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Decolouration of Model Dyehouse Wastewater with Advanced Oxidation Processes

Abstract
The article presents the results of dye decomposition in model dyehouse wastewater. Different versions of the process of advanced oxidation were used for decolouration. Such agents as ozone, hydrogen peroxide, UV and gamma radiation, and various combinations of these, were applied. In all those processes, the main oxidising agent was the hydroxyl radical. For model dyehouse wastewater, the effectiveness of decolouration reaction induced by different versions of the process of advanced oxidation was compared. The most effective version of the advanced oxidation processes proved to be the simultaneous use of all three agents. In the case of this treatment of dyehouse wastewater, a nearly complete decolouration was obtained.

Key words: *model wastewater, decolouration, advanced oxidation, ozone, gamma radiation.*

Introduction

Decolouration is one of the basic indicators that describe the quality of water used both in households and industry. Most dyes and pigments occurring in nature and used in industry do not reveal any direct high toxicity in relation to living organisms, including man. As they usually occur at low concentrations in wastewater and in water , it may be presumed that removing dyeing substances from water is not a specially difficult and important problem. However, this is not so. The disturbance of biological processes in surface water induced by changes in colour and intensity is a serious problem. This leads to changes in the quantity of light penetrating deeper water layers and the related changes in biological life. Another problem which should not be neglected either is the aesthetic aspect related to tourism and recreation.

So, decolouration is important both in wastewater treatment technology and water conditioning. In general, almost all branches of industry dispose dyestuffs into sewage. Their type and quantity vary, and mainly depend on the type of industrial plant, production size and assortment, and also the technology applied. Undoubtedly, most dyestuff is still discharged by the chemical industry in connection with the production of dyestuff, and by the textile industry in which dyestuffs are used.

Naturally, it would be most advantageous to remove all the impurities contained in wastewater and to obtain pure water. However, the costs of such an operation would be very high and not always justified. This is the case with coloured solutions. In some technological cycles, e.g. in dye industry, it is necessary only to remove the colour completely, and sometimes it is necessary to purify water slightly to enable its re-use as cooling or technological water. This enables the closing of water circulation in factories, which results not only in economic but above all ecological advantages.

An attempt to increase the efficiency of decomposition of the impurities present in the wastewater and to improve the economics of the process results in research on advanced oxidation processes in which advantage is taken of such factors as UV and gamma radiation, as well as the use of ozone and hydrogen peroxide either separately or jointly in double or treble combinations. The literature describes the positive results of this method, both in reference to dyestuff solutions [1-4] and various types of wastewater [5-8].

At this stage of our research, we present the results of experiments with the decolouration of a model textile wastewater, a dyebath, using different versions of advanced oxidation. A detailed description of the experiment has been presented in our earlier studies [9-10]. This paper is a continuation of the studies on decolouration of water solutions that include works on the mechanism of primary oxidation reaction initiated by hydroxyl radicals [11] and the development of a mathematical model of the decolouration occurring when different versions of advanced oxidation with UV and gamma radiation, oxygen peroxide and ozone are used [11].

The Mechanism of Advanced Oxidation Processes

It is postulated that the mechanism of combined action of ionising radiation and ozone is related to a simultaneous use of reactive products of water radiolysis and ozone decomposition in water. This effect was observed for the first time in water solutions of phenol and ethylene glycol [12]. The results are similar when ozone and UV radiation are used jointly.

Ozone decomposition in the aqueous solution gives rise to the formation of peroxide HO_2 radicals, then hydroxyl OH radicals:

$$O_3 + H_2O \rightarrow HO_3^+ + OH^- \quad (1)$$

$$HO_3^+ + OH^- \leftrightarrow 2\,HO_2^{\cdot} \quad (2)$$

$$HO_2^{\cdot} + O_3 \rightarrow OH\cdot + 2\,O_2 \quad (3)$$

At the same time, the primary products of water radiolysis, which were formed as a result of ionising radiation, also form peroxide HO_2 radicals in the reactions with oxygen dissolved in the system.

$$H_2O \rightarrow H\cdot + OH\cdot + e_{aq}^- \quad (4)$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot} \quad (5)$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \quad (6)$$

$$O_2^- + H^+ \leftrightarrow HO_2^{\cdot},\ pK=4.88 \quad (7)$$

When the quantity of ozone in the system is sufficient, as in reaction (3), the $HO_2^{\cdot}$ radicals formed during water radiolysis are transformed into $^{\cdot}OH$ radicals. So, in water solutions exposed to ozone and ionising radiation, apart from the low-yield reactions of immediate decomposition of organic substances (8), first of all their decomposition will take place, caused by the hydroxyl $^{\cdot}OH$ radicals that were formed during water ozonolysis and radiolysis.

$$RH \xrightarrow{\gamma} R^{\cdot} + H \quad (8)$$

$$RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O \quad (9)$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \quad (10)$$

On the other hand, while reacting with ozone, the organic peroxide $RO_2^{\cdot}$ radicals are transformed into $RO^{\cdot}$ radicals;

$$RO_2^{\cdot} + O_3 \rightarrow RO^{\cdot} + 2\,O_2 \quad (11)$$

$$RO^{\cdot} + RH \rightarrow R^{\cdot} + ROH \quad (12)$$

So, the less reactive $RO_2^{\cdot}$ and $HO_2^{\cdot}$ radicals are transformed into more reactive $HO^{\cdot}$ and $RO^{\cdot}$ radicals (3 and 11). Due to their properties, the rate of oxidation of organic compounds increases. The dominant role of $HO^{\cdot}$ radicals in the combined method is confirmed by the results of an experiment with the use of radical scavengers. The values of decomposition yield of phenol and ethylene glycol determined in the radiation-ozonation method indicate that the reaction has a chain nature.

Similar processes of organic compound oxidation, with a predominant role for the reaction of hydroxyl radicals, take place in advanced oxidation. The mechanism for generating $HO^{\cdot}$ radicals in water and their restoration in chain reactions with ozone, hydrogen peroxide and UV radiation has been presented by Benitez [13]. In the literature, there is a detailed description of water radiolysis as well as of the primary and consecutive reactions that take place in it [14]. These problems were also tackled in our studies dedicated to textile wastewater treatment by means of advanced oxidation processes [9,15].

A schematic of the oxidation processes of the organic compounds contained in water induced by hydroxyl radicals is naturally general, and is identical in all AOP versions where the main or the only oxidant is a hydroxyl radical and oxygen is present in the solution. The schematic of such an oxidation process has been presented elsewhere [16].

Materials and Methods

In the experiments, model dyehouse wastewater was used. It contained:

- anthraquinone dye, polan blue E2R (acid blue 62, C.I. 62045) - 0.04 g/dm^3
- azo dye, helion yellow G (direct yellow 44, C.I. 29000) - 0.03 g/dm^3
- azo dye, brown RC (direct brown 2, C.I. 22311) - 0.03 g/dm^3
- anionic detergent, polanol S - 0.3 g/dm^3
- table salt NaCl - 12.5 g/dm^3.

The model dyehouse wastewater was strongly concentrated. It was characterised by an intense dark green colour (colour threshold - CT=1000), a high anionic detergent content - AD content =142 mg/dm^3, and a chemical oxygen demand (COD) reaching 440 mg O_2/dm^3. The wastewater was strongly mineralised, and the content of chlorides was 8000 mg/dm^3. The reaction was neutral pH=7.5. The colour threshold number was determined according to the Polish Standards.

Advanced Oxidation Processes in Model Dyehouse Wastewater

A detailed description of the reaction system, together with a method of carrying out the process and results, have been presented elsewhere [9,10,17]. The following versions of the model dyehouse wastewater treatment were applied: ozonation, oxidation with hydrogen peroxide, UV radiation and gamma radiation, as well as all combinations of these agents, i.e. ozone and UV radiation, ozone and hydrogen peroxide, hydrogen peroxide and UV radiation, γ radiation and ozone, γ radiation and hydrogen peroxide and ozone, hydrogen peroxide and UV radiation. The effects of the gamma radiation dose and exposure rate, reaction and oxygen flow rate were studied. From the results obtained, the following conclusions on the wastewater decolouration can be drawn.

Ozone

The degree of dyestuff decomposition increases with an increase in the ozonation time, i.e. with the applied dose of ozone. Already at short reaction times (ozone doses) a very high colour reduction is obtained. Detailed results of studies on the process of ozonation applied to solutions of dyestuffs and dyebaths are discussed in other work [17].

Hydrogen peroxide

In dyehouse wastewater exposed to hydrogen peroxide, decolouration from 50 to 83% and from 67 to 90% was observed, depending on the quantity of H_2O_2 (5 to 20 cm^3 perhydrol per dm^3 wastewater) and treatment time (1 and 2 hours). Hydrogen peroxide causes quite good decolouration of the wastewater, the most significant factor being its concentration. At large quantities (20 cm^3/dm^3 wastewater) prolongation of the treatment time from 1 to 2 hours does not improve the results of decolouration.

UV radiation

In dyehouse wastewater subjected to UV radiation, decolouration ranged from 67 to 75%. The decrease in dyehouse wastewater colouration is attributed to the processes of dyestuff decomposition induced by the photochemical reaction of oxidation in the presence of oxygen. A slight increase in decolouration at prolonged exposure times is the result of secondary decomposition reactions that lead to the formation of coloured decomposition products.

Gamma radiation

Within the research on radiation process of dyebath decolouration, the effect of the following factors was investigated: the dose and exposure rate of radiation, aeration and oxidation of the solution, gas flow rates and the pH of the bath.

The effect of exposure rate on the decomposition of impurities contained in the dyebath was investigated within the range from 2.5 kGy (0.25 Mrad) to 100 kGy (10 Mrad). Two experimental series were performed: in the first one the wastewater was not oxygenated (a slight oxygen diffusion from the air over the solution might occur), while in the second series a constant flow of oxygen equal to 3 dm^3/h was applied. It was found that both in the case of non-oxygenated and oxygenated wastewater, an increase in the exposure rate caused an increase in the decomposition of impurities. The changes of the most important wastewater parameters are shown in Figure 1.

In the case of the dyebath, irradiation with 10 kGy without oxygenation is insufficient for complete decomposition of dyestuffs. This is indicated by a change in the wastewater colour from dark green into brown/yellow and a decrease of only 50% in the colour threshold number CT. A further increase of the dose up to 100 kGy had practically no effect on colour reduction. Much better results of wastewater decolouration are obtained for oxygenated wastewater. For instance, at the dose 10 kGy and oxygenation rate 3 dm^3/h, the colour reduction was 85%.

The effect of exposure rate on the decomposition of impurities was studied for non-oxygenated and oxygenated dyebaths within the range of 0.014 to 1.4 Gy/s [10,18]. A clear impact of the exposure rate on the degree of solution decolouration can be observed. Better results were obtained at low exposure

rates both in the oxygenated and non-oxygenated systems.

When analysing these results, it was observed that the effect of exposure rate was mainly due to a significant extension of the reaction time, which was particularly important in the case of wastewater oxygenation. A slower reaction at increased concentrations of oxygen dissolved in water guarantees a more efficient decomposition of impurities in water due to radiation.

The effect of oxygen flow rate was investigated within the range of 1 dm^3/h to 30 dm^3/h. It was found that with an increase in the oxygen flow rate, the decomposition of impurities also increased, while the irradiation parameters remained constant. In the systems tested it was most advantageous to apply flow rates ranging from 3 to 10 dm^3/h, which is seen in Fig. 1. Above the rate of 10 dm^3/h dm^3 of solution, no increase in the efficiency of solution decolouration is observed.

Wastewater reaction plays an important role in impurities decomposition by radiation. The highest decomposition was obtained at neutral or slightly alkaline reaction. This dependence occurred in both oxygenated and non-oxygenated systems.

As for oxygenation and aeration, the use of pure oxygen in wastewater oxygenation is too costly a process and practically not applied on an industrial scale. For this reason, differences in the efficiency of the applied dyebath decomposition by radiation in the case of oxygenation and aeration should be checked. Such experiments were carried out for the dyebath at the gas flow rate of 15 dm^3/h. A comparison was made for two radiation doses, 10 and 25 kGy. A slight difference in decolouration was reported at a higher dose, and so the final colour threshold number was 130 for air and 97 for oxygen. Hence, it is possible and economically justifiable to use air as an oxidant.

Combined processes

From the different possible combinations referring to treatment of the model dyehouse wastewater, two versions were applied: γ radiation and ozone, and γ radiation and hydrogen peroxide.

A detailed description of the experiments and a discussion of the results can be found elsewhere [9,10]. In the case of the combined action of two agents, ozone and hydrogen peroxide, ozone and UV radiation, and UV radiation and hydrogen peroxide, and also of the three agents, ozone, UV radiation and hydrogen peroxide, the process and results have been discussed in [19-27].

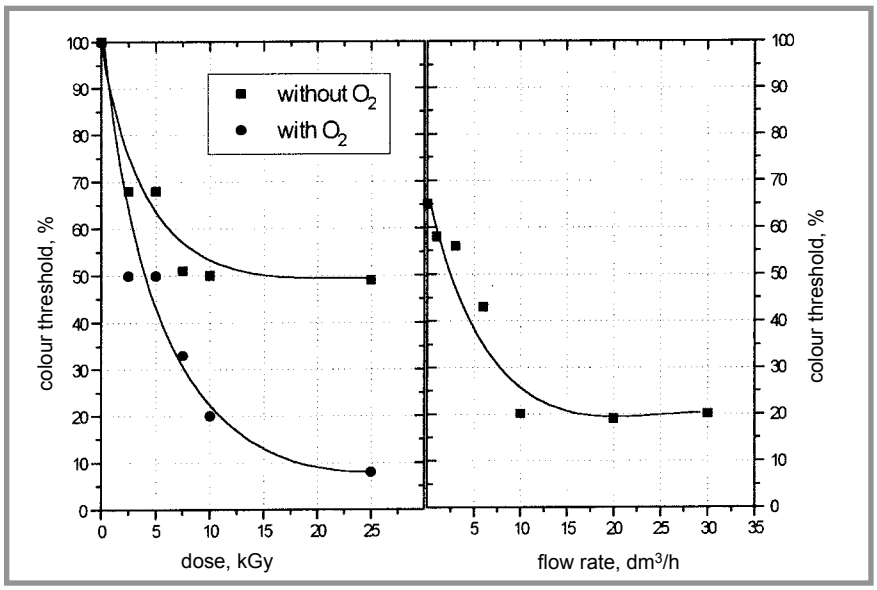

Figure 1. *The effect on colour threshold (CT) of exposure rate for the dyebath: non-oxygenated, oxygenated (left) and effect of air flow rate (right). Dose rate 0.33 Gy/s. Left - flow rate 3 dm^3/h, right - radiation dose 5 kGy.*

γ radiation and hydrogen peroxide

The effect of hydrogen peroxide on dyestuff decomposition in the irradiated dyebaths was investigated, by adding from 0.5 to 1.5 cm^3 30% H_2O_2 solution per 1 dm^3 of wastewater, and next irradiating it with 10 and 25 kGy respectively. The combined use of hydrogen peroxide and gamma radiation in the dyehouse wastewater causes its decolouration. For 1.5 cm^3 perhydrol per 1 dm^3 wastewater and a radiation dose of 25 kGy, a 95% reduction of the colour threshold number was obtained. However, this decrease is only slightly higher, reaching 90%, when solely hydrogen peroxide is used, or 50% when radiation without aeration is applied. A combined action of hydrogen peroxide and gamma radiation improves dyebath biodegradability.

γ radiation and ozone

The results of our studies on the treatment of model dyehouse wastewater with ozone and radiation have been discussed in detail elsewhere [10,27]. The preliminary investigation was aimed at verifying the applicability of the method and its optimal implementation. We had to establish whether there were any differences when ozonation is used jointly with irradiation, or separately at subsequent stages. Therefore, the wastewater was subjected to the following procedure: ozonation (just for comparison), first irradiation and then ozonation (variant I), ozonation and next irradiation (variant II), and finally simultaneous ozonation and irradiation (variant III). This research was mainly of technological significance, because it enabled future adaptation of the technology to specific industrial conditions.

As seen in Figure 2, the joint application of ozone and radiation gave much better decomposition of impurities, as compared to the case when each process was used separately.

The effect of the time of γ-irradiation, ozonation and simultaneous ozonation and γ-irradiation are presented in Figure 3. The best results of treatment were obtained when ozonation and irradiation were used jointly (variant III), and a positive synergetic effect was observed.

Ozone and UV radiation

In dyehouse wastewater subjected to the combined treatment, a significant colour reduction of between 88 and 98.3% was obtained. These results are very similar to those obtained during the ozonation process alone. It seems that in our experimental conditions the role of UV light is insignificant.

Hydrogen peroxide and UV radiation

In dyehouse wastewater subjected to the combined treatment, a 96.7 to 99.2%

colour reduction was obtained during 1 h treatment and 99.2 to 99.5% after 2 hours, so the wastewater was practically totally decoloured. In this variant, the effect of UV light on the action of hydrogen peroxide is very distinct both in the treatment time of 1 and 2 hours.

Hydrogen peroxide and ozone

In dyehouse wastewater subjected to the combined treatment, practically total decolouration was obtained. Colour reduction ranged from 98.3 to 98.8% over the treatment time equal to 1 h, and from 98.3 to 100% after 2 h.

Hydrogen peroxide, ozone and UV radiation

When three oxidising agents were used simultaneously, the dyehouse wastewater was completely decoloured during 1 h treatment.

Final Conclusions

In the case of dyehouse wastewater, no distinct positive effect of the simultaneous action of three factors on decolouration process is observed, although such an effect is very clear in reference to other wastewater parameters. This follows from a very quick process of decolouration and small doses of oxidants necessary to achieve decolouration exceeding 90%. To obtain good results, it is sufficient to use a small dose of hydrogen peroxide below 5 cm^3/dm^3 of wastewater. An increase in the amount of H_2O_2 results in the deterioration of model wastewater decolouration.

The results obtained show that the methods of advanced oxidation are very efficient in wastewater decolouration. Most efficient appeared to be a simultaneous use of three oxidants. In the case of such treatment, total decolouration of the dyehouse wastewater was achieved. Very good treatment results were also obtained when using hydrogen peroxide and ozone jointly. However, they did not differ from the results obtained when all three agents were used simultaneously. Worse treatment results were obtained when applying O_3 and UV (Figure 4). Very good decolouration was achieved by using only wastewater ozonation, which might confirm the role of this process in dyestuff decomposition (the destruction of chromophores) in water solutions.

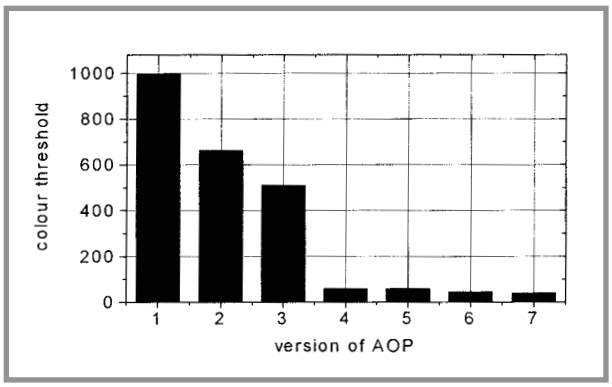

Figure 2. *The effect of treatment method on the colour threshold number, CT, of the dyebath; 1 - crude wastewater, 2 - irradiated, 3 - irradiated and oxygenated, 4 - irradiated and then ozonated, 5 - ozonated and next irradiated, 6 - ozonated, 7 - both ozonated and irradiated. Dose 5 kGy, exposure rate 0.33 Gy/s, ozone concentration 1460 mg/dm³h. Gas flow rate 10 dm³/h.*

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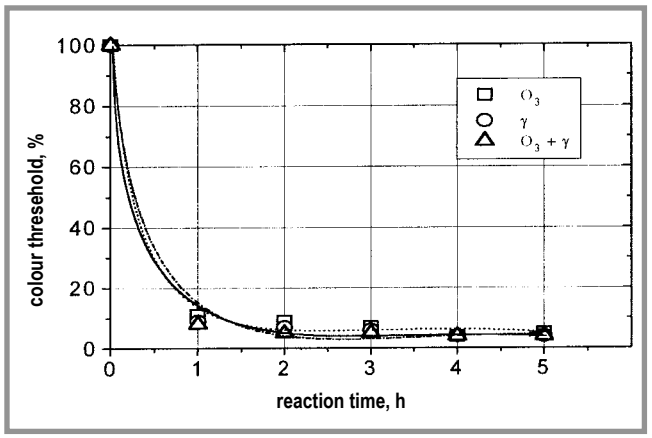

Figure 3. *The effect of the time of irradiation (□), ozonation (○), and simultaneous ozonation and irradiation (Δ) on the colour threshold of the dyebath (expressed in percent of deacy). Dose rate 0.33 Gy/s, ozone supply rate 145 mg/dm³h.*

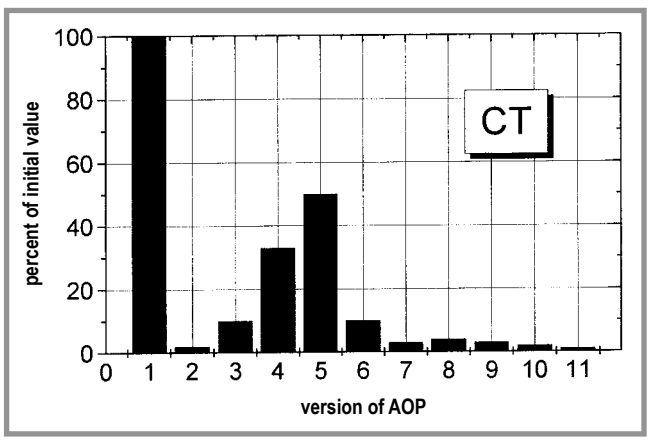

Figure 4. *Comparison of CT changes in the dyehouse wastewater obtained for different variants of the advanced oxidation process (AOP); 1- untreated, 2 - O_3, 3 - H_2O_2, 4 - UV, 5 - γ (25 kGy), 6 - γ + + O_2 (25 kGy), 7 - O_3 + UV, 8 - γ + O_3 (5 kGy), 9 - O_3 + H_2O_2, 10 - UV + H_2O_2, 11 - O_3+ UV + H_2O_2.*

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