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Fenton type processes for minimization of organic content in coloured wastewaters: Part I: Processes optimization

Hrvoje Kušić, Ana Lončarić Božić, Natalija Koprivanac*

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulicev trg 19, Zagreb 10000, Croatia

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Abstract

This study was focussed on the application of Fenton (Fe^{2+}/H_2O_2) and Fenton "like" processes (Fe^{3+}/H_2O_2 and Fe^0/H_2O_2) for the minimization of organic content of coloured synthetic wastewaters. Two reactive dyes, C.I. Reactive Blue 49 with anthraquinone chromophore and C.I. Reactive Blue 137 with azo chromophore were used as model organic pollutants. Fenton type processes were investigated in order to establish optimal operating conditions (pH, concentration of iron salts or iron powder, and ratio of Fenton reagent) for the maximal degradation of investigated model coloured wastewaters. Degradation of studied dyes as organic pollutants was monitored on the basis of decolourization and mineralization extents of model solutions, determined by UV/vis spectrophotometric, and TOC and AOX analyses, respectively. Colour removal $> 95\%$ was achieved by all the applied processes, while mineralization extents ranged between 34 and 72% depending on the dye structure and applied AOP.

Keywords: Coloured wastewater; Reactive dyes; Fenton process; Fenton "like" process; Process optimization

1. Introduction

Synthetic dyes are present in many spheres of our everyday life and their application is continuously growing. Dyes make our world beautiful, but they bring pollution. Wastewaters originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature [1,2]. So there is a clear need to treat dye wastewater prior to discharge into the effluent.

Traditional wastewater treatment technologies based on aerobic and anaerobic digestion were proven to be markedly ineffective for handling wastewater containing reactive dyes. This type of wastewater is characterized by low biodegradability due to the recalcitrant nature, i.e. chemical stability of these pollutants [3–5]. Furthermore, wastewater treatment methods based on physical processes such as reverse osmosis, adsorption on activated carbon, and coagulation/flocculation, although effective for colour removal in many cases, are non-destructive and merely transfer pollutants to other media, thus causing secondary waste [1,6,7]. Chemical treatment by chlorine, the most widely used chemical oxidant in the past, has been restricted in many countries due to the possible health effects from the generation of organochlorine compounds [8].

The limitations of conventional wastewater treatment methods can be overcome by the application of the so-called Advanced Oxidation Processes (AOPs), which present a potential alternative ability to decolorize and to reduce recalcitrant coloured wastewater loads [9]. AOPs are based on the generation of very reactive species such as hydroxyl radicals that rapidly and nonselectively oxidize a broad range of organic pollutants [10]. Common AOPs involve Fenton and Fenton "like" processes, ozonation, photochemical and electrochemical oxidation, photolysis with H_2O_2 and O_3, high voltage electrical discharge (corona) process, TiO_2 photocatalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams or γ-beams and various combinations of these methods [11–13].

When the treatment method for dye wastewater is considered, it is important to be aware of the inevitable secondary

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* Corresponding author. Tel.: +385 1 4597 124; fax: +385 1 4597 143.
E-mail address: nkopri@marie.fkit.hr (N. Koprivanac).

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considerations that go beyond the actual removal of colour. These considerations include: sludge production and handling cost requirements, the level of operational skill required, the operational and maintenance attention needed, the long-term system reliability and the total system costs [14]. Compared with other oxidation processes, processes using Fenton type reagent are relatively cheap, easily operated and maintained [15]. Fenton process, one of the most effective processes for the removal of organic pollutants from aqueous solutions [16–18], involves the application of ferrous salts and hydrogen peroxide to produce hydroxyl radical according to Eqs. (1) and (2) [19]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (2)$$

In Fenton "like" processes, ferric salts or iron powder is used as a source of catalytic iron [20–24]. In acid conditions, iron powder reacts with hydrogen peroxide producing ferrous ions, Eq. (3) [25]:

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^- \qquad (3)$$

From the environmental point of view, advantage of the implementation of iron powder (Fe^0) instead of iron salts is the avoidance of unnecessary loading of aquatic system with counter anions [26]. Furthermore, the concentration of ferrous and ferric ions in wastewater treated by Fenton "like" process with iron powder is significantly lower in comparison to Fenton type processes that utilize iron salts [27].

The efficiency of Fenton and Fenton "like" processes depends on the generation rate and concentration of the hydroxyl radicals produced through the Fenton reaction [16]. Operational parameters of Fenton type processes that directly influence their efficiency are iron concentration, source of iron catalysts (iron powder, ferrous or ferric salts), H_2O_2 concentration, iron catalysts/hydrogen peroxide ratio (Fenton reagent), temperature, pH and treatment time [28].

In this study, Fenton (Fe^{2+}/H_2O_2) and Fenton "like" (Fe^{3+}/H_2O_2 and Fe^0/H_2O_2) processes were applied for the minimization of organic content of coloured synthetic wastewaters. Two reactive dyes, C.I. Reactive Blue 49 with anthraquinone chromophore and C.I. Reactive Blue 137 with azo chromophore were used as model organic pollutants. Investigations were carried out in order to establish optimal operating conditions: pH, concentration of iron salts or iron powder, and Fenton reagent ratio for the degradation of studied dyes in model coloured wastewaters. Decolourization and mineralization extents of the model solutions were determined by UV/vis spectrophotometric analysis and total organic carbon (TOC), and adsorbable organic halides' (AOX) content measurements, respectively.

2. Experimental

Series of experiments were conducted in order to find an optimal pH for each of the applied Fenton type processes. At the beginning of the experiment, pH was adjusted to 2, 3 and 4 using 25% sulphuric acid, which was followed by the addition of Fenton reagent. Ferrous and ferric sulphates, $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$, and iron powder were used as sources of iron catalysts in the applied Fenton type processes. Furthermore, experiments for determining optimal iron catalysts/hydrogen peroxide molar ratio were performed. Iron concentrations were 0.5 and 1.0 mM, while the concentration of hydrogen peroxide was varied to give molar ratios 1:5, 1:10, 1:20, 1:30, 1:40, and 1:50. Reaction mixture ($V = 250$ mL) was continuously stirred at room temperature in an open-batch system with magnetic stirring bar and was treated for 2 h, while dye concentration and TOC values were measured at the end of each experiment to establish decolourization and mineralization extents.

Two reactive dyes, C.I. Reactive Blue 49 (RB49) with anthraquinone chromophore and C.I. Reactive Blue 137 (RB137) with azo chromophore, supplied by CIBA-Geigy, Switzerland, were used as model pollutants (Table 1). Experiments were performed using model wastewater with dye concentration 20 mg l^{-1}.

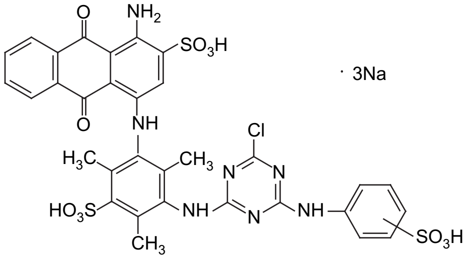
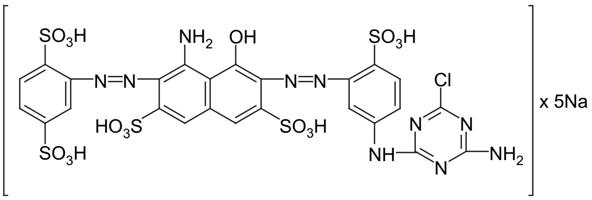
A Perkin Elmer Lambda EZ 201 UV/vis spectrophotometer was used for decolourization monitoring at λ_{max} for each dye, while mineralization extents of RB49 and RB137 were determined on the basis of total organic carbon content measurements (TOC) performed by total organic carbon analyzer, TOC-V_{CPN} 5000 A, Shimadzu, and adsorbable organic halides (AOX), performed by Organic Halide Analyzer, DX-2000, Dohrmann.

3. Results and discussion

3.1. Fenton process, Fe^{2+}/H_2O_2

Influence of iron concentration, Fe^{2+}/H_2O_2 molar ratio, and initial pH on the effectiveness of Fenton process for RB49 degradation expressed as colour and TOC removal is summarized in Table 2 and Fig. 1, respectively. It can be seen that the decolourization of model wastewater is rather successful. At applied operating parameters, decolourization extents range between 73 and 98.5%. The chromogenic part of the organic dye molecule RB49, anthraquinonic ring, with its conjugated double bound system is rather susceptible to OH radical attack. This could be the reason why the varying of operating parameters within applied ranges did not result in significant difference in decolourization efficiency. However, the best results were achieved at pH 3 with colour removal of 92–98.5%. Besides decolourization, degradation of organic dye molecule is characterized by a decrease in the total organic content i.e. value of TOC parameter. From the results presented in Fig. 1 it can be seen that the values of obtained mineralization extents are significantly lower in comparison to decolourization extents. Furthermore, mineralization extents demonstrate higher sensitivity to the changes in operating parameters. Besides decolourization at initial pH 3 the highest TOC removal was obtained, as well. Lower effectiveness at decreased pH values can be contributed to the formation of $[Fe^{2+}(H_2O)]$ which is less reactive in comparison to the free Fe^{2+} ionic form

Table 1
Molecular structures of the studied dyes

Dye	C.I. name	Structure	λ_{max} (nm)
RB49	Reactive Blue 49		590
RB137	Reactive Blue 137		610

[29–31]. Besides, at lower pH, hydrogen ions act as OH radical scavengers [28]. On the other hand, at higher pH values the concentration of free Fe^{2+} ions decreases due to the formation of ferrous complexes, thus disabling the formation of OH radical through the initial Fenton reaction. Furthermore, dye degradation efficiency by Fenton process is also influenced by the concentration of Fe^{2+} ions which catalyze hydrogen peroxide decomposition resulting in OH radical production and consequently the degradation of organic molecule. According to the literature, the minimal concentration of ferrous ions for the initiation of Fenton reaction ranges between 3 and 15 mg l^{-1} [28]. Generally, with increasing ferrous salt concentration, degradation rate of organic compound also increases, but only to that certain level where further addition of iron becomes inefficient [19,28]. From the results presented in Fig. 1 it can be seen that higher RB49 mineralization extents were obtained with lower Fe^{2+} concentration (0.5 mM) at the same pH values with all applied Fe^{2+}/H_2O_2 ratios. Concentration of hydrogen peroxide is one of the operating parameters that significantly influence the final mineralization extent. With further increasing hydrogen peroxide concentration, degradation efficiency also increases with the achievement of certain optimal Fenton reagent ratio. With further increasing of hydrogen peroxide concentration degradation efficiency is decreasing due to the scavenging nature of hydrogen peroxide towards OH radicals when it is present in higher concentration. The result is the formation of perhydroxyl radicals which are significantly less reactive species than hydroxyl radicals and thus directly influence the efficiency of dye degradation [25]. According to the literature, typical values of Fenton reagent ratio are in the range between 1:5 and 1:25 [28,32]. The optimal operating parameters for RB49 degradation by Fenton process established on the basis of TOC measurements are $Fe^{2+}/H_2O_2 = 1{:}20$, $c(Fe^{2+}) = 0.5$ mM, pH 3, where maximal TOC removal of 72.1% was achieved (Fig. 1).

As another pollutant of model wastewater, reactive dye RB137 with azo chromophoric group was used. According to the results of optimization of initial pH carried out for RB49 (Table 2 and Fig. 1), which are found to be in accordance with the literature [33–35], experiments for the optimization of other two operating parameters of Fenton process

Table 2
RB49 colour removal at different operating conditions for Fenton process

Fe^{2+}/H_2O_2	Colour removal (%)					
	pH 2		pH 3		pH 4	
	$c(Fe^{2+}) = 0.5$ mM	$c(Fe^{2+}) = 1.0$ mM	$c(Fe^{2+}) = 0.5$ mM	$c(Fe^{2+}) = 1.0$ mM	$c(Fe^{2+}) = 0.5$ mM	$c(Fe^{2+}) = 1.0$ mM
1:5	96.30	87.37	97.85	95.98	89.89	88.04
1:10	95.98	91.71	97.77	96.14	90.13	90.38
1:20	96.32	95.60	98.30	96.42	90.02	87.73
1:30	94.13	95.59	98.51	96.61	87.64	89.28
1:40	93.02	85.40	97.99	92.12	88.27	89.49
1:50	89.87	89.87	98.02	94.50	72.75	86.98

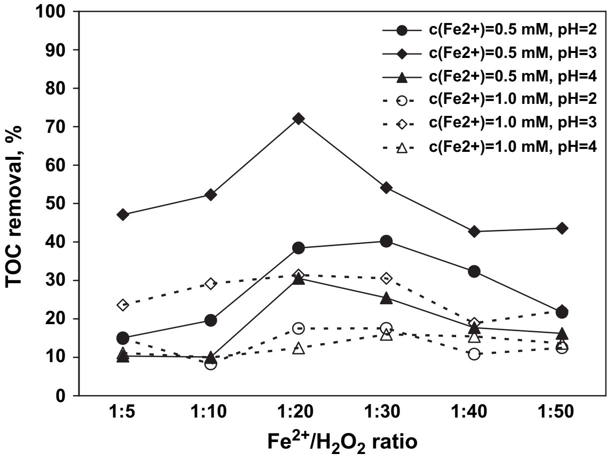


Fig. 1. Influence of the operating parameters of Fenton process, Fe^{2+}/H_2O_2, for the degradation of RB49 on TOC removal.

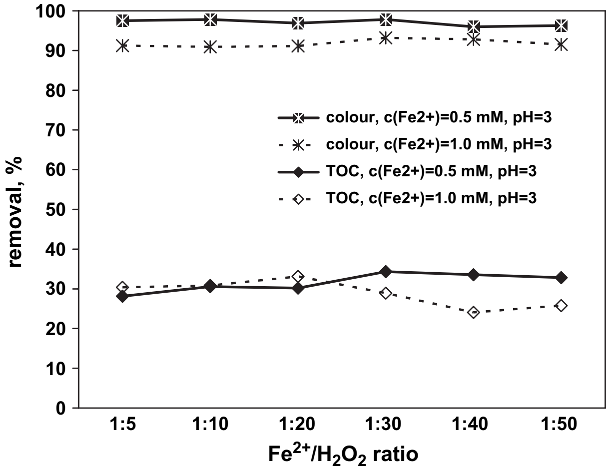


Fig. 2. Influence of ferrous concentration and Fe^{2+}/H_2O_2 ratio on colour and TOC removal in Fenton process for the degradation of RB137 at pH 3.

(Fe^{2+} concentrations and Fe^{2+}/H_2O_2 ratio) for degradation of RB137 in model wastewater were conducted at pH 3. In Fig. 2 decolourization and mineralization extents of RB137 solution depending on the concentration of ferrous ions and Fenton reagent ratio are presented. It can be seen that RB137 solution was decolourized almost completely with lower Fe^{2+} concentration (0.5 mM), 96–98% of colour removal, while in cases with higher Fe^{2+} concentration (1.0 mM) obtained colour removal ranges between 91 and 93%. It can be concluded that azo chromophores in RB137 are susceptible to OH radical attack as well as anthraquinonic chromophore in RB49 (Table 2). These results suggest that the oxidation would preferably occur on the chromophore structure rather than on the dye molecule skeletons. Again, obtained mineralization extents, 24–34.3%, are significantly lower in comparison to the decolourization extents, 91–98%, in the entire investigated range. They are also lower in comparison to mineralization extents obtained for degradation of RB49 at the same conditions. This indicates that molecular structure is an important factor that influences the effectiveness of dye degradation by Fenton process. Tang and Chen [24] studied the decolourization kinetics of three commercial dyes by H_2O_2/iron powder system, where Fenton's reactions are the dominant mechanisms contributing to dye decolourization, and they found that decolourization rates for anthraquinone dyes were higher than for azo dyes. Similar observations concerning decolourization followed by the mineralization of anthraquinone and azo type of dye by oxidation through OH radical mechanism were reported by several authors [36,37]. Since decolourization, i.e. the cleavage of bonds in the chromophoric group of dye molecule precedes further mineralization, it is expected that higher decolourization rate consequently results with the higher mineralization extent, which is in accordance with the results obtained in this study. On the basis of TOC removal, Fenton process with ratio of $Fe^{2+}/H_2O_2 = 1{:}30$ and $c(Fe^{2+}) = 0.5$ mM at pH 3 is proven to be the most efficient process for degradation of RB137, with 34.3% of TOC removal (Fig. 2).

3.2. Fenton "like" process, Fe^{3+}/H_2O_2

Like in earlier described Fenton process, the influence of optimal operating parameters to the efficiency of Fenton "like" process, Fe^{3+}/H_2O_2, for RB49 and RB137 degradation was investigated. Series of experiments were performed in order to establish optimal pH, Fe^{3+} ions concentration and Fe^{3+}/H_2O_2 ratio for the maximal degradation of RB49 and RB137 by Fenton "like" process. As it can be seen from the results presented in Table 3, Fenton "like" process, Fe^{3+}/H_2O_2, was shown to be very efficient for the bleaching of RB49 model solution with 87–99% colour removal in the

Table 3
RB49 colour removal at different operating conditions for Fenton "like" process, Fe^{3+}/H_2O_2

Fe^{3+}/H_2O_2	Colour removal (%)					
	pH 2		pH 3		pH 4	
	$c(Fe^{3+}) = 0.5$ mM	$c(Fe^{3+}) = 1.0$ mM	$c(Fe^{3+}) = 0.5$ mM	$c(Fe^{3+}) = 1.0$ mM	$c(Fe^{3+}) = 0.5$ mM	$c(Fe^{3+}) = 1.0$ mM
1:5	98.37	97.54	98.93	98.39	94.58	93.88
1:10	98.82	97.54	98.39	97.99	96.09	94.44
1:20	98.56	96.37	97.85	97.31	96.30	92.58
1:30	97.78	97.17	97.85	98.20	94.87	91.18
1:40	98.03	97.24	98.39	96.87	95.55	90.07
1:50	97.80	97.18	97.90	97.52	93.28	86.98

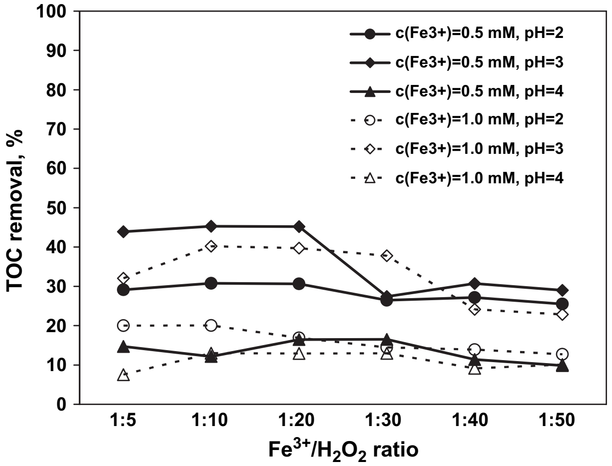


Fig. 3. Influence of the operating parameters of Fenton "like" process, Fe^{3+}/H_2O_2, for the degradation of RB49 on TOC removal.

applied range of operating parameters. In spite of such high decolourization efficiency, RB49 mineralization extents obtained by the Fenton "like" process, Fe^{3+}/H_2O_2, (Fig. 3) are significantly lower in comparison to those achieved by Fenton process (Fig. 1). It can be seen that pH value significantly influences the mineralization of RB49 by Fe^{3+}/H_2O_2. The highest mineralization extent of RB49 model solution, 45.3% TOC removal, was achieved by $Fe^{3+}/H_2O_2 = 1{:}10$ and $c(Fe^{3+}) = 0.5$ mM at pH 3 (Fig. 3). Similar colour removal, 87–95%, and mineralization extents, 32–45.3%, were obtained for the treatment of RB137 model solution by Fe^{3+}/H_2O_2 (pH 3, ferric concentration of 0.5 and 1 mM, and varied Fe^{3+}/H_2O_2 ratios between 1:5 and 1:50 (Fig. 4)).

3.3. Fenton "like" process, Fe^0/H_2O_2

Fenton "like" process, Fe^0/H_2O_2, was optimized in the same manner as described earlier. Iron powder was utilized instead of ferrous and ferric salts as a source of iron catalyst in Fenton reagent. In Fe^0/H_2O_2 process, 28 mg l^{-1} and 56 mg l^{-1} of iron powder were added which correspond to 0.5 and 1.0 mM iron concentration, respectively, as used in Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes. Colour removal results obtained after the treatment of RB 49 by Fe^0/H_2O_2 are presented in Table 4. It can be observed that slightly better bleaching, 98–100%, was achieved in the entire studied pH range with the usage of lower concentration, 0.5 mM, than with 1.0 mM of iron powder where colour removal ranged 85–98%. At pH 4, lower decolourization efficiency of Fenton "like" process, Fe^0/H_2O_2, is perceived, as well as in Fenton, Fe^{2+}/H_2O_2 and Fenton "like", Fe^{3+}/H_2O_2 processes. These results indicate that after the initial leaching of Fe^{2+} ions from the iron powder surface, dye degradation is carried out mainly throughout by the Fenton oxidation mechanism in the bulk. Since successful colour removal was achieved in all cases, the optimization of operational parameters of Fe^0/H_2O_2 process for the degradation of RB49 was conducted on the basis of TOC removal measurements (Fig. 5). The highest mineralization of RB49 model solution, 46.9% of TOC removal, was achieved in the case with $Fe^0/H_20_2 = 1{:}20$, $c(Fe^0) = 0.5$ mM at pH 3. It can be seen that higher concentration of iron powder negatively affects the degradation efficiency of RB49 by Fe^0/H_2O_2. Similar effect was observed by increasing the hydrogen peroxide concentration over Fe^0/H_2O_2 ratio 1:20. At higher hydrogen peroxide concentrations, an inert oxidative film on the iron powder surface could be created thus disabling further leaching of Fe^{2+} ions. Tang and Chen [24] investigated the application of Fenton "like" process with iron powder for the degradation of different types of dyes: Reactive Red 120, Direct Blue 160 and Acid Blue 40, and they established that the optimal operating pH value ranges between 2 and 3, depending on the molecular structure of studied dyes. The same authors reported that the optimal dosage of iron powder is also significantly influenced by the molecular structure of the studied dye. In the same manner as for RB49, the influence of iron powder concentration and Fe^0/H_2O_2 ratio for degradation of RB137 model solution were investigated (Fig. 6). Again, almost complete bleaching was achieved in all cases, while the best mineralization extent with 45.3% of TOC removal was obtained in the case with $Fe^0/H_20_2 = 1{:}20$, $c(Fe^0) = 1.0$ mM at pH 3. The efficiency of Fe^0/H_20_2 process for the degradation of RB137 was higher in comparison to Fe^{2+}/H_2O_2 process. One of the major advantages of iron powder application in Fenton type processes instead of iron salts is that the concentration of iron in wastewater after the treatment is significantly lower [24]. According to Lücking et al. [27] the amount of iron ions can be reduced up to 50%. Moreover, the utilization of Fe^0/H_2O_2 process considers the avoidance of additional loading of treated wastewater with other anions, while relatively small amount of remaining iron powder can be easily removed from the treated wastewater after the treatment. Although the major dye degradation mechanism in Fe^0/H_2O_2 process is oxidation throughout Fenton reactions in the bulk, the adsorption of dye molecule onto the iron powder surface where oxidation reaction with OH radicals occurs positively contributes to the overall efficiency of dye degradation. From the literature,

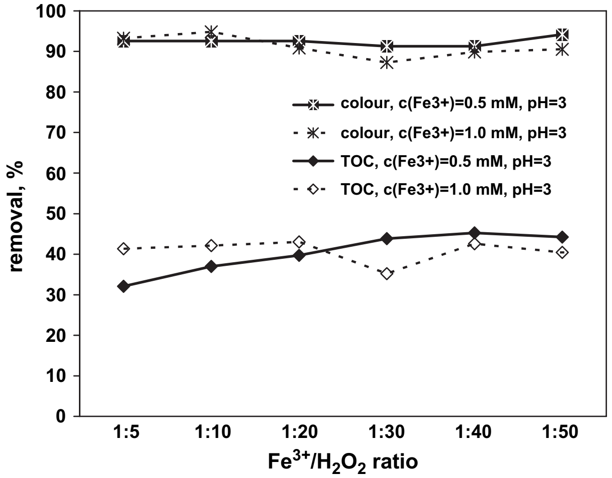


Fig. 4. Influence of ferric concentration and Fe^{3+}/H_2O_2 ratio on colour and TOC removal in Fenton "like" process for the degradation of RB137 at pH 3.

Table 4
RB49 colour removal at different operating conditions for Fenton "like" process, Fe^0/H_2O_2

Fe^0/H_2O_2	Colour removal (%)					
	pH 2		pH 3		pH 4	
	$c(Fe^0) = 0.5$ mM	$c(Fe^0) = 1.0$ mM	$c(Fe^0) = 0.5$ mM	$c(Fe^0) = 1.0$ mM	$c(Fe^0) = 0.5$ mM	$c(Fe^0) = 1.0$ mM
1:5	98.42	91.12	99.47	84.95	98.16	85.55
1:10	99.84	96.79	100	94.10	99.50	87.72
1:20	99.10	98.00	98.93	97.85	99.22	93.17
1:30	98.86	98.05	98.39	97.73	98.37	95.66
1:40	98.73	97.23	99.49	96.30	98.54	94.79
1:50	98.90	97.99	98.50	97.52	98.28	95.06

it is known that highly oxidative media promote oxidation reaction of organic molecules adsorbed onto the surface of solid particles [38,39]. This effect was also observed in the degradation of phenol in high voltage electrical discharge (corona) reactors [40]. Besides, the gradual leaching of iron powder provides continuous Fe^{2+} ions input into the Fenton reaction system that also positively contributes to the efficiency of Fenton "like" process, Fe^0/H_2O_2, for degradation of organic compounds.

In Fig. 7 final values of colour, TOC and AOX removal obtained by the studied Fenton type processes at optimal conditions for the treatment of RB49 model wastewater have been summarized. It can be observed that colour removal achieved with all the three processes was almost complete indicating that the less substituted anthraquinone chromophoric part of dye molecule is the most sensitive one to OH radical attack. Obtained TOC removal by Fenton process, Fe^{2+}/H_2O_2 (72.1%), in comparison to those achieved by Fenton "like" processes, Fe^{3+}/H_2O_2 and Fe^0/H_2O_2 (45.3% and 46.9%), indicates that regeneration of iron through the catalytic cycle (Eqs. (1)–(3)) was inhibited by organic ligands produced during the treatment [19]. In spite of the high TOC removal obtained by Fenton process, only 47.0% of AOX removal was achieved indicating that the mineralization of RB49 was more pronounced in the anthraquinone than in the triazine part of the dye molecule. For degradation of RB137 model solution, final values of colour, TOC and AOX removal by Fenton type processes at the optimal operating conditions are shown in Fig. 8. Similar to RB49 almost complete decolourization of RB137 was achieved. Final TOC removal ranged between 34.2 and 45.3%, indicating that the decolourization of RB137 occurs throughout the cleavage of azo bond in the chromogenic part of dye molecule, whereas stabile aromatic intermediates are formed. Feng et al. [41] reported that triazine ring is more stabile toward OH radical attack in comparison to the formed mono- and di-substituted benzenes and naphtholes. In this study, 59.1% AOX was removed, which with respect to the 34.2% of TOC removal obtained by Fenton process (Fig. 8) lead to the conclusion that some more persistent structures than triazine ring, presumably products of dimerization of organic radicals [24], were formed during the degradation of RB137.

4. Conclusions

Fenton, Fe^{2+}/H_2O_2, and Fenton "like", Fe^{3+}/H_2O_2 and Fe^0/H_2O_2, processes for the degradation of anthraquinone and azo reactive dyes were comparatively studied. The influence of operating parameters such as pH value, iron catalyst concentration and Fenton reagent ratio on the overall process

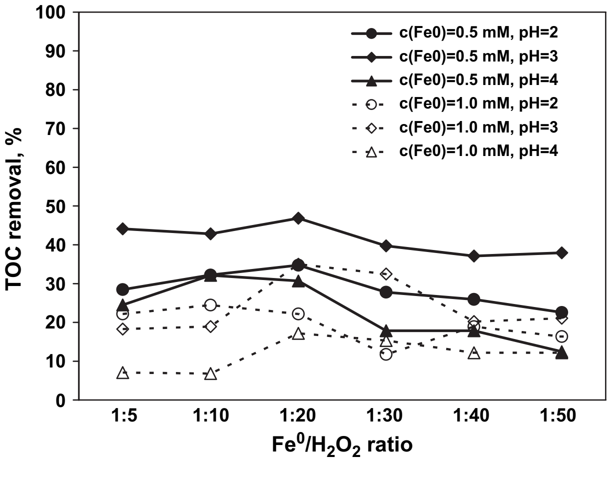


Fig. 5. Influence of the operating parameters of Fenton "like" process, Fe^0/H_2O_2, for the degradation of RB49 on TOC removal.

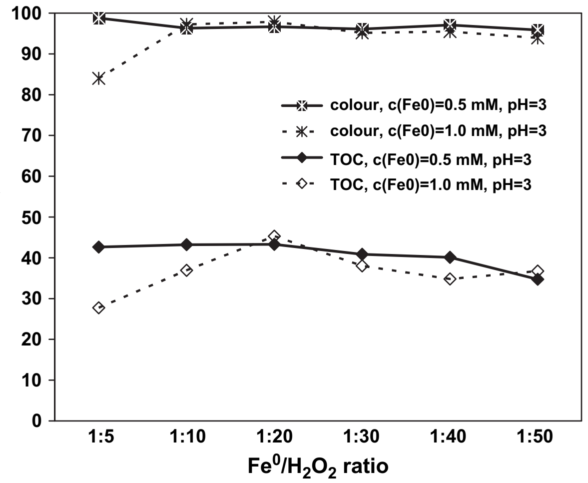


Fig. 6. Influence of iron powder concentration and Fe^0/H_2O_2 ratio on colour and TOC removal in Fenton "like" process for the degradation of RB137 at pH 3.

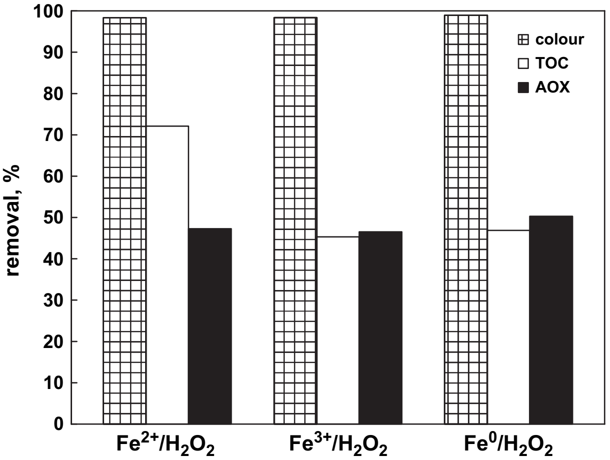


Fig. 7. Comparison of efficiency of Fenton type processes at the optimal operating parameters for RB49 degradation.

efficiency was investigated and estimated on the basis of UV/vis and TOC measurements. Optimal operating conditions for each process were established. Both the types of model wastewater were decolourized rather fast, more than 90% in all cases, indicating high susceptibility of both anthraquinone and azo chromophores to the OH radicals and consequently low sensibility of the decolourization process to the varying operating parameters within applied ranges. However, only partial mineralization was achieved for both RB49 and RB137 dyes. The best mineralization extent, i.e. maximal TOC removal, 72.1%, was obtained for degradation of RB49 by Fenton process, $Fe^{2+}/H_2O_2 = 1:20$, $c(Fe^{2+}) = 0.5$ mM at pH 3, whilst AOX value was decreased to 47.3%. On the other hand, for degradation of RB137, the best result, 45.3% of TOC removal, was achieved by both Fenton ''like'' processes, $Fe^{3+}/H_2O_2 = 1:40$, $c(Fe^{3+}) = 0.5$ mM at pH 3 and $Fe^0/H_2O_2 = 1:20$, $c(Fe^0) = 1$ mM at pH 3, with 22.7% and 42.2% AOX removal, respectively. These results indicate that the molecular structure of dyes studied has a significant role in the oxidation mechanism by Fenton type processes.

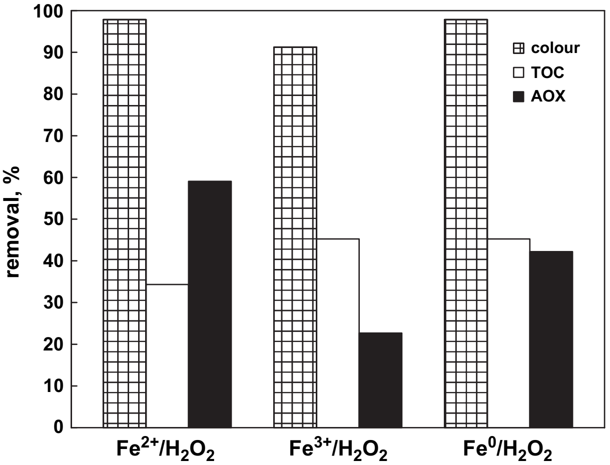


Fig. 8. Comparison of efficiency of Fenton type processes at the optimal operating parameters for RB137 degradation.

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References

[1] Papic S, Koprivanac N, Loncaric Bozic A, Metes A. Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process. Dyes and Pigments 2004;62:291–8.

[2] van der Zee FP, Letttinga G, Field J. Azo dye decolourisation by anaerobic granular sludge. Chemosphere 2001;44:1169–76.

[3] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. Environment International 2004;30:953–71.

[4] Gottlieb A, Shaw C, Smith A, Wheatley A, Forsythe S. The toxicity of textile reactive azo dyes after hydrolysis and decolourisation. Journal of Biotechnology 2003;101:49–56.

[5] Lourenco ND, Novais JM, Pinheiro HM. Effect of some operational parameters on textile dye biodegradation in sequential batch reactor. Journal of Biotechnology 2001;89:163–74.

[6] Papic S, Koprivanac N, Loncaric Bozic A. Removal of reactive dyes from wastewater using Fe(III) coagulant. Coloration Technology 2000; 116(11):352–8.

[7] Stylidi M, Kondarides DI, Verykios XE. Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO_2 suspensions. Applied Catalysis B: Environmental 2003;40:271–86.

[8] White GC. Handbook of chlorination and alternative disinfectants. New York: John Wiley & Sons; 1999.

[9] Neamtu M, Yediler A, Siminiceanu I, Macoveanu M, Kettrup A. Decolorization of disperse red 354 azo dye in water by several oxidation processes – a comparative study. Dyes and Pigments 2004;60(1):61–8.

[10] Daneshvar N, Salari D, Khataee AR. Photocatalytic degradation of azo dye Acid Red 14 in water: investigation of the effect of operational parameters. Journal of Photochemistry and Photobiology A: Chemistry 2003;157:111–6.

[11] Gogate PR, Pandit AB. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Advances in Environmental Research 2004;8:501–51.

[12] Gogate PR, Pandit AB. A review of imperative technologies for wastewater treatment II: hybrid methods. Advances in Environmental Research 2004;8:553–97.

[13] Lukes P. Water treatment by pulsed streamer corona discharge. PhD thesis. CZ: Institute of Plasma Physics; 2001.

[14] Loncaric Bozic A. Application of AOPs for organic dye removal from industrial wastewaters. PhD thesis. HR: University of Zagreb; 2004.

[15] Swaminathan K, Sandhya S, Caramlin Sophia A, Pachhade K, Subrahmanyam YV. Decolorization and degradation of H-acid and other dyes using ferrous–hydrogen peroxide system. Chemosphere 2003;50: 619–25.

[16] Kuo WG. Decolorizing dye wastewater with Fenton's reagent. Water Research 1992;26(7):881–6.

[17] Chen R, Pignatello JJ. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. Environmental Science and Technology 1997;31:2399–406.

[18] De Heredia JB, Torregrosa J, Dominguez JR, Peres JA. Kinetic model for phenolic compound oxidation by Fenton's reagent. Chemosphere 2001;45:85–90.

[19] Tarr MA. In: Tarr MA, editor. Chemical degradation methods for wastes and pollutants. Marcel Decker, Inc, 2003. p. 165–201.

[20] Gallard H, De Laat J, Legube B. Spectrophotometric study of the formation of iron(III)–hydroperoxy complexes in homogeneous aqueous solutions. Water Research 1999;33(13):2929–36.

[21] Gallard H, De Laat J. Kinetics of oxidation of chlorobenzenes and phenylureas by Fe(II)/H_2O_2 and Fe(III)/H_2O_2. Evidence of reduction and oxidation reactions of intermediates by Fe(II) and Fe(III). Chemosphere 2001;42(4):405–13.

[22] Neamtu M, Yediler A, Siminiceanu I, Kettrup A. Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes. Journal of Photochemistry and Photobiology A: Chemistry 2003;161:87–93.

[23] Rivas FJ, Beltrán FJ, Garcia-Araya JF, Navarrete V, Gimeno O. Co-oxidation of *p*-hydroxybenzoic acid and atrazine by the Fenton's like system Fe(III)/H_2O_2. Journal of Hazardous Materials 2002;B91:143–57.

[24] Tang WZ, Chen RZ. Decolorization kinetics and mechanism of commercial dyes by H_2O_2/iron powder system. Chemosphere 1996;32(5):947–58.

[25] Bergendahl JA, Thies TP. Fenton's oxidation of MTBE with zero-valent iron. Water Research 2004;38:327–34.

[26] Koprivanac N, Kusic H, Peternel I, Locke BR. In: Locke BR, editor. Proceedings of the 4th international symposium of non-thermal plasma technology. Tallahassee, FL: FAMU-FSU, College of Engineering; 2004. p. 194–8.

[27] Lücking F, Köser H, Jank M, Ritter A. Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution. Water Research 1998;32:2607–14.

[28] http://www.h2o2.com/; 1998.

[29] Lin SH, Lo CC. Fenton process for treatment of desizing wastewater. Water Research 1997;31:2050–6.

[30] Tang WZ, Huang CP. 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. Environmental Technology 1996;17:1371–8.

[31] Kang YW, Hwang KY. Effects of reaction conditions on the oxidation efficiency in the Fenton process. Water Research 2000;34:2786–90.

[32] Arslan I, Balcioglu IA. Degradation of Remazol Black B dye and its simulated dyebath wastewater by advanced oxidation processes in heterogeneous and homogeneous media. Coloration Technology 2001;117:38–42.

[33] Muruganandham M, Swaminathan M. Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology. Dyes and Pigments 2004;63(3):315–21.

[34] Meric S, Kaptan D, Olmez T. Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. Chemosphere 2004;54(3):435–41.

[35] Malik PK, Saha SK. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. Separation and Purification Technology 2003;31(3):241–50.

[36] Collona GM, Caronna T, Marcandalli B. Oxidative degradation of dyes by ultraviolet radiation in the presence of hydrogen peroxide. Dyes and Pigments 1999;41:211–20.

[37] Verma P, Baldrian P, Nerud F. Decolorization of structurally different synthetic dyes using cobalt(II)/ascorbic acid/hydrogen peroxide system. Chemosphere 2003;50:975–9.

[38] Vidic RD, Suidan MT, Brenner RC. Oxidative coupling of phenols on activated carbon: impact on adsorption equilibrium. Environmental Science and Technology 1993;27:2079–85.

[39] Abuzaid NS, Nakhla GF. Dissolved oxygen effects on equilibrium and kinetics of phenolics adsorption by activated carbon. Environmental Science and Technology 1994;28:210–21.

[40] Grymonpre DR, Finney WC, Locke BR. Activated carbon particles in aqueous phase pulsed streamer corona discharge. Journal of Advanced Oxidation Technologies 1999;4:408–16.

[41] Feng W, Nansheng D, Helin H. Degradation mechanism of azo dye C.I. reactive red 2 by iron powder reduction and photooxidation in aqueous solutions. Chemosphere 2000;41(8):1233–8.