

# Oxidative Decolorization of Methyl Violet by Fenton Reagent in the Presence of Natural Additives

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**Abstract** – *The work is aimed at studying the efficiency of the process of methyl violet decolorization by Fenton reagent by the variation of the concentration of the components of the reaction mixture, as well as the studying the influence of additives of natural substances on oxidation rate and dye conversion by Fenton reagent.*

Keywords – kinetics, oxidation, Fenton reaction, dye, methyl violet, hydrogen peroxide, ascorbic acid, fructose, UV/Vis-spectroscopy.

## Introduction

Water is one of the most important resources, without which human existence is impossible. Inappropriateness of water for consumption relates to pollution of reservoirs by industry waste, agricultural and domestic dirt. Annually thousands of chemicals fall into the water sources. Accumulation of such substances reduces the amount of oxygen in the water, negatively affects flora and fauna [1]. Synthetic dyes are one the largest groups of water pollutants.

There are many water treatment methods that can be divided into biological – using biofilters, anaerobic reactors [2], physical methods – adsorption, nanofiltration and reverse osmosis, and chemical ones, which include reduction, neutralization, oxidation [3]. One of the most common and effective are chemical methods. Recent developments in the field of chemical purification of water have resulted in a significant improvement in the oxidative discoloration of organic compounds dissolved in water [2–4].

The development of new methods for water purification includes the study of oxidation processes characterized by the generation of hydroxyl radicals as primary oxidants. Such systems include Fenton reagent and Fenton-like systems [5]. They are characterized by high efficiency in oxidation processes, moreover, they are relatively inexpensive and environmentally friendly. When H<sub>2</sub>O<sub>2</sub> interacts with Fe<sup>2+</sup> ions, OH-radicals are formed, which can destroy water-soluble compounds:



The initial rate of oxidative degradation of the substrate by the Fenton reactant is significantly influenced by the concentration of H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>, pH of the medium, etc. [5].

Since Fe<sup>2+</sup> is converted to Fe<sup>3+</sup> during the Fenton reaction, it is important to return Fe<sup>2+</sup> to the reaction mixture. Different substances can be used as reducing compounds, including natural additives, such as ascorbic acid [6] or fructose [7]. Their presence in the system can affect the efficiency and oxidation rate of the process, and the products of such additives destruction will not pollute the environment [8].

The goal of this work was to study the oxidation efficiency of the synthetic dye by Fenton reagent, as well as the influence of substances of natural origin on the oxidative destruction of the substrate.

### Materials and methods

Solutions of methyl violet (MV) dye were prepared in the distilled water. The dye oxidative decolorization was achieved by Fenton reagent which composed of a mixture of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Additives of natural origin were ascorbic acid (AA) and fructose (F).

The pH of the system was adjusted by adding sulfuric acid solution.

The kinetics of decolorization of MV dye by Fenton reagent was investigated by spectrophotometric method. The maximum absorbance wavelength of MV was found to be 585 nm. UV/Vis spectra of the solutions were received on a single-beam spectrophotometer SPECOL 2000 (Analytik Jena, Germany) in a glass cuvette with a thickness of 1 cm in the wavelength range 190–1100 nm at  $21 \pm 3$  °C.

### Results and discussion

Hydrogen peroxide is the source of  $\text{OH}\cdot$  radicals, which are formed in the reaction (1) by interaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$ . Generated  $\text{OH}\cdot$  radicals as part of Fenton reaction are used for the oxidation of the dye. Thus, it was important to study the effect of the concentration of  $\text{H}_2\text{O}_2$  on the efficiency of MV decolorization. The dependence of the degree of MV decolorization at different ratios of Fenton reagent components are given in Table 1.

Table 1

The influence of Fenton reagent components on MV dye conversion (*S*).

$[\text{MV}]_0 = 1.75 \cdot 10^{-5}$  M;  $[\text{H}_2\text{O}_2]_0 = (1.0-5.0) \cdot 10^{-4}$  M;  $[\text{Fe}^{2+}]_0 = (1.0-6.0) \cdot 10^{-4}$  M; pH = 3.5

		<i>S</i> , %				
$[\text{Fe}^{2+}]_0$ \backslash $[\text{H}_2\text{O}_2]_0$		1	2	3	4	5
1		89	98	98	98	98
2		91	95	99	100	100
3		87	96	100	100	100
4		86	93	98	99	100
5		85	87	99	96	98
6		81	88	96	94	95

The obtained data shows that maximum degree of conversion of MV is provided at concentration ranges of  $3.0-8.0 \cdot 10^{-4}$  M for  $\text{H}_2\text{O}_2$  and  $2.0-3.0 \cdot 10^{-4}$  M for  $\text{Fe}^{2+}$ . These concentrations correspond to the ratios  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0 = 3:3$  and  $4:2$ . For these systems, after 25 min from the start of the reaction, the conversion is almost 100 %. It should be noted, that for higher concentrations of  $[\text{H}_2\text{O}_2]_0$  in the system, the initial decomposition rate and the time of dye decolorization increase, while the conversion is 94–98 %.

The data given in Table 1 also demonstrate the influence of  $\text{Fe}^{2+}$  initial concentrations on the oxidative degradation of MV. It can be seen, that at concentration of  $[\text{Fe}^{2+}]_0 = 1.0 \cdot 10^{-4}$  M, the decolorization of MV can reach 98 % (within 15 min after the mixing of the components). At the same time *S*(MV) changes nonlinearly with  $[\text{Fe}^{2+}]_0$ . For all the investigated  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0$

ratios, with  $[\text{Fe}^{2+}]_0$  increase from  $3.0$  to  $6.0 \cdot 10^{-4}$  M gradual decrease of MV conversion is observed.

One of the ways to control the effectiveness of Fenton reaction is the addition of substances that can be reductors of  $\text{Fe}^{3+}$ . For example, substances of natural origin that can contribute to the oxidation-reduction cycle of iron are fructose and ascorbic acid. Ascorbic acid affects the reduction cycle of  $\text{Fe}^{2+}$  ions according to reaction (3)[9]:



In this work it was established that, depending on the concentration  $[\text{F}]_0$  or  $[\text{AA}]_0$ , the acceleration or inhibition of the oxidative decolorization reaction of MV can be observed. The results of these experiments are shown in Fig. 1.

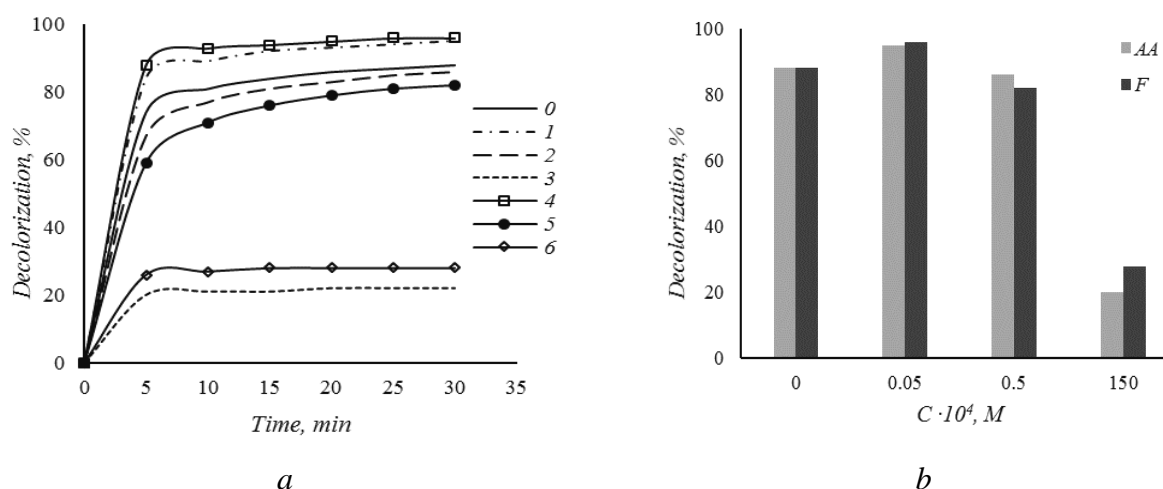


Fig.1. Effect of  $[\text{AA}]_0$  and  $[\text{F}]_0$  on the oxidative decolorization of MV by Fenton reagent:

$[\text{MV}]_0 = 1.75 \cdot 10^{-5}$  M;  $[\text{H}_2\text{O}_2]_0 = 4 \cdot 10^{-4}$  M;  $[\text{Fe}^{2+}]_0 = 1 \cdot 10^{-4}$  M; pH = 3.5.

1 –  $[\text{AA}]_0 = 0.5 \cdot 10^{-5}$  M; 2 –  $[\text{AA}]_0 = 0.5 \cdot 10^{-4}$  M; 3 –  $[\text{AA}]_0 = 1.5 \cdot 10^{-2}$  M;

4 –  $[\text{F}]_0 = 0.5 \cdot 10^{-5}$  M; 5 –  $[\text{F}]_0 = 0.5 \cdot 10^{-4}$  M; 6 –  $[\text{F}]_0 = 1.5 \cdot 10^{-2}$  M.

Fig. 1 *a* shows changes of the substrate decolorization depending on the additive concentration. One can see, that for all the systems the kinetic curves demonstrate sharp increase of dye conversion during the first 5 min of the reaction, then the process slows down, and the conversion changes are insignificant. It should be noted that the effectiveness of both additives is almost the same for all investigated reaction mixtures.

The degree of conversion of the substrate has a nonlinear dependence on the concentration of the additive in the investigated range of concentrations. Variation of additive concentration results in significant changes of the process. At low AA or F values (less than the substrate and Fenton reaction components concentration) the additive acts as accelerator of the reaction. When larger quantities of  $[\text{AA}]_0$  or  $[\text{F}]_0$  are added, the inhibition of the process is observed. E. g. at  $1.5 \cdot 10^{-2}$  M additive concentration in the reaction mixture, the extent of dye decolorization does not exceed 28 % within 30 min.

The explanation of the received dependences needs further investigations. It can be assumed, that at low content of the additive, the concentration of the reduced  $\text{Fe}^{2+}$  does not exceed the concentration of  $\text{H}_2\text{O}_2$ , and this helps to maintain the constant  $[\text{H}_2\text{O}_2]_0: [\text{Fe}^{2+}]_0$  ratio. Thus, such substances within some concentration range could be used to improve the effectiveness of oxidative decomposition of organic pollutants.

## Conclusion

Spectrophotometric method was used to study the oxidative decolorization of MV dye. The influence of the initial concentrations of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  on the degree of the substrate conversion has been established. It was shown that the higher  $\text{H}_2\text{O}_2$  concentration the higher the dye conversion. At the same time the reaction shows non-linear change with  $\text{Fe}^{2+}$  concentration. The ratio  $[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]$  which provides relatively fast discoloration of the substrate lies within 3:3–4:2.

The influence of additives of natural substances on the reaction has been investigated. The comparison of both additives showed no dependence of the the effectiveness of dye decolorization process on the used reduction agent. It was shown that depending on the concentration of ascorbic acid or fructose, such compounds could act as reaction accelerators (at low additive concentration) and inhibitors (if the concentration was higher than  $0.5 \cdot 10^{-4}$  M). Such effect could be used to change the rate of Fenton reaction in wastewater purification processes, as well as the effectiveness of other radical chain oxidation reactions of organic substances in water media.

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