FACTORS INFLUENCING EFFICIENCY OF UV/H₂O₂ ADVANCED OXIDATION PROCESS

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ABSTRACT

In recent years the textile industry is characterized as qualitative fabric industry. Raw materials and process auxiliaries (as dyes and other chemicals) are used of very good quality. Dyes are developed to be very stable and resistant to physical and biological breakdown. Therefore they are hard degradable in natural conditions. Removal of dye residual from the wastewater requires also qualitative treatment solutions.

As conventional wastewater treatment methods are unable to decompose hard degradable pollutants to the final breakdown products at the textile industry wastewater treatment unit, therefore there is a demand for more advanced treatment. Considerable attention is paid to the advanced oxidation methods.

In this paper the research results of textile reactive dyeing artificial wastewater treatment with advanced oxidation method under ultraviolet light (UV) in presence of hydrogen peroxide (H_2O_2) are described. Investigated relationships are such as pH, reaction length and wastewater composition influence to the UV/HgO₂ advanced oxidation process efficiency.

From obtained results it can be concluded that UV/H_2O_2 advanced oxidation process is inhibited by high pH level, dyeing assisting chemicals, salts and anticreasing agent. The reaction rate constant with removed disturbances is obtained up to 0.4436 min⁻¹, textile reactive dyeing artificial wastewater complete decolourisation is achieved within 4 to 15 minutes.

KEYWORDS

Reactive dyes; textile reactive dyeing wastewater; advanced oxidation processes; decolourisation; inhibition; pH importance.

1 INTRODUCTION

Since the beginning of material and other fabric use in daily life, the dyeing/coloring of fabric was also applied. Cotton and other celluloses comprise over 40% of the whole world textile consumption. Color is applied to the fiber using several types of dyes. The amount of the cotton dyes used in the world is 50% of all dyes consumption [1]. Reactive dyeing is the most common for cotton dyeing in the past years [2, 3].

The consumption of reactive dyes in industry is steadily increasing because of excellent wash fastness [4, 5]. The fastness appears because of the high-grade hydrophility of the reactive dyes. They form covalent bond either with fabric or with water, therefore from 20 to 50% of the applied initial dye concentration in dyeing process is left in the wastewater [6]. The wastewater is rich with hard degradable toxic azo dyeing compounds, also high pH value. As in the dyeing process the dyeing auxiliaries such as pH buffers (NaOH, Na₂CO₃), fastening

(NaCl), softening, anticreasing and other auxiliaries are used. The pollutants and residual color create high environmental and aesthetical problems [7, 8].

Mostly high molecular weight "colored" compounds are resistant to biological degradation, especially the reactive dyes. Usually 90% of reactive dyes concentration that present in spent textile industrial wastewater passes the conventional municipal treatment plants and enter environment, where remain in natural conditions for 40 years and longer [4]. In addition, the dyes and their intermediates are defined as toxic [9]. The solution for this problem could be application of biological, chemical, physicochemical and complex treatment methods [4-13].

In the last years a lot of research has been done in order to find the most sufficient treatment method for reactive dyeing wastewater purification. Most authors refer full pollutant degradation in artificial wastewater prepared according the real wastewater model [9, 14].

Reactive dyeing wastewater treatment methods have been widely investigated. All of them have benefits.

The biological systems have been developed to treat the wastewater contaminated with the dyes and other hazardous auxiliaries. Though biological methods are not capable to decompose dyes completely and treatment efficiency is up to 70% [10] in lab conditions. Anaerobic process for reactive dyeing wastewater treatment was used, but toxic byproducts are produced and left in the treated water [9]. Fentons, and ordinary filtration also produce toxic sludge, and the problem occurs of the toxic sludge disposal [9, 14, 11]. Advanced oxidation processes (so – called AOP's) or membrane filtration (such as ultrafiltration, nanofiltration, and hyperfiltration) – should be included to the treatment chain, in order to decompose the hard degradable aromatic compounds to the final breakdown products, and not just to convert them to colorless even more toxic intermediates [11, 14].

Lately considerable attention in the reactive wastewater treatment is given to advanced oxidation processes (AOP). The methods based on complete destruction of the pollutants by oxidation reaction [10]. Under UV light in presence of hydrogen peroxide (H_{QO_2}), active •OH radicals are formed, that have the activation energy (2.8 V) almost highest from all oxidizing agents (except active fluorine radical – 3.06 V) [16]. *The method application on reactive textile wastewater treatment* is investigated widely, although following the literature analysis there are a few questions left unclear:

- Why the efficiency of the UV/H_2O_2 AOP is dependent on the dyeing type;
- Why the higher method efficiency is reached with artificial reactive dyeing wastewater;
- What additional substances or their conditional processes inhibit UV/H2O2 AOP;

- What is the inhibition effect of $CO_3^{2^2}$ and CI^2 ions (form Na_2CO_3 and NaCl salts added) to the UV-H₂O₂ decolourisation process.

For the purpose to gain more information on $UV/H_2O_2 - AOP$ performance and to be able to answer the questions given above the investigation was done. The experiments were performed with textile reactive dyeing artificial wastewater, the composition of which was changed according to the investigated parameters.

2 MATERIALS AND METHODS

2.1 Artificial wastewater preparation

The artificial wastewater samples were prepared in the same way as were proposed by most other authors [10, 11, 12, 13]. The dye solution was prepared from commercial dye product (obtained from DyStar, Germany) to anticipate the experiment to real conditions. The dye powder was dissolved in demineralised water (further called – dyes) and kept for at least three hours under intensive stirring; after the stirrer was stopped the solution was left in dark for 12 hours that dye molecules would be completely dissolved. The amount of each kind artificial wastewater was prepared such as it could be possible to repeat each experiment at least three times, in order to avoid accidental results.

Commonly hues and shades are obtained by mixing basic colors. In the experiment for artificial wastewater preparations three basic colors were used.

Each color artificial wastewater was investigated separately (see Table 2 – experimental matrix) in order to evaluate process kinetics for separate color and their mixture. Quantities and conditions were repeated the same as are applied in industry in general to anticipate the experiment to the industrial conditions.

The concentration of dyes in artificial wastewater samples were 30% of initial dye concentration (as this amount is left after dyeing in the real wastewater [4, 15]). Four different colors artificial wastewater samples were analyzed.

Colors used for artificial wastewater preparation: - Procion yellow HE4R (according Color Index (CI)e- corresponds to reactive yellow 84 (further in the texte- RY84));

- Procion crimson HEXL (corresponds to reactive red 141 according CI (further - RR141);

- Procion navy HEXL (corresponds to reactive blue 171 according CI (furthere- RB171);

- Mixture was prepared of all three types of dyes in proportion (RY84 – 70%, RR141-30%, RB171 – 1%, (furthere- MIX). The MIX composition was the same as used in real enterprise.

Additional chemicals generally applied in dyeing process were also added to artificial wastewater. The concentrations of the chemical components and the functions of the auxiliary chemicals in the dyeing process are summarized in *Table 1*

Reactive group	Concentration
	(mg/l)
Monochlorotriazinyl	100
Disazo	100
Monochlorotriazinyl	100
Function	Concentration g/l
Transfer dyes to	40
fabric	
pH buffer	10
Anticreasing agent	1
pH buffer (instead	7.5
	Reactive group Monochlorotriazinyl Disazo Monochlorotriazinyl Function Transfer dyes to fabric pH buffer Anticreasing agent pH buffer (instead of Na ₂ CO ₃)

Table 1. Concentrations and functions of chemicals used for the preparation of the artificial reactive dyeing wastewater.

In order to investigate the impact of dyeing auxiliary chemicals to AOP kinetics and decolourisation process efficiency one or more of dyeing solution components (*see Table 2*) were eliminated from artificial wastewater and the method performance was tested under the same conditions. For investigation of pH influence on $UV/H_2O_2 - AOP$ kinetics, Na₂CO₃ was replaced by NaOH, and pH level was adjusted the same.

From the first data obtained with the artificial wastewater decolourisation the sharpest process characterization was obtained with RY84 type of artificial wastewater, therefore for process kinetics investigation it was decided to use this type of dye (*see Table 2 – samples No 5-12*).

Type of the dye and amount (mg/l)			Auxiliarie	s added cor	centration in (g/l)		
Sample number	RY84	RR141	RB171	Na ₂ CO ₃	NaCl	Anticreasing agent	NaOH
1.	30	: <= :	(-)			-	-
2.	-	30	-	÷.	-	2	-
3.	2		30		-		-
4. MIX	20.91	8.79	0.3		*	-	-
5.	30			(†	5	0.3	
6.	30	220	-	141	23	0.6	12
7.	30	-	-	(*)	-	1	-
8.	30			-	40	-	-
9.	30	120	120	10	- C	2	2
10.	30	-	-	10	40		-
11.	30	-	-	10		0.3	-
12.	30	147	: L :	~	84) 1	0.3	7.5

Table 2. Experimental matrix.

2.2 Equipment Set – Up.



low pressure UV-C lamps;
quartz glass reaction vessel;
stainless steel hexagonal reflector.

Figure 1. Principal scheme of equipment set – up.

800 ml volume reaction vessel made from quartz glass was placed to the stainless steel hexagonal reflector with fixed 6 UV-C light lamps (type-low pressure lamps maximum emission at 253.7 nm, 15W each, length of lamp 0.41m, Philips, Netherlands). UV lamps situated in a circular arrangement as shown in figure (1 A-A).

Temperature was maintained constant $20^{\circ}C \pm 2$ as it influences the process dynamics [9]. During the process the pH level changes [21], the pH was measured throughout the experiment with pH meter – MT28-280-001 (with pH electrode WTW Sen Tix 21, Netherlands). Sampling was continuous; reactor was connected to the peristaltic pump (Watson – Marlow 302, Netherlands) that was piping the sample through the UV/Vis spectrophotomether quvetes. The spectrophotometric color intensity was measured with Varian Cary 3E UV-Vis Spectrophotometer (Varian B.V., Netherlands), which was connected to the computer and the data was recorded at the certain time intervals.

The reaction was stopped after 15 minutes - time interval was set from the process efficiency calculations, and was constant in order to have possibility to compare separate reactions kinetic.

The artificial wastewater during decolourisation process was mixed hydraulically at certain time intervals with no contact with oxygen in order to get better light penetration in the depth of reaction vessel.

The light was turned on before each experiment. The irradiation power in such kind of reactor when light is going from outside to inside was calculated according [17].

2.3 Analytical procedures

 H_2O_2 amount needed for the oxidation has been infused in the range of 100- 800 mg/l [4, 18, 19, 20]. Exact H_2O_2 amount consumed during the oxidation was defined by means of determining residual (unreacted) H_2O_2 amount after each experiment by "Nanocolor Peroxid 2" (MACHEREY-NAGEL GmbH & Co, Germany). 30% purity H_2O_2 solution (Merck, Germany) was used.

Cl⁻, CO²⁻₃ ion amount (from Na₂CO₃ and NaCl added) was determined by ion chromatograph analyzer (DIONEX DX 600, Dionex Corporation, USA).

Decolourisation (color disappearance) was measured by means of change in absorption level (m^{-1}) at certain wavelength (nm) with UV-Vis spectrophotometer (Carry Varian). The wavelength for measuring oxidation absorption change was set analytically, for investigation of each color artificial wastewater samples investigated. The highest absorption value (m^{-1}) was defined by scanning the artificial wastewater sample in range 200-800 nm. Highest peaks obtained in this range, were used for UV/H₂O₂ - AOP observation in the highest signal obtained, in order to obtain the highest sensitivity of measurement. The wavelength (nm) at which the peaks were obtained (*see Table 3*).

Table 3. Different colors artificial wastewater highest absorbance at certain wavelength.

Color	RY 84	RR 141	RB 171	MIX
Wavelength (nm)	418	430	670	421
Absorbance (m ⁻¹)	0.35	0.42	0.39	0.30

3 RESULTS AND DISCUSSION

3.1 Kinetic model applied

From the data obtained and literature analyzed it is clear that under UV light in presence of hydrogen peroxide during photo catalytic process by highly active •OH radicals, dyes are oxidized to lower molecular weight substances. In order to get dye concentration value from the absorbance data the calibration curves are obtained by measuring with UV-VIS spectrophotometer.

The absorbance dependency from artificial wastewater concentration (mg/l) is derived for all four color wastewater investigated by means of calculating correlation coefficient (R^2) . Average value from four straightened curves is $R^2 > 0.99$. Obtained correlation coefficient value shows strong relation between the obtained dependency and the straightened curves. Correlation was used for estimation of dye concentration, converting light absorbance value (nm) to dye concentration (mg/l) in artificial wastewater investigated. The intensity of the light was assumed as constant value. All investigated artificial wastewater samples

corresponds the same kinetic model. Color removal rate (absorbance decrease) is proportional to concentration of the dye (C_{dyc}) and concentration of H_2O_2 (C_{112O2}). For determination of oxidation process kinetics the reaction rate constant relation was defined.

In this certain case, second order relation fits the best:

$$r = k * C_{dve} * C_{H,O_2} \tag{1}$$

If assuming that the hydrogen peroxide concentration is constant value, then the reaction could be described as pseudo first order, and it is possible to express reaction rate as follows:

$$r = k' * C_{dye} \tag{2}$$

Where: r- reaction rate; k'- reaction rate constant when C $_{11:O2}$ is constant value (min⁻¹); C_d φ_c -dye concentration (mg/l).

Dye concentration is reciprocal to the color intensity, and then it is possible to rewrite equation as:

$$\frac{d(color)}{dt} = -k^{'} * (color) \tag{3}$$

The natural logarithm plot of the color shows the plot of rate expression:

$$\ln\frac{(color_0)}{(color_i)} = -k^* * t \tag{4}$$

The $ln(color_0/color_1)$ over the time gives the value of the reaction rate constant $-k^*$ (min⁻¹). For the data expression pseudo first order reaction rate constant $-k^*$ calculated from color removal over the time was used.

3.2 Decolourisation kinetics

A) Artificial Wastewater Decolourisation.

Oxidation kinetics were investigated of artificial wastewater samples (RY84, RR141, RB171, MIX) (polluted with dyes), were exposed under UV/H₂O₂ AOP. Data given in *Table 3* characterizes the oxidation process effectiveness. The dye decomposition performance under oxidation conditions is given in *Figure 3*.

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Figure 3. Artificial wastewater decolourisation kinetics under UV/H₂O₂-AOP

Sampl	Dye title	Change in pH range		H_2O_2 amount	Reaction rate
e no.		during the		WW decolourisation	k min ⁻¹
		pro	cess	[mg/l]	k, iiiii
		Before	After		
1.	RY 84	6.17	3.35	2 li1.55	0.4436
2.	RR 141	6.8	4.68	2 li4.34	0.3253
3.	RB 171	6.59	3.09	237.77	0.0935
4.	MIX	6.0	4.3	245.2	0.0771

Table 3. Dye type in fluence to the UV/H_2O_2 -AOP.

While in the liquid were present only dyes (no additional substances) dissolved in demineralized water, artificial wastewater samples were decolorized within 5-li5 min. Decolourisation was reached with the H_2O_2 consumption 211.55 up to 245.2 mg/l.

Analyzing *Figure 3* and data given in *Table 3* it could be noted, that the artificial wastewater samples No. 1 and No. 2 are decolorized within 4 and 9 minutes respectively, though the wastewater samples No. 3 and No. 4 after 15 minutes of decolourisation still kept more than 30% of initial concentration (color). According to reaction rate constant values, the fastest decomposition of the dyes is achieved with RY84 – $k = 0.4436 \text{ min}^{-1}$ and RR141 – $k = 0.3253 \text{ min}^{-1}$. Artificial wastewater No.4 (MIX- prepared form three types of dyes) is the hardest degradable one, the reaction rate constant MIX – $k = 0.0771 \text{ min}^{-1}$ which is 6 times lower than of RY84 also shows that.

PH level drop could be observed from the obtained results (see Table 3). The pH drop under $UV/H_2O_2 - AOP$ conditions can be explained by formation of organic acids [14] upon oxidative dye degradation. For further investigation of inhibiting factors RY 84 was chosen to be used as it's decomposition under applied advanced oxidation is fastest, therefore it is the most striking example for observation of other substances caused influence on the process performance.

B) UV/H₂O₂ - AOP inhibition by auxiliary chemicals (anticreasing agent).

Anticreasing agent was included to the artificial wastewater RY84 in particular amounts -0, 0,3; 0,6; 1 g/l - of dyebath concentration. From the obtained data of artificial wastewater decolourisation under UV/H₂O₂ - AOP the reaction rate constant decrease was observed (*see Figure 4 and Table 4*).



Figure 4. Artificial wastewater decolourisation kinetics under UV/H_2O_2 - AOP with auxiliaries added (anti-creasing agent).

Small amount 0.3 g/& (30%) of anticreasing agent gives insignificant inhibition to artificial wastewater decolourisation under UV/H₂O₂ – AOP, though further enlarging concentration of anticreasing agent, significantly decreases the reaction rate (samples No 6 and No 7) in comparison with 0 g/& anticreasing agent concentration (e.g. sample No 1 in *Table 4*).

The explanation could be as follows: anticreasing agent thickens the solution (it becomes of colloidal manner), then the UV radiant is dissipated [17]. Therefore the dye molecules are not reached by UV light properly, because of are not decomposed completely.

nr. Dye Sample title No.		Change in pH range during the decolourisation process		H ₂ O ₂ amount consumed for artif. W W	Reaction rate constant k, min ⁻¹
		Before	After	decolourisation, [mg/l]	
1.	RY 84	6.17	3.35	211.55	0.4436
5.	RY 84	6.2	5.81	221.12	0.1351
6.	RY 84	5.67	5.09	242.12	0.0606
7.	RY 84	6.0	5.68	285.6	0.0462

Table 4. Anticreasing agent influence to the UV/H₂O₂ -AOP.

C) UV/H₂O₂ AOP Inhibition by Auxiliary Chemicals (salts - NaCl, Na₂CO₃).

The artificial wastewater with RY84 was prepared with the full amount of salts (NaCl; Na₂CO₃). Artificial wastewater decolourisation was investigated by UV/H_2O_2 – AOP with different salts present in solution. The amounts applied in the experiment normally are applied in the industrial dyeing process. The artificial wastewater decolourisation performance under

 $UV/H_2O_2 - AOP$ was investigated and inhibition effect was observed in comparison with no salts present in decolorized artificial wastewater samples.

The analysis was performed with one or both salts in ordinary inlet concentrations (process performance is given in *Figure 5* and summarized in *Table 5*).



Figure 5. Artificial wastewater decolourisation kinetics under UV/H_2O_2 - AOP with auxiliaries added (salts).

The highest oxidation reaction rate constant value 0.4436 min⁻¹ is obtained with the artificial wastewater No. 1 (RY84 with no salts added). When NaCl is added (artificial wastewater No. 8) the reaction rate decreases insignificantly (*see Table 5*). It could be posted that NaCl presence in dyeing wastewater has certain inhibition to the UV/H_2O_2 - AOP.

The significant inhibition of UV/H_2O_2 - AOP is observed with added Na₂CO₃, the decrease in reaction rate constant is more than 10 times (*see Table 5*).

Sample No.	Dye title	Change in pH range during the decolourisation process		H ₂ O ₂ amount consumed for artif. WW	Reaction rate constant
		Before	After	decolourisation, [mg/1]	к, шп
1.	R Y 84	6.17	3.35	211.55	0.4436
8.	RY 84	7.05	4.18	225.44	0.1328
9.	RY 84	11.08	10,45	230.46	0.04@9
10.	RY 84	7.27	3.09	204.68	0.0599

TILC	C L	· /1	1	UV/II O	100
Table 5	Salts	influence	to the	UV/H_2U_2	-AOP.

Though when both NaCl and Na₂CO₃ (defined as UV/H₂O₂ –AOP inhibitors) are added in fulk concentrations (sample No. 10), the reaction rate is bigger than of sample No. 9, in which only Na₂CO₃ (full concentration) is present. As $CO_3^{2^2}$, Cl⁻ ions in literature [14] is derived as main process inhibitors. Though difference in decolourisation process performance when both Na₂CO₃ and NaCl (sample No. 10) are present in the solution, it could be explained by salts

influence on the pH level of the liquid. The process inhibition appears because of the changed H_2O_2 equilibrium by means of change in pH level. The inhibition effect obtained in the experiment is significant as it was also found in literature [4, 21, 22, 23].

D) Hypothesis of pH inhibition was investigated.

Two artificial wastewater samples were prepared at the same manner, only in one sample instead ofiNa₂CO₃ (to avoid the CO₃²⁻ inhibition), NaOH was added (corresponding amount to adjust the same pH level in artificial wastewater). It is observed from experimental results (*see Figure 6*) that the reaction rate constants of both artificial wastewaters decolourisation under UV/H2O2 advanced oxidation process reactions are very similar. Therefore it can be stated that the UV/H₂O₂ – AOP reaction is inhibited of high pH level of decolorized liquid.

Table 6. PH buffers influence to the UV/H₂O₂-AOP.

Sample No.	Dye title	Change in pH range during the decolourisation process		H ₂ O ₂ amount consumed for artif. WW	Reaction rate constant
		Before	After	decolourisation, [mg/l]	k, min ⁻¹
11.	RY 84	11.08	10.45	230.16	0.0718
12.	RY 84	11.05	10.65	245.11	0.0695



Figure 6. Artificial wastewater decolourisation kinetics under UV/H_2O_2 - AOP with auxiliaries added (pH buffer).

4 CONCLUSIONS

In this experimental work, decolouriation of artificial wastewater polluted with three type commercial dyes (RR84, RR141, RB 171) was investigated by using UV/H_2O_2 advanced oxidation process. Influence of operating parameters, additional substances, pH value were investigated and evaluated by means of change in reaction rate.

The fastest decolourisation in artificial wastewaters RY84 and RR141 under UV/ H_2O_2 advanced oxidation process (reaction rate constant values - 0.4436 min ⁻¹ and 0.3253 min ⁻¹

respectively) was obtained. The slowest decolourisation was obtained in artificial wastewater MIX (mixture of three types of dyes), where the obtained reaction rate constant was twice lower than with RY84. From the obtained results it can be concluded that UV/H_2O_2 process decolourisation depends on the dye type present in the wastewater.

Anticreasing agent presence in artificial wastewater concentration above 0.3 g/& (e.g.30%) sample No. 9 and sample No.10 has the significant inhibition to the UV/H₂O₂ advanced oxidation process. The higher concentration of anticreasing agent makes the liquid of colloidal manner and inhibits the decolourisation process performance, the slower reaction rate occurs and half of the dye concentration remains after 15 minutes of decolourisation.

The CI'; $CO_3^{2^2}$ ions presence in the solution has significant influence to pH level in the process, though no direct inhibition on UV/H₂O₂ advanced oxidation process is observed.

The significant inhibition on UV/H_2O_2 advanced oxidation process kinetics has high pH level, as the pH in the solution has great influence to H_2O_2 equilibrium.

It can be assumed that solution acidification prior to the UV/H_2O_2 advanced oxidation process application is beneficial, this way the higher effectiveness of the process can be reached. In order to ascertain if the acidification can improve the UV/H_2O_2 advanced oxidation process, further investigation should be performed.

REFERENCES

[1] Blackburn R. S., Burkinshaw S. M., 2002. A greener approach to cotton dyeings with excellent wash fastness. *UK, The Royal society of chemistry.*

[2] Rajkumar D., Kim J.G., 2006. Oxidation of various reactive dyes with in situ electro – generated active chlorine for textile dyeing industry wastewater treatment. *Journal of Hazardous Materials B136*, 203-2&2.

[3] Roessler A., Jin X., 2003. State of the art technologies and new electrochemical methods for the reduction of vat dyes. *Dyes and Pigments 59*, 223-235.

[4] Alaton I. A., Balcioglu I. A., Bahnemann D. W., 2002. Advanced oxidation of reactive dyebath effluent: comparison of O_3 , $H_2O_2/UV-C$ and $TiO_2/UV-A$ processes. *Water* research 36, 1143 - 1154.

[5] Cisneros R. L., Espinoza A. G., Litter M. I. 2002. Photodegradation of an azo dye of the textile industry. *Chemosphere 48*, 393-399.

[6] EPA US. 1996. Best Management Practices for Pollution Prevention in the Textile Industry. EPA/625/R-96/004.

[7] Graham N., Chen X. G., Jayaseelan S., 2001. The potential application of activated carbon from sewage sludge to organic dyes removal. *Water science and technology* 43(2), 245-252.

[8] Pollard S. J. T., 1992. Low cost adsorbents for waste and wastewater treatment: a review. *Environmental science and technology* 116, 31-52.

[9] Ntampegliotis K., Riga A., Karayannis V., Bontozoglou V., Papapolymerou G., 2006. Decolourisation kinetics of Procion H-exl dyes from textile dyeing using Fenton – like reactions. *Journal of Hazardous Materials 136*, 75-84.

[10] Andreozzi R., Caprio V., Insola A., Marotta R., 1999. Advanced oxidation processes for water purification and recovery. *Catalysis today* 53, 51-59.

[11] Arslan I., Balcioglu I. A., Bahnemann D. W., 2000. Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate – Fenton/ UV-A and TiO_2/UV -A processes. *Dyes and pigments 47*, 207-218.

[12] Grimau V. L., Gutierrez M. C., 2006. Decolourisation of simulated reactive dyebath effluents by electrochemical oxidation assisted by UV light. *Chemosphere 62*, 106-112.

[13] Arslan I., Balcioglu I. A., Bahnemann D. W., 2000. Heterogeneous photocatalytic treatment of simulated dyehouse effluents using novel TiO_2 –photocatalysis. *Applied catalysis* 26, 193-206.

[14] Gultekin I., Ince N. H., 2004. Degradation of Reactive Azo Dyes by UV/H₂O₂: Impact of Radical Scavengers. *Journal of Environmental Science and Health A 39(4)*, 1069-1081i.

[15] Allegre C., Moulin P., Maisseu M., Charbit F., 2006. Treatment and reuse of reactive dyeing effluents. *Journal of membrane science 269*, 15-34.

[16] Metcalf and Eddy, 2003. Wastewater engineeringi: treatment and reuse, 4t^h edition ed. McGraw- Hill, New York. USA.

[17] Masschelein W. J., 2002. Ultraviolet Light in Water and Wastewater Sanitation. Ph.D. thesis printed in US Library of Congress Cataloging.

[18] Edwards.J. C., 2000. Investigation of Color Removal by Chemical Oxidation for Three Reactive Textile Dyes and Spent Textile Dye Wastewater. Department of Civil and Environmental Engineering.US- Virginia.

[19] Shen Y. S., Wang D. K., 2002. Development of photoreactor design equation for the treatment of dye wastewater by UV/H₂O₂ process. *Journal of Hazar dous Materials B89*, 267-277.

[20] Fung P. C., Poon S. S., Chu C. W., Tsui S. M., 2000. Degradation kinetics of reactive dye by $UV/H_2O_2/US$ process under continuous mode operation. *Water Science and Technology* 44 (6), 67-72.

[21] Mattioli D., Malpei F., Bortone G., Rozzi A., 2000. Water minimization and reuse in textile industry. Water recivcling and reuse recovery in industry : analysis, technologies and implementation. *IWA publishing, Cornwall, UK 677 pp.*

[22] Oliver J. H., Hyunook K., Chiang P.C., 2000. Decolourisation of wastewater. *Critical Reviews In Environmental Science and Technology 30(4)*, 449 – 505.

[23] Galindo C., Klat A. 1998. UV- H2O2 oxidation of monoazo dyes in aqueous media: a kinetic study. *Dyes and Pigments 40*, 27-35.