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Homogeneous photocatalytic processes for degradation of some endocrine disturbing chemicals under UV irradiation

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ABSTRACT

Advanced oxidation processes including UV, UV/H_2O_2, Fenton reaction (Fe(II)/H_2O_2) and Photo Fenton process (Fe(II)/H_2O_2/UV) for degradation of paracetamol, Bisphenol A, and dibutyl phthalate as endocrine disrupting chemicals(EDCs) are investigated in this study. A comparison among these techniques is undertaken with respect to the decrease of total organic carbon (TOC). Optimum operating conditions for each understudied process revealed the effect of the initial amounts of Fe(II) and hydrogen peroxide. Among the tested processes, the Photo Fenton process was found to be the most efficient with respect to TOC reduction of the wastewater within 50 min reaction time under low amounts of Fe(II) and hydrogen peroxide of 2.7 and 5 mmol/L respectively and amounted to 100% TOC removal for all the studied EDCs. Photo Fenton was followed by UV/H_2O_2, Fenton and UV only respectively in TOC removal.

Paracetamol showed the highest removal followed by dibutyl phthalate (DBP) while, Bisphenol A came in the end. Scavenger experiment proved that the degradation takes place mainly through hydroxyl radical mechanism. As well, studying the toxicity of produced water showed that the treated water is non-toxic.

1. Introduction

Certain pharmaceuticals or chemicals, which are harmful even in very low concentrations, can pass easily through sewage treatment plants. These chemicals can later be detected in surface water, groundwater, and drinking water [1]. An important group of such harmful compounds is endocrine disturbing chemicals (EDCs) [2]. Additional wastewater treatment methods such as ozonation and advanced oxidation processes (AOP) could be applicable for the elimination of these substances [3–5].

Pharmaceutical residuals, personal care products (PCPs) and endocrine disrupting chemicals (EDCs) are classified as emerging micropollutants as they may have significant adverse environmental and human health effects although the occurrence of these pollutants in the environment is usually in a very low concentration ($\mu g\ L^{-1}$ to $ng\ L^{-1}$) [6].

During recent decades, bisphenol A (BPA) has gained attention and became a public concern since it was recognized an endocrine disruption source [7,8]. Bisphenol A is a chemical compound widely used as a raw material in manufacturing chemical products such as polycarbonate plastics and epoxy resins. It is released into the environment during manufacturing processes and by leaching from final products [9]. Numerous studies have reported the occurrence of BPA in environmental matrices [10,11] and in waste water treatment effluent because it is not completely removed during conventional treatments [12,13]. Hence, to reduce its ubiquity in environmental matrices, it is necessary to develop sustainable treatment technologies to tackle this issue. Meanwhile, in particular, paracetamol (*N*-acetyl-4-aminophenol), is a common analgesic and anti-inflammatory that used for humans and animals. It is reported as the pharmaceutical compound that is present in high concentration in French rivers [14]. On the other hand, DBP is used in cosmetics, children's toys and child care products. It is reported to reduce sperm production and its motility, decrease rates of pregnancy and promote miscarriages [15,16].

Advanced oxidation processes (AOPs) have been proved to be a good alternative for the removal of recalcitrant compounds and the most popular AOPs studied are homogeneous photocatalysis such as ozonation, UV/H_2O_2, as well as the Fenton and Photo Fenton processes [17]. Homogeneous photocatalysis is of a special interest since UV irradiation and sunlight can be used as the irradiation source [18,19].

AOPs are based on the in situ generation of highly reactive transitory species (i.e. H_2O_2, HO^-, $O_2\cdot^-$, O_3) for mineralization of refractory organic compounds such as EDCs, water pathogens and disinfection by-products [20,21]. AOPs have been defined broadly as that aqueous

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phase oxidation processes which are based primarily on the intermediacy of the hydroxyl radical ($HO\cdot$) in the mechanism resulting in the destruction of the target pollutant or xenobiotic or contaminant compound [22].

Generation of the free radicals is commonly accelerated by combining some oxidizing agents such as hydrogen peroxide (H_2O_2), UV radiation and catalysts such as ferrous iron. Among those methods, UV, hydrogen peroxide and ultraviolet light (UV/H_2O_2), the Fenton's reagent and Photo Fenton process hold the greatest promise for detoxification and mineralization of pollutants [23]. The UV treatment method is based on supplying energy in the form of radiation to the chemical compounds, which is absorbed by reactant molecules that can pass to the excited states and have sufficient time to promote reactions [24]. The UV/H_2O_2, radiation with a wavelength lower than 300 nm is able to photolyze H_2O_2 molecules. The mechanism accepted for the photolysis of hydrogen peroxide is the cleavage of the molecule into hydroxyl radicals with a quantum yield of two $HO\cdot$ radicals formed per quantum of radiation absorbed [22], according to Eq. (1).

$$H_2O_2 \overset{h\nu}{\rightarrow} 2H\cdot \tag{1}$$

The Fenton reagent was first recognized in the 1960s and remaining as one of the most applied AOPs for its ability to degrade high loading of organic compounds. It consists of a mixture of iron(II) salts and hydrogen peroxide. Its mechanism may involve decomposition of hydrogen peroxide into hydroxyl radicals that is catalyzed by metal cations (Eqs. (2) and (3)) [25].

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

$$Fe^{3+}L_n + h\nu \rightarrow Fe^{2+}L_{n-1} + L\cdot \tag{3}$$

The process can be accelerated by irradiation of the solution up to a light wavelength of 600 nm in a process which is called Photo Fenton. Accordingly, the Photo Fenton reaction is expedited when the light source is present causing rapid H_2O_2 decomposition by ferrous or ferric ions and resulting in the formation of radicals. All these soluble iron hydroxyls or iron complexes can absorb not only UV radiation but also visible light [26].

The major objective of this study is to investigate the performance of different advanced oxidation methods and/or their combinations for TOC removal of three EDCs. Direct photolysis (UV), hydrogen peroxide with UV, Fenton and Photo Fenton processes were employed at pH 2–10, H_2O_2 concentrations 0–35 mmol/L, Fe(II) amounts from 0 to 5.4 mmol/L, for the treatment of Paracetamol, BPA, and DPP. The obtained results in this study confirm the possible application of such treatment for pharmaceutical and health care wastewater.

2. Experimental

2.1. Model substance and other materials

N-Acetyl-*p*-aminophenol (Paracetamol), Bisphenol A and Dibutyl phthalate are of high purity grade and are obtained from Sigma-Aldrich were used as received without further purification.

GP grade chemicals namely of very high purity, ferrous sulfate ($FeSO_4{\cdot}7H_2O$), hydrogen peroxide (H_2O_2) 30% (w/w basis), sulfuric acid and sodium hydroxide were used without any purification and were provided by Merck.

2.2. Set-up

The laboratory photocatalytic oxidation unit was used for the batch experiments. It consists of a cylindrical photoreactor of 0.85 L volume, made from quartz, with a coaxial and immersed medium pressure UV mercury lamp used as the UV emitter and light source (Heraeus TQ150, input energy of 150W) emitting a polychromatic radiation in the range from 100 to 280 *n*m wavelength. The lamp emitted a power of 6.2 W in the UV-C ($100 < \lambda < 280$ nm) range, corresponding to1.32×10^{-5} Einstein s^{-1} (according to the manufacturer). The UV lamp is equipped with a cooling water jacket to maintain the temperature of the reaction at room temperature. There is one cooling loop for the cooling of the UV lamp. The UV system is positioned in a coaxial direction inside the reactor vessel. The UV system is made from quartz glass, which is effective in the transfer of UV irradiation. The reaction chamber is filled with the aqueous solution, which is between the reactor walls and UV lamp system. Mixing was accomplished by means of the magnetic stirring.

2.3. Procedure

The laboratory unit was filled separately with 0.85 L of synthetic concentrations of the studied EDCs. The optimum conditions for the different photochemical oxidation were investigated for each pollutant. The pH solution was adjusted to the desired value before start-up and kept at the same value during the reaction.

For runs using UV/H_2O_2 processes, hydrogen peroxide into different amounts was injected into the reactor before the beginning of each run. In the UV/H_2O_2 process, the variable studied was the influence of the amount of hydrogen peroxide at certain pH. For runs, using Fenton and the Photo Fenton process, a given weight of iron salt was added. The iron salt was mixed very well with the synthetic solutions before the addition of a given volume of hydrogen peroxide. For the Photo Fenton process, the time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide.

Table 1
Parameters studied in different oxidation processes.

Processes	Parameter	Conditions of experiment
UV	Effect of irradiation time	pH 8, 180 min
	Effect of pH	pH studied [4, 6, 8, 10]
UV/H_2O_2	Effect of irradiation time	pH 8, H_2O_2 5 mmol/L, 60 min.
	Effect of H_2O_2 dose	Dose [0, 5, 10, 15, 20, 25, 30 mmol/L, pH3, 60 min
	Effect of pH	pH studied [2–7], H_2O_2 5 mmol/L
Fenton reaction	Effect of irradiation time	pH3, Fe(II) 2.7 mmol/L, H_2O_2 5 mmol/L, 210 min
	Effect of pH	pH studied [2–7], H_2O_2 12 mmol/L, Fe 2.7 mmol/L, 210 min.
	Effect of iron dose	Dose studied [0, 0.9, 1.8, 2.7, 3.6, 4.5, 5.4 mmol/L], pH3, at H_2O_2 12 mmol/L, 210 min.
	Effect of H_2O_2 dose	dose studied [0, 2, 4, 6, 8, 10, 12, 14 mmol/L] at pH3, Fe^{2+} 2.7 mmol/L, 210 min
Photo-Fenton	Effect of irradiation time	pH 3, Fe^{2+} 2.7 mmol/L, H_2O_2 5 mmol/L, 60 min.
	Effect of iron dose	Range studied [0, 0.9, 1.8, 2.7, 3.6, 4.5, 5.4 mmol/L], pH3, 60 min, H_2O_2 5 mmol/L.
	Effect of H_2O_2 dose	Range studied [0, 0.5, 1, 1.5, 2.5 mL/l], pH 3, Fe^{2+} 0.5 g/L, 60 min.
	Effect of pH	pH studied [2–7], H_2O_2 5 mmol/L, Fe 2.7 mmol/L, 60 min.