

Degradation of Methyl Orange in aqueous solution by UV/H₂O₂ advanced oxidation process

P. Kourani¹, Z. Samadi¹, H. Roohollahi^{2,*}

1. Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran

2. Department of Chemical Engineering, Vali-E-Asr University of Rafsanjan, Rafsanjan, Iran
Hosseinroohollahi54@gmail.com

Abstract

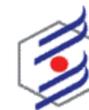
In this work, The degradation of the methyl orange (MO) dye was studied using advanced oxidation process (AOP) by exposing MO aqueous solution to UV irradiation after the addition of hydrogen peroxide (H₂O₂). The degradation of MO was accompanied by the decolorization of the solution. A thorough investigation of the AOP process was carried out by studying the influence of the dye concentration, H₂O₂ concentration, operation time, and pH. The result indicated that the maximum The degradation of the MO(91%) was achieved at pH 2.5. Also by increasing H₂O₂ concentration, the amount of The degradation of the MO increases. also color removal increased with increasing operation time. Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants in water. This operation has good efficiency for The degradation of th MO dye.

Keywords: Degradation, Methyl Orange, AOP, Wastewater.

Introduction

The textile industry has played a significant role in the economical development of many countries. different types of synthetic dyestuffs appear in the effluents of wastewater in various industries such as dyestuff, textiles, and leather. The effluents including dyes are a highly colored and serious reason for water pollution. Today there are more than 10,000 dyes with various chemical structures attainable commercially. Dyes are broadly classified as anionic, cationic and non-ionic depending on the ionic charge on the dye molecules. Cationic dyes are more poisonous than anionic dyes [1]. From an environmental point of view, the removal of synthetic industrial dyes is of great concern, since most of these dyes and their degradation products may be carcinogens and poisonous. In the last decades, the removal of color synthetic organic dyestuff from waste effluents becomes an environmental challenge. It is rather difficult to treat dye effluents because of their synthetic source and their mainly aromatic structures, which are biologically non-degradable [2].

to improvement these organic pollutants in an effective and economic method, a large number of physical, chemical, and biological methods were proposed and considered during the few ago decades. between the possible wastewater treatment methods, the advanced oxidation processes (AOPs), which mainly involve the generation of amain oxidative kinds like free



hydroxyl radicals ($\bullet\text{OH}$) and the subsequent attack of these radicals on the pollutants, are highly efficient methods for rapid oxidation/degradation of azodyes. The most widely accepted AOPs contain photodegradation[3], ozonation[4], Fenton[5], photo-Fenton[6], ultrasonication[7], catalytic H_2O_2 oxidation[8], and so forth. However, the AOPs can offer good efficiency for the oxidation of refractory organic pollutants, the complexity, high chemical consumption, and relatively high operation costs constitute main barriers for their large-scale applications [9].

In addition, advanced oxidation processes (AOPs) are very useful for the treatment of industrial wastes include organic dyes. AOP is based on the generation of highly reactive radicals, which are very powerful oxidizing factors (e.g. $\bullet\text{OH}$, $E_0 = 2.8 \text{ V/NHE}$) at situation near ambient temperature and pressure. Many researchers reported on the effectiveness of AOPs with or without its combination with other techniques [10].

Hydrogen peroxide (H_2O_2) is very significant chemical reagents, and it is widely used for bleaching of textiles and paper in the relevant industries and for important usage are the removing organic and inorganic pollutants from wastewater in the field of environmental protection. In addition, H_2O_2 plays an important role in biochemical processes, because it is essential for cellular activities and has been identified as a second messenger [11]. However, H_2O is extremely toxic to cells at high concentrations, and its toxicity is mainly a result of highly deleterious hydroxyl radicals ($\bullet\text{OH}$) generated from the Fenton reaction [12]. So, the determination of trace amounts of H_2O_2 is of considerable importance in fields of food, environmental science and technology, and clinical applications[13].

In 2011, haji et al.[10] investigated degradation of MO through the $\text{H}_2\text{O}_2/\text{UV}$ process. They reported that, the dye degradation rate increased with the increase in the initial dye concentration, UV irradiation power.

Amin et al.[14] reported on the influence of few experimental parameters such as UV intensity, pH of the solution, and H_2O_2 dosage on the degradation of Blue Sulfur dye present in synthetic aqueous solutions.

In this study, We investigated the effect of the Hydrogen Peroxide concentration, Effect of operation time, Effect of initial concentration, and Effect of pH on the degradation of MO from wastewater.

Experimental

Materials

Hydrogen peroxide (30%, w/w), Methyl orange (MO), sodium hydroxide (NaOH), hydrochloric acid (HCl) obtained from Merck co were used without any further purification. The chemical structure of MO is shown in Figure 1.

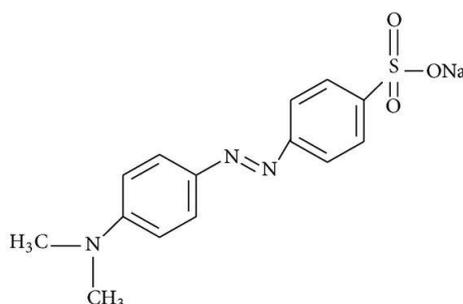
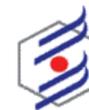


Figure 1. Chemical the structure of methyl orange dye.



Batch Degradation studies

batch experiments for the UV/H₂O₂ processes were performed in a batch photoreactor in a quartz beaker 100 mL contain different concentrations of MO solution (10-70mg/L) with different pH values (2-12) and different concentration H₂O₂(10-25mmol/L) that was put on magnetic stirring with a stirring speed of 100 rpm at 25 °C for different times(10-90 min). The initial pH of the MO solution is natural. A stock solution of 200 mg/L was prepared by dissolving accurately weighed amounts of MO separate doses of 1000 mL distilled water. The desirable experimental concentrations of solutions were prepared by diluting the stock solution with distilled water. The percent of the degradation of the MO at equilibrium condition, Degradation%, was calculated by the following equations:

$$\text{Degradation\%} = \frac{(C_o - C_e)}{C_o} \times 100$$

where C₀ and C_e are the initial and equilibrium dye concentrations (mg/L), respectively.

Results and discussion

Effect of pH

Solution pH is an important factor influencing MO degradation in a AOP system. The pH optimum for AOP is usually reported in the acidic range (pH < 4.0). In order to choose the best solution pH in this reaction system, the MO absorbance variations have been determined at different solution pH values and H₂O₂ concentrations. Figure. 2 shows that the degradation of the MO increased initially with the increasing of pH, reached a maximum at pH 2.5, and then decreased when pH > 2.5. Therefore, pH 2.5 was selected for further experiments.

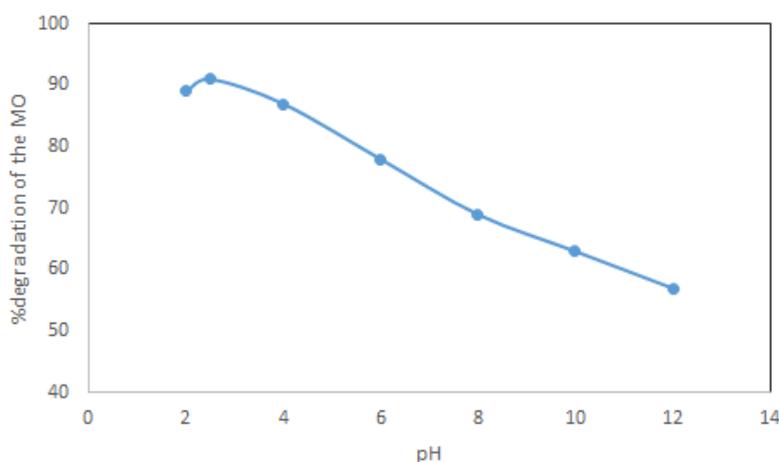
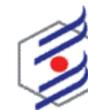


Figure 2- the effect of pH on the degradation of the MO
(initial concentration=10 ppm, H₂O₂ concentration=25mmol, operation time=30min)

Effect of Hydrogen Peroxide concentration

Figure 2 shows the effect of H₂O₂ concentration on the degradation of the MO. As expected, increasing hydrogen peroxide concentration will speed the MO oxidation as more hydroxyl radicals are produced. The MO degradation efficiency increases from 57.7 to 91.2% with increasing H₂O₂ concentration from 10 to 25 mmol/L. However, some of the hydroxyl radicals could also be scavenged by excess H₂O₂ to form hydroperoxyl radicals, which reduced the



probability of the attacking hydroxyl radical on the organic molecule. As a consequence, the MO degradation efficiency increases little with further increase in H₂O₂ concentration.

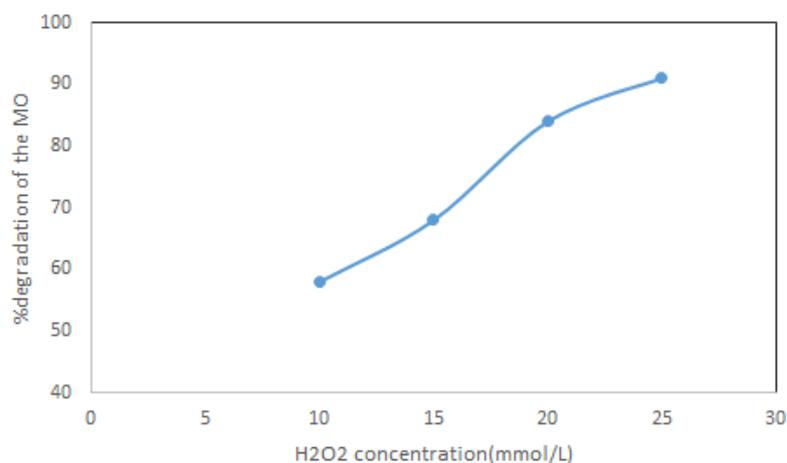


Figure 3- the effect of of H₂O₂ concentration on the degradation of the MO (initial concentration=10 ppm, contact time=30min)

Effect of operation time

Figure 4 illustrates clearly the effects of operation time on the decolorization extent, which is represented by absorbance change. increases rapidly with increase of operation time initially, and approaches an almost constant value beyond 30min. Therefore, a operation time is optimized as t=30min to reduce the total operation time for the whole measurement.

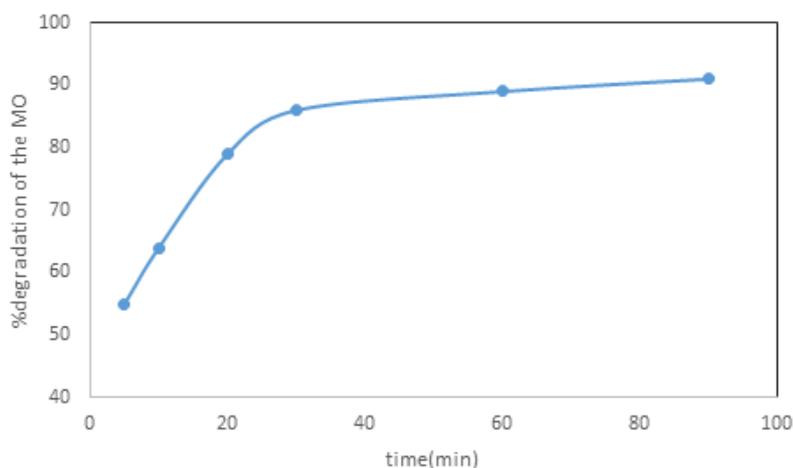
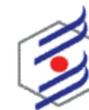


Figure 4- the effect of operation time on the degradation of the MO (initial concentration=10 ppm, H₂O₂ concentration=25mmol, pH=2.5)

Effect of initial concentration

The influence of MO concentration on the degradation of the MO is shown in Figure 5. The degradation of the MO is decreased with increasing of MO concentration. In contrast, at higher MO concentrations, only a very small fraction of the MO molecules may be degraded and the



extent of MO decolorization is very small when the H₂O₂ level is not high enough. Consequently, we selected a Low MO concentration of 10 mg L⁻¹ for further experiments in the present work

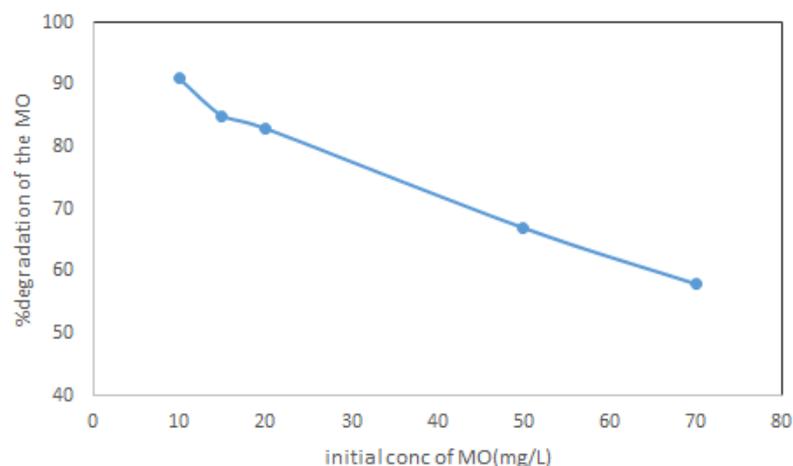


Figure 5- the effect of initial concentration of the MO on degradation of the MO (H₂O₂ concentration=25mmol, pH=2.5, operation time=30min)

Conclusions

In this study, we investigated the degradation of methyl orange dye using H₂O₂/UV As one of the methods AOP. The degradation studies were carried out under different condition including, initial concentration of MO, operation time, H₂O₂ concentration, and solution pH. The maximum degradation of the MO 91% was achieved under the conditions of H₂O₂ concentration 25 mmol/L, pH 2.5, operation time 30 min and temperature 25°C with MO concentration 10 mg/L. Finally, would be considered as efficiently and environmentally friendly method for the degradation of the MO from the aqueous phase due to its no-toxic properties, as well as high performance.

reference

- [1]O. J. Hao, H. Kim, and P. C. Chiang, "Decolorization of wastewater," Critical Reviews in Environmental Science and Technology, vol. 30, no. 4, pp. 449–505, 2000.
- [2]G. O. El-Sayed, "Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber," Desalination, vol. 272, no. 1–3, pp. 225–232, 2011.
- [3]D. Zhao, G. Sheng, C. Chen, and X. Wang, "Enhanced photocatalytic degradation of methylene blue under visible irradiation on graphene@TiO₂ dyade structure," Appl. Catal. B Environ., vol. 111–112, pp. 303–308, 2012.
- [4]M. Koch, A. Yediler, D. Lienert, G. Insel, and A. Kettrup, "Ozonation of hydrolyzed azo dye reactive yellow 84 (CI)," Chemosphere, vol. 46, no. 1, pp. 109–113, 2002.
- [5]A. Rodríguez, G. Ovejero, J. L. Sotelo, M. Mestanza, and J. García, "Heterogeneous fenton catalyst supports screening for mono azo dye degradation in contaminated wastewaters," Ind. Eng. Chem. Res., vol. 49, no. 2, pp. 498–505, 2010.
- [6]J. Macías-Sánchez, L. Hinojosa-Reyes, J. L. Guzmán-Mar, J. M. Peralta-Hernández, and A. Hernández-Ramírez, "Performance of the photo-Fenton process in the degradation of a model azo dye mixture," Photochem. Photobiol. Sci., vol. 10, no. 3, pp. 332–337, 2011.
- [7]N. H. Ince and G. Tezcanli-Güyer, "Impacts of pH and molecular structure on ultrasonic



degradation of azo dyes,” *Ultrasonics*, vol. 42, no. 1–9, pp. 591–596, 2004.

[8]C. Tizaoui, N. Karodia, and M. Aburowais, “Kinetic study of the manganese-based catalytic hydrogen peroxide oxidation of a persistent azo-dye,” *J. Chem. Technol. Biotechnol.*, vol. 85, no. 2, pp. 234–242, 2010.

[9]D. Xu, F. Cheng, Q. Lu, and P. Dai, “Microwave enhanced catalytic degradation of methyl orange in aqueous solution over CuO/CeO₂ catalyst in the absence and presence of H₂O₂,” *Ind. Eng. Chem. Res.*, vol. 53, no. 7, pp. 2625–2632, 2014.

[10]S. Haji, B. Benstaali, and N. Al-Bastaki, “Degradation of methyl orange by UV/H₂O₂ advanced oxidation process,” *Chem. Eng. J.*, vol. 168, no. 1, pp. 134–139, 2011.

[11]G. Georgiou and L. Masip, “An overoxidation journey with a return ticket,” *Science* (80-.), vol. 300, no. 5619, pp. 592–594, 2003.

[12]A. F. Li et al., “Oxidative cyclization of N-acylhydrazones. Development of highly selective turn-on fluorescent chemodosimeters for Cu²⁺,” *Org. Biomol. Chem.*, vol. 7, no. 1, pp. 193–200, 2009.

[13]W. Luo, M. E. Abbas, L. Zhu, K. Deng, and H. Tang, “Rapid quantitative determination of hydrogen peroxide by oxidation decolorization of methyl orange using a Fenton reaction system,” *Anal. Chim. Acta*, vol. 629, no. 1–2, pp. 1–5, 2008.

[14]H. Amin, A. Amer, A. El Fecky, and I. Ibrahim, “Treatment of textile waste water using H₂O₂/UV system,” *Physicochem. Probl. Miner. Process.*, vol. 42, pp. 17–28, 2008.