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THE APPLICATION OF OZONE IN REMOVAL OF REFRACTORY SUBSTANCES FROM TEXTILE WASTEWATER

Investigations were carried out on laboratory and on pilot scales to determine the suitability and effectiveness of wastewater ozonation in removal of refractory substances from textile wastewater.

The subject of the investigations was textile wastewater from the cotton industry mixed with municipal wastewater in 1:1 to 2:1 ratios and preliminarily treated in the activated sludge and filtration processes.

On laboratory scale ozonation was carried out in a batch system with single dyes introduced to wastewater, and on a pilot one in the continuous flow, in one- and two-stage systems.

It has been found that ozone oxidation is particulary effective in colour removal, the latter amounts to 67% after a 15 minute contact of wastewater with the ozone dose of 50 mg/dm^3 in a two-stage reactor.

The consumption of energy required for ozone generation was high and amounted to 1.2 KWh/m^3 of wastewater. The advantage of this process compared with other tertiary treatment processes is the lack of sediments.

1. INTRODUCTION

The necessity of high-effective treatment of wastewater from the textile industry, which is one of the sources of considerable loads of wastewater pollutants, is becoming a serious engineering problem as far as small reservoirs, and in particular those deficient in water are concerned. Wastewater from the textile industry contains great amounts of so-called refractory substances which are totally or partly resistant to biodegration. This is particulary true for such organic refractory substances as dyes, detergents and synthetic compounds used to dye and finish textile fabrics.

The ozone oxidation process is widely used in many European and American countries, but mainly in water treatment plants. It is, however, rarely used in the treatment of industrial wastewater and as the third stage of treatment. Ozone is a gas whose solublity in water

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is 13 times higher than that of oxygen, ranging from 0.57 to 0.8 mg/dm^3 at 20°C [1, 2]. Its solubility in wastewater is 10 to 30% lower than in pure water [3], as ozone is very unstable gas and its decomposition to oxygen occurs within 20-30 minutes.

The ozonation of wastewater allows to achieve [1,2,4]:

the decomposition of substances which give rise to natural colour caused by ferrous and manganese compounds and peaty substances, as well as to artificial colour caused by synthetic dyes;

the decomposition of phenol;

the detergent removal;

the decrease in COD and BOD.

2. PREVIOUS RESULTS OF THE APPLICATION OF OZONE IN THE TERTIARY WASTEWATER TREATMENT

The use of ozone to treat wastewater is based on its oxidizing properties in reactions with mineral, organic and microbiological pollutants. Ozone exceeds in many qualities the other considerably weaker oxidizers which have been used hitherto.

By applying ozone in concentrations of 5 to 15 mg/dm^3 for 1-5 minutes of contact time with wastewater, a total destruction of viruses is obtained in wastewater previously subjected to the secondary treatment [5,6].

From published research [1,3,4,7-10] it appears that oxidation of biologically treated municipal wastewater with ozone in concentrations ranging from 10 to more than 50 mg O_3/dm^3 results in a 50% removal of the organic substance content expressed in COD.

Removal of COD occurs very slowly with high consumption of ozone and its considerable losses, better effects being obtained when the concentrations of ozone fed in and the initial COD value are higher [1,3,8].

Theoretically [3] the total COD should be oxidized during ozonation. In practice, part of the COD is resistant to oxidiaton, so that a very long ozone contact time is required to achieve a removal effect of above 50-70%.

Total organic carbon is also only partly removed from wastewater under the influence of ozone. The small undissolved part is resistant to oxidation [8].

From the research on the decomposition of anionic detergents in the ozonation process it appears [1] that the level of detergent removal is high, up to about 90%, and — as in the case of the COD indicator — it depends on the concentration of the ozone fed in and on the contact time.

3. SCOPE OF PRESENT RESEARCH WORK

The investigations were carried out on a laboratory scale by the batch method and on a pilot scale under dynamic conditions in an experimental continuous flow model.

Under statical conditions the ozonation process was conducted in a batch system, and its purpose was, first of all, to check whether the selected dyes used by the textile industry were susceptible to decomposition under the influence of ozone present in wastewater.

4. CHARACTERISTICS OF WASTEWATER USED IN THE INVESTIGATIONS

The research was conducted on textile wastewater from the "Andropol" Cotton Plant in Andrychów, which had been mixed with municipal wastewater, and subjected to biological treatment by the activated sludge method and filtered through a gravel-sand bed.

Of the total amount of wastewater discharged from the textile factory, about 17% comes from the dyehouse, where the yarn is treated before weaving. Cotton yarn is dyed with indigosole, vat, glacial, sulphuric and reactive dyes, while the yearn consisting of synthetic and cotton fibres is coloured with cotestrene and dispersed-vat dyes.

The ratio of textile wastewater to municipal sewage was varied from 1:1 to 2:1. The mixed wastewater was characterized by a variable chemical composition. During the investigations its colour was a fairly intensive pink, sometimes grey-green. The wastewater pH ranged from 6.8 to 8.0, but it was predominantly 7.5 or 7.7. COD varied from 69 to 290 mg/dm^3. The anionic and non-ionic detergent contents ranged from 0.30 to 1.2 mg/dm^3 and from 4.7 to 32.0 mg/dm^3, respectively.

5. RESULTS

5.1. OZONATION OF DYES IN A BATCH SYSTEM

5.1.1. METHODS

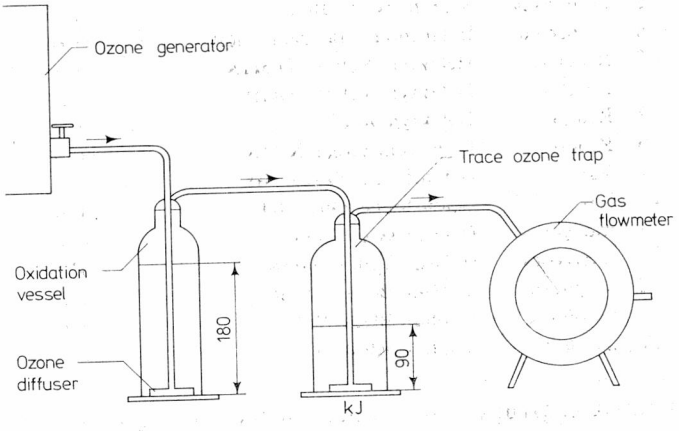

Fig. 1. Scheme of ozonation apparatus on a laboratory scale, batch system
Rys. 1. Schemat urządzenia do ozonowania w skali laboratoryjnej (układ statyczny)

The investigations were carried out a laboratory scale in a batch system, using an experimental unit shown in figure 1.

Ozone was generated from air in a Fischer Labor. Generator. The flow of the ozone — air mixture varied from 6 to 15 dm^3/h with ozone concentration of 10-14 mg/dm^3. Each of the 750 ml samples of wastewater prepared for the investigations contained 50 mg/dm^3 of a single dye. The ozonation time of three or four samples carried out for each dye studied was for each subsequent sample longer than for the previous one. Ozonation was carried out until a complete change of colour was visually confirmed. Analytical control of the process covered colour and COD determinations.

Colour was determined spectrophotometrically by continuous measurement of light absorption in the wave length range 400-650 nm. For dyes colour removal was determined from the difference in peak heights. In the case of wastewater which did not give a characteristic peak, the average absorption value was calculated from 11 points on the absorption curve corresponding to the measurement made for light wave length divided into 10 equal segments.

Table 1

COD determinations of dyes used in ozonation process on a laboratory scale
ChZT barwników stosowanych w laboratoryjnym procesie ozowania

No. of dye	Group	Dye	COD mg O_3/mg of dye
1	Glacial	Scarlet Base RG	0.95
2	Glacial	Salt of Naphtanil Blue BT	0.48
3	Dispersed	Synten Rubine P-3B	2.50
4	Dispersed	Synten Azure	1.54
5	Dispersed	Synten Navy Blue	6.50
6	Dispersed	Indanthrene Bordeaux RR	26.80
7	Reactive	Helaktyn Yellow D-5GN	5.75
8	Reactive	Helaktyn Yellow DGR	1.22
9	Reactive	Helaktyn Red	5.40
10	Reactive	Drimarene Green X-2BL	4.36
11	Vat	Helanthrene Green B5	2.24
12	Vat	Healnthrene Olive BT	21.80
13	Indygosol	Helasol Green ZG	4.75
14	Indygosol	Helasol Yellow GOK	9.45
15	Sulphuric	Sulphur Brown W4R	1.53
16	Sulphuric	Sulphur Black WT	1.15
17	Sulphuric	Sulphur Khaki G	2.44

17 dyes from different groups were selected for the investigations (table 1). The COD was used to calculate the theoretical ozone required to oxidize the dyes. The values of COD determined for 1 mg of the dye under investigations are given in table 1. They allowed

Table 2

Ozone balance and colour, COD removal in the ozonation process of water dye solutions
Bilans ozonu oraz usuwanie barwy i ChZT w procesie ozonowania wodnych roztworów barwników

Dye	Ozonation contact time min.	Amount of utilized ozone mg O_3/mg of dye	Ozone balance, %			Removal, %	
			Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas	Colour	COD
Scarlet Base RG	12	0.45	57.6	3.6	38.8	84.0	30.8
Salt of Naphtanil Blue BT	11	0.57	52.6	2.3	45.1	96.7	39.0
Synten Rubine P-3B	20	0.27	21.4	4.0	74.6	37.2	24.9
Synten Azure	33	0.73	35.5	0.9	63.6	68.1	41.2
Synten Navy Blue	43	0.58	42.6	3.1	54.3	98.8	30.8
Indanthrene Bordeaux RR	120	0.91	17.2	0.5	82.3	94.5	81.7
Helaktyn Yellow D-5GN	23	0.42	54.6	4.0	41.4	90.2	22.4
Helaktyn Yellow DGR	23	0.52	47.1	3.6	49.3	93.3	33.8
Helaktyn Red	22	0.54	55.6	3.9	40.5	98.0	34.7
Drimarene Green X-2BL	40	0.89	23.7	2.3	74.0	90.5	52.1
Helanthrene Green B5	120	2.06	50.9	0.4	48.7	48.0	76.7
Helanthrene Olive BT	120	1.23	31.8	0.7	67.5	78.5	66.6
Helasol Green ZG	15	0.21	28.3	6.6	65.1	89.0	57.2
Helasol Yellow GOK	71	0.91	36.2	1.8	62.0	97.5	79.0
Sulphur Brown W4R	15	0.20	25.9	3.0	71.1	50.2	0.0
Sulphur Black WT	15	0.15	21.6	8.6	69.8	76.2	0.0
Sulphur Khaki G	15	0.33	31.0	3.8	65.2	86.3	0.0

to calculate the amount of ozone required to oxidize the dye, the ozone concentration in the gas, the amount of gas supplied in a unit of time and the dye concentration being known. The values of ozone concentrations in wastewater and in gas leaving the column after the process made the basis for calculation of the percentage balance of ozone.

5.1.2. DISCUSSION

Table 2 presents the characteristic values obtained from the investigations, i.e. contact time, amount of ozone consumed per 1 mg of dye, ozone balance and degrees of colour and COD removal.

Only in a few cases did the ozone consumption exceed 50% of the total amount of ozone supplied. In general it ranged from 15 to 40%, thus the ozone losses were quite considerable. In most cases ozone consumption decreased with the increasing time due to the decreasing rate of oxidation. Colour removal during ozonation ranged from 37 to 98%. Changes in light absorption in the wave lenght range of 400-650 nm for two characteristic dyes — salt of Naphtanil Blue and Helanthrene Green — are given in figures 2 and 3.

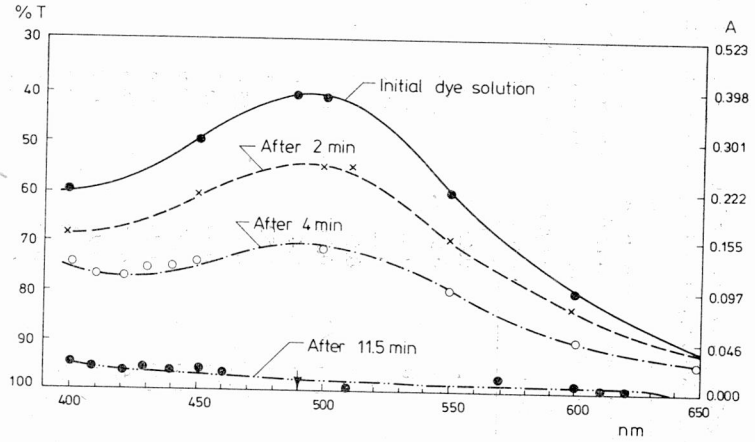

Fig. 2. Change of absorption spectrum within the λ value in the course of ozonation of the salt of Naphthanil Blue BT dye

Rys. 2. Zmiany wartości λ absorpcji światła podczas ozonowania soli błękitu naftoelanowego BT

The highest decolourization degree was stated in dyes from the glacial and reactive groups containing in their structure single benzene or naphthalene rings activated by oxygen or nitrogen functional groups. This explains their higher susceptibility to the action of ozone. The dyes of the sulphuric group (with the exception of Sulphuric Brown W4R) appeared to be susceptible to the action of ozone which splits the polysulphide chains and oxidizes thiazine rings, leading thus to the degradation of the dye. The dependence of the degree of colour removal on ozonation time is given in figure 4. The curves indicate that for the dyes investigated the required contact time was different. Most of dyes were discoloured to a large degree within 20 minutes, some of them required a prolonged time

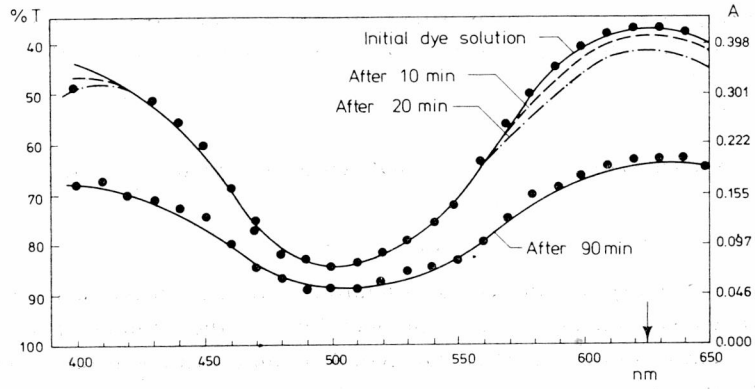

Fig. 3. Change of absorption spectrum within the λ value in the course of ozonation of Helanthrene Green B5 dye

Rys. 3. Zmiany wartości λ absorpcji światła podczas ozonowania zieleni helantrenowej B5

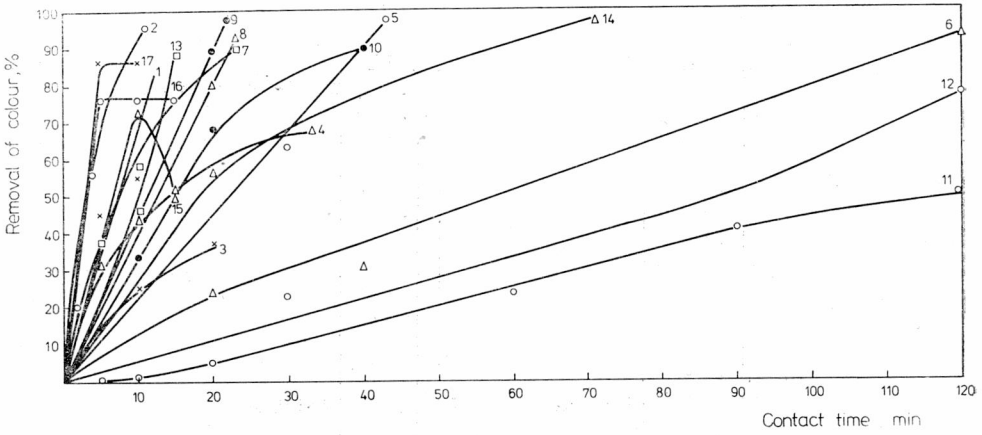

Fig. 4. Dominant colour removal depending on contact time of ozonation for particular dyes The numbers of curves on the diagram correspond to the numeration of dyes in table 1

Rys. 4. Zależność usuwania barwy od czasu kontaktu barwników z ozonem Numery krzywych odpowiadają numeracji barwników w tabeli 1

of 40 to 60 minutes. Two of the dyes studied, Indanthrene Bordeaux RR and Helanthrene Olive BT, were discoloured in 40-90% not earlier than after 120 minutes. Helanthrene Green BS proved to be resistant to ozonation; its decolourization after 120 minute contact being proved scarcely 48%.

For the majority of dyes ozone oxidation caused a fall in COD value. The reduction of COD after 15-20 minute contact time reached 25-40%. A higher level of COD removal, from 60 to 80%, was only achieved after 90 to 120 minutes. In the case of sulphuric dyes COD remained unchanged. For dyes of the reactive and sulphuric groups the COD value increased in the first phase of ozonation, being reduced only in the further phase. The most

probable reason for this phenomenon is the capacity of ozone to break up the organics present in the compounds examined and to make them more susceptible to the COD test [11].

5.2. WASTEWATER OZONATION IN A DYNAMIC SYSTEM

5.2.1. METHOD

Two variants of the system presented in figure 5 were used in the investigations. The one-stage system consisted of one column operating on the counter-current principle. A two-stage system was obtained after the second column with co-current operation was connected. The two-stage system consisted of counter-current column in one-stage and co-current column in two-stage, ensured conditions for more effective process. In one-

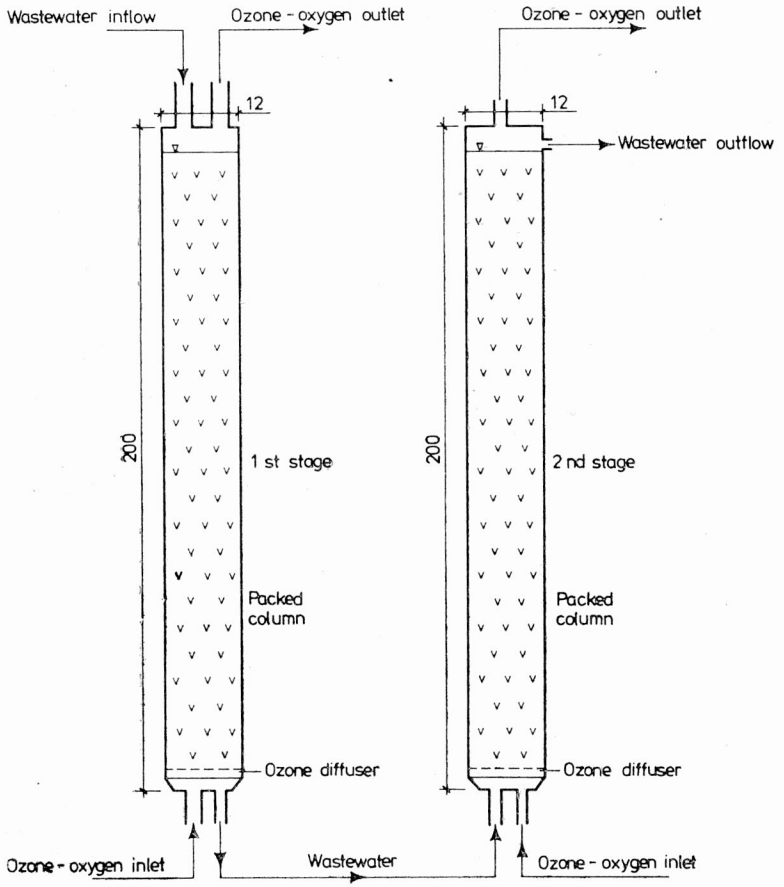

Fig. 5. Schematic flow diagram of one- and double-stage ozonation on a pilot scale
Rys. 5. Schemat jedno- i dwustopniowego urządzenia do ozonowania w skali pilotowej

age the ozone utilization is more effective as after passing upflow it contacted with unsatu-ited wastewater in upper part of column. The columns (2 m high and 12 cm in diameter) ere made of organic glass and filled (to a height of 1.5 m) with ceramic rings, in order to crease the effectiveness of the ozone — wastewater reaction. The ozone-oxygen mixture as fed into the column trough a rotametr and a diffusor which covered the bottom of e column. Before each test the column was stabilized to constant conditions for about hours. Then the required ozone concentration was regulated and the wastewater supplied. astewater flowing to and from the apparatus was sampled several times during each st, and the average sample taken for analysis consisted of the mixture of separated samples.

The following parameters were determined analytically: colour (by continuous measure-ent of light absorption within the range 400-650 nm), COD, anionic detergents, non-ionic tergents and ozone in the gas and wastewater. The ozone concentration values were ken for calculation of the percentage ozone balance.

5.2.2. RESULTS OF ONE-STAGE OZONATION

The tests (44) were carried out in the apparatus consisting of one column operating unter-currently. The average duration of the test was 6 hours. The ozone concentration individual tests amounted to 10, 30, 50 and 70 mg O_3/dm^3 of wastewater. The wastewater as retained in the column for 20, 30, 40 and 50 minutes. The amount of ozone supplied nged from 0.5 to 1.7 g/h with a wastewater flow of 19.2 to 48 dm^3/h depending on the ncentration required.

From the ozone balance made for 44 tests, it follows that the amounts of ozone con-med and decomposed in the column ranged from 61 to 66% of the total ozone supplied. nly in tests No. 6 and No. 11 the ozone consumption increased ranging within 76-79%.

During ozonation the wastewater changed its colour from pink or grey-green to natural eenish-yellow. The light absorption changes are shown in figure 6.

The greater the doses of ozone, the higher were the effects of pollutant removal. The one balance and the percentage of pollutant removal (average values from the measure-ents) are given in table 3. The optimum removal time ranges from 30 to 40 minutes, ith the ozone ranging from 50 to 70 mg O_2/dm^3 of wastewater (figure 7).

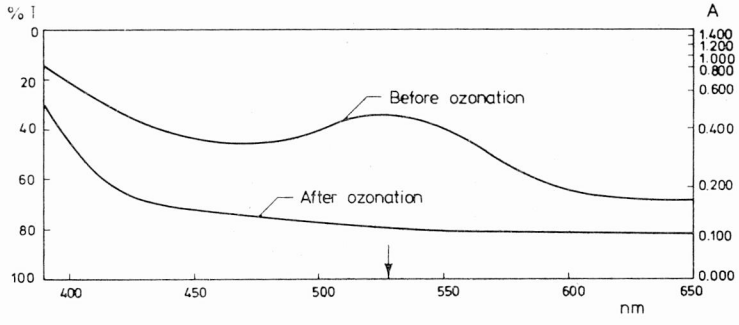

Fig. 6. Change of absorption spectrum within the λ value in the course of ozonation of wastewater
Rys. 6. Zmiany wartości λ absorpcji światła podczas ozonowania ścieków

Table 3

One-stage continuous ozonation of biologically treated and filtered wastewater. Ozone balance and colour, COD and detergent removal
Bilans ozonu oraz usuwanie barwy, ChZT i detergentów w procesie jednostopniowego ozonowania ścieków biologicznie oczyszczonych i filtrowanych

Test no.	Detention time in colum min.	Ozone concentration in wastewater in column mg/dm³	Amount of tests	Ozone balance, %			Removal, %			
				Used and decomposed in column	In effluent leaving	In exit gas	Colour, average light absorption *E*	COD	Anionic detergents	Non-ionic detergents
1-2		9.9	2	60.9	2.8	36.3	5.0	0.0	16.5	5.6
3-5		30.6	3	62.5	2.8	34.7	11.7	2.4	32.0	15.2
6-8	15	49.6	3	76.7	2.6	20.7	19.0	4.0	47.9	25.9
9-11		69.3	3	79.5	2.0	18.5	40.4	14.4	68.2	39.3
12-13		9.8	2	61.0	2.2	36.8	31.5	12.5	29.1	30.0
14-16		29.8	3	65.1	2.3	32.6	45.1	16.9	42.1	42.7
17-19	30	49.0	3	61.8	1.9	36.3	51.5	22.8	61.6	52.3
20-22		69.5	3	60.8	1.6	37.8	55.6	25.4	77.7	62.6
23-24		9.9	2	62.5	2.8	34.7	31.8	16.5	35.9	26.0
25-27		29.6	3	63.5	3.2	33.3	45.0	24.8	52.8	36.1
28-30	40	49.2	3	61.8	2.8	35.4	47.1	28.7	67.8	47.6
31-33		70.1	3	63.5	2.3	34.2	55.0	32.7	86.0	56.9
34-35		9.9	2	63.5	2.0	34.5	20.4	10.0	25.8	15.0
36-38		29.8	3	66.8	2.0	31.2	34.4	18.5	41.3	27.3
39-41	50	49.1	3	63.6	1.7	34.7	35.5	25.9	52.0	40.7
42-44		69,7	3	61,3	1,4	37,3	46,6	31,3	65.1	50.9

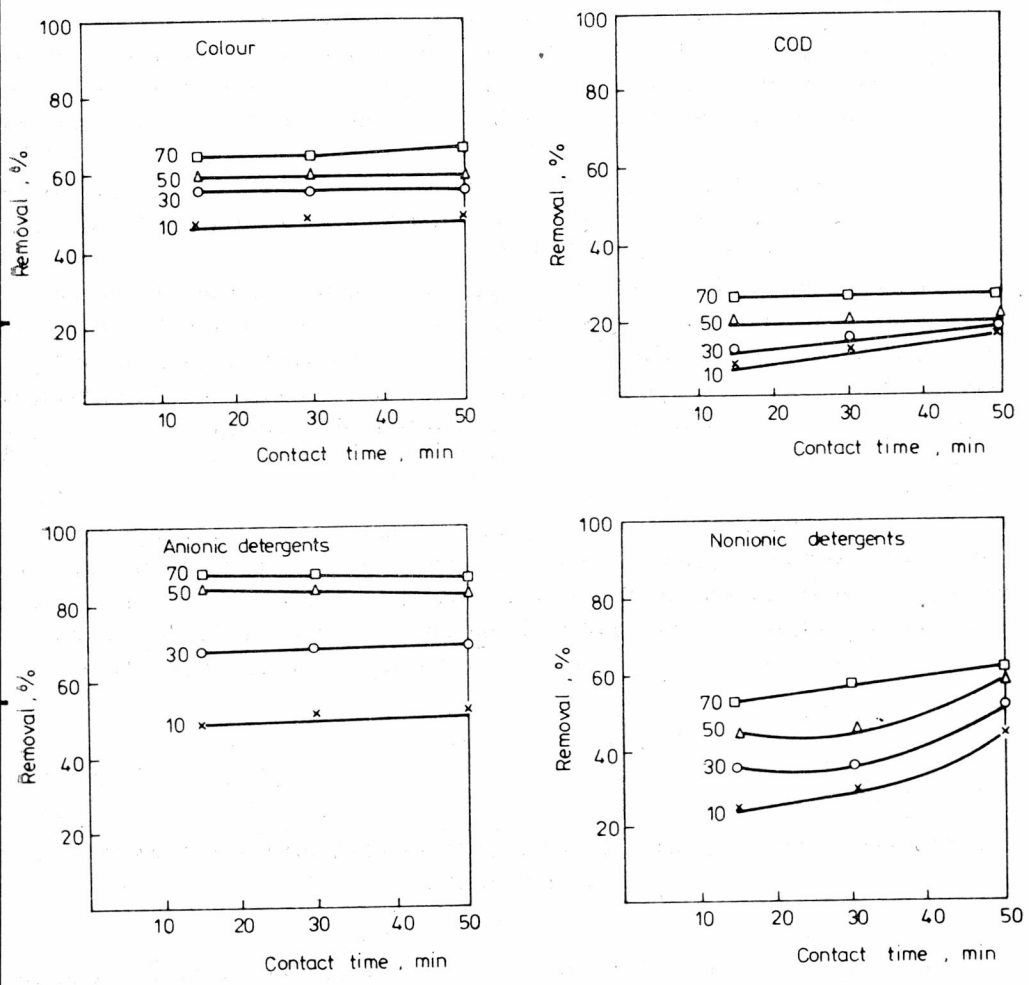

Fig. 7. Removal of contaminants in a one-stage continuous countercurrent column using 10, 30, 50 and 70 mg O_3/dm^3

Rys. 7. Usuwanie zanieczyszczeń w procesie jednostopniowego przeciwprądowego ozonowania ścieków. Zastosowane dawki: 10, 30, 50 i 70 mg O_3/dm^3

5.2.3. RESULTS OF TWO-STAGE OZONATION

The investigations were carried out on an installation consisting of two columns, of which one operated counter-currently, and the other co-currently. Wastewater was fed to the first column from the top, while ozone-oxygen mixture from the botton through a rotameter and diffusor. After passing through the first column, the wastewater supplied with a new dose of ozone was directed through the bottom of the second column.

In 24 tests conducted, 4 ozone doses, namely 10, 30, 50 and 70 mg/dm^3, were used, and the wastewater was retained for 15, 30 and 50 minutes.

Both the ozone doses and the retention times have been assumed for the two-colum set, thus to one column exactly half the ozone dose and half the reaction time were applied

The amounts of ozone supplied were from 0.5 g/h to 9.5 g/h, while the wastewate flow rates ranged from 38.4 dm^3/h to 128 dm^3/h depending on the ozone concentratio required.

The ozone balance for 24 completed tests indicates that the amount of ozone consume and decomposed in both columns ranged from 53 to 60%. Only in tests 9 and 10 the ozon consumption was higher and amounted 70%.

The gas emitted after the process contained 24 to 40% unreacted ozone. From addition al determinations of ozone in the gas emitted from the first column, it follows that the n this case of ozone exhaustion in the oxidation of organic compounds required highe amounts of ozone. The amount of unreacted ozone in the gas emitted from the first colum was on the average 25% lower than in gas emitted from the second one.

The ozone balance and the percentage of pollutant removal (average values) are give in table 4.

In the one-stage system the degree of pollutant removal depended on the ozone con centration and did not depend on the contact time ranging within 15-50 minutes. In th two-stage system the maximum effect was achieved after the process had been conducte for 15 minutes with the ozone dose of 50–70 mg/dm^3 of wastewater. Fresh dose of ozon introduced in the second-stage system increased the reaction rate, thereby the pollutan removal.

This relation is presented in figure 8.

6. DISCUSSION OF THE RESULTS OF INVESTIGATIONS ON WASTEWATER OZONATION

The ozone balance (table 3) shows that the one-stage ozonation process was conducte with an ozone deficit. This is indicated by the small concentrations of ozone remainin in the wastewater after the process.

The two-stage ozonation process (table 4) was conducted, particularly in the secon phase, with an ozone surplus.

American investigations [8] have indicated that the ozone — wastewater contact time necessary to achieve a decrease in COD from 35-40 mg/dm^3 to 15 mg/dm^3, was about 1 hour.

Since the decomposition of ozone in water takes about 20 minutes, the whole amount required should not be supplied simultaneously.

The 6-stage system with a 10-minute contact time in each column is accepted as being the most favourable and most economical. Such a system is technically complicated, as it operates on the principle that the oxygen produced from the decomposition of the ozone surplus in the wastewater is re-cycled. The oxygen undergoes compression, refrigera-

Table 4

Double-stage continuous ozonation of biologically treated and filtered wastewater. Ozone balance and colour, COD and detergent removal
Bilans ozonu oraz usuwanie barwy, ChZT i detergentów w procesie dwustopniowego ozonowania ścieków biologicznie oczyszczonych i filtrowanych

Test no.	Detention time in column min.	Ozone concentration in wastewater in column mg/dm³	Amount of tests	Ozone balance, %			Removal, %			
				Used and decomposed in column	In effluent leaving	In exit gas	Colour, average light absorption E	COD	Anionic detergents	Non-ionic detergents
1-2		10.0	2	56.5	4.7	38.8	46.3	10.0	49.6	25.7
3-4		30.0	2	55.8	2.9	41.3	56.1	13.0	68.4	35.4
5-6	15	50.8	2	55.0	2.4	42.6	59.6	21.4	84.9	43.0
7-8		70.6	2	60.7	2.4	36.9	64.5	27.2	87.0	53.1
9-10		9.6	2	70.1	5.2	24.7	46.0	13.6	59.2	29.8
11-12		29.8	2	56.2	3.2	40.6	54.2	15.3	76.1	36.9
13-14	30	50.4	2	53.8	2.2	44.0	59.8	20.0	83.3	52.8
15-16		69.4	2	57.5	1.7	40.8	67.4	26.4	85.5	58.8
17-18		9.7	2	55.2	5.1	39.7	47.0	18.8	51.0	44.6
19-20		30.0	2	57.6	3.5	38.9	56.5	17.8	69.6	51.7
21-22	50	50.1	2	59.7	2.5	37.8	60.1	20.1	82.7	60.0
23-24		69.6	2	62.4	1.5	36.1	67.3	27.2	85.3	60.8

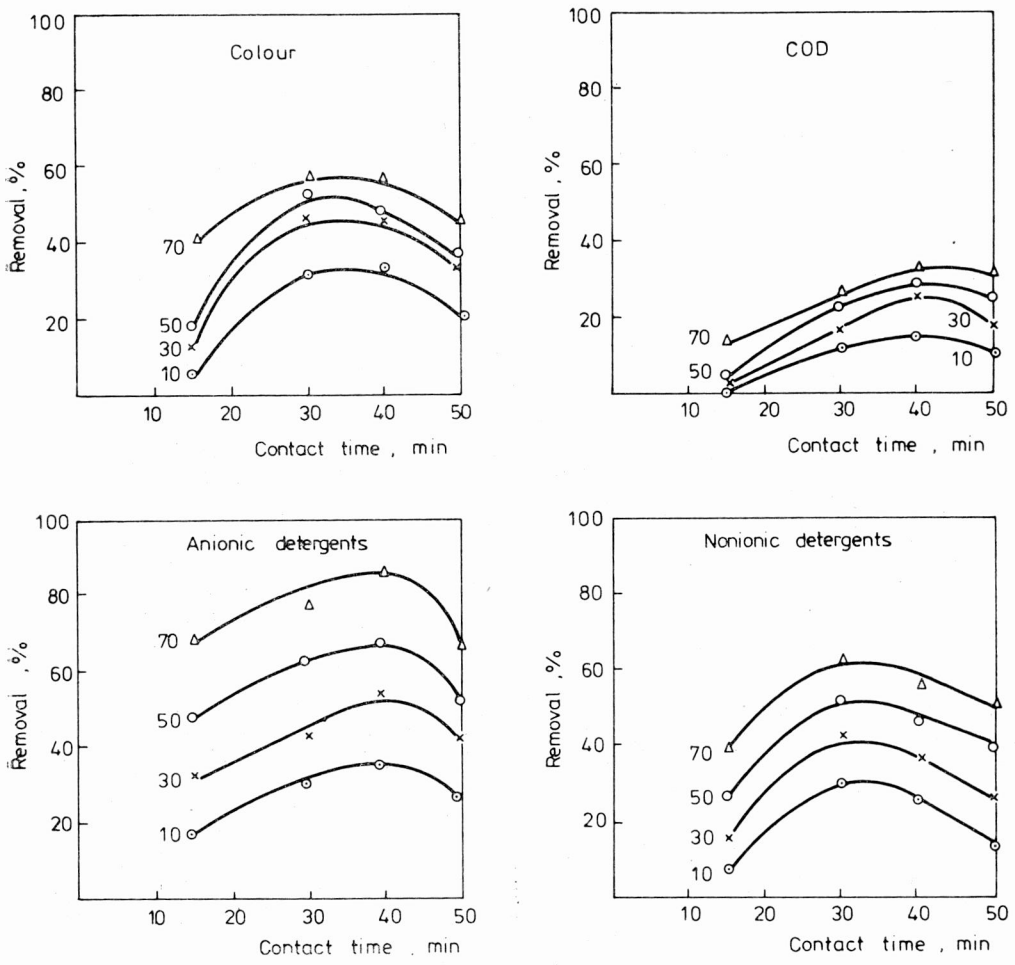

Fig. 8. Removal of contaminants in double-stage continuous columns using 10, 30, 50 and 70 mg O_3/dm^3
Rys. 8. Usuwanie zanieczyszczeń w procesie dwustopniowego ozonowania ścieków. Zastosowane dawki: 10, 30, 50 i 70 mg O_3/dm^3

tion and drying and is fed once again into the ozone generator. In this system 90% of the total amount of ozone supplied is exhausted.

The course of ozone oxidation and the degree of pollutant removal in our investigations differed depending to the system used. To obtain the highest pollutant removal in one-stage system a longer ozone — wastewater contact time is required. It ranged from 30 to 40 minutes depending on the kind of pollutant. Lengthening or shortening of the ozonation time did not bring any improvement in the treatment effects. When the time is prolonged to 50 minutes, the removal of all pollutant decreases due to earlier, spontaneous decomposition of the ozone.

A two-stage dosing of ozone accelerates the pollutant removal. The maximum effect was achieved for the reaction time of 15 minutes; no changes were practically observed at longer reaction time.

The results of colour removal (the maximum being 67%) are somewhat lower than those mentioned in the literature [1, 11-15], e.g. concentrated dye-house wastewater of c olour removal attained 80%, and for biologically treated municipal sewage it reached 92%. These differences are probably due to the method of colour measurement. In the investigations quoted [1, 12, 14, 15], the spectrophotometrical absorption was conducted exclusively for 400 nm. In order the colour be determined objectively, the light permeability of the sample studied should be investigated in the range of the visible spectrum.

In the present investigations, the maximum removal of COD was 32%. It was found that a considerable part of COD is resistant to ozone oxidation, thus in order to achieve somewhat higher removal effects the ozone contact time should be longer (multi-stage ozonation), which is not justified economically. From the investigations published [1, 3, 7-10] it follows that in biologically treated municipal sewage and subjected to ozonation with doses from as low as 10 to above 50 mg O_3/dm^3, the COD removal can be as high as 50%. Better effects of COD removal are obtained when the concentrations of ozone supplied and the initial COD concentration are higher [1, 3, 7].

The literature data [3] concerning the removal of detergents from wastewater is scarce being almost exclusively confined to anionic detergents. The 86% removal, obtained in the present investigations, is in accordance with these data. The maximum of non-ionic detergents amounted to 62%.

7. CONCLUSIONS

1. From preliminary laboratory investigations on the susceptibility of different dyes to ozone oxidation it follows that 10-14 mg O_3/dm^3 applied for 5-40 minutes resulted in 70-90% colour removal of dyes from the glacial, dispersed, reactive and indigosols groups. Colour removal of dyes of sulphuric group (70%) and vat group (20%) was lower and required a longer contact time.

2. Ozone oxidation of biologically treated textile wastewater mixed with municipal sewage is especially effective for the removal of colour, COD and anionic detergents. In the one-stage ozonation system the optimum time was 30-40 minutes, and ozone dose 50 g/m^3. In these conditions colour, COD, anionic detergents and non-ionic detergents were removed in 55%, 30%, 86% and 62%, respectively. In the two-stage system the process was completed in shorter time. 15 minute wastewater contact with the 50 mg of O_3/dm^3 dose removed 67% of the colour, 27% of COD, 85% of anionic detergents and 60% of non-ionic detergents.

3. The cost of ozonation process was high — the energy consumption necessary to generate ozone was 1.2 KWh/m^3 of wastewater. However, in comparison with other

methods used in tertiary treatment, no sediment or concentrated waste requiring treatment are formed in this process.

4. Further research should be carried out on the application of ozone with a view of using a multi-stage system which ensures the least possible losses. Alternatively, attempts should be made to decrease treatment costs by subjecting not only biologically treated but also coagulated wastewater to ozonation.

REFERENCES

[1] MAJUMDAR S. B., SPROUL O. J., *Review paper, Technical and economical aspects of water and wastewater ozonation; a critical review*, Water Research, Vol. 8 (1974), pp. 253–260.

[2] WEBER W. J., Jr., *Physicochemical processes for water quality control*, Wiley-Interscience, New York, London, Sydney, Toronto 1972.

[3] WYNN C. S., KIRK B. S., MCNABNEY R., *Pilot plant for tertiary treatment of wastewater with ozone*, EPA Series, EPA–R2–73–146, 1973.

[4] JASIŃSKI B., *Teoretyczne aspekty dyfuzji ozonu przy projektowaniu urządzeń do tej technologii*, Gaz, Woda i Technika Sanitarna, Vol. 9 (1973), pp. 297–302.

[5] CULP R. L., MCWESNER G., CULP G. L., *Handbook of advanced wastewater treatment*, second ed., Van Nostrand Reinhold Company, London, Toronto, Melbourne 1977.

[6] MAJUMDAR S. B., CECKLER W. H., SPROUL O. J., *Communication — inactivation of poliovirus in water by ozonation*, J. Water Poll. Control Fed., 1974, p. 2048.

[7] WĄSOWSKI J. P., *O zastosowaniu ozonu do oczyszczania ścieków*, Gaz, Woda i Technika Sanitarna, Vol. 9 (1973), pp. 294–296.

[8] HUIBERS D. Th., MCNABNEY R., HALFON A., *Ozone treatment of secondary effluent from wastewater treatment plant*, Robert A. Taft Water Research Center, Report No. TWRC–4, 1969.

[9] KOPPE P., GIEBLER G., *Untersuchungen über die Ozonezehrung von Wassern*, Gas, Wasserfach, Vol. 8 (1966), pp. 107–115.

[10] THIRUMURTHI D., *Ozone in water treatment and wastewater renovation*, Water, Sewage Works, Vol. (115), R–106 (1968).

[11] NETZER A., BESZEDITS S., WILKINSON P., MIYAMOTO H. K., *Treatment of dye wastes by ozonation*, Wastewater Technology Centre, Burlington, Ontario, Canada (unpublished).

[12] SNIDER E. H., PORTER J. J., *Ozone treatment of dye waste*, J. Water Poll. Control Fed., Vol. 46 (1974), p. 5.

[13] NETZER A., MIYAMOTO H. K., *The biotreatability of industrial dye wastes before and after ozonation and hypochlorination-dechlorination*, Wastewater Technology Centre, Burlington, Ontario, Canada (unpublished).

[14] ZENZ D., WEINGARDEN M. J., *Ozonation of microstrained secondary effluent*, Metropolitan Sanitary District of Greater Chicago, Research and Development Dept., 1973.

[15] SNIDER P. C., LITTLE L. N., *Characterization and treatment of textile dyeing wastewater*, Summary report presented in part at the 48th Annual Conference of the WPCF, Miami, Florida 1975.

ZASTOSOWANIE OZONU DO USUWANIA SUBSTANCJI REFRAKCYJNYCH ZE ŚCIEKÓW WŁÓKIENNICZYCH

Wykonano badania w skali laboratoryjnej i pilotowej nad określeniem przydatności i efektywności ozonowania ścieków w zakresie usuwania substancji refrakcyjnych pochodzących ze ścieków włókienniczych. Przedmiotem badań były ścieki włókiennicze z przemysłu bawełnianego zmieszane z miejskimi w proporcji 1:1 do 2:1 i wstępnie oczyszczone w procesie osadu czynnego i filtracji.

Stwierdzono, że utlenianie ozonem jest efektywne szczególnie w stosunku do barwy, która jest usuwana w 67% po 15 minutach kontaktu ścieków z dawką ozonu 50 mg/dm^3 w reaktorze dwustopniowym.

Zużycie energii na wytwarzanie ozonu było wysokie i wynosiło 1,2 KWh/m^3 ścieków. Natomiast zaletą tego procesu, w porównaniu z innymi procesami III stopnia oczyszczania, jest niepowstawanie żadnych osadów.

DIE ANWENDUNG VON OZON ZUR BESEITIGUNG VON REFRAKTÄREN SUBSTANZEN DER TEXTILABWÄSSER

Die Versuche zur Beseitigung von refraktären Substanzen die in den Textilabwässern enthalten sind, sind sowohl im Labormaßstab wie in einer Pilotanlage durchgeführt worden. Untersucht wurden Baumwollabwässer die mit dem kommunalen Abwasser im Verhältnis 1:1 bzw. 2:1 vermischt wurden — nach einer vorgehenden biologischen Reinigung mittels Belebtschlamm und anschliessender Filtration.

Die Oxydation mit Ozon ist besonders effektiv gegenüber der Abwasserfärbung, die nach etwa 15 Minuten Kontaktzeit mit einer Ozondose von 50 mgO_3/dm^3 bis zu 67% abgebaut werden konnte.

Der Energiebedarf für die Ozonherstellung war recht hoch und betrug 1,2 kWh/m^3 Abwasser. Der Vorzug dieses Verfahrens liegt darin, daß dabei kein behandlungsbedürftiger Schlamm entsteht.

ПРИМЕНЕНИЕ ОЗОНА ДЛЯ УДАЛЕНИЯ РЕФРАКЦИОННЫХ ВЕЩЕСТВ ИЗ ТЕКСТИЛЬНЫХ СТОЧНЫХ ВОД

Произведены исследования в лабораторном и полузаводском масштабах определения пригодности и эффективности озонирования сточных вод по удалению рефракционных веществ, происходящих от текстильных сточных вод. Предметом исследований были текстильные сточные воды хлопчатобумажной промышленности, смешанные с городскими стоками в соотношении 1:1 до 2:1 и предварительно очищенные в процессе активного ила и фильтрации.

Было выявлено, что окисление озоном является эффективным, особенно по отношению к цветности, которая удаляется в 67% после пятнадцатиминутного контакта сточных вод с дозой озона 50 мг/дсм^3 в двухступенчатом реакторе.

Расход энергии на изготовление озона был высоким и составлял 1,2 кВт· ч/м^3 сточных вод. Преимуществом же этого процесса, по сравнению с другими процессами трёхступенчатой очистки, является отсутствие образования каких-либо илов.