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Decolourization of dye-containing effluent using mineral coagulants produced by electrocoagulation

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Abstract

The colour and colour causing-compounds has always been undesirable in water for any use, be it industrial or domestic wastewaters. The discharge of such effluents causes excessive oxygen demand in the receiving water and then a treatment is required before discharge into ecosystems. This study examined the possibility to remove colour causing-compounds from effluent by chemical coagulation, in comparison with direct electrocoagulation. The inorganic coagulants (C_1, C_2 and C_3) in the form of dry powder tested, were respectively produced from electrolysis of $S_1 = [NaOH\ (7.5 \times 10^{-3}\ M)]$, $S_2 = [NaCl\ (10^{-2}\ M)]$, and $S_3 = [NaOH\ (7.5 \times 10^{-3}\ M) + NaCl\ (10^{-2}\ M)]$ solutions, using sacrificial aluminium electrodes operated at an electrical potential of 12 V. Reactive textile dye (CI Reactive Red 141) was used as model of colour-causing compound prepared at a concentration of 50 mg l^{-1}. The best performances of dye removal were obtained with C_2 having a chemical structure comprised of a mixture of polymeric specie ($Al_{45}O_{45}(OH)_{45}Cl$) and monomeric species ($AlCl(OH)_2 \cdot 2H_2O$ and $Al(OH)_3$). The removal efficiency (R_A) evaluated by measuring the yields of 540 nm-absorbance removal varied from 41 to 96% through 60 min of treatment by imposing a concentration of C_2 ranging from 100 to 400 mg l^{-1}. The effectiveness of the treatment increased and the effluent became more and more transparent while increasing C_2 concentration. The comparison of chemical treatment using C_2 coagulant and direct electrocoagulation of CI Reactive Red 141 containing synthetic solution demonstrated the advantage of chemical treatment during the first few minutes of treatment. A yield of 88% of absorbance removal was recorded using C_2 coagulant (400 mg l^{-1}) over the first 10 min of treatment, compared to 60% measured using direct electrocoagulation while imposing either 10 or 15 V of electrical potential close to the value (12 V) required during C_2 production. However, at the end of the treatment (after 60 min of treatment), CI Reactive Red 141 pollutant was completely removed from solution (540 nm-absorbance removal of 100%) using direct electrochemical treatment, compared to 96.4% of absorbance removed while treating dye-containing synthetic solution by means of C_2 coagulant.
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1. Introduction

The effluents of many industries (textile, leather, pulp and paper, printing, photographs, cosmetics, pharmaceutical, food) contain dyes, which represent an important environmental problem [1,2]. Colour usually appears as the result of the presence of low concentrations of specific compounds, such as azo dyes, which is the most common group of dyes used [3]. As example, the textile industry utilizes about 10,000 dyes and pigments [4]. As much as 20–50% of reactive dyes used in textile fabrics can be released into waterways [5]. Lang [6] reports that dyes are normally found in dyehouse effluent at concentrations ranging from 10 to 50 mg l^{-1}.

As example, CI Reactive Red 141 (Evercion Red HE7B) is an azo reactive dye with a molecular mass of 1634 Da (Fig. 1). This dye is representative of a dye class known to be problematic with treatment in a conventional wastewater treatment system [1]. In fact, reactive dyes are hydrophilic, therefore, they have

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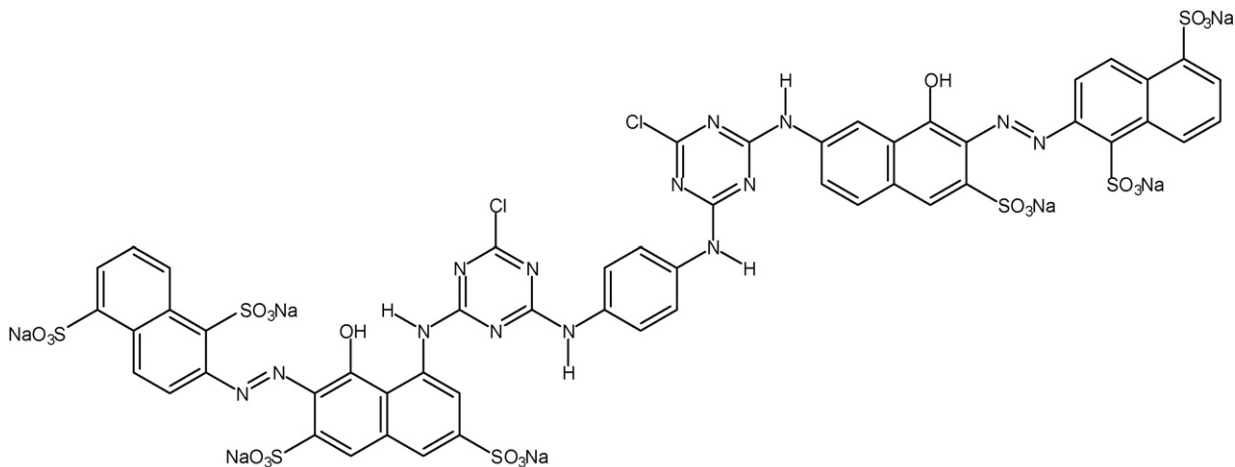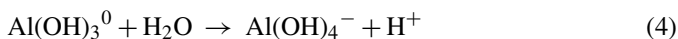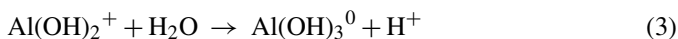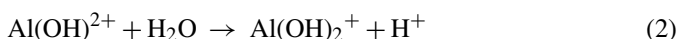*E-mail address:* blaisjf@ete.inrs.ca (J.-F. Blais).

Fig. 1. Molecular structure of red-dye CI Reactive Red 141.

low affinity to adsorb to biomass and generally pass through conventional biological wastewater systems [7,8]. Moreover, dyes molecules are highly structured molecules that are potentially toxic to organisms [9]. Therefore, it is difficult to degrade them biologically [10].

Several methods have been used or proposed for colour removal from wastewaters. This includes biological aerobic (activated sludge, SBR, biofilter, e.g.) [11–13] or anaerobic (UASB, e.g.) [1,3] treatments, enzymatic biodegradation (actinomycetes, fungi) [14], chemical oxidation (H_2O_2/Fe^{2+} (Fenton), hypochlorite, e.g.) [15,16] or reduction (Fe^0, e.g.) [17], electrochemical oxidation (O_3/UV, O_3/H_2O_2, $O_3/UV/H_2O_2$, H_2O_2/UV, e.g.) [18,19], photodegradation (TiO_2/UV, photo-Fenton, e.g.) [20,21], adsorption (activated carbons, silica, biosorbents, e.g.) [22,23], membrane separation (microfiltration, ultrafiltration, nanofiltration, e.g.) [24], chemical coagulation/flocculation (aluminium, iron or calcium salts, e.g.) [25], and electrolytic treatments, which include electrooxidation [26–28], electroflocculation [29], and/or electrocoagulation [30–34].
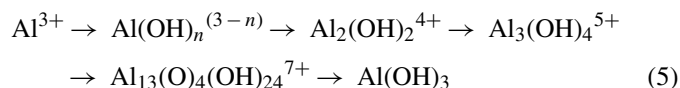
Electrocoagulation is an electrochemical technique of treating polluted effluent whereby sacrificial anodes (aluminium or iron electrodes) corrode to release active coagulant precursors into solution [35]. These molecules produce insoluble metallic hydroxide flocs which can remove pollutants by surface complexation or electrostatic attraction [36,37].

It is worth noting that, when aluminium ion (Al^{3+}) is added to water, four mononuclear complexes are initially formed as described by reactions (1)–(4).

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \qquad (1)$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \qquad (2)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3^0 + H^+ \qquad (3)$$

$$Al(OH)_3^0 + H_2O \rightarrow Al(OH)_4^- + H^+ \qquad (4)$$

The extent of hydrolysis depends upon total aluminium concentration and pH, as well as the amount of others species present in solution [38]. As the aluminium concentration increases in solution, polymeric species are formed by condensation process (or germination process) according to the following reactions [39,40]:

$$Al^{3+} \rightarrow Al(OH)_n^{(3-n)} \rightarrow Al_2(OH)_2^{4+} \rightarrow Al_3(OH)_4^{5+}$$
$$\rightarrow Al_{13}(O)_4(OH)_{24}^{7+} \rightarrow Al(OH)_3 \qquad (5)$$

where "*n*" represents the number of hydroxyl ion surrounding the metal in the coordination sphere. Most of the monomeric species ($Al(OH)^{2+}$, $Al(OH)_2^+$ $Al(OH)_3$, and $Al(OH)_4^-$) and polymeric species ($Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$) form before the precipitation of solid amorphous aluminium hydroxide [41]. Hence, soluble and insoluble pollutants can be coagulated by aluminium hydrates or hydroxide aluminium, and effectively removed from effluent.

The electrocoagulation has been tested successfully in the separation of pollutants from restaurant wastewater [42,43], potable water [44,45], groundwater [46], greywater [47], urban wastewater [48], textile wastewater [49–53], tar sand and oil shale wastewater [54], leachates containing toxic metals [55–57], liquid swine manure [58], slaughterhouse effluent [59,60], defluoridation of water [61–63], phosphate removal from wastewater [64,65], separation of ultrafine particles [38,66], arsenic removal from water [67–69], and removal of nitrate, sulfide, sulfate from water [70,71]. Direct electrocoagulation process has also been demonstrated as an efficient option for the removal of different types of dyes from effluents [4,32–34,50,72–74].

The purpose of this study is to conduct an experimental investigation on the removal of a reactive textile dye (CI Reactive Red 141) from solution using both a direct electrocoagulation process and an indirect electrocoagulation method using different aluminium hydroxides previously generated in different experimental conditions.

2. Materials and methods

2.1. Coagulant agents production

The coagulants used throughout this study was produced by direct current electrolysis at room temperature using eight parallel pieces of aluminium plate electrodes (each having $110\,cm^2$ of surface area) and individually connected to the power supply. Four anodes and four cathodes alternated in the electrode pack. The four electrodes connected to the positive outlet of power supply were consumed during the experiments while the four cathodes were insoluble (non-consumable electrodes). The electrodes were installed on a perforated acrylic plate placed at 2 cm from the bottom of the electrolytic cell. The dc power source (Xantrex, model XFR40-70, Mississauga, Ontario, Canada) had a maximum current rating of 70 A at an open circuit potential of 40 V. The potential (12 V) was held constant for each run with retention time of 300 min. The electrode sets were situated 1.5 cm apart and submerged in the liquid phase. Mixing in the cell was achieved by a Teflon-covered stirring bar installed between the perforated plate and the bottom of the cell. The liquid phase was distilled water containing different solutes. Three types of saline solutions (S_1, S_2 and S_3) were electrolysed: $S_1 = [NaOH\ (7.5 \times 10^{-3}\ M)]$, $S_2 = [NaCl\ (10^{-2}\ M)]$ and $S_3 = [NaOH\ (7.5 \times 10^{-3}\ M) + NaCl\ (10^{-2}\ M)]$. A working volume of 1.8 l was used. At the end of each experiment, the electrolysed-solution containing metallic aluminium hydroxide was carefully collected and subjected to settling for 24 h before filtration using a Whatman no. 4 membrane under vacuum. The solid fraction (wet residue) was then dried at 105 °C during 24 h. Thus, three types of coagulants (C_1, C_2 and C_3) in form of dry powder were produced from the S_1, S_2 and S_3 electrolysis. The C_1, C_2 and C_3 coagulants (aluminium salts) were then used to treat dye-containing synthetic solutions.

2.2. Chemical treatment of dye-containing solution

Synthetic solutions containing $50\,mg\,l^{-1}$ of a red colour dye (CI Reactive Red 141, Merck) was prepared with distilled water and subjected to chemical treatment using C_1, C_2 and C_3 coagulants. The treatment of dye-containing solution was conducted at room temperature with a jar-test apparatus (Phipps & Bird Inc., model PB-700, Richmond, VA, USA) comprised of six individual acrylic tank reactors, each having 2 l of capacity and contained 1 l of solution that was simultaneously mixed. Mixing was achieved by a variable speed mixer operated at 200 rpm and using a three blade axial impeller (Teflon-covered stirring bar) with a 4.5 cm diameter. Experiments were conducted at different concentrations of coagulants ($100-800\,mg\,l^{-1}$) with one reactor maintained as control. The control assay consisted of mixing the dye solution without addition of aluminium salts. Sample of 20 ml were drawn at 10 min intervals, settled and monitored for pH and the residual absorbance (540 nm) over a period of 60 min. Prior to each absorbance measurement, the samples were filtered using a Whatman 934AH membrane under vacuum.

2.3. Electrochemical treatment of dye-containing solution

In order to compare chemical coagulation with the electrochemical treatment (electrocoagulation), the dye solution was treated in an electrolytic cell using two identical aluminium electrodes each having a dimension of 3 cm (width) × 10 cm (length) × 0.2 cm (thick). The Al electrode composition is Al (98.8%), Si (0.10%), Fe (0.30%), Cu (0.010%), Mn (0.01%), Mg (0.74%), Cr (0.001%), Zn (0.01%) and Ti (0.001%). The treatment was carried out in a 1 l tank (pyrex glass) containing 500 ml of dye solution in which the two electrodes were immersed. Mixing in the cell was achieved by a Teflon-covered stirring magnetic bar installed at the bottom of the cell. The two electrodes were installed at 2 cm from the bottom of the cell and were situated 4 cm apart. The anode and cathode electrode were connected to the positive and negative outlets of a dc power supply (AL 823 ELC) having a maximum current rating of 5 A and an open circuit potential of 30 V. A potential of 12 V was held constant during the treatment at room temperature. A subsample of 10 ml of supernatant was withdrawn to measure the residual absorbance (540 nm) and monitored for pH after a short settling period. Between two assays, the electrodes (including the electrolytic cell) were cleaned with 5% (v/v) hydrochloric acid solution for at least 15 min and then rubbed with a sponge and rinsed with tap water.

2.4. Analytical techniques

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double-junction Cole-Palmer electrode with Ag/AgCl reference cell (calibration between 4.00 and 12.68). The absorbance measurements (540 nm) were carried out using an UV–vis spectrophotometer (Varian, model Cary 50, Mississauga, Ontario, Canada). The absorbance was measured after 5–10 min. The crystalline phases of coagulants was determined by X-ray diffraction using a diffract meter (Rigaku - Rotaflex, 12 kW Rotating Anode X-Ray Generator, model RU-200, The Woodlands, TX, USA) having an anode of copper for sample irradiation. Before X-ray analysis, the mineral was sieved in order to obtain a sample having 38–45 μm of particles diameter. The scanning was carried out from 2 to 80° with a step of 0.05°.

3. Results and discussion

3.1. Composition of the mineral coagulants

Table 1 presents the experimental conditions for the production of the mineral coagulants using the electrolysis technique and the corresponding major crystalline phases of the coagulants revealed by X-ray analysis. C_1 coagulant produced in highly alkaline medium was mainly in the form of monomer $Al(OH)_3$ (Bayerite, Gibbsite and Nordstrandite) (Fig. 2). The use of highly saline conditions during the production of the C_2 and C_3 coagulants has resulted in the formation of mixtures of dominant polymeric specie $(Al_{45}O_{45}(OH)_{45}Cl)$ and monomeric species $(AlCl(OH)_2 \cdot 2H_2O$ and $Al(OH)_3)$ (Figs. 3 and 4).

Table 1
Electrolysis of saline solutions and production of mineral coagulants

Parameters	Saline solutions		
	S_1 [NaOH] (7.5×10^{-3} M)	S_2 [NaCl] (10^{-2} M)	S_3 [NaOH] (7.5×10^{-3} M) [NaCl] (10^{-2} M)
Initial pH	11.4	5.0	9.8
Final pH	11.2	8.3	8.5
Current intensity (A)	0.3–0.8	0.2–0.3	0.3–0.8
Potential (V)	12	12	12
	C_1 coagulant	C_2 coagulant	C_3 coagulant
Crystalline phases of the mineral coagulant	$Al(OH)_3$	$Al(OH)_3$ $AlCl(OH)_2 \cdot 2H_2O$ $Al_{45}O_{45}(OH)_{45}Cl$	$Al(OH)_3$ $AlCl(OH)_2 \cdot 2H_2O$ $Al_{45}O_{45}(OH)_{45}Cl$

3.2. Dye removal from solution using C_1 coagulant

The effectiveness of chemical treatment using C_1 coagulant was evaluated by measuring the residual absorbance (540 nm) in the solution throughout the course of the treatment (Fig. 5a). The absorbance decreased gradually over the first 20 min of the treatment and remained quite stable between 20 and 40 min followed by a slight decrease of absorbance. At the end of the treatment, 0.77, 0.46 and 0.30 of absorbance were respectively recorded using 200, 400 and 800 mg l^{-1} of C_1 coagulant. Table 2 presents the percentage of 540 nm-absorbance removal from dye solution for various C_1 concentrations. The yields of 540 nm-absorbance removal were obtained by subtracting the residual absorbance from the initial value divided by the same initial concentration of absorbance. Removal of absorbance increased with the C_1 concentration and ranged from 12.5 to 65.9% (Table 2). Dye removal from solution can be attributed to co-precipitation or adsorption on the surface of C_1 coagulant or electrostatic attraction [31].

During the treatment, the Red 141-dye pollutant can act as a ligand (L) to bind aluminium hydrates or hydroxides according to the following reaction:

$$L\text{-}H + (OH)(OH)_2Al(s) \rightarrow L\text{-}(OH)_2Al + H_2O \qquad (6)$$
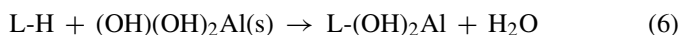
Concerning electrostatic phenomena, it can be attributed to the appearance of hydrate particles or aluminium hydroxides having positive or negative charge (such as $[Al(OH_2)_6]^{3+}$, $[Al(OH)_4]^-$ or $[Al(OH)_4(OH)_2]^-$) capable of attracting the opposite charge of dye and remove it from solution [31].

In the case of the C_1 coagulant, the highest removal capacity was observed using 400 mg C_1 l^{-1} and corresponds to 59.6 mg of Red 141 dye removed by gram of C_1 coagulant (Table 2).

3.3. Dye removal from solution using C_2 coagulant

Fig. 5b shows the change in absorbance during the treatment using C_2 as coagulant agent. The absorbance decreased rapidly over the first 10 min of the treatment and then remained quite stable until the end of experiment, using either 100, 200 or 400 mg C_2 l^{-1}. The maximum decrease in absorbance was recorded after the first 10 min of treatment regardless of the concentration of C_2 coagulant compared to 20 min required while using C_1 coagulant. Besides, C_2 coagulant was more effective in removing dye from solution than C_1 coagulant. For a given concentration of coagulant (for example 400 mg l^{-1}), the final value of absorbance recorded using C_2 was 0.03 (absorbance removal

Table 2
Chemical treatment of the dye CI Reactive Red 141 solution using C_1, C_2 and C_3 mineral coagulants at different concentrations

Parameters	Concentration of mineral coagulants (mg l^{-1})								
	C_1 coagulant			C_2 coagulant			C_3 coagulant		
	200	400	800	100	200	400	100	200	400
pH									
Initial	6.03	6.00	5.80	6.00	6.00	6.10	6.00	5.70	5.42
Final	6.63	6.74	6.96	6.15	6.28	6.53	6.10	6.18	6.45
Absorbance									
Initial	0.88	0.88	0.88	0.83	0.83	0.83	0.90	0.90	0.90
Final	0.77	0.46	0.30	0.49	0.19	0.03	0.53	0.40	0.20
R_A (%)	12.5	47.7	65.9	41.0	77.1	96.4	41.1	55.6	77.8
Dye removal capacity									
(mg dye g^{-1} coagulant)	31.3	59.6	41.2	205	193	121	205	139	97.3
(mg COD g^{-1} coagulant)[a]	29.1	55.4	38.3	191	179	113	191	129	90.5

[a] Based on the following equivalence: 1 mg CI Reactive Red 141 = 0.93 mg COD [80].
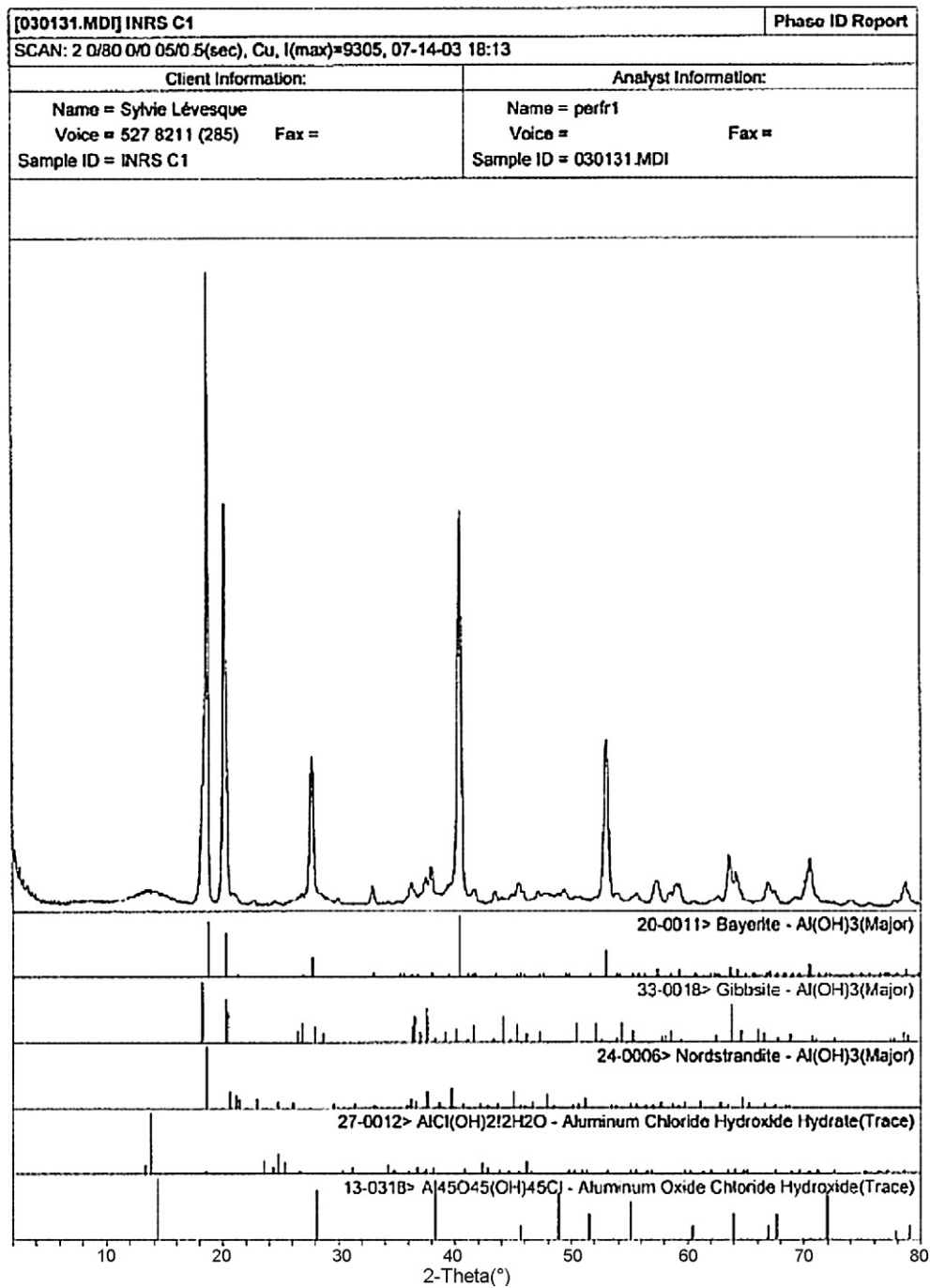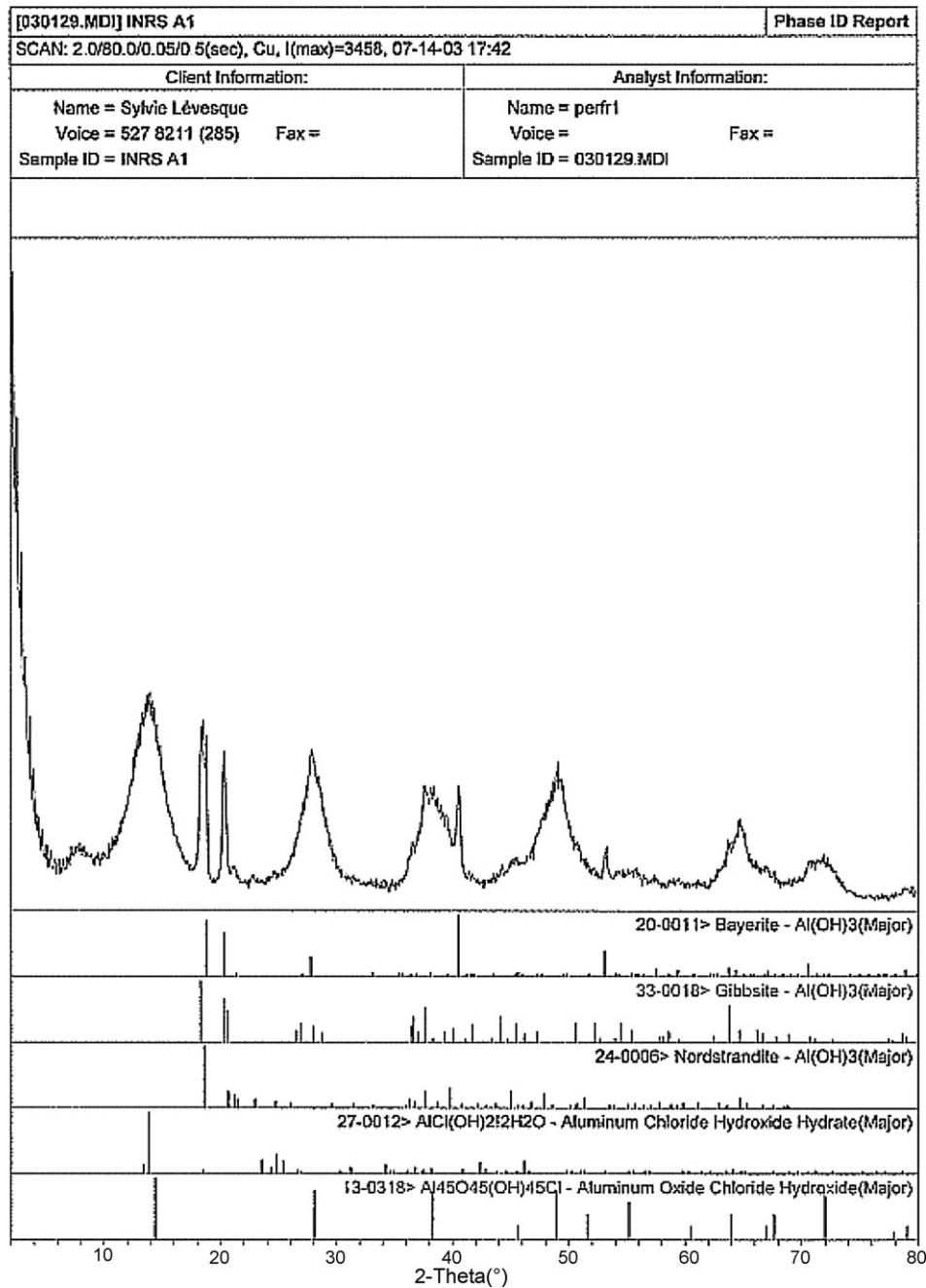
Fig. 2. XRD analyses of the coagulant C_1.

of 96.4%) while 0.46 of absorbance was measured using C_1 (only 47.7% of absorbance removal).

In fact, the good performance of C_2 as coagulating agent resulted from its chemical structure ($Al_{45}O_{45}(OH)_{45}Cl$, $AlCl(OH)_2 \cdot 2H_2O$ and $Al(OH)_3$). In addition to the reaction between the monomer species ($Al(OH)_3$) and Red 141, as indicated in reaction (6), the dye was effectively coagulated with the polymeric species and precipitated by the mechanism of adsorption and charge neutralization [75]. Indeed, the polymeric aluminium complexes can have both positive and negative charge capable of attracting the opposite charge of polluting species. Overall, the attraction phenomena occurring
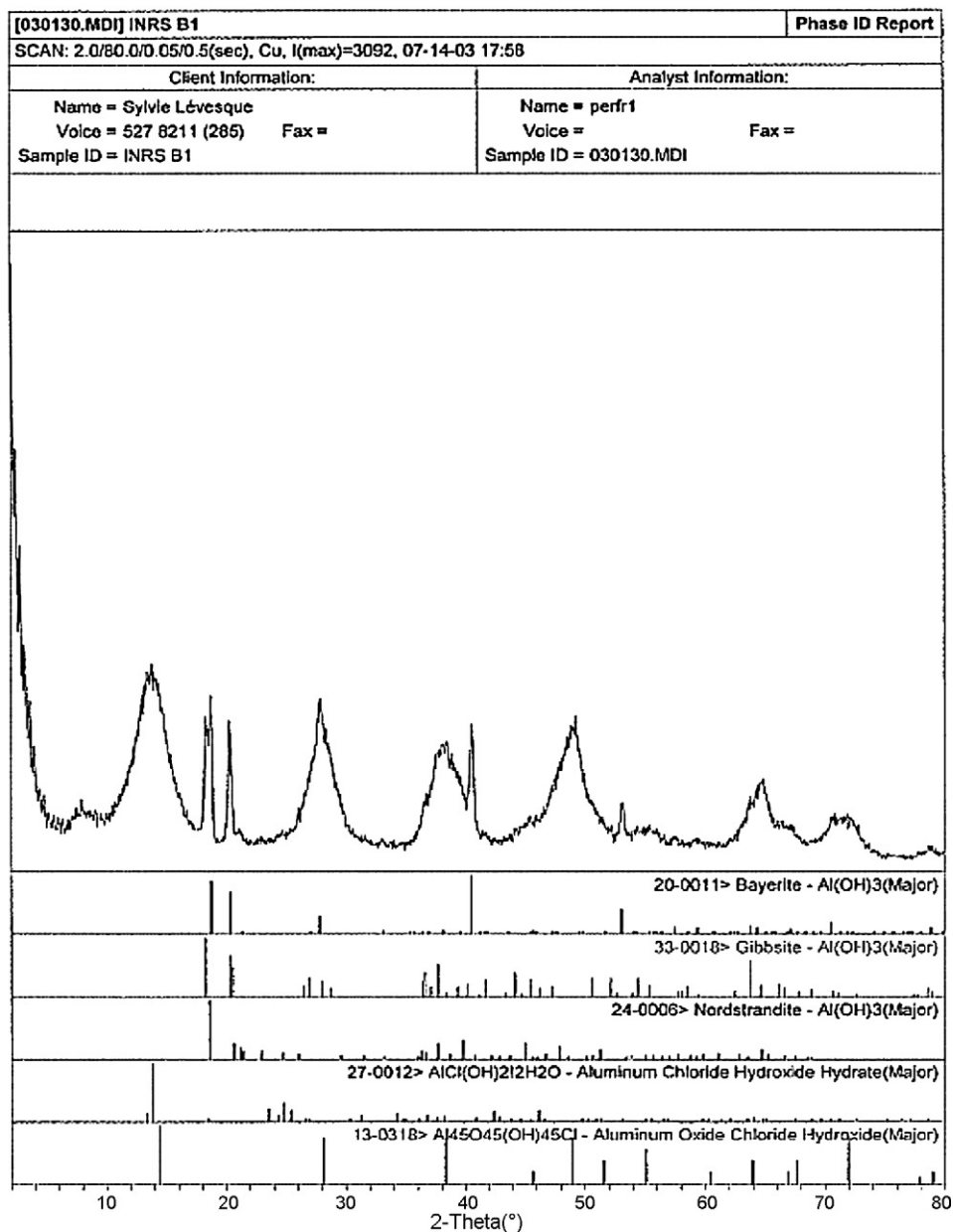
Fig. 3. XRD analyses of the coagulant C_2.

between the pollutant and the polymeric aluminium complexes are more important than that existing between the pollutants and the monomeric charged species ($Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_4^-$). The capacity of dye removal using C_2 coagulant (121–205 mg dye g^{-1} coagulant) was 2–6 times higher than that measured using C_1 coagulant (31–60 mg dye g^{-1} coagulant) (Table 2).

3.4. Dye removal from solution using C_3 coagulant

Fig. 5c shows the change in absorbance of the dye (CI Reactive Red 141) synthetic solution while applying C_3 as coagulant agent. The shape of the curves in Fig. 5c was quite similar to that recorded in Fig. 5b, confirming that the mechanism of absorbance removal based on dye co-precipitation with

Fig. 4. XRD analyses of the coagulant C_3.

metallic aluminium hydroxides ($AlCl(OH)_2 \cdot 2H_2O$, $Al(OH)_3$, $Al_{45}O_{45}(OH)_{45}Cl$) was generally the same using either C_2 or C_3 as coagulants. However, C_2 coagulant was found to be more effective than C_3 coagulant. The yields (R_A) of 540 nm-absorbance increased from 41.1 to 77.8% with increasing C_3 concentration in solution (100–400 mg l^{-1}), whereas an increase of 41.0–96.4% was recorded using similar concentration of C_2 coagulant. For a relatively lower concentration of coagulant (100 mg l^{-1}), the yield (R_A) of absorbance removal was the same using either C_2 or C_3 coagulant (Table 2). The decolourization

using the coagulant C_2 is better than that using C_3 owing to probably higher concentration of aluminium ion (Al^{3+}) in C_2 compared to that contained in C_3. In fact, the relatively high initial pH (pH 9.8) imposed in S_3 while producing C_3 limited the metallic hydroxide formation during electrolysis. Indeed, a non-negligible fraction of Al^{3+} produced by anodic dissolution in S_3 remained in solution in form of aluminate ion ($Al(OH)_4^-$), this compound being a dominant anionic specie above pH 9.0 [38]. In term of removal capacity, the best results (205 mg Red 141 dye g^{-1} coagulant or 191 mg Chemical Oxygen Demand (COD) g^{-1}
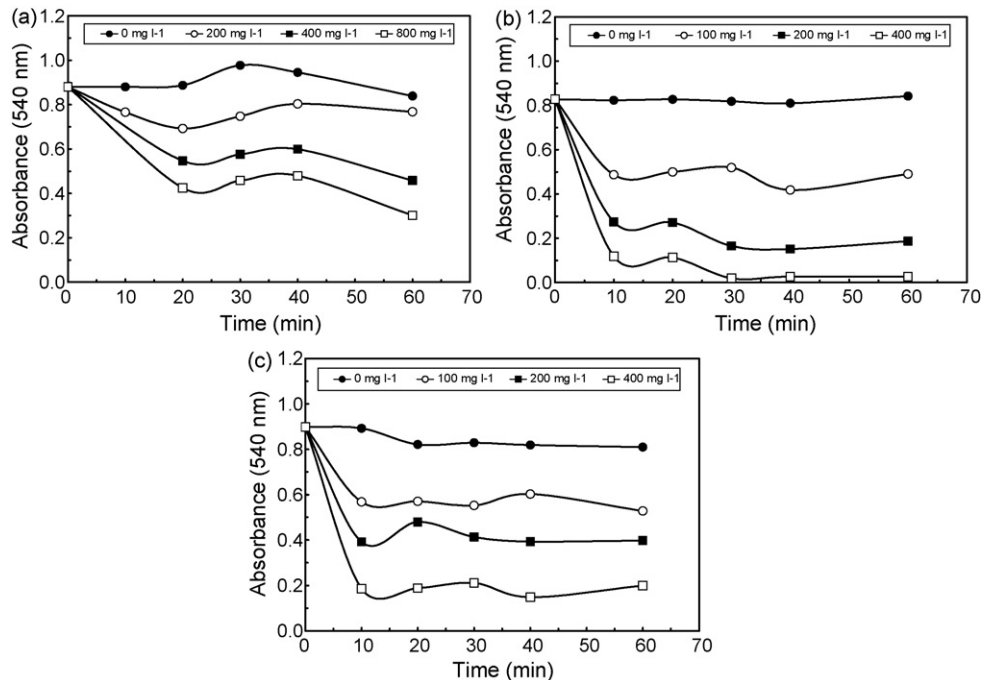
Fig. 5. Absorbance (540 nm) removal from the CI Reactive Red 141 solution ($C_0 = 50$ mg l^{-1}) during chemical coagulation assays using different concentrations of the coagulants: (a) C_1; (b) C_2; (c) C_3.

coagulant) were measured for the C_2 and C_3 coagulants, using 100 mg coagulant l^{-1} (Table 2).

The pH of the solution being quite similar at the start (pH 6.00) and at the end (6.15–6.18) of the treatment using C_2 or C_3. This difference can be probably explained by the pH of the solution measured at the start of the experiment, which can greatly influence the affinity between polymeric or monomeric aluminium species and the pollutant (red colour dye). Using 200 and 400 mg l^{-1} of concentration of C_3, the initial pH were 5.70 and 5.42, respectively, compared to pH 6.00 and 6.10 using C_2. The C_3 coagulant initially contributed to slight decrease in pH of the solution and reduced the effectiveness of the C_3 coagulant compared to C_2 coagulant, although both coagulants (C_2 and C_3) had the same chemical structure. According to the results mentioned above, C_2 reactant was found to be the best coagulant in removing red colour dye (CI Reactive Red 141) from solution.

The performance of metal hydroxides for the removal of CI Reactive Red 141 dye has been demonstrated by Netpradit et al. [76] using a multi-metallic hydroxide sludge coming from an electroplating plant. A q_{max} value (Langmuir isotherm at 30 °C) of 51.6 mg of Red 141 dye removed per gram of metal hydroxide sludge has been measured by these researchers, which value is almost similar to the removal capacity obtained using the C_1 coagulant, but is lower than the adsorption capacity values measured with C_2 and C_3 coagulants.

High adsorption capacity of CI Reactive Red 141 dye has also been observed using chitin and modified chitin [77]. Maximum dye adsorption values of 167 and 124 mg dye g^{-1} have been respectively measured using chitin (at 60 °C) and modified chitin (at 30 °C).

3.5. Comparison between electrochemical and chemical treatment of dye solution

The removal efficiency of the electrolytic cell while treating Red-141-dye-containing solution was also evaluated by measuring the residual 540 nm-absorbance in the solution throughout the course of the treatment. Fig. 6 presents the change in absorbance for various electrical potentials used (5.0, 10, 15 and 20 V) through 20–120 min of treatment. For each electrical potential, the decrease in absorbance eventually reached a steady state. The removal efficiency increased as the electrical potential increased. For instance, for an electrical potential of 20 V, the 540 nm absorbance was reduced from 1.0 to 0.1 (absorbance
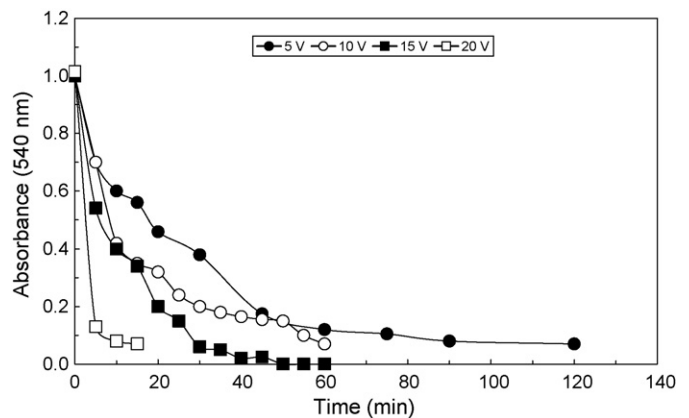

Fig. 6. Absorbance (540 nm) removal from the CI Reactive Red 141 solution ($C_0 = 50$ mg l^{-1}) during direct electrocoagulation assays using different electrical potentials imposed.

removal of 90%) after only 5 min of treatment, whereas for the same removal efficiency, a period of 60 min was required for an electrical potential of 5.0 V.

Fig. 6 shows that the absorbance decreased rapidly over the first 10 min of the treatment and the removal yield (R_A) of absorbance reached 60% by using an electrical potential of 10 and 15 V. By comparison, 63 and 88% removal of absorbance were recorded after 10 min of treatment while treating Red-141-dye-containing synthetic solution using respectively 200 and 400 mg l^{-1} of C_2 coagulant. Over the first 10 min, the yields of absorbance removal using C_2 coagulant (chemical treatment) were higher than those recorded using direct electrochemical treatment. In fact, at this period of time, polymeric aluminium species were not completely formed during electrolysis. During first few minutes of treatment, aluminium ions were produced by anodic dissolution, which reacted with hydroxide ions in solution to produce Al(OH)$_3$. It took 10–20 min for the cell to produce enough Al(OH)$_3$ and initiate the polymerization reaction. Over the first 10 min of electrolysis of dye-containing solution, 540 nm-absorbance was mainly removed by monomeric species (Al(OH)$^{2+}$, Al(OH)$_2$$^+$, and Al(OH)$_3$), whereas during the chemical treatment using C_2 coagulant the absorbance removal resulted from the mixture of polymeric specie (Al$_{45}$O$_{45}$(OH)$_{45}$Cl) and monomeric species (AlCl(OH)$_2$·2H$_2$O and Al(OH)$_3$). It is well known that, generally, the higher the molecular weight and the longer the molecular chain, the more effective the inorganic polymer is for adsorbing, coagulating, or flocculating pollutants [78,79]. This is the main reason for which chemical treatment using C_2 coagulant was more effective than direct electrocoagulation during the first 10 min of treatment. However, when electrolysis of dye-containing solution was pursued over 20 min, metallic hydroxide (Al(OH)$_3$) particles were produced up to a sufficient concentration to initiate polymerization reactions, inducing the formation of white gelatinous precipitate (polymeric species). The subsequent formation of polymeric complexes during electrolysis contributed in removing a relatively high amount of Red-141-dye in the solution. It is to be noted that, the polymeric complexes formed did not remain in solution during a long period of time. They were immediately separated from the solution and stayed on the surface of the liquid owing to the gas bubbles produced at the cathode electrodes (H$_2$) [42]. The bubbles attached to the chemical flocs moving the polymeric species up to the surface, whereas the gelatinous precipitate became increasingly red, demonstrating that Red-141-dye pollutant was adsorbed on polymeric species. Hence, after 60 min of electrolysis, Red-141-dye pollutant was completely removed from solution (540 nm-absorbance removal of 100%) by imposing 15 V of electrical potential, compared to the maximal absorbance removal (96.5%) recorded while treating dye-containing solution using C_2 at a concentration of 400 mg l^{-1}. Fig. 7 presents the change in pH for various electrical potentials imposed (5.0, 10, 15 and 20 V) during electrolysis of Red-141-dye-containing solution. The pH decreased as the electrical potential increased. Considering only the electrical potentials of 10 and 15 V which were close to the value (12 V) imposed while producing C_2 coagulant, pH varied from
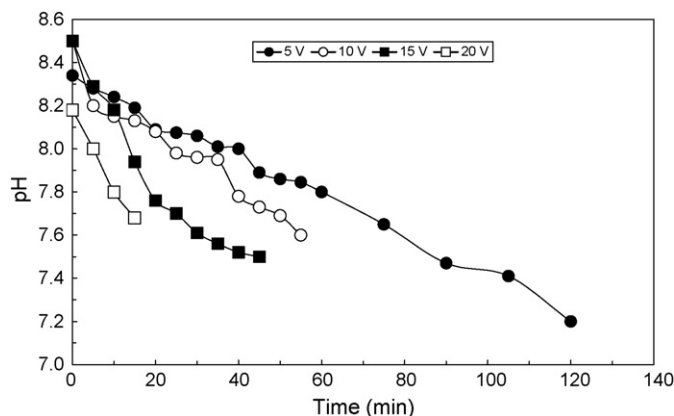

Fig. 7. pH variation of the CI Reactive Red 141 solution (C$_0$ = 50 mg l^{-1}) during direct electrocoagulation assays using different electrical potentials imposed.

the initial value of 8.6 to the final values of 7.5 and 7.6 during electrolysis. By comparison, chemical treatment using C_2 coagulant (200 and 400 mg l^{-1}) induced a slight increase of pH ranging from the initial values of 6.00 and 6.10 to the final values of 6.28 and 6.53, respectively. The slight increase in the pH using C_2 was attributed to the basic property of the product (see Table 2), while the decrease in the pH during direct electrocoagulation of dye-containing synthetic solution probably resulted from anodic parasitic reactions, such as water oxidation (in competition with aluminium anodic dissolution) leading to the formation of H$^+$ in solution according to the following reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{7}$$

As the electrical potential increased, this parasitic reaction (reaction (7)) took place, resulting in a further decrease in the pH during electrolysis. Likewise, in our experimental conditions, Eqs. (1)–(4) describing the hydrolysis of aluminium can be also used to explain the decrease in pH during direct electrocoagulation.

4. Conclusion

This study has shown the possibility to use mineral coagulants previously produced by electrolysis of saline solutions using aluminium electrodes to remove CI Reactive Red 141 dye pollutant from effluent. The best performances of dye removal were obtained with the inorganic coagulant C_2 produced by means of electrolysis of sodium chloride solution, S$_2$ [NaCl (10^{-2} M)], resulting in a mixture of polymeric species (Al$_{45}$O$_{45}$(OH)$_{45}$Cl) and monomeric species (AlCl(OH)$_2$·2H$_2$O and Al(OH)$_3$). The removal efficiency (R_A) evaluated by measuring the yields of 540 nm-absorbance removal varied from 41 to 96% through 60 min of treatment by using C_2 concentrations ranging from 100 to 400 mg l^{-1}. The comparison of chemical treatment using C_2 coagulant and direct electrocoagulation of CI Reactive Red 141 dye containing solution demonstrated the advantage of chemical treatment during the first few minutes of treatment. A yield of 88% of absorbance removal was recorded using C_2 coagulant (400 mg l^{-1}) over the first 10 min of treatment, com-

pared to 60% measured using direct electrocoagulation with either 10 or 15 V. However, at the end of the treatment (after 60 min of treatment), CI Reactive Red 141 dye pollutant was completely removed from solution (540 nm-absorbance removal of 100%) using direct electrochemical treatment, compared to 96.4% removal while treating dye-containing solution by means of the C_2 coagulant.

Additional experiments should be carried out in order to quantitatively and qualitatively compare chemical treatment using C_2 coagulant and direct electrocoagulation treatment by imposing the same Al^{3+} dosage levels while treating CI Reactive Red 141 dye containing synthetic solution. In addition, an economical study should be done to critically demonstrate the economical advantage in removing dye pollutant using either chemical coagulation by means of C_2 coagulant or direct electrocoagulation application (including energy cost, metallic residue disposal cost and the capital cost requires to build the electrochemical reactor). Likewise, in the next step, it should be interesting to compare the effectiveness of C_2 in removing CI Reactive Red 141 dye pollutant with the treatment using alum $(Al_2(SO_4)_3)$, a commercial product and the most common of coagulants used in water treatment.

Acknowledgments

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