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Mechanism and kinetics model of degradation of synthetic dyes by UV–vis/H_2O_2/Ferrioxalate complexes

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Abstract

The kinetics of photocatalytic degradation of Reactive Brilliant blue KN-R, Acid Scarlet GR and Reactive Brilliant red X-3B by UV–vis/H_2O_2/Ferrioxalate complexes were studied. Effects of initial concentration of KN-R solution, Fe^{2+}, H_2O_2 and pH were investigated. Under these optimum experimental conditions, the removal rates of COD and TOC of three dyes were more than 80% and 65%. A pseudo-first-order kinetic model was adopted to represent the reaction.

Keywords: Photocatalysis; Dye; Degradation; Kinetics

1. Introduction

The commercial dye is one of the worst environmental pollutants in industries. It is improving so rapidly that it causes great pressure on the potential of pollution of water environment. Synthetic dyes which are used extensively in textile, paper and printing industries can be classified mainly as azo, anthraquinone, vat, phthalocyanine, indigo, polymethine, carbonium, and nitro dyes. Most of these dyes are manufactured through different stages involving nitration, reduction, halogenation, amination, sulfonation, diazotization and oxidation using benzene, toluene, xylene, naphthalene, anthracene, as raw materials. The effluents from these industries vary widely in composition, contain organic and inorganic compounds and have high level of color and COD. Colored textile effluents contain persistent dyestuffs, many of which are reported to be toxic and carcinogenic [1]. Direct discharge of these effluents can cause formation of toxic aromatic amines under anaerobic conditions in receiving media and contaminate the soil and groundwater. Therefore, proper treatment is necessary before discharge into the environment.

Recent studies indicate that the advanced Fenton reagent is based on the photocatalysis of H_2O_2/Ferrioxalate. It is one of the advanced oxidation processes (AOPs) that provide a promising treatment option of commercial wastewater. Therefore, it was applied extensively all over the world [2–4]. Experimental studies of the oxidation of organic compounds have demonstrated that the $OH^{\bullet}$ concentration is the important parameter to quantify the kinetics of AOPs. Many models have been postulated over the years to describe the kinetics of these reactions using the steady-state approximation, in which the concentration of hydroxyl radicals does not change with the reaction time [5]. The kinetics are used to control reactive conditions and occult interference, thus the chemical kinetic plays very important role in the theory and the application. However, for wastewater with its many contaminants and reactions, most of the proposed models rely on the steady-state approximation to eliminate the nonmeasurable radicals' concentration, correlating it as a function of hydrogen peroxide concentration

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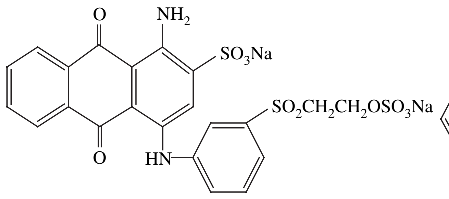
($C_{H_2O_2}$) [6]. The purpose of this work is to study the mechanism and the kinetics principle of degradation of synthetic dyes by UV–vis/H_2O_2/Ferrioxalate complexes. At the same time, the different factors on the reactive rate will be inspected and the kinetic equation will be founded for three dyes under the optimum condition at a lower cost. Thereby, these studies will accelerate the process of industrialization for the technology.

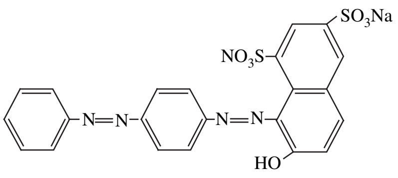
2. Materials and methods

2.1. Reagents

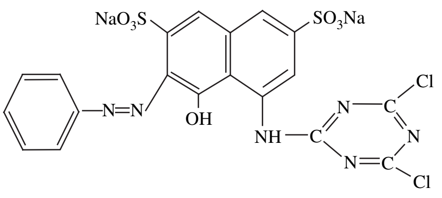
Reactive Brilliant blue KN-R, Acid Scarlet GR and Reactive Brilliant red X-3B (KN-R, GR and X-3B for short in the following paper) were obtained from the eighth dye chemical factory in Tianjin as commercially available dyes. The chemical structures of the three dyes are as following:



KN-R



GR



X-3B

2.2. Experimental process

2.2.1. Conditions

To begin with, given quantity of Fe^{2+}, H_2O_2 and $H_2C_2O_4$ was added to 100 ml beakers containing dyes' solutions (controlled ultimate concentration is 50 mg/L). After rapid and slow mixing period, pH of the supernatant was readjusted by using H_2SO_4 and NaOH when the reaction began and finished. Reactors were kept at constant temperature. The supernatant was separated by the centrifugation with 5000 rpm for 30 min. Then, the color, chemical oxygen demand (COD) and total organic carbon (TOC) removal rates were analyzed. COD removal efficiency was determined by the titration of potassium dichromate; TOC was determined by total organic carbon analysis instrument; UV–vis spectra of samples were recorded from 200 nm to 800 nm using spectrophotometer (Shanghai Model 752). The maximum absorbance wavelength (λ_{max}) of KN-R, X-3B, GR are 593 nm, 537 nm and 507 nm from the spectra. Therefore, the concentration of dyes in water was determined by the absorption intensity at λ_{max}. TOC was analyzed with Shimadzu TOC-V_{CPH} instrument. The experimental data were fitted into the following equation:

$$\text{Dye decolorization} = (C_{\text{dye},0} - C_{\text{dye},t})/C_{\text{dye},0} \times 100\%$$

$$\text{COD removal ratio} = (\text{COD}_0 - \text{COD}_t)/\text{COD}_0 \times 100\%$$

$$\text{TOC removal ratio} = (\text{TOC}_0 - \text{TOC}_t)/\text{TOC}_0 \times 100\%$$

where $C_{\text{dye},0}$ and $C_{\text{dye},t}$ are concentrations of dye at λ_{max} at reaction time 0 and t, respectively; COD_0 and COD_t are the chemical oxygen demand values at reaction time 0 and t, respectively; and TOC_0 and TOC_t are the total organic carbon values at reaction time 0 and t, respectively.

The optimum conditions were obtained for 50 mg/L KN-R case at 75 mg/L of H_2O_2 dose, 5 mg/L of Fe^{2+} and $H_2C_2O_4$ dose at pH = 3.0 in 60 min, under the common and constant temperature, by the single factor and the orthogonal experiment.

2.2.2. Kinetic models

Various types of kinetic models have been described in the literatures. They were classified into two kinds. The first type of kinetic model is a rate expression derived from an empirically determined correlation [7,8]. Another based on known reaction mechanisms has been proposed [9–11]. Most of these kinetic models were developed for low concentrations of the organic target compounds. The experiment relied on the unit reaction in which computation coefficient accords with the reactive molecule numbers. In this way, the reactive orders depend on the numbers of reactive molecule. The velocity rate equation that can be written as $-dC_A/dt = kC_A^a C_B{}^b\ldots$, could be taken as a pseudo-first-order kinetic model when $C_B\ldots$ were excesses [12]. If the $^\bullet$OH radical concentration is constant and greater than the dye concentration, the kinetics model of degradation of dye is a pseudo-first-order rate equation in UV–vis/H_2O_2/Ferrioxalate complexes system:

$$\frac{dC_t}{dt} = -k_1 C \qquad (1)$$

where, k_1 is the pseudo-first-order rate constant; C_t is the concentration of dye at t minute and t is the reactive time. In case of photo-assisted Fenton processes, UV and solar light remained almost constant during the experimental time and hence Eq. (1) was equated in evaluating the kinetics of dyes during photo-Fenton processes. When $t = 0$, C_t is equal to C_0, and the Eq. (1) becomes,

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t \tag{2}$$

and the velocity equation is founded as

$$C_t = C_0\,\mathrm{e}^{-k/t} \tag{3}$$

3. Results and discussion

3.1. Comparative experiment

From Table 1, we can see that the depredated effect was not better when Fe^{2+} or H_2O_2 was presented alone in the reactive reagent, and the reactive rate was increased under the irradiation in UV–vis/H_2O_2/Ferrioxalate complex system. Following were the reactive mechanisms [12]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{5}$$

$$\text{Under irradiation}: Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^\bullet OH + H^+ \tag{6}$$

Photocatalyst was founded and photoactivated that produced •OH. The reaction occurring in the process is as follows (from Eqs. (7) to (10)):

$$Fe^{3+} + H_2O_2 + 3C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-} + {}^\bullet OH + OH^- \tag{7}$$

$$Fe(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + {}^\bullet C_2O_4^- \tag{8}$$

$${}^\bullet C_2O_4^- + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \tag{9}$$

$${}^\bullet C_2O_4^- \rightarrow CO_2 + CO_2^{-\bullet} \tag{10}$$

$${}^\bullet C_2O_4^-/CO_2^{-\bullet} + O_2 \rightarrow O_2^{-\bullet} + 2CO_2/CO_2 \tag{11}$$

Table 1
COD and TOC removal ratios on different Fenton systems

Conditions	Fe^{2+}	H_2O_2	Fe^{2+}/H_2O_2	$Fe^{2+}/H_2O_2/H_2C_2O_4$
COD				
Irradiation	24.1	32.0	66.5	89.1
Dark	11.3	27.6	57.6	60.8
TOC				
Irradiation	12.0	24.2	33.2	65.6
Dark	5.6	19.4	30.0	45.1

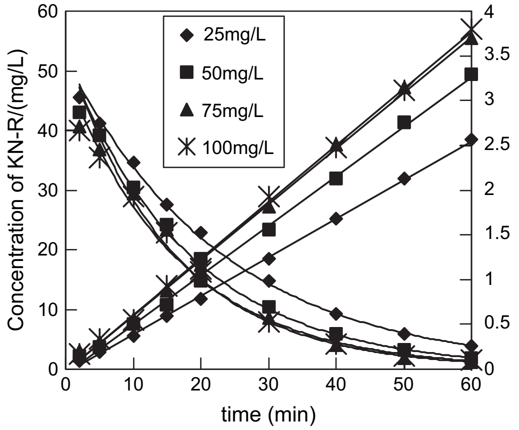


Fig. 1. Effect of H_2O_2 on the oxidation kinetics of KN-R.

$$O_2^{-\bullet} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{12}$$

The ${}^\bullet C_2O_4^-$ and $CO_2^{-\bullet}$ continued to be reactive with O_2 and produced H_2O_2 in acid conditions (Eqs. (11) and (12)). Thus Fe^{2+} and H_2O_2 were produced by the photoactivated function of Ferrioxalate complexes that can maintain source of Fenton's reaction.

The generated ${}^\bullet$OH radical reacted with the target compound, dyes, by abstracting the H-atom of the aromatic ring resulting in degradation when the organic substances existed. Fe^{3+} ion generated (in Eq. (4)) can react with either peroxide or perhydroxyl radical ($HO_2^\bullet$) or decomposed radical ($R^\bullet$) as shown in Eqs. (13) and (14) for regenerating the ${}^\bullet$OH radical to participate in further oxidation reaction.

$$RH + {}^\bullet OH \rightarrow R^\bullet + H_2O \tag{13}$$

$$R^\bullet + HO{-}HO \rightarrow R{-}OH + {}^\bullet OH \tag{14}$$

The degradation reaction continued, until the compounds were completely depleted from the aqueous solutions.

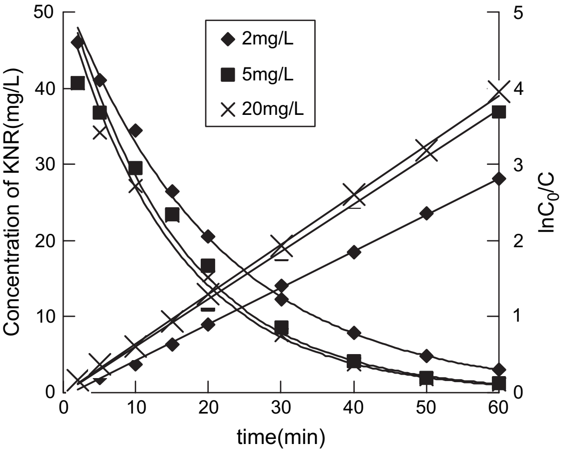


Fig. 2. Effect of Fe^{2+}on the kinetics of KN-R.

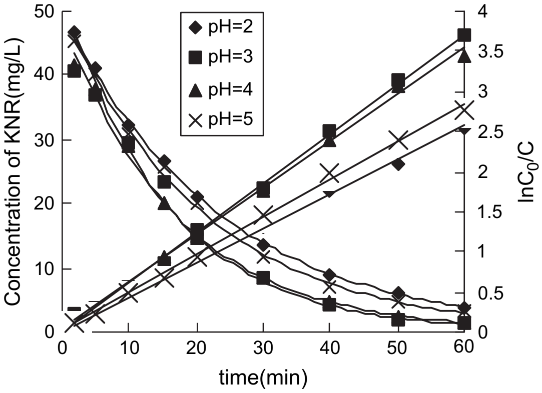


Fig. 3. Effect of pH on the kinetics of KN-R.

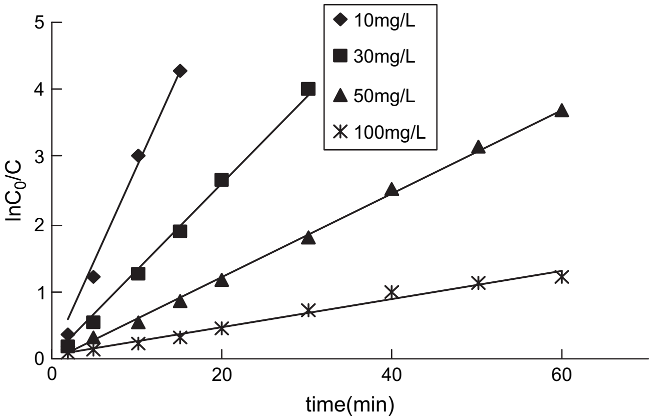


Fig. 4. Effect of the initial concentration on the kinetics of KN-R.

3.2. Effect of H_2O_2 dose on oxidation kinetics

The concentration of H_2O_2 is found to be the most important factor to achieve better performance in Fenton's reaction by the results of orthogonal experiment. The reactive rate of KN-R increased with H_2O_2 concentration, as $C_{H_2O_2}$ varied from 25 up to 100 mg/L (Fig. 1). The reactive rate was the fastest when $C_{H_2O_2}$ was 100 mg/L, and the slowest as $C_{H_2O_2}$ was 25 mg/L, but the rate has only slight acceleration at the concentration of 75 mg/L. Although the increase in $C_{H_2O_2}$ accelerates the formation of $OH^\bullet$, the decolorization rate becomes increasingly independent of $C_{H_2O_2}$. When the concentration of H_2O_2 is high, H_2O_2 can absorb $^\bullet OH$ radical, reaction is $H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O$ [13], resulted to diminish using rate of H_2O_2, and the more concentration of H_2O_2, the more strong power absorb function [14].

3.3. Effect of Fe^{2+} dose on the kinetics

Effect of Fe^{2+} was similar to the H_2O_2 dose, the reactive rate was the fastest when Fe^{2+} was 20 mg/L, but 5 mg/L of Fe^{2+} obtained rate slightly slower than 20 mg/L. The slowest rate was obtained when the concentration of Fe^{2+} was 2 mg/L (Fig. 2).

In addition, the documents reported that Fe^{2+} was the catalyst used for generating $^\bullet OH$ by motivating decomposition of H_2O_2. The amount of $^\bullet OH$ is little due to the low concentration of Fe^{2+} which resisted decomposition.

Table 2
Main effect factors on kinetics

Effect factors		k (min^{-1})	R^2	$\tau_{1/2}$ (min)
H_2O_2 (mg/L)	100	0.0631	0.9978	10.9
	75	0.0622	0.9981	11.2
	50	0.0552	0.998	12.5
	25	0.0431	0.9991	16.1
Fe^{2+} (mg/L)	20	0.0649	0.9989	10.7
	5	0.0622	0.9981	11.2
	2	0.0478	0.9992	14.5
pH	2	0.0427	0.9992	16.2
	3	0.0622	0.9981	11.2
	4	0.0588	0.9972	11.8
	5	0.0473	0.9973	14.6

3.4. Effect of pH on the kinetics

The effect of pH on the removal rate of the dissolved dye in the batch system is a complicated factor, which is shown in Fig. 3 [15].

At pH 2, the dye concentration decreased from 50, through 32.2, 20.9, 13.4, 8.8, and 6.1 to 3.9 mg/L at time 10, 20, 30, 40, 50, and 60 min, respectively, where the average removal rate was 0.77 mg/L/min. At pH 5, the average removal rate was 0.78 mg/L/min in the same interval. In the acidic region of pH 3 and 4, the dye concentration decreased rapidly during the photo-degradation. The average removal rates were added to 0.81 mg/L/min. We could conclude the same results from the data in Table 2. Maximum reactive rate of KN-R was observed at pH 3, where approximately half of the Fe(III) exists as Fe^{3+} ion and half as $Fe(OH)^{2+}$ ion. Below this pH, the concentration of $Fe(OH)^{2+}$ declines and at a higher pH the Fe(III) precipitates as oxy hydroxide and reduces the transmission of radiation. Degradation of dye wastewater by Fenton's and photo-Fenton's reaction was achieved at the pH range 3.0–4.0 [16].

3.5. Kinetics of the initial concentration

In Fig. 4, the degradation rates obtained were 0.3082 min^{-1}, 0.1373 min^{-1}, 0.0622 min^{-1}, 0.0209 min^{-1}, respectively, for the different initial concentrations of KN-R which were 10, 30, 50 and 100 mg/L. The results showed that these reactions accorded with a pseudo-first-order, and the reactive rate was decreased with increasing concentration in the KN-R's linearity range (0–120 mg/L).

3.6. Kinetics on the source of light

From Fig. 5, we can see that the UV–vis/Fenton/$H_2C_2O_4$ system is a more efficient method than others. Solar energy

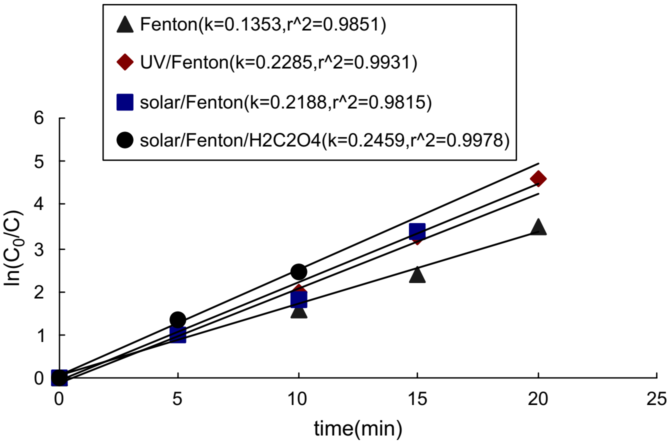


Fig. 5. Effect of light source on the kinetics of KN-R.

was made use of for the Fenton technology, which saved much cost and could be operated efficiently and effectively.

3.7. Kinetics on the different dyes

The pseudo-first-order kinetic model was certified by the linear character of $\ln(C_0/C)$ versus time. This assumption was true and right. The apparent first-order rate constant (k_1) of the degradation after 30 min of reaction time was calculated from linear regression $\ln(C_0/C)$ versus time plots with all regression coefficients greater than 0.99. The k_1 obtained for X-3B and GR was 0.1454 min^{-1} and 0.2046 min^{-1} (Fig. 6). The corresponding first-order constant of KN-R was 0.0619 min^{-1}. The photocatalytic oxidative degradation rate on the GR was 3.3 times faster than the KN-R. The results showed that the chemical structure of the dyes also influenced the reactive rate. The degradation of KN-R was more difficult than the other two dyes viz., the anthraquinone dye is harder to degrade than the azo dye.

Similar results were proved in Fig. 7(a–c). As could be observed from these spectra, before the treatment, the absorption spectrum of three dyes was characterized by three main bands in the visible region, with their maximum absorption at 593 nm, 537 nm, and 507 nm, respectively, for KN-R, X-3B, GR, and a few bands in the ultraviolet region located from 220 nm to 322 nm. The peaks between 220 nm and 322 nm were ascribed to the absorption of the $\pi-\pi^*$ or $p-\pi^*$ transition related to the group of things with aroma features, such as the naphthalene, anthracene, benzene rings, bonded to the conjugative and inductive effects of the −N=N−, C=O, S, Cl or N group in the dye molecule [17,18]. The band in the visible region was attributed to the homophones containing azo linkage of the dye molecules in the solution [19]. The adsorption peaks at $\lambda_{max} = 537$ nm and $\lambda_{max} = 507$ nm for X-3B and GR, which were diminished and finally disappeared completely under 10 min, to KN-R the peak at $\lambda_{max} = 593$ nm needed longer time than the others, the time was further more, the peaks between 220 nm and 350 nm were decreased obviously with increasing reaction time, too. The absorptions were obtained which were 0.44, 0.25 and 0.58, respectively, for KN-R, X-3B and GR under 90 min. The decrease was also meaningful with respect to the −N=N− and aroma family rings of dyes, as the most active site for attack [20].

In addition, we can see from Table 3, the COD and TOC removal ratios for three dyes. They can be degraded effectively by the solar/oxalic acid/Fenton system. The oxidation rate of dyes was in the order GR > X-3B > KN-R. Thus the method was an effective treatment method for dye-containing wastewater to some extent.

4. Results

The effect of parameters pH, H_2O_2, Fe^{2+} and $H_2C_2O_4$ concentration were synthetically evaluated in the case of KN-R (50 mg/L) on reactive rate in the improved Fenton system. The optimum condition was obtained at 75 mg/L of H_2O_2 dose, 5 mg/L of Fe^{2+} and $H_2C_2O_4$ dose at pH = 3.0 in 60 min, under the common and constant temperature, through the single factor and the orthogonal experiment.

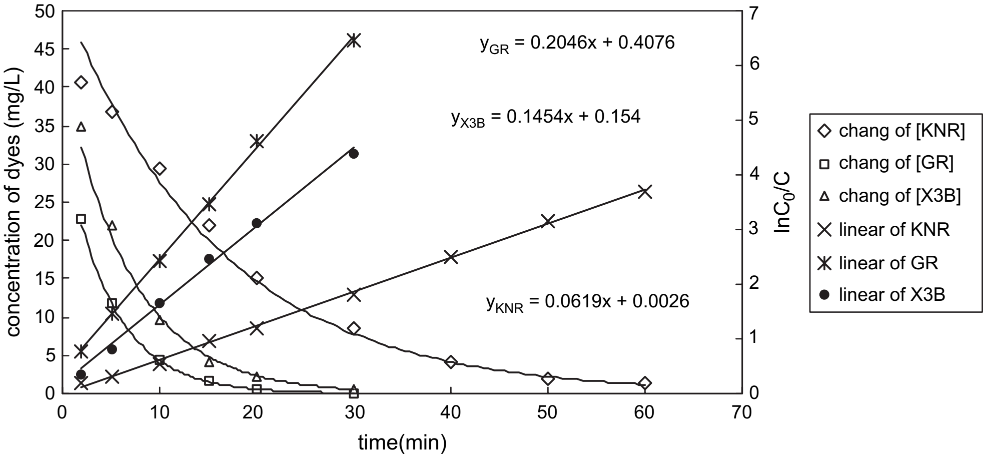


Fig. 6. Change of degradation of dyes and $\ln(C_0/C)$ with time.

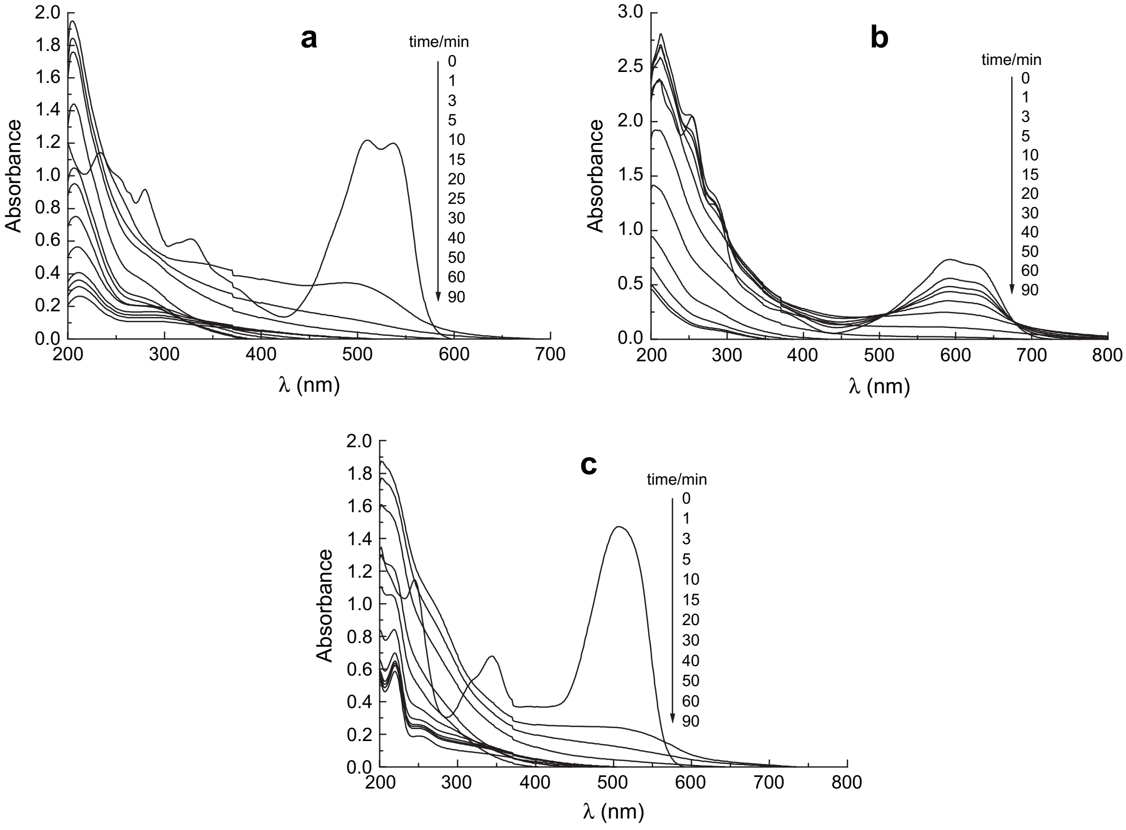


Fig .7. Comparison of degradation process on different dyes under irradiation a: X-3B, b: KN-R and c: GR.

The reactive rate was decreased with increasing concentration of dye by studying the kinetics of the initial concentration. The assumption of pseudo-first-order kinetic model was certified by the linear character of the $\ln(C_0/C)$ versus time. The results showed that these reactions accorded with a pseudo-first-order and the velocity rates of KN-R, X-3B and GR were built up, which were $C_t = 53.65e^{-0.0622t}$, $42.866e^{-0.1454t}$ and $33.227e^{-0.2045t}$, respectively.

The data of COD and TOC removal ratios for the three dyes were more than 80% COD and 65% TOC in 1 h. Therefore, the degradation was effective in the solar/H_2O_2/Ferrioxalate complexes system. The COD and TOC removal ratios were 1.5 and 2.1 times than common Fenton in this method. Thus there will be a prosperous application for the improved Fenton system, as a result of saving energy and being operated economically, efficiently and effectively in the treatment of textile wastewater.

Table 3
Degradation of dyes

Dyes (50 mg/L)	Velocity equation C_t (mg/L)	$\tau_{1/2}$ (min)	COD removal ratio	TOC removal ratio
KN-R	$53.65e^{-0.0622t}$	11.1	89.1	65.6
X-3B	$42.866e^{-0.1454t}$	4.8	82.7	69.8
GR	$33.227e^{-0.2045t}$	3.4	85.6	66.5

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