

JAN PERKOWSKI*, LECH KOS**, STANISŁAW LEDAKOWICZ****

ADVANCED OXIDATION PROCESSES OF REAL TEXTILE WASTEWATERS****

Textile wastewater is known to be highly resistant to biodegradation under both natural and wastewater treatment plant conditions. Different real textile wastewaters from knitting company located in Łódź, Poland, were subjected to treatment by advanced oxidation processes (AOPs). The following agents were used: ozone (O_3), hydrogen peroxide (H_2O_2) and UV radiation. They were applied separately and in all possible combinations: $O_3 + UV$, $O_3 + H_2O_2$, $UV + H_2O_2$, as well as all three at the same time: $O_3 + UV + H_2O_2$. The effluents before and after the treatment were analyzed according to requirements of the Polish Standards which included: pH of the effluent, specific colour and colour threshold (CT), chemical (COD) and biochemical oxygen demand (BOD_5), anionic detergent (AD), total organic carbon (TOC), dry residue (DR), soluble substances (SS) and suspensions (S). Ozonation was carried out in a lab-scale bubble column reactor with centrally located UV burner. We used two kinds of UV lamp: low-pressure mercury discharge lamp TNN, 15/32 type, of 15 W power and medium-pressure mercury discharge lamp, TQ 150 type, of 150 W power. The most effective version of AOPs proved to be a simultaneous use of all three agents. In the case of such a treatment of wastewaters, practically complete discoloration and full destruction of surface-active substances were observed at simultaneous reduction of COD and TOC and increase of biodegradation effectiveness.

The results obtained suggest that simultaneous use of O_3 , H_2O_2 and UV-irradiation can be applied successfully on a technological scale. Combination of these methods enables almost complete degradation of toxic substances and may contribute to recycling and conserving of water in textile factories.

1. INTRODUCTION

Textile industry produces large quantities of effluents which are not only very toxic and resistant to destruction by physicochemical treatment methods but hardly biodegradable. The nonbiodegradability of textile wastewater is due to high content of dyestuffs, surfactants and additives which are generally organic compounds of a complex structure [1]. Textile wastewater, being nonbiodegradable under both natural and sewage treatment plant conditions, is a potential nuisance to the environment. There-

*Institute of Applied Radiation Chemistry, Technical University, Łódź, Poland.

**Institute of Knitting Technology and Techniques, Łódź, Poland.

***Institute of Bioprocess Engineering, Łódź Technical University, Poland.

****This paper has been presented at III NEAR Conference in Cracow.

fore, it is necessary to find an effective method of the wastewater treatment capable of removing colour and toxic organic compounds from textile effluents. The literature indicates that ozone application, due to its high oxidizing power, may result in at least partial destruction or removal of many refractory organic matters [2]–[7].

Ozone application in the processes of oxidation of pollutants present in textile wastewater gives good results [7]–[13]. Advantages of ozone application lie in its easy availability, lack of secondary pollution, no hazard of overdosage and flexibility of the method. Ozone in aqueous solution causes disintegration of detergents and dyes as well as destruction of aromatic systems and chromophores. However, the sole application of ozone to achieve a complete purification is sometimes insufficient and very costly. Hence, it is advantageous to combine ozonation with other oxidizing agents or to use chemical oxidation methods as a pretreatment step before biological oxidation of wastewater.

Recently, a growing interest in the application of combined methods of chemical O_3 oxidation and UV-irradiation as well as O_3 with H_2O_2 is observed in the literature on ozonation [14]–[19]. Synergistic effects of such combinations as $O_3 + H_2O_2$, $H_2O_2 + UV$, $O_3 + UV$ and $O_3 + H_2O_2 + UV$, called advanced oxidation process (AOP), are often observed. The application of advanced oxidation allows us to reduce significantly the costs of energy needed to produce ozone. There are reports regarding installations working in few countries in this way on both semi-commercial and commercial scales [3], [6], [7], [20].

In a series of studies, we would like to present results of our investigations of advanced oxidation of real textile wastewater. This study presents a discussion of the results obtained during investigation of wastewater treatment with ozone, hydrogen peroxide and UV-irradiation and the combination of the oxidants. In our previous studies, we have presented results of decomposition of synthetic textile wastewater in APOs processes [21]–[24].

2. MATERIALS AND METHODS

Three different kinds of wastewater obtained during cotton dyeing were used. Real textile wastewater was collected in knitting company located in Łódź, Poland.

The dyeing wastewater (1) used in the experiments was a moderately concentrated wastewater of not very intensive green colour CT-50; the values of COD and BOD_5 were $320 \text{ mg O}_2/\text{dm}^3$ and $42 \text{ mg O}_2/\text{dm}^3$, respectively. The BOD_5/COD ratio reached 0.13, i.e. it was difficult to reconstruct it biologically. The content of anionic detergents was as low as $3.9 \text{ mg}/\text{dm}^3$. The content of suspended matter was also low, i.e. $10 \text{ mg}/\text{dm}^3$. The contents of both dry residue ($2270 \text{ mg}/\text{dm}^3$) and soluble substances ($2260 \text{ mg}/\text{dm}^3$) were the same within the limit of error.

The dyeing wastewater (2) was also a moderately concentrated wastewater of not very intensive blue colour CT-250, the values of COD and BOD_5 were $320 \text{ mg O}_2/\text{dm}^3$ and $64 \text{ mg O}_2/\text{dm}^3$, respectively. The BOD_5/COD ratio was 0.20. The content of anionic

detergents was low, i.e. 2.6 mg/dm^3 . The content of suspended matter was pretty high: 120 mg/dm^3 . Dry residue was 1680 mg/dm^3 and soluble substances – 1560 mg/dm^3 . Total organic carbon reached 117 mg/dm^3 .

The dyeing wastewater (3) was strongly concentrated. It was characterized by an intensive orange colour, $CT = 670$, high value of COD ($1310 \text{ mg O}_2/\text{dm}^3$), BOD_5 equal to $75 \text{ mg O}_2/\text{dm}^3$. The content of anionic detergents was 5.3 mg/dm^3 and that of soluble substances – 1040 mg/dm^3 . The BOD_5/COD ratio reached 0.06, i.e. it was difficult to reconstruct it biologically.

Both crude and treated wastewaters were analysed taking into account the following characteristics:

- specific colour,
- colour threshold (CT),
- pH,
- anionic detergent content (AD),
- chemical oxygen demand (COD),
- biological oxygen demand (BOD_5),
- dry residue (DR),
- soluble substances (SS),
- suspensions (S).

All analyses were carried out according to the Polish Standards.

In the experimental series with dyeing wastewater (2), total organic carbon (TOC) was analysed in Coulomat 702 Li/C, Ströhlein Instrument.

The experimental set-up for wastewater treatment consisted of the following elements: an ozonator with equipment, reaction vessel and a system of sorption bulbs (figure 1). Oxygen from a steel cylinder was pumped to the ozonator by two drying columns filled with CaCl_2 and P_2O_5 , and then by a flowmeter used for measuring oxygen flow rate. The ozonator was equipped with an ozone monitor produced by ELIMP to measure the ozone content in oxygen at the reactor inlet and outlet. The volume of 1.3 dm^3 of wastewater was poured into a glass reactor equipped with a thermostating jacket. The mixture of oxygen and ozone flowing to the reactor was introduced into the solution by means of a porous plate which enabled good gas dissipation. In the center of the reactor there was a quartz tube in which a light source was placed. These were the Heraeus lamps: low-pressure mercury discharge lamp, TNN 15/32 type, of 15 W power and medium-pressure mercury discharge lamp, TQ 150 type, of 150 W power. Light sources were cooled by air flow or water.

In the case of 15 W lamp, the emitted luminous energy is $1.2499 \cdot 10^{21} \text{ eV/min}$, which corresponds to 200.23 J/min , or to 3.337 W . The number of quanta is $2.96 \cdot 10^{20}$ quantum/min. Taking into account the quanta of the wavelength $\lambda < 310 \text{ nm}$, which constitute 75.9% of the total number of quanta, the corresponding energy is 87.4% of the total amount of energy, i.e. 175.1 J/min .

In the case of 150 W lamp, the luminous energy is $5.81 \cdot 10^{21} \text{ eV/min}$, which corresponds to 931 J/min , or to 15.51 W . The number of quanta is $1.95 \cdot 10^{21}$ quantum/min.

Taking into account only the quanta of the wavelength $\lambda < 310$ nm, which constitute 10.8% of the total number of the quanta, the corresponding energy is 16.02% of the total emitted energy, i.e. 149.2 J/min.

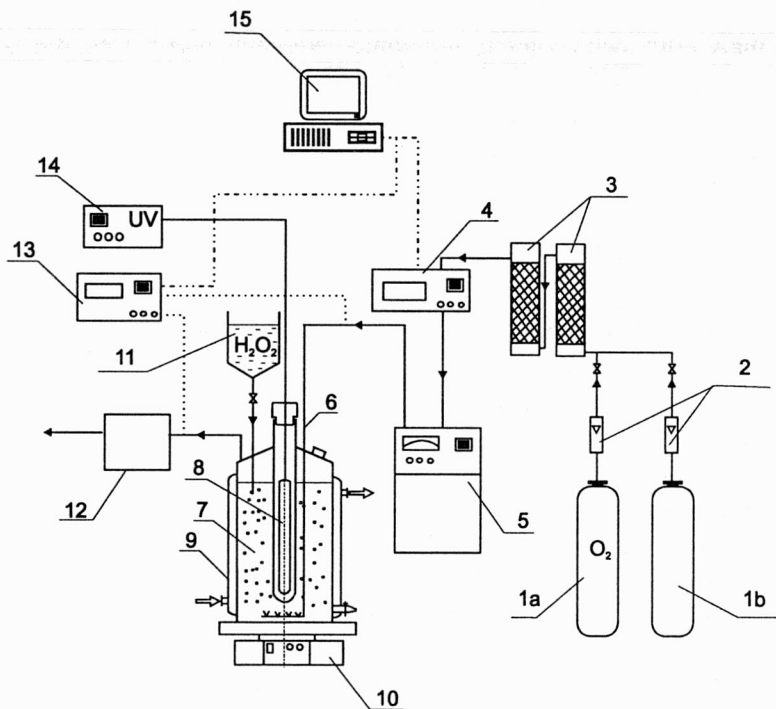


Fig. 1. Schematic of the system for wastewater treatment by advanced oxidation methods:

1a, 1b – steel cylinders with oxygen and neutral gas, 2 – rotameters, 3 – drying columns filled with CaCl_2 and P_2O_5 , 4 – gas flow meter cooperating with computer, 5 – ozonator, 6 – porous plate, 7 – glass reaction vessel, 8 – quartz tube with UV lamp, 9 – thermostating jacket, 10 – magnetic mixer, 11 – hydrogen peroxide tank, 12 – system of ozone neutralization, 13 – ozone concentration meter which measures ozone content in oxygen at the reactor inlet and outlet, 14 – UV-lamp feeder, 15 – computer

So, the amount of energy, which can be used in the process of ozone decomposition, is by 17% higher for the 150 W lamp. These values refer in general to the number of quanta and energy emitted by the lamp and transferred through the “active” volume of the reactor.

The wastewater treatment parameters were as follows:

1. Ozonation was carried out in a 1.5 dm^3 glass bubble column reactor filled with 1 dm^3 of solution at ambient temperature. The incoming ozone gas flow rate was $20 \text{ dm}^3/\text{h}$ at the initial ozone concentration of $64 \text{ mg}/\text{dm}^3$. Ozonation periods varied between 30 and 120 minutes. The corresponding ozone dosages were in the range from 640 to $2560 \text{ mg O}_3/\text{dm}^3$. The degree of ozone conversion decreased from the initial 70% to about 40% after 120 minutes.

2. UV irradiation was carried out in the same reactor as the ozonation process. A quartz tube with light source was placed centrally in the reactor. The Heraeus lamps were applied: a low-pressure mercury discharge lamp, TNN 15/32 type, of 15 W power and medium-pressure mercury discharge lamp, TQ 150 type, of 150 W power. The wastewater was UV-irradiated for 1, 2 and 6 hours and then mixed by means of oxygen flow at a rate of 20 dm³/h. Light sources were cooled by air flow or water.

3. The process of wastewater oxidation by hydrogen peroxide was carried out in the same reactor as ozonation. The solution was mixed by means of oxygen flow at a rate of 20 dm³/h. Hydrogen peroxide in the form of 30% solution (perhydrol) was added at the reaction onset in the amount of 5, 10, 15 and 20 cm³/dm³ of wastewater. The reaction time was 1 hour.

4. At the combined ozone and UV light action in the wastewater the reaction times of 60 and 120 minutes were tested. Oxygen flow rate was equal to 20 dm³/h. The ozone concentration at the inlet to the reactor was 64 mg/dm³. The degree of ozone conversion decreased from the initial 70% to about 45% after 120 minutes.

5. A combined treatment with ozone and hydrogen peroxide consisted in adding to them, at the reaction onset, 30% solution of hydrogen peroxide in the amount of 5, 10 and 20 cm³/dm³ of wastewater. The reaction times were 1 and 2 hours. The amount of ozone applied was 1280 mg/dm³.

6. Wastewater treatment by hydrogen peroxide and UV light consisted in adding first 30% H₂O₂ solution in the amount of 5, 10, 15, 20 and 25 cm³/dm³ of wastewater and then it was UV-irradiated for 1 and 2 hours. The flow rate of the oxygen–ozone mixture was 20 dm³/h. The ozone concentration at the inlet to the reactor was 64 mg/dm³, which corresponded to the ozone dosage rate of 985 mg/h·dm³ of wastewater. The degree of ozone conversion decreased from the initial 70% to about 40% after 120 minutes. A low-pressure lamp (15 W) and medium-pressure lamp (150 W) were used.

7. Wastewater treatment by means of a simultaneous action of all three agents (O₃, H₂O₂ and UV) consisted in adding first 30% H₂O₂ solution in the amount of 5, 10, 15 and 20 cm³/dm³ of wastewater. Then wastewater was subjected to simultaneous ozonation and UV irradiation for 1 and 2 hours. The oxygen–ozone mixture flow rate was 20 dm³/h. The ozone concentration at the inlet to the reactor was 64 mg/dm³ as usual. The degree of ozone conversion decreased with time from the initial 70% to about 35% after 120 minutes. A low-pressure lamp (15 W) and medium-pressure lamp (150 W) were used.

After completing the reaction the excess hydrogen peroxide was decomposed by manganese dioxide (MnO₂). In all experiments, the process temperature was kept constant at 295 K.

3. RESULTS AND DISCUSSION

Experimental results of the measurements of pH, COD, BOD₅, CT, AD for dyeing wastewaters (1), (2) and (3) and TOC for dyeing wastewater (2) are given in tables 1,

2 and 3. Changes of TOC for dyeing waste (2) obtained by applying different variants of AOPs are shown in figure 2.

Table 1

Changes of some characteristic parameters of dyeing wastewater (1) resulting from applying different variants of advanced oxidation

Type of treatment		Specific colour	CT	pH	COD [mg O ₂ /dm ³]	BOD ₅ [mg O ₂ /dm ³]	AD [mg/dm ³]
Nontreated		green	50	9.0	320	42	3.9
O ₃	0.5 h	light green	17	9.0	190	19	2.3
	1.0 h	light green	8	8.8	130	34	1.6
	1.5 h	noncoloured	–	8.6	140	47	1.3
	2.0 h	noncoloured	–	8.3	120	18	0.7
UV	1.0 h	green	50	8.9	220	26	2.4
	2.0 h	light green	33	9.0	150	24	1.8
	6.0 h	light green	17	9.0	110	27	1.5
H ₂ O ₂	5 cm ³ /dm ³	green	43	9.5	210	54	2.4
	10 cm ³ /dm ³	light green	33	9.4	170	50	1.5
	15 cm ³ /dm ³	light green	25	9.3	170	49	1.4
	20 cm ³ /dm ³	light green	17	9.3	150	10	0.7
O ₃ + UV	1.0 h	noncoloured	–	8.1	115	12	2.4
	2.0 h	noncoloured	–	8.3	105	18	1.5
O ₃ + H ₂ O ₂	1.0 h+5 cm ³ /dm ³	light green	25	8.4	130	13	1.4
	1.0 h+10 cm ³ /dm ³	light green	17	8.5	110	10	0.8
	1.0 h+20 cm ³ /dm ³	noncoloured	–	8.7	75	10	0.5
H ₂ O ₂ +UV (1 h)	5 cm ³ /dm ³	noncoloured	–	8.0	275	17	2.3
	10 cm ³ /dm ³	noncoloured	–	8.2	200	<10	2.2
	15 cm ³ /dm ³	noncoloured	–	8.4	144	<10	2.0
	20 cm ³ /dm ³	noncoloured	–	8.4	130	18	1.7
	25 cm ³ /dm ³	noncoloured	–	8.5	42	<10	0.6
H ₂ O ₂ +UV (2 h)	5 cm ³ /dm ³	noncoloured	–	8.1	195	<10	2.6
	10 cm ³ /dm ³	noncoloured	–	8.2	<20	<10	2.1
	15 cm ³ /dm ³	noncoloured	–	8.5	<20	<10	0.7
	20 cm ³ /dm ³	noncoloured	–	8.4	<20	<10	0.6
O ₃ + UV (2 h)	5 cm ³ /dm ³	noncoloured	–	8.4	<20	<10	1.5
	10 cm ³ /dm ³	noncoloured	–	7.9	<20	<10	0.9
	15 cm ³ /dm ³	noncoloured	–	8.3	<20	<10	0.0
O ₃ + H ₂ O ₂	20 cm ³ /dm ³	noncoloured	–	8.1	<20	<10	0.0
	5 cm ³ /dm ³	noncoloured	–	8.4	130	<10	1.8
	10 cm ³ /dm ³	noncoloured	–	8.4	70	<10	1.1
O ₃ + UV (1 h)	15 cm ³ /dm ³	noncoloured	–	8.3	<20	<10	0.8
	20 cm ³ /dm ³	noncoloured	–	8.4	<20	<10	0.0

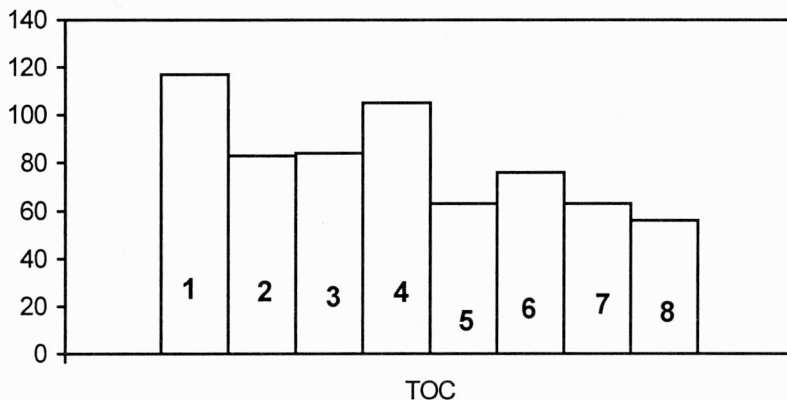


Fig. 2. Yield of TOC (mg/dm^3) for the dyeing waste (2) obtained due to application of different variants of advanced oxidation: 1 – nontreated waste, 2 – O_3 (1 h), 3 – UV low-pressure mercury lamp (15 W, 1 h), 4 – H_2O_2 (5 cm^3), 5 – O_3 + UV low-pressure mercury lamp (15 W, 1 h), 6 – O_3 + H_2O_2 (5 cm^3 , 1 h), 7 – UV + H_2O_2 (5 cm^3), low-pressure mercury lamp (15 W, 1 h), 8 – O_3 + UV + H_2O_2 (5 cm^3 , 1 h), low-pressure mercury lamp (15 W). The above values refer to 1 dm^3 of solution at ambient temperature. Ozone flow rate – $20 \text{ dm}^3/\text{h}$, initial ozone concentration – 64 mg/dm^3

For the all kinds of wastewaters and AOPs no significant changes of wastewater parameters such as DR, SS and S were observed, so they were not presented in the tables.

3.1. THE EFFECT OF O_3

From the data presented in table 1 it follows that the concentrations of pollutants in the wastewater, expressed in terms of the parameters analysed, decrease with an increase of the treatment time (the dosage of ozone). As early as after half an hour, which is equivalent to treatment with ozone dosage approaching 600 mg/dm^3 , the wastewater is completely decolourized. Reduction of COD and AD are 62.5% and 82%, respectively.

In the case of the moderately concentrated dyeing wastewater (2), the results of its treatment by ozonation are very similar to the results of treatment of the dyeing wastewater (1) (table 2).

In the case of strongly concentrated dyeing wastewater (3), the destruction of anionic detergents is almost complete, however, the COD reduction amounts to 25% only. More information on the ozonation of real and model textile wastewaters is available in our previous papers [22]–[24].

3.2. THE EFFECT OF UV

From the data presented in table 1 it follows that CT, COD and AD decreased with an increase of the reaction time (dose of UV radiation). The application of sole UV

irradiation did not guarantee a complete decolouration of the wastewater even during a 6 h process (colour reduction was 65% at most). Reduction of AD was 53% and 65% for 2 h and 6 h reaction time, respectively, while that of COD reached 54% and 61% for 2 h and 6 h, respectively.

Table 2

Physicochemical characteristics of the dyeing wastewater (2)
obtained due to application of different variants of advanced oxidation

Type of treatment		Specific colour	CT	pH	COD [mg O ₂ /dm ³]	BOD ₅ [mg O ₂ /dm ³]	AD [mg/dm ³]	TOC [mg/dm ³]
Nontreated		blue	250	8.2	320	64	2.6	117.0
O ₃	1.0 h	noncoloured	–	7.8	220	20	0.4	83.2
	2.0 h	noncoloured	–	8.0	135	14	0.0	75.7
UV	1.0 h, 15 W	l. orange	100	8.1	185	15	1.5	84.1
	2.0 h, 15 W	l. yellow	50	8.2	170	15	0.0	82.1
	1.0 h, 150 W	l. orange	67	8.2	260	18	0.7	96.2
	2.0 h, 150 W	l. yellow	33	8.3	280	18	0.0	93.9
H ₂ O ₂	5 cm ³ /dm ³	l. purple	120	8.4	300	10	0.3	104.9
	10 cm ³ /dm ³	l. purple	100	8.5	290	33	0.0	100.3
O ₃ + H ₂ O ₂	1 h + 5 cm ³ /dm ³	noncoloured	–	7.9	190	10	0.4	75.5
	2 h + 10 cm ³ /dm ³	noncoloured	–	8.0	135	63	0.7	72.9
O ₃ + UV	(15 W) 1.0 h	noncoloured	–	7.6	140	10	0.8	63.0
	(15 W) 2.0 h	noncoloured	–	7.6	125	13	0.0	52.6
	(150 W) 1.0 h	noncoloured	–	8.1	225	33	0.8	72.0
	(150 W) 2.0 h	noncoloured	–	8.0	180	12	0.0	64.7
H ₂ O ₂ + UV (1 h)	(15 W) (1 h)	noncoloured	–	8.3	125	42	0.8	62.6
	5 cm ³ /dm ³							
	(150 W) (1 h)	noncoloured	–	7.9	240	<10	1.3	48.2
	5 cm ³ /dm ³							
	(15 W) (2 h)	noncoloured	–	8.2	180	<10	0.0	48.7
	10 cm ³ /dm ³							
H ₂ O ₂ + UV (2 h)	(15 W) (2 h)	noncoloured	–	8.1	230	13	0.8	31.5
	10 cm ³ /dm ³							
	(15 W)	noncoloured	–	8.2	180	<10	0.0	48.7
	10 cm ³ /dm ³							
O ₃ (1 h), H ₂ O ₂ (5 cm ³ /dm ³) + UV(1 h)	15 W	noncoloured	–	7.8	125	16	0.0	
	150 W	noncoloured	–	7.7	175	72	0.0	69.6
O ₃ (2 h), H ₂ O ₂ (10 cm ³ /dm ³) + UV (2 h)	15 W	noncoloured	–	8.3	224	10	0.0	49.3
	150 W	noncoloured	–	7.9	245	11	0.0	59.7

*l. – light.

Moderately concentrated dyeing wastewater (2) was photochemically destructed by two kinds of UV lamps: low-pressure mercury discharge lamp and medium-pressure mercury discharge lamp. In the case of monochromatic light of wavelength of the 252 nm, the effects of COD and TOC reduction were much better than for the medium-pressure lamp.

Table 3

Physicochemical characteristics of the dyeing waste (3)
obtained due to application of different variants of advanced oxidation

Type of treatment			Specific colour	CT	pH	COD [mg O ₂ /dm ³]	BOD ₅ [mg O ₂ /dm ³]	AD [mg/dm ³]	
Nontreated			orange	670		1310	75	5.3	
O ₃	1.0 h		orange	670	6.6	990	220	0.8	
	2.0 h		orange	500	7.1	980	50	0.0	
UV	2.0 h	15 W	orange	670	7.4	1080	78	2.4	
	1.0 h	15 W	orange	670	7.3	870	95	0.0	
	1.0 h	150 W	orange	670	7.2	1010	45	0.8	
	2.0 h	150 W	orange	670	7.5	960	155	0.0	
H ₂ O ₂	5 cm ³ /dm ³		orange	670	7.1	1310	93	0.0	
	10 cm ³ /dm ³		orange	330	7.5	1280	13	0.0	
O ₃ + UV	1.0 h	15 W	orange	670	6.6	860	50	0.0	
	2.0 h	15 W	orange	170	6.8	720	24	0.0	
	1.0 h	150 W	orange	500	7.3	1020	40	0.0	
	2.0 h	150 W	l. yellow	100	7.0	960	75	0.0	
O ₃ + H ₂ O ₂	1.0 h	5 cm ³ /dm ³	yellow	120	7.2	1310	73	0.0	
	2.0 h	10 cm ³ /dm ³	l. yellow	67	6.8	1080	30	0.0	
H ₂ O ₂ + UV	1.0 h	5 cm ³ /dm ³	15 W	orange	500	7.3	1280	27	0.0
	2.0 h	10 cm ³ /dm ³	15 W	yellow	120	7.3	1210	127	0.0
	1.0 h	5 cm ³ /dm ³	150 W	orange	330	7.0	1230	107	0.8
	2.0 h	10 cm ³ /dm ³	150 W	yellow	120	6.9	1280	127	0.0
O ₃ +UV+ H ₂ O ₂	1.0 h	5 cm ³ /dm ³	15 W	l. yellow	100	7.1	1000	235	0.0
	2.0 h	10 cm ³ /dm ³	15 W	l. yellow	25	7.0	780	84	0.0
	1.0 h	5 cm ³ /dm ³	150 W	l. yellow	67	7.1	1030	15	0.0
	2.0 h	10 cm ³ /dm ³	150 W	l. yellow	17	7.0	800	87	0.0

*l. - light.

Generally there were no differences in photochemical destruction of both dyeing wastewaters (1) and (2). However, in the case of strongly concentrated dyeing wastewater (3), we did not observe decolourization in 2 h reaction time. Reduction of COD was about 30% and it was slightly higher for low-pressure 15 W lamp. The detergent

was completely destroyed. The effect observed was due to an intensive colour of the wastewater (3) – high initial value of CT and relatively low concentration of detergent.

3.3. THE EFFECT OF H₂O₂

Table 1 illustrates the effect of H₂O₂ on the changes in pollutants' concentrations in the dyeing wastewater (1). With an increase in the amount of H₂O₂ added, there was a decrease in chemical oxygen demand, biochemical oxygen demand, colour threshold value and concentration of anion surfactants. Under the experimental conditions, 80% reduction of AD, 65% reduction of colour and 50% decrease of COD were obtained. However, the amount of H₂O₂ added was significant – 20 cm³/dm³ of wastewater.

Physicochemical characteristics of dyeing wastewater (2) are given in table 2 and those of wastewater (3) – in table 3. Decolourization of wastewater (2) by means of 5 and 10 cm³ H₂O₂/dm³ was much better than that of wastewater (1), though the initial CT values were lower for the wastewater (1) than for the wastewater (2), reaching 50 and 250, respectively. The COD and TOC reductions were rather low, i.e. 10% and 15%, respectively, while the detergent destruction was complete. In the case of wastewater (3), a complete destruction of detergent was also observed, but the colour reduction amounted to 50%, while the COD practically did not change. Hence, hydrogen peroxide was mostly effective in destruction of anionic detergents.

3.4. THE EFFECT OF O₃/UV

The best results of decomposition of organic compounds measured in terms of COD value were obtained when ozone and UV (both lamps) were applied. Application of ozone only led to worse results, while UV irradiation proved to be the worst (see tables 1, 2 and 3, positions 1, 2 and 4). The low-pressure 15 W lamp was more advantageous than the medium-pressure 150 W lamp. However, these differences depended on the process version applied. So, the decomposition due to photochemical oxidation is observed when both lamps are used. However, these differences are much bigger than it might be expected from the intensity of light emitted by the two lamps in the UV range. From actinometric measurements it follows that this difference is about 17%. The differences in COD decrease reach about 40% and 60%, while for TOC – only 14%, and for BOD₅ – 20%. In the case of anion detergents, a faster decomposition was reported for a 150 W lamp. This is, however, a significantly erroneous result because of a low output value of AD.

When ozonation and UV irradiation were applied simultaneously, similar results of deteriorated decomposition efficiency measured by COD value were obtained in the case of a 150 W lamp. These differences were smaller when TOC was analysed. The results show that when a lamp of improper characteristics is used, the synergistic effect of UV radiation does not occur in relation to ozone. On the contrary, a slightly

negative effect is observed, especially for a prolonged treatment (large ozone doses and irradiation). This conclusion is undeniable; however, it has not been given in the literature in such a straightforward way yet.

Simultaneous application of ozone and UV for the wastewater (2) caused its complete decolourization within 1 hour, independently of the application of the UV lamp. The anionic detergents were decomposed very fast. The COD reduction was 61% and 34% for 15 W and 150 W lamps, respectively.

The concentrated wastewater (3) was better decolourized by the lamp of higher power. It was due to an intensive colour of the wastewater and the fact that photochemical reactions took place in the vicinity of the lamp. The COD was reduced by 45% and 27% for the 15 W lamp and for the 150 W lamp, respectively. The anionic detergents were destructed completely as well.

3.5. THE EFFECT OF O_3/H_2O_2

Table 1 shows the reduction of basic parameters of the wastewater (1) subjected to the combined $O_3 + H_2O_2$ treatment. The ozonation lasted 60 minutes, and the concentration of H_2O_2 added changed from 5 to 20 cm^3/dm^3 of wastewater. Good effects of treatment were obtained. It is evident that ozone is the main oxidizing agent. Addition of hydrogen peroxide in the amount of 5 cm^3/dm^3 of wastewater, despite the fact of not improving the process yield, even slightly deteriorates the process conditions. This can be observed in the case of deterioration of wastewater decolouration (an increase of colour threshold value) and no COD changes. An increase in the amount of hydrogen peroxide added causes a slight improvement of the treatment efficiency. In wastewater containing 20 cm^3 of H_2O_2/dm^3 of wastewater, the colour reduction after ozonation was complete, AD concentration decreased by over 85%, while that of COD by 75%.

The wastewater (2) was treated at low concentration of hydrogen peroxide. The colour completely disappeared, COD reduction reached 40%, and TOC reduction was 35% for the reaction time of 1 hour. The extension of the reaction time to 2 hours increased the COD reduction to 58% and TOC – to 48%. Detergents were not completely destructed at 5 and 10 cm^3 doses of H_2O_2 per 1 dm^3 of wastewater and their removal reached 73 and 63%, respectively.

In the case of strongly concentrated dyeing wastewater (3), the decolourization was not complete, being 82% for 1 h and 5 cm^3 of H_2O_2 per 1 dm^3 of wastewater and 90% for 10 cm^3 of H_2O_2/dm^3 of wastewater. The COD reduction was 18% only, while detergents were completely destroyed.

3.6. THE EFFECT OF UV/ H_2O_2

The combined treatment of the dyeing wastewater (1) with UV/ H_2O_2 had a very advantageous effect on colour reduction. The wastewater was completely decolour-

ized as early as at the lowest dosages of the oxidants used. On the other hand, the sole application of UV irradiation and separate use of H_2O_2 brought about poor results. When both agents were used jointly a clear positive synergistic effect was observed. In the case of anionic detergents, the results were not so explicit. A combined use of UV irradiation and H_2O_2 produced less advantageous results than separate application of the two components, especially at low doses of the oxidants. The combined use of UV irradiation and H_2O_2 in low doses caused some deterioration of COD in the dyeing wastewater (1). A positive synergistic effect occurred only at higher doses of oxidants when COD reduction was very high.

Results of the investigation of the wastewater (2) are given in table 2. The decolouration of the wastewater (2) was similar to that of the dyeing wastewater (1). In this case also a combination of UV and H_2O_2 produced excellent results which were expressed by complete wastewater decolouration although its initial colour was much more intensive than that of the dyeing wastewater (1). Worse results were obtained for anion-active detergents. In the case of COD of wastewater, the combined treatment with UV and H_2O_2 yielded good results, especially when a low-pressure lamp (15 W) was used. For example, at the dose of $5 \text{ cm}^3 \text{ H}_2\text{O}_2/\text{dm}^3$ of wastewater only a 6% reduction of COD was obtained, while at 1 h UV irradiation with 15 W lamp and 150 W lamp the reduction in COD reached 42% and 19%, respectively. When both these factors were applied the COD reduction was 61% (using 15 W lamp) and 25% (for 150 W lamp). Thus, the application of low-pressure 15 W lamp is much more advantageous than that of the medium-pressure 150 W lamp. When H_2O_2 and UV irradiation (15 W) are used jointly, the process of pollutants' decomposition is the most intensive. This is confirmed by an increase of wastewater susceptibility to biodegradation which increases from 20% for untreated wastewater to 34% after the treatment. In wastewater treated with single oxidizing agents, the susceptibility to biodegradation (BOD_5/COD) decreased to a few per cent. Thus, compounds of a simple structure were decomposed first, while the complex, organic structures, which could not be rebuilt biologically, remained practically not degraded.

In the case of concentrated wastewater, the decolourization effect was the worst for the low-pressure lamp, but this trend was not observed for the COD reduction.

3.7. THE EFFECT OF $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$

The application of all three oxidizing agents at the same time was very advantageous and evidently enhanced the degradation of organic pollutants present in the wastewater. The quickest was the degradation of dyes, while the decomposition of anion-active detergents proved to be slightly slower. This was especially evident in relation to COD of wastewater. In some samples practically a total reduction of COD was obtained. For instance, a dose of H_2O_2 equal to 5 cm^3 per 1 dm^3 of wastewater combined with 2 h treatment with ozone and UV light resulted in a practically complete COD reduction (higher than 94%). Under the conditions when each of three such agents as hydrogen peroxide, ozone and UV irradiation is applied separately, the

COD reduction equals 34%, 62%, and 53%, respectively. Experimental results for the dyeing wastewater (1) are given in table 1.

For comparison similar investigations were carried out for the second lot of wastewater (the dyeing wastewater (2), table 2). This wastewater appeared to be more resistant to oxidizing agents. Although after a simultaneous treatment with ozone, UV light and hydrogen peroxide it was completely decoloured and devoid of anion-active detergents, the COD decrease was not so evident. A positive synergistic effect was observed only at low doses of oxidizing agents. Prolonged time of treatment with ozone and UV light associated with an increase of the amount of H_2O_2 had a disadvantageous effect on ozonation, with COD reduction being higher in this case. Similarly as in the case of the dyeing wastewater (1) it was better to use a low-pressure UV lamp.

When all three agents were applied at the same time, the reduction of any particular parameter was very high. In the case of dyeing wastewater (1), beside a complete decolouration and reduction of detergents, also COD and BOD_5 values decreased below the accuracy of determination, so it was impossible to specify their susceptibility to biological decomposition. In the case of more concentrated dyeing wastewater (2), where COD reduction was not so high, the value of the BOD_5/COD ratio declined which caused that the treated wastewater showed slightly worse susceptibility to biological degradation than the untreated wastewater.

Both colour reduction and destruction of detergents in the wastewater (3) were almost complete. The COD reduction was equal to 40%, but BOD_5 slightly increased, so the biodegradability of the treated wastewater increased.

4. CONCLUSIONS

Studies on real textile wastewater treatment using H_2O_2 and UV irradiation or O_3 , H_2O_2 and UV irradiation showed that, in general, the best results of pollutants degradation were obtained when two or three agents were used simultaneously. Under experimental conditions, satisfactory results of wastewater treatment were obtained. They were expressed by complete decolouration and full degradation of anionic detergents. It was also possible to obtain a total reduction of COD. The results of treatment depended on duration of the treatment, oxidant doses, the amount of H_2O_2 added, and on the concentration and type of pollutants in wastewater. In order to obtain a satisfactory reduction of pollutants, we have to dose the oxidants very precisely. In advanced oxidation processes with simultaneous UV irradiation, low-pressure lamps with possibly mono-energy spectrum in the UV-C range should be used.

The products of degradation obtained in this way are much less toxic than the initial compounds which makes them easily biodegradable. The method proves that the oxidizing agents can be dosed with some flexibility, depending on the concentration and type of pollutants present in the wastewater. However, the wastewater composition should be under constant control, and the wastewater parameters have to be optimized when an optimum decomposition of pollutants at a minimum cost is to be obtained.

The results obtained suggest that simultaneous use of O_3 , H_2O_2 and UV irradiation can be applied successfully on a technological scale. A combination of these methods enables almost complete degradation of toxic substances and may contribute to recycling and conserving water in textile factories.

REFERENCES

- [1] CORREIA V.M., STEPHENSON T., JUDD S., *Characterization of textile wastewaters – a review*, *Environ Technol*, 1994, 15, 917–929.
- [2] PELEG M., *The chemistry of ozone in the treatment of water*, *Water Research*, 1976, Vol. 10, pp. 361–365.
- [3] LANGLAIS B., RECKHOW D.S., BRINB D.R., *Ozone in water treatment, applications and engineering*, Cooperative Research Report, Chelsea, 1991, MI, USA: Lewis Publishers Inc., 69.
- [4] ORMAD P., PUIG A., SARASA J., ROCHE P., MARTIN A., OVELLEIRO J.L., *Ozonation of wastewater resulting from the production of organochlorine plaguicides derived from DDT and trichlorobenzene*, *Ozone Science & Engineering*, 1994, Vol. 16, 6, pp. 487–503.
- [5] RICE R.G., MILLER G.W., ROBSON C.M., HILL A.G., *Ozone utilization in Europe*, *AIChE Symp.*, 1989.
- [6] RICE R.G., *Applications of ozone for industrial wastewater treatment – a review*, *Ozone Science & Engineering*, 1997, 18, pp. 477–515.
- [7] RICE R.G. *Applications and current status of ozone for municipal and industrial wastewater treatment: A literature review* [in:] *The Role of Ozone in Wastewater Treatment*, Proceedings of a seminar held at the Centre for Environmental Control & Waste Management, Imperial College of Science, Technology & Medicine, London SW7 2BU, UK.
- [8] DALANGHE B., MEKRAS C.I., GRAHAM N.J., *Aqueous ozonation of surfactants; a review*, *Ozone Science & Engineering*, 1991, Vol. 13, 6, pp. 639–673.
- [9] BALDES H.U., BACKER J., *Ozone treatment of textile and dye-house waste*, 11th Ozone World Congress, San Francisco CA, 1993, pp. S-10-76–S-10-83.
- [10] SCHULZ G., HERLINGER H., GAHR F., *Oxidativer Abbau von Farbstoffen durch Ozon*, *Textil Praxis Intern.*, 1992, 11, 1055–1060.
- [11] GREGOR H., *Oxidative decolorization of textile waste water with advanced oxidation*, [in:] *Chemical Oxidation Technologies for the Nineties*, Vol. 2, edited by W.W. Eckenfelder, A.R. Bowers, J.A. Roth, Lancaster, Basel, 1992.
- [12] UYGUR A., *An overview of oxidative and photooxidative decolorisation treatments of textile waste waters*, *JSDC*, 1997, Vol. 113, pp. 211–217.
- [13] WAGNER V., KETRUP A., *Oxidation treatment of wastewater of the textile finishing with combinations of H_2O_2 , O_3 , UV*, Proceedings of the International Ozone Symposium *Application of ozone in water and wastewater treatment*, edited by A.K. Biń, Warsaw, Poland, May 26–27, 1994, pp. 344–354.
- [14] BELTRAN F.J., GONZALEZ M., GONZALEZ J., *Industrial wastewater advanced oxidation. Part 1. UV radiation in presence and absence of hydrogen peroxide*, *Water Research*, 1997, Vol. 31, 10, pp. 2405–2414.
- [15] BELTRAN F.J., ENCINAR J.M., GONZALEZ J.F., *Industrial wastewater advanced oxidation. Part 2. Ozone combined with hydrogen peroxide or UV radiation*, *Water Research*, 1997, Vol. 31, 10, pp. 2415–2428.
- [16] BORUP M.B., MIDDLEBROOKS E.J., *Photocatalyzed oxidation of toxic organics*, *Water Sci. Technol.*, 1987, 19, pp. 381–390.

- [17] GUITTONNEAU S., DE LAAT J., DUGUET J.P., BONNEL C., DORE M., *Oxidation of parachloronitrobenzene in dilute aqueous solution by $O_3 + UV$ and $H_2O_2 + UV$: a comparative study*, Ozone Science & Engineering, 1990, Vol 12, pp. 73–94.
- [18] PREIS S., KAMENEV S., KALLAS J., MUNTER R., *Advanced oxidation processes against phenolic compounds in wastewater treatment*, Ozone Science & Engineering, 1995, Vol. 17, 4, pp. 399–418.
- [19] GLAZE W.H., KANG J.W., CHAPIN D.H., *The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation*, Ozone Science & Engineering, 1987, Vol. 9, pp. 335–352.
- [20] LUCK F., MARET A., PAILLARD H., *A review of industrial applications of advanced oxidation processes for water treatment*, Down Under 96, Proceedings, Australia.
- [21] LEDAKOWICZ S., PERKOWSKI J., MACIEJEWSKA R., *Application of advanced oxidation processes to textile wastewater*, 3-rd Int. Conf. on Advanced Oxidation Technologies for Water and Air Remediation, Cincinnati, Ohio, USA, October 1996, p. 147.
- [22] PERKOWSKI J., KOS L., LEDAKOWICZ S., *Application of ozone in textile wastewater treatment*, Ozone Science & Engineering, 1996, 18 (1), pp. 73–85.
- [23] KOS L., PERKOWSKI J., *Application of ozone and UV-radiation in textile wastewater treatment*, Fibres & Textiles in Eastern Europe, 1999, 7, 1, (24), pp. 61–64.
- [24] KOS L., PERKOWSKI J., *Application of ozone and hydrogen peroxide in textile wastewater treatment*, Fibres & Textiles in Eastern Europe, 1999, 7, 2 (25), pp. 61–64.

PROCESY POGŁĘBIONEGO UTLENIANIA PODCZAS OCZYSZCZANIA RZECZYWISTYCH ŚCIEKÓW WŁÓKIENNICZYCH

Ścieki włókiennicze są trudne do oczyszczenia i słabo biodegradowalne. Trzy rodzaje rzeczywistych ścieków włókienniczych z łódzkich zakładów oczyszczano metodami pogłębionego utleniania (AOPs). Zastosowano następujące czynniki: ozon, nadtlenek wodoru i promieniowanie UV zarówno pojedynczo, jak i we wszystkich kombinacjach ($O_3 + UV$, $O_3 + H_2O_2$, $UV + H_2O_2$ oraz trzy jednocześnie $O_3 + UV + H_2O_2$). W ściekach przed i po oczyszczaniu analizowano następujące parametry: odczyn (pH), zabarwienie specyficzne i liczbę progową barwy (Lp), chemiczne (ChZT) i biochemiczne zapotrzebowanie tlenu (BZT₅), anionowe substancje powierzchniowo czynne (ASPC), ogólny węgiel organiczny (OWO), substancje rozpuszczone (SR), suchą pozostałość (SP) i zawiesiny (Z). Oznaczenia wykonano zgodnie z Polską Normą. Procesy ozonowania prowadzono skali laboratoryjnej w szklanym reaktorze, do którego doprowadzono gaz i w którym umieszczono centralnie palnik UV. Do doświadczeń użyto dwóch typów lamp UV: niskociśnieniowej lampy rtęciowej typu TNN 15/32, o mocy 15 W i średniociśnieniowej lampy rtęciowej typu TQ 150, o mocy 150 W.

Procesy pogłębionego utleniania były najefektywniejsze wtedy, gdy zastosowano jednocześnie wszystkie trzy czynniki, tzn. O_3 , H_2O_2 i UV. Uzyskano wtedy praktycznie całkowite odbarwienie ścieków i rozkład anionowych środków powierzchniowo czynnych, znaczną redukcję ChZT i OWO oraz poprawę biodegradowalności ścieków.

Uzyskane rezultaty wykazują, że proces pogłębionego utleniania z jednoczesnym zastosowaniem ozonu, nadtlenu wodoru i promieniowania UV może być z powodzeniem zastosowany na skalę przemysłową. Metoda ta prowadzi do całkowitej degradacji substancji toksycznych, umożliwiając biologiczne doczyszczanie i zwracanie wody w zakładach włókienniczych.

ścieki włókiennicze, ozonowanie, utlenianie,
biodegradacja

