Decolorization of reactive textile dyes using water falling film dielectric barrier discharge

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ABSTRACT

Decolorization of reactive textile dyes Reactive Black 5, Reactive Blue 52, Reactive Yellow 125 and Reactive Green 15 was studied using advanced oxidation processes (AOPs) in a non-thermal plasma reactor, based on coaxial water falling film dielectric barrier discharge (DBD). Used initial dye concentrations in the solution were 40.0 and 80.0 mg/L. The effects of different initial pH of dye solutions, and addition of homogeneous catalysts (H_2O_2, Fe^{2+} and Cu^{2+}) on the decolorization during subsequent recirculation of dye solution through the DBD reactor, i.e. applied energy density (45–315 kJ/L) were studied. Influence of residence time was investigated over a period of 24 h. Change of pH values and effect of pH adjustments of dye solution after each recirculation on the decolorization was also tested. It was found that the initial pH of dye solutions and pH adjustments of dye solution after each recirculation did not influence the decolorization. The most effective decolorization of 97% was obtained with addition of 10 mM H_2O_2 in a system of 80.0 mg/L Reactive Black 5 with applied energy density of 45 kJ/L, after residence time of 24 h from plasma treatment. Toxicity was evaluated using the brine shrimp *Artemia salina* as a test organism.

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1. Introduction

Two major sources of industrial dyes released into the environment are effluents from synthesis plants and from dye-using industries, such as textile factories. For example, during textile processing, inefficiencies in the dyeing process results in 10–15% of all dyes being released directly into the wastewater. With a consumption of over 7×10^5 tons of dyes per year, this imposes a lot of pressure on the textile coloration industry, which is often considered as one of the major water polluters taking in account both volume discharged and effluent composition [1–5].

New ecolabels for textile products and tighter restrictions on wastewater discharges are forcing textile processors to reuse process water. Various traditional methods such as adsorption, coagulation, filtration, sedimentation and biological treatments have been used to treat textile dye wastewater, but none of these treatments was satisfactory because of the effluent's high degree of polarity and complex molecular structure. Furthermore, they all end up in producing a secondary waste product which needs to be dealt with further. A variety of new technologies (e.g. fixed film bioreactors, anaerobic digestion, ozone/UV-oxidation, photocatalysis (UV/TiO$_2$), aerobic treatment with fungi) have been studied for textile wastewater treatments to meet this challenge. Though several of these new technologies are promising in terms of cost and performance, they still require further research and/or need broader validation [5–7,3,8–10].

Promising results have been achieved using advanced oxidation processes (AOPs) which are based on *in situ* generation of strong oxygen-based oxidizers: hydroxyl radicals, ozone, atomic oxygen, hydrogen peroxide, perhydroxyl radicals, which promote destruction of the target pollutant until mineralization. Especially, the formation of hydroxyl radicals and ozone is desired since they are among the strongest oxidizers, and their reactions with organic compounds are characterized by very high reaction rates. The remarkable advantage of AOPs over all chemical and biological processes is that they neither transfer pollutants from one phase to the other nor produce massive amounts of hazardous sludge. Advanced oxidation processes include ozonation, photocatalytic degradation, Fenton's reagents (H_2O_2/Fe^{2+}), photo-Fenton, high energy radiation and wet air oxidation (WAO) [6,9,11].

Ozone, which is commonly used in AOP, is mainly produced from air or oxygen by electrical discharges. Beside ozone, electrical discharges in humid air also produce a variety of chemically active species, such as O•, •OH, N•, HO$_2$•, N$_2$*, N*, OH$^-$, O$_2^-$, O$^-$, O$_2^+$, N$_2^+$,
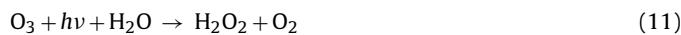
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Table 1
Chemical structure and characteristics of dyes.

C.I. (Color Index) name	Commercial name	CAS registry number	Chemical structure	Chemical nature	λ_{max} (nm)
C.I. Reactive Black 5	Drimaren Black K-3B	CAS No.: 17095-24-8		Diazo	590
C.I. Reactive Blue 52	Drimaren blue X-3LR	CAS No.: 12225-63-7		Azo	615
C.I. Reactive Yellow 125	Drimarene Gold Yellow K-2R	CAS No.: 68155-62-4		Azo	390
C.I. Reactive Green 15	Drimarene Green X 2BL	CAS No.: 61969-07-1	–	Azo (formazan) copper complex	620

N^+, and O^+. These species are short lived and decay before ozone enriched air/oxygen reaches the treated water solution. However, if the reactor is designed in such way that the electrical discharges are formed in close proximity to the water surface, i.e. just above the water, some of these species may enter the water thereby destroying the pollutants [12]. Possibility to obtain very active species like $^{\bullet}OH$ in a water solution was the basic idea which forced many researchers to design different discharges in water and above the water surface. Various discharges in water are described in a review article by Bruggeman and Leys [13]. Since we used a discharge formed above the water surface, here we only mention this type of electrical discharge, which has been used for degradation of various organic compounds: phenols, benzenes, pharmaceutical compound and less extent organic dyes [14–24]. Our discharge is based on the dielectric barrier discharge (DBD), which is a typical non-equilibrium high pressure AC gas discharge. The DBD is obtained between two electrodes, at least one of which is covered with a dielectric, with AC high voltage applied to the electrodes. The dielectric is the key factor for the proper functioning of the discharge. It limits the charge transported in the discharge, i.e. limits the current flow to the system, and distributes the discharge almost uniformly over the entire electrode area. DBD is an excellent source of energetic electrons (1–10 eV energy) with high electron density. In humid air DBD can produce UV light and many reactive species such as free electrons, negative ions, positive ions, uncharged short-lived radicals, H_2O_2 and O_3 [25–27]. It was shown that the principle reactive species involved in degradation of organic compounds are $^{\bullet}OH$ radical and H_2O_2 [28]. The $^{\bullet}OH$ radical, especially, is known to play an important role in degrading organic compounds since its oxidation potential is higher than that of atomic oxygen and ozone. The detailed formation mechanisms for these species during the discharge are as follows [12,29]:

$$e^-{}_* + O_2 \rightarrow O^{\bullet} + O^{\bullet} + e^- \tag{1}$$

$$e^-{}_* + H_2O \rightarrow {}^{\bullet}OH + H^{\bullet} + e^- \tag{2}$$

$$e^-{}_* + O_2 \rightarrow O_2{}^+ + 2e^- \tag{3}$$

$$e^-{}_* + O_2 + M \rightarrow O_2{}^- + M \tag{4}$$

$$O^{\bullet} + O_2 + M \rightarrow O_3 + M \tag{5}$$

$$2H_2O + e^-{}_* \rightarrow H_2O_2 + H_2 + e^- \tag{6}$$

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2{}^{\bullet} \tag{7}$$

$$O^{\bullet} + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \tag{8}$$

$$O_3 + H_2O_2 \rightarrow {}^{\bullet}OH + O_2 + HO_2{}^{\bullet} \tag{9}$$

$$O_3 + HO_2{}^{\bullet} \rightarrow {}^{\bullet}OH + O_2 + O_2{}^- \tag{10}$$

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2 \tag{11}$$

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH \tag{12}$$

In the present paper, the decolorization of four commercial reactive azo dyes C.I. Reactive Black 5, C.I. Reactive Blue 52, C.I. Reactive Yellow 125 and C.I. Reactive Green 15 was studied using advanced oxidation processes (AOPs) in a non-thermal plasma reactor based on coaxial dielectric barrier discharge (DBD). Coaxial DBD plasma reactor used in this research, is very similar to the recently developed reactor for treatment of various water solutions [16] which was successfully tested for removing of phenols from wastewater [17,18]. Azo dyes were chosen due to the fact that they are the major colorants in the textile industry; they provide colors with outstanding colorfastness and wide spectrum. At the same time, azo dyes are the most toxic, mutagenic and carcinogenic commercial dyes [11].

Initial dye concentration in the treated water solution was 40.0 and 80.0 mg/L. The effect of various conditions such as applied energy density (45–315 kJ/L) and pH of initial dye solutions (pH
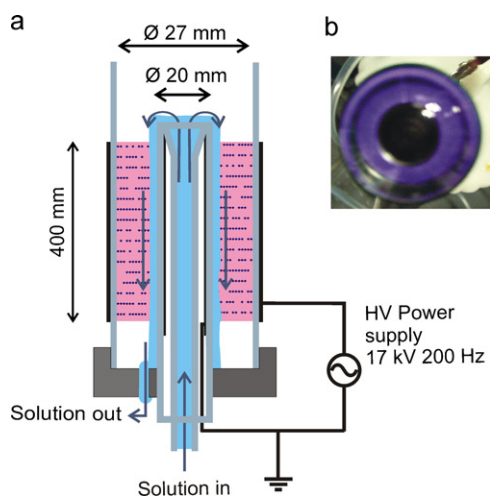
Fig. 1. (a) Schematic of coaxial DBD. (b) Photo of the discharge viewed from the top. Dimensions: inner glass barrier (diameter 20.0 mm, length 500 mm, thickness 1.5 mm); outer glass barrier (diameter 30.0 mm, thickness 1.5 mm, length 600 mm); outer metal foil electrode (diameter 30 mm, length 400 mm).

9.00, 7.00 and 5.00) were studied. Detail analysis of H_2O_2 and Fe^{2+} influence on phenol degradation in a water discharge was presented by Sharma et al. [30] and Grymonpré et al. [31]. Influence of H_2O_2 and Fe^{2+} on decolorization efficiency is investigated this paper. For this purpose different concentrations of H_2O_2, Fe^{2+} and Cu^{2+} ions as homogeneous catalysts were introduced in the dye solutions. Change of pH values and effect of pH adjustments of dye solution after each recirculation on the decolorization efficiency was tested. The influence of residence time on the absorbance of solutions after introducing the energy density of 45 and 90 kJ/L in the solution was tested for all four dyes. Toxicity was evaluated using the brine shrimp *Artemia salina* as test organism.

2. Experimental

2.1. Materials

Four commercial reactive azo dyes Reactive Black 5, Reactive Blue 52, Reactive Yellow 125 and Reactive Green 15 (Clariant, Switzerland) are used without any further purification. The molecular structures of used dyes are shown in Table 1.

For the pH adjustment, sulphuric acid and sodium hydroxide, purchased from Carlo Erba, Italy were used. Hydrogen peroxide, H_2O_2, Carlo Erba, Italy, 30% (m/m), ferrous sulphate, $FeSO_4 \cdot 7H_2O$ and copper sulphate, $CuSO_4 \cdot 5H_2O$, Merck, Germany, were used as homogeneous catalysts. All chemicals were p.a. grade. All solutions were prepared using deionized water with conductivity between 1.0 and 1.5 μS/cm. *A. salina* eggs were purchased from Sera®, Germany. Sera Artemia-Mix contains frozen dried eggs, salt and nutrition.

2.2. Instrument

The coaxial DBD was designed as an atmospheric non-thermal plasma reactor for treatment of various water solutions [16]. In this reactor water forms a falling film which is in direct contact with plasma, see Fig. 1a. The coaxial DBD is a source of a wide range of reactive species, created both in the gas and in the liquid phase. This discharge is able to produce O_3, H_2O_2, •OH and other active species. Ozone is considered as one of the most powerful molecule species because of its long lifetime and high oxidation potential. In such design of the discharge, radicals are transferred from plasma into the liquid phase, where the reactions with the pollutants take place.

Also, this discharge produces UV radiation, ions (e.g. OH^-, O_2^-, O^-, O_2^+, N_2^+, N^+, O^+) and electrons. A schematic diagram of experimental setup is shown in Fig. 1a. A cylindrical reactor is made of pyrex glass with the inner diameter of the tube 27.0 mm and length of 600 mm. An outer electrode is made of aluminum foil glued on the outer side of the glass tube on a length of 400 mm. The inner electrode is a glass cylinder with a diameter of 20.0 mm which is silverised on the inner side, see Fig. 1a. Barrier discharge is generated between the inner glass and the outer glass tubes. When the discharge source works as a falling film reactor, water flows up through a vertical hollow glass tube and flows down making a thin dielectric film over the electrode, see Fig. 1a. Power supply that we used is a high voltage transformer which is fed by a frequency inverter which allows variation of the sinusoidal voltage frequency up to 500 Hz. The frequency for the plasma reactor was set at the optimal value found, 200 Hz. The discharge is generated within the 3.5 mm gap between the glass and the water layer by applying voltage of 17 kV. To increase the total flow of treated solutions three discharges are connected in parallel. Plug-in power for this system of the discharges was 150 W.

Solutions of dyes were pumped to the top of the reactor through the inner electrodes using a peristaltic pump. From the top of the inner electrode, solution flows down in a thin layer over the electrode. After the treatment, solution is collected in a reservoir at the bottom of the reactor. Total flow rate through three parallel DBD reactors was 210 mL/min. Collected solution is introduced through the reactor for the next treatment in such way that the presently treated amount of solution is never mixed with the amount of solution treated in the previous pass. Energy density of ~45 kJ/L per one pass through the reactor, was introduced in the solution. The introduced energy density was increased using multiple passes through the reactor. Each solution was recirculated seven times. In each series of experiments, the treatment was started with 2 L of dye solutions (certain concentration and specified pH value). After each recirculation, 100 mL of the solution was sampled for analysis after the amount of 500 mL has passed through the DBD reactor. Each following recirculation was done immediately after the completion of the previous one.

2.3. Methods of analysis

The capability of the plasma reactor for decolorization of four azo dyes C.I. Reactive Black 5, C.I. Reactive Blue 52, C.I. Reactive Yellow 125 and C.I. Reactive Green 15 was tested in triplicate. Each color solution was prepared by dissolving of commercial dye without preceding purification in deionized water. In all cases water samples containing 40.0 mg/L or 80.0 mg/L of dye were passed from one to seven times through the discharge. Decolorization efficiency is defined as percent decrease of absorbance according to the following Eq. (13):

$$\%\text{decolorization} = \frac{A_0 - A}{A_0} \times 100 \tag{13}$$

where A_0 is the absorbance at the maximum absorption wavelength ($\lambda_{\max}$) of initial dye solution and A is the absorbance at the maximum absorption wavelength of dye solution after the plasma treatment. Absorbance measurements were done by using the UV-Visible Cintra 6 spectrometer (GBC Scientific Equipment Pty Ltd., Australia) immediately (after 5 min), and 24 h after the plasma treatment.

To determine the influence of pH value of the initial dye solution on the decolorization efficiency, a pH of dye solutions was adjusted to three different values (pH 9.00, 7.00 and 5.00) by adding sodium hydroxide or sulphuric acid. Also, pH of each solution was determined after each recirculation. The pH value was measured using pH monitor (Microcomputer pH-vision 6071, JENCO
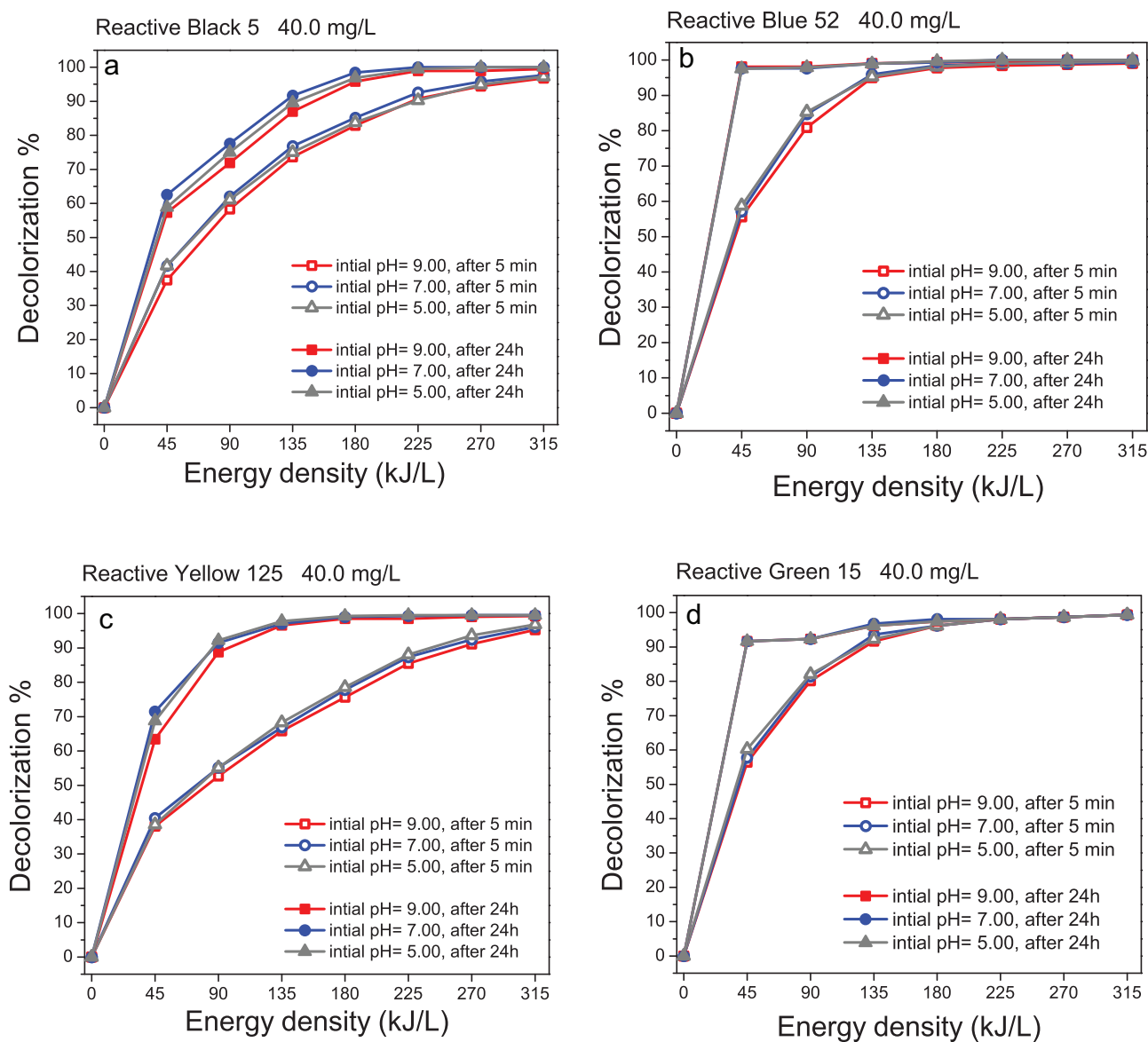
Fig. 2. Effect of initial pH value on the decolorization efficiency of azo dyes in the DBD plasma reactor: (a) Reactive Black 5, (b) Reactive Blue 52, (c) Reactive Yellow 125, and (d) Reactive Green 15 (c_0 = 40.0 mg/L).

Electronics. Ltd., Taiwan). The influence of Cu^{2+} as a homogeneous catalyst, present in some dyes is examined by adding $CuSO_4 \cdot 5H_2O$ in equimolar amount to dyes that do not comprise copper (Reactive Black 5 and Reactive Yellow 125; c_0 = 40.0 mg/L).

It was noticed during the experiments that pH value decreases after the plasma treatment. Therefore, to determine the influence of this effect, we tested the change of %decolorization with and without adjusting the pH value after each recirculation. The effect was tested for dye Reactive Black 5, c_0 = 40.0 mg/L after 5 min of treatment time. The initial pH of the solution for both series was 9.00, therefore it was adjusted to pH 9.00 after each recirculation of solution.

To find out the cause of pH decrease we used deionized water which was treated seven times through the DBD reactor. Five minutes after each recirculation concentrations of nitrite [32], nitrates [33], hydrogen peroxide [34,35], pH and conductivity (Cond 330i/SET, WTW Wissenschaftlich, Germany) were determined. The concentration of hydrogen peroxide was determined using the reaction of H_2O_2 with titanyl ions using the absorbance measurements at λ = 407 nm.

Effect of residence time on the absorbance of solutions was tested after introducing the energy density of 45 and 90 kJ/L for all four dyes (c_0 = 40.0 mg/L, initial pH 9.00). Absorbance was measured after 5–10 min, then every hour, and at the end of every 24 h over 5–6 days.

To determine the effects of adding H_2O_2 to initial dye solution on the decolorization, H_2O_2 was added just before the plasma treatment. Different concentrations H_2O_2 were added to dye Reactive Black 5 (c_0 = 80.0 mg/L; H_2O_2: 0, 2, 10 and 40 mM). The value of initial pH was 9.00. Decolorization efficiency was monitored 5 min and 24 h after the plasma treatment.

Effect of adding Fe^{2+} (1, 2, 5 and 10 mg/L) on the decolorization efficiency of Reactive Black 5 (c_0 = 40.0 mg/L, initial pH 3.00) during the plasma treatment was tested.

Toxicity test on brine shrimp (*A. salina*): *A. salina* eggs were incubated in artificial laboratory seawater illuminated by a tungsten filament light and gently sparged with air. Optimum temperature for hatching is 26–28 °C, where hatching occurs approximately after 24 h. Toxicity test is done with dyes solutions of 200 mg/L at decolorization of 50% and 90% seven days after the plasma
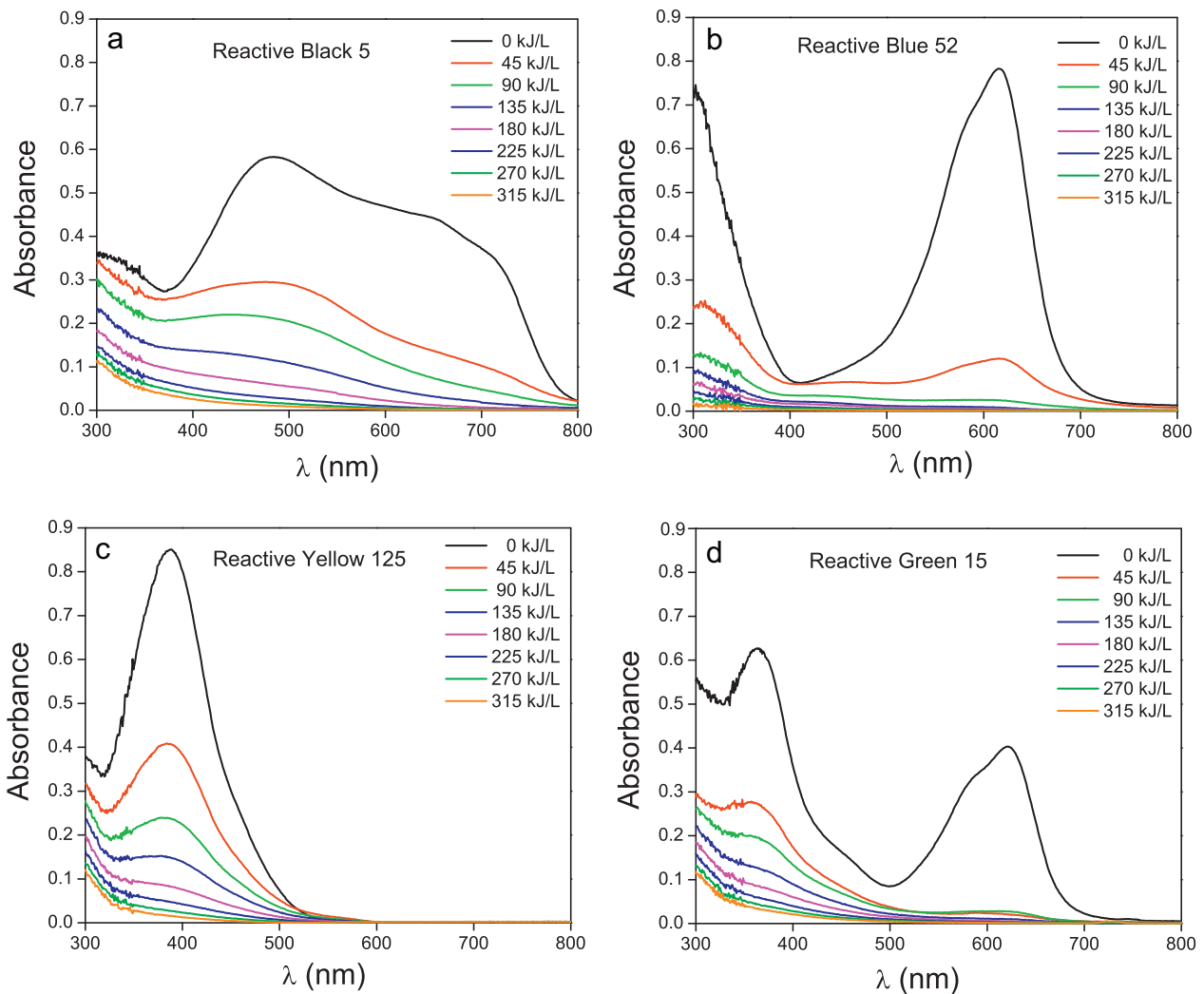
Fig. 3. Visible absorption spectra of dyes during the decolorization process: (a) Reactive Black 5, (b) Reactive Blue 52, (c) Reactive Yellow 125, and (d) Reactive Green 15 (experimental conditions: initial dye concentration 40.0 mg/L, initial pH 9.00, after 12 h (b, c) and 24 h (a, d) of treatment time).

treatment. Before the testing, pH of dye solution was adjusted to 7.00 and salinity to 3% with solid NaCl. Amount of 4.5 mL of sea water was added in the test tube, 0.5 mL shrimp (*A. salina* > 30) and 5 mL of dye solution or 2.5 mL of dye solution and 2.5 mL of sea-water. The final dye concentration in the medium was 100 mg/L and 50 mg/L, respectively. Solutions were illuminated by a tung-sten filament light for 24 h at 25 °C. The test was conducted with three replicates, after 24 h by determining the percentage of mortality [36,37].

3. Results and discussion

In order to optimize the parameters of decolorization process the effect of number of passes (respective energy density) and ini-tial pH value of dye solution on the decolorization efficiency was studied.

3.1. Effects of applied energy density

Dependences of %decolorization on applied energy density for three initial pH values is shown in Fig. 2. Introduced energy was added by multiple passes. It can be seen that initial pH value does not influence the curve dependences noticeably. In all cases decol-orization after the first treatment (i.e. 45 kJ/L) measured 5 min after passing through the DBD reactor was 40–60% while 24 h after

the plasma treatment, decolorization has increased to 70–97%, depending on dye. For the dye Reactive Black 5, decolorization value measured 24 h after one pass through DBD reactor reaches the same value as decolorization obtained in two passes (i.e. 90 kJ/L) and measured after 5 min. For the dye Reactive Blue 52, decolorization value measured 24 h after one pass is equal to decol-orization obtained after four passes (i.e. 180 kJ/L) and measured after 5 min. For dyes Reactive Yellow 125 and Reactive Green 15, decolorization value obtained 24 h after the first pass is equal to decolorization obtained after the three passes (i.e. 135 kJ/L) and measured after 5 min. This indicates that the effect of plasma treatment can be intensified in aqueous solutions by the primary products formed during water treatment. According to Magure-anu et al. [15] various oxidizing species are formed in the plasma treated aqueous solutions which contribute to the decomposi-tion of organic dyes, but most of these oxidizers have very short lifetimes. Therefore, they can only react with the dye molecules while the solution flows through the DBD reactor. Ozone and hydrogen peroxide are the only oxidizers generated in the plasma, which are stable enough to react with the dye molecules out-side of the plasma reactor, i.e. later upon the treatment. Reactions after plasma treatment can be partly attributed to reactions that are similar to the wet air oxidation and radiation. These reac-tions occur through the formation of alkyl, alkyl peroxide radicals, and hydroperoxides, with the third of these being responsible for

the autocatalytic decomposition of organic compounds, as shown in Refs. [6,9].

3.2. Spectrophotometric monitoring of dye during the plasma treatment

The changes of the visible spectra of Reactive Black 5, Reactive Blue 52, Reactive Yellow 125 and Reactive Green 15 solutions by plasma processes are shown in Fig. 3 (initial solution: $c_0 = 40.0$ mg/L, pH 9.00). Spectra were recorded after 12 h (Fig. 3b and c) and 24 h (Fig. 3a and d) of plasma treatment. The changes of the visible spectra of dyes can be used to understand dye degradation during treatments. It should be noted that absorbance maximum at 590 nm is commonly used for monitoring of decolorization in Reactive Black 5, due to smaller sensibility to pH value [38,39].

It can be seen that for all dyes, absorbance is reduced in the whole spectra with increase of introduced energy into the solution. The decrease of absorbance in the visible part of the spectrum indicates the loss of conjugated system in the compounds. This suggests that dyes were oxidized by oxidative species, and then converted into carboxylic intermediates what may finally lead to a complete mineralization of carbon into CO_2. Using absorbance measurements it is not possible to determine whether the complete mineralization occurs.

It should be noted that the absorbance in the visible range decreases faster than in the UV region. This may be explained by the destruction of a conjugated system which leads to the loss of color in the visible part of the spectra. On the other hand, opening of the aromatic rings (which absorb in the UV) is a much slower and more difficult process.

Among the oxidative species, $^\bullet OH$ is the major oxidative transient, and is known to react with benzene and azo moieties with high rate coefficients. The $^\bullet OH$ addition to the $-N{=}N-$ bond also produces the hydrazyl type radical forms, $-^\bullet N{-}N(OH)-$. This reaction probably led to the destruction of the intensive color in the visible range [40]. The effect of other oxidation species which are created in the plasma is also present. However, it should be noted that the $^\bullet OH$ radical has the highest oxidation potential and is the least selective in the reactions of degradation.

3.3. Change of pH values and effect of pH adjustments

The variation of pH values of the solution during the treatment process is shown in Fig. 4 for all three initial pH values for dye Reactive Black 5. The curves show that the pH value considerably
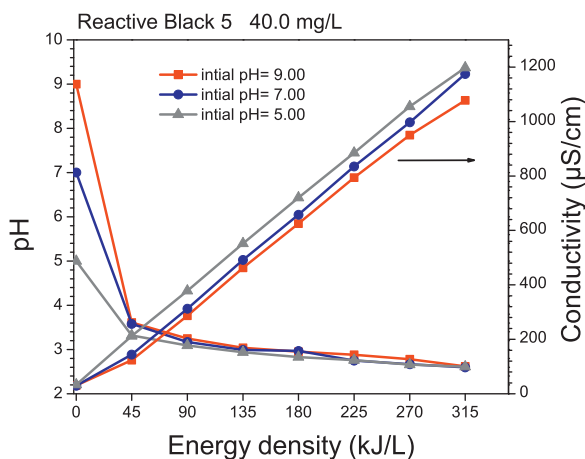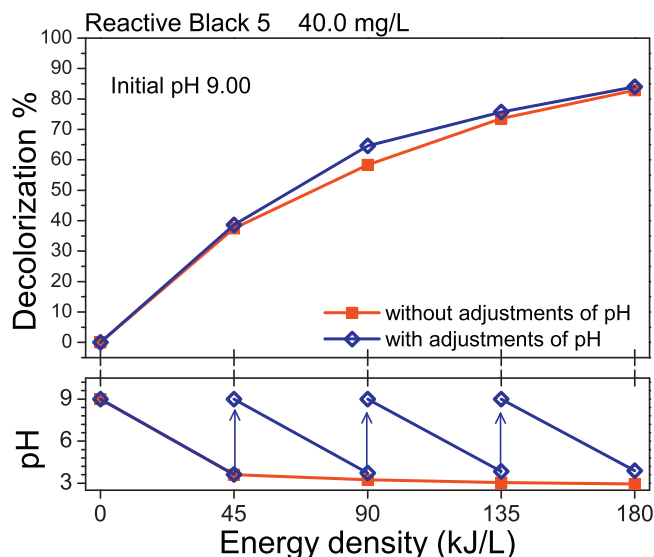

Fig. 5. The change of %decolorization and pH values during the reaction process without and with adjustments pH after each recirculation (Reactive Black 5, $c_0 = 40.0$ mg/L, initial pH 9.00).

decreases, for all three initial pH, after the first pass through the reactor to a value of about 3.5. After each subsequent pass (i.e. increase of applied energy) pH slowly declines to the value of 2.6 after the seventh pass (315 kJ/L). Dyes Reactive Blue 52, Reactive Yellow 125 and Reactive Green 15 have the same trend and values of pH. The variation of pH value is probably caused by several special acidic substances such as nitric acid and nitrous acid which are produced during the discharge process in air [41]. Also, a certain contribution to the pH variation during the plasma treatment may come from sulphuric acid and carboxylic intermediates, produced from the degradation of dyes.

To confirm acidification of the water solution caused by air plasma, deionized water without dyes was treated in the DBD reactor. NO_2^- content of 0.95 mg/L was measured after the first pass (45 kJ/L), and was reduced below the detection limit at the end of treatment (315 kJ/L). The contents of NO_3^- was increasing during the treatment and reached 90 mg/L at 315 kJ/L. Values of pH in the treated water were almost identical to that in the treated dye solutions. Conductivity of deionized water has increased during the plasma treatment from 1.8 to 1100 μS/cm for the energy density of 315 kJ/L.

Percentage of decolorization during the reaction process with and without adjustment of pH after each recirculation was examined on the example of dye Reactive Black 5. The initial pH of dye solution was 9.00. Solution pH was adjusted after each pass through the reactor using NaOH, to its initial value of 9.00. It can be concluded that adjustment of pH after each pass through the DBD reactor does not affect significantly the %decolorization of the solution, see Fig. 5. This conclusion is important for the treatment of wastewater from textile industry through eliminating the necessity of pH adjustment, i.e. reducing the number of unit operations in water treatment processes.

3.4. Effect of residence time after plasma treatment

The effects of residence time after plasma treatment on the absorbance of solutions of dyes is shown in Fig. 6. Absorbance change for λ_{max} after introducing the energy density of 45 and 90 kJ/L in the solution was tested for all four dyes ($c_0 = 40.0$ mg/L, initial pH 9.00). Absorbance was measured after the plasma treatment at different time intervals, depending on the change in its

Fig. 4. The change in the solution pH and conductivity values during the reaction process for different initial pH (Reactive Black 5, $c_0 = 40$ mg/L, after 5 min of treatment time).
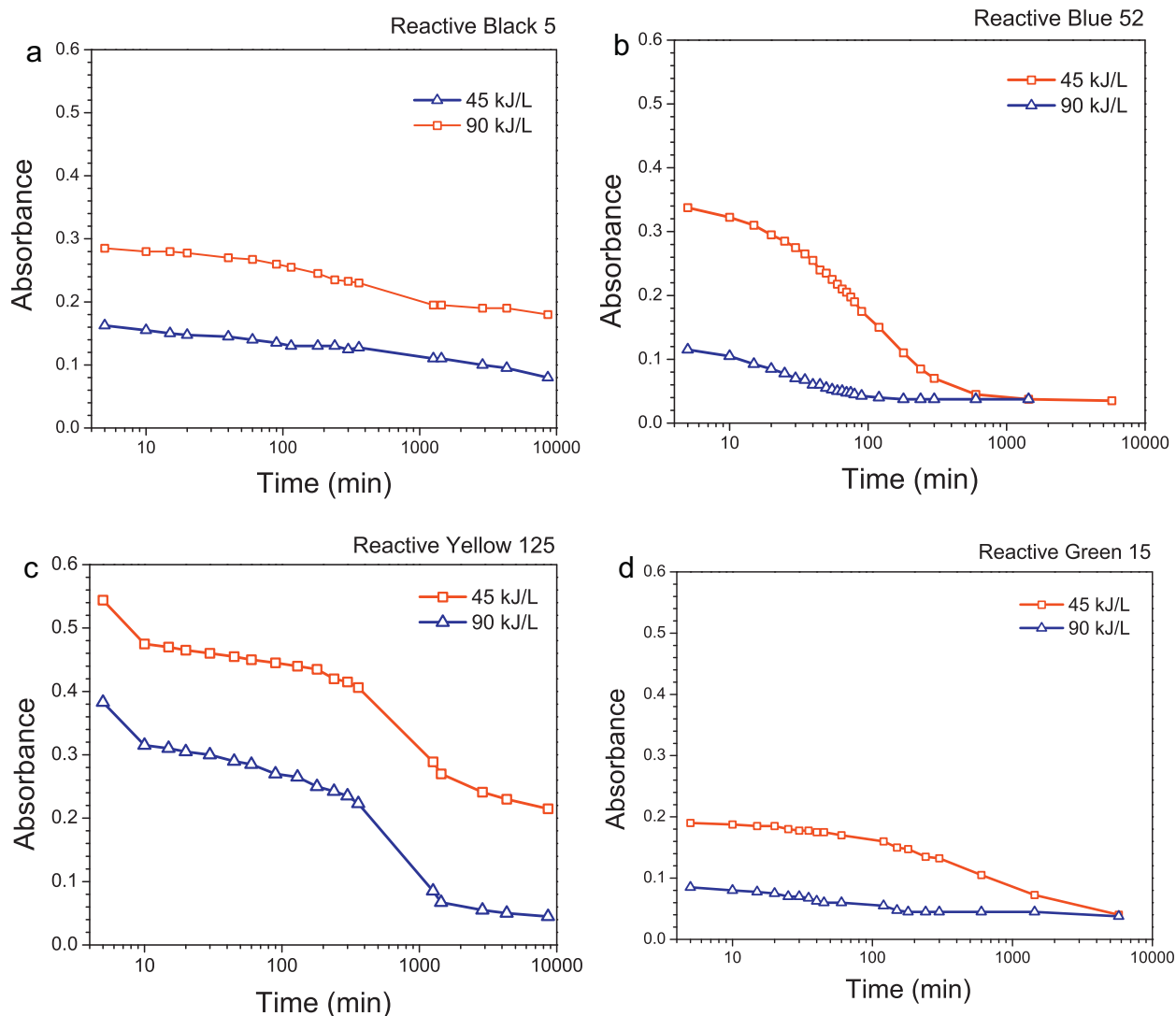
Fig. 6. Effects of residence time on absorbance for λ_{max} after introduction the energy density in the solution of 45 and 90 kJ/L: (a) Reactive Black 5 ($A_0 = 0.475$), (b) Reactive Blue 52 ($A_0 = 0.780$), (c) Reactive Yellow 125 ($A_0 = 0.855$), and (d) Reactive Green 15 ($A_0 = 0.405$); A_0 is the absorbance of initial solution, before the plasma treatment ($c_0 = 40.0$ mg/L, initial pH 9.00).

value (every 5–10 min, every hour and every 24 h) over the course of 5–6 days. Reactive Black 5 and Reactive Yellow 125 show a similar trend of decolorization with residence time for both energy densities. On the other hand, dependence of %decolorization on the residence time for dyes Reactive Blue 52 and Reactive Green 15 is different: in the first 180 min %decolorization is much higher for 90 kJ/L than for the 45 kJ/L.

For continued process of decolorization during the residence time in plasma treated dye solution, molecular species (O_3 and H_2O_2) are primarily responsible, and possibly long-lived free radicals formed during plasma treatment. Ozone was identified and quantified in the solution after the treatment in the DBD reactor [17]. In the treated deionized water the content of H_2O_2 was quantified 5 min after the treatment. During the subsequent recirculation of deionized water through the DBD reactor, H_2O_2 content gradually increased and at introduced energy density of 315 kJ/L H_2O_2 content was 13.80 mg/L (0.41 mM).

3.5. Effect of H_2O_2

Fig. 7 shows the effect of addition of different concentrations of H_2O_2 on decolorization efficiency of Reactive Black 5
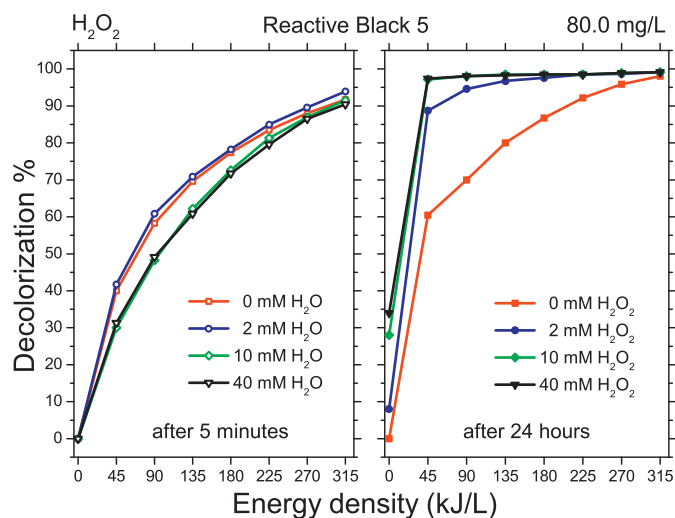

Fig. 7. Effect of adding H_2O_2 on the decolorization efficiency of Reactive Black 5 ($c_0 = 80.0$ mg/L, initial pH 9.00, after 5 min and 24 h of treatment time).

(c_0 = 80.0 mg/L). The results show that decolorization of dye could be accelerated or inhibited in the presence of H_2O_2 depending on the dosage. The decolorization efficiency of Reactive Black 5 increased with addition of low concentrations of H_2O_2 (2 mM). This addition increased the decolorization efficiency by a small amount of 1% for each passing measured 5 min after the treatment. On the contrary, for high concentration of H_2O_2 (10–40 mM), the decolorization efficiency of Reactive Black 5 decreased with increasing H_2O_2 concentration, measured after 5 min. For example, when higher concentrations of H_2O_2 were added into the solution (10 mM and 40 mM), a 10% lower decolorization efficiency was observed (at 45 kJ/L), than in the solution with no H_2O_2. Decolorization after 24 h residence time is better in systems both with low and high contents of H_2O_2, reaching value higher than 95% after the first pass, while the decolorization without H_2O_2 is 60%. For example, at the lowest energy density of 45 kJ/L measured after 24 h – addition of 2 mM of H_2O_2 raised %decolorization for 28%, and with high concentrations of H_2O_2 %decolorization was raised for 37% (from its value without H_2O_2).

The higher dye degradation efficiency and decolorization improvement with low dosage of H_2O_2 may be explained with more efficient generation of $^\bullet$OH according to the following Eqs. (12) and (14) [12,42]:

$$H_2O_2 + {}^\bullet O_2{}^- \rightarrow {}^\bullet OH + OH^- + O_2 \qquad (14)$$
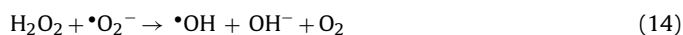
The lower degradation efficiency and decolorization at high H_2O_2 dosage may be explained with the consumption of $^\bullet$OH by H_2O_2, which could be expressed by Eqs. (7) and (15) [12,43,44]:

$$HO_2{}^\bullet + {}^\bullet OH \rightarrow H_2O + O_2 \qquad (15)$$

When higher concentration of $^\bullet$OH and H_2O_2 are both present simultaneously, this mechanism becomes more significant, which reduces the effective level of both H_2O_2 and $^\bullet$OH in the solution, and as a result, the decolorization of dye is decreased.

Without using the DBD reactor (0 kJ/L), obtained %decolorization after 24 h for 2, 10 and 40 mM of H_2O_2 was 8, 28 and 34%, respectively. Much higher final decolorization of 88% (2 mM H_2O_2) and 97% (10 and 40 mM H_2O_2) was obtained in systems with both H_2O_2 and DBD at 45 kJ/L. The case of 45 kJ/L and 2 mM H_2O_2 shows an interesting feature. Namely, simultaneous use of H_2O_2 and plasma gives higher %decolorization then the sum %decolorizations obtained with them separately. This indicates possible synergetic effects between the H_2O_2 and stable species or radicals formed in the DBD reactor.

3.6. Effect of Fe^{2+}

The DBD reactor produces H_2O_2 through reactions (6) and (11). Fe^{2+} was added to the treated solution to increase the oxidizing power of generated H_2O_2 by the production of $^\bullet$OH from Fenton reaction [45,46]:

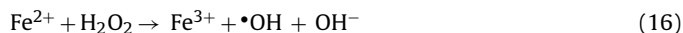$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad (16)$$

Fig. 8 shows the effect of adding different concentrations of Fe^{2+} on decolorization efficiency of Reactive Black 5 (c_0 = 40.0 mg/L). The initial pH value of dye solutions was adjusted to pH 3.00. When compared with the system without Fe^{2+} (0 mg/L), decolorization efficiency after five minutes increases by a small degree with addition of Fe^{2+} in concentrations of 1–5 mg/L. On the other hand, addition of higher concentration of Fe^{2+} (10 mg/L) slightly reduces decolorization. After 24 h, at energy density 90 kJ/L and higher, H_2O_2 which is produced in larger amounts, reacts with Fe^{2+} (1, 2 and 5 mg/L) thus contributing to the increase of %decolorization by approximately 10%, compared to the system without Fe^{2+}. For Fe^{2+} concentration of 10 mg/L, %decolorization was 5% lower than
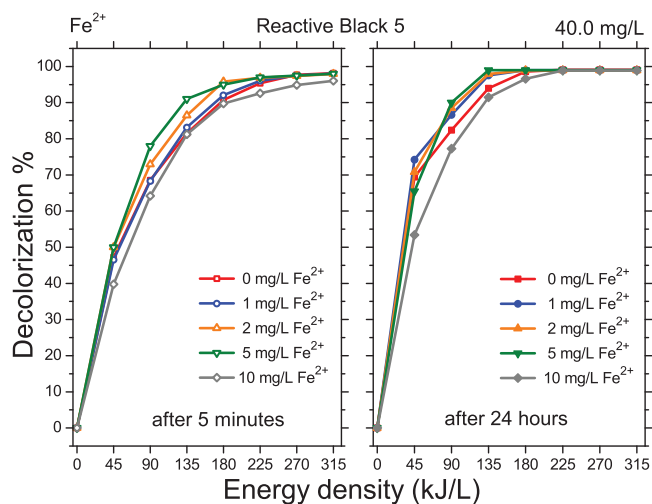

Fig. 8. Effect of adding Fe^{2+} on the decolorization efficiency of Reactive Black 5 (c_0 = 40.0 mg/L, initial pH 3.00).

in the system without Fe^{2+}, due to the reaction of excess Fe^{2+} with already generated $^\bullet$OH and the formation of Fe^{3+} and hydroxide ion [47–49].

3.7. Toxicity test (A. salina)

Before the treatment, the tested concentrations of dyes (50.0 and 100.0 mg/L), Reactive Black 5 and Reactive Yellow 125 had toxicity of about 10% mortality, while Reactive Blue 52 and Reactive Green 15 are not toxic. After the plasma treatment with 50 and 90% decolorization, Reactive Blue 52 and Reactive Yellow 125 for both initial dye concentration were not toxic (0% mortality). Reactive Green 15 for a concentration of 100.0 mg/L and at 90% decolorization, had a toxicity of 4% mortality, while the other tested systems are not toxic. For Reactive Black 5, there was no significant change in toxicity after the plasma treatment except in the case of 50 mg/L of dye and 50% decolorization when toxicity was reduced to 0% mortality.

4. Conclusion

Decolorization of four reactive textile dyes was studied using a non-thermal plasma reactor, based on coaxial water falling film dielectric barrier discharge (DBD). The treated solutions containing investigated dyes, exhibit very similar decolorization kinetics for all four dyes. The $^\bullet$OH radicals generated in DBD reactor produce long lived reactive species that provide almost complete decolorization of tested dyes with 90 kJ/L after 24 h residence time. Due to this fact the DBD reactor can be used, with reduced energy consumption, in combination with retention basin, in wastewater treatment facilities. Initial pH value of tested solutions, has shown no influence on decolorization kinetics. The effect of plasma treatment can be significantly intensified with addition of hydrogen peroxide. For example, the most effective decolorization of 97% was obtained with addition of 10 mM H_2O_2 in a system of 80.0 mg/L Reactive Black 5 with applied energy density of 45 kJ/L, after residence time of 24 h. Also, the effect of plasma treatment can be enhanced with addition or iron (II) salts if the conditions for Fenton reactions are fulfilled. During the treatment, the discharge generates other species like nitrous and nitric acids which decrease the pH values of solutions. Toxicity tests, performed using A. salina, have shown that toxicity of dye solutions was reduced or maintained at the same level after the treatment, except for Reactive Green 15 where slight increase of toxicity was detected for only one concentration value.

Our results obtained at laboratory level indicate that the coaxial DBD plasma reactor may be effectively used for decolorization of textile wastewater. Certainly, additional experiments are needed in order optimize operating conditions for a scale up, towards the final aim of using this type of plasma reactor for wastewater treatment.

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