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Application of non-thermal plasma reactor for degradation and detoxification of high concentrations of dye Reactive Black 5 in water

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Abstract: Degradation and detoxification efficiency of high concentrations of commercially available reactive textile dye Reactive Black 5 solution (40, 80, 200, 500, 1000 mg L⁻¹), were studied. Advanced oxidation processes in water falling film based on dielectric barrier discharge in a non-thermal plasma reactor were used. For the first time, this reactor was used for the treatment of high concentrations of organic pollutants such as reactive textile dye Reactive Black 5 in water. Solution of the dye was plasma treated in a thin aqueous solution film that was constantly regenerated. The reactor works as a continuous flow reactor and the electrical discharge itself takes place at the gas–liquid interphase. The dye solution was recirculated through the reactor with an applied energy density of 0–374 kJ L⁻¹. Decolorization efficiency (%) was monitored by UV–Vis spectrophotometry. Samples were taken after every recirculation (~ 22 kJ L⁻¹) and decolorization percentage was measured after 5 min and 24 h post plasma treatment. The efficiency of degradation (*i.e.*, mineralization) and possible degradation products were also monitored by determination of the chemical oxygen demand (COD) and by ion chromatography (IC). Initial toxicity and toxicity of the solutions after the treatment were studied using *Artemia salina* test organisms. Efficiency of decolorization decreased with the increase of the dye concentration. Complete decolorization, high mineralization and non-toxicity of the solution (<10 %) were accomplished after plasma treatment using energy density of 242 kJ L⁻¹, while the initial concentrations of Reactive Black 5 were 40 and 80 mg L⁻¹.

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INTRODUCTION

Advancement in technology and science by the end of the 20th and start of the 21st century undoubtedly led to increased quality of life for humankind. However, the ecological aspect of new technologies and their environmental impact were studied less than they deserved. Organic compounds are extensively used in every possible way and in great amounts. Problems that occurred were the toxicity of certain compounds and the resistance towards classic techniques for water treatment including reverse osmosis, coagulation, carbon adsorption and biological treatment as well. This could slowly lead earth's ecosystem to a problematic state, to say the least. It is a devastating fact that at the start of 21st century more than a quarter of earth's population has health problems caused by insufficient drinking water, or its low quality as the consequence of water pollution. Therefore, a lot of attention has been given to the water purification treatments, and the extensive search for new and ecological technologies for pollution control are on the way.

Synthetic organic dyes are widely used as colorants in all the industries imaginable: food, cosmetics, textile, paper, pharmaceuticals, etc. Annual production of synthetic organic dyes worldwide was estimated at 0.7 million tons and is at constant rise. There are more than 10,000 different commercially available synthetic dyes, but the reactive types are the most important category.¹

Moderate amounts of dyes were used in the past and they did not represent a serious problem. Nowadays, due to increased use of dyes the situation is different. The textile industry is the largest consumer of reactive textile dyes.² Presently, used dyeing process is not very efficient and the excess amount of dye is required in order to achieve complete colorization of textile. In such a way, a lot of wastewater containing the excess of reactive dyes is produced. The treatment in wastewater plants sometimes cannot completely remove the toxic and hazardous dyes and consequently they are released into the environment. A good overview of wastewater treatment and water recycling in textile industry is given in the study by Rott *et al.*³ These wastewaters have high chemical oxygen demand (COD), high concentrations of salts that increase ionic strength, and a lot of different, toxic substances. The reactive textile dyes were recognized as the most toxic constituents of these wastewaters. Therefore, advancement in more efficient technologies for reactive dye removal was in the focus of research in the past and will be in the future.

Reactive dyes account for 20–30 % of dye market and they are used in wide variety of applications with cotton dyeing as the most important one. Their usage is at a constant rise due to the great performance/price ratio. Great performance

could be attributed to their high solubility as well as reactivity. Nowadays, azo dyes, a type of reactive textile dyes, account for more than a half of all reactive dyes used worldwide.⁴⁻¹⁰

Toxicity, low removal rates by classical physicochemical processes and negligible biodegradability of reactive dyes demanded development of novel and effective methods for their removal from wastewaters. Among many newly developed technologies, the advanced oxidation processes (AOPs) showed great efficiency for wastewater treatment. The main goal of all degradation processes is to achieve complete mineralization of organic matter, *i.e.*, total conversion to carbon dioxide and water. Advanced oxidation processes could achieve such goals, or at least they are able to convert the toxic and non-biodegradable organic compounds into less toxic and more readily biodegradable intermediates.

The main advantage of AOPs compared to other classical methods of wastewater treatment is their extremely destructive nature. Total mineralization of organic waste is achieved through the process, while no additional waste is generated, or the amount is exceptionally low.¹¹ AOPs give rise to chemical species, mainly hydroxyl radicals ($\bullet\text{OH}$) that are able to oxidize most of the organic compounds present in wastewaters.¹² Hydroxyl radicals are short-lived, but have the strongest oxidation potential after fluorine, and low selectivity when used for degradation purposes in wastewater treatment. Due to their instability, hydroxyl radicals need to be generated continuously. Hydroxyl radicals could be accomplished by different (photo)chemical or electrochemical reactions, *e.g.*, classic ones like Fenton's or photo-Fenton's reaction,¹³⁻¹⁶ ozone,^{17,18} or the increasingly popular photocatalysis based on TiO_2 , BiVO_4 and some other semiconductors.¹⁹⁻²¹ Presently, most promising processes are based on electrical discharge technologies, *e.g.*, dielectric barrier discharge (DBD) or pulsed corona discharge (PCD).^{11,22-28} Another advantage of AOPs is that they could be used alone or in combination with other classical methods for wastewater treatment.

Electric discharge in the air induces conversion of molecular oxygen into ozone. Besides ozone, other chemically active species like O^\bullet , $\bullet\text{OH}$, N^\bullet , O_3^* , N_2^* , OH^- , O^{2-} , N^+ , O^+ are generated (*indicates high energy state).^{24,29-32} All of the species mentioned are short-lived and cannot be contained and used afterwards. Therefore, a new approach to use the oxidation potential of these species in water was required. Problem was solved by *in situ* electrical discharges in water or in contact with water.³³ The most frequently used electric discharges are DBD and PCD.

The quantification of environmental impact of certain effluent containing various organic compounds and subsequent treatment efficiency could be estimated using different bioassays.³⁴ As a model for rapid screening of toxicity, *Artemia salina* was used to estimate the non-thermal plasma reactor potential and the consequences of water treatment.^{25,35} Advantage of using *Artemia salina* for

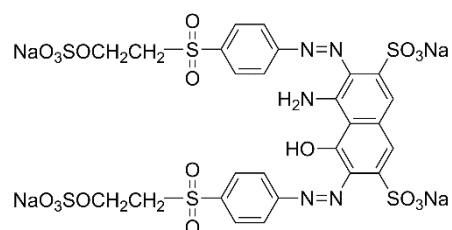
these kind of biological tests is tolerance of high salinity environment which makes it versatile and useful.³⁶

One goal of the research conducted was to test the coaxial plasma reactor system (DBD) for degradation and detoxification of high concentrations of reactive textile dye, Reactive Black 5. Another goal was to estimate capacity of DBD reactor, which was done for obtaining 50 % of decolorization of Reactive Black 5 as a model compound. UV-Vis spectrophotometry, COD and ion chromatography (IC) monitored the degradation efficiency and specific degradation products. The toxicity of the dye solution was determined before and after the plasma treatment by means of *Artemia salina* test organisms.

EXPERIMENTAL

Materials

Reactive textile dye, Reactive Black 5 (purity >98 %, Clariant, Switzerland) was used without further purification. Reactive Black 5 is a dissociated anionic sulfonate in an aqueous solution. Molecular structure and general characteristics of Reactive Black 5 are presented in Fig. 1. Potassium hydroxide (*p.a.*) was supplied by Merck, Germany. *Artemia salina* cysts (Artemia-mix) and sea salt (Tropic Marin[®]) are products of Sera[®], Germany. Artemia-mix contains lyophilized cysts and food. Synthetic seawater was prepared by dissolving 100 g of sea salt in 3 L of deionized water. Besides sodium chloride (Sigma Aldrich, USA, *p.a.*) for osmotic adjustment of samples, sodium hydroxide (Merck, Germany, *p.a.*) and sulfuric acid (Sigma Aldrich, USA, *p.a.*) were used in *Artemia salina* bioassay. Catalase from *Aspergillus niger* was supplied by Sigma-Aldrich, USA. All solutions were prepared using deionized water with conductivity ranging between 1.0 and 1.5 $\mu\text{S cm}^{-1}$.



Chemical class: Azo
 Application class: Cotton
 Maximum absorption, $\lambda_{\text{max}}=590 \text{ nm}$

Fig. 1. Molecular structure and general characteristics of Reactive Black 5.

DBD reactor

Coaxial DBD reactor used in this research was designed as a non-thermal plasma reactor which is an open type reactor operating in air, at atmospheric pressure and it is described in Kuraica *et al.*³⁷ and Dojčinović *et al.*²⁴ Briefly are mentioned only few details of the reactor characteristics. In the reactor with the peristaltic pump, the solutions of Reactive Black 5 passed through the central tube to the top and then, they were falling down forming a thin layer over the inner electrode. Therefore, the solutions were in the direct contact with plasma generated between two electrodes (Fig. 2). Plasma above the water layer generated ozone and UV radiation, as well as a wide range of reactive species like excited atoms, molecules (such

as H_2O_2 and O_3), electrons, and ions in both the gas and the liquid phase. This type of reactor was successful in phenol removal from water³⁸ and also in dye removal,²⁴ pesticide removal,²⁵ medicaments removal³⁹ and surfactants removal.⁴⁰ Electric discharges were generated in the air between the glass and the water layer at a distance of 3.5 mm, by applying a voltage up to 14 kV at frequency of 200 Hz and power of 25 W deposited in the discharge. Three discharges were connected in parallel in order to increase the total flow of treated solutions. Power of discharge for this system calculated using Q-V plots was 75 W. Flow rate through three parallel DBD reactors was 210 mL min^{-1} . Solutions were recirculated up to 17 times.

It needs to be pointed out that the currently treated solution was never mixed with a solution which has been treated in the previous passing (Fig. 2). Whenever the solution passed through the reactor, the same amount of energy density, $\sim 22 \text{ kJ L}^{-1}$, was introduced into the solution.

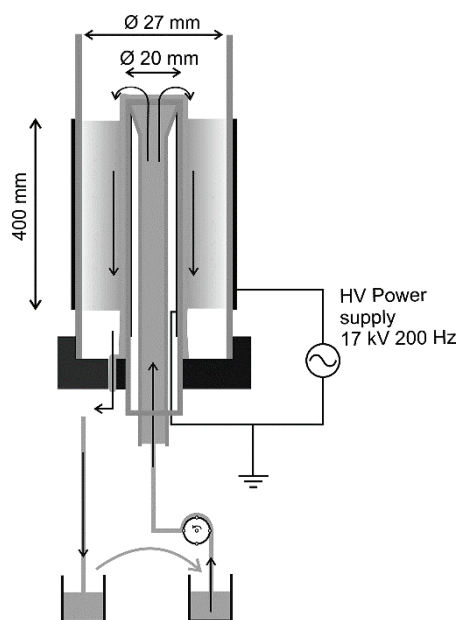


Fig. 2. Schematic image of coaxial falling film DBD reactor: inner glass barrier diameter 20.0 mm, length 500 mm, thickness 1.5 mm); outer glass barrier (diameter 30.0 mm, thickness 1.5 mm, length 600 mm); outer metal foil electrode (diameter 30 mm, length 400 mm).

Methods of analysis

Determination of decolorization efficiency at high concentrations of Reactive Black 5.

The ability of the reactor for degradation of the reactive azo dye, Reactive Black 5, was tested in triplicate. Each solution of the dye was prepared by dissolving the commercial dye without additional purification in deionized water. In series of experiments, initial concentrations of Reactive Black 5 were 40, 80, 200, 500 and 1000 mg L^{-1} , and applied the energy density was $0\text{--}374 \text{ kJ L}^{-1}$. Initial values of pH and conductivity are measured and their values are in the following range: pH from 8.44 (for 40 mg L^{-1} solution) to 10.45 (for 1000 mg L^{-1} solution) and conductivity from 32 (for 40 mg L^{-1} solution) to $722 \mu\text{S cm}^{-1}$ (for 1000 mg L^{-1} solution). Initial pH value of the solutions was not adjusted because in our previously published research,^{24,35} adjusting of initial pH value had no effect on degradation of dyes and 4-chlorophenols. In all cases, water samples containing different concentrations of the dye passed up

to seven times through the discharge. Decolorization efficiency is defined as the percentage decrease of solution's absorbance according to Eq. (1):

$$\text{Decolorization} = 100 \frac{A_0 - A}{A_0} \quad (1)$$

where A_0 is the absorbance at the maximum absorption wavelength (λ_{max}) of the initial dye solution, while A is the absorbance at the maximum absorption wavelength of the dye solution after the plasma treatment. The absorbance measurements were performed using a UV-Vis Cintra 10 spectrometer (GBC Scientific Equipment, Australia) 5 min and 24 h after the plasma treatment and then decolorization efficiency was calculated.

Determination of the chemical oxygen demand (COD)

Chemical oxygen demand ($\text{mg O}_2 \text{ L}^{-1}$) was measured for all initial Reactive Black 5 dye samples from previous series of experiments, i.e. solutions that had the initial concentrations of 40, 80, 200, 500 and 1000 mg L^{-1} . Also, COD value was determined for plasma-treated samples with applied energy density of 66 and 242 kJ L^{-1} for each of the initial concentrations except for the 40 mg L^{-1} . These measurements were performed two days after the plasma treatment.

Preparation of the samples for COD determination was performed by microwave digestion at high temperature and pressure (up to 100 bar). Microwave digester was ETHOS 1, Advanced Microwave Digestion System, Milestone, Italy, with segmented rotor HPR-1000/10S. In this type of apparatus, with poly(tetrafluoroethylene) vessels, up to ten samples can be prepared simultaneously, which considerably accelerates the process. Vessels were filled up to one-fourth with samples and other chemicals required by the method. Heating time was optimized, while the temperature was $150 \text{ }^\circ\text{C}$. Optimization was achieved by using the solution of precisely known COD value ($\text{COD} = 900 \text{ mg O}_2 \text{ L}^{-1}$). Solution was made by dissolving dried primary potassium hydrogen phthalate standard. Three temperature regimes were tested, i.e., their influence on the accuracy of the method. All three analyzed regimes required gradual sample heating for 7 min until the temperature reached $150 \text{ }^\circ\text{C}$ and then the digestion time at constant temperature of $150 \text{ }^\circ\text{C}$ differed (10, 20 and 25 min). After cooling of the samples, the contents in the vessels were quantitatively transferred to erlenmeyers and titrated with standard iron(II) ammonium sulfate solution with ferroin indicator according to the procedure described by the standard method.

Determination of inorganic and organic anions by Ion Chromatography (IC)

Ion chromatography was used for quantitative and qualitative determination of inorganic and organic anions in the initial samples of reactive textile dye, Reactive Black 5, from previous two series of experiments, i.e., for samples containing the dye in concentrations of 40, 80, 200, 500 and 1000 mg L^{-1} . Also, ion chromatography analysis was done for plasma treated samples of the dye with applied energy densities of 66 and 242 kJ L^{-1} . Determination was performed on Dionex ICS-3000 chromatographic set-up consisting of a single pump, a conductivity detector (ASRS ULTRAI (4 mm), recycle mode), an eluent generator (potassium hydroxide) with a Chromeleon® Chromatography Workstation and Chromeleon 6.7 Chromatography Management Software. All the separations were performed using IonPac AS15 Analytical, $4 \text{ mm} \times 250 \text{ mm}$ and IonPac AG15 Guard, $4 \text{ mm} \times 50 \text{ mm}$ columns. The flow rate of the mobile phase was 1.00 mL min^{-1} and the elution was gradual in the following order: 0–3.5 min, 0.75 mM KOH; 3.5–7 min, 7.5 mM KOH; 7–20 min, 60 mM KOH; 20–25 min, 60 mM KOH; 25–30 min, 60–0.75 mM KOH; 30–35 min, 0.75 mM KOH. In addition,

the following conditions were applied: column temperature was 30 °C, conductivity cell temperature was 35 °C and the suppressor current was 149 mA. The backpressure was \approx 18 MPa.

Toxicity of Reactive Black 5 towards Artemia salina test organisms

For the toxicity tests the brine shrimp *Artemia salina* was used according to Vanhaecke *et al.*⁴¹ The *Artemia salina* cysts were hatched in synthetic sea water at 32.0 ± 0.5 ‰ to produce instar larvae.⁴² An acute toxicity test was performed in darkness at a temperature of 26 ± 1 °C, for the test period of 24 h, with control and two dilutions (sample:sea water, 1:1 and 1:3 volume ratios) with three replicates per dilution, and six of control. The test was carried out with different initial concentrations of Reactive Black 5 dye (40–1000 mg L⁻¹) in 50 mL borosilicate glasses in the following way: artificial sea water was used as control solution (negative control) and as a diluent for samples. Before testing, pH value of each sample was adjusted to 7 using sodium hydroxide or sulfuric acid. Solution salinity was adjusted using solid sodium chloride. Sample volume was 10 mL. With a Pasteur pipette 20 naupliis were placed into each vessel. They were considered dead if no movement was observed within 10 seconds. Lethality for each sample dilution was expressed as the percentage of mortality. Tests were considered valid if the mortality in the control did not exceed 10 %.

RESULTS AND DISCUSSION

In the present study, the decolorization and degradation of high concentration of the commercial reactive azo dye Reactive Black 5 were studied using an advanced oxidation process (AOP) in a non-thermal plasma reactor based on coaxial dielectric barrier discharge (DBD) and the toxicity of the solutions before and after plasma treatment was determined using the test organisms *Artemia salina*. Within reactor, water formed a falling film that is in direct contact with the plasma. As water is constantly flowing over the top of the reactor, thin water film constantly regenerates, *i.e.*, reactor works as the flow reactor. Energy density of ~ 22 kJ L⁻¹ was introduced into the solution after one passing through the reactor. Applied energy density was increased by multiple recirculations of solution through the reactor. Reason for using such high concentration of the dye is for determining the DBD reactor capacity, and for evaluating DBD reactor usage in potential industrial accident situation.

Decolorization efficiency of high concentrations of reactive dye Reactive Black 5

Influence of high concentrations of reactive dye Reactive Black 5 on decolorization efficiency as function of applied energy density, was examined using dye concentrations of 40, 80, 200, 500 and 1000 mg L⁻¹, while the energy density was ranging from 22 to 374 kJ L⁻¹ (Fig. 3a). Decolorization efficiency was measured 5 min and 24 h after the plasma treatment. For different dye concentrations, decolorization increased with input energy increase, rapidly at the beginning of dye treatment and slowly after several passes through the reactor. Higher decolorization rate after 24 h, in comparison with 5 min post-plasma treatment decolorization has been observed because of longer living oxidative species (such

as O_3 and H_2O_2) remaining after treatment in the dye solution, which promoted further degradation and decolorization after initial degradation mainly caused by $\bullet OH$.

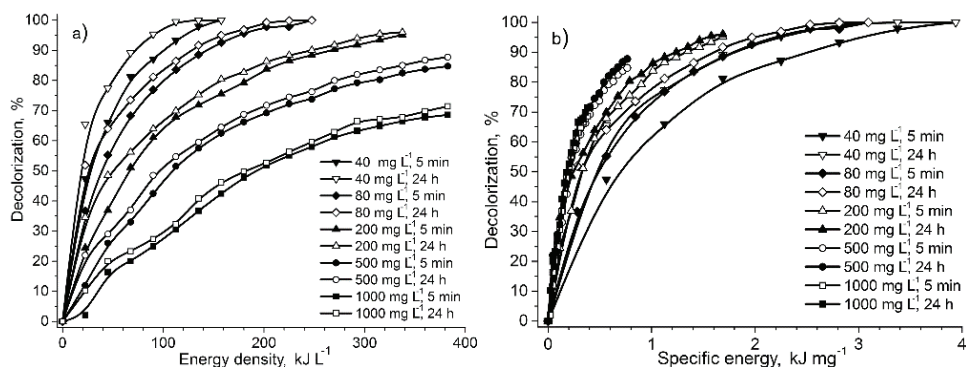


Fig. 3. a) Decolorization vs. energy density and b) decolorization vs. specific energy for various initial concentrations of reactive dye Reactive Black 5 (c_0 , 40–1000 $mg L^{-1}$) and residence time (5 min and 24 h).

Based on these results, it could be concluded that decolorization efficiency decreased with increase of dye concentration. However, if the decolorization is depended on specific energy (energy density divided by dye concentration) (Fig. 3b), it is obvious that the most efficient decolorization was obtained for the highest dye concentration. Production of $\bullet OH$, as the most important reactive species, was independent of the dye concentration, as their productions were caused by electron dissociation of water molecules.⁴³ $\bullet OH$ non-selectively reacted with surrounding molecules and as its lifetime was very short (micro-seconds in a gas phase or order of nano-seconds in a liquid phase), it reacted with the dye molecule only if it was closer than $\bullet OH$ mean free path. Otherwise, $\bullet OH$ would react with water molecule. The increase of dye concentration enabled dye molecules were in close proximity to $\bullet OH$ and increased the possibility for their interaction and, consequently, the increase of the decolorization efficiency. Analyzing the decolorization and degradation processes from point of view of specific energy, the explanation is not straightforward. Therefore, the rest of the discussion was focused on the use of energy density as a parameter. Based on the results presented in Fig. 3a, it could be concluded that oxidation species for both lower and higher concentrations of the dye are used evenly for decolorization reactions and for oxidation of intermediates. Analysis of experimental results indicated that increase in decolorization efficiency in time was decreasing as dye concentration increased (Fig. 4). Specific energy could be useful for DBD reactor capacity estimation since concentration of dye at which specific energy stops decreasing even if compound concentration is still being increased. Using Reactive Black 5

dye as a model compound for capacity estimation graph of specific energy vs. dye concentration can be plotted using data obtained for 50 % decolorization and 5 min after the plasma treatment (Fig. 5a). Specific energy was decreasing with dye concentration increase, even if the energy density was increasing. Therefore, more energy was used per dye molecule in case of lower dye concentrations. From Fig. 5a, can be concluded that capacity of reactor to obtain 50 % decolorization was reached when specific energy decreased and did not significantly change regardless of dye concentration increase. Reactor capacity was reached for Reactive Black 5 concentrations above 1000 mg L^{-1} . It was determined that reactor capacity had linear dependence of applied energy density in the tested concentration range for which effectiveness of 50 % decolorization is achieved after 5 min and 24 h after the plasma treatment (Fig. 5b).

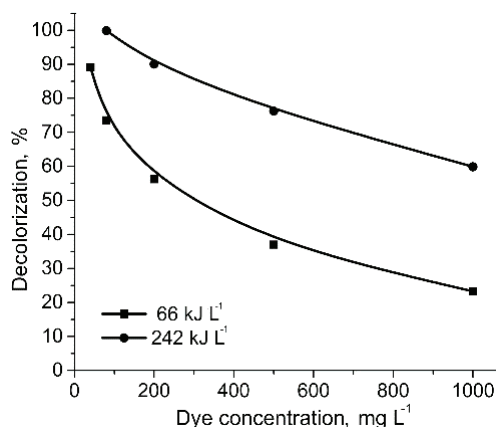


Fig. 4. Dependence of decolorization on concentration of reactive dye Reactive Black 5 ($c_0 = 40\text{-}1000 \text{ mg L}^{-1}$) for applied energy densities of 66 and 242 kJ L^{-1} (24 h after the treatment).

Determination of COD

Chemical oxygen demand ($\text{mg O}_2 \text{ L}^{-1}$) is a simple analytical method for water control. It could be used to determine the content of all substances that can be oxidized (organic and inorganic). However, it does not provide the information about the nature of organic or inorganic substances, and is more of a general indication of water pollution. If no oxidable inorganic substances in the solution are present, but only organic compounds, COD value of water is in correlation with total organic carbon (TOC) value, *i.e.*, it shows the load of water with organic substance.

COD value of initial (0 kJ L^{-1}) reactive dye Reactive Black 5 solutions ($80, 200, 500$ and 1000 mg L^{-1}) and solutions after the DBD treatment with applied energy density of 66 and 242 kJ L^{-1} were measured. COD value of plasma treated samples was measured 48 h after the treatment. Measured COD values were shown in the histogram (Fig. 6).

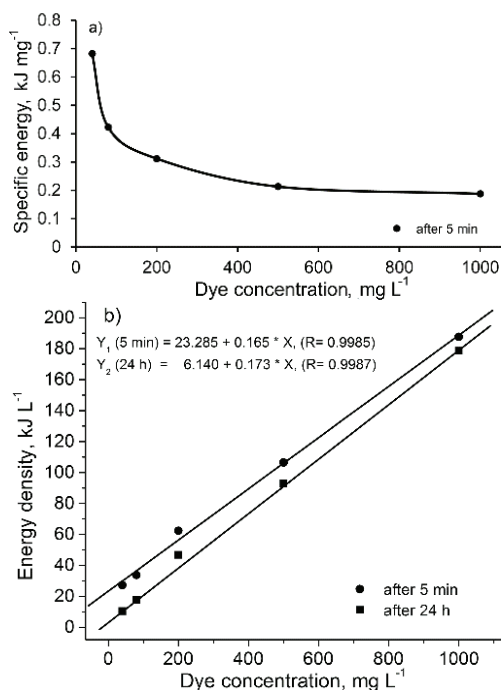


Fig. 5. Dependence of specific energy a) and applied energy density b) from the dye concentrations ($c_0 = 40\text{--}1000 \text{ mg L}^{-1}$) for 50 % decolorization efficiency.

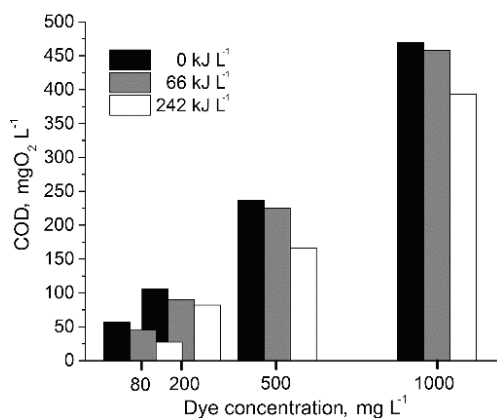


Fig. 6. *COD* values of reactive dye Reactive Black 5 solutions ($c_0 = 80, 200, 500$ and 1000 mg L^{-1}) before and after the plasma treatment (applied energy densities: 66 and 242 kJ L^{-1} ; measured after 48 h).

The decrease of *COD* with the increase of applied energy density indicate that the portion of initial dye is being completely mineralized to CO₂ during the plasma treatment in the DBD reactor. The decrease of *COD* (ΔCOD , %) as a function of initial dye concentration for applied energy densities of 66 and 242 kJ L^{-1} is shown in Fig. 7. Variation of ΔCOD values for the energy density of 242 kJ L^{-1} shown in Fig. 7 is within measurement uncertainty ($\pm 15\%$) for *COD* determination method, thus having no effect on overall data interpretation. The change of chemical oxygen demand (ΔCOD) was calculated using the equation:

$$\Delta COD = 100 \frac{COD_0 - COD_{ED}}{COD_0} \quad (2)$$

where COD_0 is chemical oxygen demand ($\text{mg O}_2 \text{ L}^{-1}$) of initial dye solution before the plasma treatment and COD_{ED} chemical oxygen demand ($\text{mg O}_2 \text{ L}^{-1}$) of dye solution after the plasma treatment, i.e. at the same energy density (ED).

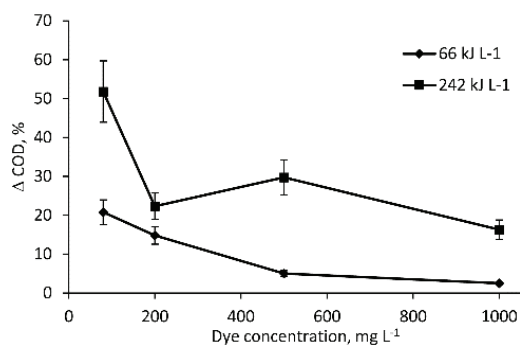


Fig. 7. The changes of chemical oxygen demand (COD) of plasma treated dye solutions for various initial dye concentrations ($c_0 = 80, 200, 500$ and 1000 mg L^{-1}) and energy densities (66 and 242 kJ L^{-1} ; after 48 h).

It could be concluded that for the energy density of 66 kJ L^{-1} increase in dye concentration resulted in gradual decrease of ΔCOD compared to energy density of 242 kJ L^{-1} (Fig. 7). These results are opposite to the ones obtained for decolorization (Fig. 4). The decolorization reaction is not always strictly followed by mineralization reaction, as the mineralization reaction could appear *via* lower intermediates. For higher applied energy density (242 kJ L^{-1}), decolorization was almost complete and decrease was more gradual with increased dye concentration, while the drop in COD value is higher due to the presence of lower intermediates at higher concentration (Fig. 8).

Determination of inorganic and organic anions using IC

Ion chromatography was used for quantitative and qualitative determination of inorganic and organic anions in initial reactive dye Reactive Black 5 solutions of $40, 80, 200, 500$ and 1000 mg L^{-1} . Also, IC analysis of anions was done for plasma treated samples of dye with applied energy densities of 66 and 242 kJ L^{-1} . Measurement was done 24 h after the plasma treatment. Qualitative and quantitative analyses were done for four anions: sulfate, oxalate, acetate and formate (Fig. 8). Chlorides, malonates, maleinates and fumarates were not detected after the plasma treatment for both applied energy densities. It is interesting to note that measured concentrations of nitrates were higher than maximum concentration of standard solution that was used for apparatus calibration. Taking into account that nitrates are being made during discharge from atmospheric nitrogen, and probably in lesser amount during dye oxidation, repeated quantification in the corresponding range of concentrations would not give the needed information about the mechanism of dye degradation.

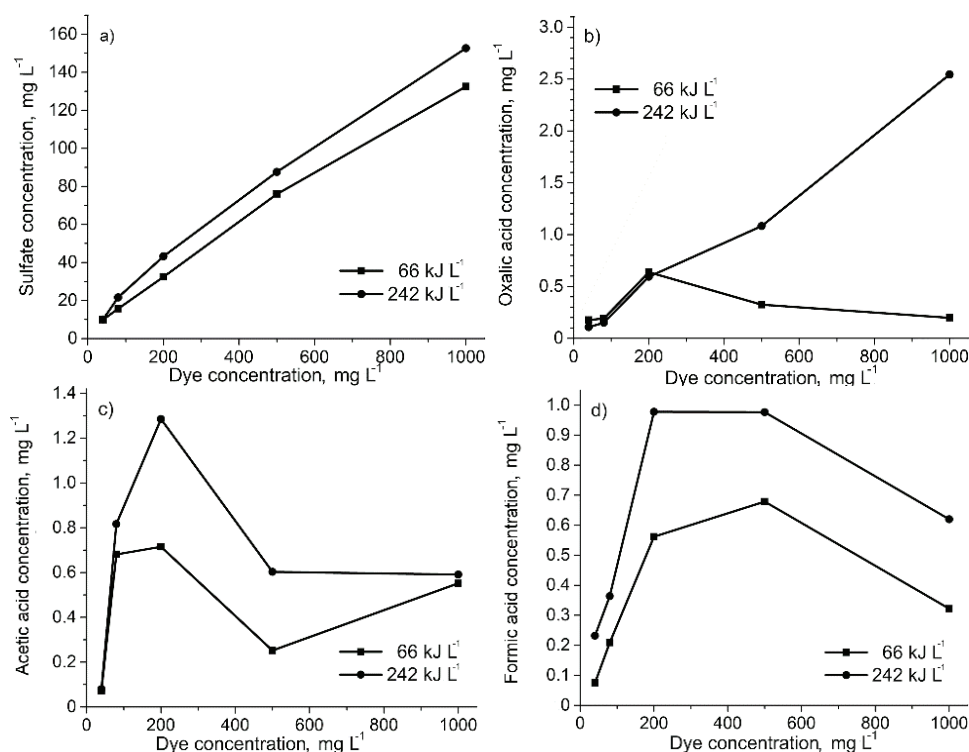


Fig. 8. The changes of concentrations of obtained anions during the plasma treatment with applied energy densities of 66 and 242 kJ L⁻¹ for various concentrations of dye Reactive Black 5: a) sulfate, b) oxalate, c) acetate and d) formate.

The change in concentration of sulfates as a function of concentration change of Reactive Black 5 after the plasma treatment and applied energy densities of 66 and 242 kJ L⁻¹ is shown in Fig. 8a. Concentration of sulfate increased with the increase of initial dye concentration for the same applied energy density. Also, increase of applied energy densities from 66 to 242 kJ L⁻¹ resulted in increased sulfate concentration. For initial dye concentration of 1000 mg L⁻¹, with applied energy densities of 66 and 242 kJ L⁻¹, measured concentrations of sulfate were 132.5 and 152.7 mg L⁻¹, respectively. Probably, sulfates originated from the part of the molecule that is linked with -CH₂CH₂- group (Fig. 1). The maximum theoretical concentration of sulfate, by this mechanism of degradation and initial dye concentration, was 193.6 mg L⁻¹. Decolorization with these applied energy densities was 23.3 and 59.6 % which indicated that the great part of the energy was spent on removal of aliphatic sulfo groups instead of decolorization process, *i.e.*, the oxidation of diazo bond. The same trend was noted for all initial dye concentrations.

The change in concentration of oxalate as a function of concentration change of Reactive Black 5 after the plasma treatment with applied energy density of 66 and 242 kJ L⁻¹ is presented in Fig. 8b. For applied energy density of 66 kJ L⁻¹, the concentration of oxalates was increased for dye concentrations up to 200 mg L⁻¹, while it decreased with further increase in dye concentration. The concentrations of oxalates were increased proportionally with the increase of initial concentration of dye in the examined range, with applied energy density of 242 kJ L⁻¹. Considering the trend of oxalate formation, it could be concluded that for lower applied energy density (66 kJ L⁻¹), and for lower dye concentrations (up to 200 mg L⁻¹), there was sufficient energy that could be used for almost complete degradation of dye to oxalates. Increase of dye concentration over 200 mg L⁻¹ and the same applied energy resulted in oxalate concentration decrease, as the applied energy was spent more on initial phases of dye degradation than on final reactions of mineralization, *i.e.*, formation of oxalates. Higher applied energy density (242 kJ L⁻¹), along with considerable degradation of the dye at all examined initial concentrations, resulted in enough energy to be spent on the final dye mineralization to oxalates and therefore there was a linear increase of their concentration.

The changes of acetate and formate concentrations as a function of the initial dye concentration change with applied energy densities of 66 and 242 kJ L⁻¹ were presented in Fig. 8c and d. It could be observed that the trend of formation of these anions for both applied energy densities was similar to the trend of oxalate formation at 66 kJ L⁻¹. Also, it can be concluded that the main reasons for such trend of acetate and formate formation are the same as for oxalates (135 kJ L⁻¹).

Results of toxicity screening bioassay

The toxicity of Reactive Black 5 dye was investigated using *Artemia salina* test organisms, and the results are shown in Fig. 9a and b. Dye toxicity was given as mortality percent of *Artemia salina* test organisms. Toxicity of untreated and treated dye solutions increased with the increase in dye concentration. Toxicity test was conducted seven days after plasma treatment, in order to ensure that possible hydrogen peroxide residues were removed by catalase. For both dilutions, the toxicity of initial dye solution increased with the increase in dye concentration. For dye concentration of 500 and 1000 mg L⁻¹ and used dilution, sample:sea water (1:1 volume ratio), the toxicity was higher than 50 %. For both dilutions, the toxicity decreased with the increased energy density (Fig. 9a and b). After plasma treatment with applied energy density of 242 kJ L⁻¹ (Fig. 9a), starting from highly concentrated dye solutions of 500 and 1000 mg L⁻¹ with mortality of 55 and 75 %, the mortality significantly decreased (below 50 %) to the values of 35 and 44 %. With the increase of dilution (sample:sea water, 1:3 volume ratio) the toxicity of non-treated and treated solutions was significantly

decreased in comparison to the less diluted solutions. After plasma treatment with applied energy densities of 66 and 242 kJ L⁻¹, the mortality for solution of 40 mg L⁻¹ decreased from 20 to 10 % (Fig. 9a). Therefore, it could be considered as non-toxic solution. For solutions of 40 and 80 mg L⁻¹ and energy density of 242 kJ L⁻¹, mortality was less than 10 % (Fig. 9b), which is below the validity criterion for mortality in the control group.

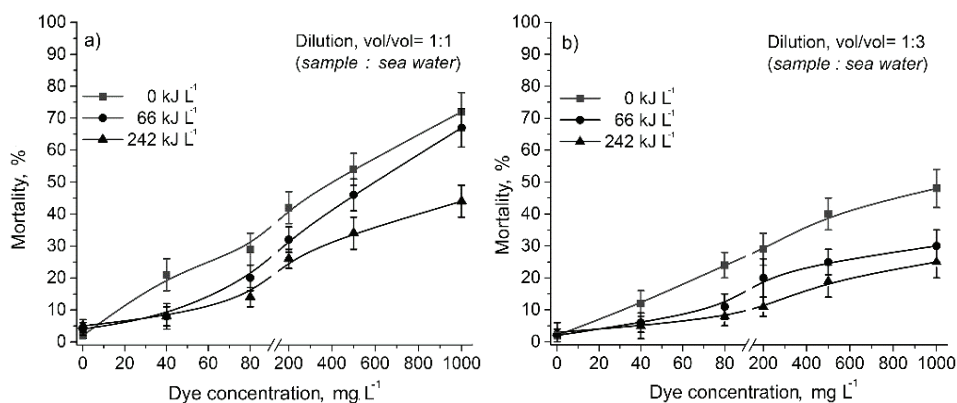


Fig. 9. Mortality of *Artemina salina* of various Reactive Black 5 solutions (c_0 , 40–1000 mg L⁻¹) before and after plasma treatment for different dilutions.

CONCLUSIONS

Degradation and detoxication of high concentrations of textile azo dye Reactive Black 5 in the range from 40 to 1000 mg L⁻¹ using non-thermal plasma reactor with gas–liquid dielectric barrier discharge were demonstrated. Applied energy density was in the range from 0 to maximal 374 kJ L⁻¹. Efficiency of decolorization at high concentrations of Reactive Black 5 (40–1000 mg L⁻¹) decreased with the increase in concentration. Complete decolorization of dye with concentrations of 40 and 80 mg L⁻¹ was achieved using applied energy densities of 110 and 198 kJ L⁻¹, respectively, while for 1000 mg L⁻¹ the maximal decolorization using energy density of 374 kJ L⁻¹ was 65 %. Also, the increase of decolorization during residence time of 24 h decreased with treated dye concentration increase. The increase of decolorization with the residence time was 10–20 % for dye concentration of 40 mg L⁻¹, while it was around 3 % for concentration of 1000 mg L⁻¹. Based on our results, the reactor capacity was reached for Reactive Black 5 concentrations above 1000 mg L⁻¹. Change in COD values of dye solutions after plasma treatment was the highest for the lowest dye concentration and applied high energy density, while it decreased with dye concentration increase. Efficient sulfate release was confirmed by IC, which indicated that larger energy portion was used for detachment of aliphatic sulfo groups than for actual decolorization process or diazo bond oxidation. This trend was observed regard-

less of the initial Reactive Black 5 concentration. Toxicological tests, with *Artemia salina* test organisms, indicated significant decrease in the toxicity of solution after treatment. Toxicity of dye solution treated with applied energy density of 242 kJ L^{-1} and dilution of sample:sea water (1:3 volume ratio) for extremely high initial dye concentration of 1000 mg L^{-1} decreased to 25 %. It could be considered as low toxic solution. For the same treatment and the same dilution for common dye concentrations in effluents (40 and 80 mg L^{-1}) toxicity is lower than 10 % which could be considered as non-toxic. Finally, it can be concluded that for common Reactive Black 5 concentrations in effluents and for low energy consumption, using DBD reactor complete decolorization, high mineralization and non-toxicity of treated solutions can be achieved.

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ИЗВОД

ПРИМЕНА НЕТЕРМИЧКОГ ПЛАЗМА РЕАКТОРА ЗА ДЕГРАДАЦИЈУ И
ДЕТОКСИКАЦИЈУ ВИСОКИХ КОНЦЕНТРАЦИЈА БОЈЕ REACTIVE BLACK 5 У ВОДИ

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У оквиру овог рада проучавана је ефикасност деградације и детоксикације високих концентрација комерцијално доступне реактивне текстилне боје Reactive Black 5 (40 , 80 , 200 , 500 и 1000 mg L^{-1}). Коришћен је унапређени оксидациони процес помоћу нетермичког плазма реактора на бази диелектричног баријерног пражњења. Овај реактор је коришћен по први пут за третман високих концентрација органских загађујућих супстанци као што је реактивна текстилна боја Reactive Black 5 у води. Раствор боје је третиран плазмом као танак слој воденог раствора који се стално обнавља. Реактор ради као континуални проточни реактор и електрично пражњење се одвија на међуфази гас-течност. Раствор боје је сукцесивно рецикулисан кроз реактор, а примењена густина енергије је била $0\text{--}374 \text{ kJ L}^{-1}$. Ефикасност деколоризације (%) је праћена помоћу UV-Vis спектрофотометрије. Узорци су узимани након сваке рецикулације ($\sim 22 \text{ kJ L}^{-1}$) и проценат деколоризације је мерен после 5 min и 24 h од плазма третмана. Ефикасност потпуне деградације (тј. минерализације) и могућих производа деградације су праћени одређивањем хемијске потрошње кисеоника (COD) и јонском хроматографијом (IC). Почетна токсичност и токсичност раствора након третмана су проучавани помоћу *Artemia salina* тест организама. Показано је да се ефикасност деколоризације смањује са повећањем концентрације боје. Потпуна деколоризација, висока минерализација и нетоксичност раствора ($<10 \%$) су постигнати након третмана плазмом при примењеној густини енергије од 242 kJ L^{-1} када су почетне концентрације Reactive Black 5 биле 40 и 80 mg L^{-1} .

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REFERENCES

1. K. Hunger, in *Industrial Dyes: Chemistry, Properties, Applications*, K. Hunger, Eds., Wiley VCH, Weinheim, 2003
2. G. M. Walker, L. R. Weatherley, *Chem. Eng. J.* **84** (2001) 125
3. U. Rott, R. Minke, *Wat. Sci. Technol.* **40** (1999) 137
4. P. C. Vandevivere, R. Bianchi, W. Verstraete, *J. Chem. Technol. Biotechnol.* **72** (1998) 289
5. J. Garcia-Montano, J. N. Ruiz, I. Munoz, X. Domenech, J. A. Garcia-Hortal, F. Torrades, J. Peral, *J. Hazard. Mater.* **138** (2006) 218
6. A. Zille, T. Tzanov, G. M. Gübitz, A. Cavaco-Paulo, *Biotechnol. Lett.* **25** (2003) 1473
7. T. Panswad, W. Luangdilok, *Water Res.* **34** (2000) 4177
8. J. T. Spadaro, L. Isabelle, V. Renganathan, *Environ. Sci. Technol.* **28** (1994) 1389
9. F. Harrelkas, A. Azizi, A. Yaacoubi, A. Benhammou, M. N. Pons, *Desalination* **235** (2009) 330
10. G. M. Walker, L. R. Weatherley, *Chem. Eng. J.* **84** (2001) 125
11. P. R. Gogate, A. B. Pandit, *Adv. Environ. Res.* **8** (2004) 501
12. S. J. Masten, S. H. R. Davies, *Environ. Sci. Technol.* **28** (1994) 180A
13. T. Krutzler, H. Fallmann, P. Maletzky, R. Bauer, S. Malato, J. Blanco, *Catal. Today* **54** (1999) 321
14. T. Zhou, X. Lu, J. Wang, F. S. Wong, Y. Li, *J. Hazard. Mater.* **165** (2009) 193
15. S. Tunç, O. Duman, T. Gürkan, *Ind. Eng. Chem. Res.* **52** (2013) 1414
16. L. Núñez, J. A. Garcia-Hortal, F. Torrades, *Dyes Pigments* **75** (2007) 647
17. E. B. Azevedo, F. R. A. Neto, M. Dezotti, *J. Hazard. Mater.* **128** (2006) 182
18. F. Javier Benitez, J. Beltrán-Heredia, J. L. Acero, F. Javier Rubio, *J. Hazard. Mater.* **79** (2000) 271
19. M. Sokmen, A. Ozkan, *J. Photochem. Photobiol., B* **147** (2002) 77
20. B. Gözmen, B. Kayana, A. M. Gizir, A. Hesenov, *J. Hazard. Mater.* **168** (2009) 129
21. K. Tanaka, K. Padermpole, T. Hisanaga, *Water Res.* **34** (2000) 327
22. B. R. Locke, M. Sato, P. Sunka, M. R. Hoffmann, J. -S. Chang, *Ind. Eng. Chem. Res.* **45** (2006) 882
23. N. Hooshmand, M. R. Rahimpour, A. Jahanmiri, H. Taghvaei, M. M. Shirazi, *Ind. Eng. Chem. Res.* **52** (2013) 4443
24. B. P. Dojčinović, G. M. Roglić, B. M. Obradović, M. M. Kuraica, M. M. Kostić, J. Nešić, D. D. Manojlović, *J. Hazard. Mater.* **192** (2011) 763
25. M. Jović, D. Manojlović, D. Stanković, B. Dojčinović, B. Obradović, U. Gašić, G. Roglić, *Chem. Eng. J.* **260** (2013) 1092
26. Y. S. Mok, J. O. Jo, J. C. Whitehead, *Chem. Eng. J.* **142** (2008) 56
27. C. M. Du, T. H. Shi, Y. W. Sun, X. F. Zhuang, *J. Hazard. Mater.* **154** (2008) 1192
28. M. Magureanu, D. Piroi, N. B. Mandache, V. Parvulescu, *J. Appl. Phys.* **104** (2008) 103306
29. M. Tichonovas, E. Krugly, V. Racys, R. Hippler, V. Kauneliene, I. Stasiulaitiene, D. Martuzevicius, *Chem. Eng. J.* **229** (2013) 9
30. X. Xu, *Thin Solid Films* **390** (2001) 237
31. U. Kogelschatz, *Plasma Chem. Plasma Process.* **23** (2003) 1
32. P. Lukes, M. Clupek, V. Babicky, V. Janda, P. Sunka, *J. Phys., D* **38** (2005) 409
33. X. Hao, X. Zhang, L. Lei, *Plasma Sci. Technol.* **15** (2013) 677
34. L. Rizzo, S. Meric, M. Guida, D. Kassinos, V. Belgiorno, *Water Res.* **43** (2009) 4070

35. M. D. Marković, B. P. Dojčinović, B. M. Obradović, J. Nešić, M. M. Natić, T. B. Tosti, M. M. Kuraica, D. D. Manojlović, *Sep. Purif. Technol.* **154** (2015) 246
36. M. Reis Da Silva, L. R. Vasconcelos de Sá, L. Vasconcelos, C. Russo, E. Scio, V. Ferreira-Leitao, *Enzyme Res.* (2010) 1
37. M. M. Kuraica, B. M. Obradović, D. Manojlović, D. R. Ostojić, J. Purić, *Vacuum* **73** (2004) 705
38. D. D. Manojlović, D. R. Ostojić, B. M. Obradović, M. M. Kuraica, V. D. Krsmanović, J. Purić, *Desalination* **213** (2007) 116
39. M. Marković, M. Jović, D. Stanković, V. Kovačević, G. Roglić, G. Gojgić-Cvijović, D. Manojlović, *Sci. Total Environ.* **505** (2015) 1148
40. M. M. Aonyas, J. Nešić, M. Jović, M. Marković, B. Dojcinović, B. Obradović, G. M. Roglić, *CLEAN – Soil Air Water* **43** (2015) 1
41. P. Vanhaecke, G. Persoone, C. Claus, P. Sorgeloos, *Ecotoxicol. Environ. Saf.* **5** (1981) 382
42. L. Yin, X. Xiaolu, L. Tian, X. Yifei, W. Xu, *Bull. Environ. Contam. Toxicol.* **88** (2012) 472
43. P. Bruggeman, D. C. Schram, *Plasma Sources Sci. Technol.* **19** (2010) 045025.