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The elimination of cancerous pollutants by an advanced oxidation processes and adsorption in monosolute solutions mixtures in water

Maria Carolina de Almeida[a,*], Tatianne Ferreira de Oliveira[a], Fernando Pereira de Sá[b]

[a]*School of Agronomy, Federal University of Goiás-UFG, Campus Samambaia, Rodovia Goiânia-Nova Veneza Km-0, Caixa Postal 131, CEP 74690-900, Goiânia, Brazil, Tel. +055 (62) 3521-1530; emails: maria.almeida@ifg.edu.br (M. Carolina de Almeida), ferreira.tatianne@yahoo.com.br (T. Ferreira de Oliveira)*

[b]*Federal Institute of Education, Science and Technology of Goiás-IFG, Avenue Universitária, CEP 75400-000, Inhumas, Brazil, email: fernandofpsa@gmail.com (F. Pereira de Sá)*

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ABSTRACT

The objective of this work was to study different treatments for the elimination of phenol compounds (PHE) and diethyl phthalate (DEP), comparing the efficiency of each treatment used individually and when mixed, to more complex matrices where these pollutants are in competition with each other. The treatment methods studied included adsorption with activated carbon (AC); advanced oxidation processes using UV-C/H_2O_2 and coupling (UV-C/H_2O_2/AC). The results obtained showed that the adsorption process using AC revealed that there was a greater elimination of the PHE pollutant in both synthetic effluent and tap water, with competition among the molecules. The results obtained in the UV-C/H_2O_2/AC coupling between the different activated carbons used in this study revealed that AC2 showed reduced efficiency in the removal of PHE. It showed a slower elimination rate when compared to AC1, which was justified by the properties of the AC, but the results showed a degradation rate higher than 90% in the two ACs used. The kinetic degradation constants of the micro-powder in the two matrices by AOP (UV-C/H_2O_2) and coupling (UV-C/H_2O_2/AC1) in tap water effluent with DEP were all higher – ranging from 0.0673 to 0.1289 min^{-1} in comparison with synthetic multi-component laboratory effluent (DEP). The results of the kinetic curves allowed us to conclude that the AC adsorption process delays the elimination of the micropollutants understudy when compared with the other UV-C/H_2O_2 and UV-C/H_2O_2/AC processes, but it can be a positive material in the generation of efficient hydroxyl radicals in these treatment processes.

Keywords: Phenol; Diethyl phthalate; Complex matrices; Hydroxyl radicals; Advanced oxidation processes

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1. Introduction

Emerging pollutants are potentially toxic substances whose effects or presence in the environment is still poorly understood. As can be seen from this definition, the term “emerging” refers to the concern that these substances have produced in the light of new knowledge acquired about their actual and potential impacts on human and environmental health. In other words, it encompasses both substances that have been used for a long time, as well as new substances resulting from technological advances [1,2].

These compounds include phthalates, which may promote adverse effects on the human endocrine and reproductive systems by their carcinogenic and mutagenic action [3,4]. The authors Gani and Kazmi [5], state that the level of contamination by phthalates in the aquatic environment is increasing in residual waters, followed by surface, underground and drinking water sources. The main source of

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* Corresponding author.

the contamination is in effluent releases even after treatment and which is still charged with phthalates.

Phenolic compounds are also very harmful to humans and animals, even at low concentration levels and are considered one of the main pollutants in wastewater [6]. Phenol has also been detected in surface waters, rainwater, sediments, drinking water, groundwater, industrial effluents, urban runoff and hazardous waste sites [7].

Phenolic compounds and phthalates comprise one of the most representative groups of priority pollutants. Phenolic compounds as well as phthalates are carcinogenic, highly toxic, and may cause death, even at low doses [8]. Hence, investigating new or improved technologies and treatments for phenol compounds (PHE) abatement is of paramount importance. Over the past three decades, research efforts have focused on developing more effective technologies to remove persistent organic pollutants from wastewater. Among these processes are the advanced oxidation processes (AOPs), which are defined as those that are capable of generating hydroxyl radicals in quantities sufficient to oxidize the chemicals present in effluents. These processes may be heterogeneous or homogeneous, and may or may not use UV radiation. These processes are based on hydroxyl radical generation ($HO^•$), a highly oxidizing and non-selective species.

In this context, the objective of this work was to study the elimination techniques, besides comparing several PHE and diethyl phthalate (DEP) processes and to compare their efficiency in each treatment when used individually and when mixed if and where these pollutants are in competition. The treatment methods studied included: adsorption with activated carbon (AC); AOP (UV-C/H_2O_2) and coupling (UV-C/H_2O_2/AC).

2. Materials and methods

2.1. Material and activated carbon characterization

The AC used in this study (AC1 and AC2) was commercially activated carbon provided by FBC Fábrica de Catalisadores, Brazil. The AC was washed before each experiment to eliminate any residual acidity resulting from the activation treatment. The DEP, from the Aldrich Chemistry brand, presents 99.5% purity. The phenol (PHE) of the Vetec brand shows 99.85% purity. All the chemical substances used were of analytical grade.

The textural analysis was performed on a porosimeter (Micromeritics, model Gemini V2380, USA). Specific surface area ($m^2\ g^{-1}$) was measured through the BET method (Brunauer–Emmet–Teller). Total pore volume ($cm^3\ g^{-1}$), micropore volume ($cm^3\ g^{-1}$), size distribution and average pore diameter (Å) were estimated from the linear part of the Dubinin–Radushkevich plot [9]. The Boehm method was performed to determine surface functional groups (acids and basic) [10]. The point of zero charge (pH_{PZC}) was obtained using the method Rivera-Utrilla et al. [11]. Adsorption spectra in the infrared region were obtained using a spectrophotometer (PerkinElmer, model Spectrum 400). Analyzes were concentrated in the infrared region between 4,000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. Scanning electron microscope analyzes were performed using (Jeol, model JSM-6610, Japan) aimed at evaluating activated carbon.

2.2. Adsorption experiments

The experimental conditions were applied in a reactor, an Erlenmeyer flask with 250 mL of the effluent, with a concentration rate of the micropollutant of 0.2 g L^{-1} chosen as the standard (this elevated concentration was chosen for better monitoring of the kinetic study). The reactor was put in shaker equipment (Tecnal brand model TE424) with a shaking control set at 150 rpm. Samples were collected at different time intervals (0, 5, 10, 15, 25, 35, 45, 60, 80, 100, and 120 min) with the objective of evaluating the elimination of the pollutant in the solution. After each collection, samples were filtered using 25 μm of qualitative filter paper and subjected to analysis on a UV-visible spectrophotometer (Femto, 700 plus) at λ = 228 nm and 265 nm (wavelength of DEP and PHE).

The adsorption experiments were carried out at pH 7.0 and 30°C, evaluating different matrices: DEP and PHE contaminated in aqueous solution separately, tap water with multi-components (DEP and PHE) and tap water contaminated with only DEP. A total of five experiments, all carried out in triplicates, totaling in full 15 separate experiments. The data obtained were analyzed using a Statistica 7.0 program (StatSoft Inc., Tulsa, Oklahoma, USA) with a significance level of ($p < 0.05$).

2.3. UV-C/H_2O_2 and UV-C/H_2O_2/AC coupling

The oxidation kinetics were performed as follows: 20 mmol of H_2O_2 concentration was added into a photo-reactor containing 250.0 ml of the effluent to a 0.2 g L^{-1} concentration of the micropollutant DEP and PHE, chosen as the standard. Experimentation started when H_2O_2 was introduced into the photo-reactor. The photo-reactor (Fig. 1) consists of a parabolic glass cell containing the micropollutant solution which was placed under a 125 W (Avant brand) mercury vapor lamp bulb with light intensity (UV-C) of 20.41 W m^2 inside the metallic cylinder. This

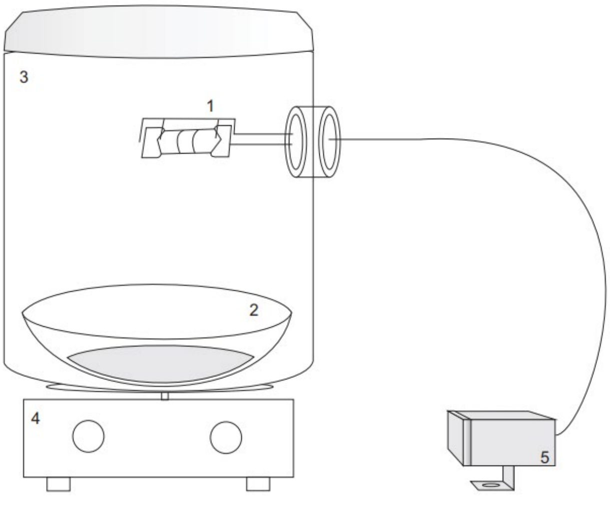

Fig. 1. Advanced oxidation processes (AOPs) pilot scheme: (1) mercury vapor lamp; (2) glass parabolic cell; (3) metallic cylindrical cell; (4) magnetic stirrer; (5) lamp reactor.

system was placed on a magnetic stirrer (Nova Técnica brand) with an agitation control set at 150 rpm at 30°C and pH 7.0. In AC coupling, the same experimental procedure was followed, with the addition of 0.4 g of AC (preliminary tests not presented in this work were completed for the choice of AC mass, as the best substance for the absorption process).

During the oxidation processes, samples were collected at different time intervals (0, 12, 24, 36, 48, 60, 80, 100, and 120 min) to evaluate the elimination of the pollutant in the solution. 2 mL of aliquot was collected at these time intervals, and 1 mL of sodium sulfite (Na_2SO_3) at 0.1 mol L^{-1} was added as a $HO^{\bullet}$ radical inhibitor, according to the methodology proposed by Keen et al. [12]. The samples were conditioned in test tubes wrapped in foil, eliminating the possibility of light degradation between collection and the moment of analysis.

2.4. Analysis

Analyzes of the DEP and PHE were performed using high-performance liquid chromatography. The chromatographic system used was fitted with the following brands of equipment: Shimadzu U C202047 (Germany); model LC-8A; detector: UV/VIS Prominence SPD-20A DAD (λ = 228 nm (DEP) and λ = 265 nm (PHE)); column: C18 (250 mm × 4.6 mm × 5 μm), Wakosil brand, model SGE 206505, mobile phase: acetonitrile (ACN P.A.)/water (Milli-Q deionized H_2O) 70:30; flow of the mobile phase: 1 mL s^{-1}; limit of instrumental detection: 0.12–0.17 μg L^{-1} for DEP and PHE; sample injection volume: 20 μL.

3. Results and discussion

3.1. Activated carbon characterization

The physical and chemical characterization of the ACs used is presented in Table 1. It shows that AC1 and AC2 share a predominantly basic character, however, the nature of their different acid groups: with 5.09% carboxylic; 36.36% phenolic and 47.72% lactone acids for AC1; and 0.142 meq g^{-1} carboxylic; 0.168 meq g^{-1} phenolic and 0.212 meq g^{-1} lactone acids for AC2, and with 2.55 meq g^{-1} for basic groups and 0.05 meg g^{-1} for acid groups, meant that practically they were composed only of carboxylic groups without phenolic and lactonic groups.

These results show that these ACs have more basic functional groups than acid functional groups. The pH_{PZC} obtained was consistent with the pH quantification of surface functional groups obtained using the Boehm method having a pH value of 7.2 for AC1 and of 7.3 for AC2. The result obtained by infrared analysis is consistent when compared to the Boehm method and shows pH_{PZC} identified in adsorption wavelength for AC1 of (a) phenol acid anhydrides; (b) carboxylic acid, anhydride and lactone; and (c) carbonyl and quinone groups [13], specific bands at 1,710–730 cm^{-1} (C=O starching vibration in carboxyl functions) and phenolic C–O groups, as the 1,000–1,250 cm^{-1} and phenol (1,175 cm^{-1}), respectively. Moreover, for AC2 there is broadband with frequency at 3,433 cm^{-1} ($HO^{\bullet}$), peaks at 2,926 and 2,854 cm^{-1} (CH), elongation at 1,630 cm^{-1} (C=C) in alkanes, a band at 1,455 cm^{-1} (CH_2) of the pyran ring and peaks with frequency at 1,091 cm^{-1} (CO) [14].

The textural characterization indicates a high S_{micro}, which is constituted by micropores with radii from 0.160 to 0.263 Å for AC 1 and AC2 respectively. The average pore diameter was 20.79 (Å). Micropore volume represents 77.63% of the total pores of the activated carbon, showing that the activated carbon is predominantly microporous, too.

3.2. Adsorption experiments: influence of the matrix used

Fig. 2 presents the comparison of the results of the treatment performed to eliminate the micropollutant of the multi-components DEP and PHE by adsorption, applied in tap water doped with DEP and PHE in the mono solution synthetic effluent and with both multi-components in a complex matrix (pH 7.0, 0.4 g AC, 30°C).

The results showed that there was greater elimination of the PHE pollutant in both synthetic effluent and tap water.

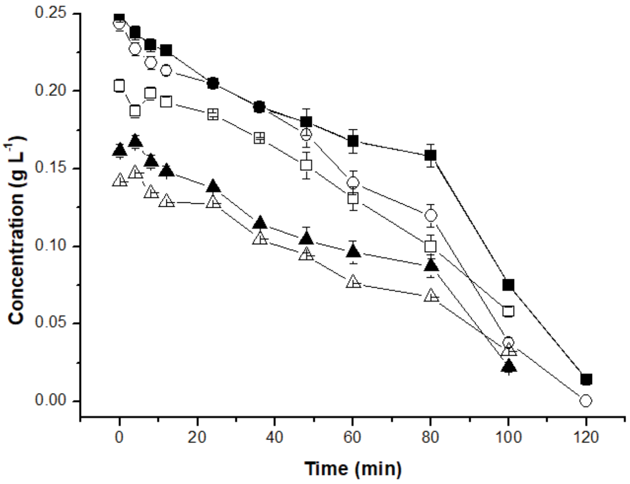

Fig. 2. Adsorption kinetics of micro pollutants DEP and PHE in AC1: tap water with DEP (■); tap water with multi-component ((DEP (○) and PHE (▲)), tap water with mono-component ((Δ) PHE and (□) DEP), all experiments in: pH 7.0, 0.4 g AC, 30°C.

Table 1
Chemical and textural characteristics AC1 and AC2

	pH_{PZC}	Carboxylics (meq g^{-1})	Phenolics (meq g^{-1})	Lactones (meq g^{-1})	Total acid (meq g^{-1})	Total basic (meq g^{-1})^a	Fourier transform infrared spectroscopy (cm^{-1})	Micropore radius (Å) Barrett, Joyner, and Halenda method	S_{total} (m^2 g^{-1})
AC1	7.2	0.071	0.169	0.211	0.523	0.845	1,500–1,800	0.16–0.263	554.228
AC2	7.3	–	–	–	0.05	2.55	2,854–3,433	0.23	512.0

It is observed that there is a competition between the molecules in the active sites of the activated carbon. These results are extremely important when compared with the actual results obtained in the treatment plants of effluents, where there is a lower efficiency rate when compared to those results obtained in laboratories.

The surface area of the PHE molecule is lower if compared to that of the DEP molecule. As in other works, where the efficiency of adsorption in treatments for removal of a pollutant and the combination of pollutants of synthetic effluents has been verified, it can be confirmed that both the porosity of the AC and the interaction between the active sites of AC and micropollutant molecules may determine the most efficient treatment for each micropollutant. In addition to the charges of both the AC surface and the pollutant molecules, as well as the texture characteristics of the AC and the surface area of each micropollutant molecule and the combination thereof, this will lead to a faster access to the AC pores. Despite the different characteristics of the pollutants studied, the smaller surface area of the PHE molecule in the competition between them, shows a higher adsorption velocity, even though there was an electrostatic attraction between DEP with a negatively charged nucleus and the AC surface of basic character. In addition, the adsorption process in AC was lower in the adsorption of DEP when compared to the adsorption of the PHE. Similar results were found by other authors [15–17], who studied the AC adsorption process and found lower elimination rates for bisphenol A when compared to the adsorption of PHE.

On the other hand, the amount of adsorbate that can be adsorbed by an adsorbent depends upon both adsorption concentration characteristics and phase liquids, such as pH and temperature [18,19]. Its adsorbent power comes from the large surface area and the presence of a variety of functional groups on its surface [20,21].

The worst results were obtained with the DEP molecule, where there was slower adsorption in relation to the PHE. These results are explained by the micro powder molecules, such as pKA (2.943) DEP and pH_{PZC} of the AC with a pH of 7.0, where the surface of AC1 presents a positive charge and the DEP a negative charge. As they are different, an electrostatic attraction occurs and adsorption is favored. For PHE, which has a pKA of (9.95), PHE and pH_{PZC} of AC1 at pH 7.0, both the AC surface and the PHE charges are positive, electrostatic repulsion occurs and adsorption is not favored.

The results presented by Cagnon et al. [22], reveal that the adsorption competition between the two molecules in the mix led to modifications in the parameters obtained in monosolute solution. The adsorption capacity of each AC with monosolute solution was higher for dimethyl phthalate (DMP) whereas in bisolute solutions it was higher for DEP. These phenomena may be due to the solubility of the molecules. DEP is less soluble in water than DMP, after DEP adsorption; there are fewer adsorption sites available for the DMP molecule.

3.3. *UV-C/H_2O_2: influence of the micropollutant used*

The elimination kinetics of DEP and PHE by advanced oxidation processes, AOPs, (UV-C/H_2O_2) are presented in Table 2.

The results obtained by the UV-C/H_2O_2 process revealed that the best elimination rates were for DEP compared to the PHE pollutant at the end of 120 min of treatment when the treatment was applied to the effluent in the mono solution condition. In addition to the effect of the pH associated with the concentration of H_2O_2 with a non-negligible micro pollutant elimination rate for both DEP and PHE in synthetic effluents with distilled water, they were higher than 96% and 76% respectively for DEP and PHE, treatment.

With the presence of tap water, the rates could have been influenced by the presence of components of the water matrix (including natural organic matter, HCO_3^-, Cl^-, SO_4^-, and NO_3^- UV/H_2O_2 where the process can generate radical hydroxyls $HO^{\bullet}$ %), and the percentage of $HO^{\bullet}$. The generated radical can react with non-selective organic compounds through electron transfer, hydrogen abstraction and electrophilic addition reactions [23–26], as reported by Zhang et al. [27]. In the same way as with the presence of carbonate or bicarbonate, nitrate, phosphate and dissolved organic matter [28–30], these factors may also interact with one another and make the optimization process challenging [31].

The percentage of $HO^{\bullet}$ radicals can react with many constituents with a constant diffusion-controlled rate and therefore is considered a non-selective oxidant with a short shelf life. For Zhang et al. [27], who evaluated the efficiency of UV/AOP treatments, to eliminate non-metabolized amoxicillin (AMX) in the UV/H_2O_2 and UV/persulfate ($S_2O_8^{2-}$, PS) systems, the degradation kinetics of AMX with percentages of $HO^{\bullet}$ and $SO_4^{\bullet}$ radicals were compared to other treatment processes at neutral pH. Similar trends were also found by Lee and von Gunten, for the oxidation of phenol, aniline, glycine, dimethylamine, and trimethylamine [32].

The diffusion of the $HO^{\bullet}$ radical may have been reduced in the presence of PHE, which is less soluble than DEP, and in the combination of the multi-components, which may have contributed to a lower action by the oxidant in a complex matrix, as it didn't demonstrate the same result

Table 2
Responses of advanced oxidation processes for the elimination rate of DEP (Y_1) and PHE (Y_2)

UV-C/H_2O_2					
Kinetics	[H_2O_2] (mmol L^{-1})	pH	Temperature (°C)	Y_1 (%) DEP	Y_2 (%) PHE
*K*1	20	7.0	30	99.92	76.92
*K*1	20	7.0	30	96.18	76.00
*K*3	20	7.0	30	98.17	78.12

when compared to the treatment of mono solutions. The study by Mondal et al. [31], revealed that for the degradation of anionic surfactant, sodium dodecyl sulfate (SDS), in municipal wastewater by UV/H_2O_2, and kinetic experiments conducted for both municipal wastewater and distilled water enriched samples containing 100 mg L^{-1} of SDS, the rate of reaction based on flow and pseudo-first-order, it was seen that the constant for the wastewater sample was 1.5 times smaller than the sample with distilled water.

In studies, with the use of the phthalates DEP and DMP, [5,33,34] it is reported that the efficiency of the process is affected by the concentration of H_2O_2, UV radiation and pH, the phthalates also returned positive results. According to Xu et al. [33], DEP elimination results obtained revealed that H_2O_2 concentration and intensity of UV radiation is directly related to the efficiency of the process to increase the production of hydroxyl radicals.

UV/AOPs have been considered as alternatives to conventional water treatment technologies due not only to the risk of reducing the formation of carcinogenic disinfection by-products (DBPs) or intermediates [32]. DBPs also lead to the generation of highly reactive radicals. The UV/H_2O_2 process can generate hydroxyl radicals ($HO^{\bullet}$ %) [35] and $HO^{\bullet}$ % can react with non-selective organic compounds through electron transfer, hydrogen abstraction and electrophilic addition reactions [23–26].

3.4. UV-C/H_2O_2/AC: influence of the AC used

The curves of DEP and PHE oxidation kinetics by UV-C/H_2O_2/AC coupling are shown in Fig. 3 and Table 3.

The results obtained in Fig. 4 revealed that the PHE degradation kinetics were faster than the DEP pollutant using the AC1/UV-C/H_2O_2 coupling. We observed that there was a complete elimination of DEP after only 40 min when using AC1 under the conditions of the present study (pH 7.0 and 30°C). AOPs, when coupled with AC, present better results than when applied separately, which was clearly shown in Fig. 2. The attack of hydroxyl radicals $HO^{\bullet}$ is a very important mechanism involved in the degradation of pollutant molecules in the aqueous phase. Some studies have shown that a hybrid process combining high oxidation capacity and high adsorption capacity of AC can be a very efficient process when compared with conventional AOPs [36,13].

Studies by Moraes et al. [37], with the PHE molecule using AC-coupled AOPs, have shown that the degradation of PHE is predominantly in the homogeneous phase, but a part occurs at the surface of the activated carbon, showing that this adsorbent material contributes significantly to the increase of the rate of removal of the PHE.

The results obtained with the activated carbon AC2 showed lower efficiency in the removal of the PHE, where there was slower elimination when compared with the AC1 (Table 4). However, the results showed a degradation rate higher than 90% in the two AC used. The difference between the efficiency of AOP using different activated carbons is justified by the properties of AC (on the surface areas and in concentrations of acidic or basic group present on the surface of the AC) which played a significant role in the degree of improvement. [34]. It is observed that the best (AC2) has a greater amount of basic functions on the surface, which could favor the interactions between the pollutant molecule and the hydroxyl radicals formed, generating a higher elimination rate. AC1 has a greater total of oxygenated groups of larger acidic surfaces, but with AC2, they have 48% fewer oxygenated groups on the surface than AC1, which results in disadvantages for hydroxyl radical generation. Some authors have also obtained similar results using AOP/AC where a greater amount of both acid functions [13,38], and basic functions [39] can increase AC interaction with the oxidizing agent thus increasing the generation of hydroxyl radicals $HO^{\bullet}$. [40,13] Other studies which coupled

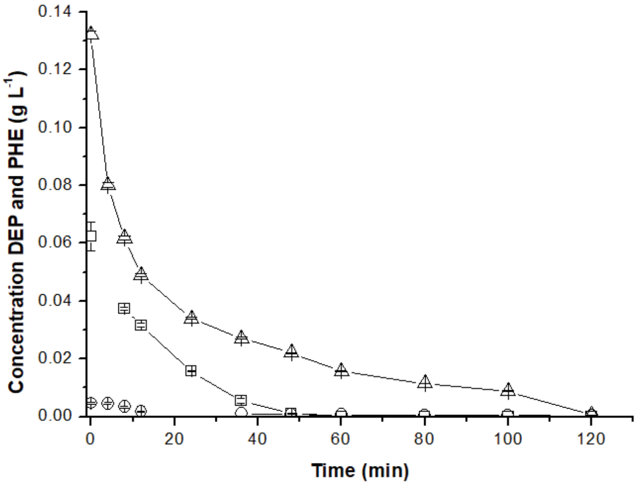

Fig. 3. Kinetics of PHE and DEP degradation during coupling AC/UV-C/H_2O_2: AC1/UV-C/H_2O_2 – multicomponent DEP: (□) and PHE: (○); AC2/UV-C/H_2O_2 – only PHE (Δ), all experiments in: 20 mmol L^{-1}, pH 7.0 and 30°C.

Table 3
Responses of advanced oxidation processes coupling AC (*A*) of the elimination rate (*Y*) of DEP and PHE by AOP+AC

	UV-C/H_2O_2/AC					
AOP + AC (*A*) Kinetics	[H_2O_2] (mol L^{-1})	pH	Temperature (°C)	Y_1 (%) DEP – CA1	Y_2 (%) PHE – CA1	Y_3 (%) PHE – CA2
*K*1	20	7.0	30	95.82	87.54	92.76
*K*2	20	7.0	30	98.41	87.09	93.32
*K*3	20	7.0	30	96.90	97.30	96.41

Table 4
Kinetic constants for the degradation of multi-components in the complex matrices AOP (UV-C/H_2O_2) and (UV-C/H_2O_2/AC1) coupling

Matrices	Treatment	k (min^{-1})	R^2
Tap water (DEP)	UV-C/H_2O_2	0.0673	0.9659
	UV-C/H_2O_2/AC1	0.1289	0.9539
	AC1	0.0089	0.8821
Multicomponent synthetic effluent (DEP)	UV-C/H_2O_2	0.0413	0.9070
	UV-C/H_2O_2/AC1	0.0537	0.9719
	AC1	0.0053	0.8638
Multicomponent synthetic effluent (PHE)	UV-C/H_2O_2	0.0765	0.9532
	UV-C/H_2O_2/AC1	0.0919	0.9424
	AC1	0.0055	0.8638

activated carbon to advanced oxidative processes also concluded that AC presented an attractive option for increasing elimination efficiency, when compared to separate processes, as was obtained in the present study [37,41,42].

3.5. Influence of the matrix when used in different processes: AC, UV-C/H_2O_2 e UV-C/H_2O_2/AC

Fig. 4 shows the kinetic curves of the three treatments studied to eliminate the DEP and PHE (adsorption, UV-C/H_2O_2 and UV-C/H_2O_2/AC) micropollutants in DEP contaminated tap water and in the multi-component synthetic effluent (DEP and PHE) at 30°C and pH 7.0. The modeling of degradation kinetics (described by the simple pseudo-first model) with the kinetic constants of the different oxidative treatments used are presented in Table 4.

The results of the kinetic curves show that the AC adsorption process retards the elimination of the studied micropollutants when compared to the other processes UV-C/H_2O_2 and UV-C/H_2O_2/AC, but it can be a positive material in hydroxyl radical generation as explained in the previous items. It is also observed that there is a competition between the DEP and PHE molecules when together in the adsorption process, with the best efficiency achieved when using DEP separately. These results were also observed by Cagnon et al. [22].

The kinetic degradation constants of the micropollutant in the two matrices by AOP (UV-C/H_2O_2) and coupling (UV-C/H_2O_2/AC1) in tap water effluent with DEP were all higher (DEP) (0.0673 and 0.1289 min^{-1}) when compared to synthetic multi-component laboratory effluent (DEP). The results also allowed us to conclude that the degradation rate of PHE is always higher than that of DEP and that in the presence of interfering materials, or other compounds, the coupling shows a reduction in the DEP elimination rate. These results are also due to the synergistic effect of adsorption with AOP, where AC will not react only as an adsorbent, but results in a combination of different effects in homogeneous (in liquid) and heterogeneous (in CA surface) phases.

Experiments with more complex matrices contaminated with phthalates have shown that the presence of natural radical scavengers and competitive reactions with other products leads to a significant decrease in phthalate degradation kinetic constants ranging from 0.262 min^{-1} (tap water) to 0.148 min^{-1} (municipal wastewater discharge). However, in all experimental conditions and with all matrices used, coupling with AC was much more efficient in removing phthalates than conventional methods [43].

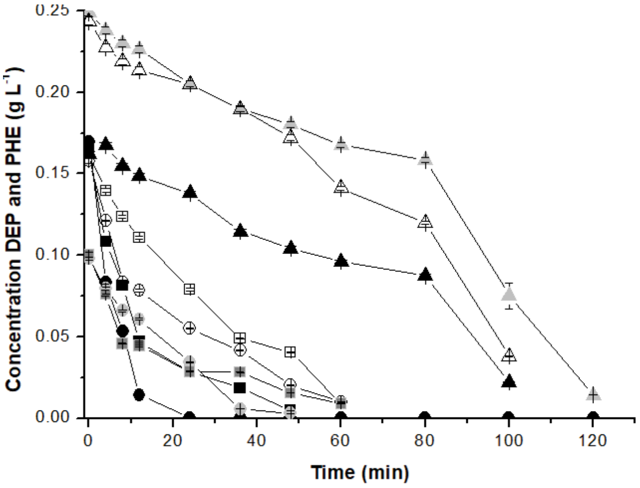

Fig. 4. Kinetics of micropollutants DEP and PHE in complex matrices: adsorption of AC1 in tap water only DEP (▲), multicomponent DEP (Δ) and PHE (▲); UV-C/H_2O_2: tap water with only DEP (■) and multicomponent DEP (□) and PHE (■); UV-C/H_2O_2/AC in tap water only DEP (●), multicomponent DEP (○) and PHE (●), all experiments in: 20 mol L^{-1}, pH 7.0 and 30°C.

According to the studies carried out by Faria et al. [44] and Oliveira et al. [45], this is due to the interactions between the basic functions present in the AC which initiate and promote radical species. The results obtained in these studies also confirmed that the textural properties influenced the coupling efficiency: the AC with a superior external and microporous surface favored the interaction between the micropollutants and the oxidative species.

The authors, Medellin-Castillo et al. [34] and Oliveira et al. [43], also obtained similar results using different effluents with AOP and concluded that inorganic and organic compounds in natural waters (surface waters and wastewater) compete with the pollutant molecules to react with radical species. However, the comparison of the results obtained with deionized water and natural matrices showed that the contribution of the heterogeneous phase is slightly lower in natural matrices, due to the higher pollution load. This finding can be attributed to the presence of radical scavengers and other compounds, leading to a slight decrease in the efficiency of the treatment process.

4. Conclusion

The different treatment methods studied for the elimination of the PHE and DEP pollutants had different but satisfactory results. AC adsorption process retards the elimination of the studied micropollutants when compared to the other UV-C/H_2O_2 and UV-C/H_2O_2/AC processes, but it can be a good material for hydroxyl radical generation efficiency in these treatment processes when taken together. The results obtained revealed that there was a difference in the removal rate for the same contaminant in different media (aqueous solution or tap water) and the difference in the rate of removal of the same contaminant in single and multi-component: PHE degradation kinetics were faster than the DEP pollutant using the UV-C/H_2O_2/AC coupling. The kinetic degradation constants of the micropollutant in the two matrices by AOP (UV-C/H_2O_2) and coupling (UV-C/H_2O_2/AC1) in tap water effluent with DEP were all higher (DEP) (0.0673 and 0.1289 min^{-1}) when compared to synthetic multi-component laboratory effluent (DEP).

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