

Decolorization of disperse red 354 azo dye in water by several oxidation processes—a comparative study

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Abstract

The degradation of the Disperse Red 354 azo dye in water was investigated in laboratory-scale experiments, using four advanced oxidation processes (AOPs): ozonation, Fenton, UV/H₂O₂, and photo-Fenton. The photodegradation experiments were carried out in a stirred batch photoreactor equipped with an immersed low-pressure mercury lamp as UV source. Besides the conventional parameters, on acute toxicity test with a LUMISTox 300 instrument was conducted and the results were expressed as the percentage inhibition of the luminescence of the bacteria *Vibrio fischeri*. The results obtained showed that the decolorization rate was quite different for each oxidation process. After 30 min reaction time the relative order established was: UV/H₂O₂/Fe(II) > Dark/H₂O₂/Fe(II) > UV/H₂O₂ = O₃ > UV/H₂O₂/Lyocol. During the same reaction period the relative order for COD removal rate was slightly different: UV/H₂O₂/Fe(II) > Dark/H₂O₂/Fe(II) > UV/H₂O₂ > UV/H₂O₂/Lyocol > O₃. A color removal of 85% and COD of more than 90% were already achieved after 10 min of reaction time for the photo-Fenton process. Therefore, the photo-Fenton process seems to be more appropriate as the pre-treatment method for decolorization and detoxification of effluents from textile dyeing and finishing processes. Sulphate, nitrate, chloride, formate and oxalate were identified as main oxidation products.

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1. Introduction

The use of disperse dyes has been continuously increased in the textile industry since the discovery

of synthetic fibers. These dyes can be applied to most synthetic fibres using simple exhaustion techniques. Disperse azo dyes, in particular, cause environmental concern due to their widespread use, their degradation products, such as toxic aromatic amines, and their low removal rate during aerobic waste treatment [1]. Therefore, the commercial Disperse Red 354 [Color Index (CI)] azo

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dye was chosen as a model substrate in the present work.

There are several methods used to decolorize the textile wastewater [2] but they cannot be effectively applied for all dyes. Advanced oxidation is one of the potential alternatives to decolorize and to reduce recalcitrant wastewater loads from textile dyeing and finishing effluents. This process implies generation and subsequent reaction of hydroxyl radicals, which are the most powerful oxidizing species after fluorine [3].

Among AOP's, treatment with ozone (often combined with H_2O_2 , UV, or both), an UV/ H_2O_2 system, or Fenton and photo-Fenton type processes have proven to yield very good results either for complete mineralization of reactive dyes or for their transformation into less complex structures that are more easily biodegradable [4–7].

The main objective of this work was to study the degradation kinetics of the azo dye Disperse Red 354 (CI) by four AOPs: ozonation, UV/ H_2O_2 , Fenton, and photo-Fenton. In addition, the toxic potential of the dye's degradation products was investigated using the bioluminescence test. The commercial disperse dyes generally contain about 50% of the dispersing agent. Therefore, the influence of this dispersing agent on the degradation process was also examined. HPICE analysis was also performed to obtain detailed information on the resulting oxidation products (organic and inorganic anions).

2. Methods

2.1. Materials

The azo dye Disperse Red 354 (CI) was kindly provided by Clariant (Germany) as a commercially available dye formulation designated as Foron Rubin S₂GLF (trade name) and used without further purification. The main characteristics of the investigated azo dye used as a substrate are represented in Fig. 1. The dispersing agent Lyocol DRN, an aromatic polyethersulfonate, was also supplied by Clariant (Germany). Hydrogen peroxide solution (30%)

and manganese dioxide of analytical grade, as well as all organic components (p.a.), were obtained from Merck (Germany).

Aqueous solutions containing 100 mg/l azo dye were prepared with ultrapure water (conductivity of 0.056 $\mu\text{S}/\text{cm}$) from a Millipore Waters Milli Q purification unit and stirred overnight. After the stirring the sample was filtered through 0.45 μm cellulose nitrate filters. As the dye was partially soluble in water, the solution was deliberately filtrated in order to use for experiments a simulated disperse dyebath effluent. It is known that Disperse dyes have a high fixation rate. Only 5% of waste dye could be found in wastewaters. Decolorization capacity was determined by absorbance measurements at the maximum visible absorbance wavelength of 462 nm.

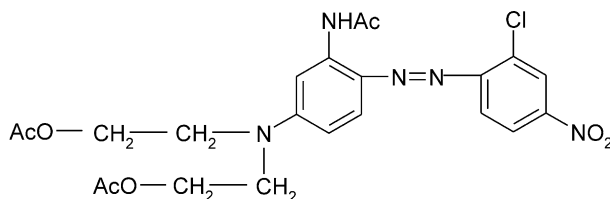
The so-prepared aqueous solution had a concentration of 45.756 μM and was characterised by COD equal to 155 mgO_2/l , $\text{TCV} = 31.41 \text{ m}^{-1}$, pH 6.70, conductivity 23 $\mu\text{S}/\text{cm}$ and $\text{TOC} = 17.55 \text{ mgC}/\text{l}$.

2.2. Photoreactor and actinometry

The photodegradation experiments were carried out in a stirred batch photoreactor, at 298 K, as described in a previous paper [8]. A Heraeus UV immersed lamp TN 15/35 with a nominal output of 15 W irradiated the solutions. The incident photonic flux was measured by photolysis of H_2O_2 ($I_0 = 1.007 \cdot 10^{-5} \text{ Einstein/s}$) [9].

2.3. Ozonation

Ozone was generated from dried air by an ozone generator “Ozon Erzeuger 24g” of the company Erwin Sander Elektroapparatenbau, Ueltzen. The ozone concentration was determined by an ozone measuring device model “Ozon Meßgerät” (Erwin Sander Elektroapparatebau). Ozonation was performed in a cylindric glass reactor (volume 1.4 l) by bubbling the ozone/air mixture into the solution, at a volume stream of 20 l/h through a sintered glass filter (pore size 50–80 μm) fixed at the bottom of the reactor. The ozone consumption was measured by means of the monitored ozone concentration at the reactor outlet. Samples of the



Molecular weight: 505.723 g/mol

Molecular formula: $C_{22}H_{24}ClN_5O_7$

Bacteria: $IC_{50} > 100$ mg/L

Phytotoxicity (salmo gairdneri, oncorhynchus mykiss) 48h: $LC_{50} = 180$ mg/L (Safety Data-Sheets)

Fig. 1. Chemical structure and essential proprieties of Disperse Red 354 (CI).

reaction medium were withdrawn at regular intervals and analyzed for UV/vis-absorbance, COD (chemical oxygen demand), TOC (total organic carbon), pH, conductivity and for inorganic/organic anions by HPIC (high performance ion chromatography). The residual hydrogen peroxide was removed by raising the pH to 9–10, adding MnO_2 and allowing the samples to sit overnight. The dye absorbance was measured before and after addition of the catalyst. No changes in absorbance were observed. The manganese dioxide remains unchanged at the end of the experiment.

2.4. Analyses

The optical absorption of each azo dye solution was determined and recorded by a UV–Vis Cary 1 spectrophotometer (Varian). The concentrations of the unconverted dye in solution were defined as the dye absorption maximum by Eq. (1), and the Translucent Color Value (TCV) was defined by Eq. (2):

$$\frac{C_A}{C_A^0} 100 = \frac{TCV}{(TCV)_{\tau=0}} 100 \quad (1)$$

$$TCV = A(\lambda) 1000 \, d^{-1} \quad (2)$$

where $A(\lambda)$ = spectral absorbance; d = length of the quartz cell (10 mm). Anion analysis was conducted using a Dionex model DX500 ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with an IonPac HPICE-AS 11 column (Dionex) and operating in suppressed conductivity detection mode. Samples, injected at a volume of 50 μ l by an

automatic sampler, were eluted by a NaOH/water gradient at a flow rate of 1.5 ml/min.

COD determination was done using commercially available test kits from Machery and Nagel (Düren, Germany) by oxidation with potassium dichromate in sulphuric acid and heating for 2 h at 421 K. The TOC content in the solution was determined using a Shimadzu model 5050 TOC analyzer. The pH was measured by means of a WTW pH-Meter Multiline P4.

2.5. Bioluminescence test

Acute toxicity tests were performed as reported by Wang et al. [10] by using the inhibition of the natural luminescence of the marine photobacterium *Vibrio fischeri*. All tests were conducted using a DR LANGE LUMISTox 300 photometer. Luminescent bacteria and all reagents required for the assay were also obtained commercially from the same company.

3. Results and discussion

3.1. Ozonation of aqueous dye solution

The results of the conventional parameter characterization of the ozonated aqueous sample of Disperse Red 354 ($TCV_0 = 31.41 \, m^{-1}$) are shown in Table 1.

Decolorization of the investigated disperse dye was 29.3% after 30 min of ozonation at ozone concentrations of 8.2 mg/l. Due to the production of organic and inorganic acid anions, the pH decreased during ozonation from 6.7 to about 4.7, whereas the conductivity increased from 23 to 74

Table 1

Conventional parameters during the ozonation (8.2 mg/l) of Disperse Red 354 at 298 K ($TCV_0 = 31.41 \text{ m}^{-1}$)

Time (min)	A/A_0 , 462 nm (%)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	COD (mg O_2/l)	COD/COD ₀ (%)	TOC ^a (mg C/l)	TOC/TOC ₀ (%)
0	100.0	6.70	23	155	100.0	12.08	100.0
5	92.80	6.37	60	149	96.13	11.21	92.80
10	88.22	6.05	60	144	92.90	10.66	82.22
15	83.64	5.40	61	138	89.03	10.10	83.62
30	70.68	4.70	74	133	85.81	8.54	70.70

^a Calculated value.

$\mu\text{S}/\text{cm}$. A 14.19% degree of COD removal was obtained after the same reaction time of ozonation. The corresponding TOC removal rates were determined to be 29.30%. These results may be explained by the production of small organic molecular fragments along with the destruction of the dyestuff, not being completely mineralized under the prevailing oxidation conditions. The TOC/TOC₀ ratio is helpful for assessing the mineralization rate but the obtained TOC values may not present the total TOC concentrations because of the losses of volatile compounds (i.e. formaldehyde, acetaldehyde) into the gaseous stream during the ozonation. To obtain detailed information on the reaction processes during ozonation, the resulting oxidation products (organic and inorganic anions) were analyzed. Sulphate, nitrate, formate and oxalate were identified as the main oxidation products. The initial sulphate concentration of the aqueous Disperse Red 354 solution is caused by the content of dispersing agent within the dye formulation. Oxidation and cleavage of the azo and amino groups results in the formation of nitrate. Due to the decreasing value of the pH during ozone treatment it can be assumed that the ozonated solution contains the analyzed organic anions in the form of their corresponding acids.

3.2. Photodegradation of aqueous Disperse Dye solution

The results of the conventional characterization of the irradiated aqueous samples of Disperse Red 354 ($TCV_0 = 31.41 \text{ m}^{-1}$) are shown in Table 2.

Table 2

Conventional parameters during photodegradation of Disperse Red 354 at 298 K ($TCV_0 = 31.41 \text{ m}^{-1}$, $\text{C}_{\text{H}_2\text{O}_2} = 24.5 \text{ mmol/l}$)

Time (min)	A/A_0 , 462 nm (%)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	COD (mg O_2/l)	COD/COD ₀ (%)
0	100.0	6.70	23	155	100.0
5	96.64	6.26	32	128	80.00
10	91.82	4.90	34	90	56.25
15	84.37	4.35	43	73	45.63
30	73.65	3.76	100	61	38.13

After 30 min irradiation with a dose of 24.5 mmol $\text{H}_2\text{O}_2/\text{l}$, 26.4% decolorization was achieved. The pH decreased during ozonation from 6.70 to about 3.76 whereas the conductivity increased from 23 to 100 $\mu\text{S}/\text{cm}$. Formate and oxalate, identified as fragmental oxidation products of Disperse Red 354 could also be detected during the irradiation of the dye. Nitrate, chloride and sulphate were also detected as reaction products (Fig. 2).

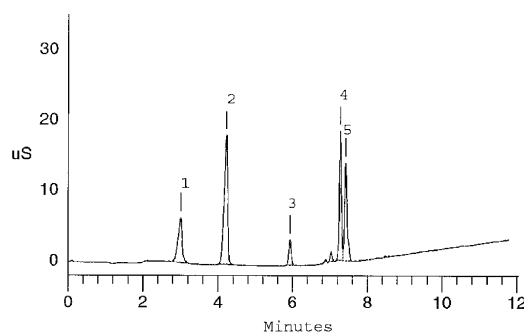


Fig. 2. HPICE analysis of Disperse Red 354 after 30 min irradiation with 24.5 mmol $\text{H}_2\text{O}_2/\text{l}$. Peak identities are as follows: 1, formate; 2, chloride; 3, nitrate; 4, sulphate; 5, oxalate.

The high initial sulphate concentration of the aqueous Disperse Red 354 solution is assumed to be caused by the content of dispersing agent within the dye formulation. A 62% COD removal rate was obtained after 30 min of irradiation time.

The existence of an optimal dose of H_2O_2 has previously been noticed by numerous authors [5, 7, 11, 12]. Shu et al. [11] investigated the decolorization of Acid Red and Acid Yellow 23 by UV/ H_2O_2 treatment. They described an optimal dose of 9.8 mmol/l H_2O_2 for a 23.56 $\mu\text{mol/l}$ Acid Red 1 aqueous solution with an initial molar ratio of $\text{H}_2\text{O}_2/\text{dye}$ of 415.96. Our previous finding in the case of RY84, for instance, leads to a ratio of 417.02 mol $\text{H}_2\text{O}_2/\text{mol dye}$ [12], that is 24.5 mmol/l H_2O_2 . In the case of azo dye Disperse Red 354 a ratio of 535.45 mol $\text{H}_2\text{O}_2/\text{mol dye}$ was found to give good results. It can be concluded that a H_2O_2 dose higher than 24.5 mmol/l corresponds to an unprofitable consumption of hydrogen peroxide.

3.3. Fenton reaction

The results of the conventional characterization of the aqueous samples of Disperse Red 354 ($\text{TCV}_0 = 31.41 \text{ m}^{-1}$) by a Fenton oxidation are summarized in Table 3.

After 30 min of reaction, 76% decolorization was achieved. Trace concentrations of oxalate, nitrate and sulphate were also identified as reaction products. Formation of nitrate and sulphate can probably be explained as above. A greater than 90% COD removal rate was obtained after 30 min reaction time at a 20:1 $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratio and at pH 3.

Table 3

Conventional parameters during treatment with $\text{H}_2\text{O}_2/\text{Fe(II)}$ /Dark of Disperse Red 354 at 298 K ($\text{TCV}_0 = 31.41 \text{ m}^{-1}$, $\text{C}_{\text{H}_2\text{O}_2} = 24.5 \text{ mmol/l}$; $\text{C}_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} = 1.225 \text{ mmol/l}$ at pH 3)

Time (min)	A/A_0 , 462 nm (%)	COD (mg O_2/l)	COD/ COD_0 (%)
0	100.0	155	100.0
5	32.38	89	57.42
10	28.49	81	52.26
15	28.36	<15	<9.67
30	23.57	<15	<9.67

3.4. Photo-Fenton oxidation

Due to its slow dissociation rate in the dark, the generation of hydroxyl radicals was reduced and consequently the Fenton oxidation was not even half as effective as when the reaction was run in the absence of light. It is obvious that the most effective AOP for treating dye solutions is a UV-enhanced $\text{H}_2\text{O}_2/\text{Fe(II)}$ solution. The results of the conventional characterization of the aqueous samples of Disperse Red 354 ($\text{TCV}_0 = 31.41 \text{ m}^{-1}$) by photo-Fenton oxidation are summarized in Table 4.

After 30 min of reaction time, the degree of decolorization was 94%. Nitrate and sulphate were also found as reaction products. More than 90% of COD and 74.77% of TOC removals were obtained after 5 min at a molar ratio of 20:1 for $\text{H}_2\text{O}_2/\text{Fe(II)}$ at pH 3. By contrast with other oxidation methods, far better results could be obtained using the photo-Fenton process under the described experimental conditions. The high removal efficiencies of this method can be explained by the fact that oxidation reactions are coupled to coagulation occurring due to the presence of ferrous/ferric cations, thus these metallic ions play a double role as a catalyst and a coagulant in the process.

Moreover, in the Fenton process the hydrogen peroxide reacting with ferrous ions forms a strong oxidising agent (hydroxyl radical), whose oxidation potential is higher than that of ozone (2.8 V compared to 2.07 V). The performance of the photo-Fenton process depended heavily on factors such as the pH of the solution, the quality of hydrogen peroxide added and the dose of FeSO_4 .

Table 4

Conventional parameters during the photo-Fenton oxidation of Disperse Red 354 at 298 K ($\text{TCV}_0 = 31.41 \text{ m}^{-1}$, $\text{C}_{\text{H}_2\text{O}_2} = 24.5 \text{ mmol/l}$; $\text{C}_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} = 1.225 \text{ mmol/l}$ at pH 3)

Time (min)	A/A_0 , 462 nm (%)	COD (mg O_2/l)	COD/ COD_0 (%)	TOC ^a (mg C/l)	TOC/ TOC_0 (%)
0	100.0	155	100.0	12.08	100.0
5	20.52	<15	<9.67	3.05	25.23
10	15.27	<15	<9.67	2.27	18.78
15	9.29	<15	<9.67	1.38	11.42
30	5.96	<15	<9.67	0.88	7.32

^a Calculated value.

The existing results on other dye (Procion Reactive red HE7B, [13]) show that the system, when operated with a source of UV light at pH 3 and a molar $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratio of 20:1, can be optimal for complete textile wastewater decolorization and mineralization. The best experimental results for the photo-Fenton process proved to be the following: after 10 min of reaction time the removal of color and COD was equal to 85% and more than 90%, respectively. The removal of color and COD was accomplished at two different rates. A quick oxidation during the first 10–15 min was followed by a much slower reaction. It can be hypothesised that in analogy to the oxidation with ozone, during the photo-Fenton process the substances which are easy to oxidize are also removed readily. The reactions which occur in the first step of the photo-Fenton process, apart from coagulation, are thus among those leading to modification of the structure of the dye, an observation which can be confirmed by the rapid decolorization of the solution at the outset of the process. It is of interest to note that the most effective removal of COD and the apparent color reduction obtained by the Fenton's reagent are confirmed by numerous authors using reactive and direct dyes [14–16].

3.5. Effect of dispersing agent (Lyocol) on the photodegradation of Disperse Red 354

During the production of disperse dyes, two or three types of dispersing agents are added to the pure dye to ensure the required dyeing quality of commercial dyes. The main problem in applying disperse dyes are the dispersing agents, which are not biodegradable and remain completely in the dye bath. In general, the commercial disperse dye contains about 50% of dispersing agent. The comparison (Table 2) of the effect of the dispersing agent Lyocol (aromatic polyethersulfonate) on the photodegradation of the azo dye Disperse Red 354 was studied (Table 5).

After 30 min of reaction time only 17% decolorization was achieved in the presence of Lyocol and 26.3% in the absence of the dispersing agent. Nitrate and sulphate were also detected as reaction products. COD removal rates obtained after 30 min of reaction time were 30% in the presence

Table 5

Conventional parameters of photodegradation of Disperse Red 354 at 298 K ($\text{TCV}_0 = 31.41 \text{ m}^{-1}$, $\text{C}_{\text{H}_2\text{O}_2} = 24.5 \text{ mmol/l}$; Lyocol concentration, 0.5 g/l)

Time (min)	A/A_0 , 462 nm (%)	pH	Conductivity ($\mu\text{S/cm}$)	COD (mg O_2/l)	COD/COD ₀ (%)
0	100.0	7.06	188	393	100.0
5	92.91	8.44	169	353	89.82
10	85.82	8.35	177	295	75.06
15	84.23	7.86	188	274	69.72
30	82.98	7.57	211	277	70.48

of Lyocol and 55% without the dispersing agent. The conductivity increased during irradiation from 188 to 211 $\mu\text{S/cm}$.

3.6. Bioluminescence test

The toxicity of pollutants is usually determined by tests performed on fish or single cell green algae. A recent review [17] presents a table of toxicities of some dyes on the single cell green algae *Selenastrum capricornutum* as well as on *Pimephales promelas*. The main disadvantages of tests on fish and algae are their long duration (24–96 h, compared to a maximum of only 30 min for bioluminescence tests) and the large error in EC_{50} because only a small number of living organisms are used in each experiment (while the bioluminescence tests use 10^6 bacteria for one analysis). Wang et al. [10] demonstrated that the toxicity assessment with luminescent bacteria is effective and of practical use for chemicals applied in the textile finishing industry. The bioluminescence tests were conducted to find out whether the methods used can cause any toxic degradation products. Aqueous dye solutions of Disperse Red 354 after oxidative treatment were submitted to bioluminescence tests using the luminescence bacterium *V. fischerii* in LUMISTox 300 according to DIN 38412 an the international standard ISO DIS 11348. Screening is the simplest way of determining the toxicity of a sample. The results expressed as the percentage inhibition of the luminescence in the test solutions relative to a control solution are summarized in Table 6.

Based on the 15 min percentage inhibition values, the $\text{UV}/\text{H}_2\text{O}_2/\text{Lyocol}$ -treated samples

Table 6

Percentage inhibition of the luminescence in the test solutions of Disperse Red 354 after 60 min of reaction time (exposure time: 15 min)

Method	Inhibition (%)
Foron solution	7.72
Photo-Fenton	7.29
Ozonation	32.29
UV/H ₂ O ₂	72.22
UV/H ₂ O ₂ /Lyocol	87.39

with the 87.39% can be scheduled as samples with the most toxic capacity. Obviously, dispersing agent Lyocol had an inhibitory effect on the degradation process. Wang et al. [10] also experienced the same phenomena in the case of dispersing agents “Dispersant PNG” and “Breviol A 69”. The photo-Fenton process can be listed as the process with the lowest toxic capacity.

4. Conclusions

The disperse dye Disperse Red 354 degradation in aqueous solution has been comparatively studied by four AOP's: oxidation by UV/H₂O₂, ozonation, Fenton and photo-Fenton processes. The decolorization rate was observed to be quite different for each system, after 30 min reaction time the relative order evaluated was: UV/H₂O₂/Fe(II) > Dark/H₂O₂/Fe(II) > UV/H₂O₂=O₃ > UV/H₂O₂/Lyocol (Fig. 3).

The relative order established for the COD removal rate after the same reaction time was also observed to be different for each system, and followed the order of UV/H₂O₂/Fe(II) > Dark/H₂O₂/Fe(II) > UV/H₂O₂ > UV/H₂O₂/Lyocol > O₃ (Fig. 4).

Based upon the toxicity results, the bioluminescence test could be applied as a rapid pre-screening test for toxicity evaluation of different process effluents. The results confirm that the photo-Fenton process, which proved to be feasible and cost-effective for degradation of dyes at a low H₂O₂ concentration, seems to be more appropriate for removal of color, COD and TOC of dye-solution.

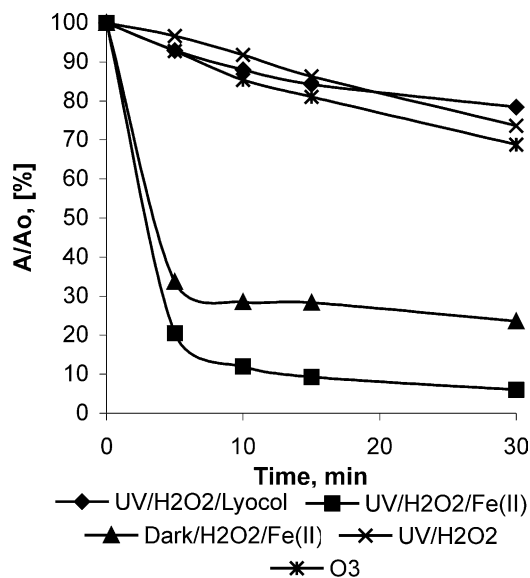


Fig. 3. Rate of color degradation of Disperse Red 354 aqueous solution during ozonation, photooxidation, photo-Fenton oxidation. Initial conditions were 24.5 mmol H₂O₂/l, 8.2 mgO₃/l, 1.225 mmol FeSO₄/l [at molar H₂O₂/Fe(II) ratio 20:1].

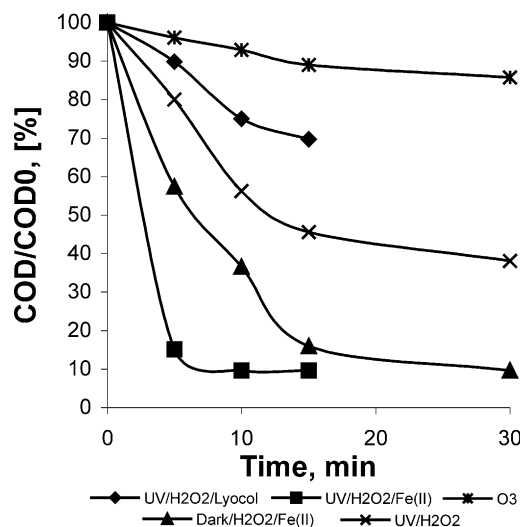


Fig. 4. Rate of COD degradation of Disperse Red 354 dye solution during ozonation, photooxidation, photo-Fenton oxidation. Initial conditions were 24.5 mmol H₂O₂/l, 8.2 mgO₃/l, 1.225 mmol FeSO₄/l [at molar H₂O₂/Fe(II) ratio 20:1].

The investigations should be continued in order to elucidate the influence of other factors such as textile auxiliaries, salts, surfactants and other impurities on the degree of mineralization.

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