

SIMULTANEOUS DEGRADATION OF SOME PHTHALATE ESTERS UNDER FENTON AND PHOTO-FENTON OXIDATION PROCESSES

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ABSTRACT. – Simultaneous degradation of some phthalate esters under Fenton and Photo-Fenton oxidation processes. In this study the assessment of the degradation efficiency of five phthalates, DEP, BBP, DEHP, DINP and DIDP, found in a mixture in a liquid phase, using the Fenton and Photo Fenton oxidation processes, was conducted. It was observed that the main parameters that influence the Fenton oxidative processes of phthalates were the concentration of the oxidizing agent, H₂O₂, the concentration of the catalyst used, Fe²⁺, the pH value, UV irradiation and the reaction time. For the Fenton oxidative process, the highest degradation efficiencies were 19% for DEP, 50% for BBP, 84% for DEHP, 90% for DINP and 48% for DIDP, when the experiments were carried out using concentrations of 20 mg L⁻¹ phthalate mixture, 100 mg L⁻¹ H₂O₂, 10 mg L⁻¹ Fe²⁺ at a pH value of 3, with a total reaction time of 30 minutes. For the Photo-Fenton oxidative process carried out in the same conditions as Fenton oxidative process, it was observed that after an irradiation time of 90 minutes under UV radiation the degradation efficiencies of phthalates were improved, being 22% for DEP, 71% for BBP, 97% for DEHP, 97% for DINP and 81% for DIDP.

Keywords: bis(2-ethylhexyl) phthalate, diethyl phthalate, diisodecyl phthalate, diisononyl phthalate, benzyl butyl phthalate, Fenton, Photo Fenton.

1. INTRODUCTION

Phthalate esters are a class of organic compounds mainly used as plasticizers in the petrochemical industry and also found in all plastic products, paints, dyes, coatings for nutritional supplements and pharmaceutical products, emulsifiers, lubricants, cosmetic products, glue, ink, detergents. Because phthalates are only physically bounded to the plastic material, without any chemical bounds, they can easily migrate into the environment or even in food products from the plastic wrappers they are packed in (Heudorf et al., 2007).

The most documented adverse effects of phthalate contamination are related with the reproductive system and refer mainly to fertility reduction and the histological modification of testicles (Heudorf et al., 2007). Studies in which the presence of bis(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), benzyl butyl (BBP) and dimethyl phthalate (DMP) metabolites were identified in human urine showed reductions in sperm count and in sperm mobility (Matsumoto et al., 2008).

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The stability of these compounds in the environmental factors is high, several studies have shown that the biodegradation process is slow and does not occur at desired efficiencies (Staples et al., 1997). Moreover if it takes into account that bis(2-ethylhexyl) phthalate (DEHP) is introduced on the list priority substances (Annex X, Directive 2000/60/EC), their removal from wastewater is necessary.

In the last time different advanced oxidation processes (AOPs) such as Fenton (H_2O_2), Photo-Fenton ($h\nu - \text{H}_2\text{O}_2$), Ozone (O_3), Photo- O_3 etc. have been developed for the treatment of different xenobiotic organic compounds which are refractive to conventional biological or physical treatment (Bauer and Fallman, 1997; Al-Tawabini, 2003; Esmaeli et al., 2011; Tay et al., 2011). One of the most applied and promising method for the removal of organic compounds from aquatic samples is the Fenton AOP, due to the fact that the reagents used in this method are cheap, easy to handle and environmentally friendly (Litter, 2005). These processes are based on the production and use of highly reactive hydroxyl radical ($\bullet\text{OH}$), using the Fenton reagent, a mixture of H_2O_2 and Fe^{2+} , which go as far as even mineralizing the organic compounds into CO_2 and H_2O (Litter, 2005).

The aim of this study was to test the efficiency of the Fenton and Photo Fenton AOPs for the removal of a mixture of five phthalates such as diethyl phthalate (DEP), bis(2-ethylhexyl) phthalate (DEHP), benzyl butyl phthalate (BBP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) from water samples. The influences of the changes in the process variables (oxidant concentration, catalyst concentration, pH, UV radiation and process time) have been studied for a better comprehension of the phenomena.

2. MATERIAL AND METHODS

2.1. Materials

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2O_2 (30% w/w), methanol, hexane, NaOH and HCl were purchased from Merck. A mixture of DEHP, DEP, DIDP, DINP, BBP, all of 99% purity, purchased from Supelco, in concentration of 50 mg L^{-1} for each compound was prepared in a mixture of ultrapure water: methanol (80:20 v/v).

2.2. Experimental

To prevent the interference of sun radiation, the oxidation experiments were carried out in a 50 mL brown beaker, equipped with magnetic stirrer, to ensure the homogeneity in the reactor. 10 mL of water sample containing 20 mg L^{-1} of each selected phthalate were placed into the reactor. Subsequent different volumes of Fenton reagent were added into the reactor. Before adding the Fenton reagent to the reactor, the pH was adjusted to 3.0 using solutions of 0.1 N NaOH and 0.1 N HCl in water to prevent changes in the iron form, in all experiments, unless stated differently. The pH was measured using a WTW InoLab multiparameter. Different volume of H_2O_2 (30% w/w) were added into the reactor for Fenton degradation. In order to estimate the degradation rate of the phthalates,

at different times, the mixtures from the reactor were taken and extracted with 2 mL of hexane in a glass separator funnel according to Esmaeli et al. (2011) method. The mixture was then vigorously shaken for 5 minutes and subsequent allowed to the aquatic and organic phases separation. Next, the hexane layer was separated in a vial and evaporated to dryness under nitrogen. The residue was then dissolved in methanol and analyzed by high performance liquid chromatography (HPLC). All the experiments were conducted at room temperature (25°C).

2.3. Analytical method

The analyses of the phthalates were carried out using a HPLC system, model Shimadzu, equipped with a 10LC module pump, a 10LD UV/Vis detector and a manual injection valve. The separation of the compounds was performed on a reverse phase column type Luna C18 (25 cm x 4.5 mm id x 5 µm particle size) purchased from Phenomenex. An isocratic elution mode using a mobile phase containing 100% methanol at a flow rate of 0.8 mL min⁻¹ was used for the HPLC analysis. The detection of the compounds was carried out at 240 nm wavelength.

The phthalate concentrations in the water samples were calculated using the calibration curve method. For this purpose, five standard solutions in concentrations of 2.5, 5, 10, 25 and 50 mg L⁻¹ of each phthalate were prepared.

The limit of detection (LOD) and limit of quantification (LOQ) were determined taking into consideration the standard deviation of the response factor of the detector (σ) for each compound and the slope (S) of each calibration curve. These parameters have been calculated according to the following equations: $LOD = 3.3\sigma/S$ and $LOQ = 10\sigma/S$. The performances of the analytical method are presented in table 1.

Table 1. The regression equations, correlation coefficients (r), LODs, LOQs and extraction recoveries of the tested compounds

Compound	Regression equations	r	σ	LOD [mg L ⁻¹]	LOQ [mg L ⁻¹]	Extraction recoveries (%)
DEP	$y = 0.596x + 0.5834$	0.9996	0.13	0.72	2.26	102.32±5
BBP	$y = 0.452x + 3.7979$	0.9921	0.16	1.17	3.65	108.26±5
DEHP	$y = 0.2993x + 2.0836$	0.9932	0.12	1.32	4.01	90.95±3
DINP	$y = 0.0956 + 0.3421$	0.9985	0.061	2.10	6.40	95.46±4
DIDP	$y = 0.1664 + 0.5409$	0.9982	0.11	2.18	6.80	92.7±5

3. RESULTS AND DISCUSSIONS

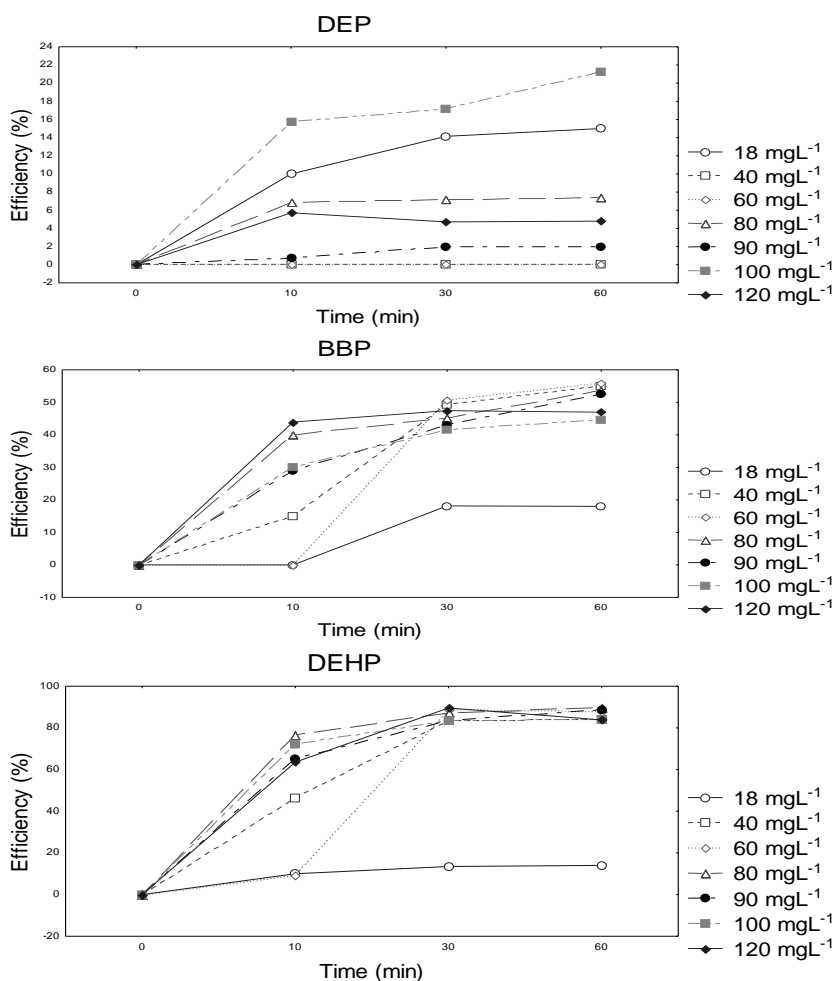
3.1. Optimization of process parameters

According to Litter (2005) the efficiency of the Fenton and Photo Fenton processes is influenced by the concentrations of the reagents (hydrogen peroxide and ferrous ion) used for reaction, by the pH, UV irradiation and total reaction time. For this reason, it is important to identify the optimum values for these parameters to ensure that the process is economical.

3.2. Effect of hydrogen peroxide concentration

To determine the H_2O_2 concentration for which optimum phthalate degradation efficiency can be obtained, concentrations of H_2O_2 between 18 mg L^{-1} and 120 mg L^{-1} were used. At different time intervals (10, 30 and 60 minutes) the reaction mixtures were extracted and analyzed by HPLC in order to monitor the phthalate degradation rate. Fe^{2+} concentration was maintained at a value of 10 mg L^{-1} (Yang et al., 2005).

As can be seen in figure 1, DEP, BBP, DEHP and DINP and DIDP showed similar patterns of degradation. More exactly, the degradation was slow in the first 10 minutes of the experiments but rose to higher percentages after 30 minutes. The analyses realized after 60 minutes showed that there were no major changes in the phthalate concentrations in the last part of the experiments.



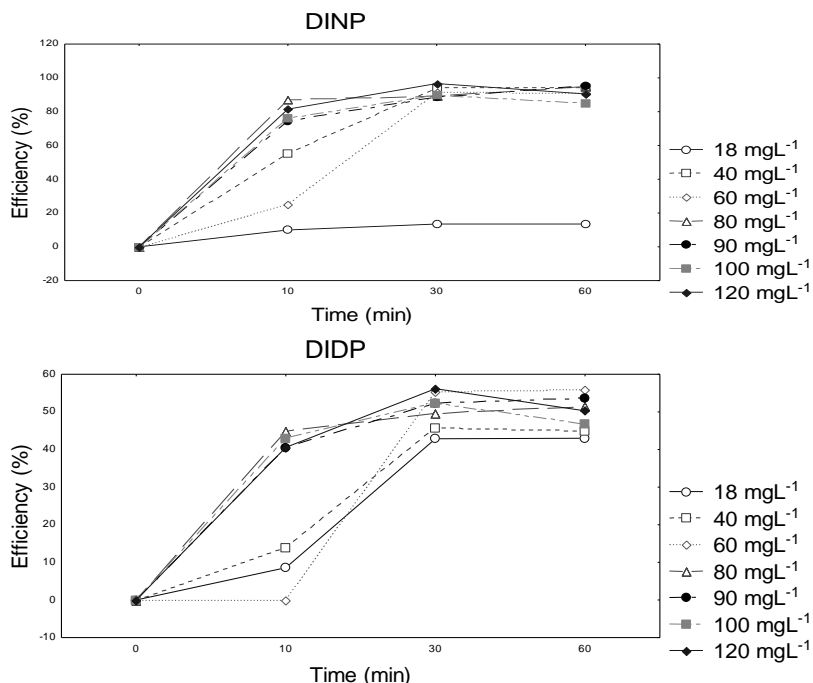


Fig. 1. Effect of H_2O_2 concentration on phthalate degradation

It can also be observed that for BBP, DEHP, DINP and DIDP, the final degradation efficiencies varied differently when the experiments were conducted using H_2O_2 concentrations between 40 mg L^{-1} and 120 mg L^{-1} . The maximum efficiency for DEP (19%) was obtained at a concentration of $80 \text{ mg L}^{-1} H_2O_2$, for BBP (56%) at 60 mg L^{-1} , for DEHP efficiencies between 88% and 90% where obtained for concentrations of H_2O_2 between 60 mg L^{-1} and 100 mg L^{-1} , for DINP (90%) at 40, 80 and 90 mg L^{-1} and for DIDP (56%) at $60 \text{ mg L}^{-1} H_2O_2$ respectively.

It can be concluded that the highest efficiency was registered at $100 \text{ mg L}^{-1} H_2O_2$. For this concentration the obtained efficiencies were 19% for DEP, 45% for BBP, 84% for DEHP, 85% for DINP and 48% for DIDP.

3.3. Effect of time

Because no significant changes were observed in the phthalate concentrations after 30 minutes in the previous experiments, another different experiment was conducted to determine the degradation pattern in correlation with the time parameter. For this purpose the degradation of the phthalates after 10, 20, 30 and 40 minutes were evaluated. The H_2O_2 concentration was set at 100 mg L^{-1} and Fe^{2+} at 10 mg L^{-1} . The results showed that the Fenton process has a powerful action on the phthalates in the first 20 minutes of the experiment and that after this time interval the degradation efficiencies tend to vary in very small intervals (Figure 2). Furthermore, it was decided that 30 minutes is sufficient reaction time

to reach the maximum efficiencies that can be obtained with the Fenton process for the tested compounds.

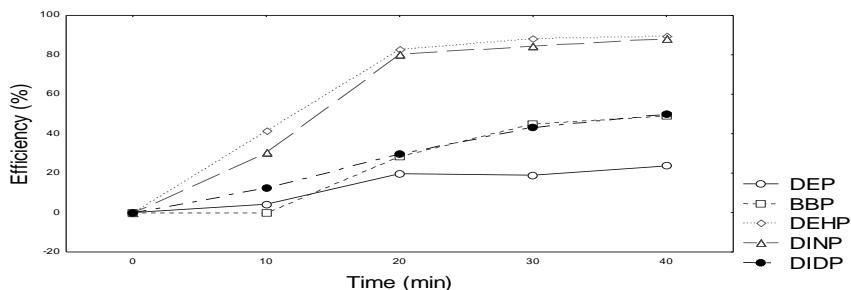


Fig. 2. Influence of time on the Fenton degradation of phthalates

3.4. Effect of Fe^{2+} concentration

In order to find the optimum concentration of catalyst for which the degradation of phthalates reaches the maximum efficiency, concentrations of Fe^{2+} between 5 mg L^{-1} and 60 mg L^{-1} were tested. The concentration of H_2O_2 was maintained constant at a concentration of 100 mg L^{-1} . The total reaction time was set at 30 minutes. As can be observed from figure 3, the maximum degradation took place at Fe^{2+} concentration of 10 mg L^{-1} for almost all the phthalate compounds, (50% degradation for BBP, 84% for DEHP, 90% for DINP and 43% for DIDP) except for DEP, which was degraded with maximum efficiency (23%) at a Fe^{2+} concentration of 20 mg L^{-1} .

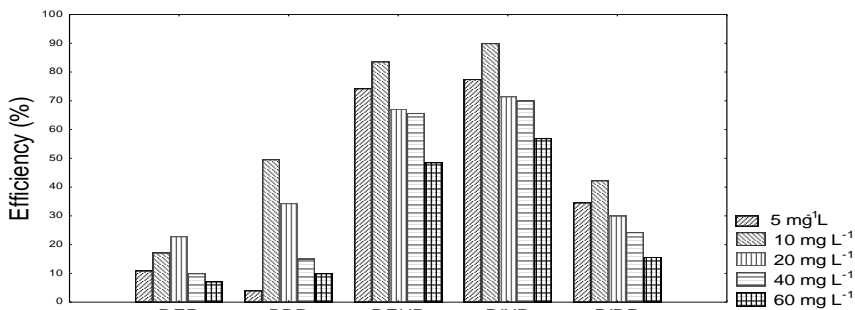


Fig. 3. Phthalate degradation efficiencies at different Fe^{2+} concentrations

3.5. Effect of Ph

In order to test the influence of pH on the Fenton degradation of phthalates, different experiments of 30 minutes were carried out at pH values between 1 and 5, with $100 \text{ mg L}^{-1} H_2O_2$, $10 \text{ mg L}^{-1} Fe^{2+}$ and 20 mg L^{-1} phthalates. As can be observed in figure 4, the maximum efficiencies were obtained at pH 3, except for DEP which proved to be less sensitive to pH changes in the reactor. Overall, the degradation efficiencies varied in very short intervals for pH values 2, 3 and 4. The

lowest efficiencies were obtained in the experiments conducted for the lowest (1) and highest (5) tested pH values.

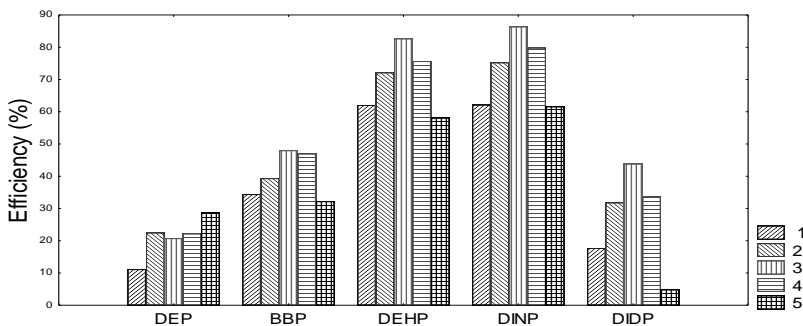


Fig. 4. Phthalate degradation efficiencies at different pH values

3.6. Photo Fenton degradation

Based on the results obtained from the Fenton oxidation experiments, an attempt to increase the degradation efficiencies was made by using a Photo Fenton system. A deuterium arc lamp of 50 watts with a spectrum from 180 nm to 370 nm was added to the experimental installation used in Fenton experiments. The mixture of selected five phthalates was irradiated for different period of time, using as Fenton mixture $10 \text{ mg L}^{-1} \text{ Fe}^{2+}$, $100 \text{ mg/L H}_2\text{O}_2$, at pH value of 3. The phthalate concentration was maintained at 20 mg L^{-1} . After 30, 60 and 90 minutes irradiation time, the reaction mixtures were extracted and analyzed. As can be seen in figure 5, only BBP and DIDP suffered noticeable increases in the degradation efficiencies compared to the results obtained in the Fenton experiments, while the degradation efficiency of DEP was almost the same and DEHP and DINP recorded an increase in efficiency of 13% and 7%.

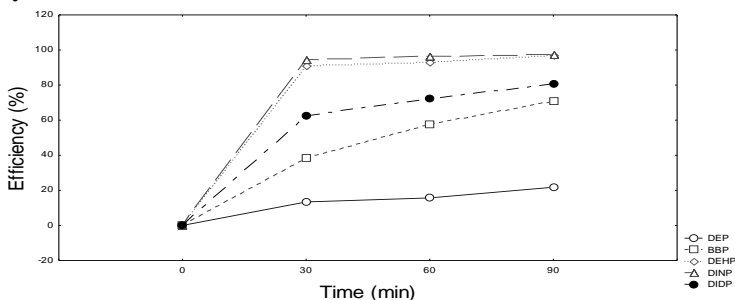


Fig. 5. Influence of time and UV radiation on phthalate degradation

4. CONCLUSIONS

The results this study show that for the Fenton AOP the degradation efficiencies of DEP, BBP, DEHP, DINP and DIDP were influenced by the concentrations of H_2O_2 and Fe^{2+} , by the pH and total reaction time.

The maximum degradation efficiencies, of 19% for DEP, 50% for BBP, 84% for DEHP, 90% for DINP and 48% for DIDP, were obtained in the experiments in which $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$, $10 \text{ mg L}^{-1} \text{ Fe}^{2+}$ were used, at pH 3 after a total reaction time of 30 minutes.

In case of Photo-Fenton AOP only BBP and DIDP suffered noticeable increases in the degradation efficiencies, rising from 50% in the case of the Fenton oxidation to 71% after 90 minutes of irradiation for BBP, and from 48% to 81% in the case of DIDP. The degradation efficiency of DEP varied in very small limits around the value of 22% throughout the 90 minutes of irradiation and the degradation of both DEHP and DINP rose to 97%.

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