

Investigation on dyes oxidation by Fenton's reagent in aqueous medium

A. Józwiak, S. Wiktorowski and A. Dębicka
*Institute of General and Ecological Chemistry,
Technical University of Łódź, 90-924 Łódź, ul. Żwirki 36*

Investigations on oxidation of two dyes: Acid Violet 1 and Direct Blue 74 were carried out with application of Fenton's reagent (hydrogen peroxide in the presence of Fe^{2+} ions). These dyes are representatives of acid and reactive dyes.

The effect of hydrogen peroxide dose and concentration of Fe^{2+} ions on efficiency of colour removal in model solutions of dyes at concentration of 100 mg/L in the pH range from 2 to 4 was determined.

The efficiency of the oxidation process was controlled by measurements of changes in TOC (total organic carbon) and absorbance values (spectrophotometric method) vs. time. Under optimum conditions of the reaction, colour removal was relatively high (90–95%) in the case of both dyes. However, their susceptibility to oxidation was found to be different.

1. INTRODUCTION

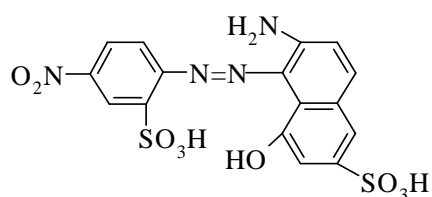
Dyes present in the wastewater from textile industry cause its dark colour and resistance to biological treatment. Specific colour is particularly burdensome because it causes that water pollution seems to be significant even if other contamination indicators have admissible values. Colour removal is very important in wastewater treatment because it can be accompanied by an increase in biodegradability [1, 2].

In the paper, a decolourisation degree in aqueous solutions of two selected organic dyes, obtained as a result of hydrogen peroxide application in the presence of a catalyst – ferrous ions, is determined.

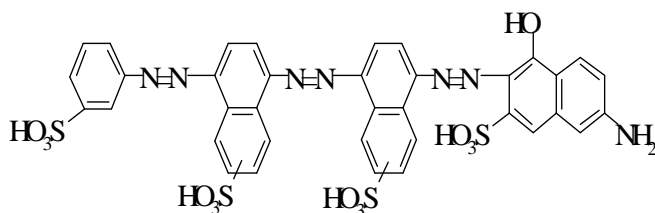
Hydroxyl radicals formed in Fenton's reaction show a high oxidation-reduction potential (2.8 V). However, they are not stable. Their activity must be checked under specified experimental conditions.

The aim of investigations was to determine an efficiency of decolourisation in model aqueous solutions of dyes as an effect of hydrogen peroxide application. An effect of pH, oxidant dose and catalyst concentration (ferrous ions) on this efficiency was also investigated. The efficiency of decolourisation was controlled by measurements of absorbance at the wavelength which corresponds to maximal light absorption and by a change in total organic carbon (TOC). Under optimal conditions of the catalytic oxidation with hydrogen peroxide, additionally a change in chemical oxygen demand (COD) was determined using a dichromate method, and UV-VIS spectra were recorded. In the investigation, solutions of two dyes: Acid Violet 1 and Direct Blue 74 were used. These dyes are representatives of acid and direct dyes. The concentration of solutions was 100 mg/L. Molecular formulas of the dyes are as follows:

Acid Violet 1



Direct Blue 74



2. EXPERIMENTAL

Experiments were carried out in a reactor with constant volume. A concentrated dye solution with specified volume (adjusted such as the final concentration was 100 mg/L) was supplied to the reactor with the volume of 250 mL. Next pH was adjusted to the selected value.

The proper amount of the catalyst Fe⁺² in the form of FeCl₂ was added to the reactor which was next filled up with deionized water to the volume of 100 mL. After stirring of the reactor content, the initial absorbance (A_0) of the solution

was determined at the specified wavelength. Next, the specified amount of an oxidant was added to the reactor. The absorbance was measured at 490 and 535 nm in the case of Direct Blue 74 and Acid Violet 1, respectively.

The decolourisation efficiency was analysed after 120 min experiment by determination of the absorbance (A). The decolourisation degree was calculated using the following equation:

$$\alpha = \frac{A_0 - A}{A_0} \cdot 100\%$$

Experiments with Acid Violet 1 and Direct Blue 74 were carried out in the temperature of 25°C and 60°C, respectively. These temperatures resulted from the investigation of the temperature effect on the progress of oxidation with hydrogen peroxide [3].

Dyes used in the investigation were products separated in a filter from a mother liquor dried in air to the constant mass. Their purity degrees were analysed by determination of organic carbon (comparison of organic carbon with the theoretical carbon amount) were as follows:

- Acid Violet 1 – 42%,
- Direct Blue 74 – 52%.

3. RESULTS AND DISCUSSION

Aqueous solutions of dyes were decoloured by hydrogen peroxide at the amount of 0.07 mg H₂O₂ per 1 mg of a dye at pH in the range from 2 to 4. The decolourisation was carried out in 25°C in the case of Acid Violet 1 solutions. Solutions of Direct Blue 74 were only slightly decoloured in this temperature. Therefore, the most of experiments with Direct Blue 74 was carried out at the temperature of 60°C.

Investigation results of an effect of ferrous ions concentration (in the range from 0 to 50 mg/L) on solution decolourisation for both dyes are presented in Figure 1. The decolourisation degree was slight if the catalyst was not added to a solution. Addition of ferrous ions causes improvement in the decolourisation. The optimal decolourisation was obtained at ferrous ions concentration of 5 mg/L and 2.5 mg/L in the solution of Acid Violet 1 and Direct Blue 74, respectively. In both cases, the decolourisation was almost total. Higher decolourisation degrees can be achieved by an increase in an oxidant dose. An effect of the hydrogen peroxide dose on the decolourisation was determined in the dose range from 0.04 to 1.00 mg per 1 mg of a dye. Results of the investigation are presented in Figure 2.

Data shown in Figure 2 indicates that an increase in the hydrogen peroxide dose causes an improvement of the decolourisation of the dye solutions. An increase in H_2O_2 dose to 1 mg per 1 mg of a dye caused the total decolourisation of the solutions of both dyes.

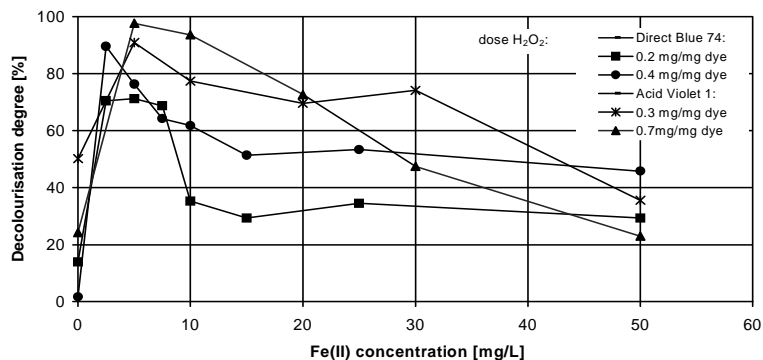


Fig. 1. A dependence of the decolourisation degree of dye solutions on the concentration of ferrous ions during the oxidation by hydrogen peroxide

Decolourisation degree, %

Ferrous ions concentration, mg/L

H_2O_2 dose, mg/mg of a dye

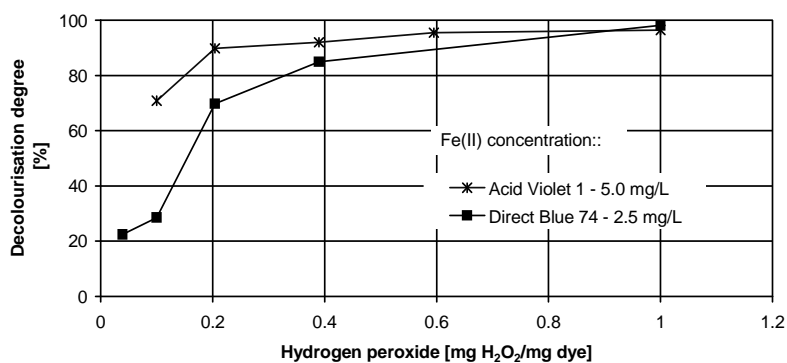


Fig. 2. A dependence of the decolourisation degree of dye solutions on a dose of hydrogen peroxide at the specified concentration of ferrous ions

Decolourisation degree, %

H_2O_2 dose, mg/mg of a dye

The concentration of ferrous ions was as follows:

Acid Violet 1 – 5.0 mg/L

Direct Blue 74 – 2.5 mg/L

Analysis of total organic carbon was carried out in samples of aqueous dye solutions before and after the oxidation. TOC was determined in TOC 505 Shimadzu analyser. Results of TOC determination are presented in Table 1.

Tab. 1. An effect of the oxidation by hydrogen peroxide on changes of oxygen indicators and the content of organic compounds; TOC – total organic carbon, α – a degree of TOC or COD decrease

Dye	Before the oxidation		After the oxidation by H ₂ O ₂		α_{COD}	α_{TOC}
	COD, mg O ₂ /L	TOC, ppm	COD, mg O ₂ /L	TOC, ppm		
Acid Violet 1	55.92	20.66	18.88	12.49	0.64	0.39
Direct Blue 74	73.16	19.33	44.84	10.44	0.39	0.46

Results of TOC analysis indicate that organic compounds are not completely oxidised to CO₂. The decrease in TOC was 39% in Acid Violet 1 solutions and 46% in Direct Blue 74 solutions

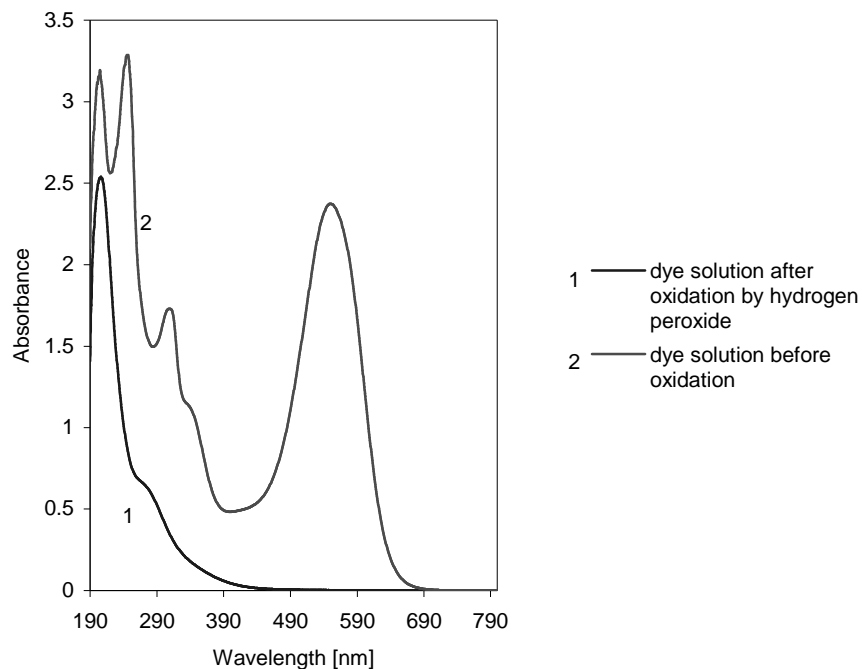


Fig. 3. Spectra of Acid Violet 1 solutions before and after oxidation by hydrogen peroxide: a dose H₂O₂ – 0.3 mg/mg dye, pH = 2.8, t = 25°C and at the concentration of Fe(II) as a catalyst – 5.0 mg/L

Determination of chemical oxygen demand using dichromate method was also carried out in the solutions before and after the oxidation under the above mentioned reaction conditions. Results of the determination are presented in Table 1. The degree of COD decrease is 64% in Acid Violet 1 solutions and 39% in Direct Blue 74 solutions.

Spectra were recorded in solutions before and after the decolourisation under the above mentioned conditions. UV-VIS spectra are presented in Figures 3 and 4. A significant decrease in a peak characteristic for aromatic groups and decay of peaks characteristic for chromophoric groups was observed after the decolourisation.

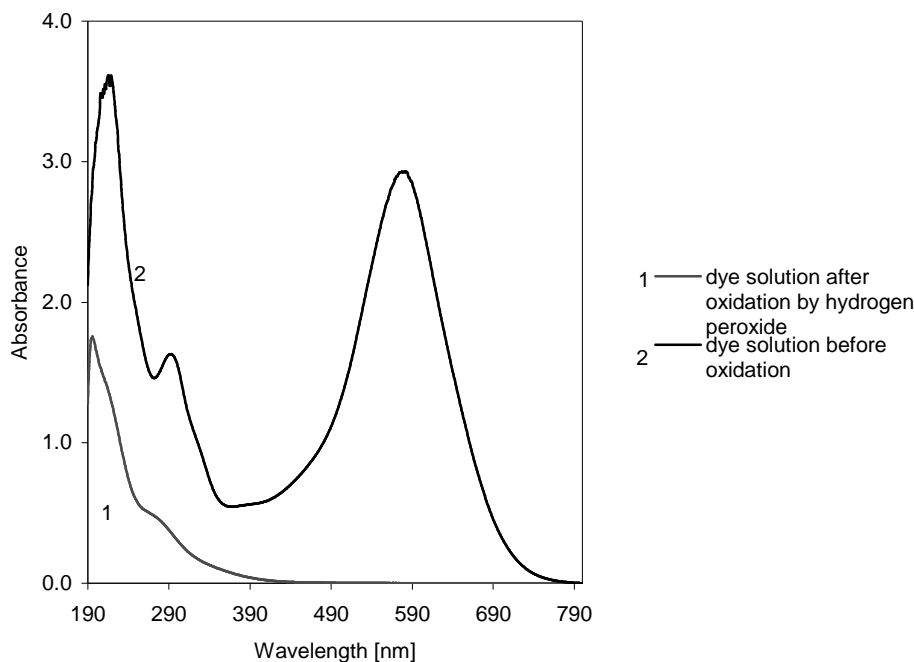


Fig. 4. Spectra of Direct Blue 74 solutions before and after oxidation by hydrogen peroxide: a dose H_2O_2 - 0.2 mg/mg dye, pH = 2.5, t = 60°C and at the concentration of Fe(II) as a catalyst - 2.5 m/L

4. CONCLUSIONS

Results of investigations allow to draw a conclusion that the dye solutions can be decoloured in 100% under the proper reaction conditions. The decolourisation proceeds with concurrent oxidation of dyes. The decrease in TOC by 39% in Acid Violet 1 solutions and by 46% in Direct Blue 74

solutions, is observed. Simultaneously, COD is decreased by 64% in Acid Violet 1 solutions and by 39% in Direct Blue 74 solutions. This fact proves that the compounds are only partially oxidised. The partial oxidation is confirmed by analysis of UV-VIS spectra.

5. REFERENCES

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CURRICULA VITAE



Anna Józwiak graduated from the Technical University of Łódź gaining her MScE in 1970. In 1979 she obtained her PhD and at present she works in the Institute of General and Ecological Chemistry (Technical University of Łódź). Her interests mainly concern technology of water treatment and waste disposal.



Dr. Stanisław Wiktorowski was born in Iwacewicz in 1935. He graduated from the Technical University of Łódź in 1957 as Ch.E. and received his MSc degree in 1962. In 1969 Wiktorowski received his E.D. from the Technical University of Łódź, Faculty of Chemistry. He was employed in Technical University of Łódź since 1962 to 2000 (until he has got retired). In that time he published over 30 papers in Polish and international journals. Now Stanisław Wiktorowski still lectures on water treatment and waste disposal (Faculties of Chemistry and Environmental Engineering Protection Technical University in Łódź).



Agnieszka Dębicka was born in Tomaszów Mazowiecki (Poland) in 1976. Graduated from the Technical University of Łódź (MSc) – environmental protection in 2002. She is post-graduate student in the Institute of General and Ecological Chemistry of Technical University of Łódź. Her research concerns treatment of wastewater from disposal industry containing organic dyes, with application of oxidation method with Fenton's reagent.