Photo Degradation of Methyl Orange by Persulfate Activated with Zero Valent Iron

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Abstract. The oxidative degradation of Methyl Orange (MO) subjected to direct photolysis (Solar) and various oxidative systems was studied. The comparative experiments have shown that MO conversion and mineralization increases in the following order: Solar ~ Solar/Fe0 ~ Solar/S2O82- < Solar/S2O82-:Fe0 < Solar/S2O82:-Fe0. The influence of the main factors (duration of exposure, the ratio of initial concentrations of MO:S2O82-:Fe0, pH and temperature of the reaction medium) on the degree of MO conversion and mineralization was studied. The optimal pH and temperature of the reaction medium were 5.8 and 25°C, respectively. The rate of MO decomposition and mineralization increased proportionally to the initial concentration of the oxidant at the molar ratios [S2O82-] :[MO] ≤ 12. Judging by the nature of the kinetic curves, a further increase of this ratio is impractical. However, an increase in the oxidant concentration had a positive effect on the degrees of conversion and mineralization of total organic carbon (TOC). Thus, at the ratios of 12:1 and 48:1, the conversion efficiency of TOC was 23 and 60 %, respectively. The optimal concentration of Fe0 was 100 mg/l.

1. Introduction

Dyes are widely used in various industries - textile, food, paper, cosmetics, etc. The wastewater generated along can contain 10-15% of the initial amount of the dye in the process solution [1,2]. The most common group of organic dyes are azo dyes [3], which are recalcitrant compounds that have a depressing effect on microorganisms [4]. In this regard, it is obvious that there is a need to develop methods to reduce the input of this type of pollutants into aquatic ecosystems. The photo-induced advanced oxidation processes (AOPs), which are based on the use of highly reactive radical particles - active forms of oxygen - as oxidants [5,6], are currently being intensively developed. In recent years, there is an increasing interest in the use of sulfate anion radicals formed through activation of peroxydisulphates (S2O82-) in water purification processes [7-9]. The activation of S2O82- could be achieved by various methods (elevated temperatures T>50°C [10], UV irradiation [11], ultrasound [12]):

\[ \text{S}_2\text{O}_8^{2-} + \text{heat} \rightarrow 2\text{SO}_4^{2-} \] (1)

\[ \text{S}_2\text{O}_8^{2-} + \text{hv} \rightarrow 2\text{SO}_4^{2-} \] (2)
\[ \text{S}_2\text{O}_8^{2-} + \text{ultrasound} \rightarrow 2\text{SO}_4^{2-} \]  

(3)

UV radiation is the most commonly used means for activating \( \text{S}_2\text{O}_8^{2-} \). The works on the use of natural solar radiation for degradation of pollutants are few, and from the point of view of energy efficiency and environmental safety of the process the research is very important [13-14]. The additional use of transition metals of (Fe\(^0\), Zn\(^0\), Ag\(^0\), etc.) leads to better results in the oxidation of organic pollutants [15-18]:

\[ \text{S}_2\text{O}_8^{2-} + \text{Me}^{n+} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{Me}^{(n+1)+} \]  

(4)

The aim of this work was to study the catalytic degradation of azo dyes (exemplified by Methyl orange (MO)) through exposure to persulfate \( \text{S}_2\text{O}_8^{2-} \) and quasisolar radiation. The photochemical oxidation catalyst used in the study were Fe\(^0\) (zero valent iron).

2. Experimental

The experiments were performed using model aqueous solutions of methyl orange. The solutions were prepared with deionized water (18.2 MΩ cm\(^{-1}\), Simplicity® UV, Millipore). Potassium persulfate \( \text{K}_2\text{S}_2\text{O}_8 \) and zero valent iron (ZVI) Fe\(^0\) were employed in the experiments.

To simulate the natural sunlight, an optical radiation source with a quasisolar spectrum, HID 4300 KH xenon lamp (MaxLight, South Korea), was used (Table1, 2).

| Table 1. The technical characteristics of the lamp. |
|-----------------------------------------------|
| Color temperature, K                        | 4300 |
| Light flux, lm                               | 3200 |

| Table 2. Lamp emission intensity in UV spectral ranges, mV m\(^{-2}\). |
|-------------------------|
| UV-A (315-400 nm)       | 2870 |
| UV-B (280-315 nm)       | 171  |
| UV-C (200-280 nm)       | 180  |

The emission intensity of the xenon lamp was measured in the bactericidal spectral ranges with a TKA-PKM UV radiometer (at a distance of 5 cm). The emission spectrum of the xenon lamp is rather wide in the visible range (300-800 nm) and close to the solar light spectrum [14]. This enables correct simulation of the operation modes of a solar photoreactor under laboratory conditions.

Figure 1 shows schematically the laboratory unit (a) and the photoreactor (b).

The solution being treated (200 ml) was vigorously agitated (flow rate of 1.25 l/min in the circulation mode) and thermostated using a tubular glass spiral cooling circuit connected to the thermostat. The photoreactor consisted of 10 quartz tubes (each was 5 cm long) connected in a sequence. The tubular photoreactor was coiled around a tube made of thin quartz glass with the diameter of 2.7 cm and wall thickness of 0.5 mm. The light source was placed along the axis of this tube. To reduce the loss of emitted light, the reactor was placed in a reflector case made of aluminum foil.

The concentration of MO was determined by HPLC using Agilent 1260 Infinity liquid chromatography with a spectrophotometric UV detector. The chromatographic separation in the isocratic elution mode was performed on a Zorbax SB-C18 analytical column with the particle size of 5 µm. A 60:40 (v/v) mixture of acetonitrile with 75 mM of CH\(_3\)COOH was used as the mobile phase, at an elution rate of 0.5 ml min\(^{-1}\), column thermostat temperature of 35°C, and sample volume of 5 µL. The discoloration of the solutions during treatments was measured using the spectrophotometer KFK-3-zoms. The degree of mineralization of the organic substrate was evaluated by the change in the content of total organic carbon (TOC), determined with a TOC-L CSN analyzer (Shimadzu, Japan).
3. Results and discussion

3.1. Oxidative system Solar/$S_2O_8^{2-}$/Fe$^0$

It was established experimentally that the molecule of MO is photoresistant and its transformation through direct photolysis is slow (Figure 2 (a), curve 1). The initial rate of the direct photolysis was $0.378 \times 10^{-6}$ M min$^{-1}$ (Table). The slow transformation of MO through direct photolysis substantiates the need for combining it with other oxidizing agents/methods. The addition of potassium persulfate leads to a significant acceleration of the oxidation process of the dye (Figure 2 (a), curve 2). At the same time the discoloration of the solution was less prominent, indicating the formation of colored reaction products (Figure 2 (b), curve 2). To increase the effectiveness of the treatment the combined oxidation system {Solar/$S_2O_8^{2-}$/Fe$^0$} was further examined. After 120 min of the treatment, 100% conversion, 95% discoloration and 37% salinity reduction were observed (Table). On the other hand in the «dark» reaction, despite the relatively high initial reaction rate and high extent of conversion and discoloration (Figure 2 (a), curve 3), the removal of TOC was only 3% (Table 3).

Table 3. The initial rate of degradation, extent of conversion, discoloration of solutions and mineralization of TOC after 120 min

| Oxidative systems | $W_0$, μM min$^{-1}$ | Effectiveness of oxidation, % | Discoloration, % | TOC, % |
|-------------------|----------------------|-----------------------------|------------------|--------|
| Solar             | 0.378                | 7                           | 3                | no change |
| Solar/$S_2O_8^{2-}$| 4.307                | 84                          | 49               | no change |
| $S_2O_8^{2-}$/Fe$^0$| 4.412                | 99                          | 86               | 3      |
| Solar/$S_2O_8^{2-}$/Fe$^0$| 4.575                | 100                         | 95               | 37     |

Figure 1. Schematic representation of (a) experimental installation and (b) solar photoreactor. (1) Tubular photoreactor, (2) quartz tube, (3) source of light, (4) reflector, (5) peristaltic pump, (6) glass homogenizer, (7) thermostat.
Figure 2. Conversion of MO (a) and discoloration of solutions (b) in various oxidative systems: 1 - Solar; 2 - Solar/S2O82-; 3 - S2O82-/Fe0; 4 - Solar/ S2O82-/Fe0; C(MO)=10 mg/l, [S2O82–]:[MO]=36:1, С(Fe0)= 100 mg/l, T=25˚C, pH=5.8, τ=120 min.

The analysis of chromatograms shows that the photo-induced combined oxidative system provides conditions for more complete oxidation of the initial MO and intermediate products (Figure 3).

Figure 3. 3-D chromatograms of MO solutions before and after 120 min of treatment in various oxidative systems C(MO)=10 mg/l, [S2O82–]:[MO]=36:1, C(Fe0)= 100 mg/l, T=25˚C, pH=5.8, τ=120 min.

3.2. Effect of initial pH and T°C on photodegradation of MO

To identify the optimal temperature and pH of the reaction medium, a series of experiments was conducted with the degree of conversion and discoloration as the measured variables. It was established that the pH values of 4, 5.8 and 7 (Figure 4 (a)) do not have a significant impact on the degree of conversion of MO. However, at pH=7 the discoloration degree of the MO solution was only 70 %, possibly due to the formation of colored compounds (Figure 4 (b)).

The selected temperature range (25, 35, and 45°C) did not affect significantly the conversion of MO and discoloration of MO solutions (Figure 5).
Figure 4. Effect of pH on the extent of conversion of MO (a) and discoloration of the solution (b); 
C(MO)=10 mg/l, [S$_2$O$_8^{2-}$]:[MO]=36:1, C(Fe$^{0}$)=100 mg/l, T=25°C, τ=120 min.

Figure 5. Effect of temperature on the extent of conversion of MO (a) and discoloration of the solution (b); 
C(MO)=10 mg/l, [S$_2$O$_8^{2-}$]:[MO]=36:1, C(Fe$^{0}$)=100 mg/l, pH=5.8, τ=120 min.

As a result, pH=5.7 and the temperature of 25°C were selected as optimal conditions for degradation of MO.

3.3. Effect of initial concentration of S$_2$O$_8^{2-}$ on removal of MO

To study the effect of the oxidant concentration on the degradation process of MO, the following molar ratios of [oxidant]:[substrate] = 12:1; 24:1; 36:1; 48:1 were selected. It was observed that the degradation rate of MO increased proportionally to the initial concentration of the oxidant at molar ratios of [oxidant]:[substrate] ≤ 12. Judging by the character of the kinetic curves, a further increase of this ratio is impractical (Figure 6). However, the increase in the concentration of the oxidant had a positive effect on the degree of mineralization of total organic carbon (TOC). At the ratios of 12:1 and 48:1 the mineralization of TOC was 23% and 60%, respectively. According to the hypothetical reaction equation, 39 moles of S$_2$O$_8^{2-}$ would be required for 1 mole of MO:

$$
\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{Na} + 78 \text{SO}_4^{2-} + 38 \text{H}_2\text{O} \rightarrow 14 \text{CO}_2 + 3 \text{NO}_3^{-} + 79 \text{SO}_4^{2-} + 90 \text{H}^{+} + \text{Na}^{+}
$$

Based on the above considerations, 36:1 was chosen as the optimal ratio of [oxidant]:[substrate].

Figure 6. The kinetics of conversion of MO (a) and discoloration of the solution (b) at different molar ratios of [S$_2$O$_8^{2-}$]:[MO], C(MO)=10 mg/l, C(Fe$^{0}$)=100 mg/l, T=25°C, pH=5.8, τ=120 min.
3.4. Effect of Fe$^0$ dosage
While selecting a catalyst, special consideration must be given to Fe$^0$ as it is not only an effective activator, but also non-toxic, environmentally friendly, and costs significantly less as compared with other transitional metals [19,20]. To determine the optimal concentration of the catalyst required for degradation of MO, the following concentrations of Fe$^0$ were tested: 50, 100, and 200 mg/l. It was found that increasing the concentration of Fe$^0$ leads to increased degree of conversion of MO and discoloration of the solution (Figure 7). However, at high concentrations of Fe$^0$, there is the possibility that SO$_4$$^-$$^-$ would be consumed (eq. 5-12). The optimal concentration of Fe$^0$ chosen was 100 mg/l.

\[
\begin{align*}
S_2O_8^{2-} + hv & \rightarrow 2 SO_4^- \\
Fe^0 + S_2O_8^{2-} & \rightarrow Fe^{2+} + 2 SO_4^{2-} \\
Fe^{2+} + S_2O_8^{2-} & \rightarrow SO_4^- + SO_4^{2-} + Fe^{3+} \\
Fe^{3+} + S_2O_8^{2-} & \rightarrow 2 SO_4^- + Fe^{2+} \\
Fe^{2+} + SO_4^- & \rightarrow SO_4^{2-} + Fe^{3+} \\
SO_4^- + H_2O & \rightarrow \cdot OH + HSO_4^- \\
SO_4^- + OH^- & \rightarrow \cdot OH + SO_4^{2-} \\
SO_4^- + SO_4^- & \rightarrow S_2O_8^{2-}
\end{align*}
\]

Figure 7. Kinetic curves of conversion of MO (a) and discoloration of the solution (b) at various concentrations of Fe$^0$; C(MO)=10 mg/l, [S$_2$O$_8^{2-}$]:[MO]=36:1, T=25°C, pH=5.8, $\tau$=120 min.

4. Conclusion
The analysis of literary data has shown that advanced oxidation processes employing natural sunlight hold promise in treatment of wastewater from azo dyes. The comparative experiments have shown that the mineralization of MO in different oxidative systems increases in the following order: Solar $\sim$ Solar/Fe$^0$ $\sim$ Solar/S$_2$O$_8^{2-}$ $< S_2O_8^{2-}/Fe^0 < Solar/S_2O_8^{2-}$ / Fe$^0$. The influence of the main factors (duration of exposure, pH and temperature of the reaction medium, the ratio of the initial concentrations of [substrate]:[oxidant]:[catalyst]) on the degree of conversion and mineralization of MO was studied. The optimal pH and temperature of the reaction medium were 5.8 and 25°C, respectively. The rate of degradation and mineralization of MO increased proportionally to the initial concentration of the oxidant at the molar ratios of [S$_2$O$_8^{2-}$]:[MO] $\leq$ 12. Judging by the character of the kinetic curves, a further increase of this ratio would be impractical. However, the increase in the concentration of the oxidant had a positive effect on TOC removal. At the ratios of 12:1 and 48:1 the efficiency of TOC removal was 23% and 60 %, respectively. Since the stoichiometric concentration ratio of persulfate to MO is 39:1, 36:1 was chosen as the optimal ratio of [oxidant]:[substrate]. The optimal concentration of Fe$^0$ was 100 mg/l. The results highlight the prospects of using solar radiation in advanced oxidation processes and arrant further research.
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