Kinetic Study of Methylorange Oxidation Process from Aqueous Solutions

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The degradation of Methylorange (MO) azo dye in aqueous solution by the Fenton oxidation process has been investigated. The effect of temperature at pH=3.5 on the oxidative degradation of Methylorange have been assessed. The UV-Vis spectral changes of Methylorange in aqueous solution during Fenton treatment process were studied. It was easier to destruct the azo group (-N=N-) of Methylorange by Fenton oxidation. The experimental results showed that the Fenton oxidation process was an effective process for the degradation of azo dye Methylorange at low H2O2 and Fe2+ concentrations.

Keywords: Methylorange; degradation; Fenton oxidation; kinetic study

Experimental part

Experimental determinations were performed for aqueous solutions of MO, with initial concentrations of 7.58·10-5 mol·L-1. Hydrogen peroxide concentration was 1.76·10-3 mol·L-1, and added ferrous sulfate concentration in the system was 4.17·10-5 mol·L-1; thus, the concentration rate between hydrogen peroxide and MO was 23.2 : 1. Experiments were conducted at a pH of 3.5 and at different temperatures: 25, 35, 45, 55 and 65°C. pH value was adjusted using a H2SO4 5% solution and checked with a pH -meter (Consort C533 model). For each experiment, Erlenmeyer glass, equipped with refrigerator bottom, which contained 100 mL solution of ferrous sulphate and MO subjected to degradation were placed in a water bath thermostat at temperatures mentioned in the experimental data. When the temperature reached the desired value, reaction was initiated by adding hydrogen peroxide. Periodically, solution samples were taken with a pipette and analyzed by spectrophotometry. The UV-Vis spectrum of the dye during the degradation process with Fenton reagent was registered between 200 and 800 nm using an UV-Vis spectrophotometer (Varian Cary 50 Bio). From the spectrum it resulted the wavelength corresponding to the maximum absorbance value, λmax (of the -N=N- bond), at 487 nm. Thus, the dye concentration in the reaction mixture at different reaction times: 1- 5 min was determined by measuring the absorbance value at λmax=487 nm. We mention that after 6 minutes, for the samples tested at 55 and 65°C, the scan reports didn’t notice any absorbance value at λmax= 487 nm, which involves a complete degradation of methyl-orange. Thus, for the kinetic evaluation, only results obtained during the first 5 min were taken into account.

Results and discussions

To observe the effect of temperature on azo dye degradation in aqueous solution with Fenton reagent at different temperatures: 25, 35, 45, 55 and 65°C, spectral changes have been assessed for 5 minutes. Samples were taken each minute for analysis at UV-Vis spectrophotometer. UV-Vis spectra obtained during the degradation of MO at different temperatures and pH = 3.5 are shown in figure 1.

Fig. 1. UV-Vis spectra obtained during the chemical degradation of MO in the presence of Fenton reagent at different temperatures: a - 25°C, b - 65°C

Synthetic dyes are used extensively in many industries, of which: textile dyes (60%), paper (10%), plastic materials (10%). Estimates indicate that approximately 10-15% of the synthetic textile dyes used are lost in rivers during manufacturing or processing operations [1]. Yearly, 800,000 tonnes of dyes are produced in the world and about 50% of them are azo dyes. Development of the appropriate techniques for treatment of dye wastewater is important for the protection of natural resources. To eliminate dyes from aqueous coloured effluents and reduce their ecological consequences, several biological, physical and chemical techniques have been proposed: catalytic oxidation [2], biological treatment [3], physical or chemical flocculation, electrofiltration, membrane filtration, electrokinetic coagulation [4], adsorption and precipitation [5] and oxidative/reductive chemical and photochemical processes [6]. The advanced oxidation processes that use hydroxyl radicals, a very strong oxidant, provide a convenient method for the treatment of organic pollutants as dyes. Oxidation using: ozon, H2O2, ozon/UV, UV/H2O2, UV/TiO2 or UV/H2O2/Fe3+ [7-13] and Fenton reagent [14-16] showed their effectiveness to eliminate organic compounds dissolved or dispersed in aqueous media.

The paper aims to study the kinetics of Methylorange degradation with Fenton reagent in aqueous solution using UV-Vis spectrophotometry.

Experimental determinations were performed for aqueous solutions of MO, with initial concentrations of 7.58·10-5 mol·L-1. Hydrogen peroxide concentration was 1.76·10-3 mol·L-1, and added ferrous sulfate concentration in the system was 4.17·10-5 mol·L-1; thus, the concentration rate between hydrogen peroxide and MO was 23.2 : 1. Experiments were conducted at a pH of 3.5

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For other temperature values, similar spectra were obtained. In figure 1 is seen that the absorbance decreases in time at the same temperature, which demonstrates the degradation and discoloring of MO. With increasing temperature, the absorbance values at the same reaction times present a significant decrease, hence a higher rate of degradation. This may be shown by determining the color removal (CR) using the equation 1.1, at time values when the spectral recordings were performed. The dependence of color removal by time and temperature is shown in figure 2. Thus, the color removal at 5 min increases from 27.9 calculated at 25°C to the value of 85.5% at 65°C.

\[ \text{CR} = (1 - \frac{A}{A_0}) \times 100 \]  

(1.1)

where: \( A_0 \) and \( A \) represents the initial absorbance and absorbance in the moment of spectrum registering.

**Setting the mechanism and reaction order**

A simple mechanism has been proposed, which assumes that MO degradation in aqueous solution in the presence of Fenton reagent occurs in a chained process in three stages: initiation, propagation and termination.

**Initiation reaction:**

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \overset{k_1}{\rightarrow} \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH} \]  

(1)

**Propagation reactions:**

\[ \cdot\text{OH} + \text{Fe}^{2+} \overset{k_2}{\rightarrow} \text{Fe}^{3+} + \cdot\text{OH} \]  

(2)

\[ \cdot\text{OH} + \text{H}_2\text{O}_2 \overset{k_3}{\rightarrow} \text{OOH} + \text{H}_2\text{O} \]  

(3)

\[ \text{Fe}^{3+} + \cdot\text{OOH} \overset{k_4}{\rightarrow} \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \]  

(4)

\[ \cdot\text{OH} + \text{dye} \overset{k_5}{\rightarrow} \cdot\text{P} + \text{H}_2\text{O} \]  

(5)

\[ \cdot\text{P} + \text{H}_2\text{O}_2 \overset{k_6}{\rightarrow} \cdot\text{OH} + \text{P}_r \]  

(6)

**Termination reactions:**

\[ 2\cdot\text{P} \overset{k_7}{\rightarrow} \text{P}_r + \text{P}_r \]  

(7)

\[ \cdot\text{OH} + \cdot\text{OOH} \overset{k_8}{\rightarrow} \text{O}_2 + \text{H}_2\text{O} \]  

(8)

\[ \cdot\text{OH} + \cdot\text{OH} \overset{k_9}{\rightarrow} \text{H}_2\text{O}_2 \]  

(9)

where:

\( \cdot\text{P}_r \) - radical species possibly obtained as a result of discoloring;

\( \text{P}_r \) - final reaction product.

Reaction rates corresponding to the stages mentioned in the mechanism were calculated using the following equations:

\[ v_1 = k_1 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] \]  

(11)

\[ v_2 = k_2 [\cdot\text{OH}] [\text{Fe}^{2+}] \]  

(12)

\[ v_3 = k_3 [\cdot\text{OH}] [\text{H}_2\text{O}_2] \]  

(13)

\[ v_4 = k_4 [\text{Fe}^{3+}] [\cdot\text{OOH}] \]  

(14)

\[ v_5 = k_5 [\cdot\text{OH}] [\text{dye}] \]  

(15)

\[ v_6 = k_6 [\cdot\text{P}]^2 \]  

(16)

\[ v_7 = k_8 [\cdot\text{OH}] [\cdot\text{OOH}] \]  

(17)

\[ v_8 = k_9 [\cdot\text{OH}] [\cdot\text{OH}] = k_9 [\cdot\text{OH}]^2 \]  

(18)

\[ v_9 = k_9 [\cdot\text{OH}] [\cdot\text{OH}] = k_9 [\cdot\text{OH}]^2 \]  

(19)

The initiation reaction consists in the generation of hydroxyl radicals capable to start the MO degradation process. The processes following after the initiation - propagation and termination - take place while new free radicals appear in the reaction mixture. Thus, the propagation is a very rapid sequence of reactions, with the regeneration, each time, of the cationic active center (Fe\(^{2+}\)) and of the \( \cdot\text{OH} \) radical, and the termination with the regeneration of a certain percentage of hydrogen peroxide, leading to the \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) system recovery, capable to reinitiate the process of degradation. The net forming rate of hydroxyl radical in time will be determined with the following relationship:

\[ \frac{d[\cdot\text{OH}]}{dt} = -k_1 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] - k_2 [\cdot\text{OH}] [\text{Fe}^{2+}] - k_3 [\cdot\text{OH}] [\text{H}_2\text{O}_2] - k_4 [\cdot\text{OH}] [\text{dye}] - k_5 [\cdot\text{OH}] [\cdot\text{OOH}] - k_6 [\cdot\text{P}]^2 - k_7 [\cdot\text{P}] [\cdot\text{OH}] \]  

(11.10)

\( \cdot\text{P}_r \) - type radicals have a very short lifetime; practically, their forming rate \( \left( v_5 \right) \) is equal to their consumption rate \( \left( v_6 \right) \).

Simplified, relation \( (1.10) \) can be written as follows:

\[ \frac{d[\cdot\text{OH}]}{dt} = -k_1 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] - [\cdot\text{OH}] \sum k_i S_i \]  

\[ \sum k_i S_i = k_1 [\text{Fe}^{2+}] + k_2 [\text{H}_2\text{O}_2] + k_5 [\cdot\text{OH}] + k_4 [\cdot\text{OOH}] + k_6 [\cdot\text{P}] \]  

(11.11)

To test the proposed mechanism it is necessary to demonstrate that it leads to an experimentally observed law rate. For this purpose, the approximate steady-state will be applied, which implies certain simplifications; thus, it is assumed that the change rate of the hydroxyl radical concentration is negligible: \( d[\cdot\text{OH}] / dt = 0 \); the relation \( (1.11) \) becomes:

\[ k_1 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] - [\cdot\text{OH}] \sum k_i S_i = 0 \]  

(12.12)
The concentration of hydroxyl radicals can be determined from the relation (I.12) as follows:

$$[\cdot \text{OH}] = \frac{k_{\text{Fe}^{2+}} [\text{H}_2\text{O}_2]}{\sum k_{\text{iSi}}}$$  
(I.13)

The consumption rate of dye means the degradation rate with the formation of possible organic / inorganic species and corresponds to equation (I.14).

$$\frac{d[\text{dye}]}{dt} = -k_{\text{dye}} [\cdot \text{OH}]$$  
(I.14)

where \([\text{dye}]\) is MO concentration.

By replacing the \([\cdot \text{OH}]\) obtained with relation (I.13), in equation (I.14) it results:

$$\frac{d[\text{dye}]}{dt} = -k_{\text{dye}} \frac{k_{\text{Fe}^{2+}} [\text{H}_2\text{O}_2]}{\sum k_{\text{iSi}}}$$  
(I.15)

In this study, the ratio of \([\text{H}_2\text{O}_2] / [\text{dye}] = 23.2 / 1\). It is noted that H_2O_2 is sufficient to form a large amount of hydroxyl radicals, but, at the same time, there are generated many species in which the •OH radical may be consumed.

$$\frac{d[\text{dye}]}{dt} = -k_{\text{dye}}$$  
(I.16)

where: $k_{\text{dye}} = -k_{\text{a}}$ \frac{k_{\text{Fe}^{2+}} [\text{H}_2\text{O}_2]}{\sum k_{\text{iSi}}}$ and represents pseudo-first-order reaction rate, in the case of MO degradation in aqueous solution in the presence of Fenton reagent.

By adapting the relation (I.16) it results:

$$\frac{d[\text{dye}]}{dt} = k_{\text{a}} dt$$  
(I.17)

By integrating the relation (I.17) it results:

$$\ln \frac{A_0}{A} = k_{\text{a}} t$$  
(I.18)

From figure 4, it can be noticed that straight lines were obtained, passing through the origin and whose slopes are equal to $k_{\text{a}}$.

Verification of first order kinetics

a) Absorbance variation in time

The absorbance is directly proportional with the concentration of MO degraded in the presence of Fenton reagent. Thus, the variation of absorbances resulted in the given experimental conditions, in time and as a function of the temperatures of the degradation process, will be evaluated.

Graphs Absorbance = f (time) are shown in figure 3.

It is noted that, for the same temperature, absorbance decreases exponentially with time, according to $A = A_o e^{-kt}$.

Verification of first order kinetics

b) Integrated equation rate verification. Determination of rate constants

The curves $\ln (A_o / A) = f (t)$ obtained from experimental data during the process of degradation of MO are shown in figure 4.

From figure 4, it can be observed that apparent rate constants increase with the increasing of temperature and have values ranging from 0.0787 min^{-1} to 0.2842 min^{-1}.

From figure 5, it can be observed that from the cases “a” and “b” are obtained values of apparent rate constants approximately equal. According to experimental data it can be concluded
that the reaction of degradation of MO dye, in aqueous medium, in the presence of Fenton reagent follows the first order reaction kinetics.

**Determination of activation energy**

Apparent activation energy was determined using the logarithmic form of Arrhenius equation:

\[
\ln k = \ln A' - \frac{E_a}{RT}
\]

where:
- \( k \) - rate constant, at temperature \( T \) (K);
- \( A' \) - preexponential factor;
- \( E_a \) - apparent activation energy;
- \( R \) - universal constant of ideal gas.

From the graphical representation of \( \ln k = f (1/T) \), a straight line with the slope \( \left( \frac{d(\ln k)}{d(1/T)} \right) = \frac{E_a}{R} \) (fig. 6) was obtained; thus, the value of the apparent activation energy was determined as being equal to 22.09 kJ / mol.

This value of the activation energy shows that most molecules acquire the amount of energy required for the degradation of the azo bond \((-N=N-)\); however, it is possible, for a very small fraction of molecules, to acquire the amount of energy required for the transformation in stable non-aromatic species.

**Conclusions**

The study of MO chemical degradation in aqueous solution with Fenton reagent revealed the following:
- the absorbance decreases in time, at the same temperature, which demonstrates the degradation and discoloring of MO;
- with increasing temperature, the absorbance values at the same reaction time present a significant decrease, so a higher degradation rate;
- the proposed mechanism supposes that the MO degradation in aqueous solution in the presence of Fenton reagent, undergoes a chained process, the predominant active species being the hydroxyl radicals;
- the process of MO degradation in aqueous medium in the presence of Fenton reagent follows the first order reaction kinetics;
- the activation energy value (22.09kJ/mol) shows that most molecules acquire the amount of energy needed for the degradation of the azo bond \((-N=N-)\); however, it is possible, for a very small fraction of molecules, to acquire the amount of energy required for the transformation in stable non-aromatic species.

**References**

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