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Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes

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Abstract

This paper evaluates the degradation of two azo reactive dyes, C.I. Reactive Yellow 84 (RY84) and C.I. Reactive Red 120 (RR120) by photo-Fenton and Fenton-like oxidation. All experiments were performed on a laboratory scale set-up. The effects of different reaction parameters such as initial pH, contact time, effect of light and hydrogen peroxide concentrations on the oxidation of the dye aqueous solutions have been assessed. Effective system conditions were found to be pH of 3, hydrogen peroxide-to-iron molar ratio of 20:1 and UV or solar irradiation. The color removal efficiency at the optimum conditions during different Fenton-like processes was also evaluated. The results show that the color removal of RY84 after 15 min reaction time follows the decreasing order: solar/Fe(II)/H_2O_2 > UV/Fe(II)/H_2O_2 > UV/Cu(II)/Fe(III)/H_2O_2 > UV/Fe(III)oxalate/H_2O_2 > UV/Fe(III)/H_2O_2 > dark/Fe(II)/H_2O_2 > solar/Fe(III)oxalat/H_2O_2 > UV/H_2O_2 > UV/Fe(II) = UV. During the same reaction period the relative order for RR120 removal rate was slightly different: solar/Fe(II)/H_2O_2 > UV/Fe(II)/H_2O_2 > UV/Fe(III)/H_2O_2 = UV/Cu(II)/Fe(III)/H_2O_2 > UV/Fe(III)oxalate/H_2O_2 = UV/H_2O_2 > UV. The toxic potential of the dye's degradation was investigated by the bioluminescence test using the LUMIStox 300 instrument and results were expressed as the percentage inhibition of the luminescence of the bacteria *Vibrio fisheri*. Formate and oxalate, identified as fragmental oxidation products of investigated dyes, could also be detected after 15 min irradiation time.

Keywords: Azo dyes; Photo-Fenton; Decolourization; UV; Solar light

1. Introduction

There are several methods currently used to decolorize textile wastewater [1] but they are not universally applicable and they are not cost-effective for all dyes.

The azo dyes contained in industrial dye wastewaters could be treated by adsorption onto activated carbon or by chemical coagulation. Unfortunately, these classic methods mainly transferred the contaminant from wastewater to solid wastes. Advanced oxidation processes (AOP), such as the H_2O_2/UV, O_3/UV, and H_2O_2/O_3/UV procedures, employ UV photolysis of H_2O_2 and/or O_3 in order to generate HO radicals. These oxidation methods can be considered as a potential alternative in decolorizing the textile dyeing and finishing effluents [2–4]. However, the high electrical energy demand and/or the consumption of chemical reagents are common problems among all the AOPs. Specially, the production of photons with artificial light sources require an important energy input [5].

Fenton-type reactions using H_2O_2 as an oxidant in the presence of iron ions at acidic pH have been among the most common homogeneous systems [6,7]. The main advantage of Fenton's reaction compared to other AOPs is that this system offers a cost effective source of hydroxyl radicals and it is easy to operate and maintain. It is particularly advantageous in situation where textile wastewater contains a high concentration of suspended solids due to the limited depth of photon penetration.

The generation of hydroxyl radicals from H_2O_2 in presence of Fe(II) has been shown to be enhanced in the presence of light. Under irradiation, Fe^{3+} ions are constantly reduced to Fe^{2+} and the Fenton reaction is improved by the participation of photogenerated Fe^{2+}. In the presence of H_2O_2, the photo-Fenton reaction is continuously promoted.

Kang et al. [8] reported that the Fenton process could be adopted readily in a textile wastewater treatment system,

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without the need for reconstructing the existing coagulation unit. The only changes in the process operation will be the addition of H_2O_2 and Fe(II) as well as pH adjustment. In addition, the rapid and slow mixing tanks can provide detention times, which are adequate for Fenton process to achieve the desired color removal. Gnann et al. [9] suggest the regeneration of Fe^{2+} from iron sludge at $pH < 1$. This process is called "Fenton Sludge Recycling System" (FSRS). Using the FSRS, there will be almost no sludge discharge in Fenton oxidation processes. Qiang et al. [10] presented the regeneration of Fe^{2+} by an electrochemical process. The unit energy consumption in this case is 2.0–3.0 kWh/kg Fe^{2+} regenerated. During the photo-Fenton process, the Fe(III) ions are continuously regenerated to Fe(II) ions.

The aim of this paper is to present results concerning the optimization and intensification of monoazodye decolorization by the photo-Fenton process. C.I. Reactive Yellow 84 (RY84) and C.I. Reactive Red 120 (RR120) have been chosen as the subject of this study because of their wide use in the textile industry.

The specific objectives of our study are the investigation of removal efficiencies of the selected commercial dyes in the presence of H_2O_2 and iron ions under UV irradiation; the determination of the optimal conditions and the reaction rate constants at the optimal conditions. Important variables such as oxidation time, effect of pH, dosages of H_2O_2, contact time, effect of light and ferrous ions were examined. The decolorization efficiency at the obtained optimum conditions during different Fenton-like processes was also evaluated. In addition, the reaction end-products, as an important indicator of the treatment effectiveness, have also been determined.

2. Experimental

2.1. Materials

The azo dyes, *C.I. Reactive Yellow 84* (Color Index) and *C.I. Reactive Red 120* (Color Index) were obtained from BASF (Germany) as commercially available dyes and used without further purification. The hydrogen peroxide solution (30%) of analytical grade, $FeSO_4{\cdot}7H_2O$, $FeCl_3$, $CuSO_4{\cdot}5H_2O$ and all organic components (p.a.) were obtained from Merck, Germany. Aqueous solution containing 100 mg/l azo dye were prepared with ultrapure water (conductivity of 0.056 μS/cm) from a Millipore Waters Milli-Q purification unit. Potassium ferrioxalate $K_3Fe(C_2O_4)_3{\cdot}3H_2O$ was prepared from reagent-grade chemicals as recommended by Hatchart and Parker [11].

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 [12]. 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 ($I_0 = 1.007 \times 10^{-5}$ einstein/s).

2.3. Analyses

The optical absorption of each azo dye solution was determined and recorded by a UV-Vis Cary spectrophotometer (Varian). Samples of the reaction medium were withdrawn at regular intervals; the reaction was then blocked by raising the pH to 9–10, adding MnO_2 and allowing the samples to sit overnight. The residual iron was removed by alkalization of the solution. Iron is precipitated at $pH \geq 9.0$ in the form of $Fe(OH)_3$. The sediment was removed by filtration using a 0.45 μm cellulose nitrate filter. The dye absorbance was measured before and after addition of MnO_2. No changes in absorbance were observed. The manganese dioxide remains unchanged at the end of the experiment.

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

COD determination was done with commercially available test kits of the company Machery & Nagel, Düren, Germany, by oxidation with potassium dichromate in sulfuric acid and heating for 2 h to 421 K.

The total organic carbon (TOC) content in solution was determined using a Schimadzu model 5050 TOC analyzer. The pH was measured by means of a WTW pH-Meter Multiline P4.

The experiments under solar irradiation were carried out in Munich, Germany on typical August summer days (29 °C, determined on the day of experiment) under clear sky conditions. Open glass vessel of 22 cm diameter and 4 cm solution depth were used. The volume of solutions and exposition areas were 1.5 l and 380 cm^2, respectively.

The bioluminescence tests were conducted using a Dr Lange LUMIStox 300 photometer; reagents and *Vibrio fisheri* luminescent bacteria were supplied by Dr. Lange, GmbH (Düsseldorf, Germany). Solvent extracts were tested according to DIN 38412 and the international standard ISO DIS 11348. The toxicity of extracts was evaluated after 5, 15 and 30 min at 15 °C. All concentrations were tested in duplicate.

3. Results and discussion

3.1. Effect of pH

The principal inorganic reactions which are considered common to the Fenton reaction system represent the interactions among various inorganic species including $OH^{\bullet}$, $HO_2^{\bullet}$, O_2^{-}, H_2O_2, Fe^{2+} and Fe^{3+} as shown in Eqs. (1)–(10), respectively.

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^\bullet + H^+ \quad (2)$$

$$Fe^{3+} + HOO^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (3)$$

$$R\text{–}H + HO^\bullet \rightarrow R^\bullet + H_2O \quad (4)$$

$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad (5)$$

$$R^+ + H_2O \rightarrow ROH + H^+ \quad (6)$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^- \quad (7)$$

$$H_2O_2 + HO^\bullet \rightarrow H_2O + HOO^\bullet \quad (8)$$

$$HOO^\bullet \rightarrow O_2{}^{\bullet -} + H^+ \quad (9)$$

$$HOO^\bullet + Fe^{2+}(+H^+) \rightarrow Fe^{3+} + H_2O_2 \quad (10)$$

Under light irradiation, Fe^{3+} is continuously reduced to Fe^{2+}:

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^\bullet + H^+ \quad (11)$$

As indicated in Eq. (1), the amount of $HO^\bullet$ generated by the Fenton process is affected by the pH. The hydroxyl radicals can be efficiently formed especially under acidic conditions. To find the optimum pH for maximum conversion of the aqueous dye solutions, reactions were carried out at different pH value in the range of 2–9.7, by adding H_2SO_4 or NaOH. Fig. 1 represents the color removal at different pH values of 2, 3, 6.5 and 9.7, i.e. under acidic, neutral and basic conditions.

The results show that the oxidation rate increases as pH value decreases. The optimum pH for RY84 was found to be pH 3, and pH 2 for RR120. For both dyes, the maximum conversion of about 99% was achieved within 15 min at pH 3. Tang and Chen [13] reported similar results for the degradation of C.I. Reactive Red 120 using H_2O_2/iron powder.

Table 1
Hydrated iron(III) species in solution, as a function of pH

Fe^{3+} species	pH range
$Fe(H_2O)_6{}^{3+}$	1–2
$Fe(OH)(H_2O)_5{}^{2+}$	2–3
$Fe(OH)_2(H_2O)_4{}^{+}$	3–4

The low activity detected for high pH has been reported in the literature [5,14,15] and can be explained by the formation and precipitation of $Fe(OH)_3$ (Eqs. (1) and (7)). Perez et al. [5] had reported that Fe(III)ions form different complex species in solution at different pH values, and that the quantum yield of light absorption by Fe^{3+} is directly dependent on the specific species responsible for the absorption (Table 1).

According to results obtained by Pignatello [16], the photo-Fenton reaction is optimal at pH 2.8 where approximately half of the Fe(III) exists as Fe^{3+} ion and half as $Fe(OH)^{2+}$. Color removal of synthetic dyes in water by Fenton's reaction was achieved at pH range 3.0–4.0 [5,8,17]. Our results correspond to those from literature.

3.2. *Effect of the initial H_2O_2 concentration and contact time*

The selection of an optimum H_2O_2 concentration for the degradation of the dyes by Fenton's and photo-Fenton's reagent is important from a practical point of view (due to the cost of H_2O_2). Several studies have been reported the existence of an optimum H_2O_2 dosage, but there is still no agreement on the ratio of H_2O_2/Fe(II) that gives the best results. The optimal ratio of chemicals in the Fenton process recommended in the literature are the ratios H_2O_2/catalyst from 10:1 to 40:1 [5,18–20]. In our experiments, the ferrous

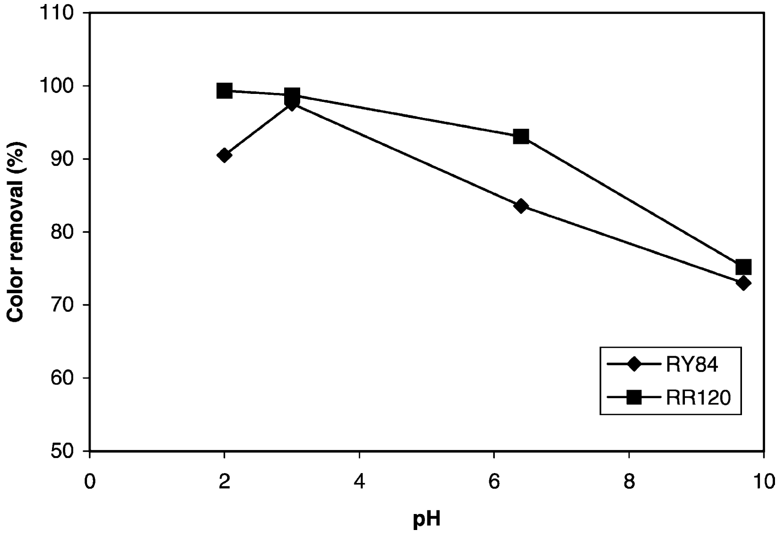

Fig. 1. Effect of pH on the decolorization of RY84 and RR120 during photo-Fenton treatment. Reaction time 15 min, $C_0(\text{dye}) = 100$ mg/l, $C_0(Fe^{2+}) = 0.25$ mM Fe(II), and $C_0(H_2O_2) = 5$ mM H_2O_2.

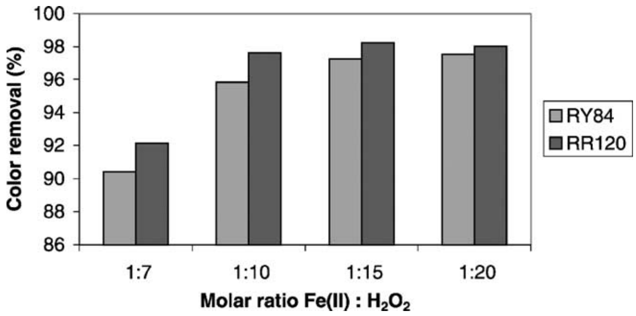

Fig. 2. Effect of H_2O_2 dose on the conversion of RY84 and RR120 during photo-Fenton treatment. Reaction time 15 min, $C_0(\text{dye}) = 100$ mg/l, pH = 3 and $C_0(Fe^{2+}) = 0.25$ mM Fe(II).

sulfate dose was based on the initial molar ratio $FeSO_4/H_2O_2$ of 1:10, 1:15, and 1:20.

In Fig. 2, the results obtained for color removal as a function of the initial molar ratio of Fe^{2+}/H_2O_2 are presented. As expected, most of the H_2O_2 dosage applied was consumed in the first stage of the fast reaction. This is in agreement with the fact that Fenton and photo-Fenton reactions dominate the first minutes of the process and a larger concentration of reactants directly increases the reaction rate [5]. Color removal increased for all H_2O_2 doses when contact time was also increased. At 5 min contact time at pH 3 and at a molar ratio of $Fe(II)/H_2O_2 = 1{:}20$, color removal observed was 88.03 and 90.81% for RY84 and RR120, respectively. At 15 min reaction time and at a molar ratio of $Fe(II)/H_2O_2 = 1{:}20$, color removal observed was 97.53% for RY84 and 98.02% for RR120. 81.34% COD removal for RY84 and 85.05% for RR120 were obtained after the same oxidation time. COD removal was more efficient than TOC reduction throughout the catalytic process. The corresponding TOC removal rates were determined to be 49.32% for RY84 and 73.52% for RR120. At the molar ratio of $Fe(II)/H_2O_2 = 1{:}15$ and after the 15 min reaction time, 97.25% color removal, 55.20% COD and 36.59% TOC removals for RY84 were achieved. The low TOC removal rates 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 [4]. The best COD and TOC removals for both dyes were obtained at the molar ratio of $Fe(II)/H_2O_2 = 1{:}20$. For further experiments this ratio has been used. Dutta et al. [21] have reported the existence of the optimum $Fe(II)/H_2O_2 = 1{:}15$ for the degradation of methylene blue by Fenton's reagent.

3.3. *Effect of light*

Photocatalytic oxidative degradation processes based on the generation of hydroxyl radicals from H_2O_2 in the presence of Fe ions have been shown to be enhanced by light [17,22]. The effect of light on the degradation of RY84 is presented in Fig. 3.

The solution depth to be irradiated is an important parameter when evaluating the efficiency of the photo-Fenton process for the degradation of dyes. This is especially the case when solar light is used as irradiation source because it influences the exposition area necessary for treatment of a certain volume [23]. In our experiments, the solution depth was 4 cm for solar irradiation and 2 cm for UV irradiation, respectively.

The apparent first-order rate constants (k_{ap}) of the degradation after 15 min of reaction time were calculated from linear regression $\ln(C_0/C)$ versus time plots with all regression coefficients greater than 0.9. The $k_{\text{solar}/Fe(II)/H_2O_2}$ obtained for RY84 was 0.338 min^{-1} and $k_{\text{UV}/Fe(II)/H_2O_2}$ – 0.275 min^{-1}. The corresponding first-order constants for RR120 were 0.393 and 0.314 min^{-1}, respectively. As can be seen in Fig. 3, no significant differences exist during the first minutes of reaction if the process is carried out in the presence of UV light or under solar irradiation.

The photocatalytic oxidative degradation processes in the presence of solar light on typical summer days are 3.90 times faster than the experiments in the dark. Photoenhanced decolorization is potentially due to direct photolysis of dye and/or photoreaction, involving H_2O_2 or iron ions. Acceleration is probably caused by photoreduction of $Fe(III)_{\text{aq}}$ or $Fe(OH)^{2+}$ (Eq. (11)), formed as a consequence of oxidative

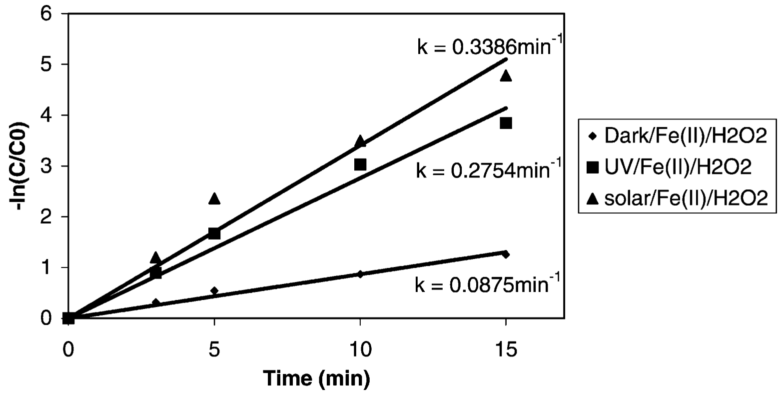

Fig. 3. Effect of light on the degradation of RY84. Initial conditions: $C_0(\text{dye}) = 100$ mg/l, $C_0(H_2O_2) = 5$ mM, $C_0(Fe^{2+}) = 0.25$ mM, pH = 2.8–3.

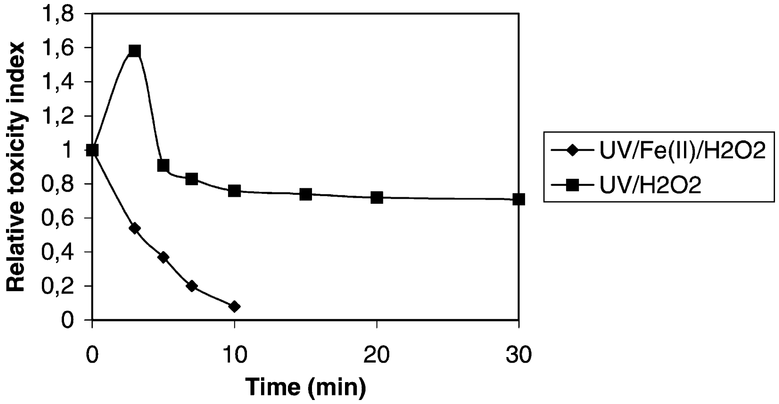

Fig. 4. Toxicity assay using the bacterium *Vibrio fisheri* in LUMIStox 300 during the treatment. Incubation time 30 min. Initial conditions: $C_0(\text{dye}) = 100$ mg/l, $C_0(H_2O_2) = 5$ mM, $C_0(Fe^{2+}) = 0.25$ mM.

processes in Fenton's system, to Fe^{2+} ions with the production of reactive OH radicals [5]. It is also known that the total rate of H_2O_2 decomposition under action of Fe(II) ions is essentially higher than in the presence of Fe(III) ions.

3.4. Comparison of hydrogen peroxide photolysis, photo-Fenton and other Fenton-like processes

A comparison of UV/H_2O_2 and UV/Fe(II)/H_2O_2 processes for degradation of RY84 have been performed. The results obtained at $pH = 3$, catalyst concentration of 0.25 and 5 mmol/l H_2O_2 are presented in Figs. 3 and 4, and Table 2.

After 15 min of irradiation time during the photo-Fenton process the decolorization was greater than 98%. A COD reduction of about 81% was observed for RY84 and 85% for RR120 at the same time. The TOC removal rates were 50% for RY84 and 73% for RR120 under identical operational conditions.

The bioluminescence test has been used for testing the progress of toxicity during the treatment. To indicate changes in toxicity, the data for percentage inhibition obtained in each experiment were converted to the relative toxicity index (RTI), where:

$$\text{relative toxicity index} = \frac{\text{inhibition at } t\ (\%)}{\text{inhibition at } t = 0\ (\%)}$$

The results expressed as the relative toxicity index values versus reaction time are presented in Fig. 4.

The increase in toxicity at 3 min during the UV/H_2O_2 treatment, most probably can be attributed to the release of toxic intermediates. A fast decrease of relative toxicity index values during UV/Fe(II)/H_2O_2 oxidation reflects the disappearance of the toxic compounds. Based on the toxicity assay, it can be concluded that photo-Fenton treatment is a suitable method also for complete detoxification.

Further investigations on decolorization efficiency during different processes at the obtained optimum conditions have been carried out. The results are presented in Figs. 5 and 6. It can be observed from the figures that the best results for both dyes are given using the photo-Fenton process and the solar light-assisted Fenton process.

The results show that the color removal of RY84 after 15 min reaction time follows the decreasing order: solar/Fe(II)/H_2O_2 > UV/Fe(II)/H_2O_2 > UV/Cu(II)/Fe(III)/H_2O_2 > UV/Fe(III)oxalate/H_2O_2>UV/Fe(III)/H_2O_2>dark/Fe(II)/H_2O_2 > solar/Fe(III)oxalat/H_2O_2 > UV/H_2O_2 > UV/Fe(II) = UV. During the same reaction period, the relative order for RR120 removal rate was slightly different: solar/Fe(II)/H_2O_2 > UV/Fe(II)/H_2O_2 > UV/Fe(III)/H_2O_2 = UV/Cu(II)/Fe(III)/H_2O_2 > UV/Fe(III)oxalate/H_2O_2 = UV/H_2O_2 > UV.

The rate of color degradation in the process UV/Fe(II) is comparable to UV irradiation. H_2O_2 alone and UV irradiation was not even half as effective, when the reaction was run in the absence of Fe(II). When Cu(II) ions were added to a solution containing Fe(III) ions, no essential difference

Table 2
Comparison of UV/H_2O_2 and UV/Fe(II)/H_2O_2 processes for degradation of RY84

Time (min)	UV/H_2O_2			UV/Fe(II)/H_2O_2, pH = 3		
	Color removal (%)	COD removal (%)	TOC removal (%)	Color removal (%)	COD removal (%)	TOC removal (%)
0	0.00	0.00	0.00	0.00	0.00	0.00
5	2.11	11.48	0.18	88.03	35.82	22.59
10	28.27	23.98	0.52	95.17	72.38	45.35
15	28.62	47.77	1.03	97.53	81.34	49.32

Initial conditions: $C_0(\text{dye}) = 100$ mg/l; $C_0(H_2O_2) = 5$ mM; $C_0(Fe^{2+}) = 0.25$ mM.

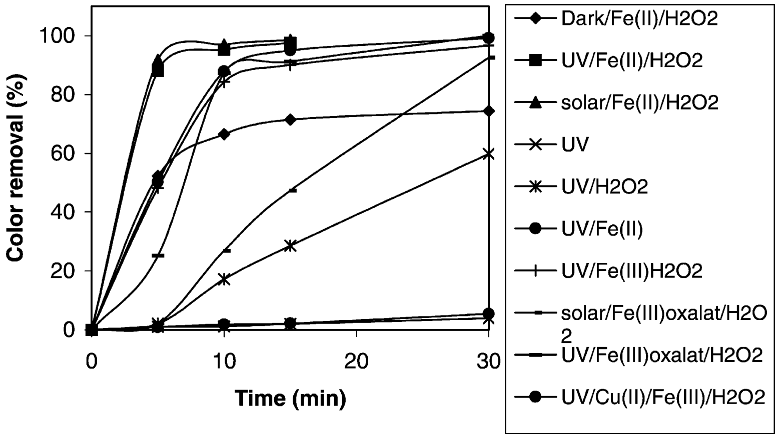

Fig. 5. Color removal of RY84 during different AOP's. Initial conditions: C_0(dye) = 100 mg/l, $C_0(H_2O_2)$ = 5 mM, $C_0(Fe^{2+})$ = 0.25 mM, $C_0(Fe^{3+})$ = 0.25 mM, $C_0(Cu^{2+})$ = 0.25 mM, molar ration Fe(II)/H_2O_2, Fe(III)/H_2O_2, Fe(III)oxalate/H_2O_2 = 1:20, pH = 3.

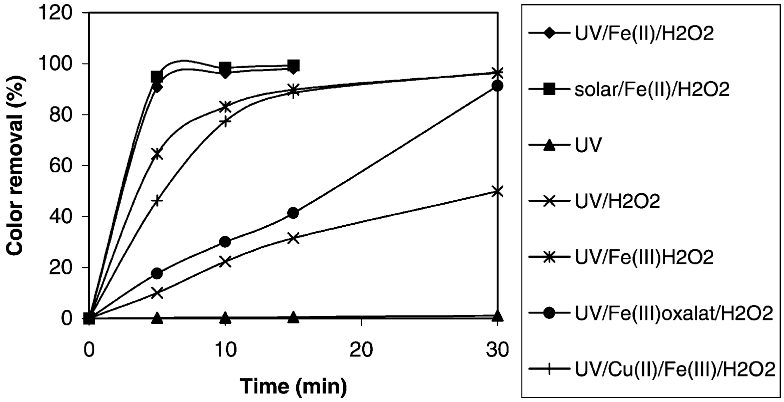

Fig. 6. Color removal of RR120 during different AOP's. Initial conditions: C_0(dye) = 100 mg/l, $C_0(H_2O_2)$ = 5 mM, $C_0(Fe^{2+})$ = 0.25 mM, $C_0(Fe^{3+})$ = 0.25 mM, $C_0(Cu^{2+})$ = 0.25 mM, molar ration Fe(II)/H_2O_2, Fe(III)/H_2O_2, Fe(III)oxalate/H_2O_2 = 1:20, pH = 3.

was observed. Formate and oxalate, identified as fragmental oxidation products of the investigated dyes, could also be detected after 15 min of irradiation.

Thus, it appears that the photo-Fenton process can be a promising treatment method. According to Goi and Trapido [24], the operating costs of the Fenton and photo-Fenton treatments are situated between US\$ 0.06 and 0.30 m^{-3} for the recommended ratios of chemicals and electrical energy for nitrophenols degradation.

4. Conclusions

The pH, initial H_2O_2 concentration, the contact time and effect of irradiation have an important influence on the photo-Fenton oxidation of the selected reactive dyes: C.I. Reactive Yellow 84 and C.I. Reactive red 120[c1]. The results indicate that the oxidation rate increases in an acidic medium, and pH 2–3 was found to be the optimum. The most favorable molar ratio Fe(II)/H_2O_2 was 1:20 for both dyes. The results also show that no significant differences exist during the first minutes of reaction if the process is carried out in the presence of UV light or under solar irradiation. Both these experimental conditions provide very good results. The photocatalytic oxidative degradation processes in the presence of solar light on typical summer days are 3.90 times faster than the experiments under dark. After 15 min of irradiation time using a photo-Fenton process, decolorization was greater than 98% for both aqueous dye solutions. Effective system conditions were found to be pH of 3, hydrogen peroxide-to-iron molar ratio of 20:1 and UV or solar irradiation.

The results confirm that the photo-Fenton process, which proved to be feasible and cost-effective for degradation of dyes at low H_2O_2 concentration, seems to be more appropriate for removal of color, COD, TOC and detoxification of dye solutions.

The application of Fenton-process for wastewater treatment using solar energy as source of irradiation, a costs-effective technology, can be a suitable treatment method for industrial applications.

The investigations should be continued for implementation of the optimum operating conditions in treatability studies with real dyeing and finishing effluents, which are known to contain considerable quantities of organic dyestuff, textile auxiliaries, salts and surfactants.

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