Removal of Some Triphenylmethane Dyes from Aqueous Solutions by Fenton Reagent. I

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The oxidative discoloration of three triphenylmethane dyes, Methyl Blue, Eriochrome Cyanine R and Phenol Red in aqueous solution has been comparatively studied using the Fenton process. The effects of different reaction parameters such as initial pH and temperature on the dyes degradation have been assessed. The UV-Vis spectral changes of triphenylmethane dyes during Fenton treatment process have been studied. The decay kinetics has also been investigated. In order to determine the concentration of unknown samples of studied dyes, the calibration curves have been achieved by measuring the absorbances at different concentration values of dyes.

Keywords: Methyl Blue, Eriochrome Cyanine R, Phenol Red, Fenton process, kinetic study

A large amount of wastewater containing dyestuffs with intensive colour and toxicity is introduced into the aquatic systems during dye production and textile manufacturing processes. Even a small quantity of dye in the water (e.g., 10-20 mg L^{-1}) is highly visible and the water transparency and the gas solubility of water body are affected as well [1].

Traditional treatments involving biological and coagulation/flocculation methods are generally ineffective for total colour removal. Advanced oxidation processes (AOPs) are treatment processes based on the generation of radicals that are highly reactive and nonselective species [2]. Therefore, AOPs have often been used for the treatment of wastewaters containing a wide range of organic pollutants. Among the AOPs, Fenton oxidation has shown pollutant removal efficiencies >90 % [3-6]. The Fenton-type process combines iron (Fe^{2+} or Fe^{3+}) with hydrogen peroxide to produce hydroxyl radicals. The general mechanism using Fenton reagent is a number of cyclic reactions which utilize Fe^{2+} or Fe^{3+} ions as a catalyst to decompose the hydrogen peroxide [2].

Azo dyes degradation study by different methods has been reported by many researchers [1, 7-15]. Triphenylmethane dyes that belong to the group of synthetic colorants are also used extensively in textile industries. Some of them such as, Aniline Blue, Eriochrome Cyanine R, Phenol Red, Methyl Blue, etc., were removed from wastewaters by using AOPs [16-21].

Methyl Blue, MB also known as Acid Blue 93 (C.I. 42780) is an anionic triphenylmethane dye used for dyeing cotton, cotton based fibers and leather. It is also used as a biological and bacteriological stain. It is harmful if swallowed and causes skin, eye and respiratory tract irritation. As evident from the literature, much research has not been done on the degradation of this dye [20].

The Eriochrome Cyanine R, ECR (C.I. 43820), frequently used in chemical analysis as an indicator for complexometry and particularly for Cu^{2+} ion detection [22], has two carboxylic groups, one hydroxyl, one carbonyl and one sulphonic group which ensure compatibility with polar solvents [23].

Phenol Red, PR (also known as phenolsulfonphtalein or PSP) is a water-soluble dye used as a *p*H indicator dye in various medical and cell biology tests. The photo-Fenton degradation of Phenol Red triphenylmethane dye was studied by A. Jain et al. [18].

The objective of this work was to investigate the application of Fenton oxidation process in the treatment of waters containing three triphenylmethane dyes: Methyl Blue, Eriochrome Cyanine R and Phenol Red. The influence of temperature and pH on dyes degradation was investigated. This study presents effective informations about the optimized reaction conditions for the discoloration of the solutions containing the mentioned compounds.

Experimental part

Materials and methods

Triphenylmethane dyes (Methyl Blue, Eriochrome Cyanine R, Phenol Red), hydrogen peroxide (30 % w/w), ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and sulfuric acid were all purchased from Fluka or Aldrich. All reagents were of analytical grade and used without any further purification. Distilled water was used to prepare the colored solutions. Chemical structures and characteristics of the tested triphenylmethane dyes are presented in table 1.

Methods

All experimental determinations were performed for aqueous solutions of dyes, with initial concentrations of 6.5×10^{-5} mol L^{-1}. The added ferrous sulfate concentration in the system was 4×10^{-5} mol L^{-1} and the hydrogen peroxide concentration was 2×10^{-3} mol L^{-1}.

For each experiment, an Erlenmeyer glass equipped with a refrigerator, containing 100 mL solution of ferrous sulphate and the dye subjected to degradation was placed in a water bath with constant temperature. The studied solution was constantly omogenized by a magnetic stirrer. The pH value of each reaction solution was measured with a model Consort C533 pH-meter and was adjusted at the desired value by using a 0.05 M H_2SO_4 solution.

The reactions were initiated by adding calculated amounts of hydrogen peroxide to the reactor. The kinetics of oxidation was followed by taking samples at regular time

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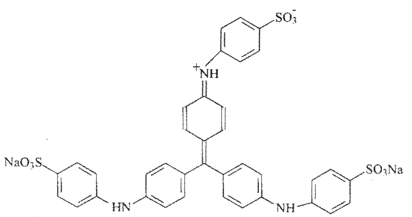
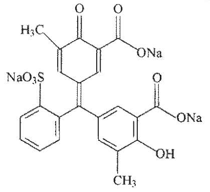
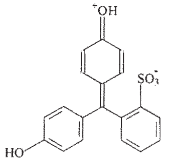
Table 1
CHEMICAL STRUCTURES AND CHARACTERISTICS OF TRIPHENYLMETHANE DYES

Dyes	Structure	Molecular formula	λ_{max} (nm)	M ($gmol^{-1}$)
Methyl blue (MB)		$C_{37}H_{27}N_3Na_2O_9S_3$	600	799.81
Eriochrome Cyanine R (ECR)		$C_{23}H_{15}Na_3O_9S$	580	536.39
Phenol Red (PR)		$C_{19}H_{14}O_5S$	430	354.38

intervals. The discoloration of dyes was monitored by registering the absorbance using an UV-Vis Varian Cary 50 Bio spectrophotometer at the maximum absorption wavelength for each considered dye. The color removal was determined using equation 1.

$$\text{Colour removal }(\%) = \left(1-\frac{A}{A0}\right)\times 100 \tag{1}$$

where A_0 and A are the absorbances at initial time ant time t, respectively.

Results and discussions

Influence of pH

The *p*H affects directly the mechanism of dye oxidation, because a change in *p*H of the solution involves a variation of the concentration of Fe^{2+} ions and therefore, the rate of production of $^{\bullet}OH$ radicals responsible for dye oxidation will be restricted [24]. The effect of *p*H on Fenton discoloration of triphenylmethane dyes was investigated at different *p*H values such as: 3, 4, 5 and 6. The temperature was maintained at 25°C. The results which are represented by the colour removal according to *p*H in figure 1 indicate that the discoloration pattern of the studied dyes is different and each dye presents a behaviour according to its chemical structure and substituents.

As it is shown in figure 1, color removal decreases with *p*H increase from 3 to 6, this being also supported by previous studies [25]. At *p*H = 3, colour removals of MB, ECR and PR obtained after 9 min were 93.06 , 51.56 and 70.92 %, respectively. At *p*H = 6, colour removals of 87.13, 27.03 and 5.96 % were obtained for MB, ECR and PR, respectively, after the same time. Phenol Red reached >99 % colour removal within only 14 min at *p*H = 3 (table 2), while at *p*H = 6, for the same dye, the discoloration process has been studied for about 9 h, the color removal obtained after this time interval being approximately 90 %.

Table 2
TIME REQUIRED FOR > 99% COLOUR REMOVALS IN CASE OF TRIPHENYLMETHANE DYES DISCOLORATION AT DIFFERENT INITIAL *p*H VALUES AND T = 25°C

Dyes	Time (min)			
	pH = 3	pH = 4	pH = 5	pH = 6
MB	11	28	60	85
ECR	26	33	41	300
PR	14	69	90	-

Influence of temperature

Because of the fact that, from the above study, the optimal *p*H value was observed as being 3, this value was used for all discoloration processes of this study. Experiments were performed for different temperature values: 25 , 35 , 45 and 55 °C. Figure 2 illustrates the effect of temperature on the Fenton oxidation of dyes.

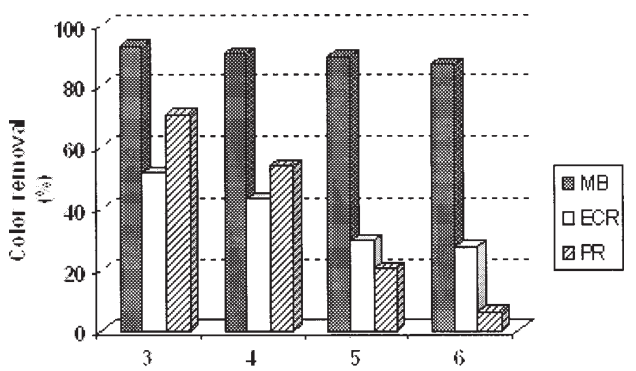


Fig. 1. Effect of pH on triphenylmethane dyes discoloration by Fenton process. Experimental conditions: $[dye]_0$ = 6.5×10^{-5} mol L^{-1}; $[Fe^{2+}]_0$ = 4×10^{-5} mol L^{-1}; $[H_2O_2]_0$ = 2×10^{-3} mol L^{-1}; temperature = 25°C; reaction time = 9 min.

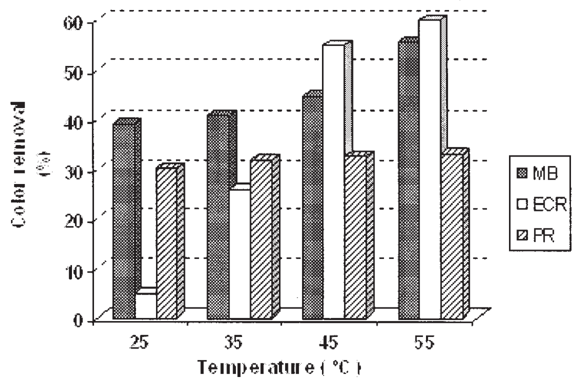


Fig. 2. Effect of temperature on triphenylmethane dyes discoloration by Fenton process. Experimental conditions: $[dye]_0$ = 6.5×10^{-5} mol L^{-1}; $[Fe^{2+}]_0$ = 4×10^{-5} mol L^{-1}; $[H_2O_2]_0$ = 2×10^{-3} mol L^{-1}; *p*H = 3; reaction time = 1 min.

Table 3
TIME REQUIRED FOR >99 % COLOUR REMOVALS IN CASE OF TRIPHENYLMETHANE DYES DISCOLORATION AT DIFFERENT TEMPERATURE VALUES AND *p*H = 3

Dyes	Time (min)			
	t = 25 °C	t = 35 °C	t = 45 °C	t = 55 °C
MB	11	9	6	3
ECR	26	8	3	1.5
PR	14	11	8	6

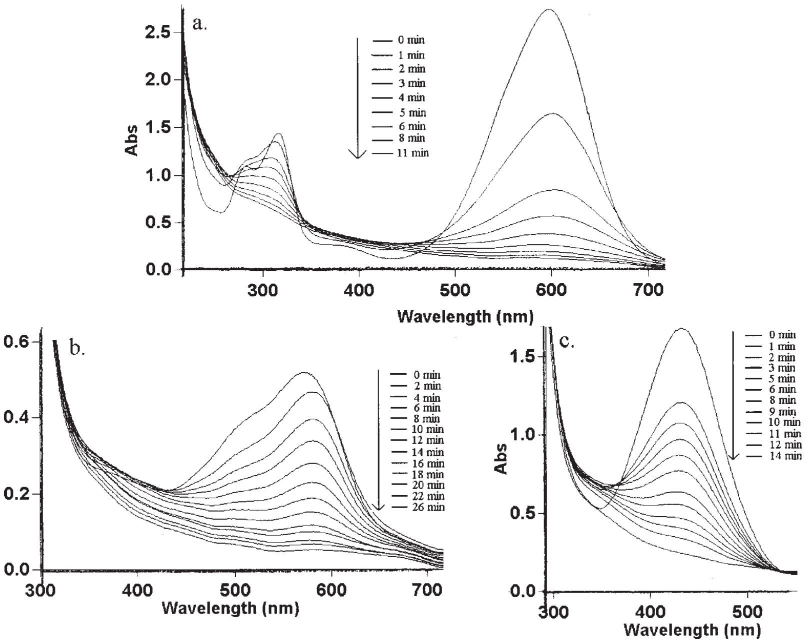


Fig. 3. Spectral changes of triphenylmethane dyes at t = 25°C and *p*H = 3: a. MB; b. ECR; c. PR

From figure 2 it can be observed that the temperature has a great effect on the rate of Methyl Blue and Eriochrome Cyanine R discoloration. With increasing temperature, the colour removal values at the same reaction time present a significant increase, hence a higher rate of discoloration. Color removals of 55.6 , 60 and 31.6 % were observed for MB, ECR and PR, respectively, at the temperature of 55 °C within 1 min, while 38.93 , 4.88 and 30.08 % of color removals were obtained for MB, ECR and PR, respectively, at the temperature of 25°C within the same time interval.

Methyl Blue reached >99 % colour removal within 3 min at the temperature of 55°C. In the case of Eriochrome Cyanine R, >99 % colour removals were obtained within 3 min and 1.5 min at 45 and 55°C, respectively (table 3).

UV-Vis spectral changes

To study the discoloration of triphenylmethane dyes solutions, UV-Vis absorption spectra of dyes solutions were recorded before and during the Fenton process at *p*H = 3 as optimal value at different times (fig. 3).

Before the treatment, the UV-Vis spectrum of MB consisted in two main characteristic bands (fig. 3a). In the UV region, a shoulder around 213 nm and a band at 312 nm were observed. These wavelengths were ascribed to π-π* transitions corresponding to the conjugated aromatic system. In the visible region, an absorbance peak was observed at 600 nm, which corresponded to the absorption of the n-π* transition related to the quinone structure and which was used in order to monitor the compound discoloration. It can be observed that not only A_{600} (quinone chromophore) significantly and rapidly decreased, but also the UV band absorption at 200-400 nm (aromatic intermediates) in the mentioned experimental conditions decreased in time.

It can be seen from the figure 3 (b and c) and from the table 1 that the maximum absorptions for ECR and PR dyes in the visible region were at 580 nm and 430 nm, respectively. Absorbance in the visible region decreases in time for each considered dye which demonstrates their discoloration. The ECR almost complete discoloration was obtained after 26 min of treatment, whereas about 11 min were necessary to obtain the same efficiency for MB. The peak at 430 nm corresponding to the PR dye has almost totally disappeared after 14 min, which was in agreement with the discoloration results. These results can be also observed from tables 2 and 3, respectively.

Kinetic studies

The kinetics of triphenylmethane dyes degradation by Fenton oxidation process under various reaction conditions have been investigated. For discoloration of dyes by Fenton reagent, first order kinetic model has been suggested [26]. Hence, the kinetic data of first 5 min were fitted into the following equation:

$$\ln\frac{A_0}{A} = k\,t \qquad (2)$$

where:

A_0 and A – absorbances of the dyes at initial time and at time t, respectively;

k – pseudo-first-order rate contant in min^{-1};

t – time in minutes.

All of the values for the pseudo-first-order rate constant, were calculated from the linear regression of the pseudo-first-order kinetic model. The effects of *p*H and temperature on the kinetic rate constants, k, for the used dyes degradation will be separately discussed in the following sections.

The role of pH

The effect of *p*H on the kinetic rate constants, k, for triphenylmethane dyes degradation was studied in the range of 3-6, at the experimental conditions of $[dye]_0 = 6.5 \cdot 10^{-5}$ mol L^{-1}; $[Fe^{2+}]_0 = 4 \cdot 10^{-5}$ mol L^{-1}; $[H_2O_2]_0 = 2 \cdot 10^{-3}$ mol L^{-1} and t = 25 °C. The plots of $\ln(A_0/A) = f(t)$ at different pH values in case of ECR discoloration were shown in figure 4. It can be seen the pseudo-first-order kinetic model is applicable to the ECR degradation at *p*H = 3-5 ($R^2 > 0.99$).

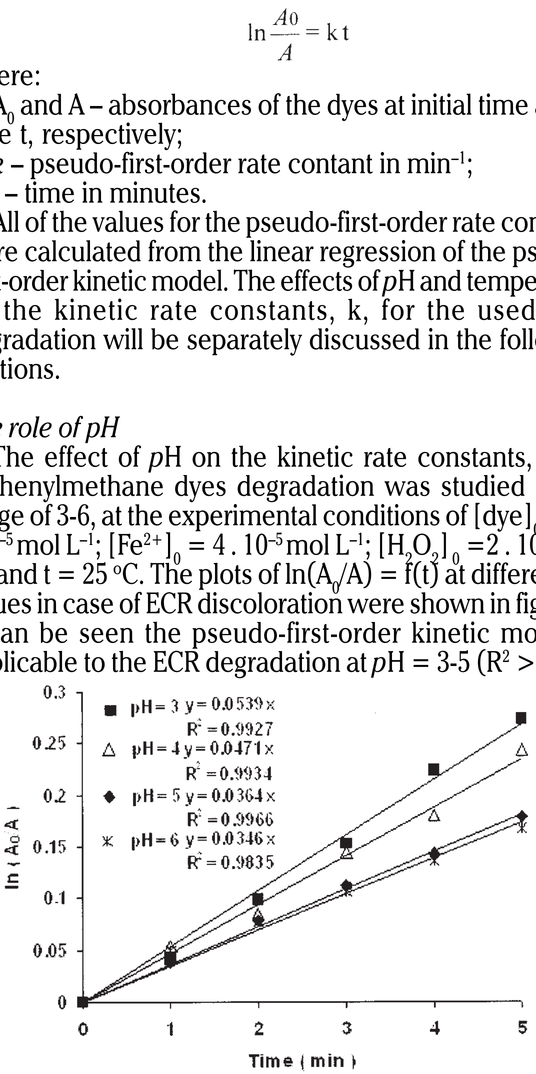


Fig. 4. Plot of $\ln(A_0/A) = f(t)$ in case of ECR discoloration at different initial *p*H values and t = 25°C

Table 4
KINETIC COEFFICIENTS AND HALF-LIFE TIMES ($t_{1/2}$) FOR A FIRST ORDER DEGRADATION REACTION OF TRIPHENYLMETHANE DYES AT DIFFERENT INITIAL pH VALUES AND t = 25°C.

Dyes	**pH = 3**			**pH = 4**			**pH = 5**			**pH = 6**		
	k	**R^2**	**$t_{1/2}$**	**k**	**R^2**	**$t_{1/2}$**	**k**	**R^2**	**$t_{1/2}$**	**k**	**R^2**	**$t_{1/2}$**
MB	0.4461	0.9914	1.553	0.3268	0.9889	2.12	0.3178	0.9628	2.18	0.3037	0.9869	2.281
ECR	0.0539	0.9927	12.85	0.0471	0.9934	14.71	0.0364	0.9966	19.03	0.0346	0.9835	20.02
PR	0.1413	0..9705	4.905	0.1031	0.6963	6.723	0.0451	0.7307	15.36	0.0108	0.9201	64.16

The rate constants and correlation coefficients values are shown in table 4. Also, to have a better knowledge on the discoloration process, the time necessary to reduce to 50 % the initial concentration of dyes (the half-life time) is presented. As it can be seen from the table 4, at constant temperature, there is an increasing trend in k values (from 0.3037 to 0.4461 for MB, from 0.0346 to 0.0539 for ECR and from 0.0108 to 0.1413 for PR) with decrease in initial pH from 6 to 3. The differences in the values of the rate constants presumably reflect the relative levels of available $^{\bullet}$OH radicals provided by each of the treatment processes [27]. It can also be observed that in case of MB degradation at *p*H = 3, R^2 is approximately equal to 1 and this proves that the MB discoloration follows the first order reaction kinetic. The smallest half-life obtained with MB at *p*H = 3 (1.553 min) indicates the fastest discoloration. A first order reaction kinetics was also reported for the electrochemical degradation of Methyl Blue from synthetic solutions containing SO^{4}_{2-} and Cl^- anions [28].

Figure 5 showed that the pseudo-first-order rate constant of dyes degradation was influenced by the *p*H value of solutions and the optimal solution *p*H was observed at *p*H = 3. Rate constants (k) decrease with the increasing of *p*H for all dyes. The poor dyes degradation at high *p*H values may be caused by the formation of ferrous and ferric hydroxide complexes [29] with much lower catalytic capability then Fe^{2+}.

The role of temperature

Temperature affects the reaction between H_2O_2 and Fe^{2+} and therefore, it should influence the kinetics of dyes degradation. Because of the fact that discoloration process in case of MB and ECR took less than 5 min for temperature values of 45 and 55°C, we have taken into account only results obtained in case of PR degradation process. The effect of temperature on the kinetic rate constants for PR discoloration was studied in the range of 25 – 55°C at the experiment conditions of $[dye]_0 = 6.5 . 10^{-5}$ mol L^{-1}; $[Fe^{2+}]_0 = 4 . 10^{-5}$ mol L^{-1}; $[H_2O_2]_0 = 2 . 10^{-3}$ mol L^{-1} and *p*H = 3.

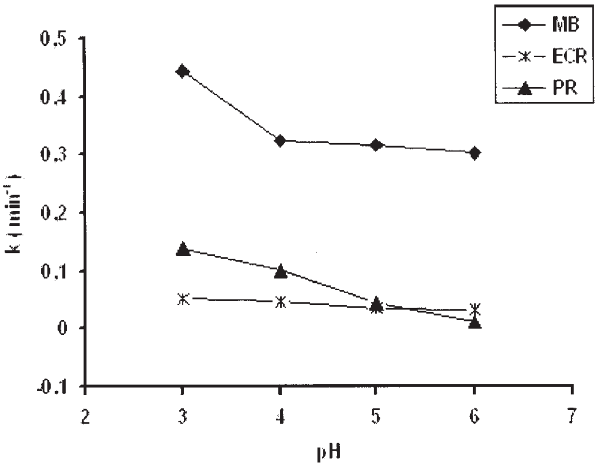


Fig. 5. Variation of rate constants with *p*H in case of dyes degradation in aqueous medium in the presence of Fenton reagent at t = 25°C

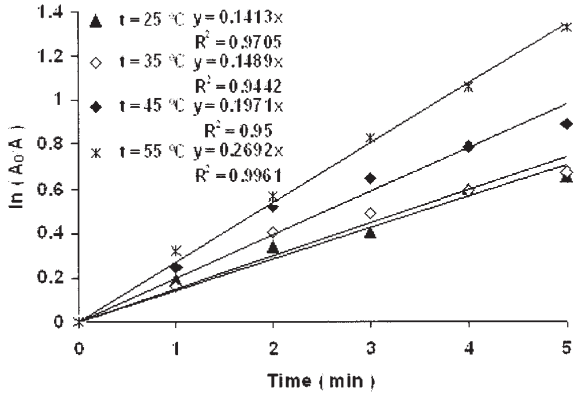


Fig. 6. Plot of $\ln(A_0/A) = f(t)$ in case of PR discoloration at different temperature values and *p*H= 3

The curves of $\ln(A_0/A) = f(t)$ obtained from experimental data during the degradation process of PR at different temperature values are shown in figure 6. It is obvious that the line is liniar at t = 55°C ($R^2 > 0.99$). Therefore, it can be deduced that the PR degradation fits the pseudo-first-order kinetic model.

From the data shown in the table 5 and from figure 7 it can be seen the rate constant (k) increases with the increasing of temperature and has values ranging from 0.1413 min^{-1} to 0.2692 min^{-1}.

Apparent activation energy was determined using the logarithmic form of Arrhenius equation:

$$\ln k = \ln A' - Ea / RT \qquad (3)$$

k – rate constant at temperature T (K);
A' – preexponential factor;
Ea – apparent activation energy;
R – universal constant of ideal gas.

From the graphical representation of ln k = f (1/T) in case of PR degradation, a straight line with the slope d(lnk) / d(1/T) = Ea / R (fig. 8) was obtained; thus, the value of the apparent activation energy was determined as being equal to 18.29 kJ/mol.

In order to determine the concentration of some unknown samples of studied dyes (MB, ECR and PR), the absorbances were measured at different concentration values: $1 . 10^{-5}$ mol L^{-1}, $3 . 10^{-5}$ mol L^{-1}, $5 . 10^{-5}$ mol L^{-1}, $7 . 10^{-5}$ mol L^{-1} and $9 . 10^{-5}$ mol L^{-1}, respectively. The calibration curves resulted by plotting the absorbance vs. dyes concentration (fig. 9). Equations obtained for the three dyes

Table 5
KINETIC COEFFICIENTS AND HALF-LIFE TIMES ($t_{1/2}$) FOR A FIRST ORDER DEGRADATION REACTION OF PR AT DIFFERENT TEMPERATURE VALUES AND *p*H = 3

t = 25 °C			t = 35 °C			t = 45 °C			t = 55 °C		
k	R^2	$t_{1/2}$	k	R^2	$t_{1/2}$	k	R^2	$t_{1/2}$	k	R^2	$t_{1/2}$
0.1413	0.9705	4.905	0.1489	0.9442	4.654	0.1971	0.95	3.515	0.2692	0.9961	2.574

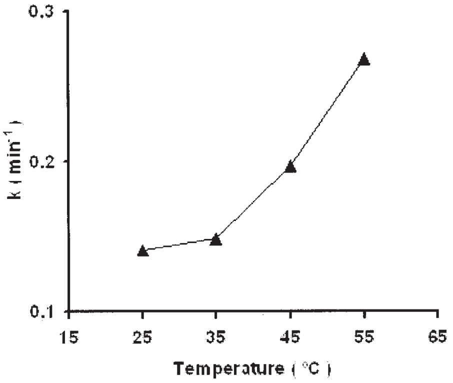


Fig.7. Variation of rate constants with temperature, in case of PR degradation in aqueous medium in presence of Fenton reagent at pH = 3

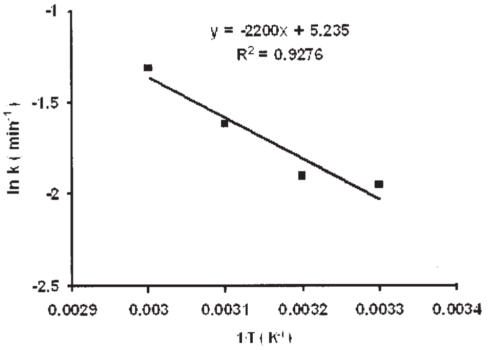


Fig. 8. Arrhenius diagrame in case of PR degradation in aqueous medium in the presence of Fenton reagent, at pH = 3

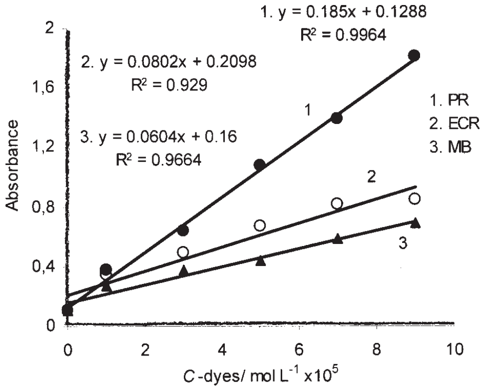


Fig. 9. Calibration curves for the studied triphenylmethane dyes

are shown in figure 9. From these equations, the concentration of each dye was calculated as being: 6.5 . 10^{-5} mol L^{-1}, 4,1 . 10^{-5} mol L^{-1} and 7.5 . 10^{-5} mol L^{-1} for PR, ECR and MB, respectively.

Conclusions

The present study demonstrated that triphenylmethane dyes, Methyl Blue, Eriochrome Cyanine R and Phenol Red, could be degraded effectively by Fenton process.

The Fenton oxidation of dyes was influenced by the initial pH value and the optimal solution pH was observed at pH = 3, the colour removals obtained in this case being 93.06 , 51.56 and 70.92 % for MB, ECR and PR, respectively, within 9 min.

The increase in temperature could greatly accelerate the discoloration. Colour removals increased from 38.93 % to 55.6 % for MB, from 4.88 to 60 % for ECR and from 30.08 to 31.6 % for PR, with increase of temperature from 25 to 55 °C within 1 min of reaction.

Kintec studies suggest that the pseudo-first-order kinetic model is applicable to the ECR and MB degradation under the pH = 3-5 and at pH = 3, respectively. Also, PR degradation fits the pseudo-first-order kinetic model at the temperature of 55°C.

From calibration curves obtained for the three dyes, the concentrations of unknown samples of dyes have been determined. The concentration values were: 6.5 . 10^{-5} mol L^{-1}, 4,1 . 10^{-5} mol L^{-1} and 7.5 . 10^{-5} mol L^{-1} for PR, ECR and MB, respectively.

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Manuscript received: 17.07.2014