Decolorization kinetics of Procion H-exl dyes from textile dyeing using Fenton-like reactions

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Abstract

The decolorization kinetics of three commercially used Procion H-exl dyes was studied using a Fenton-like reagent. The effect of the major system parameters (pH, concentration of H_2O_2 and Fe^{3+} and initial dye concentration) on the kinetics was determined. For comparison, the effect of the use of UV irradiated Fenton-like reagent and of Fenton reagent on the kinetics was also examined. In addition, mineralization rates and the biodegradability improvement as well as the effect of the addition of Cl^-, CO_3^{2-} or HCO_3^- on the decolorization rates was studied. The reactions were carried out in a 300 ml stirred cylindrical reactor with the capability of UV irradiation. The dye half-life time goes through a minimum with respect to the solution pH between 3 and 4. It also exhibits a broad minimum with respect to Fe^{3+} and H_2O_2 at molar ratios of H_2O_2/Fe^{3+} from about 100 to 10. The addition of CO_3^{2-} and HCO_3^- substantially reduces the decolorization rates, while this effect is significantly less pronounced with Cl^-. At an optimum range of parameters, the mineralization rate (TOC reduction) is very slow for the Fenton-like process (TOC decrease from an initial 49.5 to 41.1 mg/l after 30 min and to only 35.2 mg/l after 600 min), but it increases significantly for the photo-Fenton-like process (to TOC values of 39.7 and 11.4 mg/l, respectively). The biodegradability, as expressed by the BOD/COD ratio, increases significantly from an initial value of 0.11–0.55 for the Fenton-like and to 0.72 for the photo-Fenton-like processes.
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Keywords: Fenton-like reaction; Dye decolorization; Dye mineralization; Biodegradability; Procion H-exl dyes

1. Introduction

Liquid waste streams from textile dyeing industries are one of the most challenging effluents to treat successfully. One must either reduce the COD/BOD ratio, which usually ranges from 3 to 6, to values below 1.5 so that a subsequent biological treatment can be applied, or reduce the total COD to acceptable values, usually below 80 mg/l. The difficulty in treating these effluents arises from several factors, which are characteristic of most textile industry waste streams. Firstly, effluents containing dyes have a high COD to BOD ratio making it impossible to treat them by activated sludge treatment. Secondly, dyes found in effluents come from different production lines and can therefore vary significantly in their molecular structure, not only from industry to industry but also within a given processing plant. Given the fact that dye oxidation kinetics can be greatly affected by molecular structure, this inhomogeneity makes waste treatment

by oxidation difficult. Thirdly, other substances, usually various electrolytes, are added to the dyeing bath to improve color fastness, and this usually complicates the oxidation kinetics. Last, the dyeing bath pH greatly affects the oxidation kinetics, and the pH values of textile waste effluents are high, usually around 11.

Reactive dyes are most troublesome, because they are found in relatively high concentrations in textile industry effluents and because of the toxicity that many of them exhibit. Given the fact that their use is widespread (an estimated 50% of all dyes used by the textile industry are reactive), they are of great concern in regions where textile industries are concentrated. Azo dyes in particular, constitute almost 80% of the reactive dyes. Most azo dyes are not biodegradable by aerobic treatment processes [1], but they can be decolorized by anaerobic treatment [2–4]. This treatment results in the cleavage of the nitrogen double bond, and the resulting fragments, which are aromatic amines, are proven carcinogens [5]. However, the toxicity of these wastes can be reduced significantly with the use of aerobic treatment, which converts these aromatic amines into less harmful products [2].

In many textile industries, a combination of physical treatment followed by biological oxidation to reduce the non-dye

Nomenclature

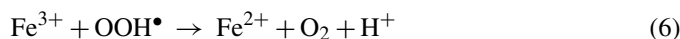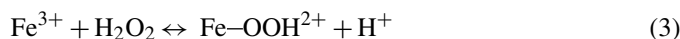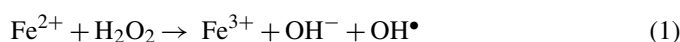|	
$C_{0,\text{DYE}}$	initial dye concentration (mg/l)
C_{0,FeCl_3}	initial $FeCl_3$ concentration (%, w/w)
$C_{0,\text{H}_2\text{O}_2}$	initial H_2O_2 concentration (%, w/w)
k_{obs}	observed pseudo 1st order reaction rate constant (1/s)
PCH	Procion Crimson H-exl dye
PNH	Procion Navy H-exl dye
PYH	Procion Yellow H-exl dye
$t_{1/2}$	half-life time (s)
TOC_0	initial total organic carbon concentration (mg/l)

BOD is used for the treatment of effluents. However, it has long been recognized that physical treatment alone, which involves coagulation and sedimentation of the dyes to form a sludge and adsorption on activated carbon, is not sufficient [6–9]. In many industries, after physical treatment, the clear fluid is sent to a biological plant, while the resulting sludge is disposed of illegally, therefore posing a significant hazard to the ecosystem. Other research has focused on treating textile effluents by activated sludge oxidation followed by membrane separation [10].

Lately, much research has been carried out on the treatment of textile industry effluents using advanced oxidation processes (AOP). This research focuses mainly on three advanced oxidation methods, namely (1) treatment with ozone or photochemical oxidation methods (either $UV + O_3$ or $UV + H_2O_2$) [11–13]; (2) photocatalysis (TiO_2 or other semiconductor particles $+ h\nu$) [14–18]; (3) Fenton or Fenton-like reactions (Fe^{2+} or $Fe^{3+} + H_2O_2$) and photo-Fenton reactions [19–22]. The end effect of all these three methods is the production of hydroxyl radicals ($OH^\cdot$), which have a very strong oxidative potential ($E^0 = +2.80\,\text{V}$), second only to fluorine [23].

In this paper, Fenton-like reactions were used for the decolorization of dilute solutions of three commercial dyes, namely Procion Navy H-exl, Procion Crimson H-exl and Procion Yellow H-exl. All three dyes belong to the category of azo dyes and are reactive dyes. The aim of the study is to examine in detail the effect of the major system parameters on the decolorization kinetics and compare the decolorization kinetics of the three dyes. The parameters, which are examined separately, are the solution pH, the concentration of H_2O_2, the concentration of the Fe^{3+} ions and the initial dye concentration. Concentrations of Fe^{3+} ions and of H_2O_2 were varied by three orders of magnitude while the solution pH was varied from 1 to more than 10. Thus, the decolorization kinetics is studied in a wide range of system parameters. In addition, for comparative reasons, the effect of the use of UV irradiated Fenton-like reagent (photo-Fenton-like process) and also Fenton reagent (Fenton process) on the decolorization kinetics specifically of Procion Navy H-exl is also examined. Because of the addition of ions such as Cl^-, CO_3^{2-} and HCO_3^- to the bath solution in textile industries, the effect of these ions on the decolorization rates is here examined. At optimum reaction conditions, the mineralization rate and the biodegradability improvement are also examined.

This method seems to decolorize dyes with a variety of molecular structures. The rate of decolorization seems to be affected very little by structure, making it an attractive option for the treatment or pre-treatment of textile effluents containing a wide range of dyes. In the literature, Fenton and Fenton-like reactions for the treatment of textile effluents are very efficient in a pH range between 2 and 5 [24–27]. Furthermore, in most papers, it is mentioned that the optimum pH value is around 3 [26,28–32]. This is a disadvantage, as the effluent pH in most textile industries using reactive dyes is around 11.

The general mechanism using Fenton reagents, via which the hydroxyl radicals are produced, is a number of cyclic reactions, which utilize the Fe^{2+} or Fe^{3+} ions as a catalyst to decompose the H_2O_2. These ions are regenerated in their original state at the end of the cyclic reactions according to the following scheme of reactions [26,32–34]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{1}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \tag{2}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^+ \tag{3}$$

$$Fe-OOH^{2+} \rightarrow Fe^{2+} + OOH^\bullet \tag{4}$$

$$Fe^{2+} + OOH^\bullet \rightarrow Fe^{3+} + {}^-OOH \tag{5}$$

$$Fe^{3+} + OOH^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \tag{6}$$

$$H_2O_2 + OH^\bullet \rightarrow H_2O + OOH^\bullet \tag{7}$$

More than 25 reactions occur, several involving the dye molecule, but the above seven are the most significant involving ions and radicals. When a Fenton-like reagent is used, the sequence of reactions begins with reaction (3). There are many bibliographic sources which report that Fenton reagent is more effective than Fenton-like reagent [31–33,35]. However, in most cases it seems that it does not matter whether Fe^{2+} or Fe^{3+} is used. The above sequence of reactions begins very quickly if there is an abundant supply of H_2O_2 and of dye. In cases, though, where reactants are in small concentrations (<10–25 mg/l H_2O_2), the use of Fe^{2+} is more effective [36].

This reaction scheme is very attractive because Fe^{2+} or Fe^{3+} ions reagents are inexpensive, while H_2O_2 is also relatively inexpensive and is environmentally safe [27]. Two disadvantages of the method are: the highly to moderately acidic environment (pH 2–5) which has to be used [37], and the need to recover the Fe^{2+} or Fe^{3+} ions at the end of the treatment. Major potential applications of this method are in the treatment of effluents from the textile industry, as well as from the cosmetic, pesticide and detergent producing industries [38].

2. Materials and methods

All experiments were conducted in a stirred 300 ml batch pyrex cylindrical reactor of diameter 7 cm and height 17 cm, which was fitted with a concentric quartz tube with diameter 3.5 cm and height 15 cm. Into the quartz tube a lamp emitting in an appropriate range was inserted. For the photo-Fenton-like

Table 1
Characteristics of the Procion H-exl dyes used

Dye	Source	Reacting group	Concentration (mg/l)	Λ_{max} (nm)	Absorbance
Procion Navy H-exl	BASF	Aminochlorotriazine	200	605.0	3.32
Procion Crimson H-exl	BASF	Aminochlorotriazine	200	549.5	3.15
Procion Yellow H-exl	BASF	Aminochlorotriazine	200	412.5	2.86

experiments the emitted wavelength was 254 nm. Also, the reactor was fitted with an air inlet and an air outlet, and the reactor contents were stirred continuously. The temperature of the reactor was held constant at $20 \pm 1\,°C$.

At various intervals, samples were withdrawn from the reactor and the concentration of the dye was determined by spectrometric analysis using Beer's law. Absorption spectra for the determination of the dye concentration were taken with a Shimadzu UV–vis 2401 PC automatic Spectrophotometer (190 nm – 1100 nm). Absorption was linear for all dyes up to about 250 mg/l. Experiments were repeated and data were found to be reproducible to within better than $\pm 20\%$. Solutions of standard concentration of 200 mg/l were prepared, kept in the dark and replaced every 3–4 days. TOC values were determined with the use of Shimadzu 5000 TOC analyzer. COD and BOD values were determined after the excess hydrogen peroxide was neutralized with sodium sulfite.

Table 1 gives the relevant information for the three dyes that were used, namely Procion Navy H-exl (PNH), Procion Crimson H-exl (PCH) and Procion Yellow H-exl (PYH). All of them are azo dyes having in common the group aminochlorotriazine as the fiber reacting group. The maximum absorption of the three dyes is at 605.0, 549.5 and 412.5 nm, respectively.

Firstly, the H_2O_2 was added to the dye solution and then the pH was adjusted to the desired value by the addition of a few drops of either HNO_3 or NaOH. Following the pH adjustment, the Fe^{3+} or Fe^{2+} ions were quickly added to the dye solution. All the solutions were of the appropriate concentration so that only up to 3 ml would be added to the 200 ml solution. This, as it was verified by measurements, changed the initial concentrations only by approximately 1%. The Fe^{3+} and Fe^{2+} ions were provided from solutions of either $FeSO_4 \cdot 7H_2O$ (Merck) or $FeCl_3 \cdot 6H_2O$ (Riedel de Haen). The H_2O_2 was from stock of 50% (w/w) (peridrol).

Samples were quickly withdrawn for spectrometric analysis, as the speed of decolorization in the initial reaction times is very fast. In order to obtain data at times close to zero, data were extrapolated. Dye half-life times ($t_{1/2}$) were calculated from the time it takes for the dye concentration to reach half its initial value (C_0). The half-life time is representative of the decolorization rates, as in most experiments the absorbance versus time curves were not found to cross each other. Another parameter that was used is the observed rate constant k_{obs} for the decolorization reaction. As is discussed in 3.1.3, the constant k_{obs} was calculated by modeling the reaction as a first order reaction with respect to the dye concentration and this was found to be the case during the initial reaction times (until about $C = 1/4C_0$) of the plot of C versus t. Therefore, the rate constant k_{obs} is a measure of the reaction rate course at a very early stage; the half-life time

is a measure of the reaction course at an intermediate stage when half of the dye is decolorized; the percent decolorization after either 10 min or 1 h reaction time is a measure of the reaction course at a relatively late stage.

3. Results and discussion

3.1. Fenton-like reagent (H_2O_2/Fe^{3+})

3.1.1. Effect of pH

Fig. 1 shows the dependence of the decolorization half-life time on the solution pH for all three dyes at a given initial concentration of dye, $FeCl_3$ and H_2O_2. It must be noted here that curves in all figures are drawn between experimental data for the purpose of elucidating them. The following can be observed from Fig. 1: (1) the dependence of the decolorization half-life time ($t_{1/2}$) on the solution pH is similar for all three Procion H-exl dyes examined; (2) the decolorization $t_{1/2}$ goes through a relatively broad minimum at an acidic pH ranging from 3 to 4 depending on the particular dye type; (3) in highly acidic solutions (below pH 2 for PNH and 3 for PCH and PYH), the decolorization rates become significantly slower with decreasing pH while a similar behavior is also found in highly alkaline solutions, where above pH 10 the decolorization half-life time becomes very large, and (4) the decolorization of the PYH dye is much slower. Therefore, it seems that the optimum pH for the decolorization of Procion H-exl dyes is in the range between 3 and 4. Generally, from the experimental data, it seems that decolorization rates are significantly faster even in slightly acidic solutions (pH 5–6) as compared to slightly alkaline ones, since the scale in Fig. 1 is logarithmic with respect to the decolorization half-life time. The findings of this study are consistent with other results reported in the literature [24–32].
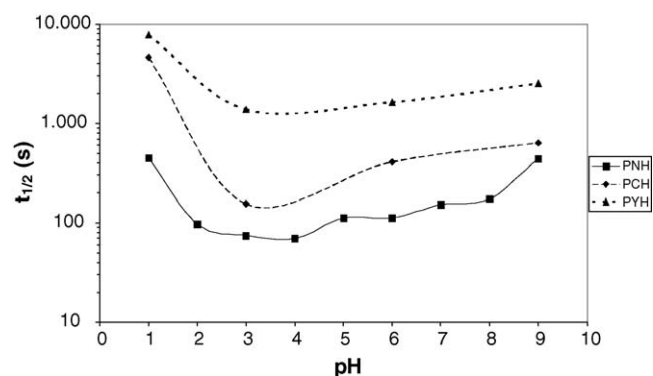

Fig. 1. Variation of the half-life time $t_{1/2}$ vs. pH for the Procion H-exl dyes ($C_{0,DYE} = 200$ mg/l; $C_{0,H_2O_2} = 0.1\%$, w/w; $C_{0,FeCl_3} = 0.02\%$, w/w).
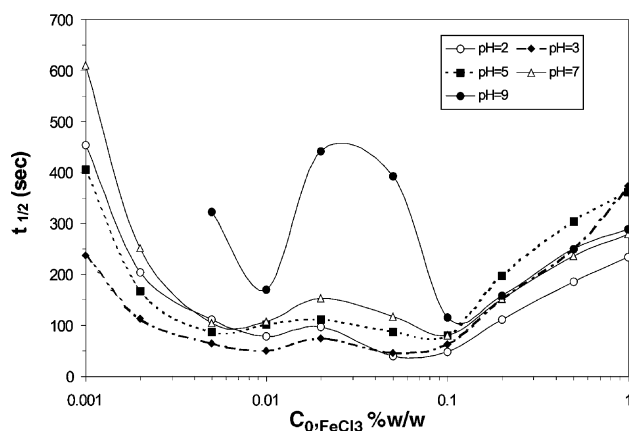
Fig. 2. Effect of the initial FeCl$_3$ concentration on the half-life time $t_{1/2}$ of the PNH dye at various pH values ($C_{0,H_2O_2} = 0.1\%$, w/w.; $C_{0,PNH} = 200$ mg/l).
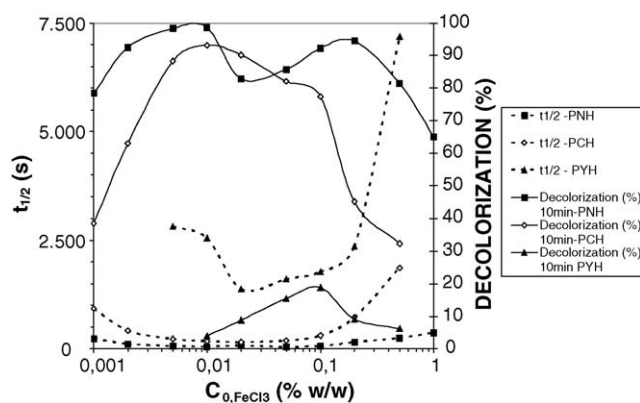

Fig. 3. Effect of the initial FeCl$_3$ concentration on the decolorization efficiency ($t = 10$ min) and the half-life time $t_{1/2}$ of the Procion H-exl dyes (pH 3; $C_{0,H_2O_2} = 0.1\%$, w/w; $C_{0,DYE} = 200$ mg/l).

The drastic increase of the decolorization $t_{1/2}$ in highly acidic solutions is due to the drastic reduction of hydroxyl radicals produced in the sequence of reactions (1) through (7). High concentrations of hydrogen ions result in the reversal of Eq. (3). Eq. (3) occurs via the following mechanism:

$$H_2O_2 \leftrightarrow HO_2{}^- + H^+ \tag{8}$$

$$HO_2{}^- + Fe^{3+} \leftrightarrow Fe\text{–}OOH^{2+} \tag{9}$$

In highly acidic conditions, H_2O_2 is stabilized and this inhibits the production of the intermediate ion $HO_2{}^-$, which reacts with Fe^{3+} to produce $Fe\text{–}OOH^{2+}$. The $Fe\text{–}OOH^{2+}$ ion decomposes to produce Fe^{2+}, which is necessary in reaction (1) in order to generate hydroxyl radicals [25,38]. Electron transfer through the solution to Fe^{3+}, which occurs by means of $HO_2{}^-$, is therefore hindered.

At highly alkaline pH, decolorization efficiency is reduced because of the reduction in the solubility of Fe^{2+} and Fe^{3+} [30] and the formation of $Fe(OH)_3$ and $Fe_2O_3 \cdot nH_2O$, resulting in the decrease in Fe^{3+} ions in the solution and subsequently in a reduction in the concentration of Fe^{2+} ions, which are more efficient than Fe^{3+} ions because they directly produce $OH^\bullet$ [25]. Also, if the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen, which reduces its concentration in the solution, potentially creating a hazardous situation [24,36].

3.1.2. Effect of the initial FeCl$_3$ concentration

The effect of the initial concentration of FeCl$_3$ introduced in the reaction mixture on the half-life time of PNH dye at pH 2, 3, 5, 7 and 9 is presented in Fig. 2. From this figure it can be concluded that there is generally an optimum range of FeCl$_3$ concentration between 0.005 and 0.1% (w/w) (molar ratio of H_2O_2/Fe^{3+} = between 100 and 5, respectively) at which $t_{1/2}$ is significantly decreased, independent the pH value, except for pH 9, where probably the phenomenon of intense Fe sedimentation observed for FeCl$_3$ initial concentrations between 0.01 and 0.1% (w/w) (molar ratio of H_2O_2/Fe^{3+} = between 50 and 5, respectively) strongly decreased Fe ions in the reaction solution. It is also obvious that in this optimum range of

FeCl$_3$ concentration, pH values between 2 and 3 give better results.

The observed decrease in decolorization reaction rate at high FeCl$_3$ concentrations (>0.1%, w/w, FeCl$_3$) is due to the fact that Fe^{2+} concentrations increase rapidly through the reactions (3) and (6) and scavenge hydroxyl radicals [24,39] through reaction (2). At low Fe^{3+} concentrations (below 0.005%, w/w, FeCl$_3$), the decolorization rate decreases even more rapidly. This is due to the lack of Fe^{3+} and subsequently of Fe^{2+}, which is necessary for the formation of hydroxyl radicals [36]. Therefore, at low Fe^{3+} concentrations the reaction is starved in $OH^\bullet$, while at high Fe^{3+} concentrations the $OH^\bullet$ concentration is reduced because of the scavenging effect by Fe^{2+}, therefore giving an optimum range between 0.005 and 0.1% (w/w) (Fig. 2).

Fig. 3 shows a comparison of the decolorization half-life times and the percent decolorization versus the concentration of FeCl$_3$ for all three dyes at the optimum pH equal to 3 determined from Fig. 1. The H_2O_2 concentration and the initial dye concentration were the same for all runs in Fig. 3. While the qualitative appearance of the three curves is similar, it is obvious that the PYH dye is much slower to decolorize. Decolorization of the other two dyes, PNH and PCH, is fast at the optimum intermediate range of FeCl$_3$ concentrations between 0.005 and 0.1% (w/w). It is also remarkable that under this optimum range, PNH and PCH are almost completely decomposed (98.63 and 93.20%, respectively) in only 10 min.

During the initial reaction times of the plot of C versus t (until about $C = 1/4C_0$), the reaction was found to follow first order kinetics:

$$-d(C_{DYE}/dt) = k_{obs}C_{DYE} \rightarrow \frac{-dC_{DYE}}{C_{DYE}}$$
$$= k_{obs}\,dt \rightarrow \ln C_{DYE} = -k_{obs}t + \ln C_{0,DYE} \tag{10}$$

The observed rate constant k_{obs}, was obtained from the slope of the dye absorbance or dye concentration versus time curve according to Eq. (10) and is shown graphically versus the FeCl$_3$ concentration for all three dyes in Fig. 4. This Figure also shows that there is an optimum range of FeCl$_3$ concentration.
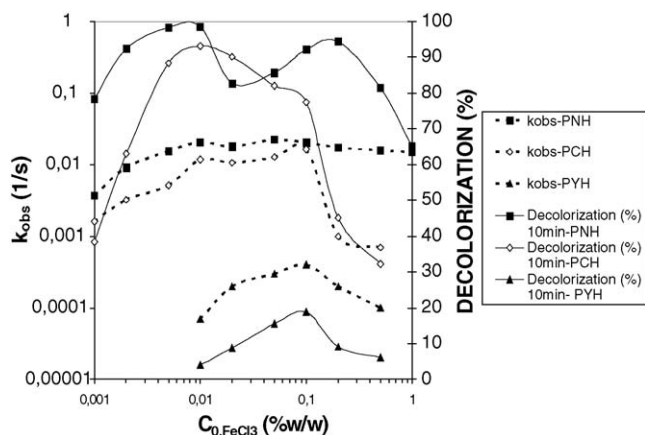
Fig. 4. Effect of the initial $FeCl_3$ concentration on the decolorization efficiency ($t = 10$ min) and the reaction rate constant k_{obs} of the Procion H-exl dyes (pH 3; $C_{0,H_2O_2} = 0.1\%$, w/w; $C_{0,DYE} = 200$ mg/l).

Fig. 6. Effect of the initial H_2O_2 concentration on the half-life time $t_{1/2}$ of the PNH dye for pH 2–9 ($C_{0,FeCl_3} = 0.1\%$, w/w; $C_{0,PNH} = 200$ mg/l).

Figs. 3 and 4 show that this optimum range in $t_{1/2}$ and k_{obs} is wider for PNH and PCH dyes and occurs between 0.005 and 0.1% (w/w) $FeCl_3$ (molar ratio of H_2O_2/Fe^{3+} = between 100 and 5, respectively).

From these two figures it is also obvious that all dyes show similar qualitative behavior with respect to the dependence of either $t_{1/2}$ or k_{obs} on the concentration of $FeCl_3$. The PYH is the most difficult to decompose and PNH the most sensitive to the Fenton-like reagent. The time variation of the dye absorbance, which is shown in Fig. 5 for all three dyes, also verifies this conclusion. Finally, extended experiments for 1 h show that the decolorization efficiency of PYH does not exceed 83.5% at the optimum parameter values, while the corresponding decolorization efficiencies for PCH and PNH are 99.3 and 100%, respectively.

3.1.3. Effect of the H_2O_2 concentration

Fig. 6 shows the dependence of the decolorization half-life time of the PNH dye on the concentration of H_2O_2 at constant dye initial concentration, pH and $FeCl_3$ concentration.
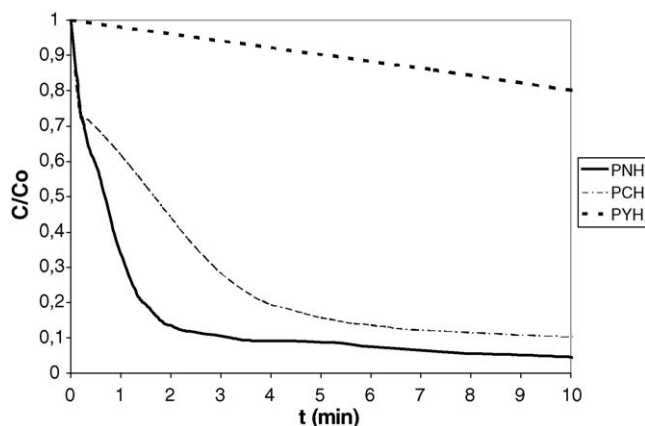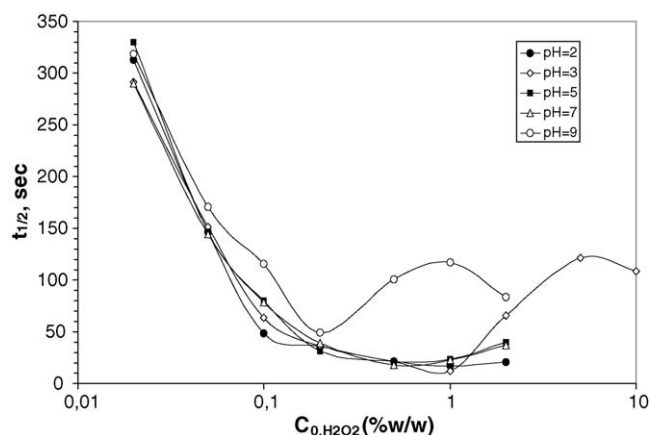
The $t_{1/2}$ almost coincides for a wide range of pH (2–7). The optimum range of H_2O_2 concentrations is between 0.2 and 2% (w/w) (molar ratio of H_2O_2/Fe^{3+} = between 10 and 100, respectively). The $t_{1/2}$ is very low (less than 50 s) at this optimum range.

At low H_2O_2 concentrations and as the H_2O_2 concentration is decreased, the $t_{1/2}$ rapidly increases. This occurs because the concentration of Fe^{2+} ions produced through reactions (3) and (4) decrease rapidly with decreasing H_2O_2 concentration. As a result, the production of hydroxyl radicals through Eq. (3) is drastically reduced. At high H_2O_2 concentrations (above 2%, w/w), the $t_{1/2}$ tends to increase with increasing H_2O_2 concentration. This is most probably due to the scavenging of the hydroxyl radicals by the H_2O_2 through Eq. (7) [26,31,39]. It was also observed from the experiments that at high H_2O_2 concentrations (above 2%, w/w), H_2O_2 decomposes into O_2 and H_2O, and this results in a rapid increase in solution temperature, decreasing in effect the oxidative power of the Fenton-like reagent because of the large decrease in the concentration of H_2O_2 [36].

Figs. 7 and 8 show a comparison of the decolorization half-life time and of the observed rate constant k_{obs} between the three

Fig. 5. Time variation of C/C_0 ratio of the Procion H-exl dyes (pH 3; $C_{0,FeCl_3} = 0.1\%$, w/w; $C_{0,H_2O_2} = 0.2\%$, w/w; $C_{0,DYE} = 200$ mg/l).
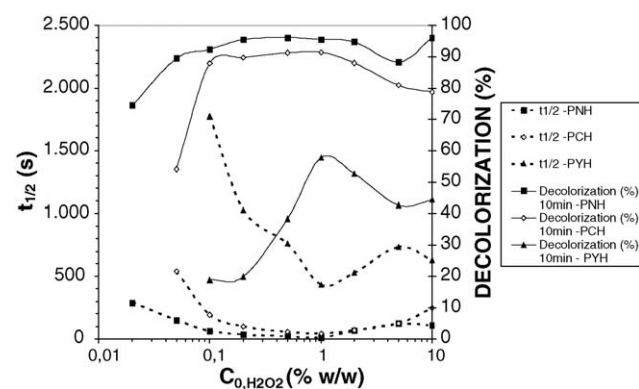

Fig. 7. Effect of the initial H_2O_2 concentration on the decolorization efficiency ($t = 10$ min) and the half-life time $t_{1/2}$ of the Procion H-exl dyes (pH 3; $C_{0,FeCl_3} = 0.1\%$, w/w; $C_{0,DYE} = 200$ mg/l).
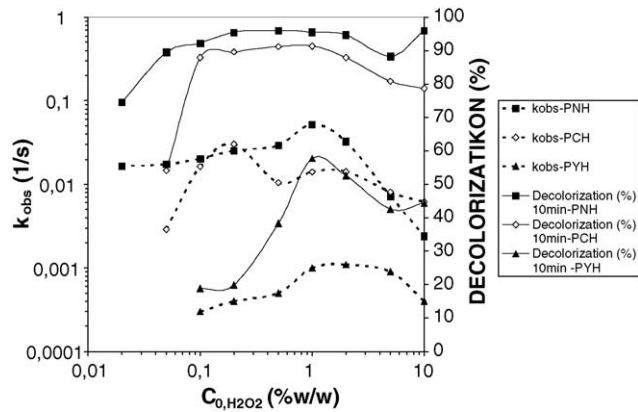
Fig. 8. Effect of the initial H_2O_2 concentration on the decolorization efficiency ($t = 10$ min) and the reaction rate constant k_{obs} of the Procion H-exl dyes (pH 3; $C_{0,FeCl_3} = 0.1\%$, w/w; $C_{0,DYE} = 200$ mg/l).
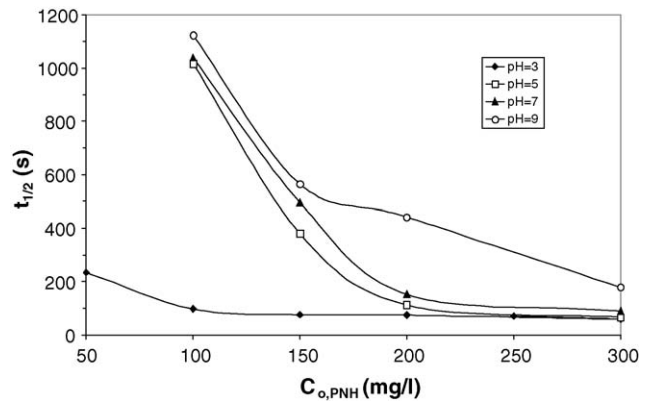

Fig. 9. Effect of the initial PNH dye concentration and pH on the half-life time $t_{1/2}$ ($C_{0,H_2O_2} = 0.1\%$, w/w; $C_{0,FeCl_3} = 0.02\%$, w/w).

different dyes versus the initial H_2O_2 concentration. The decolorization efficiency ($t = 10$ min) is also shown in the graphs. The other parameters, pH, $C_{0,FeCl3}$ and $C_{0,DYE}$, are constant at all runs in Figs. 7 and 8. From these figures, it can be deduced that the dependence of $t_{1/2}$ and the rate constant k_{obs} on the H_2O_2 initial concentration is similar for the PNH and PCH dyes throughout the H_2O_2 concentration range. At this range, the half lifetime dramatically decreases to the lowest levels, 12.1 s for PNH and 45 s for PCH. However, PYH exhibits a narrower minimum between 0.7 and 2% (w/w) (molar ratio $H_2O_2/Fe^{3+} =$ between 34 and 100), and beyond that, $t_{1/2}$ increases very sharply. At this minimum, $t_{1/2}$ is 435 s.

It is important to note from Figs. 7 and 8, that PNH can be decomposed at more than 95% in only 10 min when the H_2O_2 initial concentration is between 0.2 and 2% (w/w). Under the same conditions, the decomposition ($t = 10$ min) of PCH approaches 90%. Further experiments showed that after 1 h reaction time, an almost complete decomposition is achieved (97–99.5%). The highest decolorization efficiency of PYH after 10 min reaction time is only 57.7% at $C_{0,H_2O_2} = 1\%$ (w/w) (molar ratio of $H_2O_2/Fe^{3+} = 50$). Therefore, PYH is more stable than either PNH or PCH with respect to the examined parameters (k_{obs}, $t_{1/2}$ and decolorization efficiency).

3.1.4. Effect of the initial dye concentration

The effect of the initial PNH dye concentration on the decolorization half-life time at a wide range of pH values is presented in Fig. 9. All runs were conducted at the optimum pH and Fenton-like reagent concentrations. Dye concentrations are varied from 50 to 300 mg/l. From Fig. 9, we can observe that below a threshold concentration depending on the solution pH, $t_{1/2}$ increases with decreasing dye concentration. At the optimum pH 3, the reaction slows down below a dye concentration equal to 100 mg/l. Therefore, methods of waste treatment based on Fenton and Fenton-like reactions should be more efficient when liquid waste effluents have a high level of organic pollutants.

Generally, these methods are strongly dependent on the initial concentration of the organic substrate [32,37]. This is also consistent with the modeling of the reaction as a first-order kinetic

model ($-d(C_{DYE}/dt)) = k_{obs} C_{DYE}$), for the very early stages of the reaction. This also explains, as it can be observed from Fig. 5, the initial rapid drop in the absorbance versus time and subsequently the near leveling off of the absorbance. This implies that Fenton and Fenton-like reagents are most efficient for a pre-treatment of textile dye effluents. A combination process like a photo-Fenton, as shown in paragraph 3.2, or a Fenton-photocatalytic process may accelerate dye decolorization after the initial rapid decolorization measured in Fenton and Fenton-like processes, and is currently being examined.

A second observation made from Fig. 9 is that beyond an initial dye concentration ranging from 100 to 250 mg/l, depending on pH, there is no further decrease in the dye decolorization $t_{1/2}$. This is probably due to the formation of dimmer molecules [39] through a sequence of reactions from single dye molecules; decolorization of the dimmer molecule is more difficult, leading to the leveling off of $t_{1/2}$ in Fig. 9.

Finally, from Fig. 10, which shows the rate constant k_{obs} and the 10 min decolorization efficiency for the dye PNH versus the initial dye concentration (at pH 3), it can be seen that the reaction rate constant k_{obs}, and consequently the initial reaction rate, as well as the decolorization efficiency, are proportional to $C_{0,PNH}$, in most of its variation range.
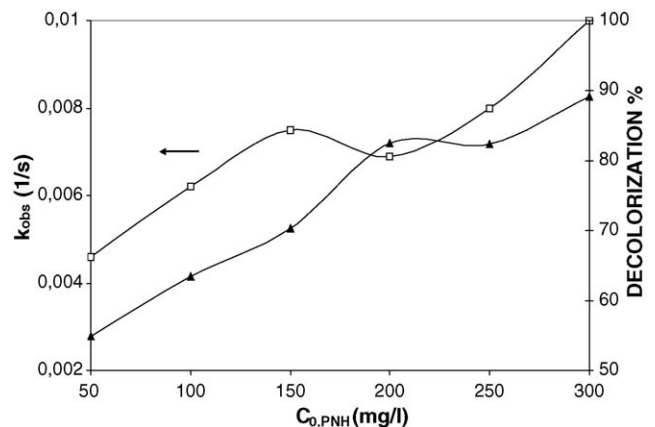

Fig. 10. Effect of the initial PNH dye concentration on the reaction rate constant k_{obs} and the decolorization efficiency ($t = 10$ min) (pH 3; $C_{0,H_2O_2} = 0.1\%$, w/w; $C_{0,FeCl_3} = 0.02\%$, w/w).
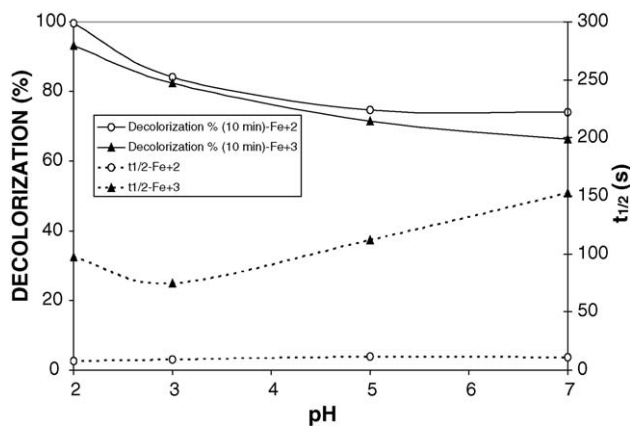
Fig. 11. Comparison between Fe^{3+}/H_2O_2 and Fe^{2+}/H_2O_2 reagent effect on the decolorization efficiency ($t = 10$ min) and $t_{1/2}$ for the PNH dye vs. pH ($C_{0,PNH} = 200$ mg/l; $C_{0,H_2O_2} = 0.1\%$, w/w; mol H_2O_2/mol Fe^{3+} or $Fe^{2+} = 24$).

Fig. 12. UV radiation effect on the Fenton like reaction for the PNH dye ($C_{0,PNH} = 200$ mg/l; pH 7; $C_{0,H_2O_2} = 0.1\%$, w/w).

3.2. Comparison with Fenton and photo-Fenton-like processes

3.2.1. Fenton-like and Fenton processes

Fig. 11 presents a comparison between the Fenton-like and the Fenton processes. In these experiments, the Fe^{3+} and Fe^{2+} concentrations as well as the molar ratios of H_2O_2/Fe^{3+} and of H_2O_2/Fe^{2+} are the same and equal to 24. The initial concentration of PNH is the same in all experiments (=200 mg/l). From Fig. 11, it seems that the use of Fenton reagent is more efficient than the use of Fenton-like reagent. This is due to reaction sequence (1) through (7). Use of a Fenton-like reagent necessitates additional steps, reactions (3) and (4), in order to produce Fe^{2+}, which then must react with H_2O_2 to produce hydroxyl radicals. Another observation is that while the $t_{1/2}$, using a Fenton-like reagent, goes through a minimum with respect to pH, the corresponding $t_{1/2}$ using a Fenton reagent remains low and flat throughout the pH range studied.

Regarding decolorization efficiency after a 10 min reaction time, the two methods achieve nearly identical decolorization efficiencies in the pH range between 3 and 5. The Fenton reagent gives better results at a pH equal to 2 and at a pH higher than 5. At pH 3, decolorization efficiencies are about 84% for both methods, while at pH 2, decolorization efficiencies are 94 and 100% for the Fenton-like and Fenton processes, respectively. All these results are in accordance with other studies reported in the literature [31–33,35].

3.2.2. Fenton-like and photo-Fenton-like processes

Fig. 12 shows a comparison between the Fenton-like process and the photo-Fenton-like process (UV-irradiated-Fenton-like reagent). Runs were made for two different concentrations of $FeCl_3$, equal to 0.02 and 0.5% (w/w) (molar ratio of $H_2O_2/Fe^{3+} = 24$ and 1, respectively), at constant H_2O_2 and PNH dye concentrations. From the time course of the absorbance readings, it can be concluded that in the early stages of the reaction, the decolorization rate for the two processes (Fenton-
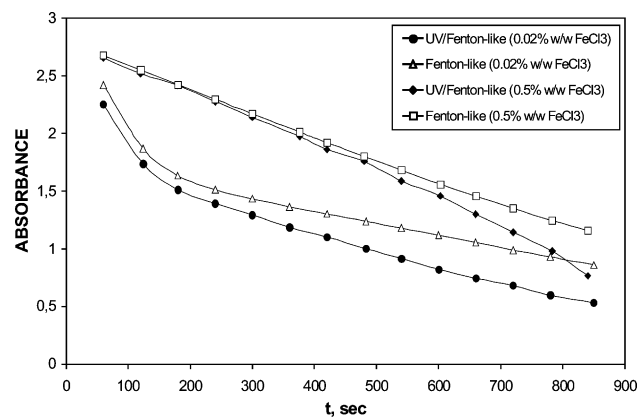
like and photo-Fenton-like) does not differ much. However, as the reaction progresses and as the decolorization rate drops, the photo-Fenton-like process increases the decolorization rate significantly.

Clearly, the following processes are occurring synchronously, contributing to the increase of the decolorization efficiency:

[A] A Fenton-like process producing hydroxyl radicals through reaction step 1,

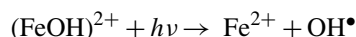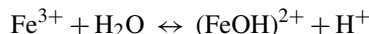[B] A photolytic process producing hydroxyl radicals through:

$$H_2O_2 + h\nu \leftrightarrow 2OH^\bullet$$
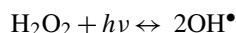
[C] Photoreduction of aqueous ferric ions:
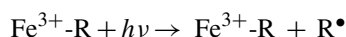
$$Fe^{3+} + h\nu \leftrightarrow Fe^{2+}$$
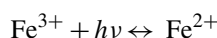
This reproduction of Fe^{2+} enhances the production of hydroxyl radicals from reaction (1)

[D] Production of hydroxyl radicals from the $(FeOH)^{2+}$ intermediate product:

$$Fe^{3+} + H_2O \leftrightarrow (FeOH)^{2+} + H^+$$

$$(FeOH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^\bullet$$

[E] Production of dye radical intermediates from Fe^{3+}-R chelates (R = dye molecule) which are degraded much faster:

$$Fe^{3+}\text{-R} + h\nu \rightarrow Fe^{3+}\text{-R} + R^\bullet$$

In the early stages of the reaction, process A is very fast, much faster than the other processes; however, as the decolorization rate drops rapidly with time, the combined contribution of processes B, C, D and E to dye decolorization predominates over that of process A and increases the decolorization rate, as has also been reported in the literature [11,23,40,41].
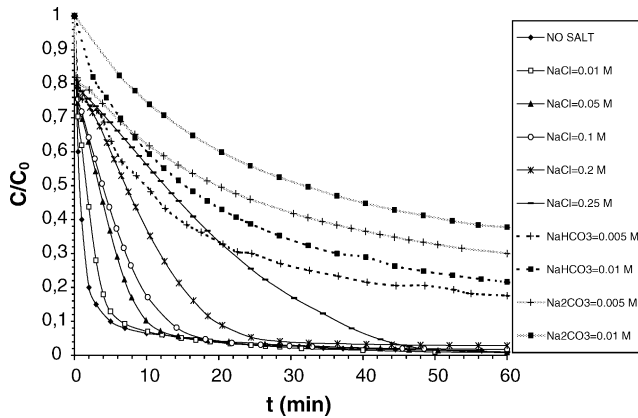
Fig. 13. Salt effect on the PNH decolorization by Fenton-like reaction ($C_{0,PNH} = 200$ ppm; $C_{0,H_2O_2} = 0.2\%$, w/w; $C_{0,FeCl_3} = 0.1\%$, w/w; pH 3).

3.3. Effect of Cl^-, CO_3^{2-} and HCO_3^- addition on the decolorization rates

Fig. 13 shows the effect of adding various amounts of the Cl^- (from NaCl), CO_3^{2-} (from Na_2CO_3) and HCO_3^- (from $NaHCO_3$) ions on the decolorization rates of dye solutions containing 200 mg/l PNH. The molar concentrations of these ions shown in Fig. 13 are in the range of typical concentrations used in the textile industry. Two points are evident from Fig. 13: (1) At the same concentrations of these three ionic species (0.01 M), the HCO_3^- and CO_3^{2-} ions (especially CO_3^{2-}) slow down significantly the dye decolorization rate, while it takes relatively very high concentrations of Cl^- to reduce significantly the decolorization rate; (2) when Cl^- is added to the solution, decolorization efficiencies (expressed by the C/C_0 ratio) become equal to the decolorization efficiency of the solution without Cl^- addition at reaction times from 10 to 45 min, depending on the concentration of Cl^- in the solution, while the decolorization efficiencies of solutions containing either CO_3^{2-} or HCO_3^- do not exhibit such a trend. It is therefore evident, that CO_3^{2-} and HCO_3^- ions decrease substantially the decolorization efficiencies, while Cl^- decreases the decolorization efficiency to a smaller extent and only in the early stages of the reaction.

3.4. TOC reduction and biodegradability increase

Fig. 14 shows the reduction of the TOC/TOC_0 ratio ($TOC_0 = 49.5$ mg/l is the TOC value at $t = 0$) versus decolorization time of solutions containing 200 mg/l PNH using the Fenton (Fe^{2+}/H_2O_2), Fenton-like (Fe^{3+}/H_2O_2) and photo-Fenton-like ($Fe^{3+}/H_2O_2/UV$) methods. This is done at an optimum combination of the system parameters determined earlier, where decolorization rates are fastest. For comparison, the reduction of the C/C_0 ratio using these three methods is also shown. It can be noted that C/C_0 decreases similarly for all three processes. Evidently, using a photo-Fenton-like process does not improve decolorization efficiencies, since decolorization efficiencies after 30 min are already about 95% for both the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes. TOC values fall much more slowly than the C/C_0 values. They fall from 49.5 mg/l to

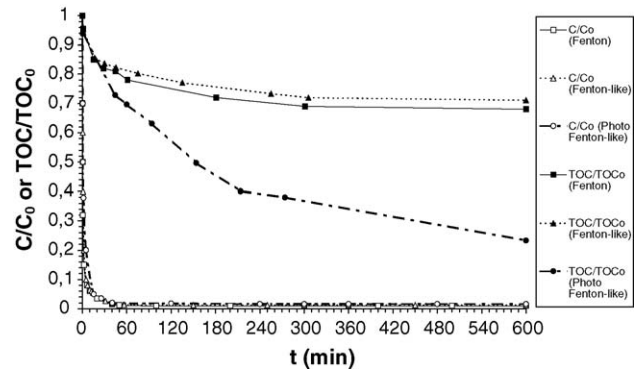
Fig. 14. Time variation of C/C_0 and TOC/TOC_0 ratio for the Fenton, Fenton-like and photo-Fenton-like processes (pH 3; $C_{0,PNH} = 200$ ppm; $C_{0,H_2O_2} = 0.2\%$, w/w; mol H_2O_2/mol Fe^{3+} or $Fe^{2+} = 10$; $TOC_0 = 49.5$ mg/l).

about 40 mg/l after 1 h reaction time for the Fe^{3+}/H_2O_2 process and to about 39 mg/l for the Fe^{2+}/H_2O_2 process, showing no further significant reduction with time. However, the TOC values are greatly reduced in the photo-Fenton like process (254 nm). After 1 h, the TOC value for the $Fe^{3+}/H_2O_2/UV$ process falls to about 34 mg/l and after 4.5 h the TOC value is about 20 mg/l.

Fig. 15 shows the change in COD, BOD and the BOD/COD ratio for solutions of the same composition using the Fenton-like (Fe^{3+}/H_2O_2) and photo-Fenton-like ($Fe^{3+}/H_2O_2/UV$) processes. It is evident that the reduction of COD values follows that of TOC in Fig. 14. However, while COD values decrease with time, the BOD values increase, leading to an increase of the BOD/COD ratio. This ratio at time zero is only 0.11 indicating that only a small fraction of the organic load is biodegradable, but it increases significantly to about 0.55 and 0.70, for the Fe^{3+}/H_2O_2 and the $Fe^{3+}/H_2O_2/UV$ processes, respectively, after a 2 h treatment. Thus, biodegradability, as expressed by the BOD/COD ratio, increases significantly with treatment time.

Hence, treatment, especially with the combined method of photo-Fenton-like ($Fe^{3+}/H_2O_2/UV$), greatly increases the mineralization rates and also increases the biodegradability of the organic load, making this process (photo-Fenton-like) attractive for the treatment of textile effluents. It seems attractive to use
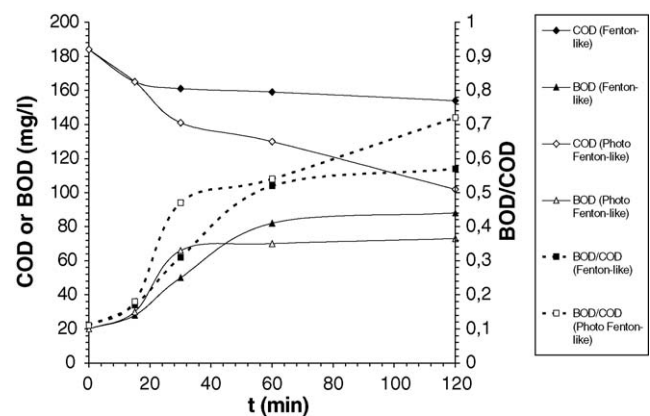

Fig. 15. Time variation of BOD, COD and BOD/COD ratio for the Fenton-like and photo Fenton-like processes (pH 3; $C_{0,PNH} = 200$ ppm; $C_{0,H_2O_2} = 0.2\%$, w/w; $C_{0,FeCl_3} = 0.1\%$, w/w).

a combined treatment of textile effluents, including a photo-Fenton-like process in the first stage in order to increase the biodegradability followed by a biological treament such as activated sludge to further reduce the COD.

4. Conclusions

From this study, it was concluded that the rate of the decolorization of the three Procion H-exl dyes is strongly dependent on the solution pH, the H_2O_2 concentration, the ferric ion concentration and the initial dye concentration. More specifically:

- The solution pH strongly influences the decolorization reaction rate. The optimum pH range is between 3 and 4. However, a pH up to 7 can be used without significantly slowing down the reaction rate. Below pH 2, the decolorization rate decreases rapidly.
- At a constant H_2O_2 concentration (equal to 0.1%, w/w), the decolorization half-life time goes through a flat minimum with increasing $FeCl_3$ concentration. This optimum range for PNH and PCH dyes occurs between 0.005 and 0.1% (w/w) $FeCl_3$. After only a 10 min reaction time, PNH and PCH dyes are almost completely decolorized.
- At a constant $FeCl_3$ concentration equal to 0.1% (w/w), the half-life time and decolorization efficiency of PNH and PCH are optimized in H_2O_2 concentration between 0.2 and 2% (w/w). For PYH, the optimum range of H_2O_2 concentration is much narrower and the decolorization rate is much slower.
- All the experimental results show that generally PYH is the most stable dye and PNH is the least stable. Also, the k_{obs}, $t_{1/2}$ and decolorization efficiency for all three dyes show relatively similar dependence on the solution pH and the concentrations of $FeCl_3$, H_2O_2 and dye. PNH and PCH have similar values of k_{obs}, $t_{1/2}$ and decolorization efficiency, especially in the optimum range.
- The decolorization rate is faster when the initial dye concentrations are above 200 mg/l. Rates are significantly lower at low initial dye concentrations (below 200–100 mg/l depending on pH).
- The speed of reaction Fe^{2+}/H_2O_2 is faster than the speed of the corresponding Fe^{3+}/H_2O_2 reaction during their early stages. However, the 10 min decolorization efficiencies of the two processes are similar in the pH range between 3 and 5. Outside this range, decolorization efficiencies become higher for the Fenton process.
- Addition of salts such as Na_2CO_3 and $NaHCO_3$ significantly reduces decolorization efficiencies. This effect is less pronounced when adding NaCl.
- TOC values drop much more slowly than the dye concentration, but it was found that the combination of Fenton-like reaction followed by UV irradiation (254 nm) increases significantly the rate of TOC reduction.
- Biodegradability, as expressed by the ratio BOD/COD, is significantly increased. After a 2 h treatment, it increases from 0.11 to 0.55 for the Fe^{3+}/H_2O_2 process and to 0.70 for the $Fe^{3+}/H_2O_2/UV$ process.

These results are encouraging because they show that dyes of Procion H-exl type can be successfully decolorized by using Fenton-like processes in which the system parameters are appropriately adjusted. Furthermore, effluent biodegradability is significantly increased and combined processes such as photo-Fenton-like processes can be used to further reduce the COD of textile effluents. Further research is currently being conducted to examine the decolorization efficiency of combined processes, especially in alkaline pH.

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