

Influence of iron on degradation of organic dyes in corona

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Abstract

In this work application of AOPs such as Fenton process, aqueous phase high voltage electrical discharge (corona) and their combination have been studied for colored wastewater treatment. Experiments were conducted on water solutions of four different organic dyes, two azo dyes C.I. Mordant Yellow 10 (MY10) and C.I. Direct Orange 39 (DO39), and two reactive of azo type C.I. Reactive Red 45 (RR45) and C.I. Reactive Blue 137 (RB137). The efficiency of studied AOPs has been estimated on the bases of UV–vis spectrophotometric and TOC measurements. The rate constants in the kinetic model have been determined. Experimental data have been compared with the developed mathematical model.

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1. Introduction

Organic synthetic dyes have been widely used as colorants in different industries such as textile, paper, color photography, pharmaceutical, food, cosmetic, etc. [1]. More than 0.7 million tons of organic synthetic dyes are produced annually worldwide. Additionally to that, over 10 000 different dyes and pigments have been applied in those industries. Recent studies indicated that approximately 12% of produced synthetic dyes per year have been lost during manufacturing and processing operations [2]. Only from the point of view of textile industries, organic synthetic dyes have been in constant expansion showing a high pollutant potential [3]. Wastewaters containing organic synthetic dyes present a very serious environmental problem because of aesthetic nature and toxicity. Namely, the coloration is visible even in a low dye concentration. The application of reactive dyes mostly for dyeing of cotton often causes colored effluents because of high solubility and hydrolysis of

those types of dyes [4]. Almost 70% of all reactive dyes are of the azo type [5]. Furthermore, commercial reactive azo dyes are intentionally designed to resist biodegradation [6]. Due to the characteristics of colored wastewaters containing reactive azo dyes, their treatment is rather difficult, especially by the conventional wastewater treatment methods based on adsorption and biodegradation [7,8]. Generally, traditional wastewater treatment methods can be broadly classified into chemical, biological, and physical–mechanical processes [9]. Physical–mechanical processes include adsorption, coagulation/flocculation, sedimentation, filtration and many other methods. Major disadvantage of those methods is that they do not concern chemical reaction, which could lead to complete mineralization, but on the contrary they produced secondary waste, which still present serious pollution problem for the environment [10]. Chemical methods, especially advanced oxidation processes (AOPs) seem to be more promising [11]. Advanced oxidation processes are a class of processes that focus on the production of hydroxyl radicals, highly reactive species, which promote oxidation of hazardous organic compounds. Common AOPs involve Fenton and Fenton “like” processes, ozonization, photochemical and electrochemical

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oxidation, photolysis with H_2O_2 and O_3 , high voltage electrical discharge (corona-in further text) process, TiO_2 photocatalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams or γ -beams and various combinations of these methods [12]. One of the most effective technologies for the removal of organic pollutants from aqueous solutions is the treatment by Fenton reagent (H_2O_2 and Fe^{2+} mixture). Chemical mechanism describing hydroxyl radicals formation [13], is presented with the chemical Eqs. (1) and (2) [14]:



Fenton reagent has been also applied successfully for colored wastewater degradation [15–17]. Recently, one of the possible methods for colored wastewater treatment without addition of chemicals is application of high voltage electrical discharge system reactors (corona reactor). Pulsed streamer high voltage electrical discharge involves application of high voltage electrical discharge in water. Various active species ($\bullet\text{OH}$, $\bullet\text{H}$, $\bullet\text{O}$, $\text{HO}_2\bullet$, O_2^- , H_2O_2 , O_3 , etc.) are considered to be produced by corona discharge in water or in an aqueous solution [18]. Among these active species, major reactive species involved in the degradation of organic pollutants are hydroxyl radicals and hydrogen peroxide. Hydroxyl radicals, aggressive and nonselective species, directly attack organic compounds leading to the oxidation of these compounds. Additionally, in the presence of iron, hydrogen peroxide produces large numbers of hydroxyl radicals through Fenton reaction [19]. Application of corona reactors for the degradation of colored wastewater containing organic dyes, including reactive and azo dyes has been reported in the literature [20,21]. Also, it has been known that addition of iron salts in pulsed streamer corona reactor enhance degradation of several organic compounds [11,12,22], including also degradation of organic dyes given in some of our previous researches [21], which induce appearance of classical Fenton process simultaneously with high voltage electrical discharge in aqueous media.

This study compares efficiency of Fenton process, pulsed streamer corona and corona reactors with addition of iron salts on degradation of several model solution based on reactive and azo dyes. Also it includes developing kinetic model for those degradation processes. Monitoring of the dye degradation was based on two criteria. First one was decolorization of model solution monitored by UV–vis. Second one was mineralization of organic dyes solutions supported by measuring of total organic carbon value (TOC).

2. Experimental

In this study experiments with the Fenton reagent were performed in a batch reactor with reaction mixture volume of 1 l. The used $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio was 1:5 and concentration of iron was 0.5 mM. Duration of experiments was 1 h and sam-

ples were taken each 10 min (0, 10, 20...60). Experiments were performed without adjusting the initial pH values.

Aqueous phase high voltage electrical discharge reactor similar like in our previous work [21] was used. The power supply circuit unit was the same like used by several other authors for degradation of different types of organic compounds in water solution [19,22–24]. Repetitive (60 Hz), fast rise time high voltage pulses with microsecond range pulse width were produced by power supply circuit unit and transported by corona discharge electrode into reactor. The point electrode (platinum wire) was placed near the bottom of the reactor. The earth ground electrode was made from reticulated vitreous carbon (RVC) [22] and submerged under the solution surface. Homogeneous mixing of solution was achieved by magnetic stirring bar. The glass vessel of 1 l was used as a reactor (see Fig. 1). The applied voltage was 45 kV and duration of each experiment was 1 h. Experiments were performed with and without addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Fe^{2+} salt). In all experiments without Fe^{2+} addition, conductivity was adjusted at $150 \mu\text{S}/\text{cm}$ with 0.1 M KCl solution. Samples were taken every 10 min (0, 10, 20...60). Experiments with iron addition were performed with concentration of iron salt of 0.05 mM. Samples were collected within 60 min. Conductivity of approximately $150 \mu\text{S}/\text{cm}$ was achieved by addition of Fe^{2+} salt. Initial and final pH and conductivity were measured.

Initial dye concentration of 20 mg/l was used in all experiments. Decolorization was monitored by the UV–vis spectrophotometers Perkin-Elmer EZ Lambda 201 and Specol 20 at maximum wavelengths (λ_{max} , Table 1). Dye mineralization grade was determinate by TOC analysis performed on Total Organic Carbon Analyzer, TOC-V_{CPN} Shimadzu. Initial and final pH and conductivity were measured by Cole-Parmer Model 1484-10 conductivity meter.

Four different types of organic dyes, two monoazo and two monochlorotriazine reactive dyes of azo type, were used (Table 1). DO39, RR45 and RB137 are commercial dyestuffs, obtained from CIBA-Geigy, Switzerland and Bayer AG, Germany, and purified while MY10 was synthesized in our laboratory following the procedure from the literature [25].

2.1. Model formulation

The mathematical model which includes 18 chemical species (ions, atoms and molecules) and 54 chemical reactions has been developed using chemical reactions and rate constants from the literature [19,22]. The general mass balance for a well-mixed, constant volume and constant temperature batch reactor is given by:

$$\frac{dc_i}{dt} = -r_i \quad (3)$$

where c_i is concentration in the bulk solution of species i , and r_i is the bulk phase rate of that species. A total of 54 simultaneous ordinary differential equations were solved using *Mathematica* 5.0 (Wolfram Research, Champaign, IL). The total rate constants for the degradation of MY10, DO39,

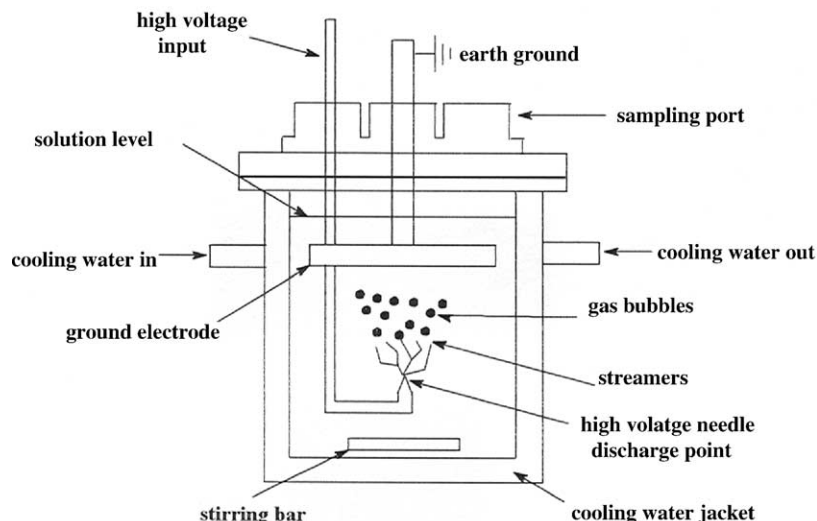


Fig. 1. Experimental setup of corona reactor used.

RR45 and RB137 by hydroxyl radicals were determined by trial and error method fitting the values for the rate constants for the degradation of the dyes into the model.

3. Results and discussion

For the decolorization and degradation of MY10, DO39, RR45 and RB137 by Fenton process, 0.5 mM of FeSO₄·7H₂O and 2.5 mM of H₂O₂ have been used. From the Fig. 2 it can be seen that obtained decolorization extents after 1 h varied from 43 to 93%. The lowest result was achieved for decolorization of MY10 by Fenton reagent. Namely, as it was mentioned before MY10 was synthesized and purified by crystallization in our laboratory and purity of MY10 dyestuff

sample it self has been almost 100%, while other studied dyes were commercial dyestuffs with less purity. For the DO39 and RB137 more than 90% color removal was obtained while with the same conditions 70% of RR45 was decolorized. Mineralization extents of the studied dyes expressed as percentage of TOC removal obtained in the Fenton process have been shown on the Fig. 3. The results have ranged between 29 and 37%. The highest mineralization extent was obtained for DO39 (37%).

The second applied AOP for the decolorization of MY10, DO39, RR45 and RB137 solutions was pulsed corona discharge process. Among the AOPs wastewater treatment methods, pulsed corona discharge was chosen for the decomposition of the studied dyes because corona by itself produces certain amount of OH•, such as in Fenton process. Within the

Table 1
Molecular structures of the studied dyes

Dye	Name	Structure	λ _{max} (nm)
MY10	C.I. Mordant Yellow 10		360
DO39	C.I. Direct Orange 39		420
RR45	C.I. Reactive Red 45		520
RB137	C.I. Reactive Blue 137		610

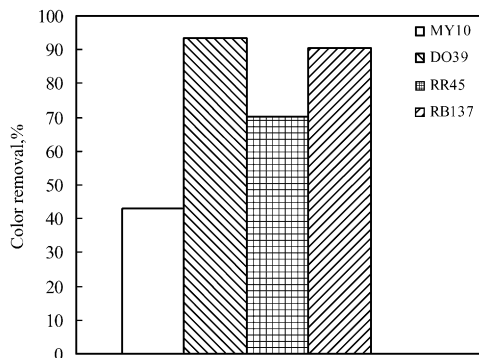


Fig. 2. Color removal after 1 h treatment with Fenton process (0.5 mM of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

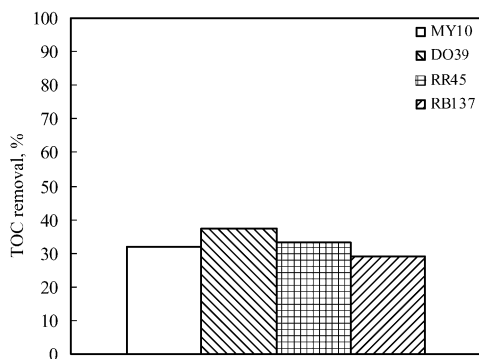


Fig. 3. Mineralization extent after 1 h treatment with Fenton process (0.5 mM of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

system in corona reactor it is possible to avoid the addition of any other chemicals, which could load treated wastewater [19]. Decolorization efficiency for the treatment of MY10, DO39, RR 45 and RB137 in corona reactor has been shown on the Figs. 4–6. Obtained color removals in 1 h of corona treatment are given with absorbance versus time and presented on the Fig. 4. Decreasing of absorbances during the reaction of corona treatment can be seen, which imply the chromophore destruction. The same results expressed as percentage of color removal versus time were presented on

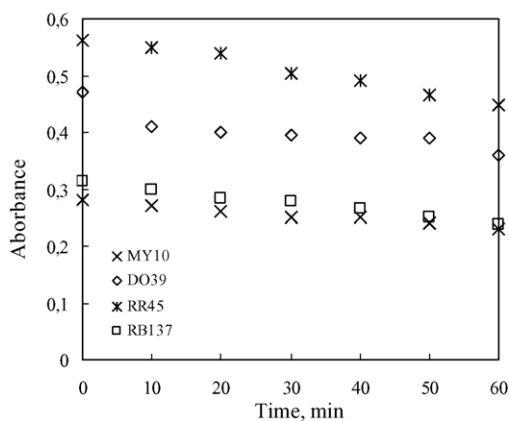


Fig. 4. Decreasing of absorbance during 1 h treatment with corona.

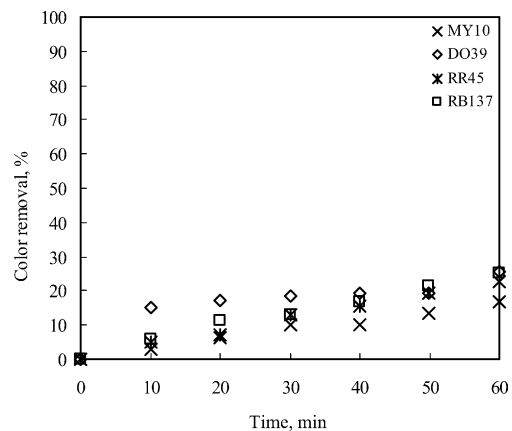


Fig. 5. Color removal increase during the 1 h corona treatment.

the Fig. 5. From these two figures it can be seen that final obtained decolorization extents were similar for the reactive dyes, 22.6% for the RR45 and 25.2% for the RB137, while results for the azo dyes of 25.6% for the DO39 and 17% have shown higher differences for resulting decolorization extents. Relatively poor decolorization extent of MY10 could be described at the same manner as in the discussion of the reason for the low decolorization extent of MY10 with Fenton process (Fig. 2).

Since it has been known that significant quantity of hydrogen peroxide was produced during the pulsed corona discharge [22] and in our study it was observed that corona process by itself was not shown efficient enough (only 25.6%) for the color removal, a set of experiments using addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ directly to corona reactor has been performed in order to enhance the production of hydroxyl radicals. The amount of 0.05 mM of Fe^{2+} has been added to the corona reactor. Results of the UV–vis spectrophotometric measurements versus time have been shown on Fig. 6. Significant increase of absorption for the MY10 decolorization can be observed and could be caused by the formation of the brownish Fe^{2+} -complex, which induces interference in the UV–vis spec-

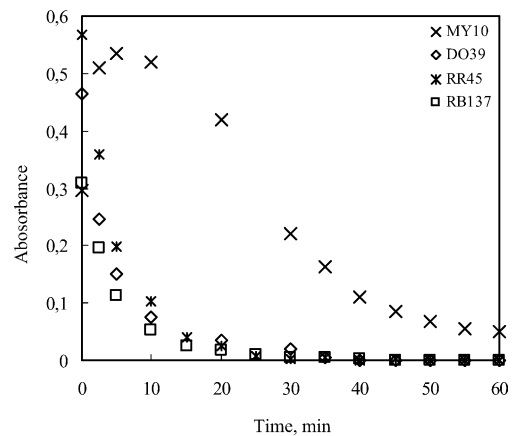


Fig. 6. Absorbance dependence during the 1 h treatment with corona and Fenton process combination (0.05 mM of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

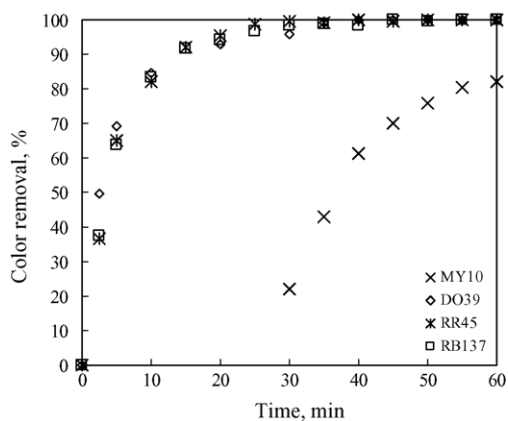


Fig. 7. Color removal increasing during the 1 h treatment with corona and Fenton process combination (0.05 mM of FeSO₄·7H₂O).

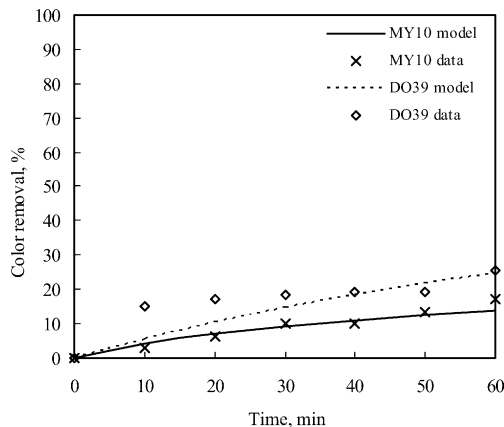


Fig. 9. Comparison of experimental and model data for decolorization extents for the studied azo dyes in corona reactor.

trophotometric measurement. Also it is known that iron complexes of mordant azo dyes would yield brown to black shades [26]. This complex absorb at higher wavelengths. As the reaction was progressing the Fe²⁺-complex has been destroyed by the attack of hydroxyl radicals formed in the corona and Fenton process as well. In the case of other studied dyes just absorption decrease versus time was observed (Fig. 6). On the Fig. 7 decolorization kinetics for the studied dyes have been shown. The slowest decolorization rate was observed in the case of MY10 due to the complex formation. It can be seen that DO39, RR45 and RB137 were 100% decolorized after 1 h in corona reactor with addition of 0.05 mM Fe²⁺, while MY10 was 83% decolorized under the same conditions. On the Fig. 8 mineralization efficiency for the combination of corona and Fenton processes have been shown. The range of mineralization extents from 39% for the MY10 up to almost 100% for the DO39 can be seen. Relatively high percentage of the TOC removal for the DO39 can be explained with the relatively simple structure of the DO39 molecule in comparison with the other molecules of reactive dyes. The relatively low mineralization extent of MY10 could be explained at the same way as it was mentioned earlier (Fig. 2).

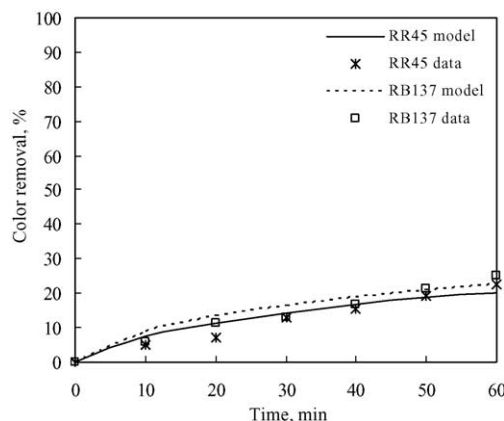


Fig. 10. Comparison of experimental and model data for decolorization extents of the studied reactive azo dyes in corona reactor.

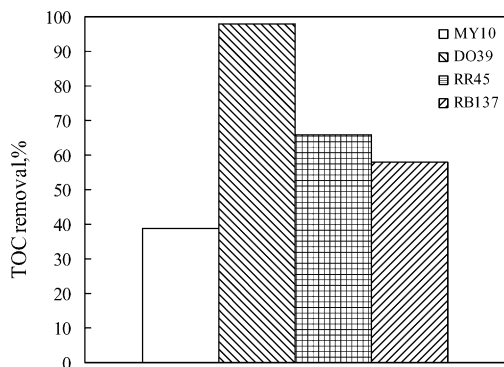


Fig. 8. Mineralization extent after 1 h treatment with corona and Fenton process combination (0.05 mM of FeSO₄·7H₂O).

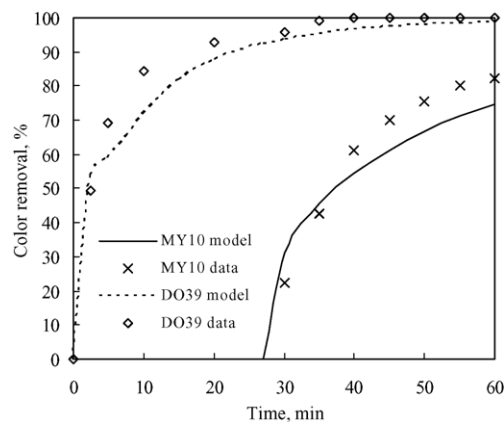


Fig. 11. Comparison of experimental and model data for decolorization extents of the studied azo dyes during the treatment with corona and Fenton process combination (0.05 mM of FeSO₄·7H₂O).

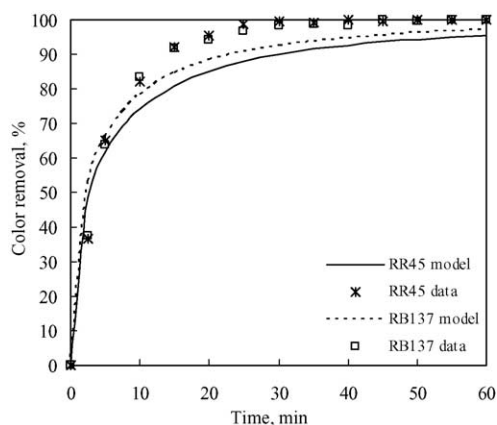


Fig. 12. Comparison of experimental and model data for decolorization extents of the studied reactive azo dyes during the treatment with corona and Fenton process combination (0.05 mM of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

Table 2
Rate constants of the studied dyes

Dye	Rate constant (M^{-1}/min)
MY10	1.3×10^8
DO39	8.4×10^{10}
RR45	1.5×10^8
RB137	1.9×10^9

degradation of the dyes by corona discharge and Fenton processes have been shown in the Table 2. It can be seen that the highest one is the rate constant for the DO39 degradation with hydroxyl radicals. From the calculations obtained using *Mathematica* 5.0 it can be seen that the concentration of hydroxyl radicals is relatively negligible in comparison to concentrations of studied dyes, 10^{-14} versus 10^{-5} . Therefore, the kinetic of reaction between HO^\bullet and a dye molecule could be considered as “pseudo-first” order [12].

4. Conclusion

For the decolorization and degradation of MY10, DO39, RR45 and RB137 Fenton and corona discharge processes as well as their combination were applied. The studied dyes were decolorized up to 93% depending on the dye molecule structure while the mineralization extents were up to 37%. Fenton process was the most successful for the DO39 decolorization and degradation, 93 and 37%, respectively. Decolorization of studied dyes with corona discharge process was achieved to 26%. The highest color removal (26%) was obtained for the DO39. Decolorization and degradation of the studied dyes with the combination of corona discharge and Fenton processes were up to 100 and 98%, respectively. Again, the highest mineralization extent was obtained for the DO39. Decolorization of the studied dyes can be described with the “pseudo-first” order reaction kinetics.

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