

DI-(2-ETHYLHEXYL) PHTHALATE OXIDATIVE DEGRADATION BY FENTON PROCESS IN SYNTHETIC AND REAL PETROCHEMICAL WASTEWATER

¹R. Esmaeli, ¹A. H. Hassani, ^{*2}A. Eslami, ³M. Ahmadi Moghadam, ⁴A. A.Safari

¹ Department of Environmental Engineering, Islamic Azad University, Sciences and Research Branch, Tehran, Iran

² Department of Environmental Health Engineering, Shahid Behashti University of Medical Sciences, Tehran, Iran

³ Department of Environmental Health Engineering, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

⁴ Department of Chemistry, Institute for Advanced Studies in Basic Science (IASBS), Zanjan, Iran

Received 5 February 2011; revised 14 May 2011; accepted 7 August 2011

ABSTRACT

Di-(2-Ethylhexyl) phthalate (DEHP) belongs to the class of phthalate esters and is used as an additive in many products including plastics, paints and inks or as a solvent in industrial formulations. The degradation of DEHP in aqueous solution using oxidative Fenton reaction (H_2O_2/Fe^{2+}) was carried out in this study. It was found that H_2O_2 concentration, Fe^{2+} concentration, and pH were the three main factors that could significantly influence the degradation rates of DEHP. The highest degradation percentage (85.6 %) of DEHP was observed within 60 min at pH 3 in H_2O_2/Fe^{2+} system. The results of our study suggested that the concentration with 90 mg/L H_2O_2 , 5 mg/L Fe^{2+} , and 20 mg/L DEHP in the solution at pH 3 were the optimal conditions. The optimized reaction parameters were preceded for treatment of real wastewater obtained from a petrochemical plant.

Key words: Oxidation; Di-(2-Ethylhexyl) phthalate (DEHP); Fenton reagent; Petrochemical wastewater

INTRODUCTION

Phthalic acid esters (PAEs) are a class of refractory organic compounds widely used as plasticizers in polyvinyl chloride (PVC) plastics (Jianlong *et al.*, 2000; Chang *et al.*, 2007; Yuan *et al.*, 2008). The stability, fluidity and low volatility of higher molecular weight phthalate esters make them highly suitable as plasticizers (Jianlong *et al.*, 2004). Experiments in animal systems, however, have provided a substantial body of evidence that PAEs are also endocrine disruptor compounds. PAEs are currently listed as priority pollutants in many countries due to their link to several human cancer diseases (Chen *et al.*, 2009). Release of PAEs into the ecosystem or wastewater occurs

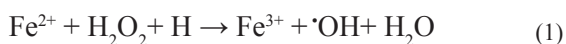
*Corresponding author: E-mail: aeslami@sbm.ac.ir
Tel: +98 21 22 43 20 40, Fax: +98 21 22 43 20 37

during manufacturing of different compounds and usage of products (Chen, 2010). Because PAEs are rather stable compounds that gradually accumulate in the environment, there is a need to search for efficient treatment methods to deal with these compounds (Chen *et al.*, 2009; Chen, 2010).

The most abundant of PAEs in the environment is di-(2-ethylhexyl) phthalate (DEHP), (Khan and Jung, 2008; Chen *et al.*, 2009). Numerous chronic effects such as hepatotoxicity, teratogenicity, carcinogenicity, adverse effects on male reproduction organs and endocrine disruption have been identified. Therefore, DEHP is classified as a probable human carcinogen (Group B2) by USEPA since 1987. Also, it has been placed

on the USEPA priority pollutants list due to its sublethal effects and ubiquity in the environment (Latini *et al.*, 2006; Chan *et al.*, 2007; Shailaja *et al.*, 2008). The water criterion of DEHP is 3 µg/L as recommended by the USEPA for the protection of aquatic organisms (USEPA, 1994), while the concentration of DEHP in drinking water should be up to 30 µg/L (Chien Chung *et al.*, 2009).

Advanced Oxidation Processes (AOPs) are ideal for the removal of recalcitrant pollutants from aqueous solutions. One of the most promising AOPs is that of Fenton reaction. The primary reactions in representative Fenton process are (Yang *et al.*, 2005; Mousavi *et al.*, 2011):



$$k_1 = 58 \text{ l/mol dm}^3/\text{s}$$



$$k_2 = 0.02 \text{ l/mol dm}^3/\text{s}$$

Where $\cdot\text{OH}$ is the hydroxyl radical and $\cdot\text{OOH}$ is the superoxide radical. If the concentration of hydroxyl radicals generated in Fenton system is sufficient, almost all organic substances can be oxidized and mineralized to carbon dioxide and water. Thus, Fenton treatment has attracted much interest for the destruction of toxic organic compounds in aqueous environment.

The primary aim of our study was to evaluate the removal efficiency of Fenton system to remove DEHP from wastewater. The effects of DEHP, Fe^{2+} and H_2O_2 concentrations in Fenton reactor are also evaluated. The second objective of the present study was to investigate the efficiency of DEHP degradation in real wastewater containing DEHP, obtained from Farabi Petrochemical Plant. Farabi petrochemical company is located in Bandar Imam Khomeini district in the south of Iran. The complex consists of two units as dioctyl Phthalate (DOP) plant with nominal capacity of 4000 Tons/year and Flaked phtalic anhydride (PAF) with 5500 Tons/year. Thereby in this study, laboratory scale feasibility for the use of Fenton process to petrochemical wastewater treatment has been assessed.

MATERIALS AND METHODS

Materials

Di-(2-Ethylhexyl) phthalate (DEHP), hydrogen peroxide (30% w/w), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and Na_2SO_3 were purchased from Merck company. The water used in the study was purified by milli-Q system (Millipore). The baseline DEHP concentration was set at 20 mg/L. Wastewater containing DEHP was obtained from Farabi Petrochemical Plant. pH was adjusted in the range of 2-6 with 0.1 M HCL and 0.1 M NaOH solutions. The high concentration of H_2O_2 was determined by a potassium permanganate method.

Experiment setup

For each oxidative degradation experiment, synthetic aqueous solution of 20 mg/L DEHP was prepared in deionized water. Then 50 mL solution of 20 mg/L DEHP was poured into the reactor. Subsequently, a series of different volumes of high concentration of H_2O_2 or Fe^{2+} solution were added into the reactor to examine the effects of the concentration on the degradation reaction. Because the volume of the added standard stock solution was minimal, no dilution effect would produce on DEHP solution. Calculated volume aqueous solution of 0.1 M Na_2SO_3 was added to each sample to quench the reaction between OH radical and DEHP. All experiments were carried out at 25 ± 1 °C.

Analysis

DEHP extraction was performed twice with dichloromethane. Dichloromethane collected after extraction was dried by passing through a column containing anhydrous sodium sulphate. The extracts were sufficiently clean for directly analysis. The concentration of DEHP was measured by high performance liquid chromatography (HPLC). All analyses were carried out on a Knauer, eurochrom HPLC system with UV detector. A Vertex C18 Column (packing material=5µm, Length×ID = 250×4.6 mm) was employed with a mobile phase of acetonitrile/methanol (90:10 v/v) at a flow rate 0.8 mL/min. UV detection was performed at 225 nm. The detection limit of HPLC for DEHP analysis was 100 µg/L. Concentrations of DEHP were calculated by calibration curves obtained from

HPLC measurements of the standard at different concentrations.

RESULTS

Optimization of reaction conditions

Effect of initial H₂O₂ concentration

In order to investigate the optimum H₂O₂ concentration, different initial concentrations ranging from 0 to 120 mg/L at room conditions with constant Fe²⁺ dosage of 10 mg/L were tested. The degradation percentages during 60 min are presented in Fig. 1.

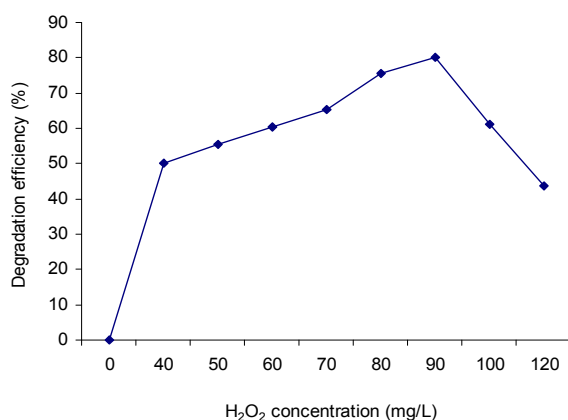


Fig. 1: Effect of initial H₂O₂ concentration on DEHP degradation efficiency; initial DEHP concentration=20 mg/L, pH=4, Fe²⁺=10 mg/L and reaction time=60 min

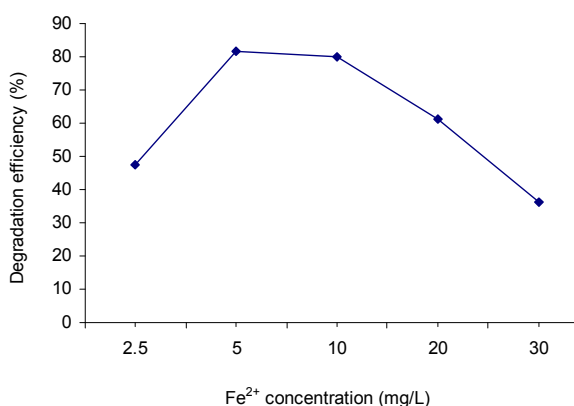


Fig. 2: Effect of initial Fe²⁺ concentration on DEHP degradation efficiency; initial DEHP concentration=20 mg/L, pH=4, H₂O₂=90 mg/L and reaction time=60 min

Effect of initial Fe²⁺ concentration

A series of experiments were performed by varying the concentration of Fe²⁺ from 2.5 to 30 mg/L for fixed H₂O₂ concentration of 90 mg/L and at pH=4. The degradation efficiency for DEHP with various Fe²⁺ concentrations is illustrated in Fig. 2.

Effect of initial pH

In Fig. 3, The effect of pH on degradation efficiency in the range of 2–6 is presented at constant initial conditions.

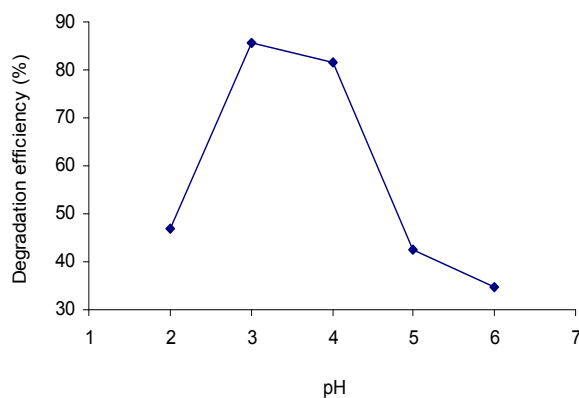


Fig. 3: Effect of initial pH on DEHP degradation efficiency; initial DEHP concentration=20 mg/L, Fe²⁺=5 mg/L, H₂O₂=90 mg/L and reaction time=60 min

Effect of initial DEHP concentration

The oxidative degradation of DEHP was investigated with different concentrations in the range of 10 – 30 mg/L. The results are shown in Fig. 4.

Effect of reaction time

The relationship between the photodegradation of DEHP and reaction time is presented in Fig. 5.

Application of the optimized H₂O₂/Fe²⁺ process for degradation of DEHP in real petrochemical wastewater

In order to investigate the efficiency of DEHP degradation in actual wastewater, samples

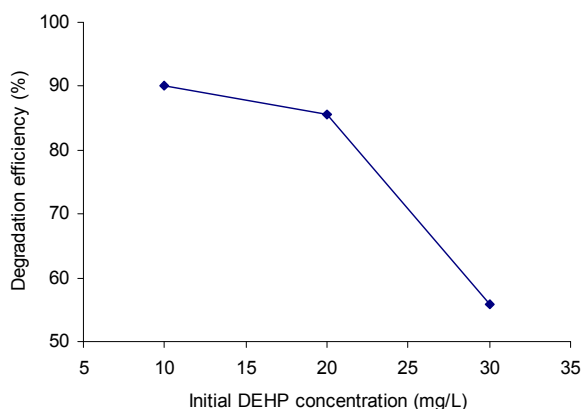


Fig. 4: Effect of initial concentration of DEHP on degradation efficiency; pH=3, Fe²⁺=5 mg/L and H₂O₂=90 mg/L

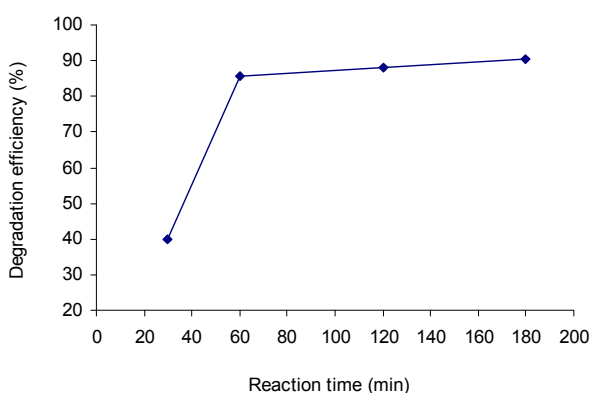


Fig. 5: Effect of reaction time on DEHP degradation efficiency; initial DEHP concentration=20 mg/L, pH=3, Fe²⁺=5 mg/L and H₂O₂=90 mg/L

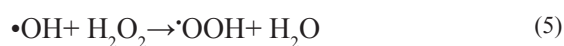
were obtained from the effluent of Farabi petrochemical plant, located in the south of Iran. The initial characteristics of water such as DEHP concentration, pH and COD were 200 mg/L, 6 and 1136 mg/L, respectively. Results are presented in Table 1.

Table 1: The degradation of DEHP in real wastewater with Fe²⁺=5 mg/L, H₂O₂=90 mg/L and pH=3 at different reaction times

Reaction time (min)	Degradation percentage (%)
60	45.5
120	65.5
180	70.4

DISCUSSION

Hydrogen peroxide plays the role of an oxidizing agent in Fenton process (Kavitha *et al.*, 2005). A low concentration of H₂O₂ did not generate enough ·OH in solution. Also, increasing H₂O₂ concentration had two opposite effects on the reaction yield. On one hand, higher initial hydrogen peroxide concentration enhanced the oxidation process leading to an increase in the concentration of ·OH radicals up to a certain concentration, when hydrogen peroxide started to react with hydroxyl radicals acting as a free-radical scavenger itself decreasing the hydroxyl radicals concentration and generating ·OOH radicals much less reactive. So there was an optimum H₂O₂ concentration to achieve the maximum percentage of removal although the definition of the concentration range varies for different contaminated wastes (Farrokhi *et al.*, 2004; Primo *et al.*, 2008). As the primary factor contributing to the chemical costs of Fenton reagent is the cost of H₂O₂, it is important to minimize the amount of H₂O₂ required, especially for treating large volumes of wastewater with pollutants such as DEHP (Yang *et al.*, 2005). The degradation of DEHP did not occur in the absence of H₂O₂, but by the addition of H₂O₂, DEHP began to be degraded and the degradation rate increased with increasing H₂O₂ concentration (Fig. 1). The degradation efficiency increased from 50.25% to 80% when H₂O₂ concentration increased from 40 to 90 mg/L. Further addition of H₂O₂, began to decrease the degradation efficiency. It may be due to self-decomposition of H₂O₂ as in Eq. (3). Moreover, the excess H₂O₂ reacts with ferric ion (Fe³⁺) to form weaker hydroperoxyl radical (·OOH) as presented in Equations (4) and (5), which is not as active as ·OH radical towards DEHP degradation (Kavitha *et al.*, 2005). Thus a concentration of H₂O₂ of 90 mg/L was selected in further experiments.



According to the results, the highest removal efficiency attained was 81.52%. When Fe^{2+} concentration increased upto 2.5 mg/L, the decomposing effect increased accordingly and the amount of hydroxyl radicals from decomposition of H_2O_2 increased. On the other hand, when the concentration of Fe^{2+} increased and especially beyond 5 mg/L, a great amount of Fe^{2+} has been competed with the DEHP in solutions for hydroxyl radicals (Chen *et al.*, 2009).

Fenton reactions are usually more effective in oxidation of organic compounds under acidic conditions than under neutral conditions (Yang *et al.*, 2005). The initial pH affects the degradation of cresols significantly by directly influencing the generation of $\cdot\text{OH}$ radical. Fig. 3 indicates that maximum degradation efficiency of 85.6% was observed. The degradation declined at $\text{pH}>3$, because iron started to precipitate as hydroxide, which lowers the concentration of free soluble iron species available for reacting with peroxide. Hence, less concentrations of $\cdot\text{OH}$ radical is generated for oxidizing DEHP and consequently the degradation efficiency decreases. Besides, the oxidation potential of $\cdot\text{OH}$ radical decreases with increasing pH (as shown in Fig. 3).

Since, contamination of DEHP from different effluent varies from locations. It is important to investigate the impact of different initial DEHP concentrations in oxidation process. Hence, with the optimized initial concentration of H_2O_2 , Fe^{2+} and pH, the effect of initial DEHP concentration was investigated by varying the initial concentration from 10 to 30 mg/L in the experiments. The results as shown in Fig. 4 indicates that degradation efficiency decreased as initial concentration of DEHP increased from 90.2% to 55.8% at the time of 60 min. The results show in Fig. 4 indicate that removal efficiency increased as the reaction time increased. It was found that DEHP removal was 85.6% at 60 min and complete removal happened in 180 min. Moreover, longer reaction time was required for complete degradation as the concentration of DEHP increased. The results show that the maximum removal efficiency for real wastewater was 70.4% according to Table 1 as compared with synthetic water (90.5%). This might be due to interference of other unknown organic

pollutants or scavengers of hydroxyl radical such as anions present in the solution. Chen *et al.* (2009) observed a similar phenomenon in their study in which the photo-Fenton process was used for the pretreatment of DEHP. These results clearly demonstrate the feasibility of Fenton system for treatment of real wastewater. Finally, in this investigation, an advanced oxidation process, Fenton reaction was utilized to degrade aqueous DEHP, which was among persistent organic pollutants in environment. The optimal concentrations of reagents such as hydrogen peroxide and iron and pH in the Fenton reaction were examined. The maximum degradation percentage (90.5%) of DEHP was observed within 180 min at $\text{pH}=3$ in the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system, with original H_2O_2 and Fe^{2+} concentrations of 90 mg/L and 5 mg/L, respectively. The present study shows that Fenton system has high potential in treating aqueous solutions containing DEHP. Hence, the optimized reaction parameters were preceded for treatment of real wastewater obtained from a petrochemical plant.

ACKNOWLEDGEMENTS

The authors would like to thank the Faculty of Health of Zanjan University of Medical Sciences for financial and technical support, and Farabi Petrochemical Plant for the facilities. We also thank Dr. Mehrasbi at the Department of Environmental Health Engineering, Zanjan University of Medical Sciences.

REFERENCES

- Chan, H.W., Chan, C.M., Ang, P.O., Wong, P.K., (2007). Integrated biosorption and photocatalytic oxidation treatment of di (2-ethylhexyl) phthalate. *J Appl Phycol*, **19**: 745-753.
- Chang, B.V., Wang, T.H., Yuan, S.Y., (2007). Biodegradation of four phthalate esters in sludge. *Chemosphere*, **69**: 1116-1123.
- Chen, Ch., (2010). The Oxidation of Di-(2-Ethylhexyl) Phthalate (DEHP) in Aqueous Solution by UV/ H_2O_2 Photolysis. *Water Air Soil Pollut*, **209**: 411-417.
- Chen, Ch., Wub, P., Chung, Y., (2009). Coupled biological and photo-Fenton pretreatment system for the removal of di (2-ethylhexyl) phthalate (DEHP) from water. *Bioresource Technology*, **100**: 4531-4534.
- Chien Chung, Y., Yu Chen, C., (2009). Degradation of Di-(2-ethylhexyl) Phthalate (DEHP) by TiO_2 Photocatalysis. *Water Air Soil Pollut*, **200**: 191-198.
- Farrokhi, M., Mesdaghinia, A.R., Yazdanbakhsh, A.R.,

- Nasseri, S., (2004). Characteristics of Fenton's Oxidation of 2, 4, 6 Trichlorophenol. Iran J Environ Health Sci Eng, **1** (1): 13-19.
- Jianlong, W., Lujun, C., Hanchang, Sh., Qian, Y., (2000). Microbial degradation of phthalic acid ester under anaerobic digestion of sludge. Chemosphere, **41**: 1245-1248.
- Jianlong, W., Xuana, Zh., Weizhong, W., (2004). Biodegradation of phthalic acid esters (PAEs) in soil bioaugmented with acclimated activated sludge. Process Biochemistry, **39**: 1837-1841.
- Kavitha, V., and Palanivelu, K., (2005). Destruction of cresols by Fenton oxidation process. Water research, **39**: 6062-3072.
- Khan, H.M., and Jung, J.Y., (2008). Ozonation catalyzed by homogeneous and heterogeneous catalysts for degradation of DEHP in aqueous phase. Chemosphere, **72**: 690-696.
- Latini, G., Vecchio, A.D., Massaro, M., Verrotti, A., Felice, C.D., (2006). Phthalate exposure and male infertility. Toxicology, **226**: 90-98.
- Mousavi, S.A.R., Mahvi, A.H., Nasseri, S., Ghaffari, Sh. (2011). Effect of Fenton process (H_2O_2/Fe^{2+}) on removal of linear alkylbenzene sulfonate (LAS) using central composite design and response surface methodology. Iran. J. Environ. Health. Sci. Eng., **8** (2): 129-138.
- Primo, O., Rivero, M. J., Ortiz, I., (2008). Photo-Fenton process as an efficient alternative to the treatment of landfill leachates. J Hazard Mater, **153**: 834-842.
- Shailaja, S., Venkata Mohan, S., Rama Krishna, M., Sarma, P.N., (2008). Degradation of di-ethylhe phthalate (DEHP) in bioslurry phase reactor and identification of metabolites by HPLC and MS. Int Biodeter & Biodegr, **62**: 143-152.
- US EPA (United States Environmental Protection Agency), (1994). Water Quality Standards Handbook-Chapter 3 'EPA August 1994', Publication EPA-823-B-B-94-005a, U.S. Environmental Protection Agency, Office of Water, Washington, DC.
- Yang, G., Zhao, X., Sun, X., Lu, X., (2005). Oxidation degradation of diethyl phthalate photochemically- enhanced Fenton reaction. J Hazard Mater, **126**: 112-118.
- Yuan, B., Li, X., Graham, N., (2008). Reaction pathways of dimethyl phthalate degradation in TiO_2 -UV- O_2 and TiO_2 -UV-Fe (VI) systems. Chemosphere, **72**: 197-204.