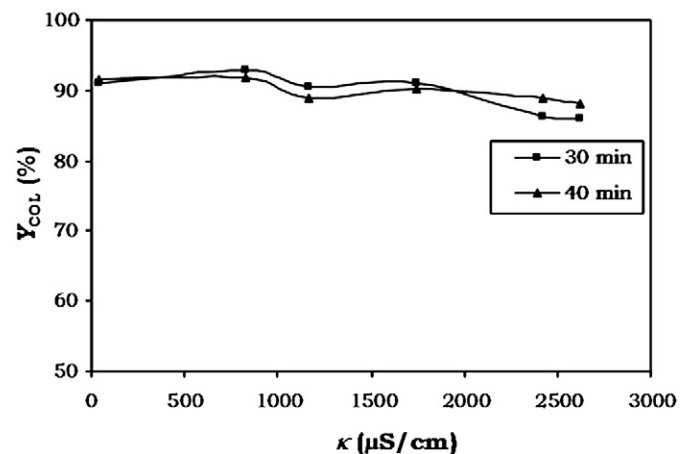


**Fig. 5.** Effect of initial dye concentration and settling time on the colour removal yield using CC: mixing speed 60 rpm, mixing time 30 min, $\kappa = 2.4$ mS/cm, initial pH 6.4 (coagulant: $Al_2(SO_4)_3$ $18H_2O$, 40 mg/L).



**Fig. 6.** Effect of settling time and NaCl addition through water conductivity on the colour removal yield using CC: $C_i$ 100 mg/L, mixing speed 60 rpm, mixing time 30 min, initial pH 6.4 (coagulant: $Al_2(SO_4)_3$ $18H_2O$, 40 mg/L).

which CC operates efficiently in Fig. 5, up to an influent dye concentration $C_i$ of 200 mg/L. Current density was shown to be the most influent parameter, as expected in EC process [28]: $j$ not only determines the production rate of coagulant, but also adjusts the production of $H_2$ bubbles, and hence affects simultaneously mixing and the growth of flocs [29]. Typical experimental results are summarized in Fig. 7 and show roughly that the values of the colour removal yield achieved for EC were similar to those of CC: an increase of current density from 20.8 to 62.5 mA/cm$^2$ yielded an increase of $Y_{COL}$ from 78% to 93%. In [37], the authors optimized the operating conditions for maximizing $Y_{COL}$ as follows: a residence time of 14 min and a current density about 31.2 mA/cm$^2$.

### 3.2.1. Economic comparison

In CC, operating costs include coagulant and power requirements for mixing. As slow mixing conditions are required during the coagulation and the settling steps, power requirements will be negligible in comparison to coagulant (alum: 0.7$/kg). In EC, operating costs derive simultaneously from the specific energy consumption $E_{dye}$ and the specific mass consumption of the electrodes $\mu_{Al}$. These quantities were estimated as a function of $j$ (mA/cm$^2$) in the optimum range of pH for $\kappa = 2.4$ mS/cm and a 14 min residence time [37]:

$$E_{dye} = 0.0036 \cdot j^2 \qquad (8)$$

$$\mu_{Al} = 0.0047 \cdot j \qquad (9)$$

For EC, operating costs can be easily deduced using the following pricing information for electricity (European electricity market *Powernext*: 0.06 $/kWh) and aluminium metal (*London Metal Exchange*: 2$/kg).

On the basis of the two equations Eqs. (5) and (6), both $E_{dye}$ and $\mu_{Al}$ are known to vary as $1/Q \sim \tau$, which is however only true when $Y_{COL}$ does not significantly change with $\tau$. From the experimental results of [37], it appears that the approximations $E_{dye} \sim 1/Q \sim \tau$ and $\mu_{Al} \sim 1/Q \sim \tau$ can be used only when $\tau$ is higher than 9 min. On the other hand, while $\mu_{Al}$ can be considered independent from water conductivity as a first approximation, $E_{dye}$ varies roughly as $1/\kappa$: this assumption results from the applicability of Ohm's law for $U$ in Eq. (5) when over-potentials at the electrodes are negligible in comparison to the contribution of the resistance of the liquid phase, which is confirmed by Eq. (8). In EC process, the addition of 5 g/L NaCl (0.02$/kg) in deionized water was therefore shown to halve power requirements [37], but at the expense of a secondary pollution by chloride anions. Even though chloride anions could also be oxidized in active chlorine

forms, such as hypochlorite anions that could contribute to pollution removal, $Y_{COL}$ was reported to remain constant or even to decrease with NaCl addition during EC [37], which is in agreement with the experimental data of CC (Fig. 6) and with the poor oxidizability of disperse dyes.

Calculations based on the above-mentioned rules are reported in Table 2, using experimental conditions that achieve a minimum of 80% colour removal yield. This table shows that CC is the cheapest process, although the difference with EC is sometimes small. However, in the optimum conditions of [37], EC is roughly 1.6 times more expensive than CC. From an economic point of view, $\mu_{Al}$ appears to play the key role on the operating costs of EC process in Table 2, in agreement with the literature in which Al consumption can constitute up to 80% of the total operating costs for EC using aluminium electrodes [31]. As shown in Table 2, this is the reason why the respective decreases of $j$ from 30.1 to 20.8 mA/cm$^2$ and of $\tau$ from 14 to 9 min have nearly the same influence on operating costs (Table 2): as $j$ and $\tau$ are roughly decreased in the same proportion, $j$ should have a stronger effect than $\tau$ on $E_{dye}$ and a similar effect on $\mu_{Al}$, but this difference vanishes due to the weak contribution of $E_{dye}$ on operating costs. This also explains why the attempt to increase wastewater conductivity raises steeply the operating cost (Table 2): as wastewaters usually exhibit high conductivity levels, large amounts of salt are required to increase $\kappa$, while conductivity acts only on $E_{dye}$.

Finally, Table 2 highlights that the amount of Al metal released is far lower in CC than in EC process. However, this table also shows clearly that EC can be optimized so that operating costs between CC and EC become close. As a result, the comparison between EC and CC is not straightforward and refined techno-economical calculations are compulsory in order to compare adequately CC and EC. These must first account for equipment cost for which EC is less expensive than CC: for CC, the residence time for coagulation/flocculation and sludge separation can be adjusted between 9 and 14 min, whereas, a minimum 40 min operation time is needed for CC, which includes 30 min for coagulation and 10 min for settling (Fig. 1). At constant wastewater volume to be treated, this leads to equipment volumes from 2.8 to 4.5 times bigger for CC. As the operating costs of CC and EC are moderate, a higher operating cost can therefore be tolerated for EC because of the lower equipment investment. However, another parameter to account for is the influence of the variability of wastewater properties on $Y_{COL}$, in particular pH and dye concentration. These are discussed in the two following subsections.

### 3.2.2. Effect of dye concentration

The sensitivity of the evolution of $Y_{COL}$ as a function of the initial/influent dye concentration $C_i$ was investigated for EC and CC. Experimental results are reported in Fig. 8. They clearly show that EC was more effective for decolourization purpose when $C_i$ was below 100 mg/L, while CC was more effective at higher $C_i$ values, as expected from Fig. 5. Actually, $Y_{COL}$ values about 90% could be achieved with CC when $C_i$ lay between 75 and 235 mg/L, while EC was more effective when $C_i$ lay between 25 and 100 mg/L. It must however be pointed out
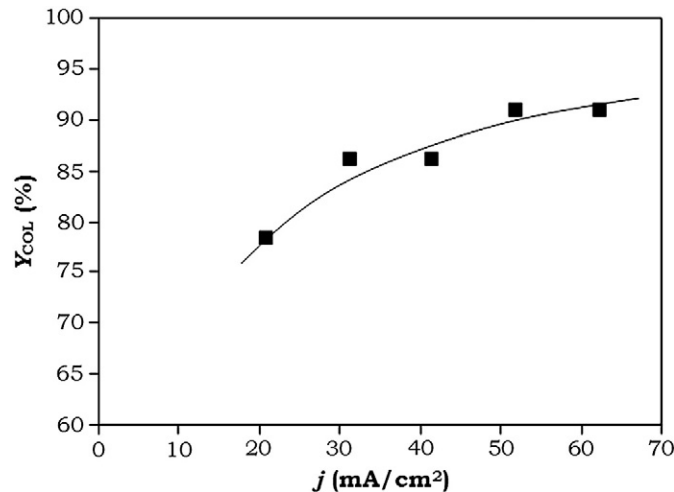


**Fig. 7.** Effect of current density $j$ on the colour removal yield using EC: $C_i$ 100 mg/L, residence time 14 min, influent pH 7.6, $\kappa = 2.4$ mS/cm.

**Table 2**
Economical comparison between CC and EC ($C_i$: 100 mg/L, wastewater pH 6.1).

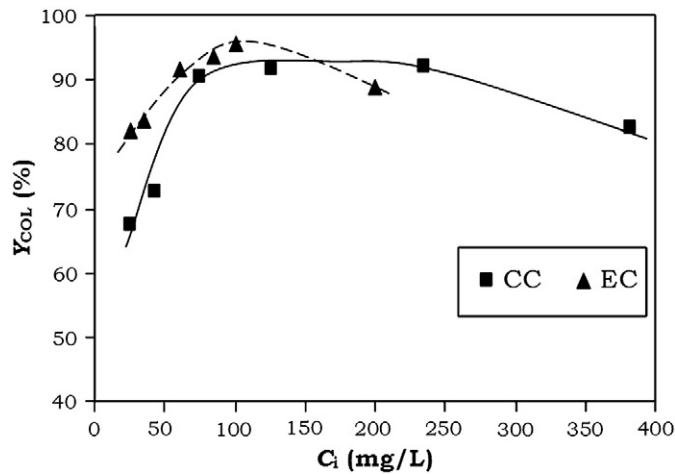|  | CC | EC | EC | EC | EC |
|---|---|---|---|---|---|
| $\kappa$ (mS/cm) | 2.4 | 2.4 | 2.4 | 2.6 | 2.4 |
| $t$ or $\tau$ (min) | 40 | 14 | 14 | 14 | 9 |
| $j$ (mA/cm$^2$) | – | 31.0 | 20.8 | 20.8 | 31.0 |
| Alum (mg/L) | 40 | – | – | – | – |
| NaCl (g/L) | – | 0 | 0 | 1.0 | 0 |
| NaCl ($/kg dye) | – | 0 | 0 | 0.20 | 0 |
| Energy cost ($/kg dye) | – | 0.21 | 0.10 | 0.09 | 0.14 |
| Al cost ($/kg dye) | – | 0.31 | 0.24 | 0.24 | 0.23 |
| $Y_{COL}$ (%) | 87 | 95 | 80 | 80 | 82 |
| Al released (mg/L) | 3.2 | 16 | 11 | 16 | 10 |
| Operating cost ($/kg dye) | 0.32 | 0.52 | 0.34 | 0.53 | 0.37 |

**Fig. 8.** Effect of wastewater dye concentration on the colour removal yield using CC (mixing speed 60 rpm, mixing time 30 min, 40 mg/L alum as a coagulant, settling time 40 min) and EC ($j = 31.2$ mA/cm$^2$, residence time 14 min), with $\kappa = 2.4$ mS/cm and wastewater pH 6.1.



**Fig. 10.** Effect of the influent/initial pH on colour removal using CC (mixing speed 60 rpm, mixing time 30 min, 40 mg/L alum as a coagulant, settling time 40 min) and EC (residence time 14 min, $j = 31.2$ mA/cm$^2$) with $\kappa = 2.4$ mS/cm and $C_i$ 100 mg/L.

that colour removal was never complete, both using EC and CC, which is a quite common result in the literature, but is not still fully understood. In Fig. 8, it also appears that the maximum $Y_{COL}$ value, close to 95%, was obtained with EC, while $Y_{COL}$ value did not overpass 92% using CC, at a pH value at which both treatments should nearly maximize decolourization. This may probably be attributed to the fact that EC was also able to oxidize pollutants, which is not the case for CC. However, the difference between both methods remained weak, probably because disperse dyes are known to be poorly oxidizable, as explained in section 1. As a conclusion, the respective ranges in which EC and CC exhibit their respective maximum $Y_{COL}$ value differ strongly; this constitutes a key criterion for the selection of the wastewater treatment process.

### 3.2.3. Effect of pH

Another possible key difference between EC and CC is the effect of the influent/initial pH. EC should exhibit, indeed, a buffering capacity which prevents more efficiently than CC high changes of pH. This statement is confirmed by Fig. 9 which compares the respective evolution of pH due to EC and CC. While CC always decreased pH when the initial pH value was above 4, the pH of the effluents tended to a buffering pH value which is about 7 using EC. Consequently, when
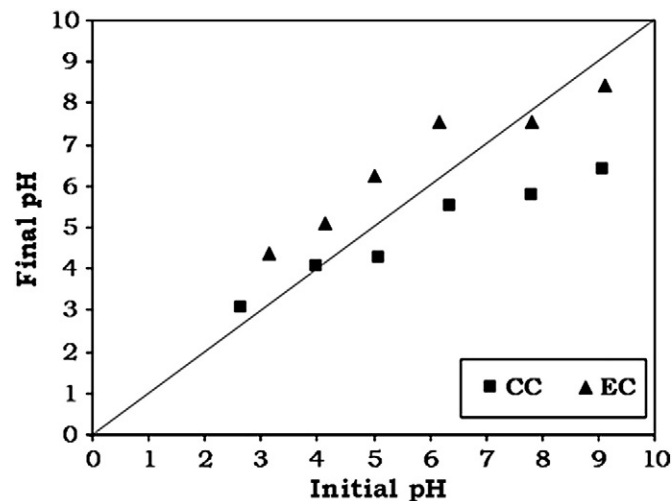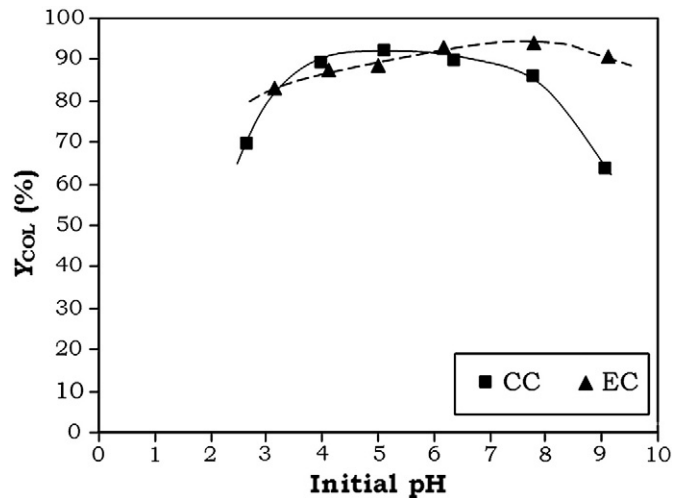


**Fig. 9.** Final/effluent pH values for different influent/initial pH values after CC (mixing speed 60 rpm, mixing time 30 min, 40 mg/L alum as a coagulant, settling time 40 min) and EC (residence time 14 min, $j = 31.2$ mA/cm$^2$) with $\kappa = 2.4$ mS/cm and $C_i$ 100 mg/L.

sweep precipitation was the key mechanism of pollution removal, EC maintained the pH values in a range in which insoluble Al(OH)$_3$ was the prevailing aluminium species. This has strong consequences on the effectiveness of colour removal, as shown by Fig. 10: the $Y_{COL}$ curve slightly increased as a function of pH up to an influent pH about 8 and then decreased only slightly for EC, while the $Y_{COL}$ curve passed through a clear maximum about an initial pH of 5 for CC. As a result, CC is far more sensitive to pH than EC, especially when the initial/influent pH value is above 7, as expected. This is in favour of the EC process, as the use of CC should probably require an additional pH adjustment in this particular situation.

## 4. Conclusions

In this work, chemical coagulation has been applied for colour removal, using a red dye of the disperse dye class, in a synthetic wastewater as a model. This dye is also representative of poorly oxidizable colloidal particles, which corresponds to a large fraction of the solids in real textile wastewater. CC has been shown to be a robust process for decolourization purpose when Al$_2$(SO$_4$)$_3$ was used as the coagulant: a removal yield about 90% could be achieved with a 40 mg/L dose of alum in a large range of pH from 4 to 8 and for a dye concentration between 60 and 235 mg/L. The comparison between CC and electrocoagulation using aluminium electrodes demonstrated that similar operating costs could be achieved with both methods, although this required a more severe optimization for the EC process. This disadvantage of EC was however shown to be counterbalanced by lower equipment investments and by a higher robustness against pH change, especially at low dye concentration. As a conclusion, CC remains probably the simplest method for the decolourization and, more generally, for the treatment of textile wastewater. However, EC is a competitive alternative process that must not be disregarded and presents a high potentiality for the treatment of textile wastewater difficult to manage with chemical coagulation.

*Nomenclature*

| | |
|---|---|
| BOD$_5$ | five-day biochemical oxygen demand (mg/L) |
| C | dye concentration (kg/m$^3$) |
| CC | chemical coagulation |
| $C_i$ | dye concentration in wastewater before treatment (kg/m$^3$) |
| COD | chemical oxygen demand (mg/L) |
| EC | electrocoagulation |
| E$_{dye}$ | specific energy consumption (kWh/kg dye removed) |
| F | Faraday's constant (96,487 C/mol e$^-$) |

| I | current (A) |
|---|---|
| j | current density (mA/cm$^2$) |
| $M_{Al}$ | molar mass of aluminium (0.02698 kg/mol) |
| Q | inlet flow rate (L/h) |
| t | electrolysis time (s) |
| U | cell potential (V) |
| $Y_{COL}$ | colour removal yield (%) |

*Greek letters*

| $\Delta m_{exp}$ | experimental weight loss of Al electrode (kg) |
|---|---|
| $\Delta m_{th}$ | theoretical weight loss of Al electrode (kg) |
| $\kappa$ | wastewater conductivity (mS/cm) |
| $\mu_{Al}$ | specific mass consumption of the anode (kg Al/kg dye removed) |
| $\tau$ | residence time in the EC cell (s) |
| $\Phi_{Al}$ | faradic yield of Al dissolution |

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