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Electrochemical degradation of Reactive Blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds

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Abstract

In the present study, electrochemical degradation experiments were conducted to degrade a textile dye namely Reactive Blue 19 (RB-19). A laboratory scale bench-top reactor was used to investigate the effect of various operating parameters using titanium based dimensionally stable anode (DSA). The oxidation of RB-19 takes place in the bulk solution with electrolytically generated chlorine/hypochlorite. Increasing the initial pH and increasing the reaction temperature decreases the de-colorization efficiency. At the same time, increasing the chloride concentration and increasing the current density showed an increase in the color removal. The complete removal of color was achieved within a short period of electrolysis for different concentrations of RB-19. However, the removal of chemical oxygen demand (COD) and total organic carbon (TOC) was 55.8% and 15.6%, respectively, for 400 mg/L RB-19 with 1.5 g/L sodium chloride concentration. The intermediate compounds formed during the degradation were identified using a gas chromatography coupled with mass spectrometry (GC/MS). In the present study, no chlorinated organic compounds were detected during the course of electrolysis. The major compounds identified were benzene, 2-hydroxy, 4,4-napthaquinoine (C.I. Natural orange 6), 1-aminoanthraquinone (C.I. Diazo fast red AL), benzyl alcohol, benzaldehyde, benzoic acid, phthalic anhydride, phthalide, phthaldehyde and 1,3-indanone.

Keywords: Reactive Blue 19; Electrochemical degradation; Wastewater treatment; DSA electrodes; Intermediate compounds

1. Introduction

Textile processing industries nowadays are widespread sectors in developing countries. Among the various processes in the textile industry, dyeing process uses large volume of water for dyeing, fixing and washing processes. Thus, the wastewater generated from the textile processing industries contains, suspended solids, high amount of dissolved solids, un-reacted dyestuffs (color) and other auxiliary chemicals that are used in the various stages of dyeing and processing. The conventional method of textile wastewater treatment consists of chemical coagulation, biological treatment followed by activated carbon adsorption. The conventional coagulation process generates huge volume of hazardous sludge and poses a problem of sludge disposal. The biological treatment of textile wastewater showed low degradation efficiency because of the presence of biologically inert high molecular weight dyestuffs [1,2]. Hence, many investigators are studying alternative oxidation methods like ozonation, photocatalytic oxidation, electrochemical oxidation, etc.

The photocatalytic oxidation experiments were conducted for Acid Blue 80 [3], Acid Orange 7 [4], Brilliant

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Orange K-R [5] and Reactive Orange 16 [6]. The electrochemically assisted photochemical degradation was also conducted to improve the degradation efficiency of the dye [7]. Ozonation process was studied for the removal of color and COD [8], however; this process showed less COD removal [9]. Researchers also investigated electrocoagulation methods for textile dye removal using aluminum [10] or iron [11] electrodes.

Several researchers have studied the feasibility of electrochemical degradation of textile dyes using various electrode materials for wastewater treatment. Electrochemical degradation of different dye compounds was studied using titanium based DSA electrodes [12], platinum electrode [13], diamond and metal alloy electrodes [14] and boron doped diamond electrodes [15,16].

Most investigators provided information on color and COD removal during the dye degradation and not much information was provided for the degradation pathway or intermediate compound formation by electrochemical degradation. Hence in the present study, an attempt was made to identify the intermediate compound formation. Since the real textile dyeing industry effluent contains larger amount of dissolved sodium chloride, electrolysis experiments were conducted in a chloride medium. Reactive Blue 19 was selected as a model compound because of its low fixation efficiency (75–80%) on cellulose due to the competition between the formation of reactive vinyl sulfone and formation of 2-hydroxyethylsulfone. The 2-hydroxyethylsulfone does not fix on the cellulose fiber [17]. The $Ti/TiO_2–RuO_2–IrO_2$ anode was selected in the present study because of its low cost and commercial availability.

2. Experimental

Electrochemical degradation experiments were conducted in a bench-top undivided electrolytic cell, with a working sample volume of 1 L. Experiments were conducted under galvanostatic conditions using a regulated dc power supply (UP-3010S model, Unicorn Co., Limited, South Korea). The anode and cathode were positioned vertically and parallel to each other with an inter electrode gap of 1 cm. The anode used in the study was a commercially available DSA® of titanium mesh (10 × 5 cm) coated with $TiO_2–RuO_2–IrO_2$ and a stainless steel plate was used as a cathode (10 × 5 cm). The total effective surface area of the anode was 27.7 cm^2. The temperature of the reactor was maintained constant using an external water re-circulation system. The solution was constantly stirred at 200 rpm using a magnetic stirrer.

The pH of the sample was measured using YSI pH meter (model 63, USA). The initial pH of the sample was set appropriately using dilute sodium hydroxide or dilute sulfuric acid. UV–visible spectra during the degradation of dye were recorded between 200 and 800 nm using a scanning UV–visible spectrophotometer (Jasco model V-530, Japan). The visible color removal was measured at 592 nm. The concentration of RB-19 during the degradation was determined based on the constructed calibration graph. Samples were diluted using distilled water if the absorbance exceeded the range of calibration curve. The total organic carbon (TOC) of the initial and the electrolyzed solutions was determined using TOC analyzer (Shimadzu, model TOC 5000A, Japan). The instrument was operated at 680 °C furnace temperature and 50 μL sample injection. The chemical oxygen demand (COD) during the electrolysis was determined by an open reflux, dichromate titrimetric method as described in Standard Methods [18]. The concentration of combined residual chlorine/hypochlorous acid/hypochlorite was analyzed by iodiometeric method as described in Standard Methods [18].

The dye sample of Reactive Blue 19 (C.I. 61200, CAS 2580-78-1) was obtained from a commercial manufacturing company (Rifa Co., Limited, South Korea). The dye sample was used as such without any purification.

The degradation products were identified using a gas chromatography coupled with mass spectrometry (GC/MS) system. The samples were collected at different time intervals during the electrolysis and were extracted with dichloromethane (HPLC grade). The sample was initially extracted under alkaline condition by adding 5 mL of 1 N sodium hydroxide followed by, in acidic condition, adding 5 mL of 1 + 1 concentrated sulfuric acid using separating funnel. Each extraction was done three times with 20 mL of dichloromethane. The extracts were dehydrated using anhydrous sodium sulfate. The extracts were concentrated to 10 mL using rotary evaporator (Eyela make, Japan) at 40 °C under reduced pressure (45 cm Hg). Further, the contents were concentrated in *n*-hexane (HPLC grade) to 100 μL under nitrogen stream at 40 °C. The operating condition of GC/MS is provided in Table 1. The intermediate compounds formed were identified by

Table 1
The operating conditions of GC/MS for the identification of intermediate compounds

GC	
Instrument	Hewlett Packard HP 6890
Injection mode	Splitless
Carrier gas	Helium (99.9999%)
Sample volume	2 mL
Injector temperature	250 °C
Column	J & W Scientific, DB-5, 30 m (length) × 0.25 mm (I.D) with 0.25 m film thickness
Temperature program	40 °C (10 min), 100 °C (12 °C/min), 200 °C (5 °C/min), 270 °C (20 °C/min), 270 °C for 5 min holding, 300 °C (10 °C/min), 300 °C for 5 min holding
MS	
Instrument	HP 5973
Mode	Scan

comparing with the standard mass spectrum of NIST library.

3. Results and discussion

3.1. Preliminary investigation with different supporting electrolytes

Initially, separate experiments were conducted with sodium sulfate and sodium chloride electrolytes at a current density of 18.05 mA/cm^2 with 100 mg/L RB-19. In the presence of sodium sulfate no color removal occurred up to 2 Ah/L. The reason is that neither any oxidative species were produced nor any direct anodic oxidation occurred at the anode surface. Increasing the mass transport by means of increasing the stirring rate also does not show any color removal. However, the color removal occurred only in the presence of sodium chloride. Thus, the de-colorization occurs in the bulk solution because of the reaction between the generated chlorine/hypochlorite and the dye molecule. The indirect electrochemical treatment involves the application of an electrical current to the wastewater containing chloride to convert chloride to chlorine/hypochlorite. The chlorine/hypochlorite oxidizes the pollutants and is then reduced to chloride ion.

$$\text{Anode}: \quad 2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$\text{Cathode}: \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

$$\text{Bulk solution}: \quad Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{4}$$

3.2. Effect of current density on the degradation of RB-19

The current density was varied from 7.22 to 36.10 mA/cm^2 with 100 mg/L RB-19 and 1.5 g/L sodium chloride. The results are presented in Fig. 1. The results clearly showed that increasing current density decreases the charge loading for the degradation of RB-19, because of the increased production of chlorine/hypochlorite at higher current densities. The reason is that increasing current density increases the over potential required for the generation of chlorine/hypochlorite. At the same time, the performance of the reactor will be affected under different current densities while altering the other operating conditions simultaneously, because the generation of chlorine/hypochlorite depends on mass, charge or mixed control. The removal of color was increased up to 18.05 mA/cm^2 current density, beyond that the color removal was not much increased.

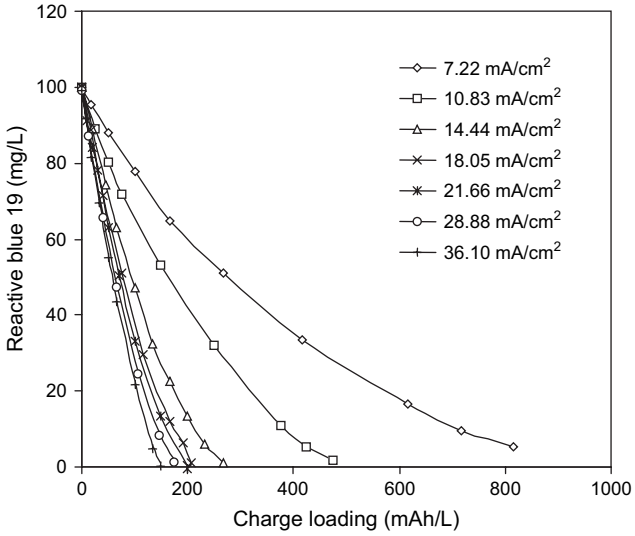

Fig. 1. Effect of current density on the electrochemical degradation of Reactive Blue 19 (conditions: initial pH = 7.0, sodium chloride = 1.0 g/L, reaction temperature = 30 °C, Reactive Blue concentration = 100 mg/L, reactor volume = 1 L).

3.3. Effect of sodium chloride on the degradation of RB-19

Fig. 2 presents the color removal with different sodium chloride concentrations under a fixed current density of 21.66 mA/cm^2. It is clear that increasing the chloride concentration increases the color removal due to increased mass transport of chloride ions to the anode surface and

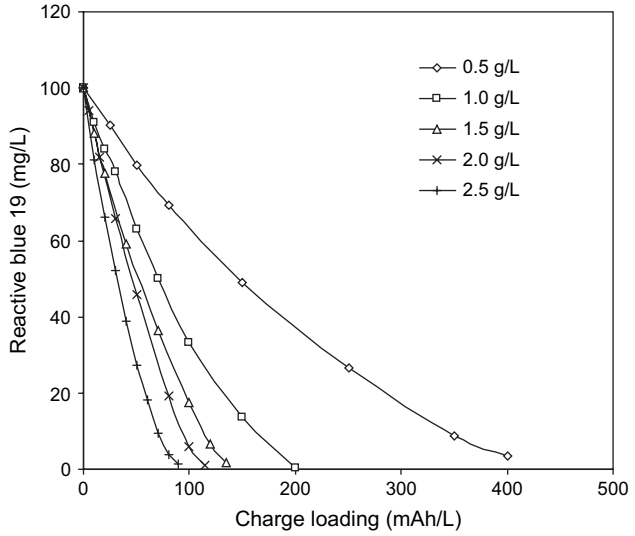

Fig. 2. Effect of sodium chloride concentration on the electrochemical degradation of Reactive Blue 19 (conditions: initial pH = 7.0, current density = 21.66 mA/cm^2, reaction temperature = 30 °C, Reactive Blue concentration = 100 mg/L, reactor volume = 1 L).

also increased diffusion in the diffusion layer of the anode. As a result, more amount of chlorine/hypochlorite will be generated. Hence the rate of color removal was increased. Though the chloride concentration is high (5000–10 000 mg/L) in real textile processing wastewater, it was decided to conduct further experiments with 1.5 g/L sodium chloride concentration, because of the implementation of stringent limits for total dissolved solid concentration for the treated wastewater by various regulatory authorities.

3.4. Effect of initial pH on the degradation of RB-19

The variation of initial pH on the de-colorization of RB-19 during the electrochemical degradation is presented in Fig. 3. The color removal decreased with increase in the initial pH of the solution. For example, the charge loading required for the removal of 95% color increased from 100 to 160 mAh/L while increasing the initial pH from 4.0 to 9.0. The color removal drastically decreased if the initial pH was 10. The reason may be due to the decreased production of chlorine/hypochlorite at higher pH conditions, because of the formation of chlorate or perchlorate according to the following equation.

$$6HOCl + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2\,O_2 + 6e^- \quad (5)$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \quad (6)$$

Another reason may be at acidic pH, the chlorine is present in the solution in the form of hypochlorous acid, which is having higher oxidation potential (1.49 V) than that of hypochlorite (0.94 V). The hypochlorite is prevalent in alkaline condition [12].

3.5. Effect of reaction temperature on the degradation of RB-19

Fig. 4 presents the color removal at different operating temperatures. It is clear that increasing temperature decreases the color removal. The reason is that increasing reaction temperature decreases the generation of chlorine/hypochlorite. The control experiments with 1.5 g/L sodium chloride generated 39.6 and 11.8 mg/L chlorine/hypochlorite, respectively, at 25 and 45 °C (Fig. 5). At high temperatures, the mass transport controlled reduction of hypochlorite may also be the reason for a decreased de-colorization according to the following cathodic loss reaction [19].

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \quad (7)$$

3.6. Effect of initial concentration of RB-19

The effect of initial dye concentration on the removal of color was studied in the range from 50 to 400 mg/L while the other conditions were fixed constant (Fig. 6). The net amount of color removal decreased with increase in the concentration. This may be explained by the fact that, under galvanostatic condition, the production rate of chlorine/hypochlorite is constant; however, the active chloro species have a nonselective property, which results in an attack on intermediate compounds produced rather than on the chromophore of the initial dye molecule while increasing the initial dye concentration. The charges

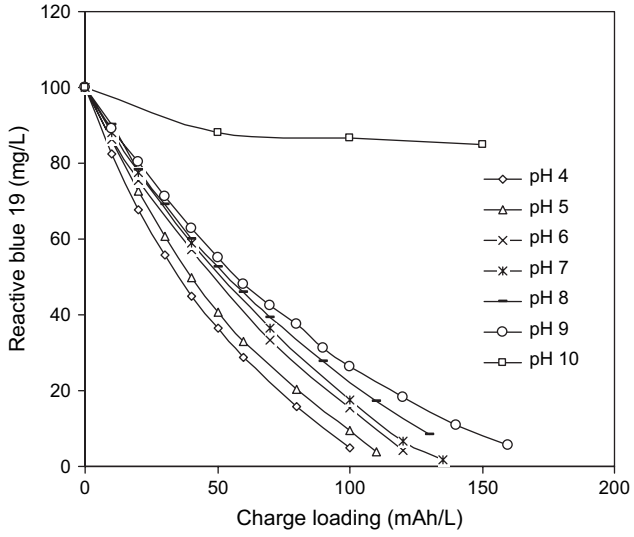

Fig. 3. Effect of initial pH on the electrochemical degradation of Reactive Blue 19 (conditions: current density = 21.66 mA/cm^2, sodium chloride = 1.5 g/L, reaction temperature = 30 °C, Reactive Blue concentration = 100 mg/L, reactor volume = 1 L).

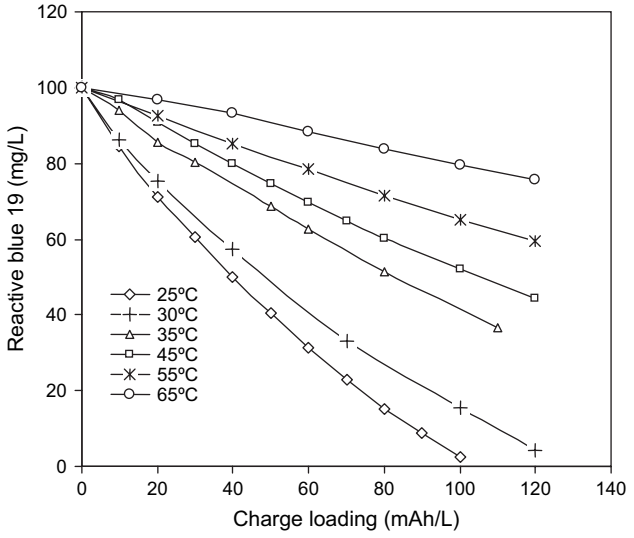

Fig. 4. Effect of reaction temperature on the electrochemical degradation of Reactive Blue 19 (conditions: initial pH = 6.0, current density = 21.66 mA/cm^2, sodium chloride = 1.5 g/L, Reactive Blue concentration = 100 mg/L, reactor volume = 1 L).

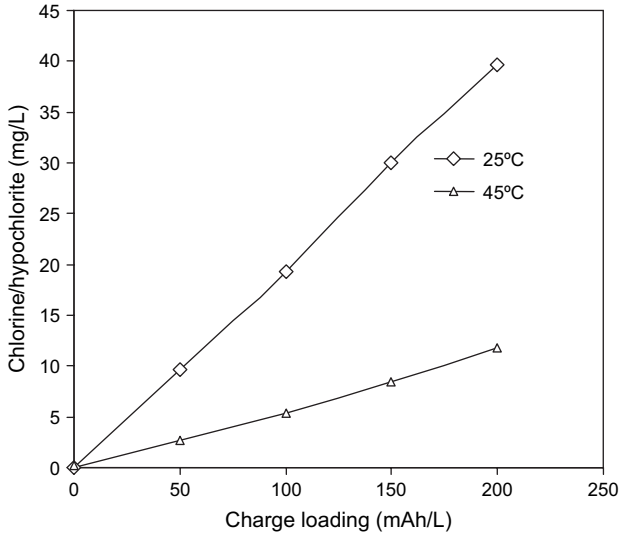

Fig. 5. Effect of reaction temperature on the generation of chlorine/hypochlorite (conditions: initial pH = 6.0, current density = 21.66 mA/cm^2, sodium chloride = 1.5 g/L, reactor volume = 1 L).

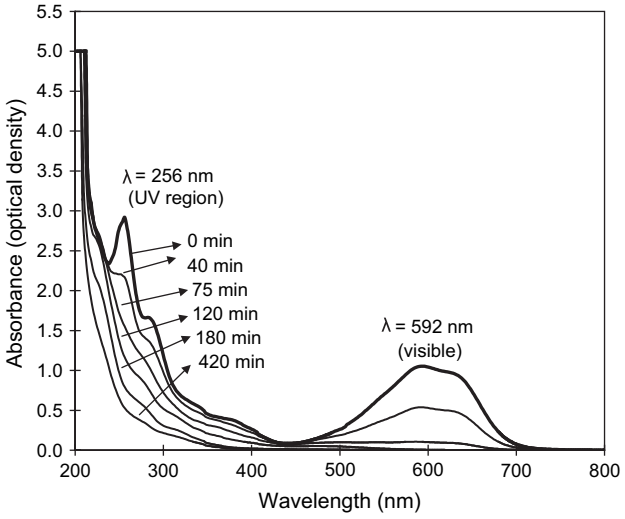

Fig. 7. UV–visible spectra during the electrochemical degradation of Reactive Blue 19 (conditions: initial pH = 6.0, sodium chloride = 1.5 g/L, current density = 21.66 mA/cm^2, operating temperature = 25 °C, Reactive Blue = 400 mg/L).

required for complete de-colorization of initial dye concentration of 50, 100, 200, 300 and 400 mg/L were 40, 100, 250, 500, 800 mAh/L, respectively.

3.7. UV–visible spectral changes during the degradation of RB-19

The UV–visible spectra of the initial and various stages of electrolysis are presented in Fig. 7. Two-absorbance peaks were observed during the scanning of RB-19 at a pH of 6.0. The peak observed in the UV region at 256 nm was due to the anthraquinone structure of the dye. The visible peak at 592 nm was due to blue color of the chromophore. It is clear that both the color removal (100%) and the degradation of anthraquinone structure is achieved at 80 min of electrolysis at 21.66 mA/cm^2 current density for 400 mg/L dye concentration.

3.8. COD and TOC removal during the degradation of RB-19

Fig. 8 presents the COD, TOC and color removal during the degradation of 400 mg/L RB-19. The complete removal of color was achieved within a short period of

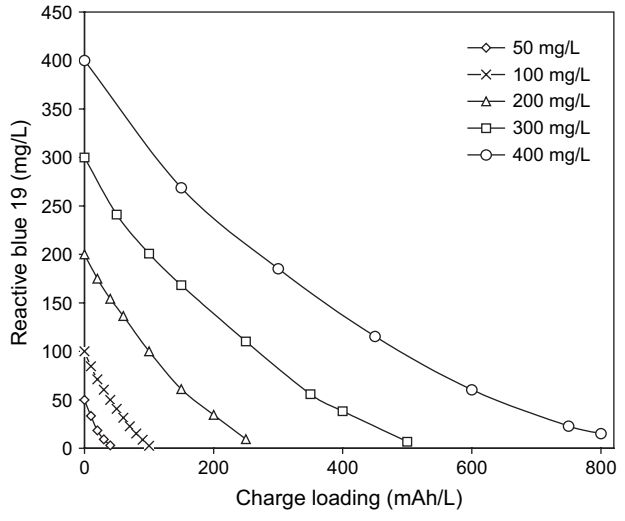

Fig. 6. Effect of Reactive Blue concentration on the electrochemical degradation (conditions: initial pH = 6.0, current density = 21.66 mA/cm^2, sodium chloride = 1.5 g/L, reaction temperature = 25 °C, reactor volume = 1 L).

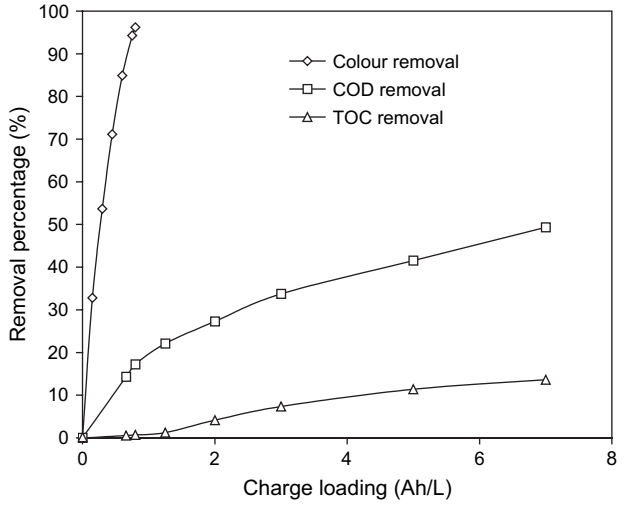

Fig. 8. Color, COD and TOC removal during the electrochemical degradation of Reactive Blue 19 (conditions: initial pH = 6.0, current density = 21.66 mA/cm^2, sodium chloride = 1.5 g/L, Reactive Blue concentration = 400 mg/L, reaction temperature = 25 °C, reactor volume = 1 L).

time (800 mA/L). At the same time, the COD and TOC removals were only 17.2% and 0.7%, respectively. However, 55.8% of COD and 15.6% TOC were removed after passing 9 Ah/L charge. It is well known that the removal of color is due to the cleavage of chromophore bond in the dye molecule. But the oxidation of aromatic ring compounds takes long time and hence the removal of COD and TOC is very less. Beyond 9 Ah/L, the removal of COD and TOC was very less because of the formation of lower molecular weight aliphatic compounds, which were resistant to chlorine/hypochlorite attack.

3.9. Electrochemical degradation pathway of RB-19

The intermediate compounds formed during the degradation of RB-19 were identified by GC/MS. Samples of different time intervals were collected during the electrolysis of 400 mg/L RB-19. The 40 min electrolysis showed the formation of benzene, 2-hydroxy, 4,4-napthaquinoine (C.I. Natural orange 6), 1-aminoanthraquinone (C.I. Diazo fast red AL), benzyl alcohol, benzaldehyde, benzoic acid, phthalic anhydride and phthalide. The compounds identified at 80 min of electrolysis were similar to compounds of 40 min with increased peak area, except 1-aminoanthraquinone, which was completely removed. In addition to the above, phthaldehyde and 1,3-indanone were detected. The samples of 180 min electrolysis showed the complete removal of 2-hydroxy 1,4-napthaquinone with increased peak area of benzaldehyde, benzoic acid and all phthalic derivatives. The final compounds detected at the end of 420 min of electrolysis showed a decrease in the peak

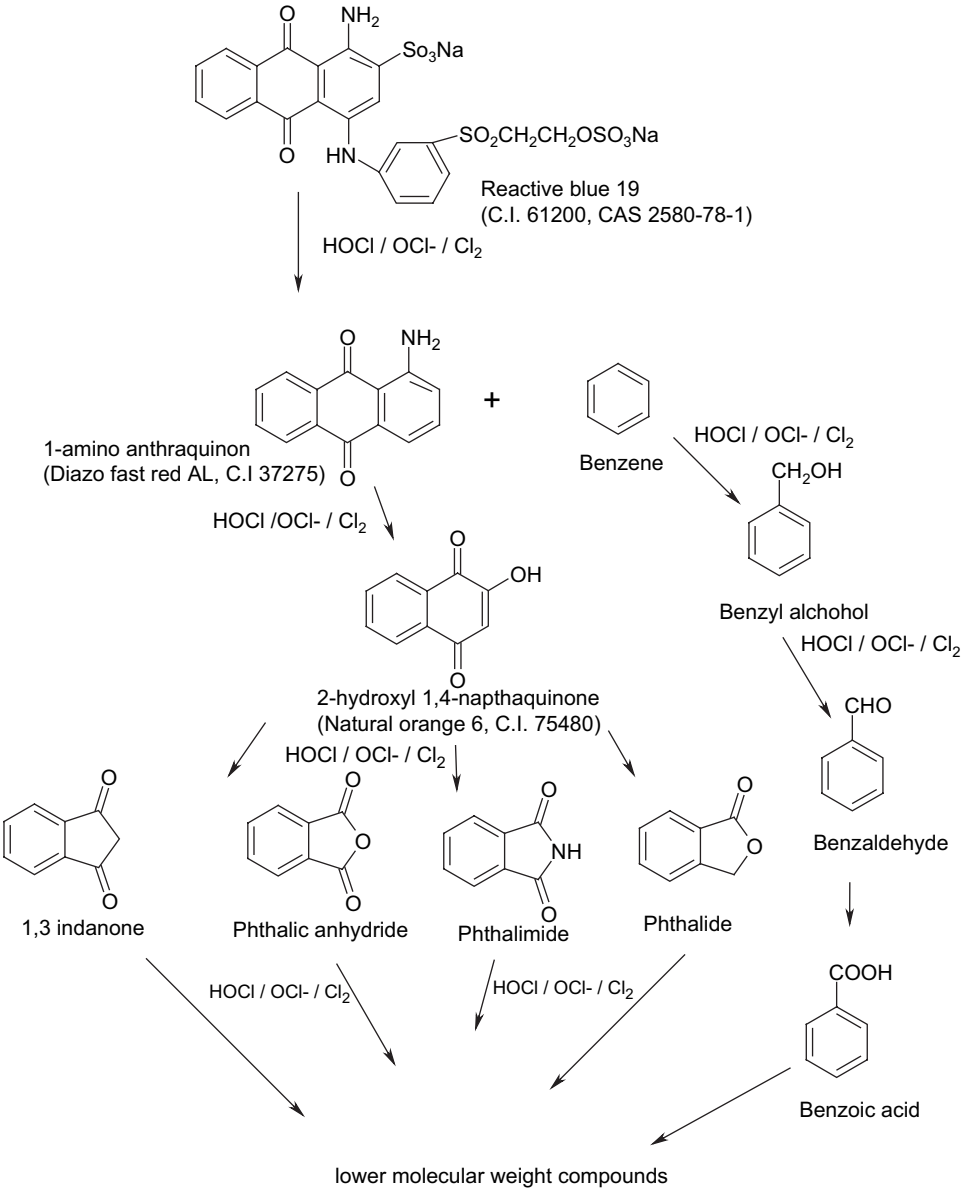

Fig. 9. Proposed pathways of electrochemical degradation of Reactive Blue 19.

area of all phthalic derivatives, benzyl alcohol, benzaldehyde and benzoic acid. It is worth to notice that no chlorinated organic compounds were detected up to 420 min of electrolysis. Based on the observation, it can be concluded that color removal by electrochemical oxidation of RB-19 in the presence of chloride does not produce any chlorinated byproducts. However, further investigation is required to identify lower molecular aliphatic acids in order to know whether any chloro acids are formed. Based on the GC/MS identification, the following pathway (Fig. 9) is proposed for the electrochemical degradation of RB-19.

4. Conclusion

Electrochemical degradation of Reactive Blue 19 was investigated using titanium based DSA in the presence of chloride. The effects of various operating parameters were studied. Operation at acidic pH (4–5), lower temperature (25 °C), higher chloride concentration, increasing current density and decreasing initial dye concentration favored the de-colorization efficiency. In the present investigation no chlorinated intermediated compounds were identified. However, further investigation is necessary in order to identify lower molecular weight aliphatic compounds. For practical applications, the degradation studies with various dye compounds with identification of intermediate compounds are required in order to know whether the other dye compounds produced chlorinated compounds or not.

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