



# Electrocoagulation treatment of simulated floor-wash containing Reactive Black 5 using iron sacrificial anode

Upendra D. Patel<sup>a,\*</sup>, J.P. Ruparelia<sup>b</sup>, Margi U. Patel<sup>c</sup>

<sup>a</sup> Civil Engineering Department, Sardar Vallabhbhai Patel Institute of Technology, Vasad, Dist. Anand 388340, India

<sup>b</sup> Chemical Engineering Department, Institute of Technology, Nirma University, Sarkhej Road, Ahmedabad, India

<sup>c</sup> Gujarat Pollution Control Board, Regional Office, Bharuch, India

## ARTICLE INFO

### Article history:

Received 23 February 2011

Received in revised form

16 September 2011

Accepted 17 September 2011

Available online 24 September 2011

### Keywords:

Floor-wash

Electrocoagulation

Reactive Black 5

Decolorization

Vinyl sulfone

## ABSTRACT

Floor-wash from dye finishing plant is a major source of color and wastewater volume for dyes industries. Batch electrocoagulation (EC) of simulated floor-wash containing Reactive Black 5 (RB5) was studied as a possible pretreatment option. More than 90% of initial 25 mg/L of RB5 was removed at current densities of 4.5, 6, and 7.5 mA/cm<sup>2</sup> in the presence of Na<sub>2</sub>SO<sub>4</sub> and NaCl as supporting electrolytes; in less than one hour. Identical  $k_{obs}$  (pseudo first-order reaction rate constant) values were obtained at initial pH of 3.74 for both electrolytes. However, at initial pH of 6.6,  $k_{obs}$  values decreased in the presence of Na<sub>2</sub>SO<sub>4</sub> and remained same for NaCl as compared to that at pH 3.74. Highest extent of decolorization and  $k_{obs}$  values were obtained at initial pH 9.0 for both electrolytes. Under identical conditions, specific energy consumption (SEC) was almost half in the presence of NaCl (~29 kWh/kg RB5) than that of Na<sub>2</sub>SO<sub>4</sub>. Vinyl sulfone (VS) was detected as one of the products of EC indicating reduction of azo bonds as a preliminary step of decolorization. Mechanism of decolorization with respect to various experimental conditions was delineated. Generation and accumulation of VS was dependent on initial pH and type of electrolyte. Results of this study revealed that EC in the presence of sodium chloride can be efficiently used as a primary treatment for decolorization of floor-wash containing RB5.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Reactive dyes are widely used for coloring cellulosic fibers such as cotton, and protein fibers such as wool. The wastewaters generated from manufacturing, and subsequently from dyeing operation of reactive dyes pose a major environmental threat due to the presence of many toxic and potentially carcinogenic organic compounds [1]. India is a global leader in manufacturing of dyes and dye intermediates. Reactive Black 5 (RB5), an azo-dye, is produced predominantly among the reactive dyes produced in India. The chemical structure and some characteristics of RB5 are given in Table 1. The manufacturing of RB5 has been improved over last one decade to make it more environment-friendly and cost effective. Briefly, H-Acid (1-amino-8-hydroxynaphthalene-3,6-disulfonic acid) is coupled with two molecules of vinyl sulfone (VS, 4-aminophenyl sulfonyl- $\beta$ -hydroxy ethyl sulfato ester sodium salt) through azo ( $-N=N-$ ) bonds. The resulting liquor is concentrated either by ultra-filtration or evaporation followed by drying using spray-dryers. The packing area where finished RB5 is packed is often subjected to dusting of RB5 due to its light weight and

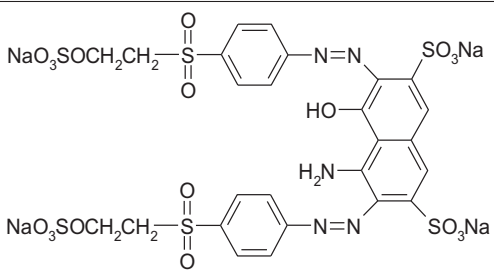
small particle size. Floor is normally washed with tap water to avoid product contamination. In contrast to liquid streams generated from occasional washing of spray-dryers and reaction vessels, floor-wash from finishing plant is generated daily and contributes significantly to wastewater color and volume. A major challenge faced by RB5 manufacturing industries is to meet with the stringent discharge limit of color in the treated effluent in India [2]. Most of the reactive dyes are designed to serve longer, resisting natural fading due to sunlight and biological activities. Thus, a major fraction of RB5 in wastewater goes unaffected through a conventional effluent treatment plant consisting of physicochemical and biological treatments [1]. Thus, evaluation of a physicochemical method as a pretreatment to decolorize RB5 floor-wash was the prime focus of this study.

Normally, granular activated carbon (GAC) filters are installed by RB5 production units to remove residual color after conventional treatment; however, this results in higher unit cost of treatment. Many other decolorization methods are available in published literature. For example, anaerobic microorganisms and some fungal species are found to decolorize RB5 partially [3,4]. Daily variation in characteristics of dye wastewater and requirement of specific redox conditions are deterrents to field scale application of biological systems for decolorization of RB5. Conventional physicochemical process consisting of application of ferrous salts under alkaline conditions achieves significant color removal in RB5 wastewater.

\* Corresponding author. Present address: Dr. Jivraj Mehta Institute of Technology, NH no. 8, Mogar, Dist. Anand 388340, India. Tel.: +91 9687961022.

E-mail address: [patelupendra@gmail.com](mailto:patelupendra@gmail.com) (U.D. Patel).

**Table 1**  
Structure and characteristics of Reactive Black 5.

Dye	Reactive Black 5
	
Chemical structure	
$\lambda_{\text{max}}$ (nm)	595
Chemical class	Diazo
Chemical name	2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3,6-bis((4-((2-(sulfoxy)ethyl)sulfonyl)phenyl)azo)-tetrasodium salt
Molecular weight (g/mol)	991.8
C.I. number	20505

However, the method is clumsy in terms of handling of chemicals and produces high volume of chemical sludge. Among the advanced physicochemical processes, electrochemical processes have gained much attention recently due to simplicity of operation and higher efficiency of color and COD removal from dye/textile wastewaters as compared to biological or conventional physicochemical processes. Application of electrochemical processes such as electrochemical oxidation (EO), electrochemical coagulation (EC), electro-Fenton (EF), and photo-electrochemical process (PEC) for decontamination of colored wastewater is reviewed by Martinez-Huitle and Brillas [5]. Electrochemical methods such as EC [6], EC followed by activated carbon adsorption [7], ozone-assisted EC [8,9], EO [10,11], and solar-photocatalytic EO [12] have been reported to efficiently decolorize aqueous RB5 solutions. EC has also been applied to decolorize textile wastewaters [13–15]. Among various electrochemical treatments narrated above, EC is simpler, efficient, and economical. For example, a comparison of indirect EO with EC for decolorization of Acid green 50 revealed that under similar operating conditions EC offered better color and COD removal, and proved more energy efficient than EO [16]. The sludge produced by EC is lesser in volume and more hydrophobic to achieve smaller volumes to be disposed as compared to conventional chemical coagulation [17,18]. Based on above literature review, the purpose of this study was to evaluate EC as a pretreatment to decolorize floor-wash. Influence of various experimental conditions such as, current density, initial pH, and type of supporting electrolyte on removal of RB5 from simulated floor-wash was studied to optimize the EC process. It has been shown that EC of reactive dyes achieves almost complete decolorization of aqueous solutions; however, TOC removal is partial [19]. This suggests that the products formed during EC are carried forward in dissolved form, with the decolorized effluent. One of the objectives of this work was to study the generation and accumulation of such products with respect to various experimental conditions in order to collect information for design of subsequent treatment units (mainly, biological) and elucidate the mechanism of decolorization. EC of aqueous RB5 solutions using sacrificial iron anode has been reported by Sengil and Ozacar [6]; however, generation and quantification of products as shown in the present study is not reported to the best of our knowledge.

## 2. Materials and methods

### 2.1. Chemicals

The RB5, H-Acid, and vinyl sulfone samples were obtained from a local dye manufacturing company. The dye was used as received

so as to include the effect of other ingredients contained in it on EC. Sodium chloride (NaCl) and sodium sulfate (anhydrous) ( $\text{Na}_2\text{SO}_4$ ) were purchased from S.D. Finechem, Vadodara, India. All chemicals were used as received.

### 2.2. EC setup

Electrochemical reactions were carried out in a single-compartment borosilicate glass beaker of 600 mL volume. Contents of the reactor were mixed through out the experiment by a magnetic stirrer (Remi, India) to maintain uniform conditions within the reactor and prevent settling of flocs. Iron plate of size 70 mm  $\times$  100 mm was used as anode and a stainless steel plate of identical size as cathode. Iron is more advantageous as compared to aluminum (Al) as an anode since EC in case of Al-anode will result in pure coagulation and adsorption; while in addition to the former, reduced iron species ( $\text{Fe}^{2+}$ ) can also cause reduction of reactive dyes [13,17]. Geometric area of each electrode in contact with the aqueous dye solution was 44 cm<sup>2</sup>. Inter-electrode gap was maintained at 20 mm. Electrodes were washed with dilute HCl, polished using D120 sand paper, and washed with water before commencing each experiment. Direct current was supplied galvanostatically using constant current/voltage regulated power supply unit supplied by Testronix 92D (India) having a range of 1–30 V and 0–10 A. Different current densities (CD) viz., 4.5, 6.0, and 7.5 mA/cm<sup>2</sup> were studied.

### 2.3. Analytical methods

Visible color absorption and detection of products of EC were carried out using UV 2600 Spectrascan double beam spectrophotometer (Thermo Scientific, India). Percentage of color removal (CR) was calculated by Eq. (1):

$$\text{CR}(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where  $A_0$  and  $A_t$  are absorbance at 595 nm of reaction solution at time  $t=0$  and  $t$ , respectively. Concentration of VS was calculated by measuring difference in absorbance at 265 nm at  $t=t$  and 0. Theoretical concentration of VS was calculated stoichiometrically, attributing all decolorization to cleavage of azo linkages. All experiments were conducted in duplicate and average values of results were used.

**Table 2**  
Characteristics of tap water used in study.

Sr. No.	Parameter	Concentration
1	pH	6.5–6.7
2	Total dissolved solids	396 mg/L
3	Hardness (as CaCO <sub>3</sub> )	174 mg/L
4	Chloride (as Cl <sup>-</sup> )	92 mg/L
5	Sulfate (as SO <sub>4</sub> <sup>2-</sup> )	52 mg/L
6	Alkalinity (as CaCO <sub>3</sub> )	46 mg/L

#### 2.4. EC of simulated floor-wash

Aqueous solutions of 25 mg/L concentration of RB5 (by diluting 10,000 mg/L stock solution of RB5) were prepared using tap water to simulate the field conditions. The characteristics of tap water are as given in Table 2. All experiments were conducted using initial reaction volume of 500 mL at room temperature. Calibration plots for RB5 and VS were prepared in concentration range of interest and were found to be linear with  $R^2$  values > 0.98. NaCl or Na<sub>2</sub>SO<sub>4</sub>, 2 g/L, was added to enhance conductivity of solution. Initial pH (3.75, 6.6, or 9.0) was adjusted using 0.1 N HCl or 0.1 N NaOH. Samples (5 mL) were drawn at specific time points using a syringe and filtered through syringe filter containing nylon filters having 0.2 μm pore size (Pall Corporation, “Ultipor N66”, 13 mm Ø).

### 3. Results and discussion

#### 3.1. Effect of current density and supporting electrolyte on EC of RB5

Fig. 1(a) and (b) shows effect of current density on RB5 decolorization using sodium sulfate and sodium chloride as supporting electrolytes, respectively. The decolorization reaction was observed to follow pseudo first-order. Fig. 2 shows dependence of pseudo first-order rate constants on current density. It may be noted from figures that rate of decolorization increases with increase in current densities for both electrolytes. Increase in decolorization with increase in CD may due to increased formation of Fe<sup>2+</sup> and iron hydroxide species according to Faraday's law. However, as shown in Fig. 2, increase in reaction rate is greater in the

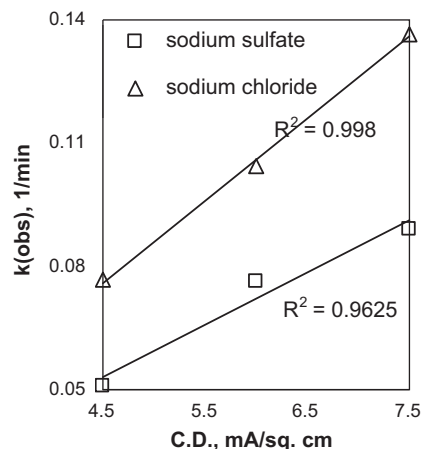


Fig. 2. Dependence of 1st-order reaction rate constants on current density.

presence of sodium chloride than that of sodium sulfate. Chang et al. [7] studied EC using cast-iron anode and reported increase in rate and extent of color removal from a RB5 solution with increase in CD from 15.8 to 55.4 mA/cm<sup>2</sup> in the presence of 1 g/L NaCl at pH 7.0. Vaghela et al. [20] also reported increase in extent of decolorization and COD removal due to EO of an industrial azo dye wastewater with increase in CD. Mohan et al. [21] studied EO in the presence of NaCl and observed increase in extent of COD removal of synthetic wastewater containing Acid Brown 14 concomitant to increase in CD. It has been shown that increase in CD increases decolorization up to a certain limit, beyond which; decolorization efficiency remains unaffected and additional electrical energy is wasted in heating up the reactor contents [7,8,22–24]. It seems that in our study, the CDs used were smaller and within the range in which the RB5 decolorization increases with increase in CD.

It seems that the effect of supporting electrolyte on removal/transformation of target compounds and electricity consumption in EC depends on: (1) the type of anode (Fe/Al) and (2) the type of target compound. For example, Yildiz et al. [25] reported that the iron anode in the presence of NaCl offered faster removal of humic substances with much lower energy

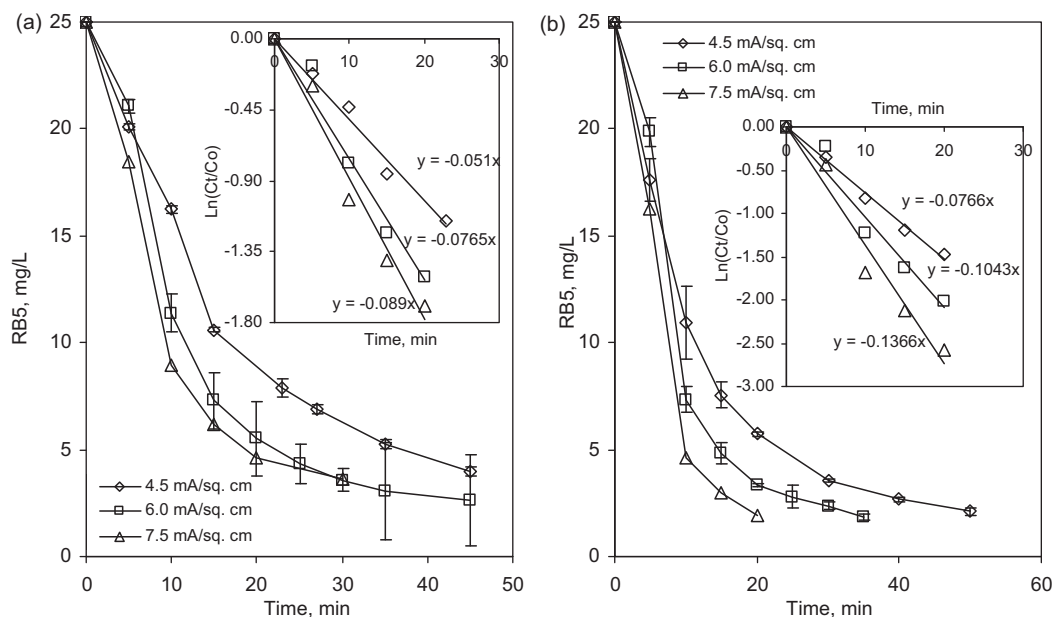
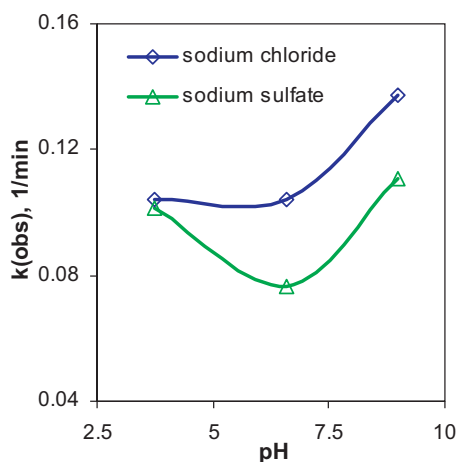


Fig. 1. Effect of current density and type of electrolyte on decolorization of RB5 using: (a) sodium sulfate and (b) sodium chloride. Inset figures show corresponding pseudo-first order kinetic plots. Reaction conditions: reaction volume, 500 mL; initial pH, 6.6; initial RB5 concentration, 25 mg/L; electrolyte concentration, 2 g/L.



**Fig. 3.** Effect of initial pH on pseudo-first order decolorization rate constant in the presence of sodium chloride and sodium sulfate. Reaction conditions: reaction volume, 500 mL; CD, 6.0 mA/cm<sup>2</sup>; initial RB5 concentration, 25 mg/L; electrolyte concentration, 2 g/L.

consumption as compared to that in the presence of Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte. In another study, Yildiz et al. [26] demonstrated that Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte offered lower energy consumption (but with slower removal rate than NaCl) for removal of humic substances with Al as anode. On the other hand, Izquierdo et al. [27] reported that both, NaCl or Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte obtained similar chemical oxygen demand (COD) removal in the presence of either Al or Fe anode for the treatment of wastewater containing soluble oil.

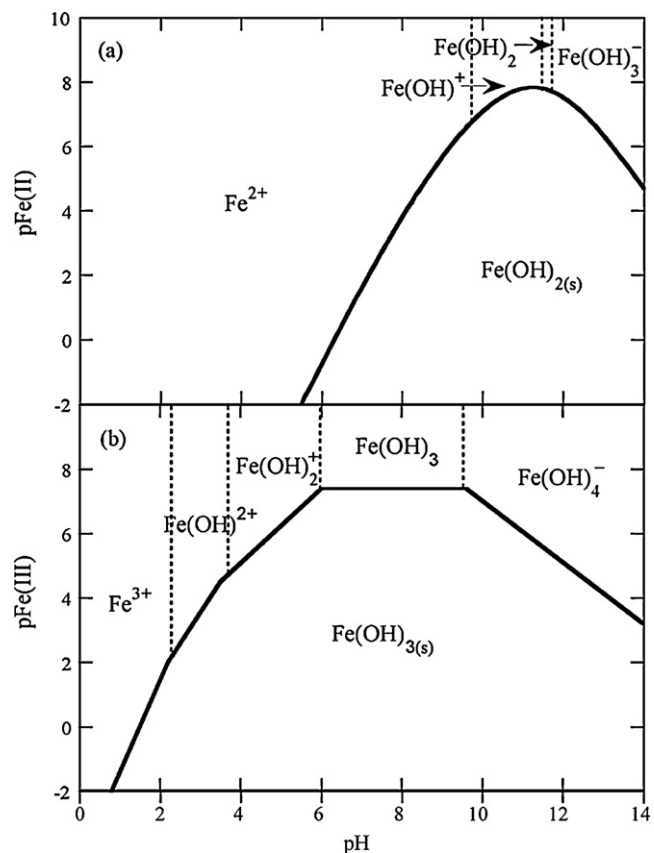
Under identical experimental conditions, chloride is more corrosive than sulfate [27]. Thus, higher rate and extent of RB5 removal in the presence of NaCl may be attributed to excess production of Fe<sup>2+</sup> species and the presence of oxidizing chlorine species generated at anode as compared to that in the presence of Na<sub>2</sub>SO<sub>4</sub>.

### 3.2. Effect of initial pH on decolorization

Fig. 3 depicts effect of initial pH on pseudo first-order reaction rate constant ( $k_{\text{obs}}$ , min<sup>-1</sup>) in the presence of sodium sulfate or sodium chloride as supporting electrolyte at CD = 6.0 mA/cm<sup>2</sup>. It may be seen from Fig. 3 that EC in the presence of sodium chloride achieves superior color removal as compared to that in the presence of sodium sulfate at all the initial pH values. It may be noted from Fig. 3 that  $k_{\text{obs}}$  values at pH 3.74 are matching in the presence of NaCl (0.104 min<sup>-1</sup>) and Na<sub>2</sub>SO<sub>4</sub> (0.104 min<sup>-1</sup>). This is interesting because stronger oxidative chlorine species exists in pH zone 3.0–8.0 (i.e. HOCl,  $E_0 = 1.49$  V vs. SHE [5]) and, thus EC of RB5 floor-wash should give faster decolorization in the presence of NaCl than Na<sub>2</sub>SO<sub>4</sub> if oxidative chlorine species react with RB5. It is well-established that oxidative chlorine species can oxidize reduced inorganic species [28] such as Fe<sup>2+</sup> which is a predominant iron species at initial pH of 3.74 [5]. It may be possible that oxidative chlorine species generated at anode in the presence of NaCl would be exhausted in oxidizing a fraction of abundantly produced Fe<sup>2+</sup> to Fe<sup>3+</sup> according to the following Eqs. (2) and (3) under acidic conditions:



At initial pH of 6.6, the  $k_{\text{obs}}$  value in the presence of NaCl remained same as that at initial pH 3.74 (0.104 min<sup>-1</sup>); however, the  $k_{\text{obs}}$  value in the presence of Na<sub>2</sub>SO<sub>4</sub> decreased (0.076 min<sup>-1</sup>) as compared to that at initial pH 3.74 (0.101 min<sup>-1</sup>). As shown in



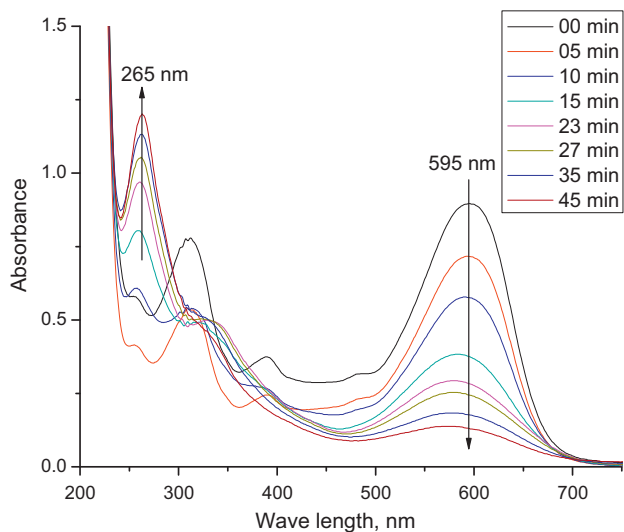
**Fig. 4.** Predominance-zone diagrams for (a) Fe(II) and (b) Fe(III) chemical species in aqueous solution. The straight lines represent the solubility equilibrium for insoluble Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub>, respectively, and the dotted lines represent the predominance limits between soluble chemical species [5].

Fig. 4, at initial pH of 6.6, Fe exists as Fe<sup>2+</sup> (predominant species) and Fe(OH)<sub>2</sub>. Thus, HOCl formed in the presence of NaCl may still be lost in oxidizing Fe<sup>2+</sup> as shown in Eqs. (2) and (3), resulting in the same value of  $k_{\text{obs}}$  at initial pH of 3.74 and 6.6. The decrease in  $k_{\text{obs}}$  value in the presence of Na<sub>2</sub>SO<sub>4</sub> appears to be due to less corrosion and hence, less formation of iron species at pH 6.6 as compared to acidic initial pH of 3.74.

The highest individual decolorization was achieved at initial pH value of 9.0 in the presence of NaCl (~94%) and Na<sub>2</sub>SO<sub>4</sub> (~88%) at the end of 25 min. The results obtained in our study are consistent with reported results; wherein, the authors have reported the highest decolorization in alkaline pH range of 8.5–10 [6,7,16,19,23].

Initial pH may affect the removal of a target compound by, (1) affecting distribution of iron species, and (2) affecting transformation of the target compound [29]. At initial pH of 9.0, Fe predominantly exists as Fe(OH)<sub>2</sub> along with some concentration of Fe<sup>2+</sup>. Moreover, sodium sulfonate (SO<sub>3</sub><sup>-</sup>Na) and hydroxyl (OH) groups of RB5 would exist as SO<sub>3</sub><sup>-</sup> and O<sup>-</sup>, and hence RB5 molecules may be negatively charged at alkaline pH. It seems that Fe<sup>2+</sup> reacts better with such negatively charged RB5 molecules at alkaline pH conditions resulting in faster reduction of azo bonds; and thereby, faster and higher decolorization.

pH at the end of reaction (30–45 min) increased to 7.8 and 7.3; respectively for initial pH values of 6.6 and 3.74. At acidic pH, H<sup>+</sup> will be reduced to H<sub>2</sub> at cathode accumulating OH<sup>-</sup> in solution; thereby increasing pH. In contrast to this, when initial pH was 9.0, the final pH decreased to 8.6; since at higher initial pH, OH<sup>-</sup> in solution will be precipitated as iron hydroxides accumulating H<sup>+</sup> and decreasing pH [22].



**Fig. 5.** UV-vis spectrophotometric changes during EC of RB5. Reaction conditions: reaction volume: 500 mL, CD: 4.5 mA/cm<sup>2</sup>, initial RB5 concentration: 25 mg/L, sodium sulfate concentration: 2 g/L, initial pH: 6.6.

### 3.3. Mechanism of decolorization

Fig. 5 shows representative time-dependent spectral profiles of RB5 floor-wash subjected to EC at CD=4.5 mA/cm<sup>2</sup>. RB5 at  $t=0$  is represented mainly by three peaks; viz., 595 nm, and 312 and 265 nm, respectively under visible and UV range. It may be noted from Table 1 that each molecule of RB5 consists of two molecules of VS and one molecule of H-Acid connected by two –N=N– bonds. Spectrophotometric analysis of solutions of varying concentrations of VS and H-Acid showed distinct peaks respectively at 265 nm and 312 nm varying linearly with concentration. Thus, the peak at 595 nm corresponds to chromophoric group –N=N–, and the peaks at 265 nm and 312 nm correspond to benzene (VS) and naphthalene (H-Acid) rings. It may be observed that as EC reaction proceeds, peak at 265 nm increases concomitant with decrease in peak at 595; indicating generation of a compound which appears to be VS.

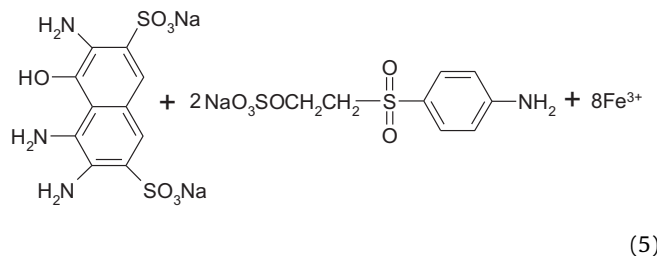
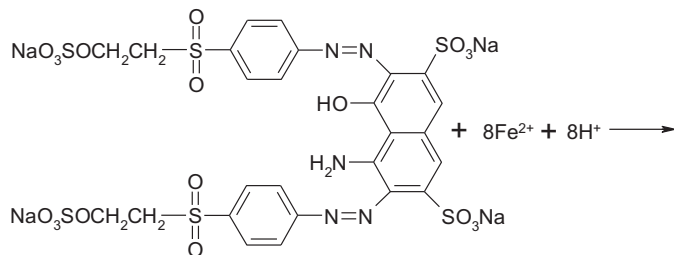
Fig. 6 compares the concentration of VS generated as a result of EC with stoichiometric concentration of VS that should have been produced as a result of actual decolorization of RB5 at various initial pH values. From Figs. 5 and 6(a) and (b), it appears that generation of VS in the presence of either electrolytes at initial pH 3.74 and 6.6 is the result of decolorization of RB5 through reductive cleavage of –N=N– bonds. It may be noted from Fig. 6(b) that generation and accumulation of VS in the presence of either salt closely matched the theoretical generation and accumulation of VS. Azo bonds are electron-deficient groups and can be easily reduced, forming corresponding amines [17]. Similar evidences of decolorization of various dyes by EC within initial pH of 4–8 through cleavage of azo bonds are reported. For example, Muthukumar et al. [19] studied EC of Acid orange 10 using iron anodes and reported formation of aniline and 1-amino-2-naphthol-6,8-disulfonic acid as products. Chang et al. [7] studied EC of RB5 using iron anode at initial pH of 7.0 and reported formation of a compound having absorbance at 265 nm. Reports showing similar mechanism (i.e. reductive cleavage of azo linkage) obtained using other treatment systems are also available. For example, Patel and Suresh [30] observed release of H-Acid while studying decolorization of RB5 using magnesium–palladium bimetallic system. Feng et al. [31] investigated products of degradation of Reactive Red 2 by zero-valent iron using GC–MS. The results revealed that the azo linkage of Reactive Red 2 was cleaved to produce hydrogenated azo structure without destroying benzene ring and naphthalene ring. Libra

et al. [32] also reported generation of compounds closely matching H-Acid and VS by anaerobic biological treatment of wastewater containing partially hydrolyzed RB5. del Rio et al. [33] demonstrated breakage of azo bond and formation of corresponding aromatic amines due to electro-reduction of Reactive orange 4 on a stainless steel cathode in the presence of Na<sub>2</sub>SO<sub>4</sub> at alkaline conditions (pH 10–13) in a divided cell. Vyjayanthi et al. [34] employed a reactor containing palladized bacterial cellulose in the presence of hydrogen for decolorization of Drimarene Red at pH 3.6–4.0. Authors noted generation of a compound having absorbance at 250 nm; however, it could not be identified. It may be noted that palladium in the presence of hydrogen is a catalytic reduction system [35]. Reductive cleavage of azo linkages by bisulfate-catalyzed sodium borohydride reaction for Acid, Direct, and Reactive dyes is already reported [36]. Based on above discussion, published literature [18,37,38], and experimental results; it was concluded that decolorization of RB5 achieved by EC in our study was primarily through reduction of azo bonds by ferrous ions as shown in following Eqs. (4) and (5):

Anode:

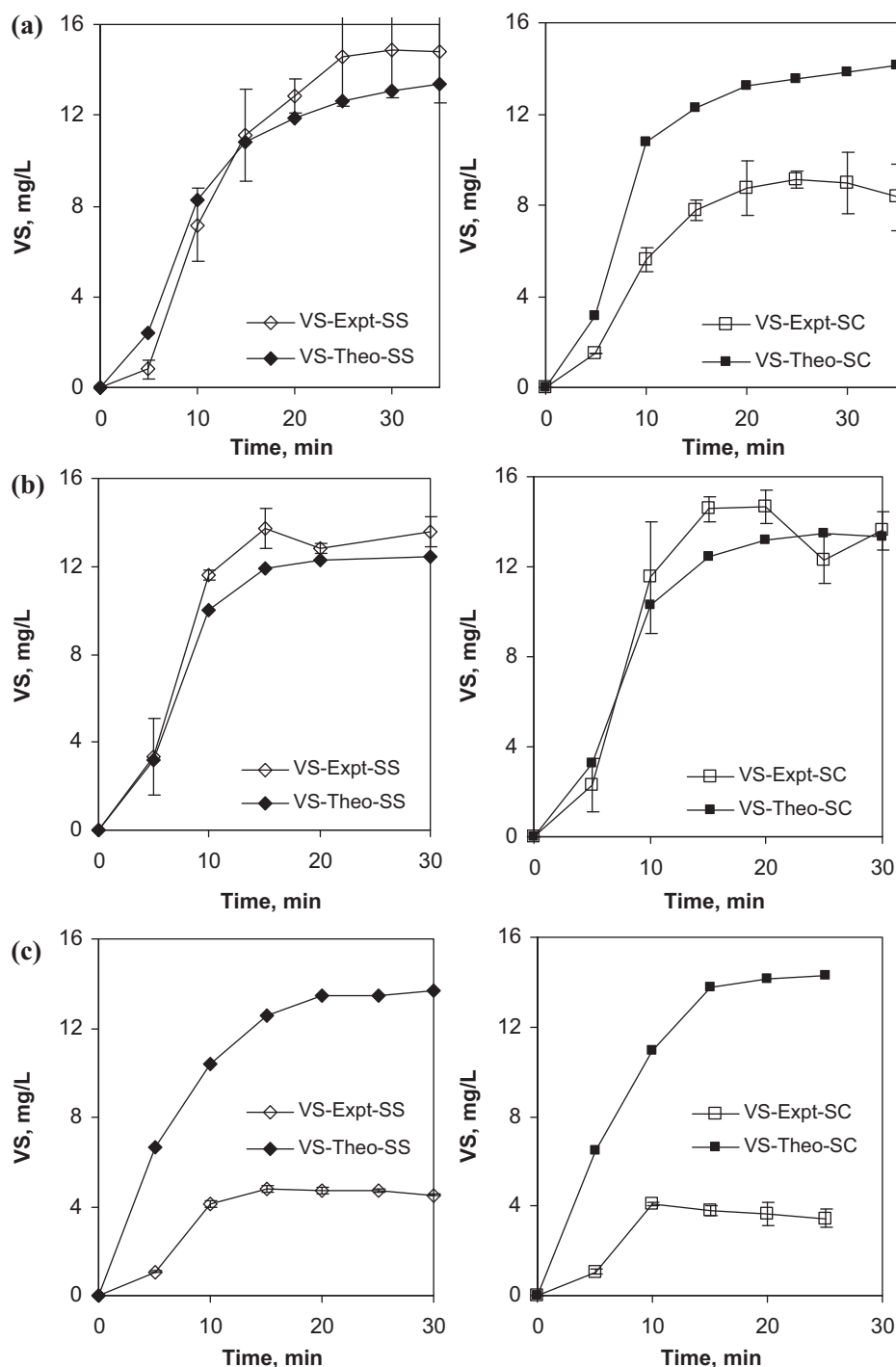


Decolorization:



### 3.4. Effect of operating parameters on mechanism of decolorization, and generation and accumulation of products

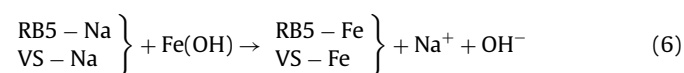
It may be noted from Fig. 6(a) and (b) that the concentration of actual VS generated as a result of EC closely matches with the stoichiometric VS concentration that would be generated if all decolorization is assumed to be due to cleavage of azo bonds. Careful observation of Fig. 6(c) reveals that concentration of actual VS generated and accumulated is much lower than the stoichiometric VS concentration at initial pH of 9.0. There could be two possible ways by which actual VS produced as a result of azo bond-cleavage is concomitantly and rapidly removed: (1) by direct or indirect oxidation; and (2) by physical interactions with iron oxy/hydroxide species. In addition to this, it may also be possible that a fraction of RB5 may be coagulated and removed without being reduced by ferrous ions, thereby producing lesser amounts of VS. To test the possibility #1, we conducted electrolysis of 20 mg/L solution of VS prepared in tap water (initial pH 9.0), using graphite as anode and stainless steel as cathode. It was noted that removal of VS by adsorption on either of the electrodes was negligible. However, ~32



**Fig. 6.** Comparison of VS generation profiles in the presence of sodium sulfate (SS) and sodium chloride (SC) as electrolytes: (a) initial pH: 6.6, (b) initial pH: 3.74, and (c) initial pH: 9.0. Reaction conditions: reaction volume, 500 mL; CD, 6.0 mA/cm<sup>2</sup>; initial RB5 concentration, 25 mg/L; electrolyte concentration, 2 g/L. Expt-Experimental, Theo-Theoretical.

and ~65% of VS was removed after 30 min of electrolysis at CD of 6.0 mA/cm<sup>2</sup>, respectively, in the presence of Na<sub>2</sub>SO<sub>4</sub> and NaCl. Excess removal of VS in the presence of NaCl as compared to that in the presence of Na<sub>2</sub>SO<sub>4</sub> may be mainly attributed to indirect oxidation by chlorine species. Although the type of anode (graphite vs. iron) may have its own influence, it appears that if VS generated as a result of EC is concomitantly oxidized, it must result in dissimilar profiles of VS generation and accumulation (i.e. more oxidation in the presence of NaCl) in the presence of Na<sub>2</sub>SO<sub>4</sub> and NaCl at initial pH 9.0. On the contrary, actual profiles of generation and accumulation of VS at pH 9.0 are almost similar in the presence of either of

the electrolytes. Thus, it seems that VS and a small fraction of RB5 were removed by surface interactions with iron hydroxide species under alkaline conditions as shown in Eq. (6). It may be noted from Fig. 4 that both, Fe<sup>2+</sup> and Fe<sup>3+</sup>, predominantly exist as Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub> at pH 8.5–9.0, respectively:



In the absence of an FTIR facility we separated and dissolved the sludge produced as a result of EC conducted at pH 9.0. The

sludge was taken in a beaker and 500 mL of tap water was added. Concentrated HCl was slowly added to reduce the pH from neutral to 6.0, 5.0, 4.0, 3.0, and 2.0 and UV–vis profiles were taken. The spectrophotometric profiles clearly showed the presence of H-Acid (315–325 nm) and a small peak of RB5 (594–605 nm, concentration < 1 mg/L). This indicated that major fraction of RB5 was decolorized by azo cleavage. However, VS could not be detected possibly because the solubility of VS decreases with decrease in pH. Thus, insoluble VS might be filtered out.

Overall, it may be concluded that decolorization of RB5 containing floor-wash by EC using iron anode is achieved by: (1) reduction of azo bonds by ferrous ions at acidic to neutral pH conditions, and (2) mainly by reduction of azo bonds by ferrous ions, and to a little extent, due to removal of RB5 by coagulation with iron hydroxide species, at alkaline pH conditions.

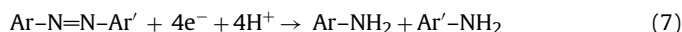
It may further be noted from Fig. 6 that accumulation of VS in the reaction medium is dependent on the type of supporting electrolyte. At initial pH of 6.6 and in the presence of sodium sulfate (Fig. 6(a)), the profiles of actual and theoretical VS generation closely match. However, in the presence of NaCl, not only that there is a gap between two profiles but also the concentration of VS generated as a result of EC decreases after a peak concentration at 25 min. This decrease and gap in the profiles may be attributed to oxidation of VS by chlorine species. On the other hand, at initial pH of 3.74 (Fig. 6(b)), profiles of actual and theoretical VS generation closely match in the presence of either of the electrolytes. This indicates that there is negligible contribution of oxidative chlorine species generated in the presence of NaCl towards removal of VS. This observation supports the similar observation noted in Section 3.2, that oxidative chlorine species may be consumed in oxidizing ferrous ions under acidic conditions. Generation, quantification, and evaluation of effect of experimental parameters on accumulation of VS, during EC of RB5 are not reported so far to the best of our knowledge. Chang et al. [7] and Song et al. [8] reported presence of a compound having absorbance at 265 nm produced by EC of RB5 solution; however, it was not quantified. In a study by Sengil and Ozacar [6], decolorization mechanism similar to that proposed by us was reported; however, no efforts were made to detect and quantify VS.

It may further be noted from Fig. 5 that peak at 312 nm, corresponding to H-Acid at  $t=0$ , was removed and did not increase as EC proceeded. This observation is consistent with that reported by Muthukumar et al. [19] who indicated that 1-amino-2-naphthol-6,8-disulfonic acid formed due to cleavage of azo bond of Acid orange 210 did not accumulate and was precipitated as insoluble metal complex. It seems that H-Acid formed similar insoluble species probably through ligand formation with iron hydroxide species [18]. O, N, and S attached to adjacent carbon of organic molecules can facilitate co-ordinate covalent bond with transi-

tional metal ions [19]. For H-Acid, O and N atoms attached to adjacent carbon atoms can facilitate co-ordinate covalent bond with Fe ions. Table 3 summarizes the proposed mechanisms of decolorization and accumulation of products with respect to various experimental conditions based on results obtained by us, and mechanisms proposed by [18,39].

### 3.5. Instantaneous current efficiency (ICE) calculations

Current efficiency (CE) is a ratio of electrons utilized for a chemical change to total electrons supplied per unit time. It was concluded based on generation and accumulation of VS that decolorization of RB5 primarily proceeds through cleavage of azo bonds. Reduction of an azo bond requires four electrons resulting in formation of corresponding amines as shown in Eq. (7) [17]:



where Ar and Ar' represent organic groups. Thus, one mole of RB5 (see Table 1), containing 2 mol of azo bonds, requires 8 mol of electron to effect the decolorization. Assuming that all decolorization is achieved through cleavage of azo bonds, ICE was calculated as shown in Eq. (8):

$$\text{ICE}(\%) = \frac{n \times (\Delta C) \times (V_s) \times 100}{(I \times \Delta t)/F} \quad (8)$$

where  $n$  is the electrons involved in chemical reaction, mol/mol ( $n=8$  in this study),  $F=96,487$  C/s,  $\Delta C$  is the change in concentration of dye between two time points, mol/L,  $V_s$  is the volume of solution (0.5 L in this study),  $I$  is the current, A, and  $\Delta t$  is the difference between two time points, s.

ICE was calculated for 50% removal of dye. Time required for 50% decolorization ( $\Delta C=0.0126$  mM) was calculated from 1st order kinetic plots for various operating conditions and it was used in Eq. (8). Electrical energy consumption (EEC, kWh/kg of dye removed) was calculated as shown in Eq. (9) [5]:

$$\text{EEC (kWh/kg)} = \frac{IVt}{M_D} \quad (9)$$

where  $V$  is the average cell voltage, V;  $I$  is the cell current, A;  $t$  is the time of electrolysis, h; and  $M_D$  is the mass of dye removed, g.

Fig. 7 shows variation of ICE and EEC with respect to CD for all experiments conducted at initial pH of 6.6. It may be noted from Fig. 7 that ICE in the presence of NaCl is consistently higher as compared to that in the presence of  $\text{Na}_2\text{SO}_4$ . EEC remains almost constant ( $\sim 40$  kWh/kg of RB5) at CDs of 4.5 and 6.0 mA/cm<sup>2</sup> and reduces to 29 kWh/kg of RB5 at CD of 7.5 mA/cm<sup>2</sup> in the presence of NaCl. Results obtained in our study are in close proximity to those reported previously. For example, Chang et al. [7] studied EC of 100 mg/L RB5 solutions using iron anode and reported EEC

**Table 3**  
Possible predominant mechanisms of decolorization and accumulation of products.

Reactions	Initial pH		
	3.74	6.6	9.0
At anode	(1) $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^-$ (2) $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$ (3) $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ (*)	(1) $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^-$ (2) $\text{Fe}^{2+}_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + e^-$ (3) $\text{Fe}_{(s)} \rightarrow \text{Fe}^{3+}_{(aq)} + 3e^-$ (4) $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ (*)	(1) $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^-$ (2) $\text{Fe}_{(s)} \rightarrow \text{Fe}^{3+}_{(aq)} + 3e^-$ (3) $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ (*)
At cathode	$2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_2$	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$
In bulk solution	(1) $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Fe}(\text{OH})_{2(s)}$ (2) $2\text{Fe}^{2+} + \text{HOCl} \rightarrow 2\text{Fe}^{3+} + \text{OH}^- + \text{Cl}^-$ (*) (3) $2\text{Fe}^{2+} + \text{Cl}_2 \rightarrow 2\text{Fe}^{3+} + 2\text{Cl}^-$ (*)	(1) $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Fe}(\text{OH})_{2(s)}$ (2) $\text{Fe}^{3+}_{(aq)} + 3\text{OH}^-_{(aq)} \rightarrow \text{Fe}(\text{OH})_{3(s)}$ (3) $2\text{Fe}^{2+} + \text{HOCl} \rightarrow 2\text{Fe}^{3+} + \text{OH}^- + \text{Cl}^-$ (*)	(1) $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Fe}(\text{OH})_{2(s)}$ (2) $\text{Fe}^{3+}_{(aq)} + 3\text{OH}^-_{(aq)} \rightarrow \text{Fe}(\text{OH})_{3(s)}$ (3) $\text{Cl}_2 + \text{OH}^- \rightarrow \text{OCl}^- + \text{HCl}$ (*)
Decolorization	$\text{Fe}^{2+}_{(aq)} + \text{RB5}_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{H-Acid}_{(aq)} + 2\text{VS}_{(aq)}$	$\text{Fe}^{2+}_{(aq)} + \text{RB5}_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{H-Acid}_{(aq)} + 2\text{VS}_{(aq)}$	$\text{Fe}^{2+}_{(aq)} + \text{RB5}_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{H-Acid}_{(aq)} + 2\text{VS}_{(aq)}$
Interaction with products of EC	$\text{H-Acid}_{(aq)} + \text{Fe}(\text{OH})_{n(s)} \rightarrow \text{H-Acid-Fe}(\text{OH})_{n(s)}$	(1) $\text{H-Acid}_{(aq)} + \text{Fe}(\text{OH})_{n(s)} \rightarrow \text{H-Acid-Fe}(\text{OH})_{n(s)}$ (2) $\text{VS} + \text{HOCl} \rightarrow \text{unknown products}$ (*)	(1) $\text{H-Acid}_{(aq)} + \text{Fe}(\text{OH})_{n(s)} \rightarrow \text{H-Acid-Fe}(\text{OH})_{n(s)}$ (2) $\text{VS} + \text{Fe}(\text{OH})_{n(s)} \rightarrow \text{VS-Fe}(\text{OH})_{n(s)}$

(\*) = (When NaCl is used as a supporting electrolyte).

H-Acid and vinyl sulfone (VS) are products formed due to cleavage of azo link between them in a Reactive Black 5 (RB5) molecule.

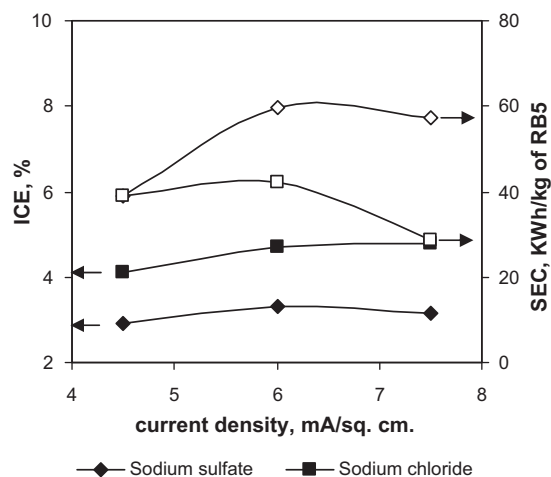


Fig. 7. Variation of ICE and SEC with respect to CD at initial pH of 6.6.

values of 17 and 34 kWh/kg of RB5, respectively for CDs of 27.7 and 54.4 mA/cm<sup>2</sup>; NaCl concentration of 1 g/L, and pH 7.0. Song et al. [8] studied ozone-assisted EC of RB5 in the presence of 5 g/L K<sub>2</sub>SO<sub>4</sub> and reported total energy consumption (i.e. EC + ozonation) of 33 kWh/kg of RB5. Sengil and Ozacar [6] reported much lower electricity consumption of 5.32 kWh/kg of RB5; however, the EEC was calculated as a function of loss of iron electrode mass during EC and thus, may not be meaningfully compared.

In the presence of Na<sub>2</sub>SO<sub>4</sub>, EEC increased with increase in CD from 4.5 to 6.0 mA/cm<sup>2</sup>, and remained almost constant thereafter (~58.5 kWh/kg of RB5). It seems that electrical energy is increasingly lost for unwanted reactions (for example, production of oxygen and hydrogen) and hence, EEC increases as CD increases in the presence of Na<sub>2</sub>SO<sub>4</sub>. On the contrary, decrease in EEC with increase in CD may be attributed to increased production of oxidative chlorine species in the presence of NaCl.

#### 4. Conclusions

Following conclusions can be drawn from the present study:

- (1) More than 90% decolorization of RB5 floor-wash could be achieved by EC in the presence of NaCl as a supporting electrolyte and at CD of 6–7.5 mA/cm<sup>2</sup> at initial pH of 9.0. Thus, EC can be effectively used as a pretreatment for RB5 floor-wash.
- (2) Reduction of azo linkage through oxidation of Fe<sup>2+</sup> appeared to be the major mechanism of decolorization of RB5. Out of the two products of RB5 decolorization, VS accumulated; while, H-Acid was concomitantly removed by surface complexation on iron hydroxide species. Accumulation of VS was found to be influenced by initial pH and the type of supporting electrolyte.
- (3) Under identical experimental conditions, energy consumption was almost half in the presence of NaCl (~29 kWh/kg of RB5) as compared to that in the presence of Na<sub>2</sub>SO<sub>4</sub> (~58.5 kWh/kg of RB5). This suggested that NaCl is a better supporting electrolyte.
- (4) A treatment consisting of EC with iron anode in the presence of NaCl, followed by aerobic biological treatment system, may achieve complete removal of RB5 since VS has been reported to be biodegradable under aerobic conditions [32].
- (5) The results of this study are important because of following reasons: (1) the floor-wash used in this study is prepared from normal tap water and thus, closely simulates the actual floor-wash and (2) it discusses the generation and accumulation of intermediates under various experimental conditions which is important to design subsequent treatment systems to get rid of aromatic amines.

#### Acknowledgements

Authors thank SVIT, Vasad, India, for providing experimental facilities and Mr. H. Patel for helping with experimental work.

#### References

- [1] N. Koprivanac, H. Kusic, Hazardous Organic Pollutants in Colored Wastewaters, Nova Science Publishers, Inc., New York, 2009.
- [2] Ministry of Environment and Forest, Government of India, Notification GSR 485 (E), New Delhi, India, 2010.
- [3] B. dos Santos, F.J. Cervantes, J.B. van Lier, Review paper on current technologies for decolorisation of textile wastewaters: perspectives for anaerobic biotechnology, *Bioresour. Technol.* 98 (2007) 2369–2385.
- [4] Y. Fu, T. Viraraghavan, Fungal decolorization of dyes wastewater: a review, *Bioreour. Technol.* 79 (2001) 251–262.
- [5] A. Martinez-Huitle, E. Brillas, Decoloration of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, *Appl. Catal. B* 87 (2009) 105–145.
- [6] I.A. Sengil, M. Ozacar, The decolorization of C.I. Reactive Black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes, *J. Hazard. Mater.* 161 (2009) 1369–1376.
- [7] S.-H. Chang, K.-S. Wang, H.-H. Liang, H.-Y. Chen, H.-C. Li, T.-H. Peng, Y.-C. Su, C.-Y. Chang, Treatment of Reactive Black 5 by combined electrocoagulation–granular activated carbon adsorption–microwave regeneration process, *J. Hazard. Mater.* 175 (2010) 850–857.
- [8] S. Song, Z. He, J. Qiu, L. Xu, J. Chen, Ozone assisted electrocoagulation for decolorization of C.I. Reactive Black 5 in aqueous solution: an investigation of the effect of operational parameters, *Sep. Purif. Technol.* 55 (2007) 238–245.
- [9] S. Song, Z. He, J. Qiu, J. Chen, Effect of operational parameters on the decolorization of C.I. Reactive Blue 19 in aqueous solution by ozone-enhanced electrocoagulation, *J. Hazard. Mater.* 152 (2008) 204–210.
- [10] D. Rajkumar, J.G. Kim, Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment, *J. Hazard. Mater. B* 136 (2006) 203–212.
- [11] E. Chatzisympson, N.P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mantzavinos, Electrochemical treatment of textile dyes and dyehouse effluents, *J. Hazard. Mater. B* 137 (2006) 998–1007.
- [12] H.-Y. Chen, L.-C. Huang, Y.-C. Su, S.-H. Chang, Degradation of Reactive Black 5 using combined electrochemical degradation-solar-light/immobilized TiO<sub>2</sub> film process and toxicity evaluation, *Chemosphere* 72 (2008) 299–305.
- [13] C.-L. Yang, J. McGarrah, Electrochemical coagulation for textile effluent decolorization, *J. Hazard. Mater. B* 127 (2005) 40–47.
- [14] O.T. Can, M. Kobya, E. Demirbas, M. Bayramoglu, Treatment of the textile wastewater by combined electrocoagulation, *Chemosphere* 62 (2006) 181–187.
- [15] M. Bayramoglu, M. Eyvaz, M. Kobya, Treatment of the textile wastewater by electrocoagulation: economical evaluation, *Chem. Eng. J* 128 (2007) 155–161.
- [16] E.-S.Z. El-Ashtoukhy, N.K. Amin, Removal of acid green dye 50 from wastewater by anodic oxidation and electrocoagulation – a comparative study, *J. Hazard. Mater.* 179 (2010) 113–119.
- [17] K. Rajeshwar, J.B. Ibanez, *Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement*, Academic Press, San Diego, 1997.
- [18] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, *J. Hazard. Mater. B* 84 (2001) 29–41.
- [19] M. Muthukumar, M. Thalamadai Karuppiyah, G. Bhaskar Raju, Electrochemical removal of CI Acid orange 10 from aqueous solutions, *Sep. Purif. Technol.* 55 (2007) 198–205.
- [20] S.S. Vaghela, A.D. Jethva, B.B. Mehta, S.P. Dave, S. Adimurthy, G. Ramachandrabhai, Laboratory studies of electrochemical treatment of industrial azo dye effluent, *Environ. Sci. Technol.* 39 (2005) 2848–2855.
- [21] N. Mohan, N. Balasubramanian, C. Ahmed Basha, Electrochemical oxidation of textile wastewater and its reuse, *J. Hazard. Mater.* 147 (2007) 644–651.
- [22] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38 (2004) 11–41.
- [23] Q. Zhuo, H. Ma, B. Wang, L. Gu, Catalytic decolorization of azo-stuff with electrocoagulation method assisted by cobalt phosphomolybdate modified kaolin, *J. Hazard. Mater.* 142 (2007) 81–87.
- [24] Phalakornkule, S. Polgumhang, W. Tongdaung, B. Karakat, T. Nuyut, Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent, *J. Environ. Manage.* 91 (2010) 918–926.
- [25] Y.S. Yildiz, A.S. Kopal, S. Irdemez, B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, *J. Hazard. Mater.* 139 (2007) 373–380.
- [26] Y.S. Yildiz, A.S. Kopal, B. Keskinler, Effect of initial pH and supporting electrolyte on the treatment of water containing high concentration of humic substances by electrocoagulation, *Chem. Eng. J.* 138 (2008) 63–72.
- [27] C.J. Izquierdo, P. Canizares, M.A. Rodrigo, J.P. Leclerc, G. Valentin, F. Lapique, Effect of the nature of the supporting electrolyte on the treatment of soluble oils by electrocoagulation, *Desalination* 255 (2010) 15–20.
- [28] C.N. Sawyer, P.L. McCarty, G.F. Parkin, *Chemistry for Environmental Engineering and Science*, McGraw-Hill Publication, 5th ed., New Delhi, India, 2003.



- [29] A.S. Kopalal, Y.S. Yildiz, B. Keskinler, N. Demircioglu, Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, *Sep. Purif. Technol.* 59 (2008) 175–182.
- [30] R. Patel, S. Suresh, Decolourization of azo dyes using magnesium–palladium system, *J. Hazard. Mater.* 137 (2006) 1729–1741.
- [31] W. Feng, D. Nansheng, H. Helin, Degradation mechanism of azo dye C.I. reactive red 2 by iron powder reduction and photooxidation in aqueous solutions, *Chemosphere* 41 (2000) 233–238.
- [32] J.A. Libra, M. Borchert, L. Vigelahn, T. Storm, Two stage biological treatment of a diazo reactive textile dye and the fate of the dye metabolites, *Chemosphere* 56 (2004) 167–180.
- [33] A.I. del Rio, J. Molina, J. Bonastre, F. Cases, Study of the electrochemical oxidation and reduction of C.I. Reactive Orange 4 in sodium sulphate alkaline solutions, *J. Hazard. Mater.* 172 (2009) 187–195.
- [34] J.P. Vyjayanthi, U.D. Patel, S. Suresh, Decolourization of drimarene Red dye using palladized bacterial cellulose in a reactor, in: *Proceedings of Water Environment Federation, WEFTEC 2008 held during 18th–22nd October at Chicago, USA, 2008*, pp. 169–182.
- [35] U.D. Patel, S. Suresh, Complete dechlorination of pentachlorophenol using palladized bacterial cellulose in a rotating catalyst contact reactor, *J. Colloid Interface Sci.* 319 (2008) 462–469.
- [36] A. Reife, H.S. Freeman, *Environmental Chemistry of Dyes and Pigments*, Wiley-Interscience Publication, USA, 1996.
- [37] Noubactep, A. Schöner, Metallic iron for environmental remediation: learning from electrocoagulation, *J. Hazard. Mater.* 175 (2010) 1075–1080.
- [38] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, *J. Hazard. Mater. B* 114 (2004) 199–210.
- [39] D. Ghernaout, B. Ghernaout, A. Boucherit, M.W. Naceur, A. Khelifa, A. Kellil, Study on mechanism of electrocoagulation with iron electrodes in idealized conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes 8 (2009) 91–99.