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Evaluation of peroxide based advanced oxidation processes (AOPs) for the degradation of ibuprofen in water

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ABSTRACT

The occurrence and fate of pharmaceutically active components in the aquatic environment has been recognised as one of the emerging issues in environmental chemistry. One key component, which is found in considerable concentrations in European natural waters and is only partially eliminated during biological wastewater treatment is ibuprofen (IBU). This paper studies the application of classic Fenton, photo-assisted Fenton, H_2O_2/UV and peroxymonosulphate (POMS) oxidation for degrading IBU from wastewater. It is seen that the applied advanced oxidation processes are capable of effectively degrading the IBU, with the photo-assisted Fenton oxidation having the highest efficiency. The IBU in the mixture (at an initial concentration of 22 mg/L) is completely removed by a H_2O_2 concentration of 0.024 and 0.03 mg/L for the photo-assisted Fenton and classic Fenton oxidation, respectively. A POMS concentration of 37 mg/L is required to remove all IBU. No complete mineralization is obtained: a chemical oxygen demand (COD) removal by 89 and 88% was obtained for a H_2O_2 concentration of 0.023 and 0.03 mg/L for photo-assisted Fenton and classic Fenton, respectively. A POMS concentration of 37 mg/L resulted in a 86% reduction of COD. Finally, the main degradation products produced during the Fenton oxidation are identified and are similar to those identified in other studies dedicated to oxidative IBU removal.

Keywords: Ibuprofen; Advanced oxidation processes (AOP); Wastewater; Pharmaceutical

1. Introduction

The occurrence and fate of pharmaceutically active compounds (PhACs) in the aquatic environment has been recognised as one of the emerging issues in environmental chemistry [1,2]. Thousands of tons of pharmaceuticals are annually consumed for the prevention, diagnosis, cure and mitigation of diseases or to improve the state of health of humans and animals [3]. Although pharmaceuticals are present in wastewater streams in amounts comparable to other micropollutants such as pesticides, they are not subjected to the same rigorous treatment to reduce their presence in the environment [4]. In fact most PhACs are often not or only partially eliminated during biological wastewater

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treatment since they are not biodegradable, nor they adsorb in significant amounts to solid particles (i.e. sludge flocs). Their presence in the effluent of municipal waste water treatment plants has been reported by various authors [5–8]. It is hence of prime importance to develop methods that effectively remove PhACs from wastewater. Membranes (reversed osmosis and nanofiltration) have been reported to retain various pharmaceuticals [9], but have the inherent drawback of merely producing a concentrate and not decomposing the compounds. Therefore, in most cases, a secondary treatment is necessary to degrade the concentrated organics.

Non-steroidal anti-inflammatory drugs (NSAID), with more than 70 million annual prescriptions worldwide [10], rank among the most consumed medications. The NSAID ibuprofen (IBU) has been confirmed to be present in effluents of wastewater treatment plants [11] and concentrations of IBU in the environment are reported between 10 and 169 μg/L [3], since IBU is only partially removed during biological wastewater treatment [12]. IBU is one of the pharmaceuticals most abundantly present in European natural waters [13]. It is frequently used for its analgesic properties and ranks among the top-3 pharmaceuticals used in the EU. It is persistent, highly stable and only partially (<10%) taken up in the human body.

In recent years, advanced oxidation processes (AOPs) have been intensively investigated for their use in wastewater [14] and sludge treatment [15–17]. They are generally considered as a very promising alternative for conventional wastewater treatment systems since they are capable of (non-selectively) oxidizing a large number of non biodegradable and persistent pollutants [18]. In this paper, some peroxide based AOP methods are evaluated for their capability of effectively disintegrating IBU.

H_2O_2 is a strong oxidant (standard potential 1.80 and 0.87 V at pH 0 and 14, respectively) and its application for the treatment of various inorganic and organic pollutants is well established. Oxidation by H_2O_2 alone is not effective for the abatement of high concentrations of refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low reaction rates at reasonable H_2O_2 concentrations [19]. Transition metal salts (e.g. iron salts), ozone and UV-light can, however, activate H_2O_2 to generate hydroxyl radicals, which are stronger oxidants than ozone and H_2O_2 themselves (oxidation potential: 2.8 V). The reaction mechanisms have been reviewed by Neyens and Baeyens [19]. Hydroxyl radicals non-specifically oxidize target compounds at high reaction rates in the order of $10^9\,M^{-1}\,s^{-1}$. Hydroxyl radicals can add to aromatic or heterocyclic rings, as well as to the unsaturated bonds of alkenes or alkynes. They can also oxidize organics by abstraction of protons producing organic radicals, which are highly reactive and can be further oxidized.

Peroxymonosulphate (POMS), chemical structure: H_2SO_5 is applied in numerous industrial processes because of its oxidative capacity, and applications include disinfection, chlorine free bleaching of recycled paper and linen, the extraction of precious metals, the specific oxidation of organic molecules (e.g. epoxidation reactions) in organic synthesis and the generation of free radicals in polymerisation reactions. In wastewater treatment, POMS is used for the oxidation of hydrogen sulphide and other reduced sulphur compounds such as mercaptanes, disulphides and sulphites [20]. The compound can be used in its acid form (H_2SO_5) or as salt ($NaHSO_5$ or $KHSO_5$). Because of their instability, these compounds, however, cannot be stored. Therefore, for practical use, the active component $KHSO_5$ is incorporated in the triple salt $2KHSO_5$ $KHSO_4$ K_2SO_4, which is stable under ambient conditions and is commercially available under the brand names Oxone®, Caroat® and Curox®. The peroxymonosulphate ion is a derivate of hydrogen peroxide (one H-atom is replaced by a SO_3-group). Its standard oxidation/reduction potential is 1.44 V. The reaction rates are 3–4 times faster than for H_2O_2 for all nucleophilic reactions.

The main objective of this paper is to study the applicability of Fenton oxidation, photoassisted Fenton, H_2O_2/UV and POMS to effectively degrade IBU in water. The degradation of IBU is followed for various oxidant concentrations. In the second part, the degradation products that are formed by the classic Fenton oxidation are identified and characterized, and the evolution of degradation products is discussed.

2. Materials and methods

2.1. *Ibuprofen solution*

All tests were performed on a solution containing 22 mg/L IBU. This concentration is some orders of magnitude higher than encountered in natural waters or wastewaters, but lies within the same order of magnitude as in the concentrate after membrane purification (and is hence relevant for practical applications). This higher concentration, moreover, enabled a more accurate analysis and a more detailed study of the oxidative degradation to be achieved. The IBU was of analytical grade. It was dissolved in ultra pure water (resistivity <10 μS/m).

2.2. AOP treatments

2.2.1. Classic Fenton oxidation

The Fenton oxidation is carried out in a reactor at ambient temperature and pressure. Approximately, 1 L of the IBU solution was introduced into the reactor. Firstly, the pH was adjusted to 2.8 using H_2SO_4. This value was previously found to be the optimum pH for the reaction to take place [21]. Fe^{2+} from $FeSO_4$ was added as a catalyst at a 1/10 proportion to H_2O_2 on a weight basis. The H_2O_2 (from a solution containing 390 g/L) was subsequently added. During treatment, the mixture was gently stirred. The reaction was considered complete after 60 min.

2.2.2. Photo-assisted Fenton

This method is nearly identical to the classic Fenton oxidation. The only difference is that a UV lamp was immersed into the solution during the treatment. The lamp had a power of 12 W and a maximum intensity at a wavelength of 254 nm.

2.2.3. H_2O_2/UV

The H_2O_2/UV oxidation was carried out in a reactor at ambient temperature and pressure. About 1 L of the IBU solution was introduced into the reactor. The H_2O_2 (from a solution containing 390 g/L) was subsequently added. A UV lamp was immersed into the solution during the treatment. The lamp had a power of 12 W and a maximum intensity at a wavelength of 254 nm. During treatment the mixture was gently stirred. The reaction was considered to be complete after 60 min.

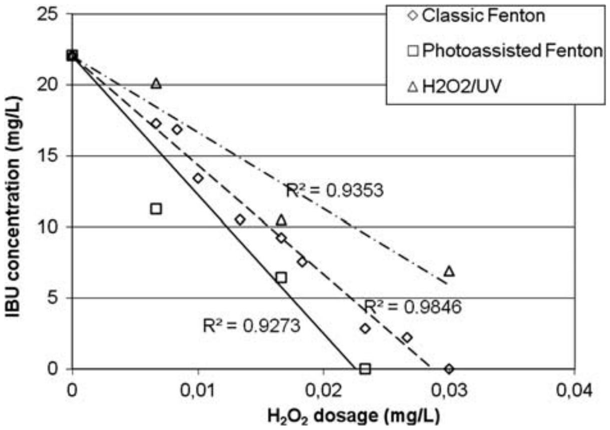


Fig. 1. Residual IBU concentrations after reaction for H_2O_2-based treatments.

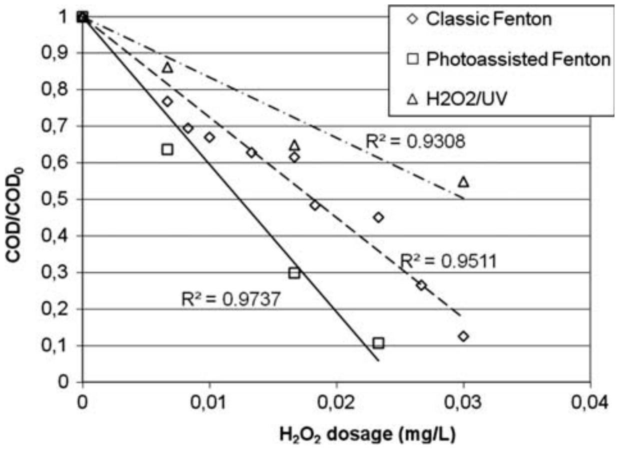


Fig. 2. COD values after reaction for H_2O_2-based treatments.

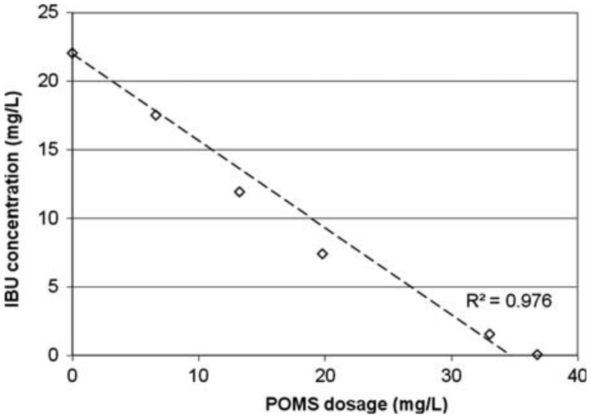


Fig. 3. Residual IBU concentrations after reaction for POMS oxidation.

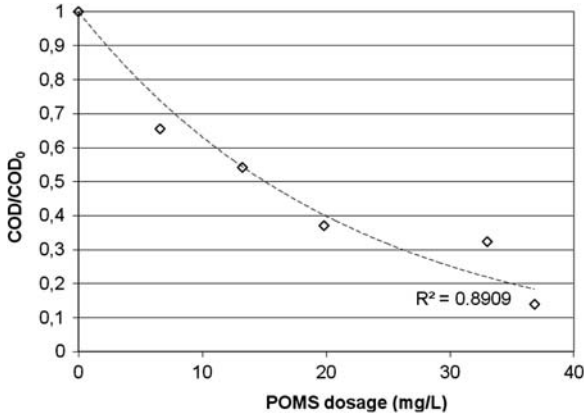


Fig. 4. COD values after reaction for POMS oxidation.

2.2.4. POMS oxidation

The POMS oxidation was carried out in a reactor at ambient temperature and pressure. No pH correction was necessary for this treatment. About 1 L of the IBU solution was introduced into the reactor. The POMS was subsequently added (Oxone).

2.3. Analytical procedures

The analysis of the IBU concentrations was performed on a Waters High-Performance Liquid Chromatography (HPLC), equipped with a Waters 510 HPLC pump, and a Waters 486 tunable adsorbance UV-detector. The injector was a Rheodyne manual injection valve, Model 7725i fitted with a 20 µL injection loop. The separation was carried out on a Symmetry C8 (reversed phase) column. The elution fluid was a mixture of 80% methanol and 20% water (both HPLC grade quality).

The chemical oxygen demand (COD) was measured using Spectroquant COD Cell tests (Merck) in combination with a Merck Spectroquant NOVA 60

Table 1
Main degradation products observed for IBU during classic Fenton oxidation

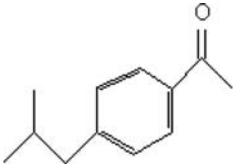
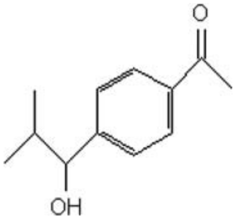
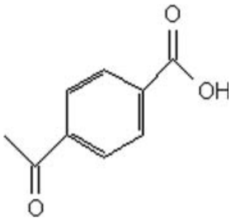
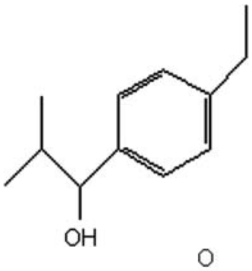
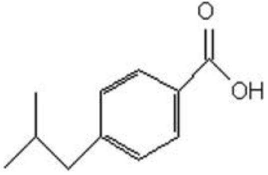
	Molecule	Retention time (min)	Abundance		Also identified by
			Sample A	Sample B	
I	DOP contaminant	27.366	–	–	
II	IBU	14.976	+++	+	
III		10.130	+++	+	[25,26]
IV		18.786	+++	++	[26]
V		9.071	+++	++	[27]
VI		9.770	++	+	[26]
VII		9.580	+	+	[27]

Table 2
Working costs associated with the total removal of IBU for 1,000 m^3 of wastewater (IBU concentration of 0.23 mg/L)

	Photo-Fenton	Classic Fenton	POMS
Cost oxidant (€)	0.01	0.0135	127.65
Cost other chemicals ($FeSO_4$, H_2O_2) (€)	0.014	0.018	–
Electricity cost (assuming 1,000 W UV lamp) (€)	0.12	–	–
Total (€)	0.144	0.031	127.65

photometer. Prior to COD analysis, the solution was tested for the presence of residual oxidant, which may possibly interfere with the COD measurement, using a Merckoquant peroxide test. No residual oxidant was found at any of the tested oxidant dosages, hence no correction of the COD was required.

The mass spectra of the degradation products were obtained using a Varian Saturn 2000 Gas Chromatography–Mass Spectrometry (GC-MS) system, equipped with an ion trap mass spectrometer and an electron multiplier detector. The instrument contained a 25 m Varian VF-1 ms column with internal diameter of 0.32 mm. Prior to the analysis, IBU and its degradation products were extracted from the water phase using ethylacetate, which was subsequently vaporised using a Rotavap. The remaining components in the Rotavap were dissolved in n-hexane. The analytes were derivatized using *N*-methyl-*N*-(*tert*.-butyldimethylsilyl)trifluoroacetamide before the injection, according to the method described by Rodríguez et al. [22].

3. Results and discussion

3.1. Degradation efficiency of the selected methods

The degradation efficiency of the various methods was followed by determining the residual concentration of IBU and the COD of the water sample after reaction for various oxidant dosages.

It was seen from the experimental results (depicted in Figs. 1 and 2) that all treatments were able to effectively degrade IBU. For all treatments, both IBU and COD concentration decreased linearly with increasing H_2O_2 dosage. Nevertheless, some differences could be observed. The photoassisted Fenton gave superior results. Using this treatment a complete removal of IBU was already achieved at a H_2O_2 dosage of 0.024 mg/L, while a concentration of 0.03 mg/L was necessary for the classic Fenton and a even higher concentration was needed for the H_2O_2/UV system.

The decrease of IBU concentration is obviously a measure for IBU reduction but presents no information on the extent to which the molecules are degraded. Indeed, only a minor change in the IBU structure (removal of one or more characteristic groups from the molecule), may already lead to the fact that a molecule is not identified as IBU by the HPLC measurement. Therefore, also the evolution of the COD of the mixture was measured as a function of H_2O_2 dosage. A complete COD removal was not achieved at the tested H_2O_2 dosages, but a significant reduction took place for all treatments. Here again, the best results were obtained by the photoassisted Fenton. At the considered H_2O_2 dosages, the H_2O_2/UV treatment only resulted in a COD reduction of 50% at the highest H_2O_2 dosage applied (0.03 mg/L).

The results for the POMS treatment are shown in Fig. 3 (reduction of IBU concentration) and Fig. 4 (COD-reduction). A complete removal of IBU was only achieved for a dosage of 37 mg/L oxone (POMS) triple salt. A residual COD-concentration of 21 mg/L was still present at that dosage.

Here again, the IBU concentration decreases linearly with increasing POMS dosage. However, an exponential relationship between COD decrease and POMS dosage was identified (the R^2-value for the linear fit was only 0.79, compared to values higher than 0.91 for the H_2O_2 oxidations). After an initial steep decrease, the COD removal rate decreased gradually for increasing POMS dosage. This behavior can be explained as follows. Initially, a high concentration of molecules that are readily degradable by POMS oxidation is present and the oxidation takes place well. The degradation products that are being formed seem, on the other hand, to be less susceptible to further oxidation by POMS. This observation indicates a lower oxidation capacity for POMS, compared to the hydrogen peroxide based treatments.

For being able to compare the POMS treatment with the H_2O_2-based treatment regarding IBU removal, the dosage of both chemicals is recalculated into the dosage of OH^*-radicals that is theoretically released from H_2O_2 and POMS. Each mole of H_2O_2 (molecular weight of 34 g/mol) splits into 2 OH^* radicals, whereas each mole of oxone (POMS) triple salt (molecular weight of 614.76 g/mol) also releases two OH^*-radicals. This means that 35 mg/L POMS generates the same amount of OH^* radicals as 1.93 mg/L H_2O_2. This leads to the conclusion that the efficiency of POMS towards IBU degradation is much lower than the efficiency of any of the H_2O_2 treatments. On the other hand, from a practi-

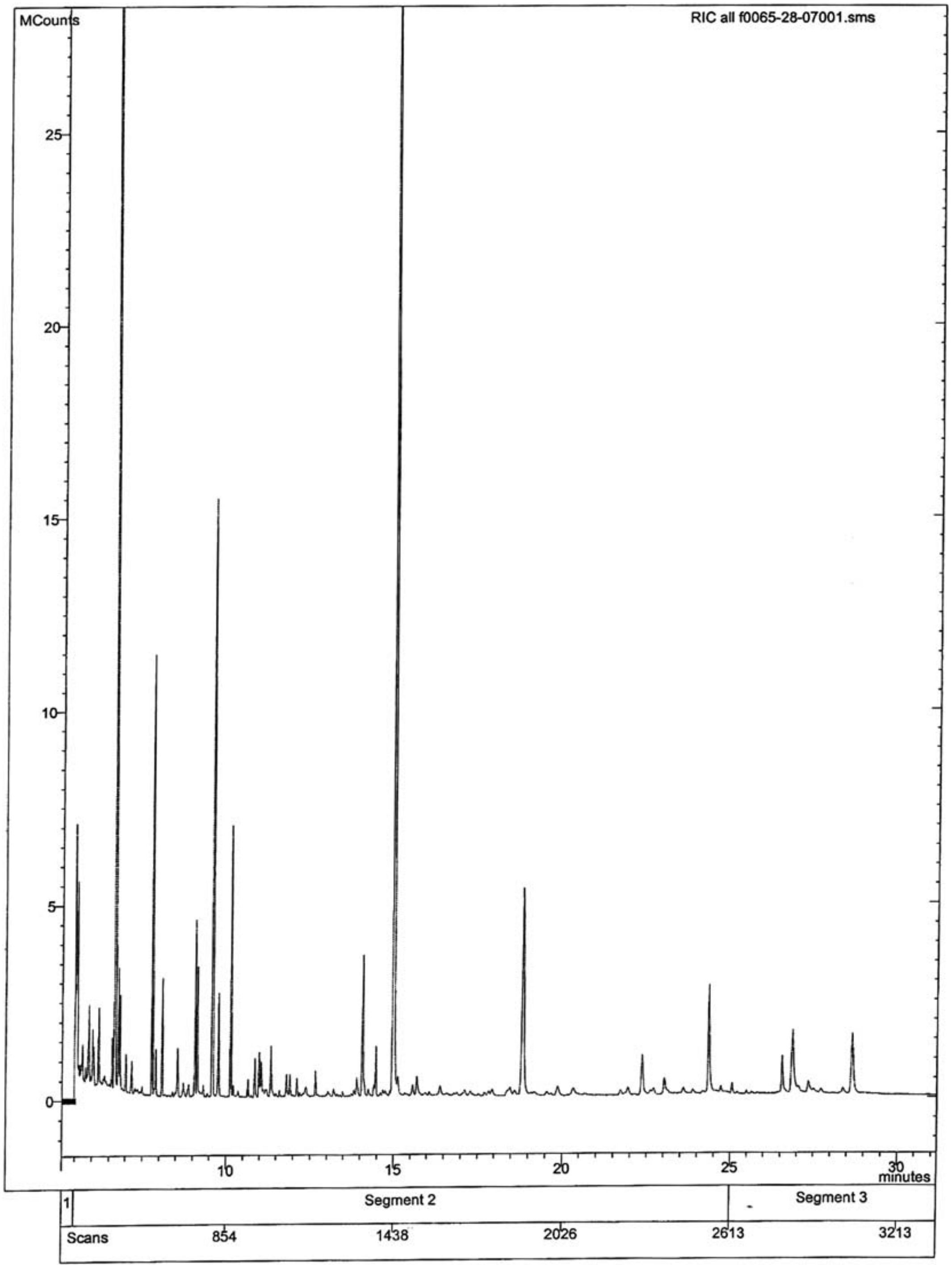


Fig. 5. Chromatogram for water samples treated with 0.015 mg/L H_2O_2.

cal point of view, the POMS treatment is much more easy, since it does not require a pH decrease or the addition of a catalyst.

3.2. Economic evaluation

The costs associated with the treatment are obviously an important factor that should be taken into account in the selection of the most suitable treatment option. A limited economic evaluation was carried out to compare the different treatment methods with each other, based on the costs of the chemicals and the electricity to power the UV lamp. As a basis for the evaluation, the oxidant concentrations leading to a complete IBU removal

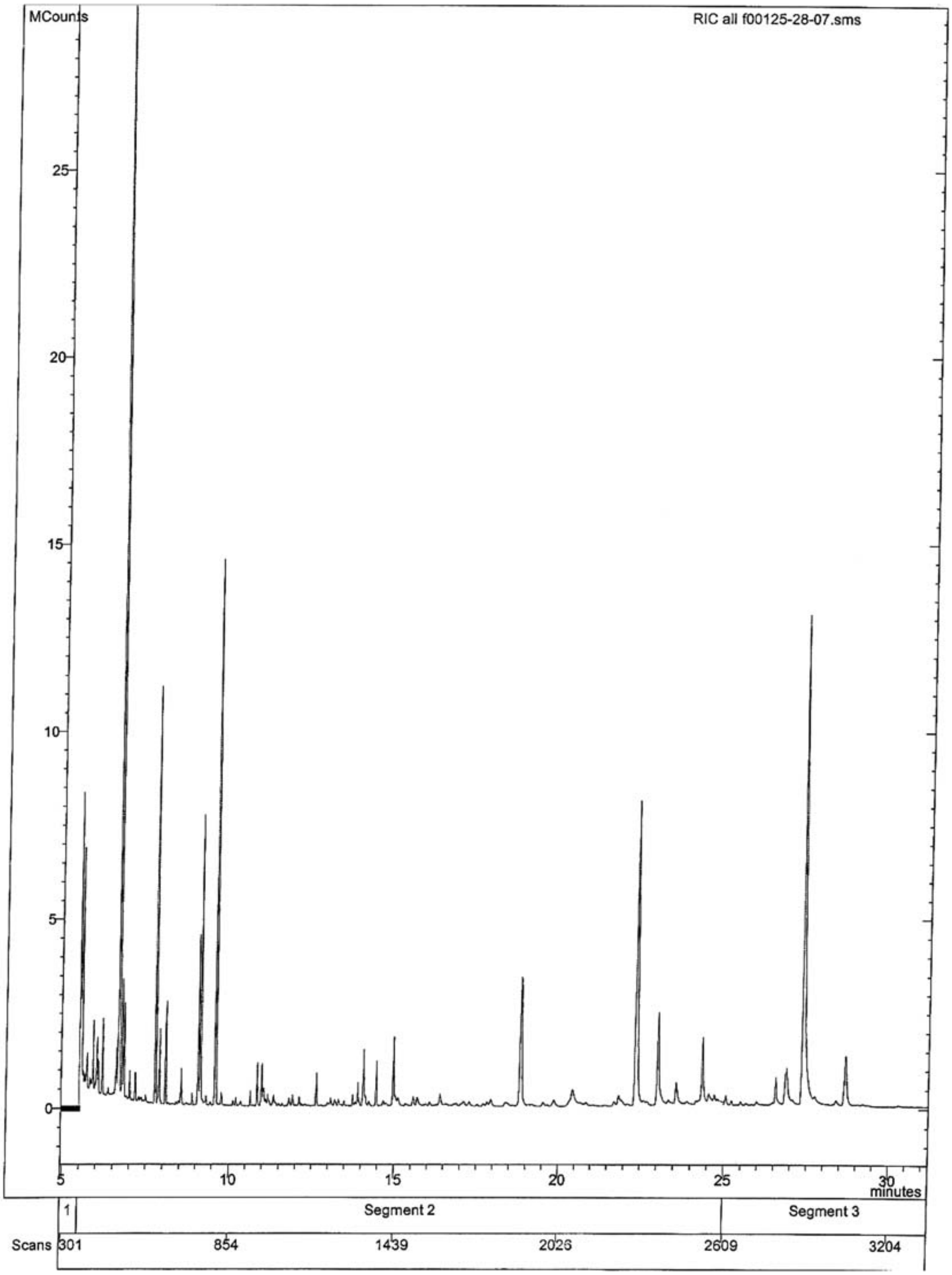


Fig. 6. Chromatogram for water samples treated with 0.03 mg/L H_2O_2.

were chosen. The results of the assessment are presented in Table 2.

From the results it can be seen that the costs associated with the classic Fenton oxidation are the lowest, followed by the photo-assisted Fenton (approximately 5 times higher). The cost of POMS is much higher, and this treatment is not economically feasible. It should be pointed out, however, that the costs were calculated using the treatment conditions applied in the labscale tests on synthetic wastewater only containing IBU. In practice, other impurities will surely be present, possibly inducing matrix effects leading to other oxidant dosages.

3.3. Identification of degradation products

It has been reported in various studies (e.g. [23,24]) that intermediate products formed during the degradation of organic compounds by AOPs can be more toxic and carcinogenic than the original compounds themselves.

Therefore, it is important to identify the reaction by-products formed during IBU oxidation. The composition of two samples, subjected to classic Fenton oxidation, was analyzed using GC-MS. Sample A was treated with a dosage of 0.015 mg H_2O_2/L resulting in an IBU concentration after treatment of 9.14 mg/L and sample B was treated with a dosage of 0.03 mg H_2O_2/L resulting in a complete removal of IBU (concentration below detection limit of HPLC). By considering two different dosages, the evolution of by-product concentration could be evaluated. Fig. 5 depicts the obtained chromatogram for sample A and Fig. 6 the chromatogram of sample B. The chromatogram of the original (untreated) sample is not shown, since only one sole peak, i.e. the one corresponding to IBU itself, was present.

The degradation products most abundantly present in the samples (corresponding with the highest peaks in the chromatogram) were identified and are listed in Table 1, together with the associated retention times and the relative concentration in both samples. It was seen that all degradation products found in this study have also been identified in other literature sources studying sonolysis, photocatalysis and sonophotocatalysis [25], photo Fenton [26] and biological metabolism [27].

Unfortunately, the compound associated with the peak with retention time 23.05 min could not be identified. Dioctylphtalate (DOP) should be considered as an impurity frequently encountered during GC-MS analysis of organic compounds and should therefore not be considered to be relevant in the present study.

It was seen that the relative concentrations of all identified components decreased with increasing H_2O_2 concentration, hence confirming the more complete mineralization at high H_2O_2 concentrations.

The height of the IBU peak dropped spectacularly, hence confirming its almost complete removal at high H_2O_2 dosage.

4. Conclusions

This paper studied the application of various peroxide based AOPs for the removal of IBU from water. All processes were able to effectively degrade IBU. Photoassisted Fenton yielded superior results, necessitating the lowest H_2O_2 concentration for complete IBU removal. Compared to the H_2O_2-based treatments, the POMS treatment needed the highest dosage of oxidant, but has the advantage to be a very simple process, which is carried out without lowering the pH of the solution or the presence of a UV lamp. The main degradation products were identified for the classic Fenton oxidation. It was seen that their abundancy decreased with increasing H_2O_2 dosage, hence confirming the more complete mineralization of IBU at high H_2O_2 dosages.

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