

TREATMENT OF WATER CONTAMINATED WITH DI-N-BUTYL PHTHALATE BY PHOTO-FENTON PROCESS

B.S. AL-TAWABINI

Research Institute,
King Fahd University of Petroleum & Minerals
P.O. Box # 952, Dhahran 31261, Saudi Arabia

Selected from papers presented at the 7th Conference
on Environmental Science and Technology,
3-6 September 2001, Ermoupolis, Syros island, Greece.

to whom all correspondence should be addressed:

tel : + 966-3-860-4386

fax: + 966-3-860-4029

e-mail: bassamst@kfupm.edu.sa

ABSTRACT

This study was conducted to assess the removal efficiency of Di-n-butyl phthalate (DnBP) from aqueous medium using the photo-Fenton process. The Fenton's reagent that consists of a mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) was used to generate the hydroxyl radical (OH^0) that attacks the target contaminant and degrade it. An ultraviolet (UV) source was used to provide the radiation needed in the photo-Fenton method (i.e. $UV/H_2O_2/Fe^{2+}$). The results demonstrated that photo-Fenton process was more effective and faster than Fenton's reagent in removing DnBP and that photolysis by UV irradiation was the dominant mechanism in degrading the compound. The results also showed that enhancing the removal via UV irradiation was achieved by increasing either the temperature or the H_2O_2 concentration.

KEYWORDS: Ultraviolet light, hydrogen peroxide, hydroxyl radical, phthalates, advanced oxidation processes, Fenton's reagent.

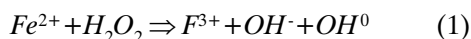
INTRODUCTION

Recent progress in chemical water treatment has lead to the development of Advanced Oxidation Processes (AOPs). These processes employ chemical, photochemical, sonochemical or radiolytic techniques to bring about chemical degradation of pollutants (Huston and Pignatello, 1999). AOPs are based on the generation of hydroxyl radical (OH^0), which has a high oxidation potential (2.8 V) that can sometimes completely convert the organic contaminant into CO_2 and H_2O (Ruppert and Bauer, 1994, Andreozzi *et al.*, 2000).

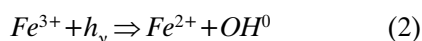
Fenton (H_2O_2/Fe^{2+}) and photo-Fenton ($UV/H_2O_2/Fe^{2+}$) methods have proved to be effective and economical AOP methods used for the detoxification and degradation of many organic compounds (Lin *et al.*, 2000). Research Studies using Fenton's reagent have demonstrated its ability to oxidize pesticides (Huston and Pignatello, 1999), phenols, (Kwon *et al.*, 1999, Kiwi *et al.*, 1994, Wang *et al.*, 1999), aromatics (Casero *et al.*, 1997, Chen *et al.*, 1997), dyes (Li *et al.*, 1999), surfactants (Lin *et al.*, 1998) and polychlorinated biphenyls (PCBs) (Sedlak *et al.*, 1991).

Fenton's reagent is a mixture of H_2O_2 and ferrous

iron, which generate hydroxyl radicals according to the following reaction:



In the presence of substrate, such as a target contaminant, the hydroxyl radicals generated are capable of detoxifying the contaminants via oxidation. Various competing reactions, which involve Fe^{2+} , Fe^{3+} , H_2O_2 , OH^0 radicals, super-oxide radicals, and derived from the substrate, are also possible during Fenton's reagent treatment (Venkatadri, 1993). The catalytic effect of Fe^{2+} can be enhanced by irradiating the solution with ultraviolet (UV) light. The so-called photo-Fenton process increases the regeneration rate of Fe^{2+} and generates more species of hydroxyl radicals as shown by reaction (2). This is expected to enhance the oxidation process (Kim et al., 1998). Thus, the photo-Fenton process can be basically represented by combining reactions (1) with reaction (2).



Di-n-butyl phthalate (DnBP) (Figure 1) was used as a model compound. This chemical is one of phthalic acid diesters and it is slightly soluble in water (11.2 mg l⁻¹) (Staples *et al.*, 1997). It has low volatility and it is widely used in epoxy resins and cellulose esters and specialized adhesive formulations. It is also listed as a priority pollutant by the U. S. Environmental Protection Agency (Bauer *et al.*, 1998). Release of DnBP into the environment can occur during manufacturing, use, and disposal

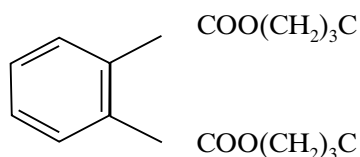


Figure 1. Di-n-Butyl Phthalate (DnBP)

where they become ubiquitous pollutants.

Some researchers studied the degradation of several phthalate esters by microorganisms under aerobic and anaerobic conditions (Cartwright *et al.*, 2000), while others investigated the fate of phthalates by adsorption on solid medium (Hunter *et al.*, 2000). However, little work has been done to study the degradation of phthalate esters in aqueous

medium by photo-oxidation mechanism.

The main objective of this study is to evaluate the efficiency of removing DnBP from contaminated water using photo-Fenton processes.

Materials & methods

A bench-scale batch reactor of 1.2 l Pyrex-glass cylindrical vessel equipped with an outer Plexiglas cylindrical vessel used as a water jacket. A low-pressure ultraviolet (UV) lamp irradiating at a wavelength of approximately 254 nm with an output intensity of about 100 mWatt was used for illumination purpose. In the Fenton's experiments, the residual DnBP concentrations were measured after 1, 2 and 3 hours, while they were measured at fractions of an hour in photo-Fenton experiments.

The DnBP standard solutions from Chemical Service, England with purities of approximately 99 % were used. Stock standard dilutions were prepared in methanol. DnBP concentrations of 0.02 mM (i.e. 5.6 ppm) were spiked in a distilled, deionized distilled water. This concentration was selected as half of the chemical solubility in aqueous medium according to Staples *et al.* (1997).

Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) from Riedel-De Haen AG was used to prepare the ferrous solutions, which were prepared daily. Stock hydrogen peroxide (H_2O_2) of 35% purity from Fluka AG was used to prepare the H_2O_2 solution. The H_2O_2 solution was standardized with potassium permanganate solution (0.1 N $KMnO_4$) by titration method.

The residual DnBP concentrations were measured by a Gas Chromatograph (GC) equipped with a Photo-Ionization Detector (PID). A DB-5 fused silica capillary column of 30m long and 0.53 mm i.d. was used for the separation purpose. The oven temperature was programmed from 80 °C to 200 °C at a ramp rate of 20 °C, with an initial and final hold time of 2 and 12 minutes respectively. Both detector and injector temperatures were set at 280°C. Helium gas was used as a carrier at a flow rate of 3 ml and a makeup of 27 ml. One (1) µl of the extract was injected into the GC by split/splitless mode. The extracts were prepared using a liquid-liquid extraction (LLE) procedure. Twenty (20) ml water samples were extracted, by shaking for one minute, with 10 ml mixture of methylene chloride (MDC) and n-hexane (v/v 1:3). The non-aqueous phase was then concentrated to 2 ml by purging with nitrogen gas. This procedure was found to have a recovery of about 90 to 95%. Due to the low sol-

Table 1. Percentage of DnBP removal by Fenton's Reagent at various Fe²⁺ and H₂O₂ concentrations.

DNBP _i (mM)	H ₂ O ₂ (mM)	Fe(II) (mM)	H ₂ O ₂ /DNBPi	H ₂ O ₂ /Fe	Fe/DNBPi	pH	Temp. (° C)	% DNBP Removed after 3 hrs
0.02	0	0	0			3	25	0.0
0.02	5	0	250			3	25	5.94
0.02	1	0.1	50	10	5	3	25	22.89
0.02	1	0.5	50	2	25	3	25	19.67
0.02	1	1	50	1	50	3	25	29.43
0.02	2	0.1	100	20	5	3	25	17.34
0.02	2	0.5	100	4	25	3	25	25.35
0.02	2	1	100	2	50	3	25	22.33
0.02	5	0.1	250	50	5	3	25	7.77
0.02	5	0.5	250	10	25	3	25	18.58
0.02	5	1	250	5	50	3	25	16.67
0.02	2	0.5	250	4	25	3	45	39.8
0.02	5	0.5	250	10	25	3	45	40.3

ubility of DnBP in water, the DnBP - contaminated water samples were stirred for along time to ensure that DnBP was dissolved in the water.

RESULTS AND DISCUSSION

Degradation of DnBP by Fenton's Reagent

In this phase of the experiment, 400 ml water samples spiked with 0.02 mM DnBP was treated with a mixture of Fe²⁺ at concentrations of 0.1, 0.5 and 1.0 mM and H₂O₂ at concentrations of 1, 2 and 5 mM. The results are listed in Table 1. The results in this table indicate that even though H₂O₂ is considered as a powerful oxidizing agent, its efficiency in oxidizing DnBP was negligible (5.9%). It can be concluded that DnBP was not removed by the action of H₂O₂ alone.

Similarly, when H₂O₂ was combined with Fe²⁺ (Fenton's reagent), only partial removal of DnBP was observed. The removal percentages in this phase under all combinations tested were below 40%. This is an indicative of the slow degradation process and can be attributed to the slowness of the reaction between the OH[•] radicals and the DnBP. Another reason can be due to the existence of the co-solvent (i.e. methanol), which was used to enhance the solubility of DnBP in water. Methanol may inhibit the reaction of the OH radical with the DnBP.

It is worth-mentioning here that pH values were kept in the range of 2.5 to 3.0 since this range is the one proved to work best for Fenton's reagent. On

the other hand, to evaluate the effect of temperature on the DnBP removal efficiency by Fenton's reagent, the temperature of the contaminated water was increased from 25°C to 45°C. The results showed that a slight improvement in the removal efficiency was observed at high temperatures irrespective of the initial concentration of H₂O₂ used. This indicates that the reaction in equation (1) is temperature dependent. However, the extent of removal of DnBP under these conditions is still considered low and need to be improved. Thus UV irradiation source was introduced to enhance the removal efficiency as explained earlier.

Degradation of DnBP by Photo-Fenton Process

UV light is expected to enhance the generation of OH[•] radicals and therefore more removal of DnBP will take place as revealed by equation 2. In this phase of the experiment, a UV lamp was used to supply the radiation. DnBP residual concentrations were measured at 0, 15, 30, 45 and 60 minutes. When UV irradiation source was combined with Fenton's Reagent (i.e. 2 mM H₂O₂ and 0.1 mM Fe²⁺) the removal of DnBP was increased to 70 % as shown in Figure 2. However, when Fe²⁺ concentration was increased to 0.5 mM, the removal efficiency decreased to only 43%. This loss of efficiency can be due to the deposition of iron particles on the UV lamp sleeves. These particles obstruct the passage of the UV light and reduce the amount of OH radicals generated and thus cause a

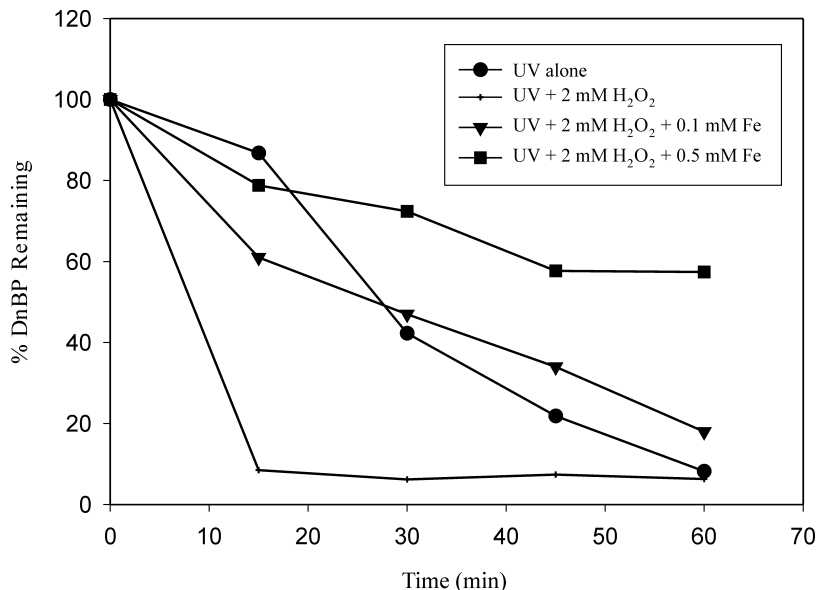


Figure 2. Removal of DnBP by Photo-Fenton Process

reduction in the removal efficiency of the DnBP. Furthermore, Figure 2 also shows that an exposure time of 60 minutes was needed to remove the DnBP when the sample was irradiated by a UV source alone without introducing any other chemical, while only 15 minutes was needed for the removal of the contaminant when a 2 mM of H₂O₂, was used without Fe²⁺, to remove the contaminant. In this case, both actions of photolysis by UV and oxidation by H₂O₂ were combined to degrade the target compound. This clearly indicates that the removal efficiency by UV/H₂O₂ is superior over Fenton and photo-Fenton process.

This result indicates that DnBP is susceptible to degradation by photolysis with UV light. This mechanism of DnBP degradation seems dominant over other degradation mechanisms.

Again, the effect of temperature was investigated in this phase. Figure 3 shows that when the UV was combined with heat source (by elevating the temperature of the contaminated water to 45 °C), more than 90% DnBP removal was observed without the addition of H₂O₂. In this case, the action of thermal degradation was probably combined with the action of photolysis to enhance the degradation efficiency.

SUMMARY AND CONCLUSION

In this study, the degradation of DnBP was investigated under a combination of UV, H₂O₂ and Fe²⁺. Several proportions of Fe²⁺ to H₂O₂ were tested.

The pH was kept in the range of 2.5 to 3.0 while the temperature was set at 25 and 45 °C ± 2 °C by a water jacket. Residual concentration of DnBP compound was taken after 1, 2, and 3 hours in the Fenton's experiments and after 15, 30, 45 and 60 minutes in the photo-Fenton process. The results of this study demonstrated that the Fenton's reagent (i.e. Fe²⁺ + H₂O₂) system was not very effective in degrading the DnBP at the conditions used. This might be attributed the slowness of the reaction of compound with the OHo radical species or the inhibition caused by the co-solvent (methanol).

On the other hand, UV irradiation alone was found to be effective in removing 50% DnBP in half an hour and more than 90% in one hour. Moreover, the results showed that when UV source was combined with H₂O₂ or with heat, excellent removal was achieved in less than 15 minutes. The deposition of iron particles on the UV lamp sleeves and increase turbidity of the solution reduced the intensity of radiation and hence, the removal efficiency of DnBP decreased. Finally, it can be concluded that the treatment process consists a UV source combined with H₂O₂ and or heat is better than photo-Fenton process for degrading the DnBP.

ACKNOWLEDGEMENT

The author wish to acknowledge the support of the Research Institute of King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

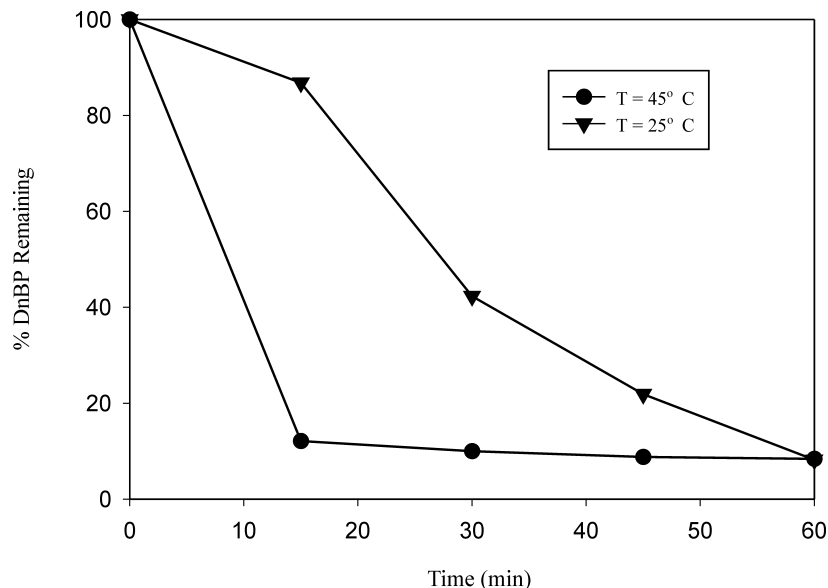


Figure 3. Effect of Temperature on The Removal of DnBP

REFERENCES

- Andreozzi, R., Caprio, V., Insola, A., Marotta, R. and Sanchirico, R. (2000), Advanced Oxidation Processes For the Treatment of Mineral Oil-Contaminated Wastewaters, *Water Res.*, **34**, 620 - 628.
- Bauer, M., Herrmann, R., Martin, A. and Zellmann, H. (1998), Chemodynamics, Transport Behaviour and Treatment of Phthalic Acid Esters in Municipal Landfill Leachates, *Wat. Sci. Tech.*, **38**, 185 - 192.
- Bauer, R. (1994), Applicability of Solar Irradiation For Photochemical Wastewater Treatment, *Chemosphere*, **29**, 1225-1233.
- Cartwright, C., Thompson, I. And Burns, R. (2000), Degradation and Impact of Phthalate Plasticizers on Soil Microbial Communities, *Environ. Toxicol. Chem.*, **19**, 1253 - 1261.
- Casero, I., Sicilia, D., Subio, S. and Perez-Bendito, D. (1997), Chemical Degradation of Aromatic Amines by Fenton's Reagent, *Water Res.*, **31**, 1985 - 1995.
- Chen, R. and Pignatello, J. (1997), Role of Quinone Intermediates as Electron Shuttles in Fenton and Photoassisted Fenton Oxidations of Aromatic Compounds, *Environ. Sci. Technol.*, **31**, 2399-2406.
- Hunter, J. and Christopher, G. (2000), Adsorption of Phthalate Esters on Soil at Near Saturation Conditions, *J. Environ. Sci. Health*, **A 35**, 1503-1515.
- Huston, P. and Pignatello, J. (1999), Degradation of Selected Pesticide Active Ingredients and Commercial Formulations in Water by the Photo-Assisted Fenton Reactio, *Water Res.*, **33**, 1238 - 1246.
- Kim, S-M and Vogelpohl, A. (1998), Degradation of Organic Pollutants by the Photo-Fenton Process, *Chemical Engineering & Technology*, **21**, 187-191.
- Kiwi, J., Pulgarin, C. and Peringer, P. (1994), Effect of Fenton and photo-Fenton reactions on the degradation and biodegradability of 2 and 4-nitrophenols in water treatment, *Applied Catalysis B: Environmental*, **3**, 335-350.
- Kwon, B., Lee, D., Kang, N. and Yoon, J. (1999), Characteristics of P-Chlorophenol Oxidation by Fenton's Reagent, *Water Res.*, **33**, 2110 - 2118.
- Li, Y-S, Liu, C-C and Fang, Y-Y. (1999), Decolorization of Dye wastewater by Hydrogen Peroxide in the Presence of Basic Oxygen Furnace Slag, *J. Environ. Sci. Health*, **A 34**, 1205-1221.
- Lin, J-G. and Ma, Y-S. (2000), Oxidation of 2-Chlorophenol in Water by Ultrasound/Fenton Method, *J. of Env. Eng.*, **126**, 130 - 137.
- Lin, S., Lin, C. and Leu, H. (1999), Operating Characteristics and Kinetic Studies of Surfactant Wastewater Treatment by Fenton Oxidation, *Water Res.*, **33**, 1735 - 1741.
- Naddtochenko and Kiwi, J. (1998), Primary Photochemical Reactions in the Photo-Fenton System with Ferric

- Chloride. 1. A Case Study of Xylidine Oxidation as a Model Compound, *Environ. Sci. Technol.*, **25**, 1419.
- Ruppert, G. and Bauer, R. (1994), UV-O₃, UV-H₂O₂, UV-TiO₂ and the Photo-Fenton Reaction-Comparison of Advanced Oxidation Processes For Wastewater Treatment, *Chemosphere*, **28**, 1447-1454.
- Sedlak, D. and Andrin, A. (1991), Aqueous-Phase Oxidation of Polychlorinated Biphenyls by Hydroxyl Radicals, *Environ. Sci. Technol.*, **25**, 1419.
- Staples, C., Peterson, D. Parkerton, T. and Adams W. (1997), The Environmental Fate of Phthalate Esters: A Literature Review, *Chemosphere*, **35**, 667 - 749.
- Venkatadri, R. and Peters, R. (1993) , Chemical Oxidation Technologies: Ultraviolet light/Hydrogen Peroxide, Fenton's Reagent and Titanium Dioxide-Assisted Photocatalysis, *Hazard. Waste Hazrd. Mater.*, **10**, 107-149.
- Wang, T-H., Kang, S-F and Lin Y-H. (1999), Comparison Among Fenton-Related Processes to Remove 2,4-Dinitrophenol, *J. of Env. Sci. & Health.*, **A34**, 1267 - 1281.