

OPTIMIZATION OF HOMOGENOUS OXIDATION PROCESS WITH HYDROGEN PEROXIDE USING BOX METHOD APPLIED FOR WASTEWATERS CONTAINING METHYLENE BLUE DYE♦

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Abstract: Delivery of textile or chemical wastewaters in river streams or pipeworks without an adequate treatment determines undesired consequences. Moreover, most dyes used nowadays are refractory compounds. Conventional biological treatments are not effective for most of synthetic dyes especially due to their polyaromatic structure. That is why advanced oxidation processes (e.g., $\text{H}_2\text{O}_2/\text{Fe}^{2+}$) for decomposition of non-biodegradable organic contaminants into industrial effluents are attractive alternatives to conventional treatment.

The paper proposes the study of homogenous oxidation (Fenton reagent) with hydrogen peroxide applied for some wastewaters containing Methylene Blue dye in different operational conditions in order to get the maximum decolourization removal using the empirical Box method. All kinetic experiments were performed on wastewater samples of 100 mL (100 mg

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dye/L) under continuing agitation, at a temperature of 17 °C, pH of 6.5 and different concentrations (or volumes) of H₂O₂ and FeSO₄ solutions.

The methodology of the empirical Box procedure is experimentally applied and permitted to get the optimal values at pH = 6.5 for decolourization degree (92 %) that corresponds to 7.9 mL FeSO₄ (stock FeSO₄ concentration of 17.67 mmol Fe.L⁻¹) and 1.18 mL H₂O₂ (stock H₂O₂ concentration of 8.235 mmol.L⁻¹).

Keywords: *wastewater, dye, Methylene Blue, Fenton oxidation, optimization, Box method*

INTRODUCTION

Many industries use dyes to colour their products. Wastewaters generated from textile industry contain various pollutants including a high content of organic matter and colour depending on forms of dyes, surface active materials and textile additive materials used in the textile dyeing process [1]. Almost 15% from the dyes used in textile industry are lost in dyeing processes and are recovered in the wastewaters [2 - 3]. The legislation settlements in many states impose strict quality standards for the delivery of such wastewater in receiving basins not only for aesthetic reasons but also because many azo dyes and their intermediate products are toxic to aquatic life and mutagenic to humans [3].

To reduce both colour and organic content must be applied the most adequate treatments. Conventional bio-treatment methods are not effective for the most of synthetic dyestuffs due to the complex polyaromatic structure and recalcitrant nature of the dyes [4]. Coagulation/flocculation, adsorption on activated carbon or membrane techniques are not efficient methods because they can only transfer, more or less effectively, the contaminants from one phase to another, leaving the final environmental problem unsolved [5-6]. Therefore, it is more indicated to transform the toxic and hazardous pollutants into harmful or easy-to-treat compounds [7].

Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganic or, at least, at their transformation into harmless products [8].

The advanced oxidation processes with hydrogen peroxide for the decomposition of non-biodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods [9].

Fenton processes (FP) represent the simplest way to produce hydroxyl radicals and do not require special apparatus. The Fenton reagent is a mixture of hydrogen peroxide and ferrous ions which generates hydroxyl radicals [7, 10]. Fenton oxidation (FO) was studied by many researchers to remove colour and COD from textile wastewaters. Some of these studies have focused on the dyes [11-13], textile additives [14] and textile wastewater [15-17]. FO process has been suggested to treat recalcitrant/toxic pollutants from textile wastewaters, but the sludge produced contains high amount of Fe (III) which needs to be managed by a safe disposal method [11, 15-16].

Decolourization of textile effluents is of major environmental concern that remains to be solved. AOPs have been thoroughly and comparatively evaluated for a variety of

organic compounds and wastewaters in the past. Also many investigations have demonstrated that AOPs are effectively removing colour and partially organic content of dyestuffs [9, 10, 15]. The present paper continues these FO studies by experimental optimization of a dye decolourization process by Fenton oxidation.

Thus, this paper proposes the study of homogenous Fenton oxidation with hydrogen peroxide applied for some synthetic wastewaters containing Methylene Blue dye in different operational conditions in order to get the maximum decolourization removal using the empirical Box procedure [17-18]. All kinetic experiments were performed on wastewater samples of 100 mL (100 mg dye/L), at a temperature of 17 °C, pH of 6.5 and under continuing agitation conditions using different concentrations (or volumes) of H₂O₂ and FeSO₄ stock solutions. The methodology of the empirical Box procedure is experimentally applied and permitted to get the optimum values at pH = 6.5 for decolourization degree.

EXPERIMENTAL

The molecular structure of Methylene Blue dye is illustrated in Figure 1 and corresponds to the chemical formula C₁₆H₁₈N₃S⁺Cl⁻. The main properties of this dye are: molecular mass of 319.86 g.mol⁻¹, maximum absorption wavelength at 713 nm, dark blue colour; it was produced as fine solid powder by BRD Chemicals LTD Poole England. It is a basic dye of the thiazine dyes' category, used for dyeing and printing on cotton, silk etc., but is used also in medicine for its antiseptic properties.

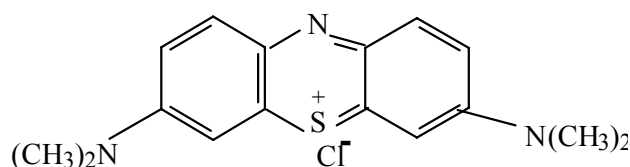


Figure 1. Chemical structure of Methylene Blue dye

In all kinetic experiments it was used a stock aqueous dye solution containing 1 g.L⁻¹ dye. The working samples (containing 100 mg.L⁻¹ dyes) were prepared by appropriate dilution of stock solution with doubly distilled water.

The continuous kinetic experiments were performed by the limited bath technique, under constant slowly stirring for different doses of Fenton reagent (*i.e.* 0.1 - 2.18 mL of H₂O₂ 30% and 0.5 – 8.88 mL FeSO₄ of 17.67 mmol.L⁻¹ Fe). Series of kinetic experiments were performed at different pH values (*i.e.* acidic conditions – pH = 2.65; neutral medium – pH = 6.5 or alkaline medium – pH = 8.75 or 9.65) and the tested pH value was adjusted using HCl 1M or NaOH 1M. After the predetermined time intervals, varying from 5 to 60 minutes, samples were taken for measurements of colour or dye content.

Analysis of colour or Methylene Blue dye was carried out by spectrophotometric method (*i.e. colour* – absorbance measurements at 436, 525 and 620 nm [19] or Hazen colour units [20], and *dye* – absorbance measurements at 713 nm) with a DRELL DR 2000 spectrophotometer, HACH Company [21].

The oxidation efficiency was expressed by the decolourization degree, DD (%) $= \frac{C_t - C_0}{C_0} \cdot 100$ where, C_t is the colour or absorbance value at the indicated wavelength

after t oxidation time and A_0 is the initial colour or absorbance of aqueous sample.

The experimental study was designed to obtain maximum colour or dye removal at an optimum pH value, temperature of 17 °C and different FeSO₄ and H₂O₂ doses chosen by use of empiric Box optimization method.

Experimental optimization with Box method

Box method is one of the empirical methods in searching of optimum values. The experiments were performed on the directions that give the best experimental results with a fixed step for each tested variable variation.

The Box procedure takes into account a basic regular geometric figure, named *Simplex*, defines into the n-dimensional region as a geometric figure having (n + 1) peaks, the distance between certain two peaks being the same, a .

Into the bi-dimensional space, the *Simplex* is an equilateral triangle (ABC) having a side; one of the peak can be into the origin or into an experimental point (A) characterized by the values given for two experimental variables, X_1 and X_2 (i.e. volume or concentration of H₂O₂ (X_1), and volume or concentration of FeSO₄ (X_2) into each studied wastewater sample). The values of each peak (i.e. A peak (X_{A1} , X_{A2}) or B peak (X_{B1} , X_{B2}) or C peak (X_{C1} , X_{C2})) into the first experimental Simplex triangle (ABC) are calculated in order to perform the oxidation processes into the calculated experimental values. If the peaks are A (0, 0), B (p , q) and C (q , p), the values of p and q are calculated with the equations (1-2):

$$p = a(1 + \sqrt{3}) / 2\sqrt{2} = 0.9657a \quad (1)$$

$$q = a(\sqrt{3} - 1) / 2\sqrt{2} = 0.2587a \quad (2)$$

For example, if the starting point (A) is not the origin (0, 0), but is considered into the $X_{A1} = 0.1$ and $X_{A2} = 0.5$ (that corresponds to the experimental dye Fenton oxidation with 0.1 mL H₂O₂ 30% and 0.5 mL FeSO₄ stock solution added into 100 mL wastewater sample having 100 mg.L⁻¹ dye), (X_1 , X_2), the co-ordinates of the peaks into the first Simplex are as into the Table 1. The a value can be equal to 1 ($a = 1$) or has a lower value. Into each peak is performed a kinetic experiment of dye Fenton oxidation that gives an final decolourization degree (considered after 30 minutes of Fenton oxidation) named Y or DD (%).

Table 1. The (X_1 , X_2) peak values into the first Simplex

Peaks	X_1	X_2	Y or DD (%)
A	0.1	0.5	Y_A
B	$0.1 + 0.9657 \cdot a$	$0.5 + 0.2587 \cdot a$	Y_B
C	$0.1 + 0.2587 \cdot a$	$0.5 + 0.9657 \cdot a$	Y_C

There are evaluated the decolourization degree (DD) performed into each peaks of *Simplex* and eliminated the peak with the worst value of DD.

A new peak (D) for a new *Simplex* (i.e. ACD, the B peak is eliminated from the new Simplex) must be obtaining using the equations (3-4):

$$X_{D1} = X_{A1} + X_{C1} - X_{B1} \quad (3)$$

$$X_{D2} = X_{A2} + X_{C2} - X_{B2} \quad (4)$$

where, the A and C are peaks into the new *Simplex*, B peak is eliminated, and D is the new peak into the *Simplex*, ACD, (D peak is the mirror of B peak over the AC segment). Into the new experimental point is performed a dye Fenton oxidation experiment and find a new decolourization degree (Y_D) after 30 minutes. The values of DD are compared into this new Simplex and the the worst peak is also eliminated. A new *Simplex* must be obtained, but the experimental search is always done into the opposite direction of the worst experimental result.

The optimal values are found into a Simplex peak that is the rotation or gravitation centre (point) into some different experimental *Simplex triangles*.

RESULTS AND DISCUSSION

Kinetic experiments of dye Fenton oxidation were performed into each peak of different Simplex triangles in order to get good decolourization degrees. Each experiment corresponds to different volumes of H_2O_2 30 % and $FeSO_4$ stock solution added as Fenton reagent into 100 mL synthetic wastewater sample having 100 mg.L^{-1} dye concentration and in different pH media (acidic, neutral and alkaline).

Influence of pH on dye Fenton oxidation

For the same volumes of H_2O_2 and $FeSO_4$ (0.1 mL H_2O_2 and 0.5 mL $FeSO_4$ stock solution) added into 100 mL sample containing 100 mg.L^{-1} dye were performed Fenton oxidations at pH = 2.65, pH = 6.50, pH = 8.75 and pH = 9.65. The total oxidation time was of 30 minutes ($T = 17^\circ\text{C}$), after that period slowly variations of DD were performed. The experimental results were synthetically presented into Table 2.

It seems that the best experimental results were performed into the neutral medium. The application of Box optimization procedure for Methylene Blue decolourization using Fenton reagent will be performed into an almost neutral medium (pH = 6.50).

Experimental optimization with empirical Box method, neutral medium

There were performed kinetic oxidation experiments on 100 mL synthetic wastewater sample containing Methylene Blue dye using different doses of Fenton reagent at pH = 6.50, temperature of 17°C and under continuing stirring. The total oxidation time was of 30 minutes in order to get high decolourization efficiency into relatively short time.

The first starting point (A) was considered for 0.1 mL H_2O_2 30% (X_1) and 0.5 mL $FeSO_4$ stock solution (X_2), the other experimental points were calculated using the Box methodology described above considering $a = 1$ (i.e. B, C, U).

The experimental results for each kinetic experiments of homogenous dye Fenton oxidation were synthetically presented into Table 3.

Table 2. The influence of pH on dye Fenton oxidation

Oxidation time [min]		0	5	10	15	20	25	30
pH = 2.65 (1 mL H₂SO₄ conc.), 100 mg.L⁻¹ dye, continuing stirring								
DD [%]	$\lambda = 436$ nm	-	7.62	14.46	14.46	15.11	18.84	25.37
	$\lambda = 525$ nm	-	11.17	12.22	12.80	12.88	13.33	14.44
	$\lambda = 620$ nm	-	0.57	1.54	1.80	2.40	3.75	4.07
pH = 6.50, 100 mg.L⁻¹ dye, continuing stirring								
DD [%]	$\lambda = 436$ nm	-	8	15	16	16.5	20	26.50
	$\lambda = 525$ nm	-	21	33	39	48	49	51
	$\lambda = 620$ nm	-	6	22	26	31	37	37.52
pH = 8.75 (0.5 mL NaOH 1M), 100 mg.L⁻¹ dye, continuing stirring								
DD [%]	$\lambda = 436$ nm	-	3.86	11.60	14.98	17.87	18.84	21.74
	$\lambda = 525$ nm	-	20.18	32.58	36	42.11	45.80	45.93
	$\lambda = 620$ nm	-	2.64	20.7	25.26	29.91	35.13	35.36
pH = 9.65 (1 mL NaOH 1M), 100 mg.L⁻¹ dye, continuing stirring								
DD [%]	$\lambda = 436$ nm	-	2.38	4.76	5.24	8.57	10.95	17.14
	$\lambda = 525$ nm	-	11.19	24.26	30.15	34.64	37.40	38.55
	$\lambda = 620$ nm	-	1.67	15.74	21.93	27.39	28.69	30.48

Table 3. Results of the kinetic oxidation for different doses of Fenton reagent obtained using the optimization methodology of Box method

Oxidation time [min]		0	5	10	15	20	25	30
A: 0.1 mL H₂O₂ and 0.5 mL FeSO₄								
DD [%]	$\lambda = 436$ nm	-	8	15	16	16.5	20	26.50
	$\lambda = 525$ nm	-	21	33	39	48	49	51
	$\lambda = 620$ nm	-	6	22	26	31	37	37.52
B: 0.36 mL H₂O₂ and 1.46 mL FeSO₄								
DD [%]	$\lambda = 436$ nm	-	9.56	22.99	26.71	31.80	35.21	37.54
	$\lambda = 525$ nm	-	52.92	61.98	64.34	66.09	68.40	69.95
	$\lambda = 620$ nm	-	57.98	68.80	70	72	73.75	74.68
C: 1.1 mL H₂O₂ and 0.76 mL FeSO₄								
DD [%]	$\lambda = 436$ nm	-	1.10	2.14	3.09	10.35	15.53	19.36
	$\lambda = 525$ nm	-	24.51	36.08	45.66	70.76	57.74	59.36
	$\lambda = 620$ nm	-	9.20	25	29.23	41.75	46.87	48.26
D: 1.36 mL H₂O₂ and 1.72 mL FeSO₄								
DD [%]	$\lambda = 436$ nm	-	4.52	6.85	15.32	23.83	27.26	32.29
	$\lambda = 525$ nm	-	48.15	57	64.20	68.66	70.13	72.46
	$\lambda = 620$ nm	-	22.18	43.78	57.70	62.71	64.30	67.00
E: 1.1 mL H₂O₂ and 0.76 mL FeSO₄								
DD [%]	$\lambda = 436$ nm	-	23.73	35.82	42.80	44.62	48.91	51.84
	$\lambda = 525$ nm	-	66.20	72.90	75.67	76.85	79	80.30
	$\lambda = 620$ nm	-	53.71	65.67	68.94	70.19	73.32	75.19
F: 1.62 mL H₂O₂ and 2.68 mL FeSO₄								
DD [%]	$\lambda = 436$ nm	-	8.19	11.12	18.53	25.59	32.25	35.73
	$\lambda = 525$ nm	-	27.35	47.64	57.60	59.16	67.13	68.91

	$\lambda = 620 \text{ nm}$	-	8.88	21.41	45.08	53.86	59.41	60.72
G: 0.88 mL H₂O₂ and 3.38 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	35.22	41.70	45.20	57.65	61.30	<i>64.08</i>
	$\lambda = 525 \text{ nm}$	-	71.27	75.16	78.61	81.80	83.38	<i>94.64</i>
	$\lambda = 620 \text{ nm}$	-	64.29	70.84	75.75	77.57	80.10	81.66
H: 1.88 mL H₂O₂ and 3.64 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	19.20	31.60	43.70	46.75	51.45	<i>54.45</i>
	$\lambda = 525 \text{ nm}$	-	63.00	74.56	78.44	80.13	81.46	<i>82.98</i>
	$\lambda = 620 \text{ nm}$	-	46.54	65.34	69.26	72.42	73.92	76.09
I: 1.14 mL H₂O₂ and 4.34 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	34.07	45.72	58.09	62.64	66.07	<i>70.08</i>
	$\lambda = 525 \text{ nm}$	-	71.70	77.91	82.47	84.38	85.62	<i>87.23</i>
	$\lambda = 620 \text{ nm}$	-	70.14	76.22	80.63	82.75	83.55	85.37
J: 0.14 mL H₂O₂ and 4.08 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	42.83	52.02	55.76	57.81	58.21	<i>58.26</i>
	$\lambda = 525 \text{ nm}$	-	79.79	82.48	83.92	84.53	84.77	<i>84.94</i>
	$\lambda = 620 \text{ nm}$	-	77.22	80.03	81.15	82.18	82.30	82.36
K: 0.4 mL H₂O₂ and 5.04 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	39.90	55.57	59.46	64.32	65.75	<i>69.13</i>
	$\lambda = 525 \text{ nm}$	-	81.75	85.52	87.30	88.95	89.38	<i>90.71</i>
	$\lambda = 620 \text{ nm}$	-	79.53	82.07	84.97	86.97	87.33	89.09
L: 1.4 mL H₂O₂ and 5.30 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	31.53	53.15	57.65	59.58	63.41	<i>67.86</i>
	$\lambda = 525 \text{ nm}$	-	72.55	79.33	81.57	84.21	85.53	<i>87.39</i>
	$\lambda = 620 \text{ nm}$	-	67.83	76.38	77.45	81.20	82.34	84.60
M: 0.66 mL H₂O₂ and 6.00 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	57.31	66.27	71.93	74.03	76.75	<i>76.80</i>
	$\lambda = 525 \text{ nm}$	-	84.02	87.04	89.73	90.41	91.65	<i>91.65</i>
	$\lambda = 620 \text{ nm}$	-	81.84	87.07	89.06	89.64	91.11	91.11
N: 1.66 mL H₂O₂ and 6.26 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	43.60	53.71	58.36	63.82	65.63	<i>69.29</i>
	$\lambda = 525 \text{ nm}$	-	62.38	70.75	74.96	77.60	78.86	<i>81.33</i>
	$\lambda = 620 \text{ nm}$	-	65.18	71.38	76.48	78.20	79.87	82.18
O: 0.92 mL H₂O₂ and 6.96 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	40.64	53.20	58.27	64.43	69.16	<i>72.42</i>
	$\lambda = 525 \text{ nm}$	-	75.41	82.44	85.10	87.03	88.67	<i>89.85</i>
	$\lambda = 620 \text{ nm}$	-	72.00	81.20	84.20	86.30	87.85	89.10
P: 1.92 mL H₂O₂ and 7.22 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	35.72	45.32	54.47	60.14	65.56	<i>69.34</i>
	$\lambda = 525 \text{ nm}$	-	71.28	79.27	82.52	84.63	86.68	<i>88.66</i>
	$\lambda = 620 \text{ nm}$	-	60.49	76.90	79.35	81.44	84.00	86.89
Q: 1.18 mL H₂O₂ and 7.92 mL FeSO₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	67.38	75.00	81.87	83.81	86.00	<i>87.19</i>
	$\lambda = 525 \text{ nm}$	-	88.27	91.64	93.54	94.47	95.30	<i>95.86</i>
	$\lambda = 620 \text{ nm}$	-	87.33	92.00	93.21	94.57	95.00	95.88

R: 0.18 mL H ₂ O ₂ and 7.66 mL FeSO ₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	60.80	71.84	75.22	77.69	78.69	79.66
	$\lambda = 525 \text{ nm}$	-	88.50	91.17	92.53	93.17	93.80	94.10
	$\lambda = 620 \text{ nm}$	-	89.18	90.54	92.27	92.60	93.53	93.62
S: 0.44 mL H ₂ O ₂ and 8.62 mL FeSO ₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	64.14	76.15	80.53	82.90	83.84	85.47
	$\lambda = 525 \text{ nm}$	-	88.08	82.51	94.35	95.12	95.84	96.46
	$\lambda = 620 \text{ nm}$	-	86.51	91.89	94.33	95.21	95.80	96.50
T: 1.44 mL H ₂ O ₂ and 8.88 mL FeSO ₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	53.62	64.23	74.12	77.39	80.70	83.97
	$\lambda = 525 \text{ nm}$	-	83.62	88.50	91.39	92.38	93.57	94.58
	$\lambda = 620 \text{ nm}$	-	84.32	88.87	91.36	92.26	93.37	94.42
U: 2.18 mL H ₂ O ₂ and 8.18 mL FeSO ₄								
DD [%]	$\lambda = 436 \text{ nm}$	-	37.79	53.52	60.72	68.84	74.65	79.43
	$\lambda = 525 \text{ nm}$	-	76.42	82.70	85.95	88.67	90.71	92.50
	$\lambda = 620 \text{ nm}$	-	74.58	80.30	83.52	87.21	89.46	91.64
V: 1.92 mL H ₂ O ₂ and 7.22 mL FeSO ₄ \cong P								

It seems that the values for X_1 (H₂O₂ volume) and X_2 (FeSO₄ volume) into the last **V** peak are the same as into the **P** peak. The **Q** peak appears to be the *rotation centre* into some different *Simplexes* as QPO, OQR, QRS, TQS, QTV, and QUV.

Also, it can be observed that the optimum point was found for $a = 1$ and corresponds to the values of **Q** peak (*i.e.* 1.18 mL H₂O₂ and 7.90 mL FeSO₄) and DD = 92 %.

The variation of decolourization degree vs. oxidation time is shown into Figure 2 and DD variation vs. pH values for 0.1 mL H₂O₂ and 0.5 mL FeSO₄ into Figure 3.

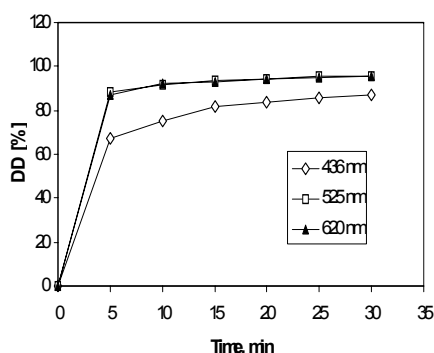


Figure 2. Variation of dye decolourization degree vs time

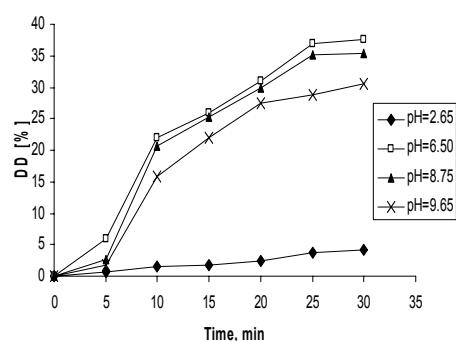
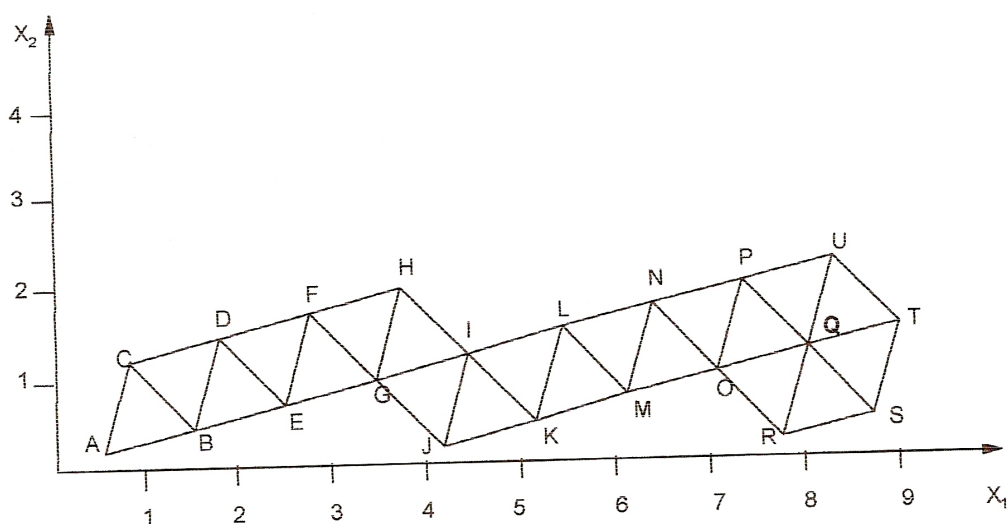


Figure 3. Variation of dye decolourization degree vs pH, for 0.1 mL H₂O₂ and 0.5 mL FeSO₄

The methodology of Box optimization procedure is synthetically presented into Table 4 and corresponds to the graphical representation of all tested Simplex triangles from Figure 4.

Table 4. Optimization procedure of Box method applied for decolourization of synthetic wastewaters containing Methylene Blue dye

Peak	X ₁	X ₂	Y [%]	Simplex	Eliminated peak
A	0.10	0.50	22.00	ABC	A
B	0.36	1.46	68.80		
C	1.1	0.76	12.11		
D	1.36	1.72	43.78	BCD	C
E	0.62	2.42	65.67	BDE	B
F	1.62	2.68	21.41	DEF	D
G	0.88	3.38	70.84	EFG	E
H	1.88	3.64	65.34	FGH	F
I	1.14	4.34	76.22	GHI	H
J	0.14	4.08	80.03	GIJ	G
K	0.40	5.04	82.07	IJK	J
L	1.40	5.30	76.38	IKL	I
M	0.66	6.00	87.07	KLM	K
N	1.66	6.26	71.38	LMN	L
O	0.92	6.96	81.20	MNO	M
P	1.92	7.22	76.90	NOP	N
Q	1.18	7.92	92.00	OPQ	P
R	0.18	7.66	90.54	OQR	O
S	0.44	8.62	91.89	ORS	R
T	1.44	8.88	88.87	QTS	S
U	2.18	8.18	80.30	OTU	T
V	1.92	7.22	76.90	QUV \cong QUP	-

**Figure 4.** Graphical representation of optimization procedure applied for the decolourization of synthetic wastewaters containing Methylene Blue dye (100 mg.L⁻¹)

The optimum values of X₁ and X₂ variables correspond to 1.20 mL H₂O₂ 30% (8.235 mmol.L⁻¹) and 7.90 mL FeSO₄ (17.67 mmol.L⁻¹ Fe) in order to get a maximum decolourization degree (DD) of 92%.

CONCLUSIONS

Different kinetic experiments were performed based of homogenous Fenton oxidation applied for synthetic wastewater containing 100 mg.L⁻¹ Methylene Blue dye. The best decolourization degrees were obtained for a pH value of 6.50 at a temperature of 17 °C and under continuing stirring. The different concentrations of Fenton reagent added into each wastewater sample for dye oxidation were calculated using the empirical Box optimization procedure.

The optimum value of decolourization degree (92%) at pH = 6.5 was performed when is added as Fenton reagent the optimal values that correspond to 7.9 mL FeSO₄ (stock FeSO₄ concentration of 17.67 mmol.L⁻¹ Fe) and 1.18 mL H₂O₂ (stock H₂O₂ concentration of 8.235 mmol.L⁻¹) for 100 mL wastewater containing 100 mg.L⁻¹ dye (*Q* peak of the Simplex, according to the Box optimization procedure).

REFERENCES

1. Grau, P.: Textile industry wastewater treatment, *Water Sci.Technol.*, **1991**, **24**, 97-103;
2. Zaharia, C., Surpateanu, M., Macoveanu, M.: Optimization of some water treatment containing organic dyes (Brown Vopsider DNRL 101) by oxidation with hydrogen peroxide associated with UV irradiation, *Studia Universitatis Babes-Bolyai, Chemia*, **2001**, **XLVI** (1-2), 89-98;
3. Sauer, T., Neto, G.C., Jose, H.G., Moreira, R.F.P.M.: Kinetics of photocatalytic degradation of reactive dyes in TiO₂ slurry reactor, *J.Photochem.Photobiol. A: Chem.*, **2002**, **149**, (1-3), 147-154;
4. Pagga, U., Brown, D.: The degradation of dyestuffs, Part II: Behaviour of dyestuffs in aerobic biodegradation tests, *Chemosphere*, **1986**, **15** (4), 479-491;
5. Colonna, G.M., Caronna, T., Marcandalli, B.: Oxidative degradation of dyes by ultraviolet radiation in the presence of hydrogen peroxide, *Dyes and Pigments*, **1999**, **41**, 211-220;
6. El-Dein Mohey, A., Libra, J.A., Wiesmann, U.: Mechanism and kinetic model for the decolourization of the azo dye Reactive Black 5 by hydrogen peroxide and UV radiation, *Chemosphere*, **2003**, **52**, 1069-1077;
7. Surpateanu, M., Zaharia, C.: Advanced oxidation processes. Decolourization of some organic dyes with H₂O₂, *Environmental Engineering and Management Journal*, **2004**, **3** (4), 629-640;
8. Andreozzi, R., Caprio, V., Insola, A., Marotta, R.: Advanced oxidation processes (AOP) for water purification and recovery, *Catalysis Today*, **1999**, **53**, 51-59;
9. Azbar, N., Yonar, T., Kestioglu, K.: Comparison of various advanced oxidation processes and chemical treatment methods for COD and colour removal from a polyester and acetate fibber dyeing effluent, *Chemosphere*, **2004**, **55**, 35-43;
10. Zaharia, C.: *Wastewater Chemical Treatment (in Romanian)*, Performantica Publishing House, Iasi, **2006**, 97-123;
11. Meric, S., Kaptan, D., Olmez, T.: Colour and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process, *Chemosphere*, **2004**, **54**, 435-441;

12. Solozhenko, E.G., Soboleva, N.M., Goncharuck, V.V.: Decolorizing of azo dye solutions by Fenton's oxidation, *Water Res.*, **1995**, **29**, 2206-2210;
13. Aslan, I., Balcioglu, A.: Degradation of Remazol Black B dye and its simulated dyebath wastewater by advanced oxidation processes in heterogeneous and homogeneous media, *Color. Technol.*, **2001**, **117**, 38-42;
14. Kang, S.F., Liao, C.H., Chen, M.C.: Pre-oxidation and coagulation of textile wastewater by the Fenton process, *Chemosphere*, **2002**, **46**, 923-928;
15. Neamtu, M., Zaharia, C., Catrinescu, C., Yediler, A., Kettrup, A., Macoveanu, M.: Fe-exchanged Y zeolite as catalyst for wet peroxide oxidation of reactive azo dye Procion Marine H-EXL: *Applied Catalysis B: Environmental*, **2004**, **48** (2), 287-294.
16. Zaharia, C., Surpateanu, M., Braunstein, H.: Optimization of photooxidation with hydrogen peroxide of some aqueous solution containing Acid Red azo dye, *Analele Stiintifice ale Univ. Al.I.Cuza Iasi, seria Chimie*, **2004**, **XII** (2), 41-50;
17. Curievici, I.: *Optimization into chemical industry (in Romanian)*, Didactical and Pedagogical Ed., Bucuresti, **1980**, 102-108;
18. Macoveanu, M., Nicu, V., Curievici, I.: *Basis of chemical technology. Methodology of mathematical model elaboration (in Romanian)*, vol. **IV**, Rotaprint Ed., Iasi, **1987**, 65-110;
19. Romanian Standard: *SR ISO 7887-1997*, Colour Examination and determination, **1997**
20. Leeuwen, J., Schell, H., Berger, M., Drikas, M., Bursill, D., Chow, C., Closen, V.: Colour and organic matter analysis into eight German surface waters, *J. Water SRT – Aqua*, **1997**, **46** (5), 261-273;
21. * * * *Guide Manual for DRELL spectrophotometer*, Hach Co., Loveland, Colorado, **1991-1993**.