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Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation

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ABSTRACT

In this paper, application of electrocoagulation using common electrode materials (aluminum and stainless steel) to a simulated reactive dyebath effluent was investigated. A mixture of dyes and auxiliary chemicals rather than a single dyestuff was employed to reflect actual reactive dyeing conditions. The experimental study focused on the effect of individual reactive dyebath components on color and COD removal rates and efficiencies by electrocoagulation. Electrocoagulation using stainless steel electrodes was found to be more effective particularly for color abatement. Na_2CO_3 significantly reduced the process efficiency both in terms of color and COD removals. An adverse effect on COD removal efficiency was also observed for the sequestering agent. On the other hand, increasing the NaCl concentration not only enhanced color and COD removal efficiencies but also compensated the adverse effects of Na_2CO_3 and sequestering agent on the electrocoagulation process. The dominant mechanism of color and COD removals from reactive dyebath effluent by electrocoagulation seemed to be coagulation and adsorption at pH values above 11.

1. Introduction

During last few decades, electrocoagulation (EC) using various electrode materials such as cast iron, stainless steel, aluminum or graphite have been successfully applied to “hard” industrial wastewater. EC is a complex, enigmatic process with a multitude of several reaction/removal mechanisms operating synergistically (coagulation, flotation and electrochemical reactions simultaneously) [1,2]. Most studies have focused on the effect of manipulating parameters (e.g. conductivity, pH, current density) on removal efficiencies of certain pollutants, rather than a fundamental, holistic and systematic approach to understand EC mechanism and its controlling parameters. Despite than more a century of application, the basic science and engineering behind EC design and modeling is still largely empirical and heuristic [3]. EC has proven to be effective in the removal of color and organic matter as well as heavy metals or oil and grease from industrial wastewaters such as the textile finishing industry [4–6] metal finishing industry [7], restaurant wastewaters [8], laundry wastewaters [9], distillery wastewaters [10], olive oil mill wastewaters [11], and oil refinery wastewaters [12]. The inherent advantages of these applications over well-known physicochemical treatment processes have also been mentioned in related studies that can be found in the recent literature [13–16].

Recently, a huge number of scientific work indicated that color of effluents originating from textile dyeing operations employing water-soluble reactive dyes could be successfully treated by electrochemical processes including EC. These studies have mostly been carried out with aqueous dye solutions bearing a single dye and these samples were called “synthetic dye wastewater” [13,16–20]. On the other hand, numerous papers have also recently been published dealing with the EC of real, combined textile preparation, dyeing and finishing wastewaters [1,2,21]. Besides, few scientific studies reported the treatability of reactive dyebath effluent [22–24], since among the different exhausted dyebath types (disperse, acid, vat, etc.) effluents from the reactive dyeing process are known as the most serious water polluters due to the relatively low fixation efficiencies of reactive dyestuffs (typically less than 80%) [25]. However, none of these papers focused on the effects reactive dye auxiliaries on EC performance, as for the fact that almost all reactive dyebath recipes comprise of a mixture of at least two dyestuffs together with a variety of dye auxiliaries such as NaCl (20–40 g/L), Na_2CO_3 (5–15 g/L) and biologically difficult-to-degrade sequestering agents [25,26]. NaCl enhances dye diffusion and adsorption onto the fiber, whereas Na_2CO_3 increases the dyebath pH and enables dye fixation through the formation of covalent bonds. Sequestering agents (carboxylic acids) chelate metal ions such as Fe^{2+}, Mn^{2+} that adversely affect the dyeing quality [25,26].

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On the other hand, NaCl is also used as an electrolyte chemical and is an important EC process variable. Na_2CO_3 may interact with the EC process in several ways; e.g. as a pH buffer of the reaction as it progresses, an electrolyte and/or electrode passivating agent. Since sequestering agents are usually of organic nature that create an additional organic pollution load (other than the dyes) in the total reactive dyebath, they are expected to interfere with decolorization and organic matter removal. Consequently, the individual/combinative synergistic effects of dye auxiliaries on the EC performance should be investigated and this evaluation is a crucial part of establishing an efficient EC system for decolorization and organic carbon removal from dyehouse effluent.

Other aspects of the EC reaction also need to be considered to decide whether it is feasible to apply EC for the treatment of reactive dyebath effluent; the presence of NaCl may results in the formation of chlorine gas and/or hypochlorite at the anode depending on the reaction pH [18,19]. These chlorine compounds on one hand may help to remove pollutants (dyebath ingredients in our case) via oxidation, but on the other hand may generate potentially toxic/carcinogenic chlorinated organic compounds, e.g. adsorbable organic halogens, known as AOX [18,19,27]. Since EC involves several removal mechanisms, AOX formation cannot be ruled out under reactive dyebath conditions and the fate of AOX/changes in toxicity should be followed during EC applications. In some cases, the net effect of EC may demonstrate a decrease in AOX and toxicity.

With the aforementioned facts in mind, the present study aimed at investigating color and organic matter (COD) removals during EC of a simulated reactive dyebath effluent bearing several reactive dyes and dye auxiliaries using aluminum and stainless steel as the electrode materials. A kinetic analysis was also carried out to determine effect of dyebath auxiliaries on treatment efficiency, for the fact that evaluation of color and COD abatement rates seemed to be useful as a quantitative tool to reveal these effects.

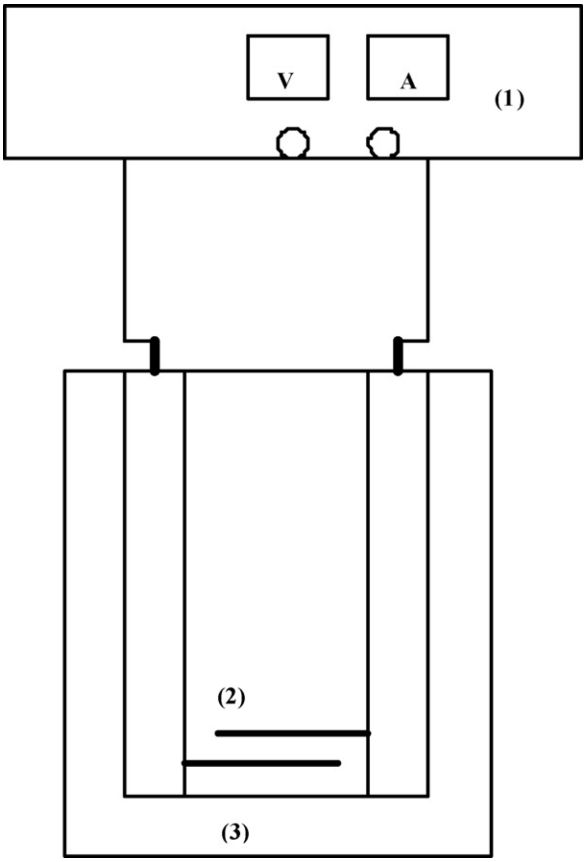

Fig. 1. Schematic diagram of the electrocoagulation unit (1) high-precision DC power supply with volt- and ampere-meters, (2) horizontally located, parallel-connected, monopolar SS or AL electrodes), and (3) EC reactor.

2. Materials and methods

2.1. The electrocoagulation unit

The electrocoagulation unit is a 1800 mL-effective capacity rectangular reactor with a height of 28.3 cm, a length of 34.3 cm and a width of 12.5 cm. The reactor is made of polyethylene (PE 1000) and equipped with six monopolar, parallel connected electrodes. Either stainless steel (SS 304) or aluminum electrodes were used as both anodes and cathodes with effective surface areas of 38.5 cm^2 (L = 11.9 cm and d = 1.02 cm). The distance between the electrodes was fixed at 3 mm. The applied current density was kept constant by means of a high precision DC power supply (E_{max} = 20 V). The schematic diagram of EC unit is depicted in Fig. 1. After each experimental run, the electrodes were treated as follows; the EC reactor and electrodes were carefully rinsed twice with 50% (v/v) nitric acid solution for 2–4 min and several times with distilled deionized water to remove impurities and metal hydroxide precipitates from the electrodes and reactor. The electrodes were replaced each time whenever more than 10% of electrode material was lost.

2.2. The reactive dyebath effluent and sample definition

The reactive dyebath recipe and ingredients were kindly provided by a local dyehouse located in Istanbul. This recipe was selected because of its frequent application in Turkey as well as worldwide. The exhausted reactive dyebath effluent was prepared according to the instructions of the technical staff of the dyehouse as follows; three reactive dyestuff formulations (Reactive Red (RR; with a confidential color index (CI) number), CI Reactive Yellow 145 (RY145) and CI Reactive Blue 221 (RB221)) were dissolved in deionized, boiling water. Thereafter, the dye auxiliaries, NaCl, Na_2CO_3, and a proper amount of polycarboxylic acid type sequestering agent were added to the aqueous dye mixture. The recipe was mixed for at least 8 h at T = 50 °C to ensure complete alkaline hydrolysis. In this manner, the sample represented a typical exhausted reactive dyebath effluent. The ingredients of the simulated reactive dyebath effluent are given in Table 1 together with their physicochemical properties and functions in the reactive dyeing process.

In Table 2, the EC experiments conducted with stainless steel and aluminum electrodes were denoted as SS and AL, respectively. As mentioned in the related literature, increasing the electrolyte (NaCl) concentration accelerates color and organic matter removals and shortens the reaction time [18,19,27]. As the extremely high NaCl concentration (40 g/L) in the present reactive dyebath effluent was expected to make the kinetic evaluation rather difficult if not impossible, it was decided to decrease the NaCl concentration of the reactive dyebath in some experimental runs to 3 g/L NaCl, i.e. the minimum electrolyte concentration that had to be added to achieve reasonable currents in the reaction solution.

Sample I (SS1-AL1) was prepared by dissolving actual amounts of the three reactive dyestuffs used in the dyebath (together with 3 g/L NaCl) as a blank sample in order to reveal the effects of other dyeing auxiliaries on color and COD abatement rates. Sample II (SS2-AL2) was prepared by adding the actual amount (40 g/L) of NaCl used the real reactive dyebath recipe to exhibit the effect of NaCl on treatment efficiencies. Na_2CO_3 and the sequestering agent were added to Sample I at their actual reactive dyebath concentrations to reconstruct Samples III (with 13 g/L Na_2CO_3) and Sample IV

Table 1
Physicochemical properties and environmental characterization of the simulated reactive dyebath effluent

Reactive dyebath ingredient	Property	Amount
Dyes		
Synazol Red KHL	An azo dye, CI number confidential (unknown)	41 mg/L
Synazol Blue KR	A formazane dye, CI Reactive Blue 221	86 mg/L
Synazol Yellow KHL	An azo dye, CI Reactive Yellow 145	25 mg/L
Dye auxiliaries	Function	
NaCl	Enhance dye diffusion onto fabric	40 g/L
Soda ash	Reagent causing covalent bond formation between dyes and fabric	13 g/L
Sequestering agent	Reduces the effect of cations (Ca^{2+}, Mg^{2+}) to the dyeing process	0.8 g/L
Parameter	Concentration	
Total COD (mg/L)	303[a]	
Color[b]	A_{436}(0.527); A_{525}(0.693); A_{620}(0.808)	
Alkalinity (mg $CaCO_3$/L)	12650	
pH	11.23	

[a] COD contribution of the three reactive dyes to the total reactive dyebath effluent = 130 mg/L (43%).

[b] as absorbance (A) at the wavelengths 436, 525 and 620 nm, in cm^{-1}.

(containing 0.8 g/L sequestering agent), respectively. Sample V was prepared upon the addition of both Na_2CO_3 and the sequestering agent to Sample I at concentrations corresponding to actual reactive dyebath conditions, but with the lower (3 g/L) NaCl content. Sample VI was prepared to examine the role of the sequestering agent on COD removal rates. Table 2 outlines the sample definitions and the content of each sample used in the experimental runs.

Besides, all chemicals used throughout the experiments and analytical measurements were of analytical grade except the dyestuffs that were commercial grade and used without further purification in order to represent actual dyeing conditions.

2.3. *Experimental procedures*

All EC experiments were performed for 30 min at the original, initial pH 11.5 of the reactive dyebath effluent and at a fixed current density of 22 mA/cm^2 (applied current was 5 A) that was found as the optimum current density for EC of the same reactive dyebath effluent sample [23]. The initial pHs of the samples which did not contain Na_2CO_3 were adjusted with 6 N NaOH solution in order to achieve the original pH of the actual dyebath effluent. Then, the EC experiments were commenced and samples were taken from the reactor at convenient time intervals during the course of the reaction to follow changes in pH as well as color and COD parameters. Thereafter, the samples were allowed to settle for 30 min before being subjected to vacuum filtration through Millipore membrane filters with a pore size of 0.45 μm. In the sample filtrates, color (absorbance), COD and pH were measured. During each run, approximately 12 sample aliquots were taken from the reactor for COD and color analyses. The sample volume was around 10 mL. Hence, not more than 10% (v/v) of the total sample volume was removed for consecutive analysis of process parameters as the total effective volume of the reactor was 1800 mL.

2.4. *Analytical procedures*

Absorbance measurements were carried out on a Pharmacia KB–Novaspec II model spectrophotometer in 1 cm glass cuvettes according to German environmental legislations [28] at three different wavelengths, namely 436 nm, 525 nm and 620 nm, representing yellow, red and blue color, respectively. This was done since no color consents exist in Turkey yet but are expected in the nearest future. Due to the fact that TOC analyses would be inaccurate and erratic because of the high inorganic carbon (Na_2CO_3) content of the reactive dyebath samples, COD was preferentially measured in all reaction solutions to follow the organic matter abatement during the process. All analyses were performed as defined in Standard Methods [29] except for COD measurements. The COD measurements were made as defined in DIN 38 409, H 41-2 Method [30] because of the high chloride content of the samples. This method is basically the same as the COD measurement method using dichromate and specified in Standard Methods except the removal of chloride interference by HCl gasification. At the end of EC experiments, the amount of formed sludge (metal hydroxide flocs together with removed pollutants) was determined by means of total suspended solid measurements according to Standard Methods [29].

2.5. *Kinetic evaluation of color and COD abatement rates*

Reaction kinetics for COD and color removals by electrochemical processes was expressed as first-order kinetics or its modification (pseudo-first-order kinetics or self-retardant first-order kinetics) as mentioned in the studies of Golder et al. [31], Kim et al. [16], Lin et

Table 2
Sample definitions

Sample identity	Dyes (mg/L)	NaCl (g/L)	Na_2CO_3 (g/L)	Sequestering agent (g/L)
Exhausted dyebath (DB)	RR: 41; RB221: 86; RY145: 25	40	13	0.8
SS1-AL1	RR: 41; RB221: 86; RY145: 25	3	–	–
SS2-AL2	RR: 41; RB221: 86; RY145: 25	40	–	–
SS3-AL3	RR: 41; RB221: 86; RY145: 25	3	13	–
SS4-AL4	RR: 41; RB221: 86; RY145: 25	3	–	0.8
SS5-AL5	RR: 41; RB221: 86; RY145: 25	3	13	0.8
SS6	–	40	–	0.8

al. [32], Rajkumar and Kim [19], and Rajkumar et al. [18]. During EC, substrate (color or COD) removal rate was proportional to substrate concentration;

$$\frac{dS}{dt} = -k \times S \tag{1}$$

where S is the remaining color (absorbance, in cm^{-1}) or COD (in $mg\,L^{-1}$) at time t (in min) and k is the pseudo-first order reaction rate constant (in min^{-1}).

3. Results and discussion

3.1. Color removal

3.1.1. Stainless steel electrodes

It is expected that in the case of iron or stainless steel electrodes, not only phase transfer (as in the case of aluminum electrodes) but also redox reactions may contribute to color removal. This may be attributable to the fast oxygen depletion occurring in the reaction solution during Fe(II) oxidation to Fe(III) after the anodic iron dissolution

$$Fe^{2+} + 2H_2O + O_2(g) \rightarrow 4Fe(OH)_3(s) + 8H^+ \tag{2}$$

Under anoxic conditions, reductive abatement of certain dyestuffs may be possible and has been reported previously [33].

Table 3 summarizes the results of EC experiments conducted using stainless steel electrodes. Almost complete decolorization was obtained for all cases. As can be seen from Fig. 2 (a) and (b), the color of the samples except those of SS3 and SS5 completely disappeared within 5 min. Therefore, due to the swiftness of these reactions in terms of decolorization, no kinetic evaluation could be made for these samples. The absorbance values of samples SS3 and SS5 gradually diminished during the course of the reaction; this

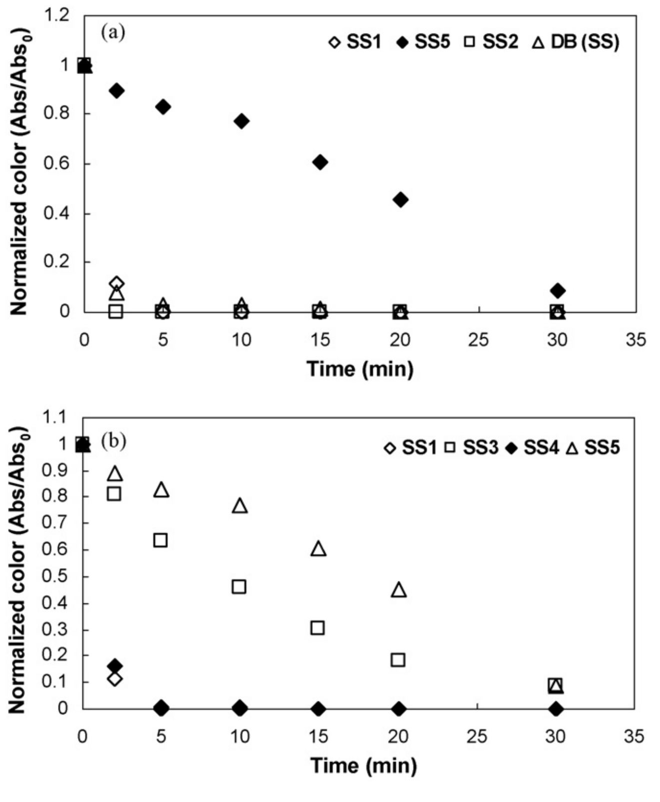

Fig. 2. Color abatements by electrocoagulation with stainless steel electrodes (at 620 nm).

Table 3
The results of electrocoagulation experiments using stainless steel electrodes (applied current density = 22 mA/cm^2)

	COD		Color						Time interval[b] (min)	COD		Color[c]		pH		Produced sludge[a] (mg/L)
	Initial (mg/L)	Removal[a] (%)	Initial (cm^{-1})			Removal[a] (%)				k ($\times 10^{-2}$ min^{-1})	R^2	k ($\times 10^{-2}$ min^{-1})	R^2	Initial	Final[a]	
			436 nm	525 nm	620 nm	436 nm	525 nm	620 nm								
DB	311	54	0.542	0.709	0.830	100	100	100	0–30	2.55	0.95	–	–	11.21	12.02	2160
SS1	145	27	0.597	0.774	1.074	90	100	100	0–20	1.42	0.98	–	–	11.53	11.56	245
SS2	106	63	0.591	0.761	0.972	100	100	100	5–30	2.84	0.90	–	–	11.53	12.27	2420
SS3	140	23	0.579	0.757	0.977	85	88	91	0–20	1.01	0.98	8.1	0.99	11.53	11.62	165
SS4	326	25	0.603	0.812	1.072	100	100	100	0–30	0.86	0.96	–	–	11.53	11.86	455
SS5	319	12	0.574	0.747	0.984	85	86	100	0–20	0.71	0.94	3.64	0.96	11.53	11.84	945
SS6	201	35	–	–	–	–	–	–	0–20	1.62	0.95	–	–	11.07	12.92	2300

[a] At the end of 30 min reaction time.
[b] The time interval used for kinetic evaluation
[c] For color removal at 620 nm.

behavior may be attributed to the presence of Na_2CO_3. Increasing the NaCl concentration compensated this adverse effect of Na_2CO_3 as is evident from the respective experiments (DB-SS). Regression analyses were applied to fit the data obtained for samples SS3 and SS5 to the pseudo-first order kinetic expression. The fitness to the data was very satisfactory ($R^2 > 0.95$). The pseudo-first order decolorization rate constants were calculated as 8.10×10^{-2} min^{-1} and 3.64×10^{-2} min^{-1} for SS3 and SS5, respectively (Table 3). When SS3 and SS5 samples were compared, the only one difference was the existence of the sequestering agent in sample SS5 and hence the decrease in decolorization rate may be attributed to the presence of the sequestering agent. On the other hand, the high color removal found for DB-SS sample implied that adverse effect of the presence of Na_2CO_3 and the sequestering agent on the decolorization rate was totally compensated when the NaCl concentration was increased. NaCl is known to increase the conductivity of the reaction solution which in turn reduces the voltage needed to achieve a certain current [27].

3.1.2. Aluminum electrodes

EC using aluminum electrodes appeared to be less efficient than employing stainless steel electrodes in our case. Therefore, decolorization efficiencies found for experiments with aluminum electrodes were much lower than those obtained for EC with stainless steel electrodes. The color removal efficiencies were limited to 20% except for AL2 as evident in Table 4 and Fig. 3 (a). These unsatisfactory decolorization results may be explained by the relatively short EC time and presence of reactive dyebath auxiliaries. The results of an earlier study implied that extending the EC time from 30 min (17% color reduction) to 90 min brought about additional 60% decolorization (76% overall color reduction) under the same operation conditions for the same reactive dyebath sample [23]. A significant increase in decolorization rate found in the case

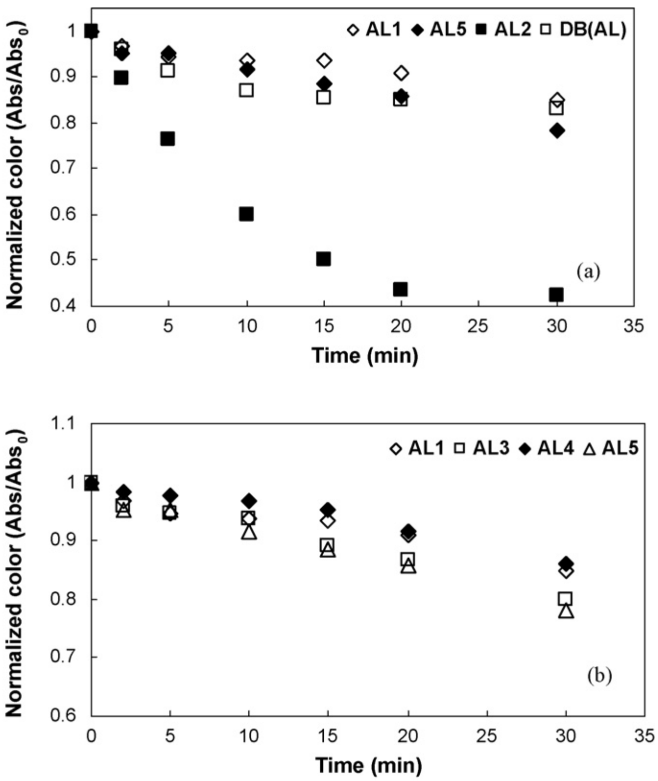

Fig. 3. Color abatements by electrocoagulation with aluminum electrodes (at 620 nm).

Table 4
The results of electrocoagulation experiments using aluminum electrodes (applied current density = 22 mA/cm^2)

	COD		Color						Time interval[b] (min)	COD		Time interval[b] (min)	Color[c]		pH		Produced sludge[a] (mg/L)
	Initial (mg/L)	Removal[a] (%)	Initial (1/cm)			Removal[a] (%)				k ($\times 10^{-2}$ min^{-1})	R^2		k ($\times 10^{-2}$ min^{-1})	R^2	Initial	Final[a]	
			436 nm	525 nm	620 nm	436 nm	525 nm	620 nm									
DB	300	28	0.546	0.740	0.842	14	22	17	0–20	0.79	0.97	0–10(10–30)	1.40 (0.21)	0.97	11.27	11.61	2600
AL1	127	17	0.593	0.753	1.051	13	16	15	0–30	0.64	0.94	0–30	0.46	0.92	11.66	9.82	2055
AL2	104	50	0.573	0.716	0.908	40	67	58	0–15	4.27	0.99	0–20	3.26	0.97	11.66	9.98	2540
AL3	136	12	0.591	0.780	0.980	15	25	20	0–30	0.45	0.94	0–30	0.68	0.97	11.66	11.27	75
AL4	330	59	0.589	0.785	1.062	8	13	14	0–30	3.30	0.80	0–30	0.47	0.95	11.66	9.91	2000
AL5	330	14	0.584	0.782	0.987	15	29	22	5–30	0.50	0.99	5–30	0.75	0.98	11.66	11.24	65

[a] At the end of reaction time of 30 min.
[b] The time interval used for kinetic evaluation.
[c] For color removal at 620 nm.

of AL2 as compared to AL1 may not be simply explained by the increase in NaCl concentration and hence conductivity since both reaction pH and sludge production were similar for these experimental runs (see Table 4); the extremely high chloride content of AL2 might have supported chlorine-mediated oxidation at pH of 9.9 (cf. decolorization rate constants $k = 0.46 \times 10^{-2}\ \text{min}^{-1}$ for AL1 and $k = 3.26 \times 10^{-2}\ \text{min}^{-1}$ for AL2). This is also evident from the high initial reduction in pH (about 1.5 unit) and associated color removal observed within the first 5 min of reaction (Fig. 3). This oxidation mechanism was by far less important in AL1 due to its relatively low NaCl content. The effectiveness of oxidation was claimed to be suppressed at alkaline pH (>10) due to formation of chlorate and perchlorate [18]. Therefore, the contribution of chlorine/hypochlorite oxidation to color abatement was also negligible for AL3, where the reaction pH was above 11. Thus, the dominant decolorization mechanism for AL1 and AL3 should be the same and most probably adsorption. Since in both cases color abatement kinetics were comparable (Table 4), but sludge production rates were quite different, it may be postulated that the decolorization process was not a function of sludge production. The reason why sludge production of AL3 was limited to 75 mg/L might be passivation of the anode due to the presence of Na_2CO_3. A comparison of the color abatements as well as process conditions indicated that the effect of the sequestering agent on the decolorization was negligible (cf. results of AL1 and AL4). A closer inspection of AL5 and DB-AL justified the evaluation made so far, and also clearly revealed that changes in sludge production rates affected color abatement rates only at a limited, higher pH range. This deduction can be supported by a previous article of Kabdaşlı et al. [24], where coagulation conducted with the same reactive dyebath sample using alum at near neutral pH (6.5) indicated that an increase in the alum dose from 350 mg/L to 2000 mg/L had no significant effect on color reduction that remained 18% for both alum doses.

On the other hand, the effects of reactive dyeing auxiliaries on color abatement rates are obvious from Fig. 3(b) depicting the results of AL3 and DB-AL experiments. In the case of sample DB-AL, color removal (with $k = 1.4 \times 10^{-2}\ \text{min}^{-1}$) during the initial course of the reaction was high and about 20% color reduction was achieved after 10 min EC. Thereafter, decolorization proceeded very slowly (k was found as $0.21 \times 10^{-2}\ \text{min}^{-1}$ for t = 10–30 min) whereas decolorization was the fastest for AL3 ($k = 3.26 \times 10^{-2}\ \text{min}^{-1}$) for the time interval of 0–30 min.

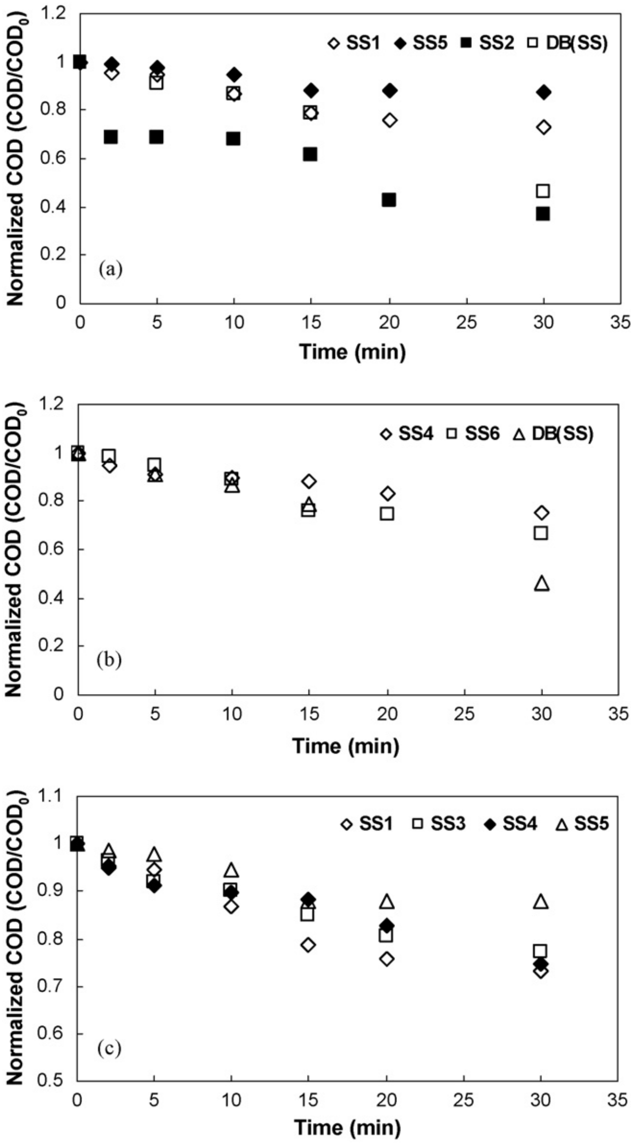

Fig. 4. COD abatements by electrocoagulation with stainless steel electrodes.

3.2. COD removal

3.2.1. Stainless steel electrodes

A comparison of SS1 and SS2 clearly indicated that increasing the NaCl concentration improved COD removal within a reasonable reaction duration (Fig. 4a). Neither significant degradation nor adsorption of the sequestering agent was expected and thus significantly contributed to the high residual COD of the SS6 sample (Fig. 4(b)). Experiments SS1 and SS4 further justified this point in that both initial and final COD's of sample SS4 reflected the sum of SS1 and SS6 samples, while COD removal in SS4 was only 25% (residual COD for SS4 = 244 mg/L; see Table 3). A comparison of SS1 and SS3 indicated that the effect of Na_2CO_3 on color and COD removal efficiencies was negligible, although sludge production decreased in the presence of Na_2CO_3. This was misleading, however, and as the initial COD increased, the effect of Na_2CO_3 became important as evident from SS4 and SS5 (Fig. 4(c)). Therefore, it should be noted here that the addition of Na_2CO_3 suppressed COD reduction in the case of the experiments performed with low NaCl concentration, whereas this effect was largely compensated by the increasing NaCl concentration for experiment DB-SS, where 54% COD removal was obtained due to its high electrolyte concentration (Fig. 4(a)). Final COD of DB experiment was even lower than sum of final CODs of SS2 and SS6, while the amount of sludge produced in SS2 and DB experiments was comparable.

A kinetic evaluation of EC with stainless steel electrodes indicated that the pseudo-first-order COD abatement kinetics fitted fairly well. This quantitative interpretation is consistent with the studies given in the former literature [16,18–20] and also supports the finding that COD removal seemed to be mainly due to adsorption on the freshly produced flocs since chlorine-mediated, indirect oxidation was not expected at pHs > 11 [18]. Increasing the NaCl concentration from 3 g/L to 40 g/L increased the decolorization rate constant from $1.42 \times 10^{-2}\ \text{min}^{-1}$ (SS1) to $2.84 \times 10^{-2}\ \text{min}^{-1}$ (SS2). The rate of dye removal (SS2) was higher than the removal of the sequestering agent ($k_{COD} = 1.62 \times 10^{-2}$ min for SS6) in terms of COD removal, the combination of dyes with the sequestering agent decreased COD abatement kinetics ($k_{COD} = 1.42 \times 10^{-2}\ \text{min}^{-1}$ for SS1 and $k_{COD} = 0.86 \times 10^{-2}\ \text{min}^{-1}$ for SS4). The effect of Na_2CO_3 was well reflected by the rate constants obtained as $1.42 \times 10^{-2}\ \text{min}^{-1}$ for SS1, $1.01 \times 10^{-2}\ \text{min}^{-1}$ for SS3, $0.86 \times 10^{-2}\ \text{min}^{-1}$ (SS4) and

0.71×10^{-2} min^{-1} for SS5. The highest COD abatement rate constant was found for SS2 with $k_{COD} = 2.84 \times 10^{-2}$ min^{-1}; the reaction rate was not significantly affected by the addition of the sequestering agent and Na_2CO_3 ($k_{COD} = 2.55 \times 10^{-2}$ min^{-1}; see DB-SS).

3.2.2. Aluminum electrodes

COD removal patterns were fitted to pseudo-first order kinetics for EC with aluminum electrodes as well. However, the response of the process to chemical composition was more variable than that observed for EC with stainless steel electrodes. The positive effect of increasing NaCl was again evident for experiments AL1 ($k_{COD} = 0.64 \times 10^{-2}$ min^{-1} and 17% COD removal for 30 min) and AL2 ($k_{COD} = 4.27 \times 10^{-2}$ min^{-1} and 50% of COD removal for 15 min). This point is consistent with the results presented in the related literature [4,5] and also supports an additional removal via chlorine-mediated oxidation. A comparison of AL1 and AL4 yields the following discussion.

Firstly, the presence of the sequestering agent did not affect the COD removal pattern according to Fig. 5(a). However, COD removal of the sequestering agent was relatively high resulting in a total COD removal of 59% (see Table 4). On the other hand, closer inspection of the COD removal pattern indicates a lag-phase up to 15 min where COD removal remained quite low, followed by a sudden enhancement in COD abatement. This pattern manifests the importance of the amount of sludge produced for COD removal during EC. Comparison of AL1 ($k_{COD} = 0.6 \times 10^{-2}$ min^{-1}, 17% COD removal) with AL3 ($k_{COD} = 0.45 \times 10^{-2}$ min^{-1}, 12% COD removal), and AL4 ($k_{COD} = 3.3 \times 10^{-2}$ min^{-1}, 59% COD removal) with AL5 ($k_{COD} = 0.50 \times 10^{-2}$ min^{-1}, 14% COD removal) clearly revealed that the presence of Na_2CO_3 had a detrimental effect on treatment efficiency. This negative effect may be associated with passivation of the anode material thus reducing the current density and sludge production, but diminishes in the presence of increased electrolyte concentration (see DB in Fig. 5(b)). This observation was in complete agreement with Chen who reported that chloride ions could significantly reduce the adverse effect of other anions such as bicarbonate and sulfate [14]. On the other hand, it should be emphasized that this compensation was less effective for aluminum electrodes than in the case of stainless steel electrodes, as the increase in the overall COD removal was rather limited (28%) in the DB experiment conducted with Al electrodes, despite a significant increase in the amount of sludge produced for sample AL5. The increase in the sludge production rate had a positive influence on COD removal, as was pointed out in the conclusion made for the sequestering agent upon comparison of experiments AL4 and AL5. This point was also verified by Kabdaşlı et al. [24] who demonstrated that an increase in alum dosage from 350 mg/L to 2000 mg/L increased the COD removal from 34% to 63% of the same reactive dyebath effluent.

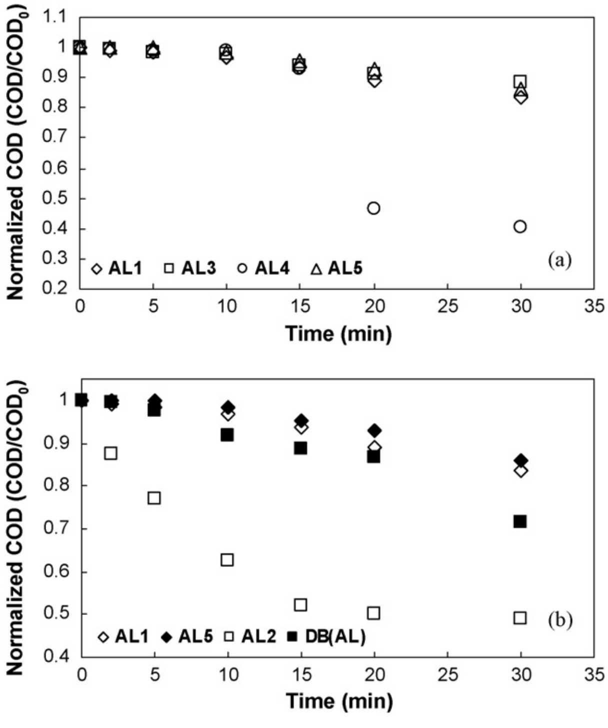

Fig. 5. COD abatements by electrocoagulation with aluminum electrodes.

3.3. Comparison of removal rates

As mentioned above, color and COD abatement rates could be satisfactorily represented by pseudo-first-order kinetics for EC with stainless steel and aluminum electrodes in our study. However, the removal rates appreciably varied depending on the electrode materials used and the pollutant parameter, e.g. COD and color. Working conditions also affected the pollutant removal rates. Below a brief comparison of pollutant removal rates on the basis of electrode material and pollutant parameters with related literature data is given. Rajkumar and Kim [19] calculated several removal rate constants in terms of COD and color parameters obtained via electrochemical process using a titanium-based dimensionally stable anode for aqueous reactive dye solutions (containing 100 mg/L of a single dye). Their working conditions were selected as an applied current density of 36.1 mA/cm^2, an electrolyte concentration of 1500 mg/L NaCl and a reaction pH of 6.2–6.5. The pseudo-first-order rate constants calculated in their study varied between 0.19×10^{-2} and 0.71×10^{-2} min^{-1} for COD removal and 5.92×10^{-2} and 28.48×10^{-2} min^{-1} for decolorization. In our study, color removal was very fast with SS electrodes and approximately an order of magnitude faster (e.g. 0.46×10^{-2} min^{-1} for AL1 and 1.4×10^{-2} min^{-1} for DB) using for Al electrodes than those reported by Rajkumar and Kim [19]. The difference may be attributed to sample as well as reaction conditions. On the other hand, COD removal rate constants calculated in the present study for the samples AL1, SS1, DB-AL and DB-SS varied between of 0.64×10^{-2} min^{-1} and 2.55×10^{-2} min^{-1} and were in the same order of magnitude as those found by Rajkumar and Kim [19].

3.4. Other aspects of electrocoagulation application

As aforementioned, one of the main issues that need to be considered when applying EC is the toxicity change brought about during the reaction, particularly for the applications involving iron (or stainless steel) anodes and high chloride concentrations as in our case. Chlorine and hypochlorite may react with organic substances and yield AOX. In our previous study [24] conducted using the same reactive dyebath recipe as in the present study it was experimentally observed that the AOX content of the reactive dyebath effluent (originally being 6.1 mg Cl/L) decreased to 3.7–5.5 mg Cl/L after EC with stainless steel and aluminum electrodes. In the same study, biodegradability (biotoxicity) of raw and electrocoagulated reactive dyebath effluents was also determined and obtained findings indicated that the biodegradability either remained unchanged (EC with stainless steel electrodes) or markedly improved (EC with aluminum electrodes). Therefore, EC application can be considered as environmentally/ecologically safe in terms of AOX formation and toxicity.

Operation costs (electrical energy requirements) of EC is another important factor for judging the feasibility of the process. A cost evaluation in terms electrical energy requirements during EC using stainless steel and aluminum electrodes was also carried out with a reactive dyebath sample having a similar composition with that of the present study. Our experimental data and electrical energy calculations indicated that the specific energy consumption was about 5 kWh/m^3 wastewater EC with aluminum electrodes and 9 kWh/m^3 for EC with stainless steel electrodes [22]. Both values were below 10 kWh/m^3 which is commonly accepted to be the feasibility limit of EC and other chemical treatment processes [34].

The advantages of EC such as high efficiency in removing color and organic matter proved to be valid for present case due to its high chloride content that is naturally present in reactive dyebaths and thus does not have to be added externally. On the other hand, the disadvantages typically being attributed to EC such as AOX formation potential and high operation cost did not seem to be valid limiting factors in the present study.

4. Conclusions

This study attempted to investigate color and COD removals from a simulated reactive dyebath effluent by means of EC using the cheap and common electrode materials aluminum and stainless steel. A step-by-step addition of dye auxiliary chemicals was realized to assess their impact on the treatment efficiency. The use of stainless steel electrodes proved to be more efficient than employing aluminum electrodes, particularly, in terms of color removal. The performance of aluminum electrodes can be meaningful provided that NaCl concentrations are high (i.e. 40 g/L) in our case. The presence of Na_2CO_3 adversely affected both color and COD removal efficiencies, whereas the effect of the sequestering agent was more pronounced on COD removal. NaCl concentration was determining the rate and efficiency of EC process and high NaCl concentration were required to compensate adverse effect of Na_2CO_3 and sequestering agent on treatment efficiency. The dominant color and COD removal mechanism at pH 11–12 seemed to be coagulation + adsorption. Obtained color and COD abatement rates could be quantified and compared by employing pseudo-first order kinetics.

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