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

ADVANCED OXIDATION OF TEXTILE WASTEWATER FROM POLYESTER DYEING PROCESS

Textile wastewater treatment by biological methods is difficult. The application of ozone, hydrogen peroxide and UV irradiation leads to decomposition of pollutants resistant to biological treatment, thus increasing wastewater susceptibility to biodegradation. In the investigations real wastewater from polyester dyeing, collected in one of Łódź textile plants, was used. The wastewater was treated with ozone, hydrogen peroxide and UV irradiation in all possible combinations. The wastewater samples were analyzed prior to and after treatment by measurement of pH, determination of specific colour and threshold number, COD, BOD_5, TOC, anionic surfactants and soluble substances. The aim of the experiments was to optimize the efficiency of waste degradation by selecting the optimum doses of the oxidizing agents, their mutual interactions and pH of the solution. The best results were obtained in the acid medium for the combination of $O_3 + H_3O^+ + H_2O_2 + UV$.

1. INTRODUCTION

Textile wastewater treatment by biological methods is difficult and troublesome. The method of advanced oxidation ensures a decomposition of toxic substances, including dyes, detergents and other organic compounds present in textile wastewater which are resistant to biochemical degradation [1]–[8].

In our previous studies the results of investigations of advanced oxidation of wastewater from dyeing cotton and bistor were presented [9]–[14]. In the present study the effects of treatment of real wastewater from polyester dyeing are discussed. Beside cotton, polyester is one of the main raw materials processed in the Polish textile industry.

2. MATERIALS AND METHODS

Real textile wastewater from dyeing of polyester with acidic dyes was investigated. This wastewater was taken from one of textile plants in Łódź.

[*] Institute of Knitting Technology & Techniques "TRICOTEXTIL", Łódź, Poland.

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

[***] Department of Bioprocess Engineering, Technical University of Łódź, Poland.

The dyeing wastewater had an intensive red colour (CT – 330), the value of COD was 510 mg O_2/dm^3, while BOD_5 was 125 mg O_2/dm^3. The content of anionic detergents amounted to 31 mg/dm^3 and that of soluble substances 520 mg/dm^3.

Prior to and after treatment the wastewater underwent an analytical control which covered the following determinations:

– specific colour,
– colour threshold (CT),
– pH,
– chemical oxygen demand (COD),
– biochemical oxygen demand (BOD_5),
– anionic detergent content (AD),
– total organic carbon (TOC).

All analyses were carried out according to the Polish Standards. Total organic carbon (TOC) was analyzed in Coulomat 702 Li/C, Ströhlein Instrument.

The experimental system for wastewater treatment consisted of the following elements: an ozonator with equipment, reaction vessel and a system of sorption bulbs (figure 1).

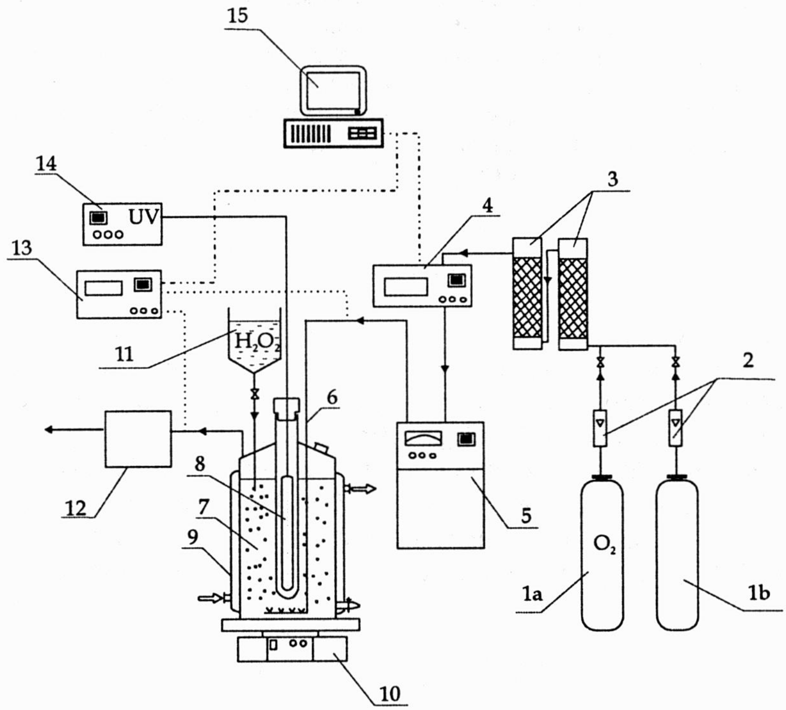

Fig. 1. Schematic of the system for wastewater treatment by advanced oxidation methods: 1a, 1b – steel cylinders with oxygen and neutral gas, 2 – rotameters, 3 – drying columns filled with $CaCl_2$ and P_2O_5, 4 – gas flow-rate meter cooperating with computer, 5 – ozonator, 6 – porous plate, 7 – glass 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 to measure ozone content in oxygen at the reactor inlet and outlet, 14 – UV lamp feeder, 15 – computer

Oxygen from a steel cylinder was pumped to the ozonator by two drying columns filled with $CaCl_2$ and P_2O_5 and mounted on a glass packing, and then by a flowmeter used for monitoring the oxygen flow rate. The ozonator contained an ozone concentration meter ELIMP to measure ozone content in oxygen at the reactor inlet and outlet. 1 dm^3 of wastewater was introduced into a glass reactor, 1.5 dm^3 in volume, 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. The reactor was equipped with a dropper used for dosing H_2O_2. In the center of the reactor there was a quartz tube in which a low-pressure UV lamp, type TNN 15/32 (Heraeus), of 150 W power was installed.

The parameters of wastewater treatment were as follows:

1. In the case of ozonization, the oxygen flow rate was 20 dm^3/h. The concentration of ozone in the gas at the reactor inlet was 45 mg/dm^3 which gave a dose of 900 mg O_3/dm^3 of wastewater. The time of ozonization was 30, 60, 90 and 120 minutes. The degree of ozone conversion decreased with the time of reaction from 70% to about 15%.

2. In the case of UV irradiation of the wastewater, the reaction time was 30, 60, 90 and 120 minutes. The wastewater was mixed by means of oxygen flow at a rate of 20 dm^3/h.

3. Wastewater treatment with hydrogen peroxide consisted in adding 30% H_2O_2 solution in the amount of 1, 2, 3, and 5 cm^3 per 1 dm^3 of wastewater. The time of treatment was 120 minutes. The wastewater was mixed by means of oxygen flow at a rate of 20 dm^3/h.

4. Wastewater treatment with H_2O_2 and O_3 consisted in adding first 30% H_2O_2 solution in the amount of 1, 2, 3, and 5 cm^3 per 1 dm^3 of wastewater. Next, the wastewater was ozonated for 60 and 120 minutes. Oxygen flow rate was 20 dm^3/h. The concentration of ozone at the reactor inlet was 45 mg O_3/dm^3. The degree of ozone conversion decreased with the time of reaction from 70% at the beginning of the reaction to about 15% after 120 minutes. The investigations were carried out in an acidic medium (pH = 4), alkaline medium (pH = 10) and in a slightly alkaline medium (pH = 7.9).

5. A simultaneous ozonization and UV irradiation were used for 60 and 120 minutes. Oxygen flow rate was 20 dm^3/h. The concentration of ozone at the reactor inlet was 45 mg O_3/dm^3.

6. Wastewater treatment with H_2O_2 and UV irradiation consisted in adding first 30% H_2O_2 solution in the amount of 1, 2, 3, and 5 cm^3 per 1 dm^3 of wastewater. Next, the wastewater was UV-irradiated for 60 and 120 minutes. The wastewater was mixed by means of oxygen flow at a rate of 20 dm^3/h.

7. Wastewater treatment with a simultaneous action of three factors: O_3, H_2O_2 and UV irradiation consisted in adding first 30% H_2O_2 solution in the amount of 1, 2, 3, and 5 cm^3 per 1 dm^3 of wastewater, and next a simultaneous treatment with ozone and UV irradiation for 60 and 120 minutes. Oxygen flow rate was 20 dm^3/h. The concentration of ozone at the reactor inlet was 45 mg O_3/dm^3.

In all experiments the process temperature was 295 K (22 °C).

3. RESULTS AND DISCUSSION

The results of advanced oxidation of real wastewater from polyester dyeing using ozone, hydrogen peroxide, UV irradiation and a combination of these factors have proved that these methods are suitable for textile wastewater treatment. Satisfactory results of contaminant decomposition were obtained. This referred mainly to such parameters as colour and surfactants content. COD of the wastewater was reduced to a lesser extent, which followed probably, on the one hand, upon a relatively high initial level, and on the other one, upon a high resistance of wastewater components to decomposition. The efficiency of contaminants removal was higher when a combination of all methods was used than when each method was applied separately.

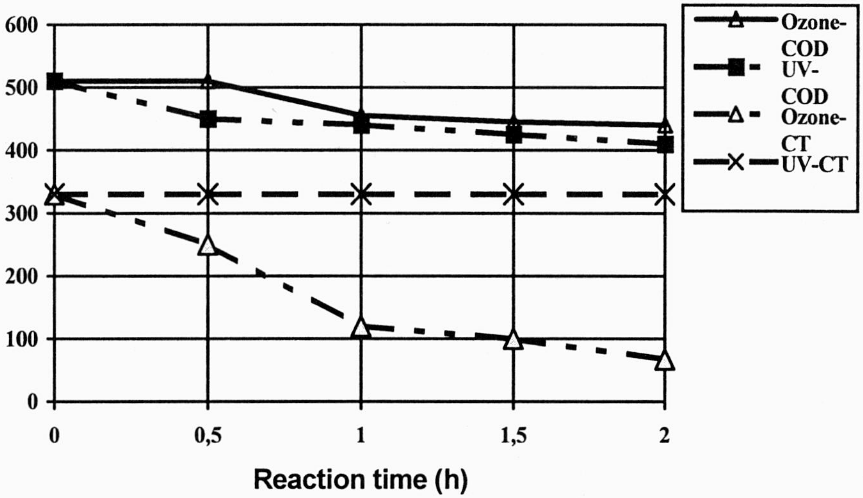

Fig. 2. The effect of reaction time on the colour threshold (CT) and chemical oxygen demand (COD) for wastewater treated with ozone and UV irradiation. Initial parameters: CT = 330, COD = 510 mg O_2/dm^3

The most efficient appeared to be the joint use of all three oxidizing agents (ozone, hydrogen peroxide an UV irradiation) simultaneously and ozonization combined with the treatment with hydrogen peroxide. This referred mainly to COD of the wastewater. In the case of decolouration, a simultaneous ozonization and UV irradiation appeared to be most efficient. It should be noted that acidic dyes applied in the process of dyeing appeared to be resistant to oxidation. For instance, a single use of UV irradiation and H_2O_2 treatment did not produce any decolouration effect (figures 2 and 3). Good effects of decolouration (ca. 90%) were obtained using O_3 + UV + H_2O_2 and O_3 + H_2O_2 (figure 4). A very good decomposition of surfactants was achieved (figures 3 and 4). Even the lowest doses of the oxidizing agents allow us to obtain practically complete decomposition of surfactants. A prerequisite was, however, that at least two oxidizing agents were applied simultaneously. Experimental results of wastewater treatment in terms of the main parameters: COD, BOD_5, AD, CT and TOC, are illustrated in figures 4 and 5.

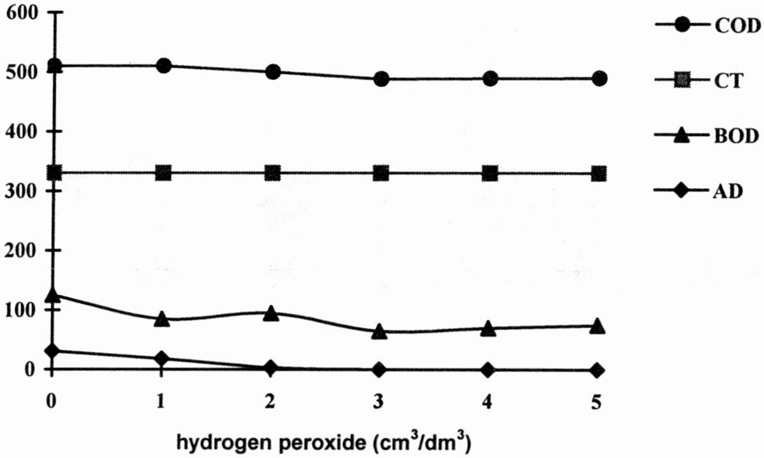

Fig. 3. The effect of hydrogen peroxide on colour threshold (CT), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5) and anionic detergent content (AD). Initial parameters: CT = 330, COD = 510 mg O_2/dm^3, BOD_5 = 125 mg O_2/dm^3, AD = 31 mg/dm^3

Figure 5 shows additionally the value of BOD_5/COD ratio for the wastewater prior to and after its treatment with ozone, hydrogen peroxide, UV irradiation and the combination of all these agents. This value is a measure of wastewater susceptibility to biochemical decomposition, and proves that its biological treatment is possible. Thus, an increase in the value of this parameter is advantageous. Such dependence was observed when most combinations of advanced oxidation were applied. The best results were obtained when wastewater oxidation with ozone was combined with hydrogen peroxide.

The results discussed corroborate the statement that the combonations of oxidizing agents, namely $O_3 + H_2O_2$ and $O_3 + H_2O_2$ + UV, seem to be most efficient. In order to improve more significantly the wastewater treatment, the effect of pH on the oxidation efficiency for these combinations was investigated. Examples of the results are shown in figure 4. They corresponded to the time of treatment with ozone and UV irradiation for 1 h with the addition of hydrogen peroxide in the amount of 5 cm^3 per 1 dm^3 of wastewater. The results discussed proved that the wastewater treatment was most effective when the process run in an acidic medium (pH ~ 4). It manifested itself as a complete decolouration of wastewater and full degradation of surfactants. COD decreased by ca. 60%. In the case of wastewater colour, the worst results of dye decomposition were obtained in an alkaline medium (pH ~ 10). Practically no decolouration was achieved compared to the colour of initial wastewater. In the case of COD and surfactants, the effects were similar to those in which pH was not adjusted

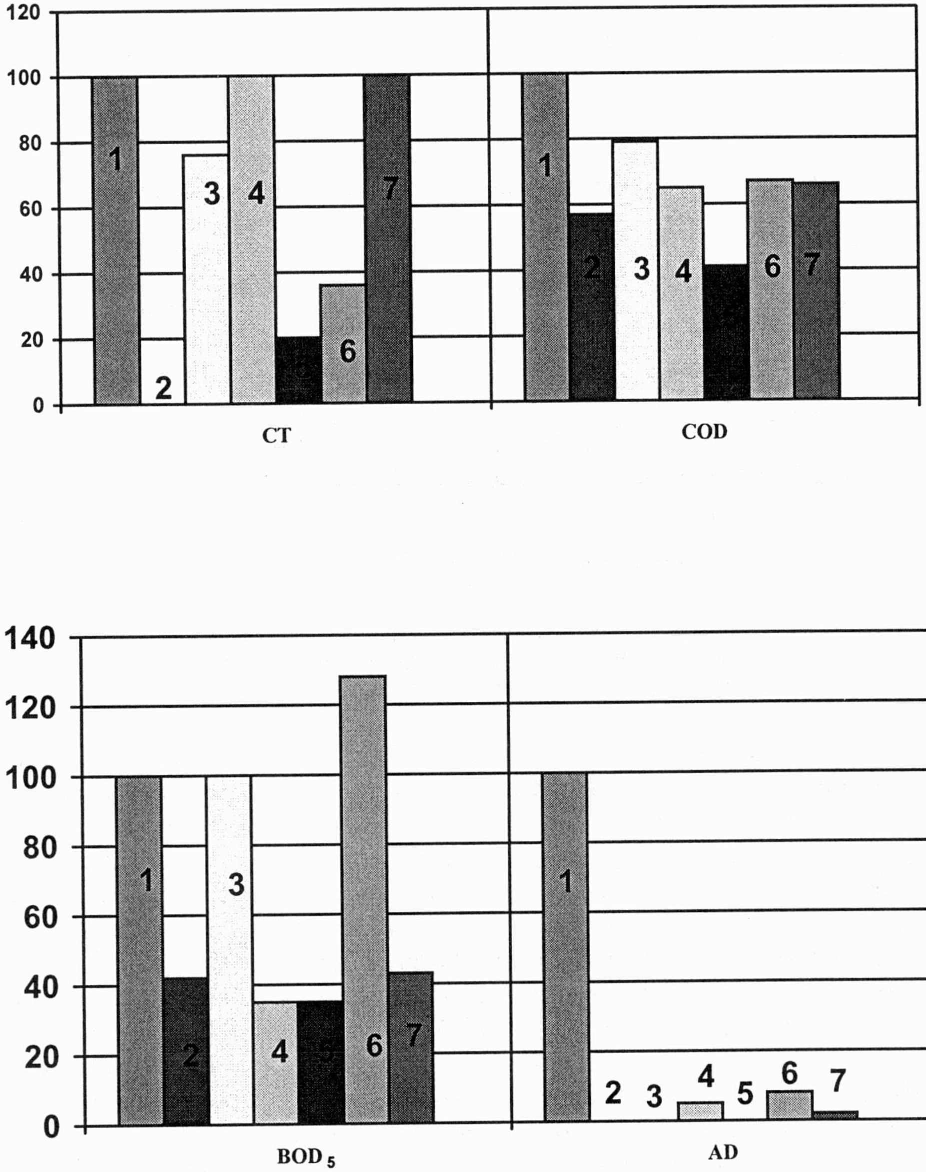

Fig. 4. Basic chemical parameters (CT, COD, BOD_5, AD) of wastewater in percent of the initial values obtained using different combinations of advanced oxidation, depending on the pH value of the solution: 1 – untreated wastewater; 2 – O_3 (1 h) + H_2O_2 (5 cm^3), pH = 4; 3 – O_3 (1 h) + H_2O_2 (5 cm^3), pH = 7.9; 4 – O_3 (1 h) + H_2O_2 (5 cm^3), pH = 10; 5 – O_3 (1 h) + UV + H_2O_2 (5 cm^3), pH = 4; 6 – O_3 (1 h) +UV + H_2O_2 (5 cm^3), pH = 7.9; 7 – O_3 (1 h) +UV + H_2O_2 (5 cm^3), pH = 10; initial parameters: CT = 330, COD = 510 mg O_2/dm^3, BOD_5 =125 mg O_2/dm^3, AD = 31 mg/dm^3

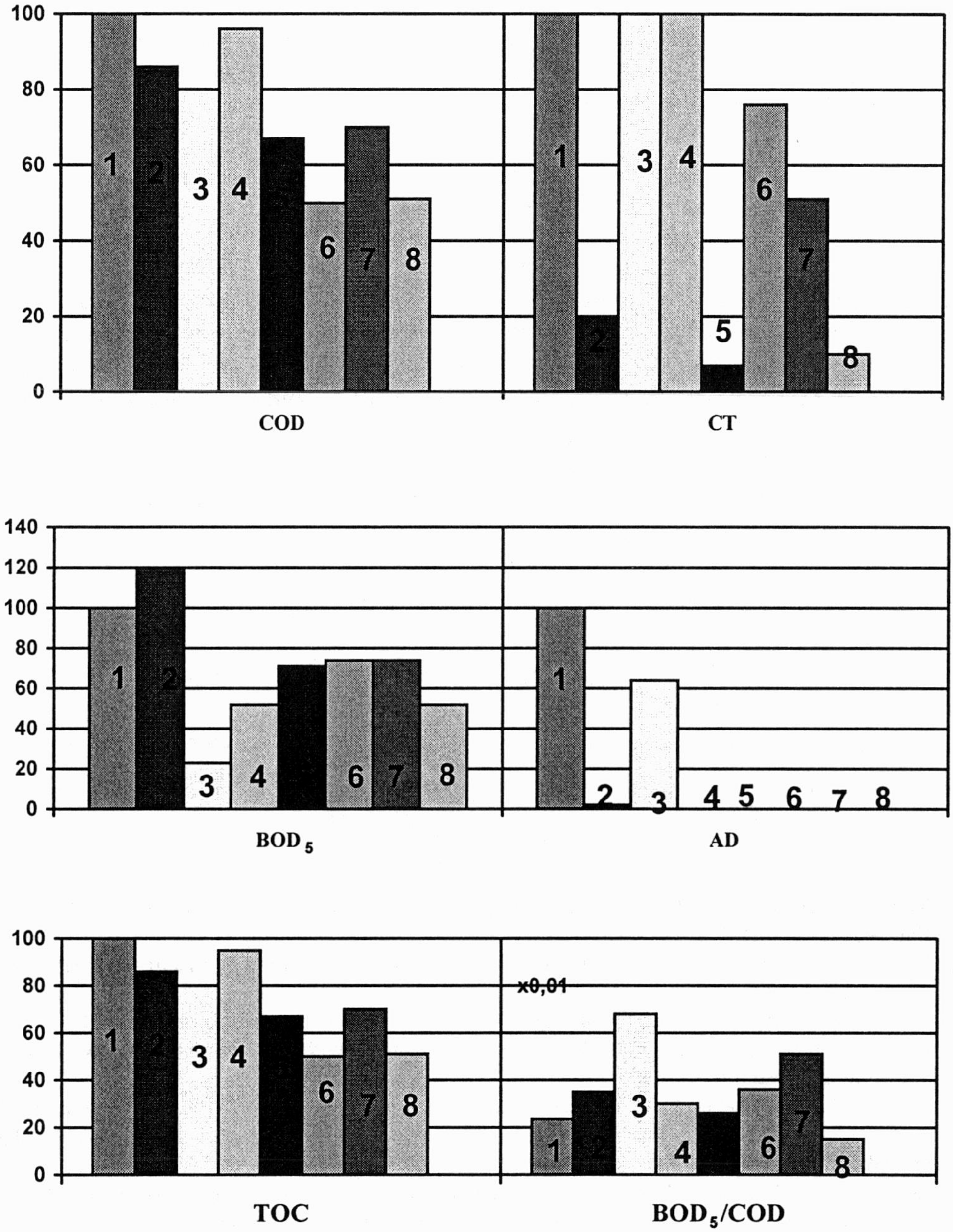

Fig. 5. Basic chemical parameters (COD, CT, BOD_5, AD, TOC and BOD_5/COD) of wastewater in percent of the initial values obtained using different combinations of advanced oxidation: 1 – untreated wastewater; 2 – O_3 (2 h); 3 – UV (2 h); 4 – H_2O_2 (3 cm^3); 5 – O_3 + UV (2 h); 6 – O_3 (2 h) + H_2O_2 (3 cm^3); 7 – UV (2 h) + H_2O_2 (3 cm^3); 8 – O_2 (2 h) + UV (2 h) + H_2O_2 (3 cm^3); initial parameters: COD = 510 mg O_2/dm^3, CT = 330, BOD_5 =125 mg O_2/dm^3, AD = 31 mg/dm^3, TOC = 118.6 mg/dm^3, BOD_5/COD = 0.235

(at the initial pH value being 7.9). From the point of view of further wastewater treatment by biological methods, the most advantageous results were obtained for the case where pH was not adjusted. The value of BOD_5/COD ratio was 0.31, while at pH ~ 4 it was 0.17, and at pH ~ 10 it was 0.13.

4. CONCLUSIONS

The application of the combined methods in wastewater treatment using ozone, hydrogen peroxide and UV irradiation appeared to be advantageous. On the one hand, it enables a better degradation of contaminants, and on the other one, the reduction of oxidant doses, which decreases the treatment costs. The results of contaminant degradation depend on the type and doses of oxidants applied and the type and concentrations of pollutants in the wastewater and pH of the solution. For textile wastewater from polyester dyeing with acid dyes, the best results of treatment were obtained for the combination of $O_3 + H_2O_2$ and O_3 + UV + H_2O_2 in the acid medium. Due to the degradation of toxic compounds, which are resistant to biodegradation, and owing to their transformation into easily recoverable compounds, it is advantageous to combine the processes of advanced oxidation with biological treatment of wastewater.

ACKNOWLEDGEMENT

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NOWOCZESNE UTLENIANIE ŚCIEKÓW POWSTAŁYCH PODCZAS BARWIENIA TKANIN POLIESTROWYCH

Nie jest łatwo za pomocą metod biologicznych uzdatniać ścieki powstające podczas barwienia tkanin. Ozon, nadtlenek wodoru i promieniowanie UV rozkładają zanieczyszczenia, których nie da się usunąć metodami biologicznymi, i zwiększają w ten sposób podatność ścieków na biodegradację. W badaniach użyto ścieków powstających podczas farbowania tkanin poliestrowych w jednym z łódzkich zakładów włókienniczych. Ścieki oczyszczano, używając ozonu, nadtlenku wodoru i promieniowania UV w różnych kombinacjach. Próbki ścieków analizowano przed i po oczyszczaniu, mierząc ich pH oraz określając ich specyficzny kolor i liczbę progową, ChZT, BZT_5, CWO, anionowe surfaktanty i substancje rozpuszczalne. Celem badań była optymalizacja efektywności rozkładu zanieczyszczeń dzięki doborowi pH roztworu, optymalnych dawek utleniaczy i ich wzajemnych interakcji. Najlepsze wyniki otrzymywano w kwaśnym środowisku dla następującej kombinacji: $O_3 + H_3O^+ + H_2O$ po naświetleniu próbek promieniowaniem UV.