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Decomposition of Anthraquinone Dye Acid Blue 62 by the Decoloration of Textile Wastewater by Advanced Oxidation Process

Abstract

The results of the decomposition of anthraquinone dye Acid Blue 62 are discussed in the paper. Different versions of the advanced oxidation process were used for decoloration of the aqueous solution of this dye. Such agents as ozone, hydrogen peroxide, UV and gamma radiation, as well as various combinations of those factors, were applied. The effectiveness of the decoloration reaction induced by the different process versions was compared. In all those processes, the main oxidising species was hydroxyl radical. Therefore, using pulse radiolysis, the rate constant of the primary reaction of hydroxyl radical with the anthraquinone dye Acid Blue 62 molecule was determined. Based on the results obtained, a mechanism of the primary decomposition reactions was proposed.

Key words: anthraquinone dyes, decoloration, advanced oxidation, hydroxyl radical, ozone.

se disturbances in the operation of biological wastewater treatment plants. So, efficiency of the biological treatment is low, and the treated wastewater is insufficiently decolourized.

This refers, among other things, to textile wastewater, whose main feature is strong colouration induced by the residues of dyestuffs unbound during technological processes. The content of dyestuffs in textile wastewater is low (near the limit of technical concentration), although the wastewater is strongly coloured. Some aniline dyes are still visible at the concentration of 0.05 g/m³ [1].

Removing dyes from textile wastewater is a difficult and expensive process. It is not necessary to remove all the dye molecules in the treatment processes. However, it is required to decolour the dye completely, and to transform it into such a chemical form which would be non-toxic and easy to remove by classical methods.

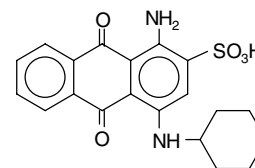
Decolouration processes have been extensively studied in many countries, involving various physicochemical and chemical processes to this end [2-10].

On the basis of the literature data, the most advantageous method of wastewater decolouration seems to be chemical oxidation, and then (if necessary) elimination of decomposition products by biological methods [11-12]. Recently, oxidation pro-

cesses have become predominant, especially advanced oxidation processes (AOPs) consisting in the simultaneous action of several oxidising agents, generating highly reactive hydroxyl radicals [13]. Advanced oxidation induces considerable degradation of molecules, including the destruction of aromatic structures. This decreases the solution toxicity, which largely improves the biodegradation processes, and allows for effective elimination of various dyes from wastewater [14].

Object and Analytical Method

As a model arrangement, the aqueous solutions of the anthraquinone dye Acid Blue 62, C.I. 62045 were selected. It was a pure substance synthesised and purified by repeated crystallisation at the Research Centre of the Boruta Chemical Plant in Zgierz, and subsequently called the Alizarin Brilliant Sky Blue R (ABSBR).



The dye decomposition was followed using a spectrophotometric method in which the spectrum was analysed at the wavelength ranging from 190 to 800 nm. Quantitative measurements were made at

Introduction

Coloured wastewater disposed to surface waters deteriorates the aesthetic values of the waters received after mixing and prevents their recreational and economic use. The presence of dyestuffs causes reduced sunlight transmittance, which results in a decrease in intensity of the assimilation processes of water plants. In such conditions, the ability of self-purification is limited and an indirect unfavourable effect on fish resources is observed. Besides, dyes are compounds that are difficult to degrade biologically, and are usually characterised by high toxicity. They often cau-

maximum absorbency in the visible range at 620 nm. A Hewlett-Packard HP 8452A spectrophotometer was used in the measurements.

Experimental

Investigations by the pulse radiolysis method were made in the Institute of Applied Radiation Chemistry. The radiation source was the 6-8 MeV ELU6 linear electron accelerator. A detailed description of experiments is given by Perkowski et al. [15]. Decolouration of the aqueous solutions of ABSBR under the influence of hydroxyl radicals was carried out by the stationary radiolysis method. The irradiation was performed in a radiation chamber in the Institute of Applied Radiation Chemistry. The research method was described by Perkowski & Mayer [16].

The decolouration of ABSBR aqueous solutions was investigated using the following versions of the advanced oxidation process: ozone, UV radiation, ionising radiation γ , hydrogen peroxide H_2O_2 and a combination of the two factors, ozone + UV, ozone + H_2O_2 and H_2O_2 + UV. The experimental system was described in our previous studies dedicated to advanced oxidation processes [17,18,19].

The dye was oxidised in a glass Sovirel reactor, 1.5 dm³ in volume, and equipped with a thermostating jacket. In the central part of the reactor there was a quartz tube where the light sources were located. The gas flowing to the reactor was supplied to the solution by means of a porous plate. The process temperature was constant at 20°C, the reaction of the solution was natural, i.e. pH ~4 depending on the dye concentration. The reaction mixture volume was 1 dm³, 2 cm³ samples for analysis were taken every 5 minutes.

Other experimental parameters were as follows:

- The process of photochemical dye decomposition was investigated for the ABSBR solution at the concentration of 100 mg/dm³. In the experiments, the light sources applied differed in their power and emission spectra. A high-pressure mercury discharge lamp of power 2x80W, a 150W medium-pressure mercury discharge lamp and a 15W low-pressure monochromatic lamp ($\lambda=254$ nm) were used.
- 10 cm³ hydrogen peroxide in the form of 30% water solution (perhydrol) was added to the dye solution at the

concentration of 100 mg/dm³, which corresponded to the initial concentration of hydrogen peroxide 9.79×10^{-2} mol/dm³.

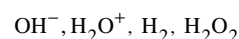
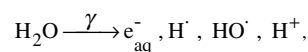
- The ozonation of ABSBR solution was studied at two oxygen flow rates, 17 and 30 dm³/h. The ozone concentration in gas at the reactor inlet ranged from 6 to 35 mg O₃/dm³. The dye concentration was 100 mg/dm³. For ozone production a type 802X BMT laboratory generator was applied. The ozone concentration in gas at the reactor inlet and outlet was measured using a BMT meter, type 963.
- The process of decolouration of the ABSBR solution at the concentration of 100 mg/dm³ using the combined action of hydrogen peroxide and UV radiation was investigated at changing initial concentrations of H₂O₂ and for different dosing rates during the reaction. Hydrogen peroxide was dosed continuously into the 1 dm³ reactor at the rate of 6 and 12 cm³/h. The solutions of H₂O₂ at concentrations 30% and 0.3%, i.e. 9.8 and 9.8×10^{-2} mol/dm³ were used. The reaction mixture was irradiated by a 150 W medium-pressure and 2x80 W high-pressure lamps.
- The decolouration of ABSBR solution in the case of simultaneous use of ozone and UV radiation was studied at an oxygen flow rate of 17 dm³/h and ozone concentration in gas equal to 6 mg O₃/dm³. A high-pressure lamp 2x80 W was used. The dye concentration was 100 mg/dm³.
- A combined action of hydrogen peroxide and ozone on the decolouration of ABSBR solution was tested depending on the concentration in the H₂O₂ system. Four concentrations of H₂O₂ were used: 9.8×10^{-6} , 4.9×10^{-5} , 9.8×10^{-5} and 2.0×10^{-4} mol/dm³. The total amount of hydrogen peroxide was added at the beginning of the reaction. The oxygen flow rate was 17 dm³/h and the ozone concentration in gas at the reactor inlet was 7 mg O₃/dm³. The dye concentration was 100 mg/dm³.
- The decolouration of water solutions of ABSBR by radiation was tested using a stationary method. 5 cm³ of the dye solution at the known concentration was placed in glass ampoules. After saturation of the solution with the appropriate gas (N₂O, argon or oxygen) the ampoules were sealed and irradiated. The following dye concentrations were used: 6, 30, 50 and 100 mg/dm³. Depending on the dye concentration and decolouration rate, the process was in-

vestigated at the lowest range of 0-300 Gy every 25 Gy until the highest range 0-10 kGy, taking measurements every 500 Gy. Three doses were used: 8.3(10-3 Gy/s, 0.19 Gy/s and 1.67 Gy/s.

The reaction of ABSBR with hydroxyl radical

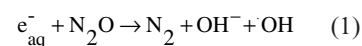
The reaction of the ABSBR dye with the basic products of water radiolysis was investigated using the pulse and stationary method [15,16]. In diluted solutions of organic compounds, at the concentration lower than 1 mmol/dm³, the products of water radiolysis exert the most important effect on their decomposition. In more concentrated solutions, the mechanism of radiolysis of organic compounds is more complex, because their direct radiolysis and the consecutive reactions between decomposition products and the products of water radiolysis play a very significant role. The mechanism of radiolysis is also affected by pH, as well as the presence of oxygen and other factors oxidising and scavenging radicals [20].

The absorption of ionising radiation in water causes various reactions resulting in stable and unstable products of water radiolysis: ions, radicals, ion radicals and molecular products.



If oxygen is present in the solution, additional products appear, the most important being HO₂[·] radical and O₂⁻ ion. To keep a single selected original product of water radiolysis and to eliminate others, various types of scavengers at relevant concentrations are used. A high rate constant of the scavenger with the product of water radiolysis practically eliminates their participation in the reactions of organic compounds present in water.

To assure the action of hydroxyl radicals alone during experiments, the aqueous solution is saturated with nitrous oxide N₂O. This induces the conversion of reducers resulting from water radiolysis, mainly hydrated electron, into oxidising agents, according to the following reaction:



The constant rate of the reaction is 9.1×10^9 mol⁻¹dm³s⁻¹ which under experimental conditions disables the reaction of the dye molecules with the hydrated electron e_{aq}⁻

and causes its quantitative conversion into $\cdot\text{OH}$ radicals.

The spectrum of transient products formed during the reaction of hydroxyl radicals with ABSBR has two characteristic ranges: the first one in which decolouration occurs (220-270 nm and 500-700 nm), and the second, where absorption bands of transient molecules can be observed (280-500 nm). The absorption bands of transient molecules in the range from 300 to 500 nm are similar to the spectra that occur during pulse radiolysis of aqueous solutions of anthraquinones and attributed to the $\cdot\text{OH}$ adduct (hydroxycyclohexadienyl type) [21].

In the spectrum of intermediate products arising from the reaction of $\cdot\text{OH}$ radicals with ABSBR, two characteristic ranges can be distinguished: the first in which decolouration occurs (220-270 nm and 500-700 nm), and the second in which absorption bands of transient molecules (from 280 to 500 nm) can be observed. The absorption bands of transient molecules within 300-500 nm are similar to the spectra occurring in pulse radiolysis of aqueous solutions of anthraquinones and those attributed to $\cdot\text{OH}$ adduct (hydroxycyclohexadienyl type).

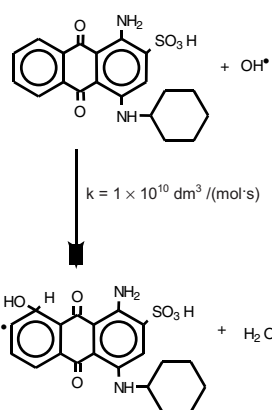
The reaction rate constant for ABSBR and $\cdot\text{OH}$ is $1.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The decay of adsorption measured at equal wavelengths proceeds according to the second-order kinetics. The rate constant of absorption increase and decay as determined is independent of the wavelength, which suggests that in this case we have one product of hydroxyl radical attack on the dye molecule.

The rate constant of the reaction of ABSBR with $\cdot\text{OH}$ reaches $1.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The increase and decay of the rate constant of absorption as determined are independent of the wavelength, which implies that we have here one product of the attack of the $\cdot\text{OH}$ radical on the dye molecule.

The secondary decay of the absorption band within 350-500 nm at the constant rate of $1.3 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ seems to be a result of the dismutation process that causes stable hydroxylated product ($\lambda_{\text{max}} = 425 \text{ nm}$) and reproduction of the dye molecule.

ABSBR decolouration induced by $\cdot\text{OH}$ is a very quick process with rate constant

$1.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, which is similar to the constant found for the formation of an adduct with $\cdot\text{OH}$.



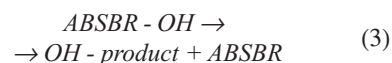
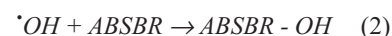
The calculated value of the extinction coefficient of ABSBR adduct with radical $\cdot\text{OH}$ for 390 nm amounts to 2.85, hence the secondary rate constant of the adduct decay reaches the value of $9.0 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

The decolouration of ABSBR solution under the influence of basic products of water radiolysis, in this number hydroxyl radical, was investigated by the method of stationary radiolysis for a solution of natural pH [16]. Changes in the solution spectrum are shown in Figure 1.

Within the reaction, the ABSBR band decays in a visible range. At the same time, a very wide absorption band within 400-500 nm (probably extended up to 700 nm) is observed. This is related to the forma-

tion and then decomposition of the stable product. ABSBR bands in the visible range are decreased to minimum values for doses within the range of $1-2 \times 10^3 \text{ Gy}$. The characteristic band of the product decays when at least tenfold doses are used. The band within the UV range is observed even at $2 \times 10^4 \text{ Gy}$, which implies that the total degradation of the dye molecule requires much higher doses. In the spectra obtained, an isobestic point occurred at 525 nm, which allowed us to calculate the product absorbance coefficient at 430 nm, which is $4.68 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.

Decolouration of ABSBR aqueous solutions when affected by $\cdot\text{OH}$ can be accounted for by the following reactions:



where: ABSBR - OH is the adduct of the dye molecule with the radical $\cdot\text{OH}$.

All these products were identified by pulse radiolysis. The results of pulse radiolysis clearly indicate that reaction (3) presents the dismutation process. This mechanism is confirmed by the obtained concentrations of the product, which are almost equal to the initial concentrations of ABSBR in the irradiated solution.

The product resulting from the adduct dismutation with $\cdot\text{OH}$ exhibits a very wide

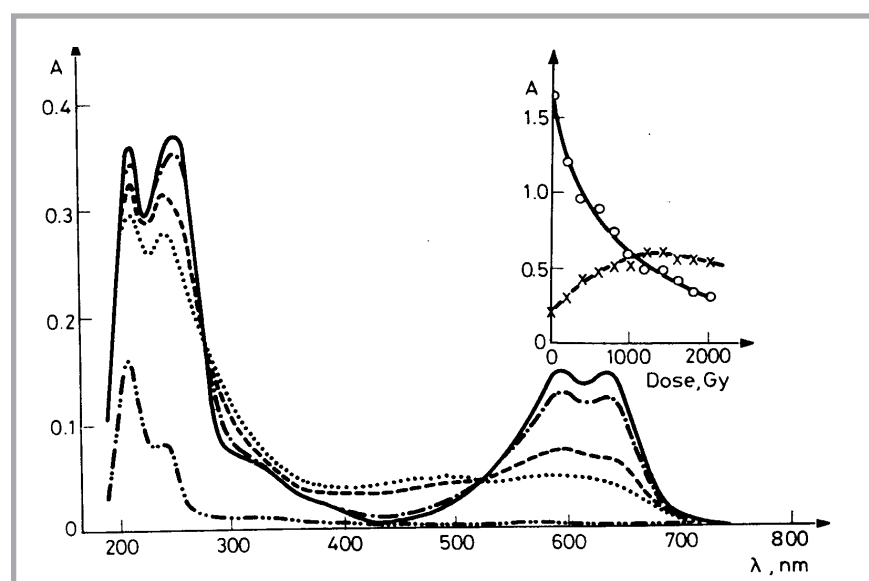


Figure 1. Effects of the dose of γ radiation (amount of hydroxyl radicals) on ABSBR absorption spectrum ($1.3 \times 10^{-4} \text{ mol dm}^{-3}$, in N_2O saturated aqueous solution at $\text{pH}=5$; before irradiation — 0 Gy, - - - $2 \times 10^2 \text{ Gy}$, - - - $1 \times 10^3 \text{ Gy}$, ··· $2 \times 10^3 \text{ Gy}$, - · - · $2 \times 10^4 \text{ Gy}$. Insert: Effects of the dose on ABSBR absorption at 598 nm (o) and formation of the product at 430 nm (x).

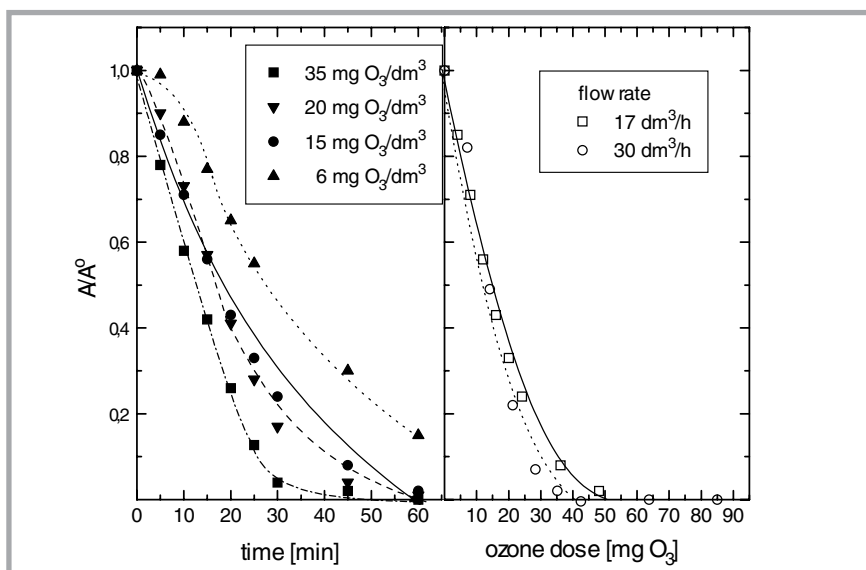


Figure 2. Decolouration of ABSBR solution by ozone. Depending on time, at different ozone concentrations in the oxygen-ozone mixture: 6, 15, 20 and 35 mg O₃/dm³, gas flow rate 17 dm³/h and depending on ozone dose for two gas flow rates 17 and 30 dm³/h at the constant ozone concentration of 17 mg O₃/dm³. Temperature 20°C, dye concentration 100 mg/dm³ and pH ~4.

absorption spectrum, reaching from UV to 700 nm. After the fast decolouration observed for low doses (up to 10³ Gy), the decrease of absorption within 500-700 nm is distorted by overlapping of the absorption band of the initial product.

The product of the reaction of the radical [•]OH and ABSBR, arising from reaction (3), participates in consecutive reactions causing its decomposition (doses > 2 × 10⁴ Gy). At this stage the degradation of the aromatic ring should occur, which is reflected by the decay of absorption bands within UV.

Decolouration of ABSBR solutions in advanced oxidation processes

In general, the main factor is the hydroxyl radical [•]OH. However, in some cases there are also other reactions, e.g. direct oxidation. A more detailed discussion of the theoretical basis of reactions for subsequent versions of the advanced oxidation process can be found in our earlier studies, as well as in many publications and monographs of other authors.

The radiation process has a different character, and although the hydroxyl radical is a dominant factor here, in the reaction

medium we have many reactive products of water radiolysis, radical and ionic, both oxidising and reducing.

Photochemical process

The anthraquinone dye ABSBR appeared resistant to UV radiation. During 1 h photolysis, the solution was decolourised only to some percent. The best results were obtained using a monochromatic lamp, for which the quantum yield of decomposition was determined. The intensity of light absorbed by the solution was calculated on the basis of actinometric measurements. The intensity was 2.45 · 10²⁰ quantum/min dm³. The quantum yield of Acid Blue 62 decomposition at 254 nm in experimental conditions is equal to 0.001 molecule/quantum.

Oxidation by hydrogen peroxide

Hydrogen peroxide is not a strong oxidant and causes a slight ABSBR decomposition. For a dye concentration of 2.1 × 10⁻⁴ mol/dm³ at initial hydrogen peroxide concentration of 9.79 × 10⁻⁴ mol/dm³, after 19 hours of the process an 11% decrease in solution absorbency was obtained; after 24 hours it was 12%, while after 43 hours the colour reduction was 19%.

Ozonation process

At low ozone concentration in gas (6 mg/dm³), the decolouration curve is different than in other cases (Figure 2), where decolouration curves are typical. For the lowest ozone concentration at the initial stage no decolouration is observed, and only after 10 minutes the process of decolouration starts. This can be related to

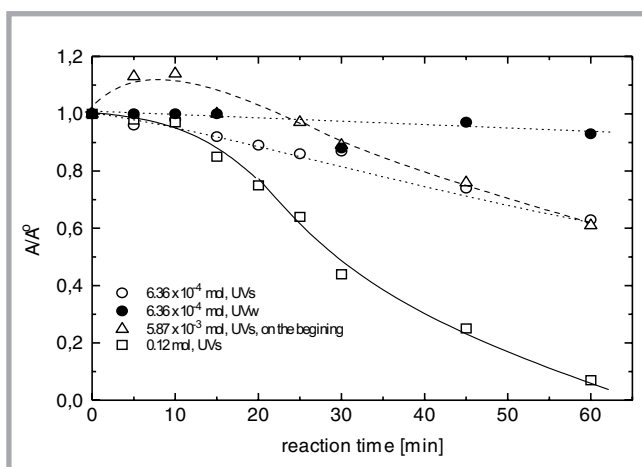


Figure 3. ABSBR decomposition induced by H₂O₂/UV for various amounts and methods of supplying H₂O₂. Hydrogen peroxide was supplied continuously; ○ - 6.36 × 10⁻⁴ mol/h dm³, high-pressure lamp (2 × 80 W); ● - 6.36 × 10⁻⁴ mol/h dm³, medium-pressure lamp (150 W); □ - 0.12 mol/h dm³, medium-pressure lamp. Hydrogen peroxide was supplied in one dose at the beginning of the reaction Δ - 5.87 × 10⁻⁴ mol/h dm³, high-pressure lamp.

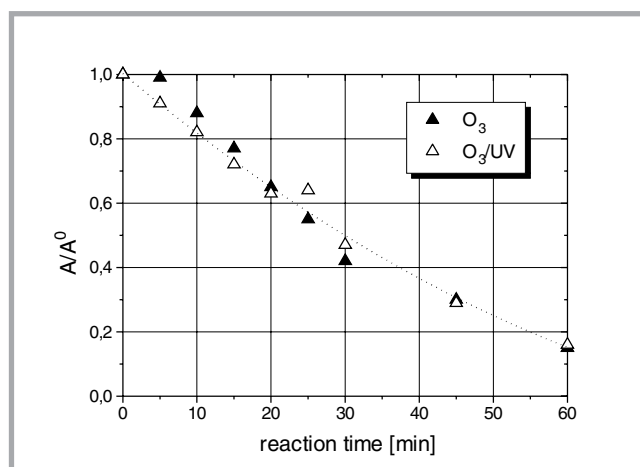


Figure 4. Kinetics of decolouration of aqueous ABSBR solution at concentration 100 mg/dm³ during combined action of ozone and UV radiation, and comparing to ozonation. Gas flow rate 17 dm³/h, ozone concentration in gas 6 mg/dm³. High-pressure lamp 2 × 80 W; ▲ - ozonation, Δ - combined action of ozone and UV radiation.

the slow saturation of the solution with ozone in this case, and also to the hyperchromium effect. At the initial stage of the ozonation process, products with spectra of a similar or slightly higher absorbency at $\lambda=620$ nm can be formed.

It follows from Figure 2 that the dose of ozone added to the reaction is most significant for dye decomposition. The flow rate with which mass transfer conditions are connected has a much smaller impact. Hence, it can be concluded that the ozonation in our experimental conditions was controlled by diffusion.

Simultaneous action of hydrogen peroxide and UV radiation

Decolouration was studied at different initial concentrations of H_2O_2 and various dosage rates during the reaction. Hydrogen peroxide was supplied either continuously to the reactor or in one dose at the beginning of the reaction. Examples of the reaction are shown in Figure 3.

The following conclusions can be drawn from the above results. In experimental conditions, it was more advantageous to introduce hydrogen peroxide continuously than in one dose at the beginning of the process. By increasing the amount of peroxide 200 times such a high decolouration rate was obtained that after 1 hour of the reaction practically a complete decolouration of the solution was achieved. When lamps of similar power and different emission spectra were used, it was found that the medium-pressure lamp with a spectrum richer in ultraviolet enabled better reaction yield than the high-pressure lamp with continuous spectrum. If the process of decolouration is slow, one can observe in its initial period a significant increase in the solution absorbency, amounting to around 10% of the initial value.

The main oxidising factor in this case is undoubtedly the hydroxyl radical that is formed during hydrogen peroxide photolysis. The similarity of decolouration curves obtained in the case of ozonation and during the combined application of H_2O_2 and UV proves that both oxidising factors have a similar impact on the ABSBR chromophore.

Combined action of ozone and UV radiation

The process of ABSBR decolouration in the case of combined action of ozone and UV radiation is shown in Figure 4, where for comparison we can also observe the

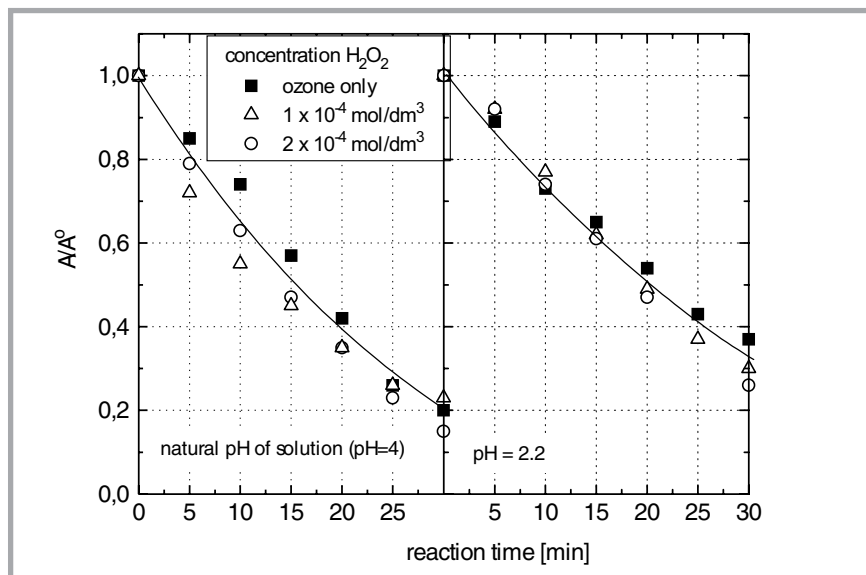


Figure 5. The effect of H_2O_2 concentration (1×10^{-4} and 2×10^{-4} mol/dm³) in the reaction system on dye oxidation in the O_3/H_2O_2 system: ozone concentration - 7 mg/dm³; oxygen flow rate - 17 dm³/h; at two pH values of the solution: for natural pH around 4 and for pH=2.2. For comparison, results of ozonation in the same conditions are presented.

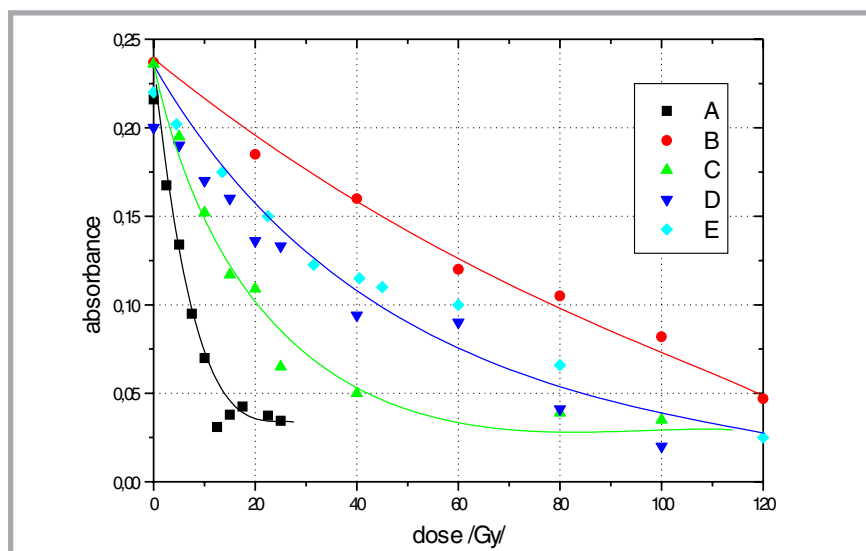


Figure 6. ABSBR decolouration induced by selected products of water radiolysis. A) as a result of the reaction with hydroxyl radicals; B) all products of water radiolysis and oxygen dissolved in the solution (non-deaerated solution) take part in the reaction; C) the reaction with $\cdot OH$ and H^\cdot radicals and with hydrated electron (argon-saturated solution, without oxygen), D) and E) HO_2^\cdot radicals and $O_2^{\cdot-}$ ions (oxygenated solution) take part in the reaction; the reaction was carried out with two doses: 1.66 and 8.33×10^{-3} Gy/s (600 and 3 krad/h). Dye concentration 6 mg/dm³.

decolouration of solution using ozone only.

The use of UV radiation along with ozone in the experimental conditions did not cause any remarkable enhancement of decolouration of the ABSBR solution. Slight differences could be observed only in the initial period of reaction (about 15 minutes), when differences exceed 5%. According to literature, the combined use of ozone and UV radiation leads to increased concentration of hydroxyl radicals,

which should increase the rate of solution decolouration remarkably. The result obtained can be explained only by the lack of hydroxyl radicals in the tested system, owing to a slightly acid reaction of the solution and the high rate constant of the direct reaction of ozone and ABSBR.

Simultaneous ozone and hydrogen peroxide action

The effect of H_2O_2 concentration on the decolouration rate in the case of the combined action of O_3 and H_2O_2 was investigated.

stigated for four H_2O_2 concentrations, namely: 9.8×10^{-6} , 4.9×10^{-5} , 9.8×10^{-5} and 2.0×10^{-4} mol/dm³. Hydrogen peroxide was added in one dose at the beginning of the reaction.

As seen in the diagram (Figure 5), no significant effect of hydrogen peroxide concentration on ABSBR decomposition is observed in the tested range of concentrations. In the initial period there is a slight increase in the rate together with an increase in H_2O_2 concentrations; however, at higher decolouration degrees (>60%) there is no such tendency and the results are practically the same. This is even more clearly observed when the process is conducted in acidic solution at pH=2.2. Such a reaction was much slower and the impact of peroxide concentration was negligibly small.

An increase in acidity of the solution from pH = 4 to 2 caused a slight decrease in the decolouration rate (by around 10%). This effect was observed at both the combined action of H_2O_2 & O_3 and in the case of single ozone use. Also, the main role in this system is played by the direct ozonation of the dye leading to decolouration of the solution. The lack of any positive impact of peroxide presence provides evidence of the lack of hydroxyl radicals formed in chain reactions as postulated in literature. As in the previous case, this can be explained by a predominant role of direct ozonolysis reaction.

Radiation process

The decolouration of ABSBR solutions was studied depending on the factors initiating the reaction. From the point of view of AOPs, oxidants are very interesting, mainly the hydroxyl radicals $\cdot\text{OH}$ and the peroxyhydroxyl radicals $\text{HO}_2\cdot$. The role of these agents is dominant when the dye solution has been saturated with nitrous oxide or oxygen prior to irradiation. In the case of the solution saturated with argon, initiators of the decolouration process are all main primary products of water radiolysis: $\text{H}\cdot$, $\cdot\text{OH}$ and e_{aq}^- . In the case of non-deaerated solution, beside main products of water radiolysis, there is also the HO_2 radical and competitive reactions with oxygen. The results of ABSBR solution decolouration with the application of the

above-mentioned versions of the radiation process are shown in Figure 6.

It follows from this relationship that the most advantageous decolourating agent is the hydroxyl radical. When it occurs alone at high concentrations (other products of radiolysis have been transformed into hydroxyl radicals using N_2O) the process of complete decolouration occurred for the dose equal to around 20 krad. The remaining value of absorbency (ca. 9%) was constant and did not decrease with the dose absorbed. In the solution saturated with argon, when we have oxidising and reducing products of water radiolysis, the process of decolouration is around 2 times slower. The $\text{HO}_2\cdot$ radicals dominating in the oxygenated solution are much less reactive. No effect of the dose on decolouration process was observed in this case. Both at 8.33×10^{-3} and 1.66 Gy/s the process was identical. Worse results were reported for the non-deaerated solution. In that case the amount of dissolved oxygen was lower, and consequently the quantity of reactive peroxide radicals was smaller. So, oxygen took part in consecutive reactions but did not contribute to the primary decolouration of the solution.

Summary of AOPs

The application of hydrogen peroxide as an oxidant or dye photolysis in the presence of oxygen does not bring about very good results of ABSBR decolouration. Reaction time is long, and the necessary light intensity or H_2O_2 concentration is high. Contrary to this, the process of ABSBR decomposition by means of ozone is very efficient and results in a complete decolouration of the solution.

When, beside ozone, such factors as hydrogen peroxide or UV radiation are used, the process rate does not increase. Hence, it can be assumed that the ABSBR ozonation takes place mainly by means of a direct attack of ozone molecule. It is surely so in the case of solutions at pH=2.4. This is also backed up by the fact that the process is faster in the acidic medium than in the neutral and alkaline media, as has been confirmed in the studies of the reaction kinetics by the 'stopped-flow' technique [22]. The other argument is that the rate of decolouration does not increase when ozone and H_2O_2 or UV radiation are used

in combination. The fast reaction of ABSBR molecules with ozone does not enable the formation of hydroxyl radicals or the extension of the chain reaction of oxidation postulated in literature for these versions of AOPs [23].

The reactivity of hydroxyl radicals in relation to ABSBR is revealed not only by the value of primary reaction rate constant determined by the method of pulse radiolysis. High efficiency of decolouration is observed in the radiation process taking place in the presence of nitrous oxide and during the combined use of H_2O_2 and UV radiation. Under the influence of UV radiation itself, ABSBR practically did not decompose at all; however after adding hydrogen peroxide to the reaction medium, 70 to 90% decolouration of the solution was achieved in 1 hour. An increase in the process rate proceeded with an increase in hydrogen peroxide concentration. In the H_2O_2 + UV system we have photochemically generated hydroxyl radicals that, irrespective of pH, decompose ABSBR molecules in an efficient way.

According to the literature data, the anthraquinone dyes are very resistant to external conditions and are barely degradable by UV radiation. They also decompose much more slowly during oxidation in comparison to azo dyes [24].

The relations observed of the decolouration rates of ABSBR solutions are undoubtedly the result of several intermediate reactions with compounds characterised by absorption spectra at the wavelength $\lambda_c=620$ nm. Studies on Acid Blue 62 decomposition by the 'stopped-flow' technique showed that at the first stage of the reaction the hyperchromium effect occurred [22]. This was visible in the case of combined action of H_2O_2 and UV. Due to the formation of a coloured intermediate product, the decolouration rate is much lower than might follow from the determined values of the primary reaction of the hydroxyl radical with ABSBR molecules.

The radiation process showed that the most efficient factor of decolouration was the hydroxyl radical. In the solution saturated with nitrous oxide, the OH formation is most efficient and there are no other

products of water radiolysis. In that case the process of ABSBR decomposition is most efficient. In the case when the solution was saturated with argon and when the reactions with all primary products of water radiolysis took place simultaneously, the rate of decolouration was slower. Saturating the solution with oxygen, which gives HO₂ and O₂⁻ radicals, causes subsequent decrease in the decolouration rate despite their high reactivity. Taking this process as an example, it was shown that the dose ranging from 3 to 600 krad/h had no significant impact. So, it can be concluded that the rate of formation of [•]OH radicals (their concentration) has no effect on the decolouration process, which confirms the high value of its rate constants. The slowest was the process of decomposition in the dye solution which was in contact with the air. Nitrogen dissolved in water decreases oxygen concentration and hampers the formation of hydroxyperoxide radicals. When comparing it with the argon-saturated solution, it may be observed that the other primary products of radiolysis formed during the process did not react with ABSBR molecules, but were subjected to other reactions which were useless from the point of view of decolouration of the solution.

It should be kept in mind that the decolouration effects observed in our study are a result of many consecutive and parallel reactions involving different initiators. Even when analysing the changes in the spectrum of the solution throughout the entire UV-VIS range, we are not able to determine explicitly the efficiency of subsequent oxidants and their effect on final solution decolouration.

Final Conclusions

Anthraquinone dyes belong to the group of most durable dyes, so they are often used in products that must satisfy strict requirements concerning resistance to solar radiation and ambient conditions. This useful feature of dyes is naturally a problem in their neutralisation. The classical processes of chemical and biological oxidation used in their degradation are not always sufficient, and so it becomes necessary to introduce new, more efficient oxidants. This demand can be met by the advanced oxidation processes.

The investigations provide more information on the decomposition of anthraquinone dyes in water solutions. The results obtained were used to develop a general mathematical model of the decolouration process for different versions of AOPs. A practical aim of this work is to optimise the process in industrial conditions. This is very important for local wastewater treatment plants, where the wastewater is subjected only to decolouration to make it suitable for re-use in technological processes.

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