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Photodegradation of the endocrine-disrupting chemicals benzophenone-3 and methylparaben using Fenton reagent: Optimization of factors and mineralization/biodegradability studies

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ABSTRACT

Benzophenone-3 (BP3) and methylparaben (MPB) are two emerging pollutants, whose endocrine disrupting activity on different living beings has been reported. Therefore, removal of these pollutants from aqueous samples using photo-Fenton technology was assessed. Effects of Fe^{2+} and H_2O_2 initial concentrations on pollutants photo-degradation were analyzed and a face centered, central composite design was carried out for determining the optimal conditions, in the evaluated range, that conducted to higher substrate elimination.

Results indicated that Fe^{2+} and H_2O_2 initial concentration and the interaction between them affect significantly the process. In addition, experiments varying BP3 and MPB initial concentrations showed that elimination rate increases with an increase in the substrate initial concentration and a pseudo-first-order kinetic can be used to describe pollutants degradation. Under optimal conditions compounds were eliminated totally after 120 min of treatment. Dissolved organic carbon studies illustrated that more than 60% of contaminants were mineralized and biodegradability analysis indicated that this factor increased gradually during 300 min of photo-Fenton treatment.

1. Introduction

At present, water has become an essential resource to the development of human life. However, many activities related to agriculture, industrial processes, urbanization, and even everyday activities such as bathing, have caused that different substances are being introduced into water bodies [1]. This is the case of the denominated emerging pollutants, which include a wide range of organic compounds (pharmaceuticals, industrial additives, synthetic drugs, UV filters, *etc.*), that are suspected in many cases to generate endocrine disruption in different organisms, including human beings, and whose presence in different compartments has not been completely regulated [1–3]. Benzophenone-3 (BP3) is one of the most used UV filters, which together with methylparaben (MPB), an organic compound used mainly as an antibacterial and antimicrobial agent in the manufacture of different personal care products, has been classified as an emerging contaminant [4,5]. In this regard, reports of different research groups have indicated that exposure to high levels of benzophenone type compounds can be associated with some disorders related to estrogen production [6,7]. Additionally, the oral and dermal administration of BP3 to populations of mice has shown alteration in different organs such as liver and kidney, also BP3 presumably could cause contact eczema, melanoma and breast cancer because a high percentage of this compound can penetrate skin and reach the bloodstream [8,9]. Meanwhile, *in vivo* and *in vitro* assays have shown that parabens, including MPB, may affect human health due to its endocrine disrupting activity [10,11].

Both compounds can reach the aqueous environment primarily through discharges of wastewater treatment plants [12,13], in the specific case of benzophenone, it can be introduced directly through domestic discharges after daily activities such as bathing or washing clothes, but also through renal excretion [13–16]. Parabens in turn also can be released into water bodies as a runoff from non-point sources and deposition of particles from the atmosphere [12].

On the other hand, advanced oxidation processes have demonstrated to be an effective alternative for the elimination of pollutants from different matrices. This is mainly due to the formation of reactive transient species, including the hydroxyl radical, which has the ability to oxidize a wide range of organic compounds [3,17]. Among the different advanced oxidation processes, those using the Fenton reagent (solution of hydrogen peroxide and an iron catalyst) are relatively inexpensive and the oxidizing agent is easy to handle [18]. Additionally, the combination of the conventional Fenton process with visible UV radiation results in the photo-Fenton reaction, which

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Table 1
Experimental design factors.

Factor	Benzophenone-3 Levels			Methylparaben Levels		
	Low	Medium	High	Low	Medium	High
Fe^{2+} concentration (mg/L)	56	112	168	7	14	21
H_2O_2 concentration (mg/L)	1000	2500	4000	50	125	200

satisfies a simple reaction mechanism and is highly efficient for degrading different types of organic substrates such us 4-chlorophenol, nitrobenzene and anisole, herbicides and ethyleneglycol [19]. In short, the ferrous ions (Fe^{2+}) catalyze the hydrogen peroxide decomposition promoting the generation of hydroxyl radicals ($OH^{\cdot}$), hydroxide anions (OH^-) and ferric ions (Fe^{3+}). Subsequently, Fe^{2+} is regenerated due to the reaction of Fe^{3+} with light (hv) and the reaction continues, as indicated in Eqs. (1) and (2) [18,20,21].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \tag{1}$$

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + OH^{\cdot} + H^+ \tag{2}$$

Additionally, it has been reported that BP3 has a high photostability under both UV and artificial solar light, which implies that direct photolysis is not able to remove all this pollutant from aquatic environments [22,23]. Thus, considering the potential harmful effect of BP3 and MPB on different organisms and the strong performance of photo-Fenton in removing pollutants of this type, the main objective of this study is to report the effect of Fe^{2+}, H_2O_2 and substrate concentrations on BP3 and MPB removal. In this way, the optimal process conditions were selected using the response surface methodology and a central composite face-centered experimental design. Additionally, some biodegradability and mineralization studies were carried out.

2. Materials and methods

2.1. Reagents

BP3 and MPB containing more than 98% of pure compound were purchased from Alfa-Aesar and used as received. All the aqueous solutions were prepared using ultra-pure water. Isopropanol and hydrogen peroxide (35% w/w) were supplied by Merck. Benzophenone-d10 and ethylparaben-d4 (CDN isotopes) were used as internal standard in analytical methods. pH adjustments were done using concentrated solutions of NaOH and HCl obtained from Alfa-Aesar, and sodium thiosulfate pentahydrate (Sigma–Aldrich) was used for quenching remaining H_2O_2. Methanol and formic acid of LC/MS grade and ultra-high purity (UHP) grade argon (Praxair) and nitrogen were employed for chromatographic analysis. Iron(II) chloride tetrahydrate (Sigma–Aldrich) was used as Fe^{2+} source.

2.2. Photodegradation experiments

Photodegradation experiments were carried out using a Suntest CPS/CPS+ (Atlas) photosimulator equipped with a xenon lamp capable of emitting radiation of light in a spectrum similar to the sun (wavelength range of 300–800 nm, irradiance: 350 ± 10 W/m^2). Pyrex flasks containing 200 mL of solution were used for light exposition. Substrates initial concentration in most of the experiments was 1 mg/L and solution pH was maintained at a value close to 3 (2.85–3.1). In order to ensure homogeneous conditions of reaction, system was stirred during experiments, and temperature was maintained at 35 °C using the Suntest CPS/CPS+ control and ventilation system.

2.3. Experimental design

In order to determine the most favorable conditions for pollutants photodegradation, the effects of the concentrations of Fe^{2+} and H_2O_2 were assessed. A face centered, central composite design was carried out for the identification of significant factors or interactions that allow the determination of the conditions under which the compounds suffer the highest rates of degradation. This kind of designs is used to find the best set of values, for a set of factors, giving an optimal response and to infer the influence of a parameter in a process [24,25]. Before carrying out the optimization experiments, some preliminary test were conducted to define the levels of each factor that allowed identifying the most significant parameters and their effects on removal of pollutants.

Table 1 shows the employed levels of each parameter in the experimental design. Statistical analysis was performed with a confidence level of 95%. The chosen experimental response was the substrate degradation percentage after 30 min of treatment, the total of experiments was 11 (three center points) and data were analyzed using the Statgraphics Centurion XVI software. All the runs were conducted in triplicate and the standard deviations and coefficients of variation of the data were below 5%.

2.4. Analytical methods

2.4.1. Sampling procedure

During experimental process, samples of 1 mL were withdrawn at different time intervals and analyzed after quenching remnant H_2O_2 using a sodium thiosulfate solution.

2.4.2. Pollutants concentration determination

An Acquity UPLC system (Waters Corporation) coupled to a triple quadrupole (TQD) mass spectrometer with an orthogonal Z-spray-electrospray (ESI) was employed to quantify pollutants concentration. Chromatographic separation was performed using an Acquity UPLC BEH C18 column (2.1 × 50 mm, 1.7 µm, Waters) at a flow rate of 0.3 mL/min. Mobile phase consisted in a mix of water 0.01% HCOOH (A) and methanol (B). In the case of BP3 quantification, an isocratic flow A/B: 65/35 was employed while in MPB samples A/B relation was 90/10 during the first 0.5 min, then 10/90 for 1 min, and finally 90/10 until the end of the running time. Benzophenone-d10 and ethylparaben-d4 were used as internal standard. Masslynx 4.1 (Micromass) software was used to process quantitative data. Table S1 (supplementary material) shows optimized conditions for pollutants and internal standards quantification.

2.4.3. Mineralization and biodegradability analysis

Transformation of organic matter into CO_2 and H_2O was evaluated quantifying the dissolved organic carbon (DOC) using an Apollo 9000 series TOC analyzer (Teledyne Tekmar). Chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) were calculated according to the methodology described in the Standard methods for the examination of water and wastewater [26], methods 5220 C and 5210 respectively.