

Treatment of gasoline-contaminated waters by advanced oxidation processes

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Received 22 February 2005; received in revised form 2 June 2005; accepted 4 June 2005

Available online 26 July 2005

Abstract

In this study, the efficiency of advanced oxidative processes (AOPs) was investigated toward the degradation of aqueous solutions containing benzene, toluene and xylenes (BTX) and gasoline-contaminated waters. The results indicated that BTX can be effectively oxidized by near UV-assisted photo-Fenton process. The treatment permits almost total degradation of BTX and removal of more than 80% of the phenolic intermediates at reaction times of about 30 min. Preliminary investigations using water contaminated by gasoline suggest a good potentiality of the process for the treatment of large volumes of aqueous samples containing these polluting species. Heterogeneous photocatalysis and H₂O₂/UV system show lower degradation efficiency, probably due to the heterogeneous character of the TiO₂-mediated system and lost of photonic efficiency of the H₂O₂/UV system in the presence of highly colored intermediated.

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Keywords: BTX; Advanced oxidation processes; Remediation

1. Introduction

In the last years, the contamination of soils and groundwater by volatile organic petroleum hydrocarbons has been extensively documented, mainly as a result of continuous leaking of fuels from old underground storage tanks [1,2]. In Brazil, there are more than 27,000 gas station, most of them operating with storage tank with more than 25 years old [3]. In these conditions, the leakage of fuels represents one of the most common sources of soil and groundwater contamination [4,5].

Petroleum derivatives such as benzene, toluene and mixed xylenes (BTX) are classified into the group of most dangerous compounds to the environment because of their large migration abilities, both in aquatic and land environments, and their acute and chronic toxicities [6]. Recent study revealed that the metabolic transformation of benzene, which is caused by specific enzyme, can lead to toxicity in human,

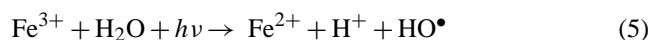
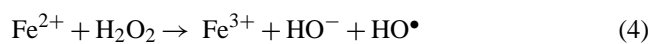
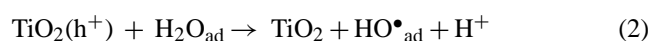
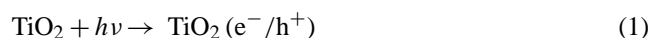
damaging the blood formation cells that can ultimately progress to leukemia [7]. In Brazil, the gasoline is mixed with about 25% of ethanol, fact that increases its migration in the subsurface after spill or leak, dramatically enhancing its environmental impact. The ethanol causes the cosolvency effect by reducing the polarity of the aqueous phase, causing higher concentrations of hydrophobic organic compounds such as BTX [3,8]. Early investigations have suggested that the presence of ethanol in gasoline is likely to hinder the natural attenuation of BTEX releases, due to an ethanol-driven consumption of nutrients and electron acceptors [9]. In view of limitations like this, conventional remediation processes show low degradation capacity of petroleum hydrocarbons from contaminated sites. Thus, the development of alternative technologies is absolutely essential.

Currently, the advanced oxidation processes (AOPs) have been investigated for application in the treatment of several organic pollutants, mainly due to its high degradation capacity toward substrates that are highly refractory with respect to conventional treatments [10]. The AOPs are characterized by the presence of highly reactive HO• radicals, which are

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suitable for rapid and indiscriminate reaction with a great number of organic compounds inducing its almost total mineralization [11,12].

Among the several processes that can be used to generate hydroxyl radical the photocatalytic decomposition of water over TiO_2 (Eqs. (1) and (2)) occupy a prominent place, mainly due to its massive exploration toward the degradation of substrates of environmental relevance [13,14]. More recently, the homogeneous $\text{UV}/\text{H}_2\text{O}_2$ (Eq. (3)), Fenton (Eq. (4)) and photo-Fenton processes (Eqs. (4) and (5)) had been used in the treatment of several organics pollutants [15], showing important advantages with respect to processes based on the irradiation of suspend solid photocatalysts [16].



Recent investigations have demonstrated that photo-Fenton reactions can accelerate the degradation processes, when compared with the conventional Fenton reactions. Furthermore, photo-Fenton processes have been used for degradation of many recalcitrant contaminants using reactors based on the use of natural sunlight to [17,18].

In the present work, the potentiality of oxidative advanced processes (TiO_2/UV , $\text{UV}/\text{H}_2\text{O}_2$, Fenton and photo-Fenton) was investigated, regarding the degradation of aqueous solution containing benzene, toluene and xylenes (BTX) and water contaminated with gasoline.

2. Materials and methods

2.1. Materials

Benzene (Biotic), toluene (Merck) and xylenes (Merse) were used without previous purification as aqueous solutions of 20 mg l^{-1} . Aqueous solutions of H_2O_2 (10% m/v) were prepared from a 50% stock solution, gently provided by Peroxidos do Brasil Ltda. Degussa P25 titanium dioxide (75% anatase–25% rutile, specific surface: $50.0 \text{ m}^2 \text{ g}^{-1}$), commercially grade oxygen (White Martins) and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Isofar) were used as received.

2.2. Photochemical treatment

The treatment of aqueous solution of benzene, BTX and gasoline-contaminated water was carried out in a glass conventional photochemical reactor with capacity of 300 ml, equipped with water refrigeration, magnetic stirrer and oxygenation system (flow of about 45 ml min^{-1}). The radiation was proportioned by a medium-pressure mercury vapor lamp

(125 W, Philips), placed in the solution by mean of a quartz (radiation UV) or Pyrex glass (radiation UV-A) jacket. The radiation intensity was determined by uranyl/oxalate actinometry as 9.7×10^{-5} and $7.1 \times 10^{-7} \text{ Es}^{-1}$ for quartz and Pyrex glass jackets, respectively.

The photocatalyst was used as suspensions of 50 mg l^{-1} .

2.3. Gasoline-contaminated water samples

Samples of gasoline-contaminated water were prepared by contacting commercial gasoline (200 ml), containing about 25% of ethanol and 4 l of distilled water during 48 h.

Samples of the aqueous fraction were collected in intervals of 12 h and characterized by gas chromatography and molecular fluorescence spectroscopy.

2.4. Analytical methods

The BTX were measured by gas chromatography (system headspace) using a Varian CP3800 chromatograph, equipped with flame ionization detector and DB624 column. Standard calibration curves were made from stock solution of 30 mg l^{-1} of benzene, toluene and xylenes in methanol.

Fluorescence UV–vis spectra were obtained in a HITACHI UVF 4500 spectrophotometer.

The organic carbon content was determined in a SHIMADZU VCPH TOC Analyzer. The calibration curve was made from standard aqueous solution of potassium hydrogenphthalate.

The concentrations of residual hydrogen peroxide, total phenol and $\text{Fe}^{2+}/\text{Fe}^{3+}$ were determined by UV–vis spectroscopy, using methodologies based in reaction with ammonium metavanadate [19], Folin-Ciocalteu reagent (APHA standard method [20]) and *o*-phenathroline (APHA standard method [20]), respectively. The measurements were carried out in a SINCO S-1150 spectrophotometer, using quartz cells of 1 cm.

3. Results and discussion

3.1. Photochemical degradation of BTX

Preliminarily, the effect of relevant experimental variables (such as pH, mass of photocatalyst and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ concentrations) on the efficiency of the four studied AOPs was investigated by factorial design systems. In this stage, benzene was used as model substrate mainly on account of its high toxicity and resistance toward conventional biological processes [21]. Subsequently, the degradation capacity of the AOPs toward BTXs was studied in the previously optimized experimental conditions and using the total phenol content as analytical response. In general, it is admitted that the photochemical degradation of aromatic structures involves preliminary addition of hydroxyl radicals, with the consequent generation of phenolic intermediates [22]. In view of this fact, the

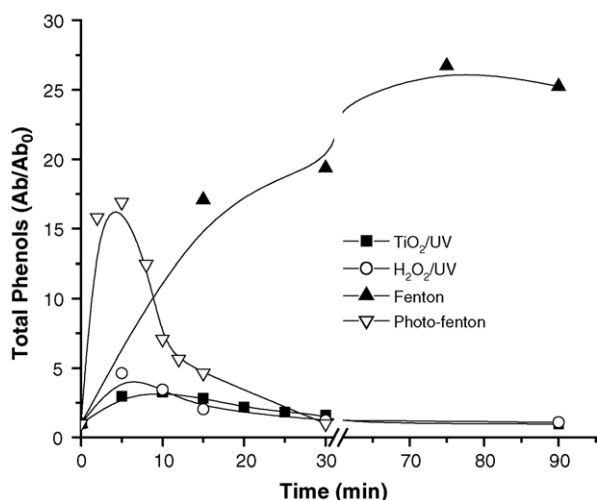


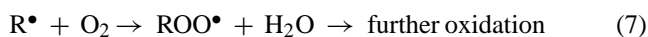
Fig. 1. Evolution of the total phenols (Abs/Ab_0) during the BTXs degradation (BTXs: 20 mg l^{-1} , 250 ml). TiO_2/UV (TiO_2 : 50 mg l^{-1} ; pH 6); UV/H_2O_2 (H_2O_2 : 100 mg l^{-1} ; pH 6); Fenton and photo-Fenton (Fe^{2+} : 10 mg l^{-1} ; H_2O_2 : 100 mg l^{-1} ; pH 3).

evaluation of phenolic structures represents a solid argument to infer some mechanistic differences between the processes.

In this study (Fig. 1), the photo-Fenton system showed a higher activity, fact confirmed by the generation of large amount of phenolic intermediates (typically phenol, catechol and hydroquinone) that accumulate at the first reaction times and that are almost completely degraded at reaction times lower than 30 min. In contrast, long times are necessary to formation of these transient species under conventional Fenton process, species that remain even after long reaction times (90 min). Heterogeneous photocatalysis and H_2O_2/UV system show an interesting difference, represented by no accumulation of large amounts of transient phenolic species. The relatively low activity showed by these processes must be a function of the heterogeneous character of the TiO_2/UV system and the loss of photonic efficiency of the H_2O_2/UV system on account of the presence of highly colored intermediated.

Taking into account its higher reactivity, the simplicity represented by its homogeneous character and the economy represented by the possibility of uses natural sunlight the photo-Fenton process was selected for further experiments.

To well characterize the photo-Fenton system, the effect of the radiation nature (UV or UV-A) and oxygenation on the BTXs degradation was studied. The results (Fig. 2) show that under UV-A irradiation the phenolic intermediates can be more easily removed in the presence of oxygen, probably due to formation of superoxide structures (Eqs. (6) and (7)) that are highly reactive and can be further decomposed [23].



For the UV photo-Fenton process the presence of oxygen is not decisive, probably on account of the higher amounts of

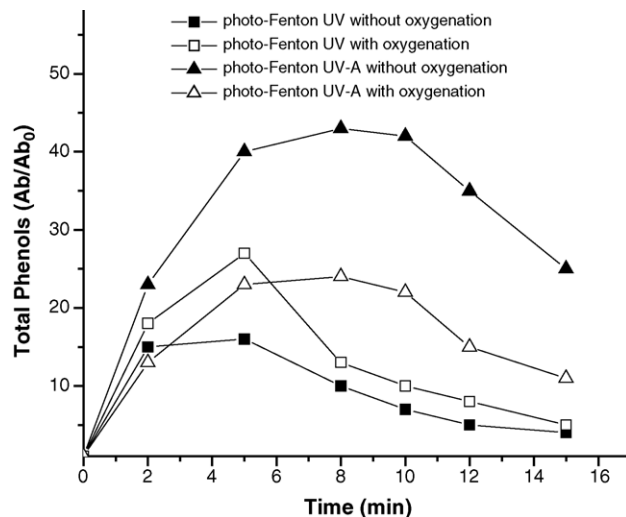


Fig. 2. Evolution of the total phenols (Abs/Ab_0) during the BTXs degradation by UV and UV-A photo-Fenton system (BTX: 20 mg l^{-1} , 250 ml; Fe^{2+} : 10 mg l^{-1} ; H_2O_2 : 100 mg l^{-1} ; pH 3).

hydroxyl radicals generated by photoreduction of Fe^{3+} (Eq. (5)) and direct photolysis of hydrogen peroxide (Eq. (3)).

In the presence of high hydroxyl radical concentrations, the degradation mechanism of phenolic intermediates involves the aromatic ring cleavage with formation of muconic acid and finally formation of carboxylic acid [24].

Even when the favorable effect of the UV irradiation and the presence of oxygen were demonstrated further experiments were carried out with UV-A radiation and in absence of oxygen, mainly due to a relative equivalency observed on the degradation capacity at slightly higher reaction times (Fig. 3). Monitoring the degradation of benzene, toluene and xylenes by gas chromatography a fast degradation was observed, with residual BTXs concentration of about 5 mg l^{-1} after

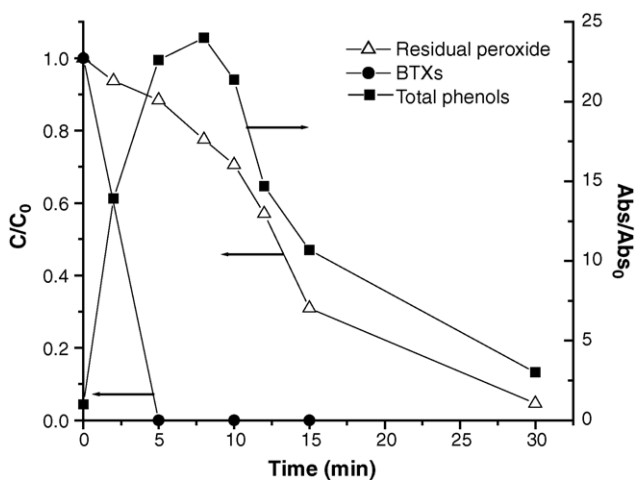


Fig. 3. Evolution of BTXs (C/C_0), total phenols (Abs/Ab_0) and hydrogen peroxide (C/C_0) during the BTX degradation by UV-A photo-Fenton system (BTX: 20 mg l^{-1} , 250 ml; Fe^{2+} : 10 mg l^{-1} ; H_2O_2 : 100 mg l^{-1} ; pH 3).

Table 1
BTXs concentration in samples of water contaminated with gasoline

Specie	Concentration ($\mu\text{g l}^{-1}$)	
	24 h	48 h
Benzene	4497.65	4113.39
Toluene	5165.26	3053.67
Xylenes	3991.53	2621.09

treatments of just 5 min. In addition, the chromatographic analysis not revealed the presence of any other volatile intermediate, indicating that the photochemical processes induces a very fast modification of the original molecular structure, with formation of high polarity intermediates. The phenolic transient species are removed in a long extension (90%) at reaction times of 30 min. Hydrogen peroxide was almost totally consumed in 30 min, fact that guarantee the no introduction of additional hazardous substances.

The mineralization capacity of the process was evaluated by total organic carbon (TOC) measurements. Even when BTXs can be removed with high efficiency, the maximum removal of TOC corresponds to 30%, at reaction time of 90 min. This behavior can implicates the accumulation of short-chain carboxylic acids (maleic, oxalic, acetic, malonic), typical oxidation products of larger molecules [25], effect allowed by the premature consumption of hydrogen peroxide. The mineralization of BTXs via UV-A photo-Fenton process shows apparent first order kinetics, with a rate constant (K) of $4.83 \times 10^{-3} \text{ min}^{-1}$.

As the cost of a photochemical process is predominantly a function of the consumed energy, a preliminary evaluation of these aspects can be done by mean of the electrical energy per order (EE/O), parameter defined as the electrical energy (kWh) required to degrade a pollutant by one order of magnitude in 1 m^3 of contaminated water [26]. At the experimental conditions studied here the UV-A photo-Fenton process show a EE/O of 11.52 kWh m^3 , value that is comparable with those related in the specialized literature [26].

3.2. Treatment of gasoline-contaminated water

Gasoline-contaminated water samples were prepared by contacting commercial gasoline (mixed with 25% of ethanol) and water and the solubilization of BTXs in the water column was evaluated by gas chromatography (Table 1). BTXs concentrations of approximately 5 mg l^{-1} were found after contacting time of 24 h, concentration that is reduced after 48 h probably due to volatilization. High concentrations of other hydrocarbons were also solubilized, fact that contributed with a total chemical oxygen demand (COD) higher than $10,000 \text{ mg l}^{-1}$. It is accepted that COD contents higher than 2000 mg l^{-1} can be not adequately treated by AOPs, mainly due to consumption of too large amounts of reactants [27]. For that reason, after use the samples were diluted in a 1:10 ratio.

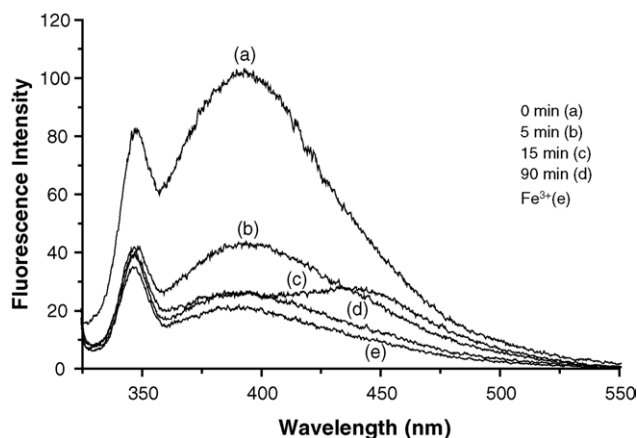


Fig. 4. Evolution of the fluorescence spectra during the UV-A photo-Fenton degradation of water contaminated by gasoline. Sample: 250 ml (24 h of contamination); Fe^{2+} : 10 mg l^{-1} ; H_2O_2 : 500 mg l^{-1} ; pH 3).

Monitoring the process by molecular fluorescence spectroscopy (Fig. 4) an intense signal was observed between 320 and 540 nm for untreated samples, indicating the presence of aromatics and phenolic compounds. A high degradation degree was observed after reaction times of 5 min, fact confirmed by the reduction of the fluorescence intensity by more than 50%. At the end of the process (90 min), the fluorescence was almost completely removed, remaining a residual signal of about 20% that resembles the characteristic signal of ferric ion complexes (e.g., $[\text{Fe}(\text{OH})]^{2+}$ and $[\text{Fe}(\text{RCO}_2)]^{2+}$).

As shown in Fig. 5, BTXs can be almost completely removed at reaction times of 15 min, even in the presence of large amounts of other hydrocarbons. The total phenol content evolved according to an expected behavior, represented by initial formation followed by progressive degradation. Additionally, hydrogen peroxide is almost totally consumed at reaction times of 60 min.

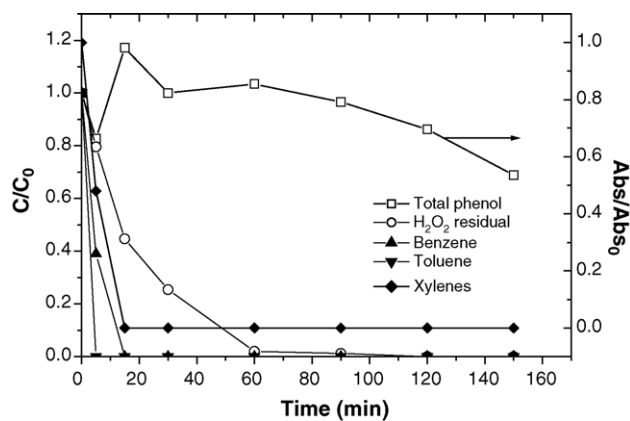


Fig. 5. Evolution of BTXs, total phenols (Abs/Abs_0) and hydrogen peroxide during the UV-A photo-Fenton degradation of water contaminated by gasoline. Sample: 250 ml (24 h of contamination); Fe^{2+} : 10 mg l^{-1} ; H_2O_2 : 500 mg l^{-1} ; pH 3).

4. Conclusions

The results discussed here demonstrated the high degradation capacity of AOPs toward aqueous samples containing BTXs. Specially remarkable are the results obtained with UV-A photo-Fenton processes, which permitted almost total degradation of BTXs and phenolic intermediates at reaction times of 5 and 30 min, respectively. The results also show that the system can be very efficient for the treatment of water contaminated with hydrocarbons derived from gasoline. In this case, the degradation of about 75% of the total amounts of hydrocarbons at reaction times of 90 min was demonstrated by fluorescence spectroscopy.

Thus, photo-Fenton system could be one good alternative in the treatment of water contaminated after spill of gasoline. Furthermore, the one important conclusion is the fact that the solar light could be used how source energy since the energy cost is its the mainly disadvantage.

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