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PHOTODEGRADATION OF DI(2-ETHYLHEXYL)PHTHALETE IN AQUEOUS MEDIUM

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ABSTRACT

Di(2-ethylhexyl)phthalate (DEHP), a toxic phthalate ester, is a ubiquitous contaminant due to its extensive use and persistence. Degradation of Di(2-ethylhexyl)phthalate (DEHP) by Fenton oxidation was evaluated in this study. The results indicate that the pH, H_2O_2 and Fe^{2+} concentration were three main operating factors considerably affecting the decomposition of Di(2-ethylhexyl)phthalate. The optimum conditions were observed at pH 3 and the molar ratio of [H_2O_2 :Fe^{2+}:DEHP] 10: 5: 1. Under such condition, the maximum removal of DEHP was max. 10 % at a time of 60 minutes. The photo-degradation of Di(2-ethylhexyl)phthalate in oxygenated aqueous medium was studied in the presence of hydrogen peroxide, ferric ions, hydrogen peroxide and suspended titanium dioxide (150 mg/l) under UV lamp. In this case was achieved degradation of DEHP about 35% at a time 60 minutes. The combined effect of hydrogen peroxide and ferric ions on the photo-degradation of Di(2-ethylhexyl)phthalate may possibly be considered as a photo-Fenton reaction.

Keywords: photo-Fenton, oxidation, DEHP, phthalate, PVC, water environment

1. INTRODUCTION

In recent years, various photo-chemically advanced oxidation processes (AOPs) such as O_3/UV, UV/H_2O_2, TiO_2 /UV and Fenton/UV, have been successfully utilized to degrade most of the organic compounds present in polluted water. The reason for the utilizations of AOPs is mainly due to the inability of biological processes to treat highly contaminated and toxic waste water. In AOP, the hydroxyl radicals are generated in solution and are responsible for the oxidation and mineralization of the organic pollutants to water and carbon dioxide.

Fenton reagent, one of AOPs, mixed by hydrogen peroxide and iron salts, is an oxidant with highly oxidative effect. The primary reactions of representative Fenton process are

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \qquad (k_1 = 58\ mol^{-1}\ dm^3\ s^{-1}) \qquad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OOH + H+ \qquad (k_2 = 0.02\ mol^{-1}\ dm^3\ s^{-1}) \qquad (2)$$

where
•OH is the hydroxyl radical and •OOH is the superoxide radical.

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^+ + \bullet OH \qquad (3)$$

Owing to hydroxyl radicals’ high oxidation potential (E0 = −2.80 V) [1], they can oxidize almost all the organic substances and mineralize them to carbon dioxide and water [2]. The degradation rate is influenced by the pH of solution and the amount of hydrogen peroxide and iron salt (Fig.1). Thus, Fenton treatment has attracted much interest for the destruction of toxic organic compounds in wastewater [2,3].

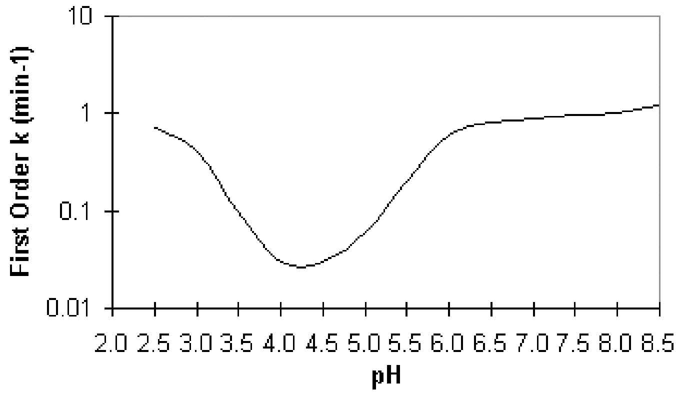

Figure 1. Influence of pH on rate of Fenton reaction

In recent years, many studies have shown that the decomposition of various organic pollutants using hydrogen peroxide as an oxidants under UV illumination have been proven to be very effective [4].
To maximize the cost effectiveness of the advanced oxidation processes system, the physicochemical parameters including reaction time, pH, TiO_2 concentration, UVA intensity, concentrations of H_2O_2 and di-n-butyl phthalate were optimized [5]. Di(2-ethylhexyl)phthalate (DEHP) (Fig. 2) is the most commonly used and persistent of the phthalate esters. It is slightly soluble in water. Its annual production amounts to 3–4 million tons, which is primarily used as a plasticizer in polyvinyl chloride (PVC) resins. Numerous chronic effects such as hepatotoxicity, teratogenicity, carcinogenicity, adverse effects on male reproduction organs andendocrine disruption [6] have been identified. Therefore, di(2-ethylhexyl)phthalate has been classified as a probable human carcinogen.

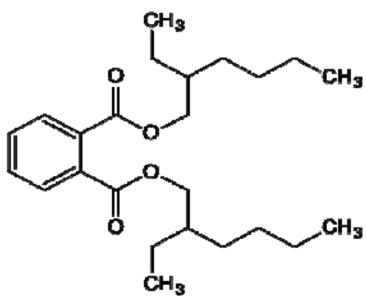

Figure 2. Di(2-ethylhexyl)phthalate (DEHP)

This study was conducted to assess the removal efficiency of di(2-ethylhexyl)phthalate from a aqueous medium using Fenton and photo-Fenton process.

2. EXPERIMENTAL

Experimental conditions (*Fenton reaction):*
A 20, 50, 100, 200 mg L^{-1} emulsion of di(2-ethylhexyl)phthalate in water was prepared by shaking and sonification. Ferrous sulfate $FeSO_4.7H_2O$ was used to prepare the ferrous solution, which were prepared daily. Hydrogen peroxide H_2O_2 of 35 % purity from Fluka AG was used. 100 ml emulsion of di(2-ethylhexyl)phthalate was placed in 250 ml bottle and and added HCl to reach pH 3, then ferrous sulfate and an aliquot of 34% H_2O_2 was added to the mixture of di(2-ethylhexyl)phthalate to reach a molar ration (DEHP : Fe^{2+} : H_2O_2) 1 : 5 : 5 a 1 : 5 : 10, 1 : 5 : 20, 1 : 5 : 40, 1 : 5 : 60 and 1 : 5 : 80. The mixture was stirred for 60 min. In Fenton`s experiments, the residual di(2-ethylhexyl)phthalate concentration was measured after 1 hours.

Determination of di(2-ethylhexyl)phthalate concentration
The residual di(2-ethylhexyl)phthalate concentration was measured by UV-VIS spectrophtometry (224 nm) UNICAM UV 500, Thermo Spectonic, England. The extracts were prepared using a liquid-liquid extraction procedure. 100 ml water samples were extracted by shaking for one hour with 25 ml n-hexan. This procedure was found to have a recovery of about 94-97 %.

Optimization of degradation of di(2-ethylhexyl)phthalate by advanced oxidation process (Photo-Fenton process):
100 ml emulsion 20 mg/l of di(2-ethylhexyl)phthalate was placed in 250 ml bottle and added HCl to reach pH 5,5 , 150 mg /l TiO_2 and molar ratio's (DEHP : Fe^{2+} : H_2O_2) 1: 5 : 10-80. The reaction mixture was placed under UV lamp. The residual di(2-ethylhexyl)phthalate concentration was measured after 1 hours.

3. RESULTS AND DISCUSSION

Degradation of DEHP by Fenton Process
The effect reaction time on the oxidation of DEHP by Fenton reaction is demonstrated in Fig.3. The effect of H_2O_2 concentration on degradation of di(2-ethylhexyl)phthalate by Fenton process is shown in Fig. 4. The pH was kept in the range of 3 to 5,5 the temperature was set at 25 °C The effect of pH was significant, and the degradation of DEHP was favorable at lower pH. Under such condition, the maximum removal of DEHP was max. 10 % after 1 hour.

Degradation of DEHP by Photo-Fenton Process
UV light is expected to enhance the generation of •OH radicals and therefore more removal of di(2-ethylhexyl)phthalate. In this phase of the experiment, a UV lamp was used to supply radiation. The effect of TiO_2 concentration on **Photo-Fenton Process** of di(2-ethylhexyl)phthalate is shown in Fig. 4. The Removal efficiencies of the reaction mixture without TiO_2 was determined as 9.84%. The removal efficiencies increased gradually and reached a maximum (28.8%) at 150 mg /l TiO_2.
The effect of H_2O_2 concentration on **Photo-Fenton Process** of di(2-ethylhexyl)phthalate is shown in Fig. 5.

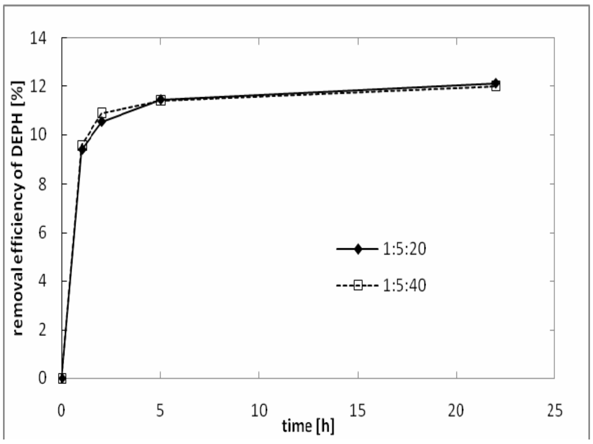

Figure 3. The effect of the reaction time on the oxidation of DEHP by Fenton reaction The experimental conditions were follows: pH=3, molar ration (DEHP : Fe^{2+} : H_2O_2) 1:5:40, 1:5 :20

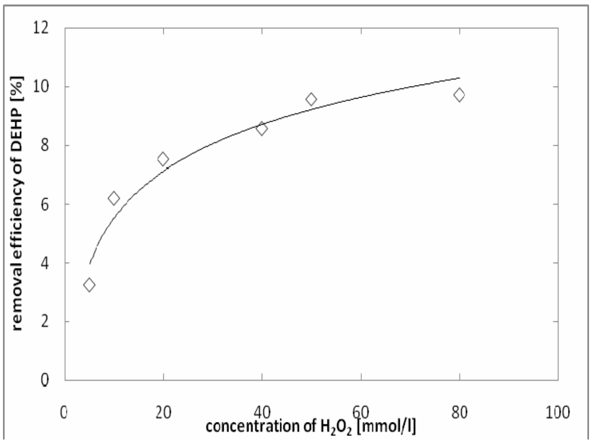

Figure 4. The effect of the initial concentration of H_2O_2 on the oxidation of DEHP by Fenton reaction: The experimental conditions were as follows: pH=3, DEHP 20 mg/l

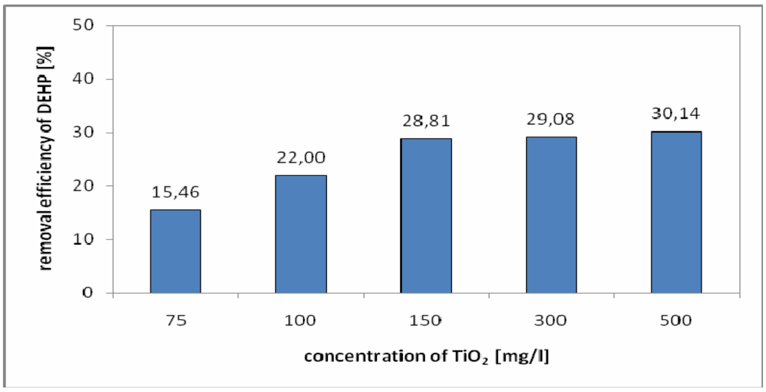

Figure 4. The effect of the initial TiO_2 concentration on the photo-catalytic oxidation of di(2ethylhexyl)phthalate. The experimental conditions were as follows: pH=5.5, concentration of DEHP 20 mg /l, DEHP : Fe2+ : H_2O_2 1: 5 : 10, UV light

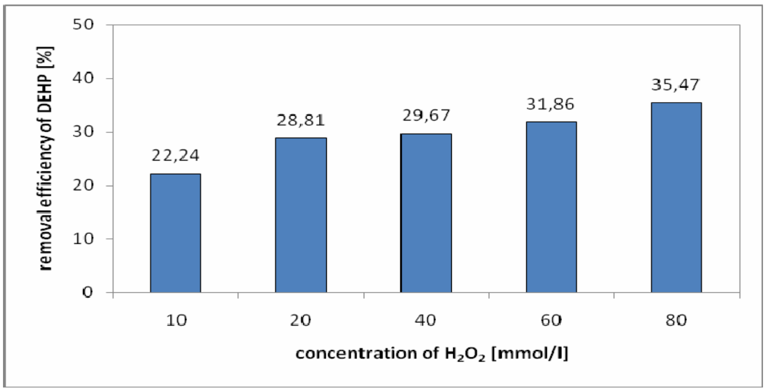

Figure 5. The effect of the initial H_2O_2 concentration on the photo-catalytic oxidation of di(2ethylhexyl)phthalate. The experimental conditions were as follows: pH=5.5, concentration of DEHP 20 mg/l, DEHP : Fe^{2+} : H_2O_2 1: 5 : 10, UV light

4. CONCLUSION

In this study, the degradation of DEHP was investigated under combination UV, H_2O_2, Fe^{2+} and TiO_2. Several proportion of Fe^{2+} : H_2O_2 were tested. The results of this study demostrated that the Fenton's reagent (Fe^{2+}+H_2O_2) system was not very effective but Photo-Fenton process was more effective. In this case was achieved degradation of DEHP about 35%.

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5. REFERENCES

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