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Decomposition of Anthraquinone Dye in the Aqueous Solution during Advanced Oxidation Processes

Introduction

Efficient treatment of many types of wastewater requires (after an initial mechanical treatment) a chemical process in which toxic, hardly degradable compounds would be decomposed into those which can be easily removed from wastewater by biological methods. One relevant method is oxidation, and especially the so-called advanced oxidation process (AOP) which consists in the simultaneous action of several oxidising agents, resulting in the generation of very highly reactive hydroxyl radicals.

In general, the methods of advanced oxidation include application of the following agents:

1. ozone - O_3 (ozonolysis)
2. hydrogen peroxide - H_2O_2
3. UV radiation - UV (photolysis)
4. ozone and hydrogen peroxide jointly - $O_3+H_2O_2$
5. ozone and UV radiation jointly - O_3+UV
6. hydrogen peroxide and UV radiation jointly - H_2O_2+UV
7. ozone, hydrogen peroxide and UV radiation - $O_3+H_2O_2+UV$ used jointly.

Some authors complete this list with:

8. Fenton reagent - hydrogen peroxide in a solution of divalent iron salts - $H_2O_2+Fe^{2+}$.
9. photocatalysis on titanium dioxide - UV/ TiO_2 .

When completing the classification presented above, versions with ionising radiation and different combinations of the Fenton process should be added to the advanced oxidation methods. In literature, this completion of the classification has so far gained some supporters.

10. ionising radiation, mainly gamma radiation - γ (radiolysis)
11. hydrogen peroxide and gamma radiation jointly - $H_2O_2+\gamma$
12. combined use of ozone and gamma radiation - $O_3+\gamma$
13. combined use of ozone, hydrogen peroxide and gamma radiation - $O_3+H_2O_2+\gamma$
14. Fenton reagent and UV radiation jointly
15. Fenton reagent and gamma radiation jointly.

Abstract

The results of investigations into the decomposition of an anthraquinone dye (polan blue E2R) in an aqueous solution by means of advanced oxidation with ozone, hydrogen peroxide and UV radiation are discussed in the paper. The decolouration efficiency in combined systems was compared. The best results were obtained using ozone, hydrogen peroxide and UV radiation simultaneously. Only slightly worse was the version in which ozone and hydrogen peroxide were applied. In industrial processes, when it is sufficient to decolour a solution before reuse of water in a technological cycle, advanced oxidation processes can be applied successfully. For conditions in a given plant, the process should be optimised and an appropriate version should be chosen. It seems that in the present conditions a combined use of ozone and hydrogen peroxide offers the best results.

Key words: decolouration, advanced oxidation, ozone, hydrogen peroxide, UV radiation, hydroxyl radicals, anthraquinone dye.

All the methods listed above were used in the investigation of the oxidation of model objects, and some of them were applied in the treatment of various types of wastewater.

Interest in advanced oxidation methods is a result of their high potential. The chain mechanism of oxidation which involves hydroxyl and hydroperoxide radicals guarantees efficiency and quick rate of the process. The high reactivity and low selectivity of the reaction enable the method to be applied to a large number of organic compounds present in the wastewater. Further advantages include a lack of by-products which can produce secondary pollution of the environment and thus risk over-dosage of the oxidising agents.

Since the 1970s attempts have been made at improving the oxidation processes to make them faster, more efficient and safer for the natural environment, that is in such a way which would not cause secondary pollution.

Garrison was the first to apply advanced oxidation methods to oxidise wastewater from photographic studios, in the form of joint application of O_3 and UV radiation at the wavelength of $\lambda=254$ nm [1]. The same system was used by Prengle for solutions containing pesticides and hydrocarbochlorides [2,3].

Nakayane used the $O_3+H_2O_2$ system for the first time to oxidise wastewater which contained organic compounds (acetic acid, alcohols, ketones, amines, ethylene glycol and others) [4].

The first installation in which AOP was used was built in North Hollywood

(USA) in 1992 [5]. A combined O_3/H_2O_2 method was applied to remove trichloroethylene (TCE) and tetrachloroethylene (PCE) from ground water.

A year later (in 1993), in South Gate near Los Angeles, an installation was built to treat water for consumption purposes where a triple system $O_3/H_2O_2/UV$ ($\lambda=254$ nm) was used [6,7]. The first water treatment installation for industrial purposes was built by IBM.

The next systems built in the USA mainly included installations in which ozone and hydrogen peroxide were used jointly. It was only in 1994, in a military plant in Milan (USA), that a triple $O_3/H_2O_2/UV$ system was used to oxidise explosives which had infiltrated the sewage.

At present, advanced oxidation processes are used in many countries for treatment of drinking water. In the case of industrial wastewater, pilot-plant installations are operating in several countries:

- the tanning industry (Germany);
- the paper industry, wastewater from bleaching (USA, Germany, France);
- the textile industry (USA, Germany, Canada);
- the chemical industry (Spain, USA, Germany);
- the petroleum industry (Estonia);
- the synthetic fuel industry (Republic of South Africa).

Since 1999, over 100 installations using the advanced oxidation method for treating leachates, toxic wastewater in electronic industry and for industrial water recirculation have been operating [8-12].

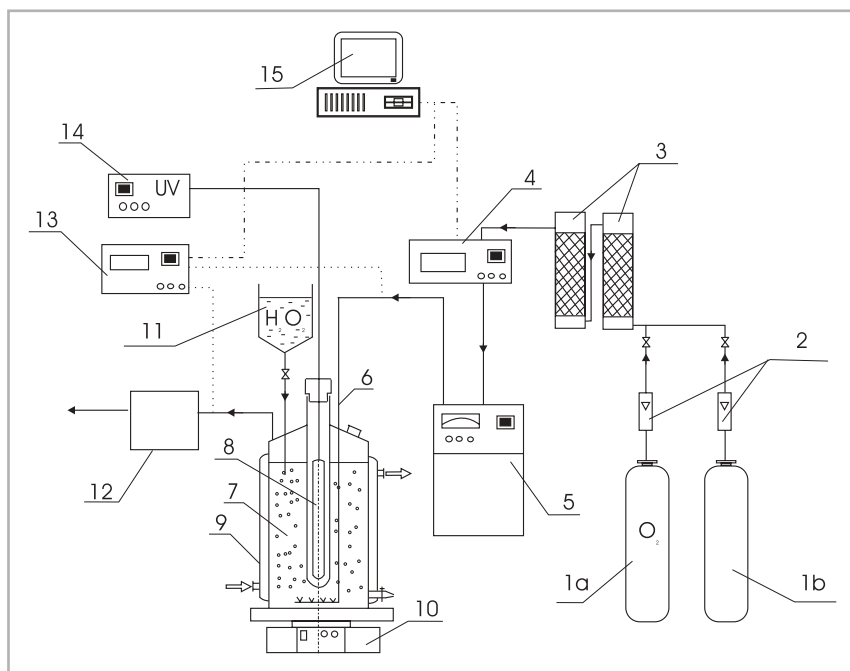


Figure 1. Schematic of experimental rig for studies of pollutant decomposition in water solutions by advanced oxidation methods: 1a, 1b - steel cylinders with oxygen and inert gas, 2 - rotameters, 3 - drying columns filled with CaCl_2 and P_2O_5 , 4 - gas flow meter connected to computer, 5 - ozonator, 6 - gas supply to the solution by porous plate, 7 - glass tank, 8 - quartz tube with UV lamp, 9 - thermostating jacket, 10 - magnetic stirrer, 11 - hydrogen peroxide dropper, 12 - ozone neutralisation system, 13 - ozone concentration meter in the gas mixture at reactor inlet and outlet, 14 - UV lamp supply system, 15 - computer.

$\text{O}_3/\text{H}_2\text{O}_2$ systems are mainly used; O_3/UV installations are less frequently applied. These systems are more efficient and economical than the use of ozone only. O_3/UV systems are applied in small-size treatment systems. In the installations of higher efficiency, the $\text{O}_3/\text{H}_2\text{O}_2$ version prevails.

Attempts at applying advanced oxidation methods for various purposes are the subject of growing interest from both researchers and big industrial companies. As a consequence, an increasing number of publications are appearing, but of greatest importance are the new ideas emerging with the aim of efficiently treating sewage and protecting the natural environment.

The decomposition of dyes in water solutions by advanced oxidation methods was investigated in detail, both with respect to model systems [13-16] and in various types of wastewater [17,18], particularly textile by-products [19-22]. Wastewater decolouration is important when closing water circulation systems in some branches of industry. A decoloured solution can be recycled and reused without the necessity for complete purification via many technological processes.

In our previous study, we presented the applicability of ozone, hydrogen peroxide and UV radiation in decolouration of solutions that contained anthraquinone dye [23]. Now

we shall discuss the results of the combined action of these factors on the decomposition of polan blue in water.

Material and Experimental Rig

The material investigated was the anthraquinone dye polan blue E2R, Acid Blue 62 (C.I. 62045). This is an acid dye used for dyeing polyamide fibres and wool.

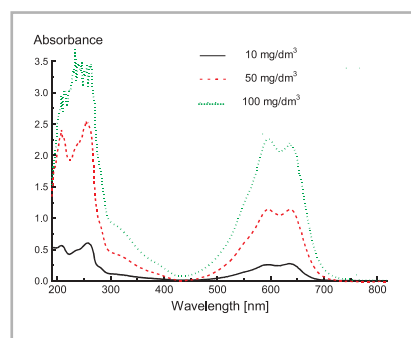
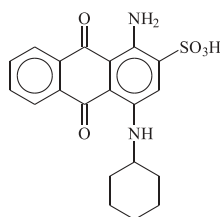


Figure 2. Absorption spectrum of anthraquinone dye polan blue E2R, Acid Blue 62.

A schematic of the experimental system for dye decomposition in the water solution by advanced oxidation methods is shown in Figure 1. The experimental system consisted of an Alford ozone generator and auxiliary equipment, a reactor and a system of sorption washers. Oxygen was pumped from a steel cylinder to the ozonator through two drying columns filled with CaCl_2 and P_2O_5 , and then through a flowmeter for reading the oxygen flow rate. The ozonator was equipped with an ozone concentration meter (Elimp) to measure ozone concentration in oxygen at the inlet and outlet from the reactor. A 1.2 dm³ solution was placed in a Sovirel glass reactor, 1.5 dm³ in volume and equipped with a thermostating jacket. An oxygen-ozone mixture flowing to the reactor was supplied to the solution by means of a porous plate which enabled good gas distribution. In the centre of the reactor there was a quartz tube in which a light source was placed.

Analytical Methods

The solutions were analysed by measuring absorbency in a Hewlett-Packard HP8452A spectrophotometer. Determinations were made in cuvettes 1 mm thick, with water used as a carrier. Spectrum of the solution was analysed in the range from 190 to 800 nm; for quantitative determinations, the absorbency of the solution at the wavelength 620 nm (where the maximum occurred) was taken. The absorption coefficient was $\epsilon_{620} = 0.020706$ [dm³/g·cm], ($M = 400.44$ g/mol). An example of the dye spectrum used in the experiments is given in Figure 2.

Experimental procedure

To investigate the decolouration process, aqueous solutions of polan blue E2R at the concentrations of 100 and 200 mg/dm³ were used. The solution volume was 1.2 dm³. The experimental procedure was as follows.

1. Decolouration of the solutions by means of H_2O_2 and O_3 consisted in adding 1 to 20 cm³/dm³ of 30% H_2O_2 (perhydrol) solution to the wastewater. The flow rate of the oxygen-ozone mixture was 17 dm³/h. Ozone concentration in the gas at the reactor inlet was 7 mg O_3 /dm³, which gives an ozone dose of 99 mg O_3 /h·dm³.

2. When ozone and UV radiation were used jointly, the following process parameters were applied: an oxygen flow rate of 17 dm³/h and 30 dm³/h; ozone concentration in the gas at the reactor inlet was 7 mg O_3 /dm³, which corresponded to an ozone dose of 99 and 175 mg O_3 /h dm³ solution respectively. The source of UV radiation was a Q-400 electric power 400W quartz burner (Hanau GmbH, Germany).

3. Decolouration with H_2O_2 and UV consisted in adding 1, 5 or $20\text{ cm}^3/\text{dm}^3$ of 30% hydrogen peroxide solution to the dye solution with simultaneous UV irradiation. The solution was mixed by oxygen at a flow rate of $17\text{ dm}^3/\text{h}$. The 400 quartz burner Q-was applied.

4. Dye decomposition by simultaneous action of all three factors (i.e. O_3 , H_2O_2 and UV) consisted in adding a 30% hydrogen peroxide solution to the dye solution in the amount of $5\text{ cm}^3/\text{dm}^3$, and simultaneous treatment with ozone and UV radiation. The Q-400 quartz lamp was used. The oxygen flow rate was $17\text{ dm}^3/\text{h}$. Ozone concentration at the reactor inlet was $7\text{ mg O}_3/\text{dm}^3$, which gives an ozone dose of $99\text{ mg O}_3/\text{h dm}^3$.

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

Results and Discussion

Combined action of O_3 and H_2O_2

In the case of the simultaneous action of ozone and hydrogen peroxide in the process of polan blue decolouration, the effect of hydrogen peroxide concentration was investigated. The results obtained are presented in Figure 3. It was found that decolouration took place fastest at a low H_2O_2 concentration of 1 and $2.5\text{ cm}^3/\text{dm}^3$ solution, which corresponded to the peroxide concentration of $0.024\text{ mol}/\text{dm}^3$. Both higher and lower peroxide concentrations caused a decrease in the efficiency of the decolouration. The negative effect was similar when taken in terms of hydrogen peroxide units.

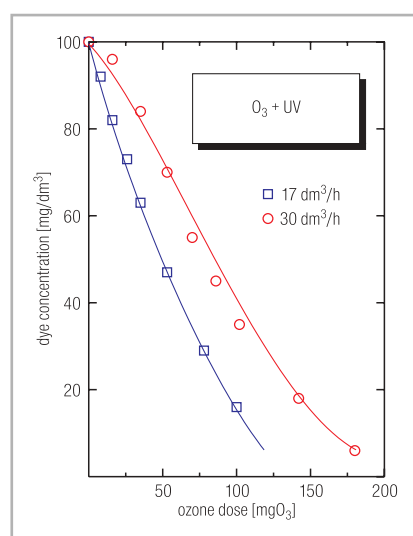


Figure 4. The effect of ozone dose on dye decomposition under the influence of simultaneous action of ozone and UV radiation. Oxygen flow rate 17 and $30\text{ dm}^3/\text{h}$, ozone concentration in the gas mixture $7\text{ mg O}_3/\text{dm}^3$, dye concentration $100\text{ mg}/\text{dm}^3$

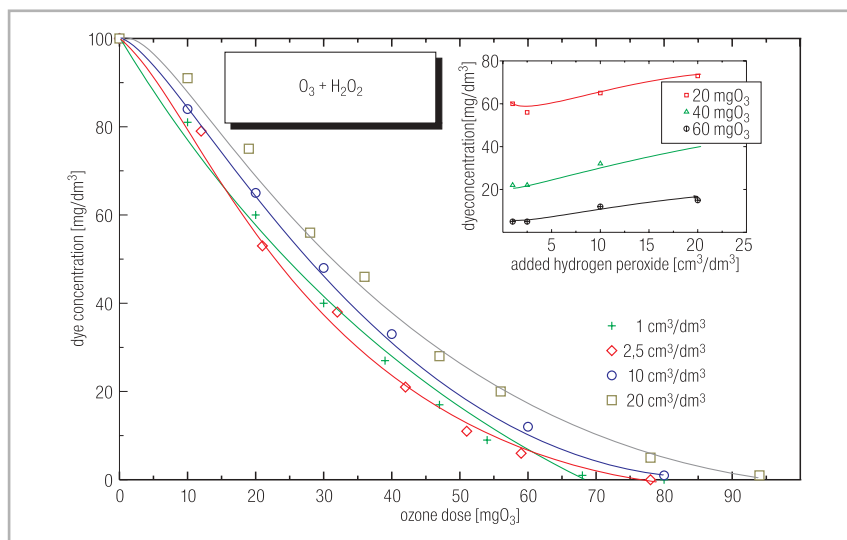


Figure 3. The effect of ozone dose on dye decomposition due to simultaneous action of ozone and hydrogen peroxide. Oxygen flow rate $17\text{ dm}^3/\text{h}$, concentration ozone in gas mixture $7\text{ mg O}_3/\text{dm}^3$, dye concentration $100\text{ mg}/\text{dm}^3$. Amount of added H_2O_2 - 1, 2.5, 10 and $20\text{ cm}^3/\text{dm}^3$ solution. Inset. The effect of added hydrogen peroxide on dye concentration for three ozone doses, 20, 40 and 60 mg O_3 .

If the decolouration efficiency is considered in reference to the amount of ozone reacted, then the maximum dye decomposition rate was obtained for H_2O_2 concentration in the range of 1 and $2.5\text{ cm}^3/\text{dm}^3$ (0.01 and $0.024\text{ mol}/\text{dm}^3$); and with a further increase in the quantity of added peroxide, the decolouration efficiency decreases almost linearly. It is worth noting that the percentage of the unreacted ozone decreases with the increase in hydrogen peroxide concentration from 22.5% for the amount of H_2O_2 reaching $1\text{ cm}^3/\text{dm}^3$ (concentration of about $0.01\text{ mol}/\text{dm}^3$) to 12.4% for $20\text{ cm}^3\text{ H}_2\text{O}_2/\text{dm}^3$ ($0.196\text{ mol}/\text{dm}^3$) when the reaction time was 60 minutes.

Joint action of O_3 and UV

In the case of the combined use of UV radiation and ozone, two experimental series were carried out for the two flow rates of the ozone-oxygen mixture of 17 and $30\text{ dm}^3/\text{h}$, and the constant ozone concentration of $7\text{ mg O}_3/\text{dm}^3$. This corresponded to the ozone doses at the reactor inlet of 119 and $210\text{ mg O}_3/\text{h}$, respectively. The results are shown in Figure 4. Despite the poor results of photolysis obtained earlier in this case, this light source was chosen because we wanted to investigate the process of decolouration in the least favourable conditions.

As expected, a higher rate of ozone dosage allowed us to obtain a higher rate of dye decomposition in time. The time required to obtain an 80% decolouration degree was 55 and 42 minutes. Hence the difference of 13 minutes constituted about 24% of the reaction time at the rate of $17\text{ dm}^3/\text{h}$.

The relationships obtained are reversed when the reaction is investigated as a function of reacted ozone. Better results of dye decomposition are obtained at low gas flow rates, i.e. at slow ozone supply rate to the reaction medium. The amount of non-reacted ozone in a 1-hour reaction for the flow rate $17\text{ dm}^3/\text{h}$ was 8%, and for $30\text{ dm}^3/\text{h}$ it was 12.1%. To obtain an 80% decolouration degree, it was necessary to use an ozone dose of $90\text{ mg}/\text{dm}^3$ at the flow rate, and $17\text{ dm}^3/\text{h}$ and $133\text{ mg}/\text{dm}^3$ at $30\text{ dm}^3/\text{h}$. Thus, the difference was $43\text{ mg O}_3/\text{dm}^3$, which constituted almost 50% of the total amount of supplied ozone at a lower flow rate ($17\text{ dm}^3/\text{h}$).

Combined action of H_2O_2 and UV

When testing the reaction induced by simultaneous action of hydrogen peroxide and UV radiation, quite unexpected results were obtained. For reaction times ranging from 30 to 40 minutes, when the decolouration degree was about 50%, the best decolouration was obtained for a H_2O_2 concentration of $5\text{ cm}^3/\text{dm}^3$ ($0.049\text{ mol}/\text{dm}^3$). Higher decolouration degrees were obtained more quickly for a high hydrogen peroxide concentration of $20\text{ cm}^3/\text{dm}^3$ ($0.196\text{ mol}/\text{dm}^3$). The use of a low H_2O_2 concentration of about $1\text{ cm}^3/\text{dm}^3$ ($0.01\text{ mol}/\text{dm}^3$) gives a practically very poor decolouration of the solution. This is observed in the decolouration curves during the reaction (Figure 5) and in the decolouration degree as a function of added hydrogen peroxide for various reaction times (Figure 5, inset).

Simultaneous action of O_3 , H_2O_2 and UV

The simultaneous application of all three oxidising agents gave interesting results of polan dye decomposition. At

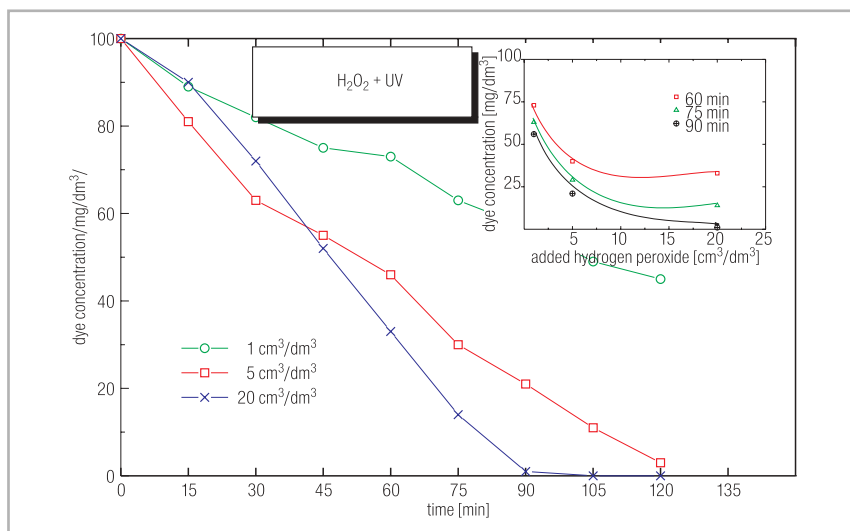


Figure 5. Dye decomposition in time for the process induced by hydrogen peroxide and UV radiation. Oxygen flow rate $17 \text{ dm}^3/\text{h}$, dye concentration $100 \text{ mg}/\text{dm}^3$. Amount of added H_2O_2 - 1, 5 and $20 \text{ cm}^3/\text{dm}^3$ solution. Inset. The effect of added hydrogen peroxide on dye concentration in the solution for three reaction times, 60, 75 and 90 min.

gas flow rate of $17 \text{ dm}^3/\text{h}$, a low ozone concentration of the gas mixture at the reactor inlet of $7 \text{ mg}/\text{dm}^3$, and the average hydrogen peroxide concentration is $5 \text{ cm}^3/\text{dm}^3$ ($0.049 \text{ mol}/\text{dm}^3$), the rate of decolouration increased with the process time (Figure 6).

There is a reaction resembling an abrupt growth in the concentration of the oxidising agents and a continuous increase in the amount of decomposed dye in time. This is undoubtedly a result of the chain character of the formation of hydroxyl radicals. On the one hand, these consist of ozone, and during the oxidation processes they reproduce organic compounds contained in water. On the other hand, their concentration grows due to the photochemical decomposition of hydrogen peroxide and the introduction of subsequent portions of the radicals into the dye decomposition cycles. It is also probable that with the proceeding decomposition, the recovery of coloured substances (deep destruction) becomes less important, which is taken as an enhancement of the decolouration process. The amount of unreacted ozone for a 30-minute reaction and a high decolouration degree (above 90%) was small, reaching 7.3%.

Comparison of the Yield of Advanced Oxidation Processes

To compare subsequent versions of the process of advanced oxidation is a difficult task. The difficulty lies first of all in the necessity of choosing process conditions, in particular the versions whose results will be used for comparison. This not only concerns the problems of ozone concentration and gas flow rate, hydrogen peroxide concen-

tration, lamp spectrum and light intensity, reaction time, etc. Of great importance is the choice of reaction degree, which in most cases determines the smaller or greater differences between particular versions.

The choice of an optimum version on the basis of a chemical effect alone is ambiguous from the technological point of view. Advanced oxidation encompasses unit processes with different investment and operating costs. Undoubtedly the cheapest is the process of oxidation which takes place in the presence of hydrogen peroxide. Ozonation and photochemical processes are characterised by high equipment costs (batteries of ozonators, UV lamps and feeding systems) and operating costs (electrical energy). Therefore, proving that one version is best without stating all its initial conditions may be tendentious.

Because decolouration processes are carried out in textile factories in order to recycle water for production mainly in dyeing departments, and the problem is not to decrease all parameters but solely to eliminate coloration, a comparison will be made for high degrees of the dye reaction. In the case of industrial wastewater treatment, the assumptions are usually different: the barely biodegradable structures should be subjected to preliminary decomposition so that the biological process, which is the cheapest wastewater treatment method, can be efficient and quick. For comparison, the mean values of gas flow rates and ozone and H_2O_2 concentrations were also selected. The comparison is shown in the bar graph in Figure 7.

On the basis of the results shown in Figure 7, one can see that the applica-

tion of two or three combined factors yields significant growth in dye decomposition efficiency. In the case of the decomposition of polan blue solution, there was a positive synergy effect in all cases of the combined use of ozone, hydrogen peroxide and UV radiation. The most interesting results were obtained using jointly $\text{O}_3 + \text{H}_2\text{O}_2$ and $\text{O}_3 + \text{H}_2\text{O}_2 + \text{UV}$. The use of three factors becomes more efficient over longer reaction times (higher reaction degrees). From the technological point of view, the combined application of ozone and hydrogen peroxide is more advantageous. The additional use of UV radiation results in a slight increase in efficiency with a remarkable cost increase. The economic aspect of the advanced oxidation version was thoroughly analysed with respect to textile wastewater [24].

Conclusions

In the case of industrial coloured solutions which do not require accurate treatment but only decolouration in order to reuse them in technological processes, the processes of chemical oxidation, and particularly advanced oxidation, can be used successfully. From the experiments carried out in water solutions of polan blue E2R, it follows that the most efficient version is a simultaneous use of ozone, hydrogen peroxide and UV radiation. However, taking into account the costs of such a process, it seems justified to apply ozone and hydrogen peroxide jointly, which is only slightly worse as far as the efficiency of the process at high decolouration degrees is concerned, but is much cheaper.

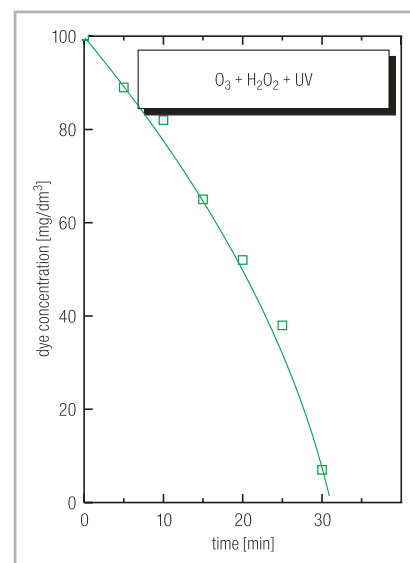


Figure 6. Dye decomposition in time for the process which takes place under the influence of ozone, hydrogen peroxide and UV radiation. Oxygen flow rate $17 \text{ dm}^3/\text{h}$, ozone concentration in the gas mixture $7 \text{ mg}/\text{dm}^3$, dye concentration $100 \text{ mg}/\text{dm}^3$. Amount of H_2O_2 added - 1, 5 and $20 \text{ cm}^3/\text{dm}^3$ solution.

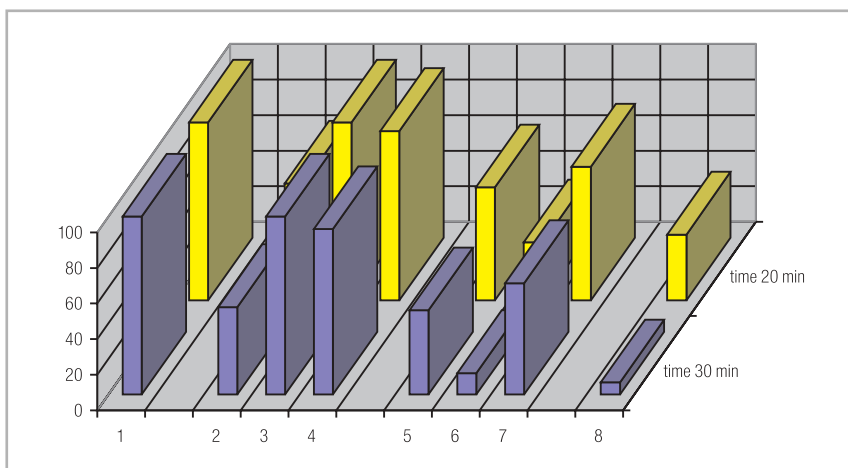


Figure 7. Comparison of the efficiency of polan blue ERN decomposition at the initial concentration of 100 mg/dm^3 using different versions of advanced oxidation for reaction times of 20 and 30 minutes. Temperature 293°K ; 1) initial solution, 2) ozone, oxygen flow rate - $17 \text{ dm}^3/\text{h}$, $7 \text{ mg O}_3/\text{dm}^3$, 3) UV radiation, 4) hydrogen peroxide $5 \text{ cm}^3/\text{dm}^3$, 5) ozone and UV radiation, oxygen flow rate - $17 \text{ dm}^3/\text{h}$, $7 \text{ mg O}_3/\text{dm}^3$, 6) ozone and hydrogen peroxide; oxygen flow rate - $17 \text{ dm}^3/\text{h}$, $7 \text{ mg O}_3/\text{dm}^3$, $5 \text{ cm}^3 \text{ H}_2\text{O}_2/\text{dm}^3$, 7) UV radiation and hydrogen peroxide $5 \text{ cm}^3 \text{ H}_2\text{O}_2/\text{dm}^3$, 8) ozone, hydrogen peroxide and UV radiation; oxygen flow rate $17 \text{ dm}^3/\text{h}$, $7 \text{ mg O}_3/\text{dm}^3$, $5 \text{ cm}^3 \text{ H}_2\text{O}_2/\text{dm}^3$.

When determining the optimum parameters of the advanced oxidation process and taking into account the industrial applications of the method, it was found that the choice of a method on the basis of a single value, e.g. process time, oxidising agent dose or decolouration efficiency, was dubious. The process conditions should be chosen each time, taking into account the specific requirements of any given industrial plant, the quantity of solution being treated, purity requirements, buildings, grounds and funds available. All these elements determine the selection of the method and parameters of wastewater treatment.

In general, no attention should be paid to the temperature of the solution in the technological process. In view of the effect obtained when an optimum temperature is maintained, it appeared unprofitable to maintain temperature at a constant level. Minimising the ozone and peroxide doses may prolong the reaction time and lead to a significant increase of equipment costs. The H_2O_2 concentration may only be chosen only when other values have been selected. However it should be borne in mind that it must decompose completely before any further action on the solution is to be undertaken.

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