

Effectiveness of Fenton Reagent in Oxidation Process of Methyl Violet Dye

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Abstract – Decoloration methyl violet dye by Fenton reagent was investigated spectrophotometrically. Reagents concentration, pH value, and metal ion were varied. It was shown that substrate oxidation rate depends non-linearly on dye concentration, Fe^{n+} , H_2O_2 , and pH value. The composition of the reaction mixture providing maximum oxidation rate and MV conversion is proposed.

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

I. Introduction

Dyes are a common model in the studying of water purification processes. Oxidation of dyes is not only a methodological but also a practical interest, since it is of great importance for reducing the impact of textile, paper, food, and pharmaceutical industry wastes on the environment. Fenton reagent may be effectively used as oxidizing agent because it is environmentally friendly and rather cheap. In classical Fenton system, Fe(II) ions are used for the catalytic decomposition of hydrogen peroxide [1]. Fenton reaction produces Fe(III) and hydroxyl radical, the latter initiates radical-chain oxidation process. It is known that this process consists of number of stages, including oxidation–reduction reactions. Some authors showed that Fe(III) could also be used in Fenton-like systems instead of Fe(II) [2]. The goal of this work was investigation of regularities of oxidation reaction of organic compounds with both classical Fenton reagent and $H_2O_2/Fe(III)$ system under different conditions using methyl violet dye as the substrate.

II. Experimental part

Methylene violet (MV), $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, H_2O_2 (60 % w/v), H_2SO_4 , were all G.R. grades and used as received. All solutions were made in distilled water. The pH value of the $FeSO_4$ solution was adjusted using 0.25 M H_2SO_4 .

The kinetics of dye decoloration was studied using SPEKOL® 1500 UV/Vis spectrophotometer (Analytik Jena AG, Germany) at 585 nm. Digital pH-meter was used for pH measurements. The experiments were carried out at 21 ± 2 °C.

It was shown that in the range $1.2 \cdot 10^{-5}$ – $2.7 \cdot 10^{-5}$ M, the absorbance of methyl violet solution at 585 nm versus concentration plots were linear ($r \sim 0.99$) with zero intercept for both Fenton systems.

III. Results and discussion

The kinetics of oxidative destruction of methyl violet (MV) by hydrogen peroxide in the presence of Fe(II) or Fe(III) ions was investigated. It was shown that such Fenton-like reactions could be effectively controlled by initial concentrations of dye, Fe^{n+} , H_2O_2 , and pH value of the reaction media.

Analysis of kinetic curves demonstrated that the decoloration of MV solution by Fenton reagent occurs in two stages (Figs. 1 and 2). The first stage is faster (1–2 min or less), and the second one is ~4 times slower, regardless Fe^{n+} ion used. The rate of each stage essentially depends on the concentration of the components of the reaction mixture. It has been shown that the initial rate of the oxidative destruction of dye and process duration depends on each component concentration (substrate, hydrogen peroxide, Fe^{n+}). It should be noted that type of metal ion used is also important – change of Fe^{2+} in classical Fenton system to Fe^{3+} results in changes of kinetic curves form (see Figs. 1 and 2). The duration of the first faster stage is much shorter for $Fe^{3+} + H_2O_2$ system.

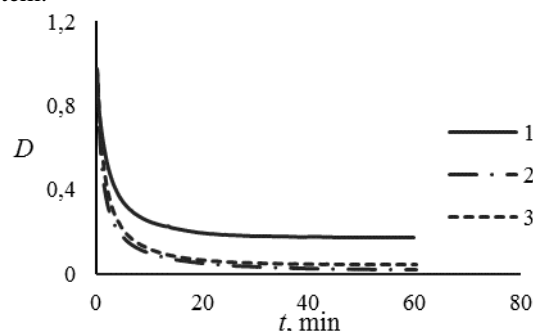


Fig. 1 Change in optical density (D) at different $[H_2O_2]_0$: (1) $-1.15 \cdot 10^{-4}$ M; (2) $-2.28 \cdot 10^{-4}$ M; (3) $-4.57 \cdot 10^{-4}$ M; $[MV]_0 = 1.75 \cdot 10^{-5}$ M; $[Fe^{2+}]_0 = 1.0 \cdot 10^{-4}$ M; pH = 3.

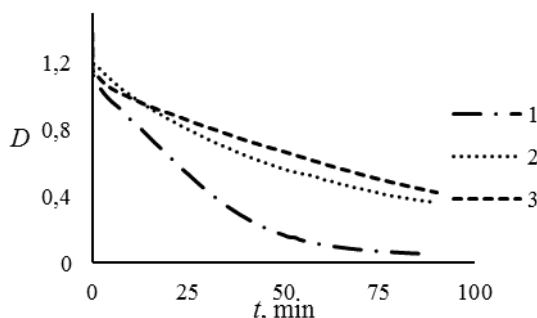


Fig. 2 Change in optical density (D) at different $[H_2O_2]_0$: (1) $-0.99 \cdot 10^{-3}$ M; (2) $-2.01 \cdot 10^{-3}$ M; (3) $-3.99 \cdot 10^{-3}$ M; $[MV]_0 = 1.75 \cdot 10^{-5}$ M; $[Fe^{3+}]_0 = 1.0 \cdot 10^{-4}$ M; pH = 3.

To investigate the effect of hydrogen peroxide concentration on dye degradation kinetics, experiments were conducted at different H_2O_2 concentrations. From Figs. 1 and 2 it can be seen that change of H_2O_2 concentration significantly influences the initial rate of

dye oxidation reaction. At comparatively low concentrations of H_2O_2 , relatively high initial rates are observed. When the concentration of H_2O_2 increased significantly ($0,02\text{ M}$) (not given), the form of the kinetic curve has changed: the initial rate decreased, but remained almost constant throughout the measurement period. This may indicate a nonproductive decomposition (in terms of the formation of $\bullet\text{OH}$ radicals, which are essential in the degradation of the dye) of hydrogen peroxide in such conditions. The analysis of the received dependences demonstrated that the initial rate of dye decomposition (V_0) and substrate conversion depended non-linearly on H_2O_2 concentration. V_0 reached maximum values at $[\text{H}_2\text{O}_2]_0 = 5,7 \cdot 10^{-4}\text{ M}$ for $\text{Fe}^{2+} + \text{H}_2\text{O}_2$, and $[\text{H}_2\text{O}_2]_0 = 6,02 \cdot 10^{-3}\text{ M}$ for $\text{Fe}^{3+} + \text{H}_2\text{O}_2$.

Fig. 3 demonstrates the kinetic curves of MV decoloration by H_2O_2 in the presence of Fe^{2+} . At high Fe^{2+} concentrations gradual decrease in the initial rate of dye destruction process is observed. The possible explanation is the growth of hydrogen peroxide decomposition rate, which means that the concentration of reactive OH^\bullet radicals in the system decreases: $2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$. As for system $\text{Fe}^{3+} + \text{H}_2\text{O}_2$, larger concentrations of reagents should be taken to achieve similar results (Fig. 4).

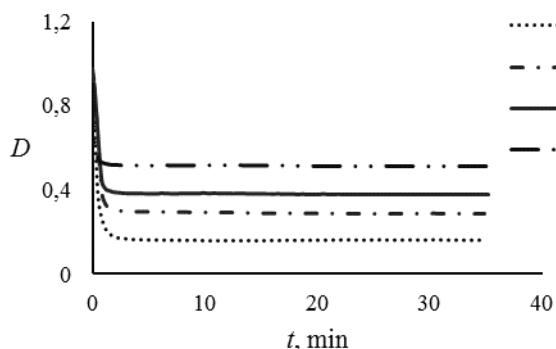


Fig. 3 Change in optical density (D) at different $[\text{Fe}^{2+}]_0$: (1) $- 0,91 \cdot 10^{-4}\text{ M}$; (2) $- 1,82 \cdot 10^{-4}\text{ M}$; (3) $- 22,8 \cdot 10^{-4}\text{ M}$; (4) $- 27,4 \cdot 10^{-4}\text{ M}$; $[\text{MV}]_0 = 1,75 \cdot 10^{-5}\text{ M}$; $[\text{H}_2\text{O}_2]_0 = 4,0 \cdot 10^{-4}\text{ M}$; $\text{pH} = 3$.

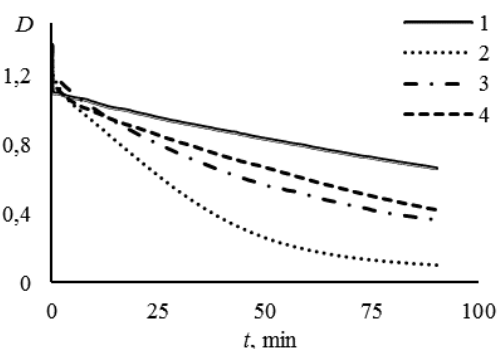
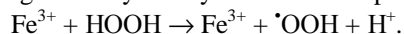


Fig. 4 Change in optical density (D) at different $[\text{Fe}^{3+}]_0$: (1) $- 1,0 \cdot 10^{-3}\text{ M}$, (2) $- 1,85 \cdot 10^{-3}\text{ M}$, (3) $- 2,0 \cdot 10^{-3}\text{ M}$, (4) $- 4,0 \cdot 10^{-3}\text{ M}$; $[\text{H}_2\text{O}_2]_0 = 1 \cdot 10^{-3}\text{ M}$; $[\text{MV}]_0 = 2 \cdot 10^{-5}\text{ M}$; $\text{pH} = 3$.

In the presence of only Fe^{3+} ions and hydrogen peroxide, significantly slowly reaction takes place:



Generated $\bullet\text{OOH}$ radical is less active than hydroxy radicals, therefore, they react with MV much more slowly. For the investigated concentrations range initial decoloration rate shows non-linear dependence: maximum initial rate of decoloration and dye conversion was observed at $[\text{Fe}^{3+}]_0 = 1,85 \cdot 10^{-3}\text{ M}$.

Additional experiments were made to determine the influence of pH value on the studied process. It was established for $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ system, that maximum conversion and rate of dye decomposition was observed for $\text{pH} 2,2-3$.

In order to determine the optimum ratio of $[\text{Fe}^{n+}]/[\text{H}_2\text{O}_2]$ for dye degradation, experiments were conducted by varying the Fe^{n+} and H_2O_2 concentrations, keeping the dye concentration fixed. The results of the experiments are listed in Table 1.

TABLE 1

COMPARISON OF THE INITIAL RATES OF MV OXIDATION (V_0) BY FENTON SYSTEMS DEPENDING ON $[\text{Fe}^{n+}]/[\text{H}_2\text{O}_2]$ RATIO AND METAL ION USED ($[\text{MV}]_0 = 2 \cdot 10^{-5}\text{ M}$)

| $[\text{Fe}^{n+}]/[\text{H}_2\text{O}_2]$ | $V_0 \cdot 10^7, \text{ mol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$ | |
|---|---|------------------|
| | Fe^{2+} | Fe^{3+} |
| 2/1 | 1.8 | 1.0 |
| 3/1 | 1.5 | 4.9 |
| 4/1 | 1.3 | 3.4 |
| 6/1 | 0.9 | 2.9 |

It can be seen from the Table that for Fe^{2+} as the catalyst maximum initial oxidation rate is observed at $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2] = 2/1$, while for $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2] = 3/1$. The higher the concentration of Fe^{n+} the lower the V_0 value is observed.

Conclusion

The oxidation of methylene violet dye by Fenton reagent at ambient temperature was studied spectrophotometrically. The effects of the initial concentrations of dye, Fe^{2+} (Fe^{3+}), and H_2O_2 , pH of the solution on dye decoloration reaction were established. It was shown that the initial rate of dye decoloration changes non-linearly with concentration of hydrogen peroxide and Fe^{n+} . Substitution of classical $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ system to $\text{Fe}^{3+} + \text{H}_2\text{O}_2$ showed lower efficiency. In order to reach similar effect in dye conversion and reaction rate the concentrations of reagents should be increased approximately by order of magnitude. It was shown That the higher the concentration of Fe^{n+} in the system compared to H_2O_2 the lower the dye decoloration rate was observed.

References

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