

Electrochemical degradation and toxicity reduction of C.I. Basic Red 29 solution and textile wastewater by using diamond anode

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Abstract

Electrochemical oxidation of Basic Red 29 (BR29) was studied in a bipolar trickle tower (BTT) reactor by using Raschig ring shaped boron-doped diamond (BDD) electrodes, which were originally employed by the present researchers, in a recirculated batch mode. The model solution was prepared with BR29 using distilled water. The effects of initial dye concentration, Na_2SO_4 concentration as supporting electrolyte, current density, flow rate and initial pH on the removal efficiency were investigated, and practically, complete BR29 removal (over 99%) was obtained in all the studies. After optimum experimental conditions were determined, textile wastewater has also studied by monitoring the destruction of color and COD. With the textile wastewater, 97.2% of color and 91% of COD removal were, respectively, achieved at the current density of 1 mA/cm^2 . Microtox toxicity tests were performed in both BR29 solution and textile wastewater under optimum experimental conditions, and relatively good toxicity reductions were obtained with respect to the initial values. According to the results, BDD anode was seen to be a unique material for the degradation of BR29 and COD and also the reduction of toxicity simultaneously.

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Keywords: Electrochemical oxidation; Dye; Textile wastewater; Boron-doped diamond; Toxicity; Bipolar trickle tower reactor

1. Introduction

Textile wastewater is characterized by strong color, large amount of suspended solids, broadly fluctuating pH, high chemical oxygen demand (COD) and biotoxicity and causes coloring of the receiving water environment [1]. Different dyes result in wastewater with different colors and the variations in color induce variation in chemical oxygen demand (COD) of the wastewater [2]. The pH change is primarily caused by different kinds of dye stuffs used in the dyeing process. The pH value of the wastewater can range from 2 to more than 12. Textile wastewater, depending on dye used, can have a toxic effect on the living organisms in the receiving water, affects the ecosystem adversely, and reduces the assimilative capacity of the environment. The temperature of textile wastewaters is unusually high (typically 40°C because of hot rinse waters and the temperatures up to 90°C used in various steps in the dyeing

process) in comparison with most industrial wastewaters [3]. For all these reasons, textile wastewater needs to be treated to satisfy discharging standards.

Textile wastewater is typically treated by conventional methods. During chemical precipitation, although additives increase treatment efficiency, a sludge disposal problem is created [3]. Ozone and hypochlorite oxidation are efficient decolorization methods, but they are not desirable due to the high investment and operational cost, and the secondary pollution arising from the residual chlorine [1]. The wide range of pH and elevated temperatures are also additional problems encountered when textile wastewaters are treated by conventional methods [3]. Azo dyes like BR29 (contain $-\text{N}=\text{N}-$ bonds) are resistant to biodegradation under aerobic conditions whereas anaerobic treatment is applied successfully. However, textile wastewater is not proper to use anaerobic process because the breakdown of azo dye leads to the formation of aromatic amines, which may be more toxic than the dye molecules themselves [4]. Electrochemical methods are also used successfully for the degradation of dyes and treatment of textile wastewaters.

In recent years there has been an increasing interest in the use of electrochemical methods for the destruction of toxic and biorefractory organic pollutants. These methods use the electron

Abbreviations: BDD, boron-doped diamond; BR29, basic red 29; BTT, bipolar trickle tower; COD, chemical oxygen demand; HF CVD, hot filament chemical vapor deposition

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as the main reagent, but also require the presence of supporting electrolytes. In general, the supporting electrolytes exist in the wastewaters to be treated, but not always in sufficient concentrations. These processes can operate at ambient temperature without a need of temperature control [5].

Decolorization can be achieved either by electrooxidation with insoluble anodes [1,5–12] or by electrocoagulation using consumable materials [13–18]. The degradation products in the oxidation of azo dyes are typically carbon dioxide, nitrate and sulfate, with the possible formation of aromatic esters, phenols, aromatic carboxylic acids, cyclic and aliphatic hydrocarbons, etc., as intermediates. Usually, the oxidation of azo group occurs, followed by the oxidation of the decomposition products [5].

Electrode material can influence the mechanism and consequently the products of anodic reaction. Electrode material is the most important parameter in the electrochemical oxidation of organics. BDD has a great potential for electrochemical applications, especially for the treatment of wastewater and drinking water because of the extraordinary chemical inertness offering the opportunity to use such electrodes (anodes as well as cathodes) in very aggressive media. The electrochemical properties of diamond provide a wide range of applications due to the extreme electrochemical window (>3 V) for almost any reaction at the surface, before hydrogen forms at the cathode and oxygen at the anode [19,20].

BDD anodes allow the direct production of hydroxyl radicals (OH^\bullet) from aqueous electrolysis with very high current efficiencies as dominant degradation mechanism in dye oxidation [21,22] according to Eq. (1).



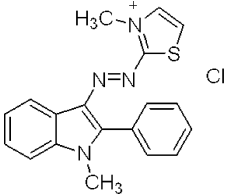
Dissimilarity of this study from the others in the literature is the shape (Raschig ring) of BDD electrodes and BTT reactor used. Furthermore, toxicity studies performed in both model solution and textile wastewater could be a remarkable contribution to the literature.

2. Materials and methods

Aqueous solution of BR29 was chosen as the model wastewater. BR29 has been reported by the manufacturer as the mutagenic to the microorganisms and mammalian somatic cells at the chronic exposure [23]. The chemical structure and other characteristics of BR29 are shown in Table 1.

Experimental setup is illustrated in Fig. 1. BTT reactor had a volume of 125 mL and consisted of two concentric glass pipes with the inner diameters of 4 and 2.5 cm. The distance between the feeding electrodes was about 22.5 cm. BDD Raschig rings were used as working electrode and placed in the inner glass pipe at the bipolar electrode configuration. Raschig rings employed in the reactor had a height of 8 mm, and inner and outer diameters of 6 and 8 mm, respectively. Total surface area of BDD electrodes was 352 cm^2 . BDD electrodes were provided from Magneto Special Anodes B.V. (Schiedam, The Netherlands) shaped as Raschig rings had an outer diameter of 0.8 cm and a height of 0.8 cm. The BDD electrodes consisted of thin (2–7 (m), highly

Table 1
Properties of Basic Red 29 (BR29)

Structural formulae (chemical structure)	
Synonym	Basacryl Red GL
Molecular formula	$\text{C}_{19}\text{H}_{17}\text{ClN}_4\text{S}$
MW (g/mol)	368.88
λ_{max} (nm)	511
Source/purity	Aldrich/19%

conductive (<0.1 cm) BDD films, deposited on niobium substrates via the hot filament chemical vapor deposition technique (HF CVD) from a gaseous feed of methane and a boron doping agent in dihydrogen.

Experiments were carried out in a recirculated batch mode at ambient temperature and wastewater was fed to the reactor by means of a peristaltic pump. Model solution was recirculated through the electrochemical reactor with the flow rates of 24.83, 36.3 and 47.8 mL/min (1.5, 2.2 and 2.9 L/h). Current densities of 0.25, 0.5, 0.75 and 1 mA/cm^2 were studied to observe their effects. pH values of 3, 5.8 (original pH of the BR29 solution) and 11 were studied to investigate the effect of initial pH of the solution. In addition, supporting electrolyte concentration was also studied using the solutions of 0.01, 0.03, 0.04 and 0.05 M Na_2SO_4 . pH of the working solution was monitored throughout the studies.

Wastewater characteristics of textile wastewater which was provided from a local plant are given in Table 2.

2.1. Analysis

BR29 (ALDRICH) was preferred to prepare the model solution and, Na_2SO_4 (MERCK) for the formation of the supporting electrolyte solution. pH of the solutions were adjusted with H_2SO_4 (MERCK) and NaOH (MERCK). All chemicals used were analytical grade.

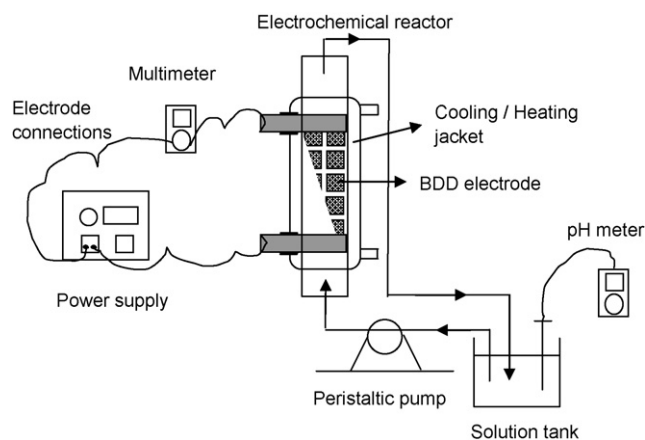


Fig. 1. Experimental setup used in the studies.

Table 2
Physical and chemical characteristics of textile wastewater

Parameter	Value
pH	12.51
Conductivity (mS/cm)	5.74
COD (mg/L)	566.45
TOC (mg/L)	380
SS (mg/L)	155
Cl ⁻¹ (mg/L)	350

During the model solution studies, BR29 concentration was determined spectrophotometrically at $\lambda_{\max} = 508$ nm according to Lambert–Beer law by using a Shimadzu UV-1700 model spectrophotometer.

The rate of the electrochemical degradation of BR29 solution and textile wastewater was monitored by COD tests besides being followed by UV–visible spectrophotometry. COD tests were carried out using a COD reactor (HACH) according to the standard methods.

Toxicities of the model solutions and textile wastewater were established with Microtox Model 500 Analyzer. The Microtox[®] system was supplied by AZUR Environmental (Carlsbad, CA), and consisted of lyophilized bacterial reagent *Vibrio fischeri*, reconstitution reagents and the Model 500 Toxicity Analyzer (AZUR Environmental), which utilizes freeze-dried luminescent bacteria (*V. fischeri*, previously named *Photobacterium phosphoreum*) as test organisms. The short-term luminescent bacteria assay was done according to the supplier's protocol for the duplicate basic test [24]. Each test consisted of one control and four serial dilutions of each sample. Toxic effects were

Table 3
Typical results of the study with BR29 solution (40 mg/L BR29 + 0.03 M Na₂SO₄, $i = 1$ mA/cm², $Q = 36.3$ mL/min, pH = original)

Time (min)	pH	Remaining dye concentration (mg/L)	Dye removal efficiency (%)
0	6.07	40	–
1	7.40	0.71	98.2
2	9.57	0.53	98.7
3	9.95	0.47	98.8
4	10.09	–	–
5	10.25	–	–

monitored as a percent decrease of the light emission of *V. fischeri* after 5 min of incubation at 15 °C with 95% confidence intervals by using the Microtox calculation software (version 1.18).

In the experimental studies, Statron 3234.9 model power supply, OGSM 3900 digital multimeter, Multifix MC 1000 PEC model peristaltic pump, Polyscience 9605 model water bath, Orion 420 A model pH meter were employed as auxiliary equipments.

3. Results and discussion

In this section, electrochemical oxidation of BR29 was searched in preliminary experiments. After the best experimental conditions had been determined, electrochemical oxidation of textile wastewater was studied. COD kinetics and toxicity results were also given in separate subtitles.

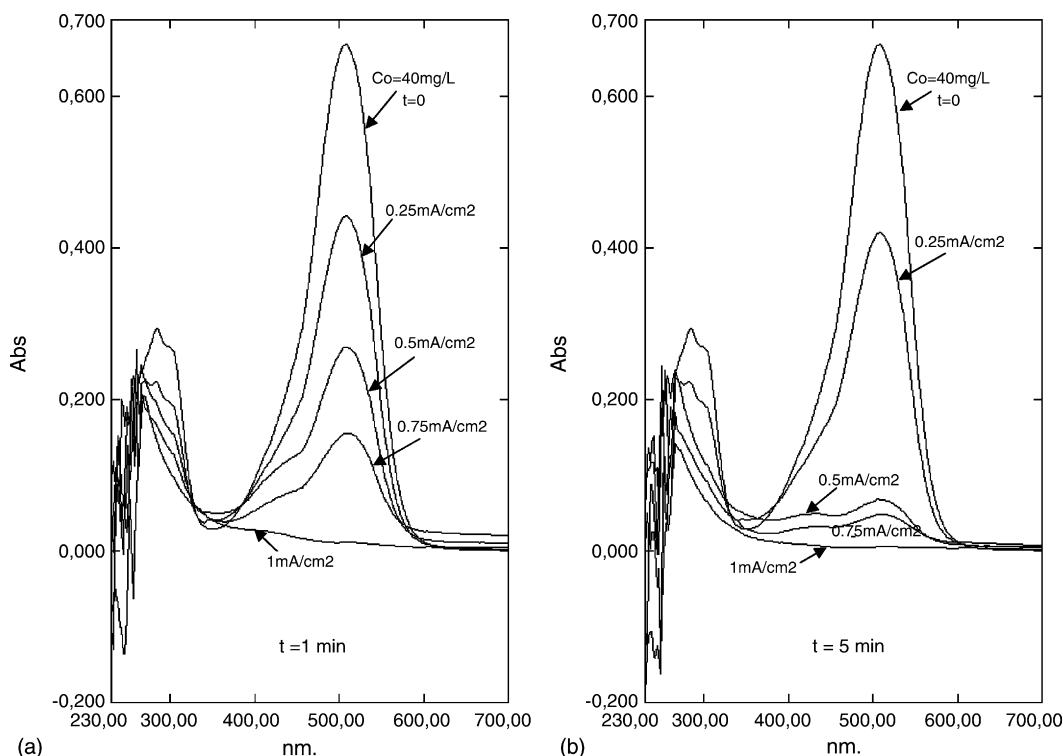


Fig. 2. Remaining amount of dye for different current densities (40 mg/L BR29 + 0.03 M Na₂SO₄, $Q = 36.3$ mL/min, pH = original) (a) 1 min of electrolysis and (b) 5 min of electrolysis.

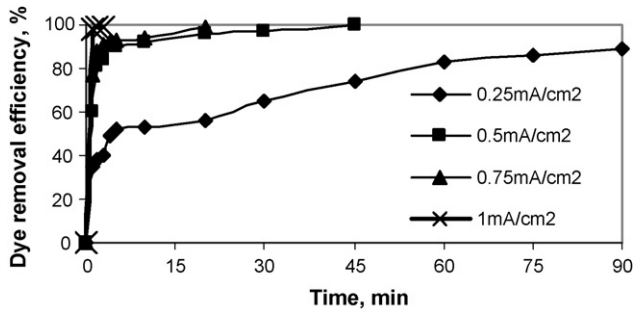


Fig. 3. Variation of removal efficiency vs. time for different current densities (40 mg/L BR29 + 0.03 M Na₂SO₄, $Q = 36.3$ mL/min, pH = original).

3.1. Electrochemical oxidation of BR29

The effects of current density, initial pH, supporting electrolyte concentration, initial BR29 concentration and solution flow rate on the removal efficiency were examined to obtain best values. Current density of 1 mA/cm², flow rate of 36.3 mL/min, Na₂SO₄ concentration of 0.03 M and original pH of the solution were found as the best values. Since BR29 solution has a lower electrical conductivity, sodium sulfate was used as supporting electrolyte in the studies.

It is clear that the method employed is very effective for dye removal as can be seen from Table 3. After only 1 min of electrolysis, final dye concentration of 0.71 mg/L was reached

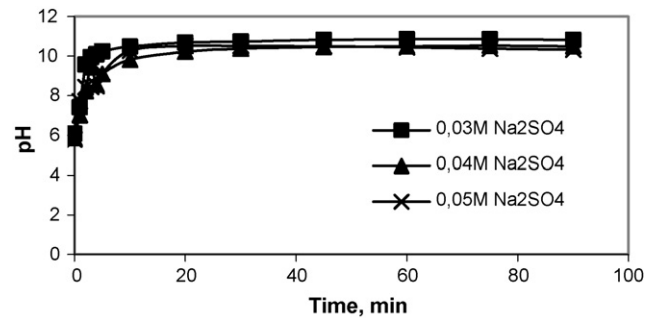


Fig. 5. Variation of pH with time in BR29 solution for different supporting electrolyte concentrations (40 mg/L BR29, $i = 1$ mA/cm², $Q = 36.3$ mL/min, pH = original).

for an initial dye concentration of 40 mg/L at a current density of 1 mA/cm².

Current density was an important parameter for dye removal as presented in Fig. 2. In this figure, UV–vis spectra of BR29 can be seen for different current densities both after 1 and 5 min of electrolysis. Increase in the current density resulted in a decrease in the BR29 concentration. About 1 mA/cm² was obtained as the most appropriate current density value. As it can also be seen from Fig. 2 that almost same UV–vis spectrums were obtained at the current density of 0.25 mA/cm² after 1 and 5 min of electrolysis. Variation of dye removal efficiency versus time for different current densities is depicted in Fig. 3.

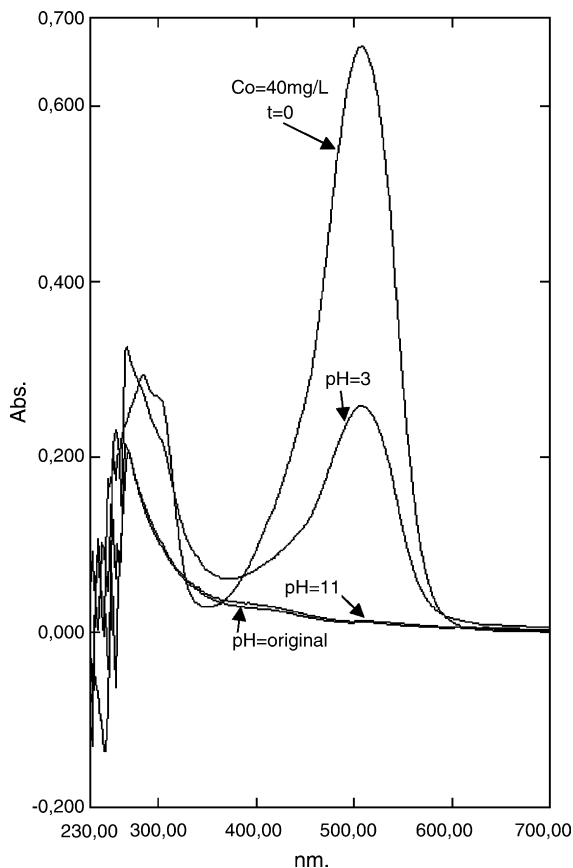


Fig. 4. Remaining amount of dye for different initial pH's (40 mg/L BR29 + 0.03 M Na₂SO₄, $i = 1$ mA/cm², $t = 1$ min, $Q = 36.3$ mL/min).

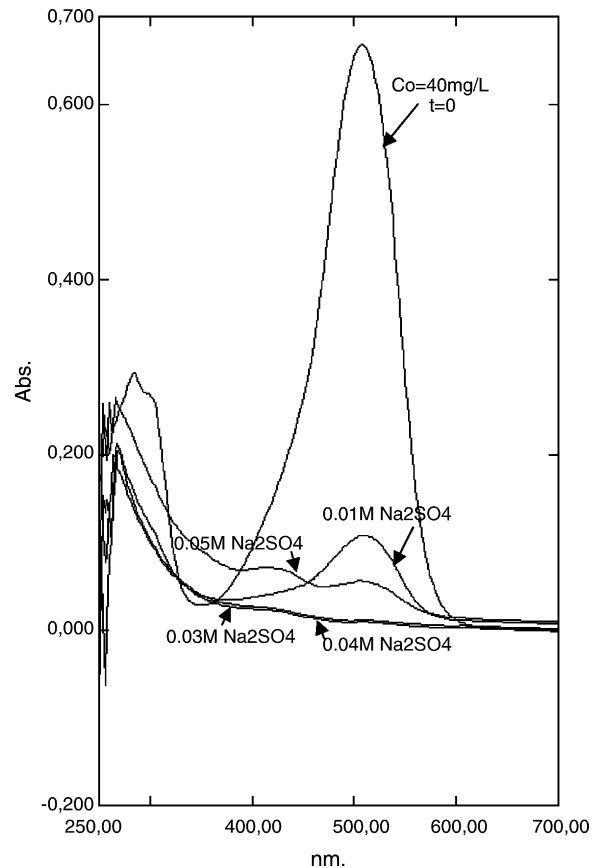


Fig. 6. Remaining amount of dye for different supporting electrolyte concentrations (40 mg/L BR29, $i = 1$ mA/cm², $t = 1$ min, $Q = 36.3$ mL/min, pH = original).

Over 98% dye removal was achieved for all current densities, except 0.25 mA/cm², relating with the duration of electrolysis. Dye removals of over 98% were obtained after 1, 20 and 45 min of electrolysis with the current densities of 1, 0.75 and 0.5 mA/cm², respectively, whereas it was 88.9% at the current density of 0.25 mA/cm² after 90 min of electrolysis. Higher the current density, shorter the time to reach desired effluent dye concentration.

Studies were performed in three different initial pH values to investigate their effects as depicted in Fig. 4. It was found that acidic initial pH caused the reduction in the efficiency of the study, and the performances in the initial pH of 11 and original pH studies were similar. Consequently, experiments were carried out at the original pH of ~5.8 without any pH adjustment. Thus, additional chemical usage was not required and this makes the process more cost effective. When the studies were performed in the different pH values, pH of the solutions generally increased as shown in Fig. 5. This is probably due to the degradation of dye and the electrode reactions. As the studies were performed under uncontrolled pH conditions, initial pH of ~6 increased up to ~10 as illustrated in Fig. 5.

The results obtained from the studies on the investigation supporting electrolyte effect can be seen in Fig. 6. Dye removal efficiencies were higher in the 0.03 and 0.04 M sodium sulfate concentrations than that in the 0.01 and 0.05 M. There-

fore, 0.03 M was preferred because lower amount of additional chemical usage was necessary. As well known, supporting electrolyte concentration is inversely proportional to the energy consumption. Therefore, an increase in its concentration results in increase in the electrical conductivity and decrease in energy consumed. Electrical conductivities of dye solutions containing 0.01, 0.03, 0.04 and 0.05 M sodium sulfate were 2.82, 5.54, 7.38 and 8.92 mS/cm and energy consumptions for these solutions after 1 min of electrolysis were 0.466, 0.342, 0.311 and 0.303 kWh/g, respectively.

BR29 concentrations of 20, 40 and 60 mg/L were studied and the results were shown in Fig. 7. According to the UV–vis spectra results, not only the dye removal but also the organics degradations were seen in UV region for different initial dye concentrations. Over 95% of dye removal efficiencies were achieved in 1 min of electrolysis for all dye concentrations. Variation of initial dye concentration did not affect the performance of process. Actually, BR29 concentration of 60 mg/L can be thought as quite high when the characteristics of a textile wastewater are considered. However, it can be concluded that electrochemical degradation by using BDD electrode in a BTT reactor is very efficient method for dye removal even if in relatively higher dye concentrations.

Remaining amount of dye and degradation of organics for different flow rates were given in Fig. 8. In general, insignificant differences have been observed between the results of different

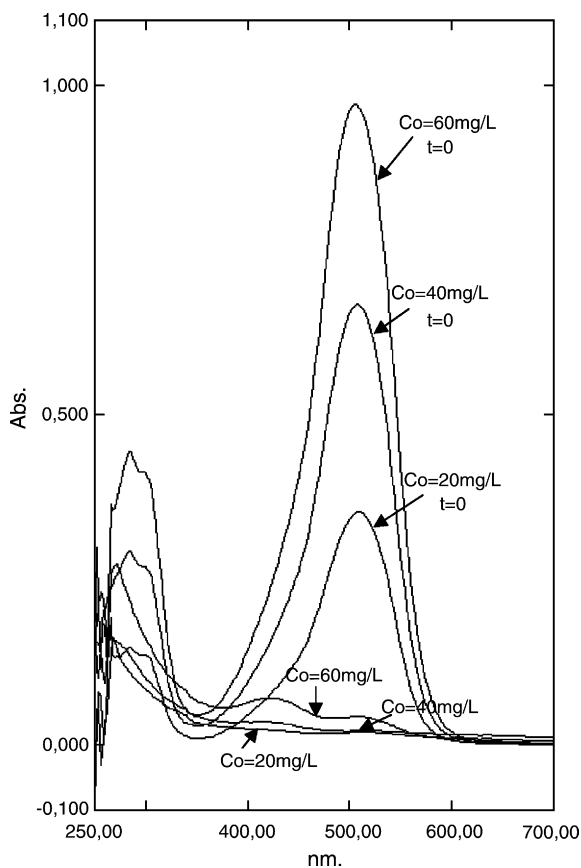


Fig. 7. Remaining amount of dye for different initial dye concentrations (40 mg/L BR29 + 0.03 M Na₂SO₄, $i = 1$ mA/cm², $t = 1$ min, $Q = 36.3$ mL/min, pH = original).

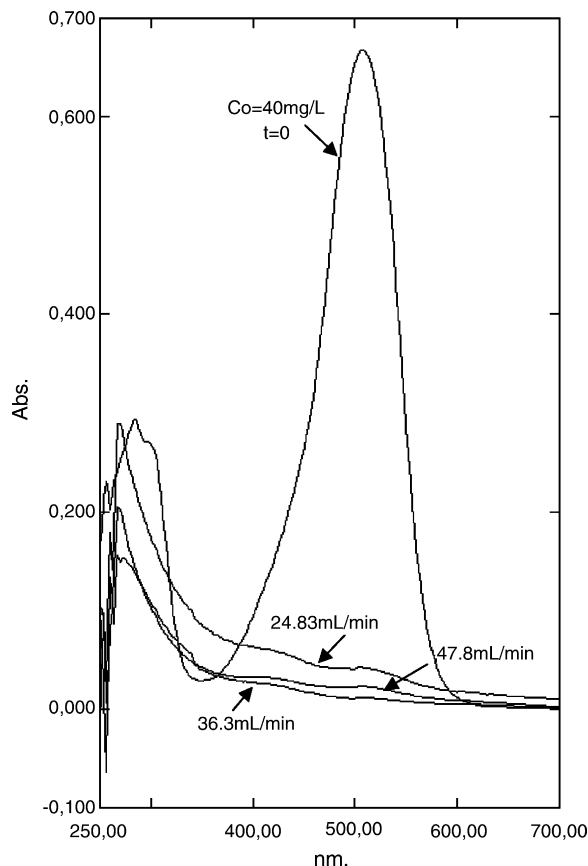


Fig. 8. Remaining amount of dye for different flow rates (40 mg/L BR29 + 0.03 M Na₂SO₄, $i = 1$ mA/cm², $t = 1$ min, pH = original).

flow rates. However, 36.3 mL/min was chosen as optimum flow rate since the results of organics spectrums in the UV region indicated this flow rate. Thus, the other studies were performed at this flow rate.

Time course changes of UV–vis spectra of BR29 for different current densities were given in Fig. 9. When the current

density of 0.25 mA/cm^2 was applied, initial BR29 concentration of 40 mg/L decreased to lower concentrations. Faster BR29 degradation rates were observed at the current density of 0.5 mA/cm^2 than that seen at 0.25 mA/cm^2 . However, dye degradations were also realized gradually at the current density of 0.5 mA/cm^2 . On the other hand, sharp decrease in the

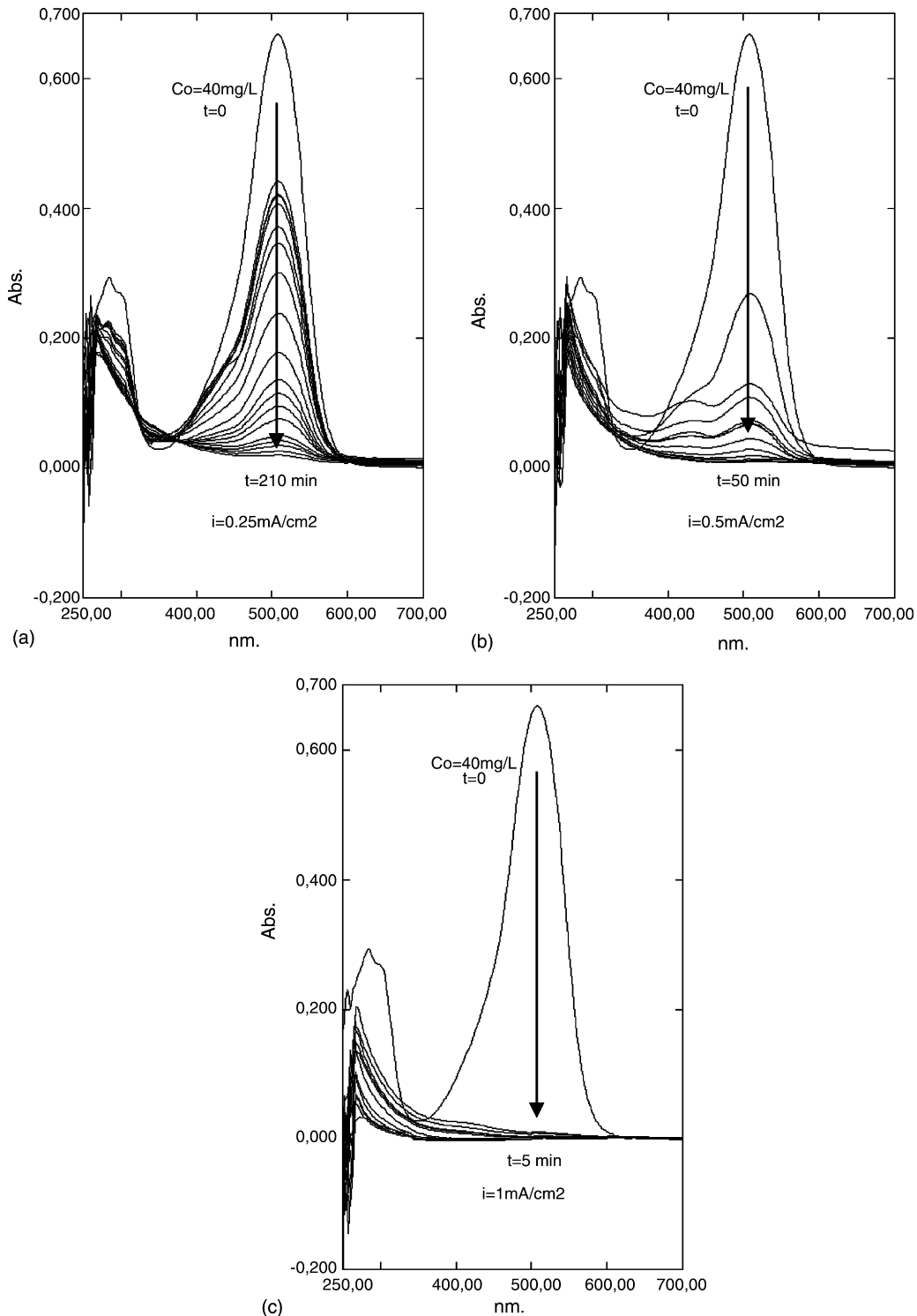


Fig. 9. Time course changes of spectrums for different current densities (40 mg/L BR29 + 0.03 M Na_2SO_4 , $Q = 36.3 \text{ mL/min}$, $\text{pH} = \text{original}$) (a) 0.25 mA/cm^2 (b) 0.5 mA/cm^2 (c) 1 mA/cm^2 .

BR29 concentration was experienced at 1 mA/cm^2 . In addition to the BR29 spectrums in the VIS region, organics degradations were also investigated in the UV region between 250–300 nm. It can be said that high removal efficiencies can be achieved for BR29 at all current densities in the VIS region without a time concern. However, while the organics degradation was investigated in the UV region, only the current density of 1 mA/cm^2 was found to be efficient whereas the other current densities were insufficient. Decomposition of organics at 1 mA/cm^2 in the region of 250–300 nm was shown in Fig. 9. Although BR29 removal rate is higher at 0.5 mA/cm^2 than that of 0.25 mA/cm^2 , organics removal rates were almost equal (Fig. 9).

3.2. Electrochemical oxidation of textile wastewater

Under the optimum experimental conditions, a textile wastewater was treated by electrochemical oxidation using BDD Raschig ring anodes and BTT reactor. Wastewater was obtained from a local plant and had a COD of 566.45 mg/L . Electrical conductivity of the wastewater was 5.74 mS/cm and pH 12.51.

In a textile wastewater, total organics removal is more important than dye removal, because organics removal is more difficult. In this study variation of the concentrations of organics and dye was also monitored by UV–vis spectroscopy (Fig. 10). According to the Fig. 10, concentrations of total organic pollu-

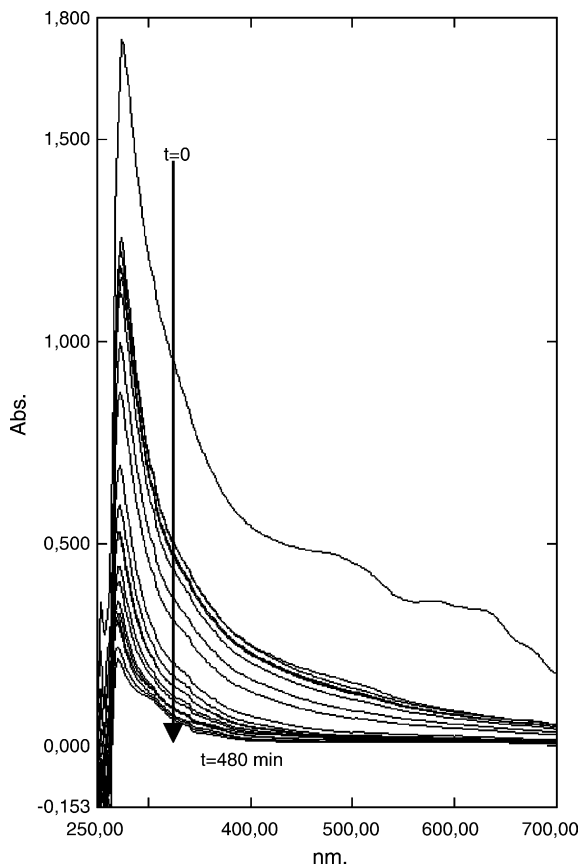


Fig. 10. UV–visible spectra of textile wastewater study ($i = 1 \text{ mA/cm}^2$, $Q = 36.3 \text{ mL/min}$, pH = original).

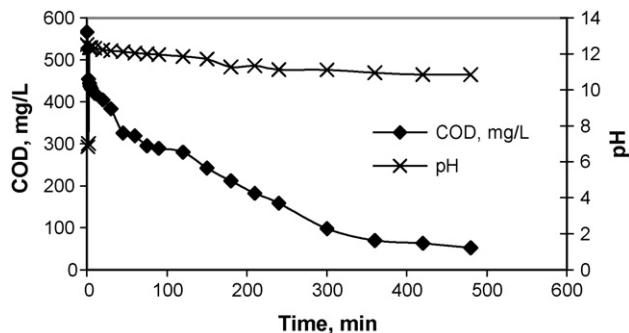


Fig. 11. Variation of COD and pH with time in textile wastewater study ($i = 1 \text{ mA/cm}^2$, $Q = 36.3 \text{ mL/min}$, pH = original).

tants decrease regularly as depicted between 250 and 300 nm. As it can be seen from Fig. 11, initial COD of 566.45 mg/L decreased gradually to final COD of 52.38 mg/L in a period of 8 h. COD removal of 91.0% was achieved with an energy consumption of 1.4 kWh/g COD removed. Change of wastewater pH between 10 and 12 with time was also given in the same figure

3.3. COD kinetics

In direct electrochemical oxidation process, the COD removal rate is proportional to the concentration of the organic pollutant. Therefore, the kinetics for COD removal is written as:

$$-\frac{d}{dt}[\text{COD}] = k[\text{COD}] \quad (2)$$

Rearranging and integrating the Eq. (2) gives:

$$\ln \frac{[\text{COD}_t]}{[\text{COD}_0]} = -k.t \quad \text{or} \quad \ln \frac{C_t}{C_0} = -k.t \quad (3)$$

where, C_0 is the initial COD of the solution in mg L^{-1} , and C_t is the COD in mg L^{-1} at time t .

Plotting C_t/C_0 on the y-axis versus t on the x-axis on semilog paper will result in straight line with the slope of k . According to the Fig. 12, the rate constant (k) and r^2 values for COD removal were $5.5 \times 10^{-3} \text{ min}^{-1}$ and 0.9326, respectively.

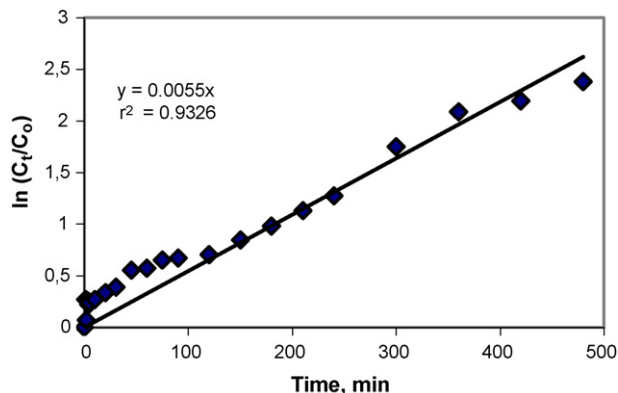


Fig. 12. Variation of $\ln(C_t/C_0)$ with time for the electrochemical degradation of textile wastewater.

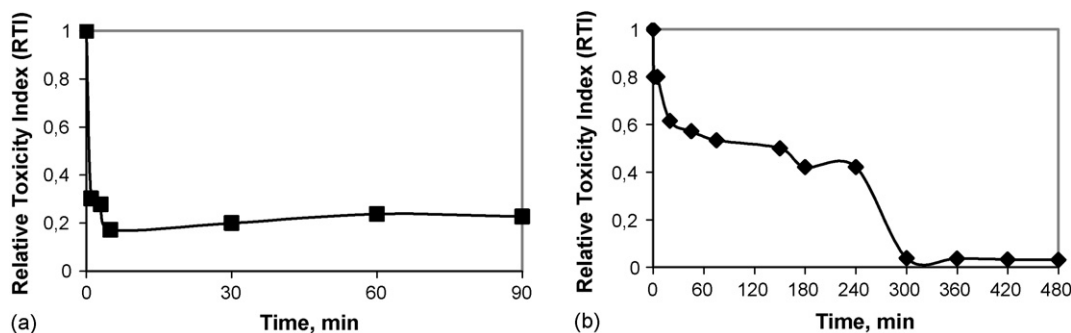


Fig. 13. Variation of toxicity with time in: (a) 40 mg/L BR29 (+0.03 M Na₂SO₄) and (b) the textile wastewater (*i* = 1 mA/cm², *Q* = 36.3 mL/min).

3.4. Toxicity studies

Microtox[®] bioassay tests were performed to measure the toxicity of model solution and textile wastewater treated in the electrochemical reactor in a given time intervals including the time zero. Toxicity results were given as relative toxicity index (RTI) [25]:

$$RTI = \frac{EC_{50}\% (t = 0)}{EC_{50}\% (t = t)} \quad (4)$$

where, $EC_{50}\% (t = 0)$ and $EC_{50}\% (t = t)$ are the 5 min Microtox toxicity of the sample at times 0 and *t*.

The toxicity results obtained from studies were given in Fig. 13 as a function of time. Initial toxicity values showed that both BR29 solution and textile wastewater were highly toxic themselves. Since BR29 has a mutagenic toxicity, toxicity studies for both model solution and textile wastewater become important. According to the results given above, this method was found to be successful for dye and COD removal. If it is also successful for toxicity reduction, it can be evaluated as a useful method from the environmental point of view. It can be seen from Fig. 13(a) and (b) that toxicity reduction was also achieved by using electrochemical oxidation. In BR29, a rapid decrease in toxicity was recorded in the first 5 min of electrolysis, and then the stable value of about 0.2 was observed (Fig. 13a). On the other hand, toxicity was decreased a much lower values for textile wastewater as indicated in Fig. 13b.

4. Conclusion

BDD Raschig ring electrode, which has high rate hydroxyl radical (OH[•]) production potential, was used to degrade BR29 dye and remove COD in a BTT reactor from model solution. Complete BR29 removal was succeeded in model solutions.

Electrochemical oxidation by using same electrode arrangement was also applied successfully to treat textile wastewater under the best experimental conditions, and the method was found to be quite efficient for COD and color removal from textile wastewater.

Toxicity tests were also performed in both BR29 solutions and textile wastewater under the best experimental conditions. According to the toxicity test results, electrochemical treatment by using BDD Raschig ring anode in BTT reactor is an effective way of reducing toxicity besides color and COD removal.

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