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CATALYTIC OZONATION OF AQUEOUS MODEL SOLUTIONS OF REACTIVE DYE BLUE-1

Catalytic ozonation of aqueous solutions of reactive dye simulating textile waste effluents was studied. The efficiency of ozonation was enhanced by nickel oxide catalyst. It was also established that the effect of the catalyst on the removal of the dye Blue-1 depends on pH of the medium and is noticeable at pH 7, whereas at higher pH values it is negligible. The effectiveness of catalytic ozonation and ozonation was estimated based on the degree of conversion. The effect of temperature and the amount of the catalyst on the Blue-1 removal was investigated. At a room temperature and a minimum amount of the catalyst the degree of Blue-1 conversion due to catalytic ozonation was 81% compared to 53% due to ozonation alone under the same conditions. The COD reduction at pH 7 due to catalytic ozonation and the ozonation itself was 50% and 22%, respectively, which evidences an improvement in the dye removal.

1. INTRODUCTION

The textile waste effluents can be characterized by an intense colour due to the highly structured dye molecules. An intense colour of the wastewater effluent, if not removed, would cause disturbance in the ecosystem of the receiving waters.

Ozonation is a powerful method for decomposing organic compounds of different nature which makes it an appropriate method for treatment of textile wastewater. The potential of ozonation for decolorization of textile effluents has been studied in recent years [3], [5] as an alternative to their treatment with chemical agents.

A short time of reaction of ozone with effluent and the lack of increase in effluent present the advantages of ozonation, while the dependence of ozone oxidation potential on pH and formation of toxic intermediate products constitute its disadvantages.

Despite the fact that ozone is a very strong oxidant, complete mineralization of textile dyes in wastewater by ozonation is usually unachievable. Therefore a combined method for complete destruction of dye molecules should be developed.

Positive results of the combination of ozonation and chemical coagulation for treatment of dye waste effluents are reported [15]. It has been observed that the time neces-

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sary for effluent decolorization can be shorter than 10 min. In conjunction with chemical coagulation, COD can be reduced by up to 70%. The effect of ozonation and electro-flocculation on the treatment and reuse of wastewater in the textile industry was studied by GIARDELLI et al. [8]. They reported decolorization of intensely coloured effluents by means of ozone treatment (95–99%) and a decrease in COD up to 60%.

Heterogeneous catalytic ozonation is a novel type of advanced oxidation which combines ozone with the solid-phase metal oxide of absorptive and oxidative proper-ties to achieve mineralization of dissolved organics at a room temperature [12].

An alternative ozonation process catalysed by transition metals has been investi-gated by LEGUBE et al. [11]. The results obtained show that ozonation in the presence of catalysts leads to a significant increase of the TOC removal compared to ozonation alone. In [1], the effect of catalysts in the form of metal salts on ozonation of dye ef-fluents is reported.

Investigations conducted by GARCIA et al. [4] revealed that the content of organic matter in humic substances was reduced by ozonation in the presence of catalysts.

This paper discusses the efficiency of ozone oxidation and the combined effect of ozonation and nickel oxide catalyst in the removal of aqueous reactive dye Blue-1 from model solutions.

2. MATERIALS AND METHODS

The experiments were carried out using model solutions of reactive dye Blue-1 with initial concentration of 110 mg $\cdot$ dm^{-3}, simulating diluted mill effluents.

Ozone was generated by a laboratory ozonizer described elsewhere [13]. The ozone concentration was 5 mg $\cdot$ dm^{-3}. The pre-treatment of the air for ozonation consisted in passing it through silicagel. The constant flow of ozone–air reached the solution of 0.05 dm^3 through a porous glass plate of 20–30 μm pore diameter. All the experiments were carried out at ozone–air rate of 20 cm^3 $\cdot$ min^{-1}. As for a catalytic ozonation experiment the catalyst was in contact only with the solution containing dissolved ozone and dye. Catalyst was added to ozonated solution and stirred permanently. The amount of the catalyst added to dye solution of 0.05 dm^3 varied from 100 mg to 200 mg. The amount of ozone was determined iodometrically in a liquid phase [9].

The concentration of dye was determined spectrophotometrically. The absorbance was measured with a Perkin-Elmer λ uv/vis. The concentration of dye was estimated based on the absorbance at $\lambda_{max} = 516$ nm. A relative standard deviation of the method is ± 6.0%.

The effectiveness of the process was estimated on the basis of the degree of con-version α, %, calculated from the formula $C_0 - C/C_0$.

The nickel oxide was synthesized according to the procedure described in [6]. It was characterized by means of IR, X-ray photoelectron spectroscopy (XPS), X-ray

diffraction and chemical analysis. The chemical analysis proved that the content of total oxygen O* approaches 7%. The specific surface area of the catalyst (particle size of 0.3–0.6 mm) determined by conventional low-temperature nitrogen absorption according to the BET method was 30 $m^2 \cdot g^{-1}$.

3. RESULTS AND DISCUSSION

The oxidation potential of ozone ranges from 2.08 V in acidic solutions to 1.4 V in alkaline solutions. Therefore the oxidizing power of ozone depends on pH of the medium.

Ozone always reacts according to two different mechanisms: direct reaction of ozone with organic compounds and indirect reaction by free hydroxyl radicals. In the direct ozonation, dissolved pollutants are oxidised with ozone molecules, whereas in the indirect reaction ozone decomposes to highly reactive hydroxyl radicals (OH·). The concentration of OH· radicals increases with the increase of pH [10]. The direct reactions are often slow but highly selective. On the other hand, the indirect reactions are highly effective but less selective [2]. The hydroxyl radicals are generated by ozone decomposition and catalyzed by hydroxide ions or intermediate products of decomposing-promoting properties. Therefore pH influences the relationship between the oxidation potential and decomposition behaviour of ozone. The decomposition rate of ozone is affected by pH, which allows us to determine quantitatively the ratio of direct/indirect ozonation by studying the kinetics of ozonation of aromatic dyes [16]. Ozone and hydroxyl radicals generated in aqueous solutions are capable of opening aromatic rings. During the ozonation of dyes they lose their colour by the oxidative cleavage of chromophors.

The effectiveness of ozonation can be enhanced by oxidative properties of catalytic systems. The nickel oxide system is characterized by a high content of active oxygen O* and high oxidation degree.

3.1. EFFECT OF INITIAL pH

The effectiveness of ozonation depends on pH of the medium. Investigations conducted by CHRISTOSKOVA et al. [7] show that the activity of the nickel oxide catalytic system in the liquid-phase oxidation strongly depends on pH. At pH ≥ 10 the effectiveness of catalytic degradation of the substrate decreases. Our investigations [14] indicate that in contrast to catalytic oxidation the effect of ozonation is stronger in alkaline medium. Consequently it is interesting to investigate the possibility of destructing aqueous solutions of dye by catalytic ozonation.

Figure 1a shows the effect of pH on the rate of dye degradation during ozonation. It can be seen that with the increase in solution pH the dye decomposition increases.

The reduction in dye concentration is higher at pH 10, which is due to the higher concentration of hydroxyl radicals at pH 10. The decrease in dye concentration was monitored by recording UV spectra of solutions ozonized at pH 7.0 and pH 8.5 (figure 1b, figure 1c).
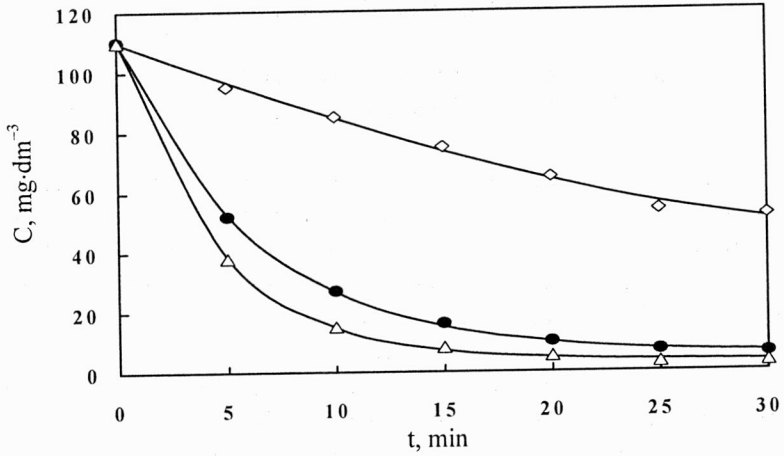

Fig. 1a. The effect of the time of ozonation on the dye concentration at various pH values:
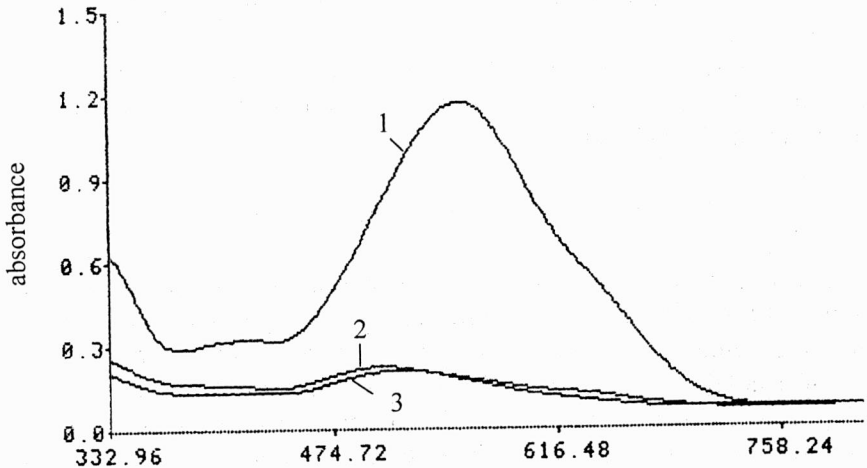$T = 298$ K; -◇- pH 7.0, -●- pH 8.5, -△- pH 10.0

Fig. 1b. UV spectra of: 1 – unozonized dye; 2 – dye ozonized at pH 7.0;
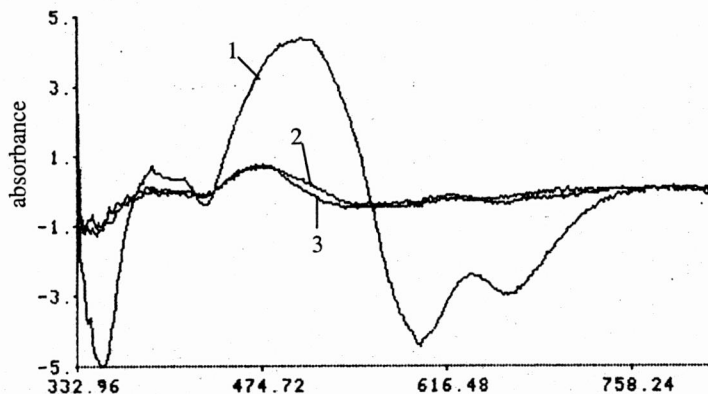3 – dye ozonized at pH 8.5

Fig. 1c. UV–D' spectra of: 1 – unozonized dye; 2 – dye ozonized at pH 7.0;
3 – dye ozonized at pH 8.5

In order to study the effect of the catalyst under the same operating conditions, the experiment was carried out in the presence of 100 mg of the catalyst. The results obtained are shown in figure 2a. In this case, the combined effect of ozone and the catalyst on the rate of decomposition is considerable at pH 7.0, whereas at higher pH values there is only a slight enhancement of the dye decomposition. This can be explained by the highest oxidizing power of ozone in the alkaline medium and low activity of the catalyst at pH 10. The UV-spectra demonstrating the decrease in the dye concentration during the ozonation alone and in the presence of catalyst at pH 7.0 are shown in figure 2b, c. It can be seen that catalytic ozonation leads to a complete degradation of the dye.
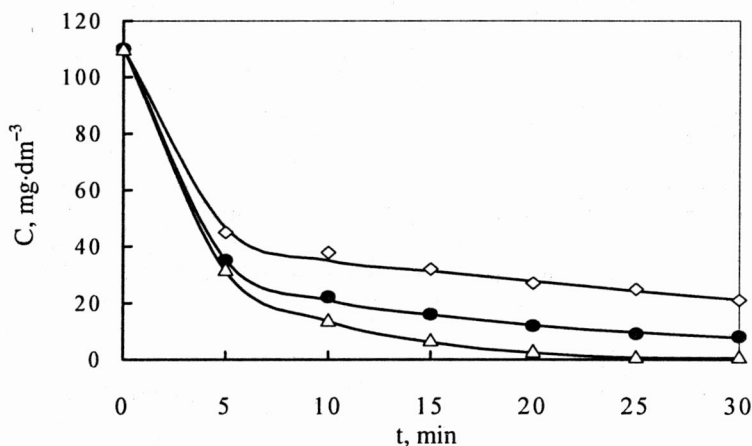

Fig. 2a. The effect of the time of catalytic ozonation on the dye concentration at various values of pH:
$T = 298$ K; -◊- pH 7.0; -•- pH 8.5; -∆- pH 10.0
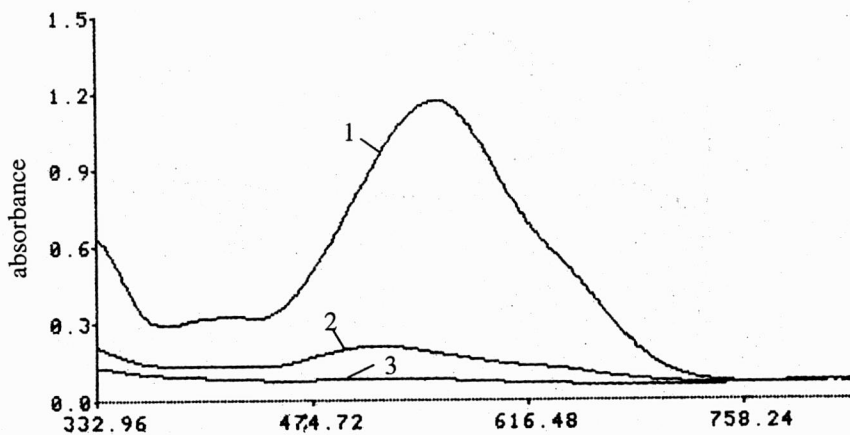
Fig. 2b. UV spectra of: 1 – unoxidized dye; 2– ozonation at pH 7.0;
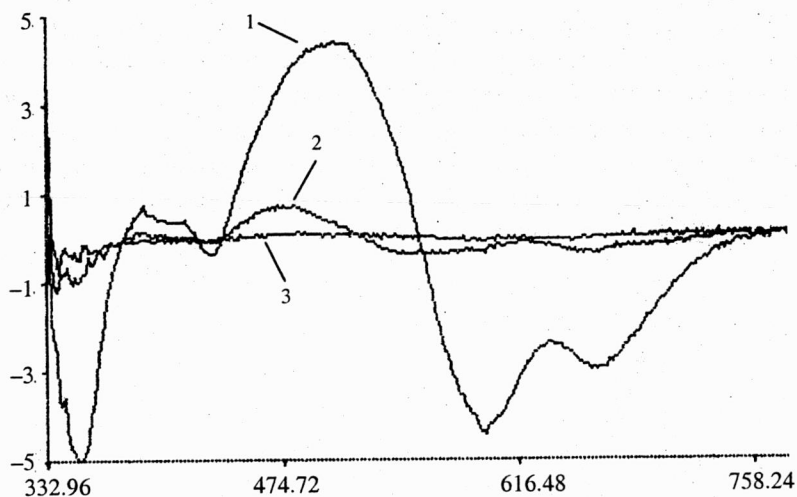3 – catalytic ozonation at pH 7.0

Fig. 2c. UV–D' spectra of: 1 – unoxidized dye; 2– ozonation at pH 7.0;
3 – catalytic ozonation at pH 7.0

3.2. EFFECT OF TEMPERATURE AND THE AMOUNT OF THE CATALYST

Figure 3 presents the effect of temperature on catalytic ozonation at pH 7.0. It shows that at a room temperature (298 K) the reduction in dye concentration is higher.
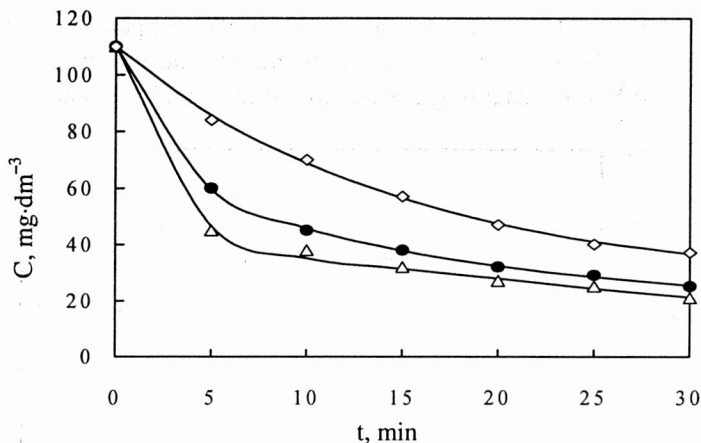
Fig. 3. The effect of the temperature on the dye concentration in catalytic ozonation: pH 7.0, amount of catalyst 100 mg, -◊- T = 283 K, -•- T = 308 K, -Δ- T = 298 K

The amount of the catalyst was varied in the range of 100–200 mg. Figure 4 illustrates the degradation of the dye investigated at pH 7.0 and 298 K in the presence of different amounts of the catalyst. It indicates that catalytic ozonation is most effective at a minimum amount of the catalyst.
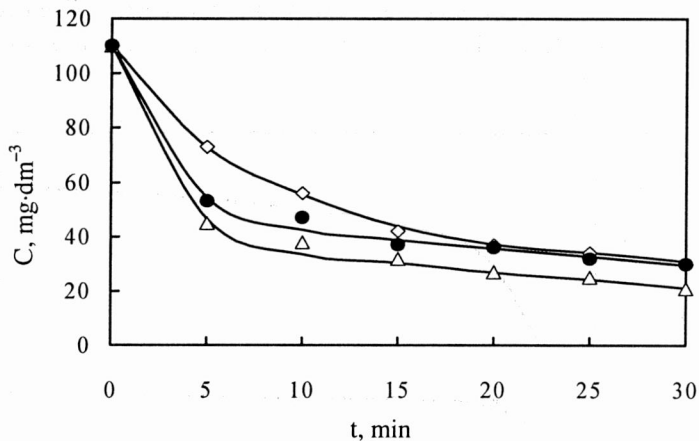

Fig. 4. The effect of the quantity of catalyst on the dye concentration in catalytic ozonation: T = 298 K, pH 7.0; -◊- 150 mg, -•- 200 mg, -Δ- 100 mg

The effect of a combined action of ozone and the catalyst is shown in figure 5, which presents the dependence of the time of ozonation and catalytic ozonation at pH 7.0 on the degree of conversion α (%). It can be seen that in 10 min the degree of

conversion during catalytic ozonation increases to 65% compared to 23% during ozonation alone. This indicates that at a room temperature and minimum amount of catalyst the range of pH values enabling destruction of dye can be extended.
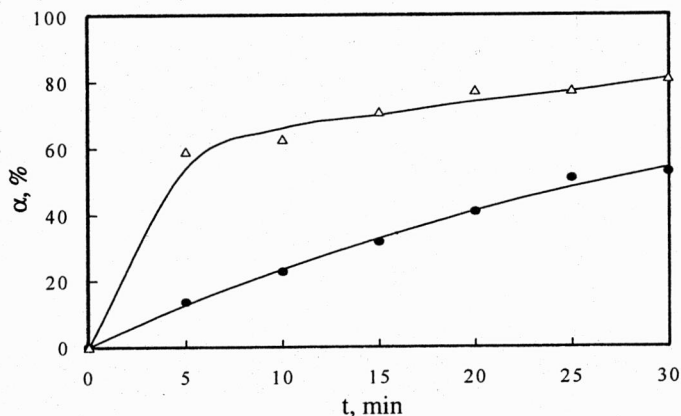

Fig. 5. Dependence of the degree of conversion α on the time of ozonation and catalytic ozonation: $T = 298$ K, pH 7.0, amount of catalyst 100 mg; -Δ- catalytic ozonation, -$\bullet$- ozonation

By comparing the obtained values of α at pH 10.0 during catalytic degradation and catalytic ozonation (figure 6) it can be concluded that catalytic ozonation is more effective than catalytic degradation under the same conditions. The results for catalytic degradation were obtained by using only a catalyst of the same amount (100 mg per 0.05 dm^3 of dye effluent).
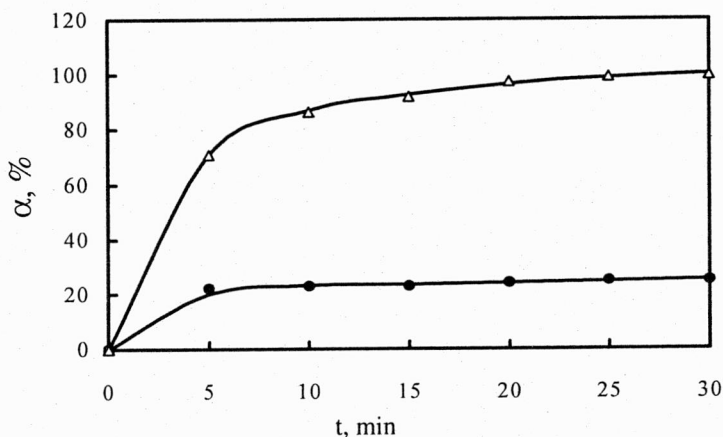

Fig. 6. Dependence of the degree of conversion on the time of catalytic ozonation
and catalytic degradation:
$T = 298$ K, pH 10.0, amount of catalyst 100 mg; -Δ- catalytic ozonation, -$\bullet$- catalytic degradation

Typically ozonation rarely produces complete impurity mineralization to CO_2 and H_2O but leads to such products of partial oxidation as organic acids, aldehydes and ketones. A relatively small COD reduction during dye ozonation is attributable to the fact that the structured polymer dye molecules are oxidized by ozonation to small molecules, which still possess a considerable amount of COD.
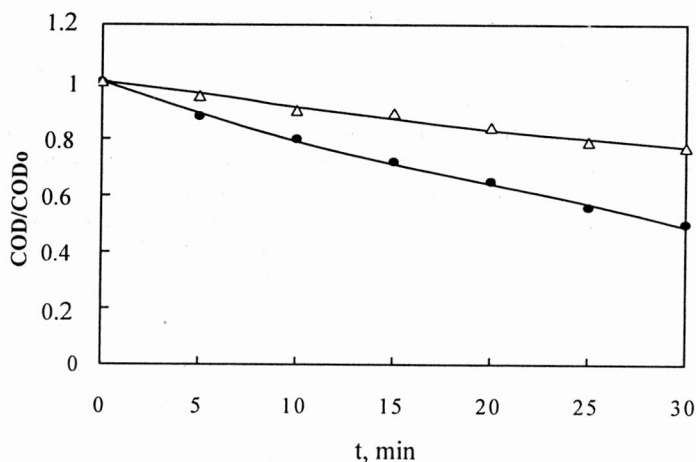

Fig. 7. Dependence of COD elimination on the time of ozonation and catalytic ozonation: $T = 298$ K, $COD_o = 316$ mg O_2 dm^{-3}; -△- ozonation, -●- catalytic ozonation

The COD reduction during ozonation alone and catalytic ozonation is shown in figure 7. The COD reduction during ozonation reaches 22% for ozonation alone and approaches 50% for catalytic ozonation. This evidences that catalytic ozonation yields an improvement in the dye removal.

4. CONCLUSIONS

The results obtained for catalytic ozonation of reactive dye Blue-1 confirm the efficiency of the combined effect of ozone and catalyst. This advanced oxidation technology combines the advantages of both ozonation and catalytic degradation. On the basis of the experimental results the following conclusions can be drawn:

• The combined effect of ozone and catalyst on the degree of conversion α (%) is considerable at pH 7.0, whereas at higher pH values it is negligible. This is due to the highest oxidation power of ozone in the alkaline medium and the low activity of the nickel oxide catalyst at pH about 10.

• The highest degree of conversion is achieved at $T = 298$ K and a minimum amount of the catalyst – 100 mg per 0.05 dm^3 of dye effluent.

• The reduction of COD during catalytic ozonation at pH 7.0 is higher than the reduction of COD during ozonation alone.

• The UV-spectra recorded during catalytic ozonation indicate complete degradation of the dye as a result of catalytic ozonation.

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KATALITYCZNE OZONOWANIE MODELOWYCH ROZTWORÓW REAKTYWNEGO BARWNIKA BŁĘKIT-1

Badano katalityczne ozonowanie wodnych roztworów reaktywnego barwnika symulujących ścieki z zakładów przemysłu włókienniczego. Efektywność ozonowania poprawia tlenek niklu użyty jako katalizator. Ustalono, że wpływ katalizatora na usuwanie barwnika zależy od pH środowiska i jest duży, gdy

pH = 7, a niewielki dla wyższych jego wartości. Efektywność katalitycznego ozonowania i samego ozonowania określono na podstawie stopnia konwersji. Badano wpływ temperatury i ilości katalizatora na usuwanie barwnika. W temperaturze pokojowej i przy minimalnej ilości katalizatora stopień konwersji barwnika w wyniku katalitycznego ozonowania osiąga 81% w porównaniu z 53% w przypadku samego ozonowania. Redukcja ChZT przy pH = 7 wskutek katalitycznego ozonowania wynosiła 50%, a wskutek jedynie ozonowania – 22%, co świadczy o lepszym usuwaniu barwnika