

Comparison of ultraviolet radiation/hydrogen peroxide, Fenton and photo-Fenton processes for the decolorization of reactive dyes

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Abstract

The effectiveness of UV/H₂O₂ process, Fenton and photo-Fenton process on decolorization of commercially important textile dyes Reactive Orange 4 (RO4) and Reactive Blue 19 (RB19) was evaluated. The effect of operational condition such as initial pH, initial H₂O₂ concentration, initial Fe²⁺ concentration and initial dye concentration on decolorization of RO4 and RB19 was studied. The photo-Fenton process is found to be more efficient than UV/H₂O₂ and Fenton process for decolorization of simulated dye bath effluent and solutions of the dyes in water alone under optimum conditions. In simulated dye bath the removal efficiency was slightly lower than for the solutions of the dyes in water alone for both dyes types. The results revealed that the tested advanced oxidation processes were very effective for decolorization of RO4 and RB19 in aqueous solution.

Keywords: dyes, Fenton process, oxidations, photo-Fenton process, UV/H₂O₂ process.

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Synthetic dyes are widely used in the textile and dyestuff industries for textile dyeing, paper printing, food, cosmetics, pharmaceutical and colour photography [1]. Nearly 10000 different dyes and pigments are used industrially and 0.7 million tons of synthetic dyes are produced each year all over the world [1,2]. The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Wastewaters from the textile industry are discharged into the environment and can be highly contaminated due to extensive use of dyes [3]. It was reported that the loss of the dyes during processes can be from 1 to 15% [4]. Dyes are very resistant to biological degradation [5,6] and thus strongly influence on aquatic ecosystem [7].

Textile dyes are divided as acid, reactive, metal complex, disperse, vat, mordant, direct, basic and sulfur dyes, as to their way of application [8]. Azo dyes make the largest group of colorants with the respect to both the number and production volume. These compounds contain one or more azo groups (–N=N–) mostly linked to benzene or naphthalene rings [9]. Some azo dyes via metabolic cleavage of azo linkage can produce potentially carcinogenic aromatic amines [10]. Therefore, more attention should be paid to the azo dyes release in the environment. Anthraquinone reactive dyes are the second most commonly used group of dyes. Because of their structure which is

highly stabilized by resonance, these dyes are very resistant to chemical oxidation. Thus, there is a need to remove dyes from wastewaters before discharging them to receiving waters. Chemical and physical processes such as chemical precipitation, coagulation, electrocoagulation, elimination by adsorption on activated carbon and reverse osmosis are used for the dye removal from textile effluents [11]. Nevertheless these (traditional methods) processes merely transfer the contamination from one phase (wastewater) to another (solid waste-sludge) and as a result make secondary waste and the problem remains still unsolved [12,13].

Alternatively, advanced oxidation processes (AOPs), such as homogeneous and heterogeneous photocatalysis, are promising technologies which aim at the decolorization and mineralization of the largest number of dyes or their transformation into biodegradable and harmless products [14–16]. AOPs refer to a set of different methods leading to the generation of highly oxidative species such as hydroxyl radicals ([•]OH) which are capable of oxidizing the pollutants to such an extent that the treated wastewater may be reintroduced into receiving streams. The use of homogeneous degradation or photodegradation systems such as Feⁿ⁺/H₂O₂ (Fenton), H₂O₂/UV and Feⁿ⁺/H₂O₂/UV (photo-Fenton) have attracted much attention due to their high efficiency in the oxidation of different pollutants including dyes [17,18]. Some advantages of use AOPs in comparison to other systems are no sludge formation, no salt formation, considerably safe and easy operation, short reaction time, reduction of COD [19]. Reaction of hydroxyl radicals with organic contaminant inc-

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ludes three different mechanisms: hydrogen abstraction, electrophilic addition and electron transfer [20].

For practical use of these processes in wastewater treatment, there is a need to determine the optimal conditions of experimental parameters (pH, initial concentration of dye, H_2O_2 and Fe^{2+}) for efficient removal. In the present study, we have investigated the decolorization of azo dye Reactive Orange 4 (RO4) and anthraquinone dye Reactive Blue 19 (RB19) by three different AOPs.

EXPERIMENTAL

Reagents

The commercial samples of textile dyes, Reactive Orange 4 (RO4) and Reactive Blue 19 (RB19), were obtained from Farbotex (Italy) and used without further purification. H_2O_2 (30%), acetic acid, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, HCl and NaOH were of reagent grade and purchased from Merck (Germany). Kutregal PN (commercial product) was purchased from Chromos (Croatia). The pH of solutions was adjusted pH-metrically, without buffering. All other used reagents were of analytical grade. All solutions were prepared with deionized water.

Apparatus

UV-Vis spectra were recorded on UV-vis spectrophotometer UV-1650 PC (Shimadzu, Japan). UV irradiation experiments were carried out using batch UV photoreactor (originally manufactured) [21].

Photodecolorization procedures

The photoreactor was operated with an initial working volume of 100 cm^3 . Solutions were prepared

by dissolving the required quantity of the dye, H_2O_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (for Fenton and photo-Fenton processes where $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as a source of Fe^{2+}) in deionized water. During the irradiation, the solution was magnetically stirred in a constant rate (200 rpm) and the temperature was maintained at $25.0 \pm 0.5 \text{ }^\circ\text{C}$ by thermostating. The pH of solutions was adjusted using NaOH or HCl ($0.1, 0.01 \text{ mol dm}^{-3}$) with pH-meter (Senslon5, HACH, USA). At regular time intervals samples were taken and absorbance was measured using UV-vis spectrophotometer, to determine degree of decolorization of the dye.

RESULTS AND DISCUSSION

UV/ H_2O_2 process

Initial results demonstrate that neither H_2O_2 nor UV alone was able to noticeably decolorize these two reactive dyes in period of 24 h (result not shown). Combination of UV and H_2O_2 is necessary for production of hydroxyl radicals by photolysis of the hydrogen peroxide [22,23]. This radical is a non-selective and very powerful oxidiser with an oxidation potential of 2.8 V and can initiate the decolorization reactions by reacting with the dye molecules [24,25]. The changes in UV-Vis spectrum of RO4 and RB19 during UV/ H_2O_2 process are presented in Fig. 1.

Figure 2 shows semi-logarithmic graphs of the concentration of reactive dyes versus illumination time. The apparent rate constants (k) for photodecolorization of RO4 and RB19 in the presence of hydrogen peroxide are obtained from above graphs. The inset of Figure 2 shows the change of removal efficiency *versus* time.

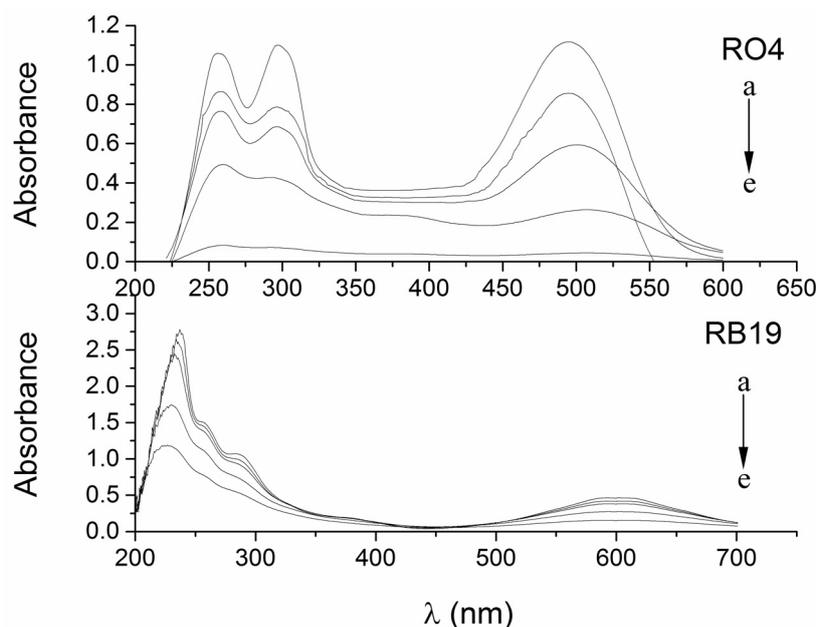


Fig. 1. The changes in UV-Vis spectrum of RO4 and RB19 in UV/ H_2O_2 process after: a) 0, b) 2, c) 4, d) 10 and e) 20 min.

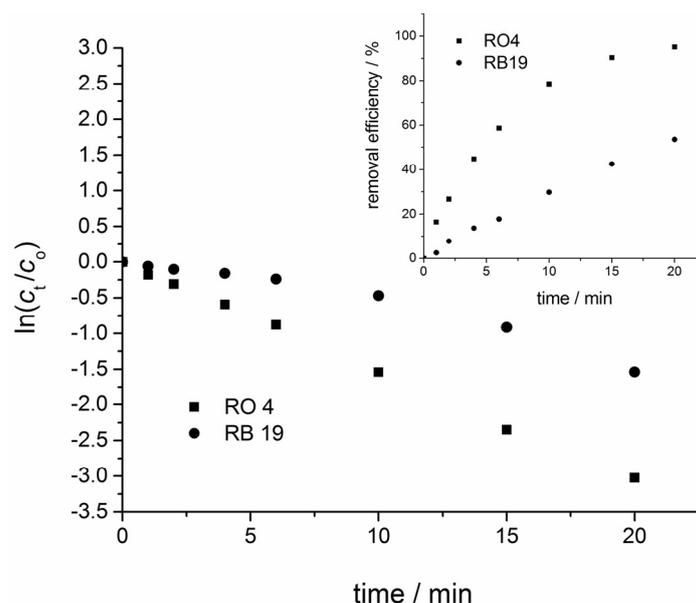


Fig. 2. Effect of UV/H₂O₂ process on decolorization of RO4 and RB19. [dye]₀ = 50 mg dm⁻³, [H₂O₂]₀ = 25 mmol dm⁻³, initial pH 7, UV radiation intensity 730 μW cm⁻², temperature 25.0±0.5 °C. Inset shows the relation between removal efficiency and illumination time.

This is a typical pseudo-first-order reaction with respect to dye concentration [21,23,26–28]. The kinetic constant can be linked to dye concentration by the following equation:

$$\ln(c_t/c_0) = -kt \quad (1)$$

where c_t is the concentration of dye after irradiation time t , c_0 is dye concentration at $t = 0$ and k (min⁻¹) is apparent pseudo-first rate constant. A linear fit was done for the first 15 min of the treatment. In all experimental results, the values of square of relative correlation coefficients (R^2) were higher than 0.98 which confirmed proposed kinetic model.

Effect of H₂O₂

Hydrogen peroxide concentration is an important parameter for the decolorization of the color in the UV/H₂O₂ process. Due to a low molar absorption coefficient of H₂O₂ at 254 nm [29], an excess of H₂O₂ is theoretically needed to produce enough hydroxyl radicals.

However in our previous work [21] in addition to other reports [30,31], we observed that the concentration of H₂O₂ may either enhance or inhibit the photoreaction rate depending on concentration. Therefore, an optimum concentration of H₂O₂ in the reaction course must be reached. The effect of the initial concentration of H₂O₂ (10, 20, 30, 40, 60, 80 and 100 mmol dm⁻³) on the photodecolorization efficiency of the system was investigated using fixed concentrations of dyes (50 mg dm⁻³) at pH 7.0 and 25.0±0.5 °C. The applied UV light intensity was 730 μW cm⁻², because of too fast decolorization at maximal value (1950 μW cm⁻²),

which made the investigation of this operational parameter difficult. The apparent rate constants versus different initial concentrations of H₂O₂ have been summarized in Fig. 3.

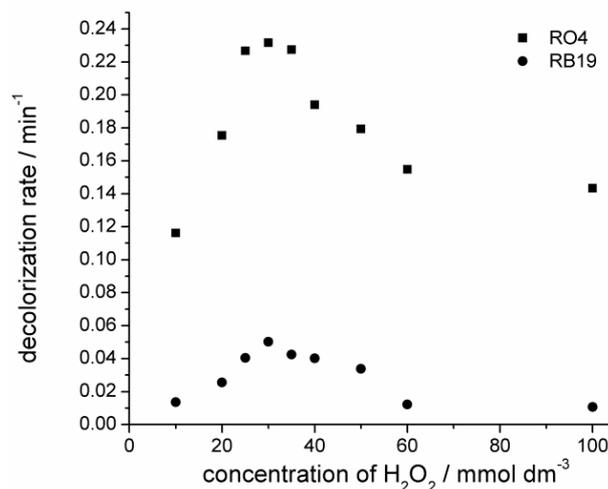


Fig. 3. Effect of initial peroxide concentration on the rate of decolorization of RO4 and RB19 by UV/H₂O₂ process. [dye]₀ = 50 mg dm⁻³, initial pH 7, UV radiation intensity 730 μW cm⁻², temperature 25.0 ± 0.5 °C.

Figure 3 shows that the addition of H₂O₂ from 10 to 30 mmol dm⁻³ increases the apparent constant rate from 0.116 to 0.232 min⁻¹ for RO4 and from 0.015 to 0.053 min⁻¹ for RB19. Further increase of H₂O₂ concentration above 30 mmol dm⁻³ decreases the apparent constant rate from 0.232 to 0.143 min⁻¹ for RO4 and from 0.053 to 0.017 min⁻¹ for RB19. This occurrence

can be explained by two opposing effects with increasing H_2O_2 concentration:

1) At low concentration of H_2O_2 , relatively low concentration of $\cdot\text{OH}$ was formed for dye oxidation, which results in low decolorization rate. Nevertheless, by increasing peroxide concentration, more $\cdot\text{OH}$ were generated upon its photodissociation [32].

2) The $\cdot\text{OH}$ free radicals produced upon photolysis of H_2O_2 can react with dye molecules, but also with an excess of H_2O_2 . Excess of hydrogen peroxide and high $\cdot\text{OH}$ concentration result in competitive reactions, producing an inhibitory effect on the decolorization. $\cdot\text{OH}$ radicals are prone to react or to recombine [33].

When the initial peroxide concentration is very high, the generated $\cdot\text{OH}$ mostly react by excess of peroxide and produce hydroperoxyl radical, $\text{HO}_2\cdot$, which are less reactive than $\cdot\text{OH}$, and the rate of dye removal decreased. Generated $\cdot\text{OH}$ can also react with $\text{HO}_2\cdot$ and produce water and dioxygen or dimerize to H_2O_2 and the concentration of $\cdot\text{OH}$ available for dye decolorization also decreased [34]. A very important parameter for the optimization of the method is the determination of adequate amount of H_2O_2 , to avoid reagent surplus which can slow down the decolorization. The results of Fig. 3 point out the negative effect of a defect or excess of concentration of H_2O_2 on the decolorization rate. We can observe an optimum value at about 30 mmol dm^{-3} for the hydrogen peroxide concentration.

Effect of pH

Since the waste water from the textile industry can be of different pH values, we have studied the effect of pH on the decolorization rate. The solutions of the dyes were adjusted to the desired pH by addition of HCl or NaOH. The different concentrations of acid or base have been chosen in order to add the minimum quantity of these species to avoid the volume change of the reaction mixture.

To investigate the effect of initial pH, the solutions of RO4 and RB19 were irradiated at various initial pH (2,3,5,7,9, 10 and 11), during 20 min of treatment time, using 50 mg dm^{-3} dye solutions, 25 mmol dm^{-3} H_2O_2 and radiation intensity $730 \mu\text{W cm}^{-2}$. The decolorization rate constants of dyes as a function of the reaction pH are shown in Fig. 4.

The decolorization rate of RO4 increases from 0.062 to 0.152 min^{-1} with increasing pH from 2 to 7. After this value we have observed a decrease of the decolorization rate to 0.067 min^{-1} as the pH increases to 11. In case of other dye RB19, a steady increase in rate constants with increasing pH was observed. This is perhaps a consequence of different structures of these two dyes.

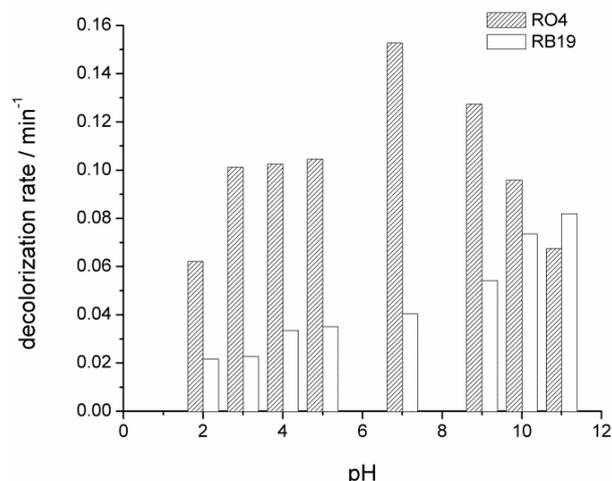


Fig. 4. Effect of pH on the rate of decolorization of RO4 and RB19 by UV/ H_2O_2 process. $[\text{dye}]_0 = 50 \text{ mg dm}^{-3}$, $[\text{H}_2\text{O}_2]_0 = 25 \text{ mmol dm}^{-3}$, UV radiation intensity $730 \mu\text{W cm}^{-2}$, temperature $25.0 \pm 0.5 \text{ }^\circ\text{C}$.

Effect of initial dye concentration

The pollutant concentration is one of the important parameters in UV/ H_2O_2 process. The effect of the initial RO4 concentration on the efficiency of dye decolorization was investigated at a concentration range from 10 up to 100 mg dm^{-3} , using fixed concentrations of H_2O_2 (25 mmol dm^{-3}) at pH 7.0, $25.0 \pm 0.5 \text{ }^\circ\text{C}$ and UV light intensity $730 \mu\text{W cm}^{-2}$ during 20 min of treatment time. The results are shown in Fig. 5.

It is evident that removal efficiency (RE) decreased with the increase of initial dyes concentrations from 10 to 100 mg dm^{-3} . This can be explained by considering that both aromatic dyes and H_2O_2 absorb UV radiation in the range emitted by the lamp. However, the molar absorption coefficient of dyes at 254 nm is higher than that of H_2O_2 , so that an increase in dyes concentration induces a rise of the internal optical density and the solution becomes more and more impermeable to UV radiation. Then, H_2O_2 can only be irradiated by a smaller portion of UV light to form lower free radicals and the removal efficiency decreases.

Fenton and photo-Fenton process

As described above, the photodecolorization of reactive dyes was mainly initiated by the production of $\cdot\text{OH}$ resulting from the direct photolysis of H_2O_2 . Degradation experiments using Fenton and photo-Fenton processes were studied to investigate the effect of increased production of $\cdot\text{OH}$.

In these processes $\cdot\text{OH}$ radicals are produced by catalytic decomposition of H_2O_2 in the reaction with Fe^{2+} (Eq. (2)) and UV light (for photo-Fenton process) [35]. The mechanism of the Fenton's process can be summarized by the following steps:

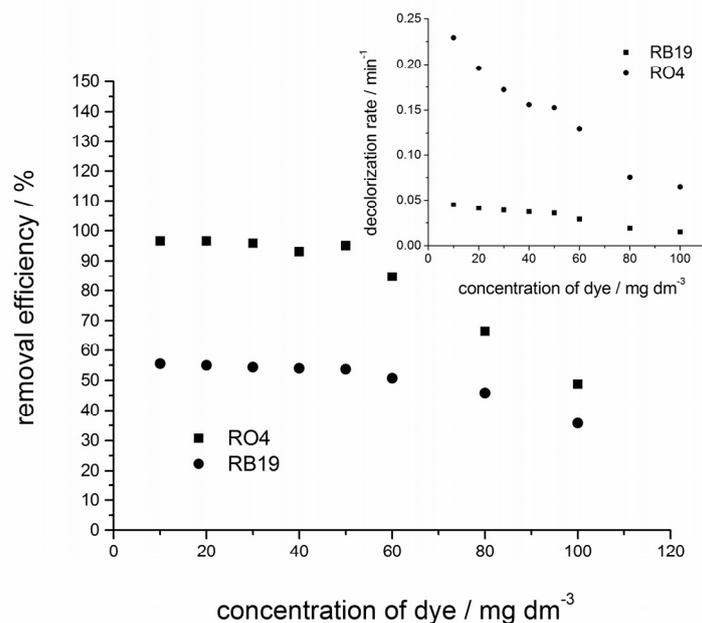
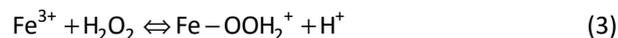


Fig. 5. Effect of initial dye concentration on the removal efficiency of RO4 and RB19 by UV/H₂O₂ process. [H₂O₂]₀ = 25 mmol dm⁻³, initial pH 7, UV radiation intensity 730 μW cm⁻², temperature 25.0±0.5 °C. Inset shows the relation between decolorization rate and initial dye concentration.

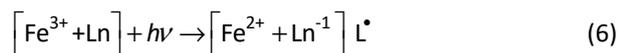
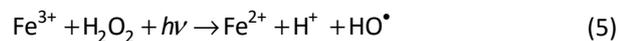
1) Mixture of H₂O₂ and Fe²⁺ in acidic solution generates the [•]OH (Eq. (2)) [36,37], which will subsequently attack the organic compounds present in the solution:



2) As Fe²⁺ acts as a catalyst, it has to be regenerated, which happened through the following scheme:



The photo-Fenton process is nearly similar to the Fenton one, but includes also radiation. Additional reactions occur in the presence of light that produce [•]OH [32] or increase the production rate of [•]OH [38]. The obtained Fe³⁺ or its complexes behave as the light absorbing species that produces another radical, and the initial Fe²⁺ is regenerated as seen in Eqs. (5) and (6) [38,39]:



The conclusion is that in this process, the regeneration of Fe²⁺ by photo-reduction of Fe³⁺ (Eqs. (5) and (6)) is accelerated and photo-reduction is an additional source of highly oxidative [•]OH (Eq. 5), as compared with the Fenton's process. This is the reason of higher efficiency of photo-Fenton than Fenton process.

Effect of Fe²⁺ on Fenton and photo-Fenton process

For Fenton and photo-Fenton processes, the concentration of Fe²⁺ is one of the important parameters. To investigate the effect of Fe²⁺ on the decolorization of RO4 and RB19, a series of experiments were conducted by varying Fe²⁺ concentration from 0.05 to 1 mmol dm⁻³, at fixed pH, initial concentration of H₂O₂ and dyes.

The RO4 and RB19 initial decolorization rate for various concentrations of Fe²⁺ was presented in Fig. 6.

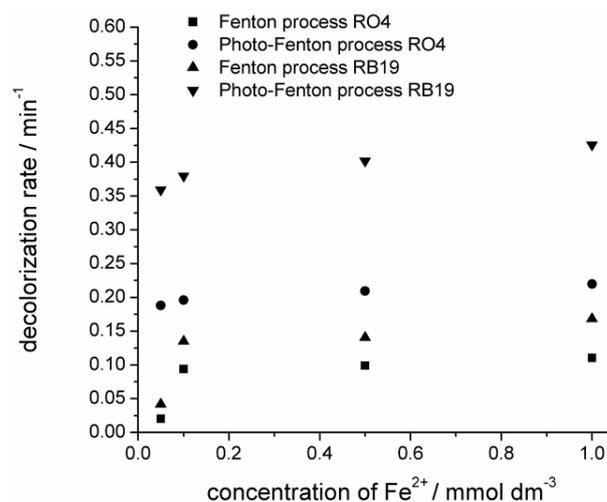


Fig. 6. Effect of initial Fe²⁺ concentration on the rate of decolorization of RO4 and RB19. [dye]₀ = 50 mg dm⁻³, [H₂O₂]₀ = 25 mmol dm⁻³, UV radiation intensity 730 μW cm⁻², temperature 25.0±0.5 °C.

From the Fig. 6. it can be seen that there is slight difference in the efficiency of Fenton and photo-Fenton processes at concentrations of Fe^{2+} from 0.1 to 1 mmol dm^{-3} . Therefore for further experiments as an optimal concentration of Fe^{2+} was used 0.1 mmol dm^{-3} in order to lessen risk of the ions excess and eventual forming of an iron sludge. The results showed that in Fenton process addition of Fe^{2+} from 0.05 to 1 mmol dm^{-3} increases decolorization rate from 0.020 to 0.110 min^{-1} for RO4 and from 0.042 min^{-1} to 0.168 for RB19. In photo-Fenton process the increase is from 0.188 to 0.220 min^{-1} for RO4 and from 0.359 to 0.425 min^{-1} for RB19 for the same addition of Fe^{2+} . Hence, photo-Fenton process is more efficient than Fenton process. Decolorization of dyes is mainly due to hydroxyl radical generated by chemical and photochemical reactions of each process. The reason of this increase is more produced $\cdot\text{OH}$ with the increase in the concentration of Fe^{2+} .

Effect of H_2O_2

Initial concentration of H_2O_2 plays an important role in the Fenton and photo-Fenton processes. The effect of addition of H_2O_2 from 5 to 50 mmol dm^{-3} , at fixed pH, initial concentration of Fe^{2+} and dye, on the decolorization of RO4 and RB19 by both processes is shown in Fig. 7.

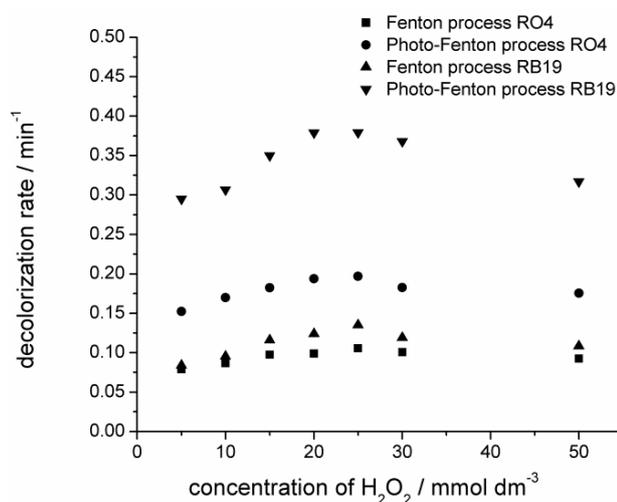


Fig. 7. Effect of initial peroxide concentration on the rate of decolorization of RO4 and RB19 by Fenton and photo-Fenton processes. $[\text{dye}]_0 = 50 \text{ mg dm}^{-3}$, $[\text{Fe}^{2+}]_0 = 0.1 \text{ mmol dm}^{-3}$, UV radiation intensity $730 \mu\text{W cm}^{-2}$, temperature $25.0 \pm 0.5 \text{ }^\circ\text{C}$.

In Fenton and photo-Fenton processes, the addition of H_2O_2 from 5 to 25 mmol dm^{-3} increases the decolorization rate. Further increase from 25 to 50 mmol dm^{-3} causes the decrease of decolorization rate for both processes.

The increase in the decolorization by the addition of H_2O_2 is due to increase in the $\cdot\text{OH}$ concentration [32].

But at high dosage of H_2O_2 the decrease in decolorization is due to the $\cdot\text{OH}$ radical scavenging effect of H_2O_2 and recombination of $\cdot\text{OH}$ [34,40]. Hence, 25 mmol dm^{-3} of H_2O_2 appear as optimal dosages for Fenton and photo-Fenton processes.

Effect of initial dye concentration

Influence of concentration of the RO4 and RB19 dye on its decolorization was examined in this study, varying dye concentration from 10 to 100 mg dm^{-3} , at fixed pH, initial concentration of H_2O_2 and Fe^{2+} . The effect of initial dye concentration in these processes is shown in Fig. 8.

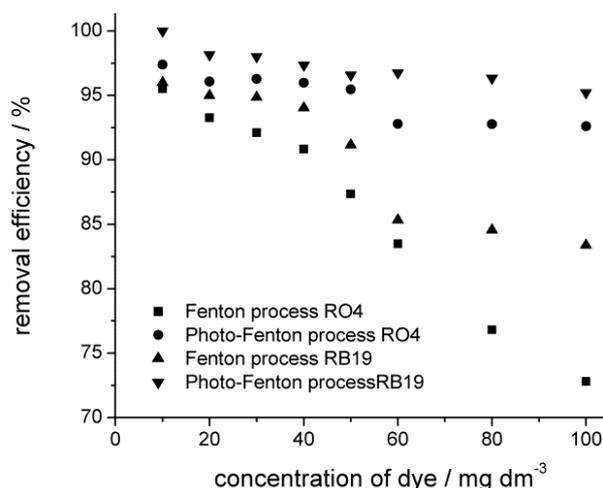


Fig. 8. Effect of initial dye concentration on the removal efficiency of RO4 and RB19 by Fenton and photo-Fenton processes. $[\text{H}_2\text{O}_2]_0 = 25 \text{ mmol dm}^{-3}$, $[\text{Fe}^{2+}]_0 = 0.1 \text{ mmol dm}^{-3}$, UV radiation intensity $730 \mu\text{W cm}^{-2}$, temperature $25.0 \pm 0.5 \text{ }^\circ\text{C}$.

The figures clearly reveal that the increase in dye concentration from 10 to 100 mg dm^{-3} decreases the removal efficiency for Fenton and for photo-Fenton process in 20 min. The results are shown in Fig. 8. $\cdot\text{OH}$ is mainly responsible for dye decolorization and its concentration remains constant for all dye concentrations. The increase in dye concentration increases the number of dye molecules and not the $\cdot\text{OH}$ radical concentration and so the removal efficiency decreases. Photochemical processes extremely depend on solution absorption. In solutions with high absorption, e.g., dye solution, the penetration of light can be very limited. In photo-Fenton process there is a strong light absorption of the dye solution at high concentration which causes lowering concentration of $\cdot\text{OH}$ radicals and decrease of removal efficiency.

Comparison of UV/ H_2O_2 , Fenton and photo-Fenton processes

Comparison of efficiencies of UV/ H_2O_2 , Fenton and photo-Fenton processes on decolorization of RO4 and RB19 was presented in Fig. 9. For comparison of these

processes we studied decolorization on optimum conditions for all processes.

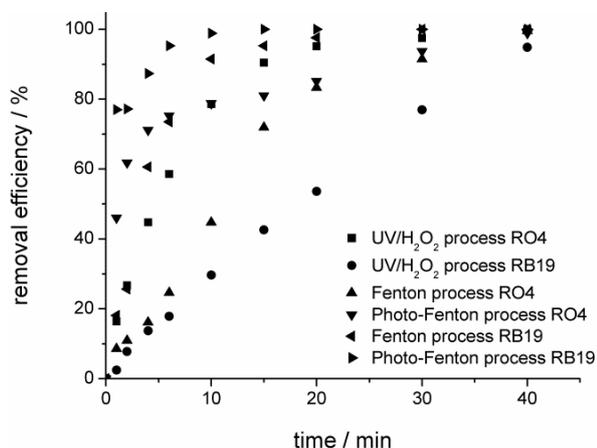


Fig. 9. Comparison of removal efficiency of RO4 and RB19 by UV/H₂O₂, Fenton and photo-Fenton processes.

Among the processes tested here for RO4 and RB19 dyes decolorization, the ranking of efficiency of color removal was as follows: photo-Fenton process > UV/H₂O₂ > Fenton reagent for RO4 and photo-Fenton process > Fenton reagent > UV/H₂O₂ for RB19. The photo-Fenton process achieved decolorization in 15 min for RO4 and 10 min for RB19, UV/H₂O₂ process in about 20 min for RO4 and 40 min for RB19 and Fenton process in about 30 min for RO4 and RB19.

From these results, it can be concluded that the photo-Fenton process is highly efficient at degrading RO4 and RB19 dyes. Purification of water and wastewater using the Fenton and photo-Fenton processes tend to be less expensive to build and operate than most other AOPs. But on the other hand, the operations of Fenton-type processes usually require strict pH control as they are most efficient at pH 2.8 [41]. Iron sludge usually forms, after the process is completed and neutralization is carried out, which requires appropriate disposal [14]. In the case of UV/H₂O₂ the final products of dyes degradation are carbon dioxide, water and inert salts. Therefore this process is a promising environmental engineering technique.

Decolorization of dyes in simulated dyebath effluent

According to previous research [42], wastewater composition from textile industries can greatly influ-

ence the photochemical oxidation process. Certain ions found at high concentrations in textile wastewater can affect the process.

In order to relate the present study to the real situation which comes out from the commercial dyeing of cotton, a simulated spent dye bath was formulated and its response to photodecolorization was tested. The reactive dyebath effluent was simulated by dissolving proper amounts of two commercial reactive dyestuff formulations and dye assisting chemicals in hot ($T = 70$ °C) deionized water. Acetic acid for neutralization and Kutregal PN as surfactant were used as assisting chemicals. Surfactants are used for the purpose of improving dispersing properties. They are also used to achieve a better contact between dyestuff formulations and fabric and improve dye diffusion through the fabric pores. The exact composition of the simulated reactive dyebath is given in Table 1. For preparing a model effluent, simulated dyebath effluent was diluted to get a new solution with 50.0 mg dm⁻³ of dyes. The highest percentage of the removal of RO4 and RB19 by photo-Fenton process was achieved after 15 min irradiation. Based on the results previously shown for the solutions of the dyes in water alone and the results for the simulated dyebath effluent shown in Table 2, it can be concluded that the decolorization efficiency is higher for solutions of the dyes in water alone than for the dyes in a simulated dyebath effluent for both dyes types.

Table 1. Composition of the simulated reactive dyebath

Reactive dyebath component	Concentration in the dyebath, g dm ⁻³
Reactive Orange 4 (azo type)	2.5
Reactive Blue 19 (anthraquinone type)	2.5
“Kutregal PN” (dispersing properties)	0.5
Acetic acid (neutralization)	0.79

CONCLUSION

In this study, we assessed the possibility of different AOPs for RO4 and RB19 decolorization. UV/H₂O₂ process was obviously affected by the initial pH and the amount of hydrogen peroxide. Desired amount of peroxide was 30 mmol dm⁻³, with RO4 and RB19 concentrations of 50 mg dm⁻³ for UV/H₂O₂, Fenton and photo-Fenton processes, while optimum UV light intensity for

Table 2. Removal efficiency of RO4 and RB19 in simulated dyebath effluent after 15 min. $[dye]_0 = 50$ mg dm⁻³

Process	Removal efficiency (RO4), %		Removal efficiency (RB19), %	
	The solutions of the dyes in water alone	The simulated dyebath effluent	The solutions of the dyes in water alone	The simulated dyebath effluent
UV/H ₂ O ₂	90.45	46.49	42.57	32.57
Fenton	71.94	35.59	81.06	72.31
Photo-Fenton	95.29	91.63	98.25	87.72

UV/H₂O₂ and photo-Fenton processes was 730 μW cm⁻². The best working condition was found for an initial Fe²⁺ concentration of 0.1 mmol dm⁻³ for Fenton and photo-Fenton processes. The removal efficiency of these three processes is in the following order: photo-Fenton process > UV/H₂O₂ > Fenton reagent for RO4 and photo-Fenton process > Fenton reagent > UV/H₂O₂ for RB19. The decolorization efficiency is higher for solutions of the dyes in water alone than for dyes in a simulated dyebath effluent.

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REFERENCES

- [1] S. Padmavathy, S. Sandhya, K. Swaminathan, Y.V. Subrahmanyam, T. Chakrabarti, S.N. Kaul, Aerobic decolorization of reactive azo dyes in presence of various cosubstrates, *Chem. Biochem. Eng. Q.* **17** (2003) 147–151.
- [2] H. Zhang, L. Duan, Y. Zhang, F. Wu, The use of ultrasound to enhance the decolorization of the C.I. Acid Orange 7 by zero-valent iron, *Dyes Pigm.* **65** (2005) 39–43.
- [3] C. Galindo, P. Jacques, A. Kalt, Photochemical and photocatalytic degradation of an indigolid dye: a case study of acid blue 74 (AB74), *J. Photochem. Photobiol., A* **141** (2001) 47–56.
- [4] T. Sauer, G.C. Neto, H.J. Jose, R.F.P. M. Moreira, Kinetics of photocatalytic degradation of reactive dyes in a TiO₂ slurry reactor, *J. Photochem. Photobiol., A* **149** (2002) 147–154.
- [5] W.S. Kuo, P.H. Ho, Solar photocatalytic decolorization of methylene blue in water, *Chemosphere* **45** (2001) 77–83.
- [6] Z. Sun, Y. Chen, Q. Ke, Y. Yang, J. Yang, Photocatalytic degradation of cationic azo dye by TiO₂/bentonite nanocomposite, *J. Photochem. Photobiol., A* **149** (2002) 169–174.
- [7] L.G. Devi, S.G. Kumar, K.M. Reddy, C. Munikrishappa, Photo degradation of Methyl Orange an azo dye by Advance Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism, *J. Hazard. Mater.* **164** (2009) 459–467.
- [8] S. Parsons, *Advanced oxidation processes for water and wastewater treatment*, IWA, London, 2004.
- [9] H. Zollinger, *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*, Wiley, Germany, 2003.
- [10] M.H. Habibi, A. Hassanzadeh, S. Mahdavi, The effect of operational parameters on the photocatalytic degradation of three textile azo dyes in aqueous TiO₂ suspensions, *J. Photochem. Photobiol., A* **172** (2005) 89–96.
- [11] N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar, Decolorization of orange II by electrocoagulation method, *Sep. Purif. Technol.* **31** (2003) 153–162.
- [12] K. Tanaka, K. Padermpole, T. Hisanage, Photocatalytic degradation of commercial azo dyes, *Water Res.* **34** (2000) 327–333.
- [13] C. Hachem, F. Boequillon, O. Zahraa, M. Bouchy, Decolorization of textile industry wastewater by the photocatalytic degradation process, *Dyes Pigm.* **49** (2001) 117–125.
- [14] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, *Catal. Today* **53** (1999) 51–59.
- [15] W.M. Ralph, Photooxidative degradation of coloured organics in water using supported catalysts. TiO₂ on sand, *Water Res.* **25** (1991) 1169–1176.
- [16] W.Z. Tang, H. An, UV/TiO₂ photocatalytic oxidation of commercial dyes in aqueous solutions, *Chemosphere* **31** (1995) 4157–4170.
- [17] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, Degradation of azo dyes using low Fe concentration of Fenton and Fenton-like system, *Chemosphere* **58** (2005) 1409–1414.
- [18] N. Daneshvar, A.R. Khataee, Removal of azo dye C.I. Acid Red 14 from contaminated water using Fenton, UV/H₂O₂, UV/H₂O₂/Fe(II), UV/H₂O₂/Fe(III) and UV/H₂O₂/Fe(III)/oxalate processes: a comparative study, *J. Environ. Sci. Health, A* **41** (2006) 315–328.
- [19] M. Le Marechal, Y.M. Slokar, T. Taufer, Decolorisation of chlortriazine reactive azo dyes with UV/H₂O₂, *Dyes Pigm.* **33** (1997) 281–298.
- [20] O. Legrini, E. Oliveros, A.M. Braun, Photochemical Processes for Water Treatment, *Chem. Rev.* **93** (1993) 671–698.
- [21] J. Mitrović, M. Radović, D. Bojić, T. Anđelković, M. Purenović, A. Bojić, Decolorization of textile azo dye Reactive Orange 16 with UV/H₂O₂ process, *J. Serb. Chem. Soc.* **77** (2012) 465–481.
- [22] C.G. Nambodri, W.K. Walsh, Ultraviolet light/hydrogen peroxide system for decolourizing spent reactive dye-bath waste water, *Am. Dyest Rep.* **85** (1996) 15–25.
- [23] J.R. Guimaraes, M.G. Maniero, R.N. De Araujo, A comparative study on the degradation of RB-19 dye in aqueous medium by advanced oxidation processes, *J. Environ. Manage.* **110** (2012) 33–39.
- [24] M. Muruganandham, M. Swaminathan, Photochemical oxidation of reactive azo dye with UV-H₂O₂ process, *Dyes Pigm.* **62** (2004) 269–275.
- [25] A.R. Khataee, V. Vatanpour, A.R. A. Ghadim, Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO₂, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: A comparative study, *J. Hazard. Mater.* **161** (2009) 1225–1233.
- [26] P.K. Malik, S.K. Sanyal, Kinetics of decolourisation of azo dyes in wastewater by UV/H₂O₂ process, *Sep. Purif. Technol.* **36** (2004) 167–175.
- [27] A. Aleboye, Y. Moussa, H. Aleboye, The effect of operational parameters on UV/H₂O₂ decolourisation of Acid Blue 74, *Dyes Pigm.* **66** (2005) 192–134.

- [28] B. Xu, N. Gao, H. Cheng, S. Xia, M. Rui, D. Zhao, Oxidative degradation of dimethyl-phthalate (DMP) by UV/H₂O₂ process, *J. Hazard. Mater.* **162** (2009) 954–959.
- [29] K. Li, D.R. Hokanson, J.C. Crittenden, R.R. Trussell, D. Minakata, Evaluating UV/H₂O₂ processes for methyl tert-butyl ether and tertiary butyl alcohol removal: Effect of pretreatment options and light sources, *Water Res.* **42** (2008) 5045–5053.
- [30] H. Ghodbane, O. Hamdaoui, Decolorization of anthraquinonic dye, C.I. Acid Blue 25, in aqueous solution by direct UV irradiation, UV/H₂O₂ and UV/Fe(II) processes, *Chem. Eng. J.* **160** (2010) 226–231.
- [31] D. Jiraroj, F. Unob, A. Hagege, Degradation of Pb–EDTA complex by a H₂O₂/UV process, *Water Res.* **40** (2006) 107–112.
- [32] F.H. Al Hamedi, M.A. Rauf, S.S. Ashraf, Degradation studies of Rhodamine B in the presence of UV/H₂O₂, *Desalination* **239** (2009) 159–166.
- [33] J.H. Baxendale, J.A. Wilson, The photolysis of hydrogen peroxide at high intensities, *Trans. Farad. Soc.* **53** (1957) 344–356.
- [34] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants of hydrated electrons, hydrogen atoms and hydroxyl radicals (AOH/AO[•]) in aqueous solution, *J. Phys. Chem. Ref. Data* **17** (1988) 513–886.
- [35] E. Chamarro, E. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, *Water Res.* **35** (2001) 1047–1051.
- [36] C. Walling, Fenton's reagent revisited. *Accounts of Chemical Research, Acc. Chem. Res.* **8** (1975) 125–131.
- [37] W. Li, V. Nanaboina, Q. Zhou, G.V. Korshin, Effect of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products, *Water Res.* **46** (2012) 403–412.
- [38] H. Fallmann, T. Krutzler, R. Bauer, S. Malato, J. Blanco, Applicability of the Photo-Fenton method for treating water containing pesticides, *Catal. Today* **54** (1999) 309–319.
- [39] C.R. Silva, M.G. Maniero, S. Rath, J.R. Guimaraes, Degradation of flumequine by Fenton and photo-Fenton processes: Evaluation of residual antimicrobial activity, *Sci. Total Environ.* **445–446** (2013) 337–346.
- [40] K. Schested, O.L. Rasmussen, H. Fricke, Rate constants of [•]OH with HO₂[•], O₂^{•-} and H₂O₂⁺ from hydrogen peroxide formation in pulse-irradiated oxygenated water, *J. Phys. Chem.* **72** (1968) 626–631.
- [41] C. Fan, L. Tsui, M.C. Liao, Parathion degradation and its intermediate formation by Fenton process in neutral environment, *Chemosphere* **82** (2011) 229–236.
- [42] I. Arslan, I.A. Balcioglu, T. Tuhkanen, D. Bahnemann, H₂O₂/UV-C and Fe²⁺/H₂O₂/UV-C versus TiO₂/UV-A treatment for reactive dye wastewater, *J. Environ. Eng.* **126** (2000) 903–911.

IZVOD

POREĐENJE ULTRALJUBIČASTO ZRAČENJE/VODONIK- PEROKSID, FENTON I FOTO-FENTON PROCESA ZA DEKOLORIZACIJU REAKTIVNIH BOJA

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U ovom radu ispitivana je efikasnost dekolozacije komercijalno važnih tekstilnih boja Reactive Orange 4 (RO4) i Reactive Blue 19 (RB19) procesima UV/H₂O₂, Fenton i foto-Fenton. Tretmani fotodekolozacije su vršeni u UV reaktoru, originalne izrade, sa živinim lampama niskog pritiska čiji je maksimum energije zračenja na talasnoj dužini 254 nm. Ispitivan je uticaj parametara procesa kao što su inicijalni pH, inicijalna koncentracija H₂O₂, inicijalna koncentracija Fe²⁺ i inicijalna koncentracija boja, na efikasnost dekolozacije boja RO4 i RB19. Rezultati su pokazali da je potpuna dekolozacija UV/H₂O₂ procesom postignuta za manje od 20 min za tekstilnu boju RO4, odnosno za manje od 40 min za tekstilnu boju RB19. Fenton procesom potpuno uklanjanje boje bilo je postignuto u vremenskom periodu od 30 min. Najefikasnija metoda za dekolozaciju ove dve boje bio je foto-Fenton proces gde je efikasnost dekolozacije od 95% postignuta za 15 min. Daljim istraživanjem utvrđeno je da je foto-Fenton proces bio efikasniji od UV/H₂O₂ i Fenton procesa za dekolozaciju boja u simuliranim otpadnim vodama kada za bojenje, pri optimalnim uslovima procesa. U simuliranim kadama za bojenje efikasnost uklanjanja je nešto niža u odnosu na efikasnost uklanjanja u vodenim rastvorima boja. Rezultati su pokazali da se ispitivani unapređeni oksidacioni procesi mogu primeniti kao efikasni tretmani za uklanjanje boja RO4 i RB19 iz otpadnih i prirodnih voda.

Ključne reči: Boje • Fenton proces • Oksidacija • Foto-Fenton proces • UV/H₂O₂ proces