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Removal of a mix of endocrine disrupters from different natural matrices by ozone/activated carbon coupling process

Tatianne Ferreira de Oliveira[a], Benoît Cagnon[b], Olivier Chedeville[b,*], Henri Fauduet[a]

[a]*ICOA, CNRS-Université, Rue d'Issoudun, BP 16729, 45067 Orléans, France*
[b]*CRMD, CNRS-Université, 1B, Rue de la Ferollerie, 45071 Orléans, France*
Tel. + 33 02 38 41 72 64; Fax: + 33 2 38 49 44 25; email: olivier.chedeville@univ-orleans.fr

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ABSTRACT

Ozone (O_3)/activated carbon (AC) coupling was studied for the removal of phthalates. These compounds, intensively used as additives (particularly as plasticizers), are suspected to be endocrine disrupters and carcinogenic compounds. The aim of this work was to study the removal of a mix of different phthalates (dimethylphthalate [DMP], diethylphthalate and diethylhexylphthalate) present in different matrices (deionised water, tap water, surface water and municipal wastewater treatment plant [WWTP] outflow) by O_3/AC coupling. Two different ACs (basic and acid) were used to study the influence of the material on the coupling process. Results were compared to those obtained with both ozonation and adsorption processes. Degradation kinetics was modelled by a global pseudo-first-order kinetic model based on the sum of all the effects occurring during the treatment process. The results obtained with deionised water show that the degradation kinetics strongly depends on the pH value. Experiments performed with more complex matrices doped with phthalates show that the presence of natural radical scavengers and competitive reactions with other products lead to a significant decrease in the phthalate degradation kinetic constants, which vary for DMP from $0.262\,\text{min}^{-1}$ (tap water) to $0.148\,\text{min}^{-1}$ (municipal WWTP outflow). Nevertheless, in all experimental conditions, and with all the matrices used, O_3/AC coupling was much more efficient at removing phthalates than conventional methods.

Keywords: Ozone/activated carbon coupling; Phthalates; Wastewater treatment; Natural matrices

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1. Introduction

Ozone (O_3)/activated carbon (AC) coupling is a wastewater treatment process based on different effects: direct or indirect oxidation by ozone in the bulk liquid, adsorption on AC and direct or indirect oxidation of adsorbed compounds [1]. Besides, interaction between O_3 and AC surface groups, both acid and basic, leads to radical generation [2,3]. In recent studies, it was proven that in the coupling, AC acts mainly as a radical initiator and promoter and as a reaction site. The great potential of this process to remove some micropollutants has been shown [2,4–6]. Among micropollutants, phthalates can be found in significant concentrations in surface water and groundwater [7,8]. These compounds are present in a very large number of industrial applications and are particularly used as additives in plastics to increase the flexibility of the material. These additives are generally

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*Corresponding author.

not bonded to the material and can easily migrate to the environment. These compounds can be found in surface waters at very different concentrations, depending on many factors such as geographical location or season [9,10]. Moreover, significant concentrations of phthalates have been detected in municipal wastewater treatment plant (WWTP) outflows, showing the inefficiency of classical methods in removing these micropollutants from water [11]. Phthalates are often mentioned as suspected endocrine disrupters and carcinogenic compounds [12–14]. Due to their potential risks for human health and the environment, diethylhexylphthalate (DEHP) has been listed as a priority substance in the European Union Water Framework Directive (2000/60/EC) and a 30% reduction in phthalates discharged in industrial wastewaters has to be achieved by 2021. They have been also included in the list of priority pollutants established by the US Environmental Protection Agency [15]. Thus, it is necessary to study and develop appropriate treatment methods that can be integrated into water and wastewater treatment to prevent the release of these compounds into the environment [16]. O_3/AC coupling is a highly promising solution to attain this objective. In previous studies concerning diethylphthalate (DEP) removal, Ferreira et al. showed that this method permits the fast and complete removal of the target pollutants, a significant decrease in toxicity and an advanced mineralisation [1,4,16]. However, these studies, and others reported in the literature, were performed in deionised water, generally doped with only one target compound. To validate the treatment process, it is necessary to study its efficiency with several pollutants in more complex natural matrices.

The aim of this work was to study the removal of three different phthalates (dimethylphthalate [DMP], DEP and DEHP) present in different matrices (deionised water, tap water, surface water and municipal WWTP outflow) by O_3/AC coupling. Results were compared to those obtained with conventional methods (ozonation and adsorption). The degradation kinetics of pollutants was modelled by a global pseudo-first-order model based on the sum of the effects occurring during the treatment process. Moreover, the influence of pH on phthalate removal was studied by performing experiments at pH values ranging from 2.5 to 7.2 and with two different ACs.

2. Material and methods

2.1. Chemical reagents and ACs

DMP, DEP and DEHP (>99.5%) and high pressure liquid chromatography (HPLC) acetonitrile (>99.9%) were supplied by Sigma-Aldrich. The commercial ACs used (L27 and X17) were provided by Pica. Their porosity was characterised by conventional nitrogen adsorption isotherm at 77 K using a Micromeritics ASAP 2020 [18]. The chemical properties of the materials were also determined according to the Boehm method [19]. The point of zero charge (pH_{PZC}) was obtained by the method proposed by Lopes-Ramon [20]. The ACs were washed and dried overnight at 100°C before each analysis and experiment to eliminate any residual acidity or basicity due to the activation treatment.

The municipal WWTP outflow investigated was collected at the WWTP of L'Ile Arrault, which treats the wastewaters coming from Orléans (France). This WWTP has a treatment capacity of 100,000 population equivalent. The surface water was collected from the Loire River in Orléans (France).

2.2. Ozone reactor and ozonation experiments

For the phthalate degradation experiments performed in deionised water, the reactor was filled with 750 mL of phosphate buffered solution containing the three phthalates. The buffer solutions were prepared with a mixture of different amounts of H_3PO_4 (purity up to 85%, obtained from Sigma-Aldrich), KH_2PO_4 (purity up to 99%, obtained from Fluka) and Na_2HPO_4 (purity up to 99%, obtained from Fluka) at pH 2.5, 5.6 or 7.2. For the experiments performed in natural matrices, no buffer was introduced. The pH value was measured with a pH-metre at the beginning and at the end of the experiments. It was observed that no significant modification of the pH value occurs during the experiment. All the experiments were performed with a mix of phthalates. The initial concentrations were $0.08\,\mathrm{g\,L^{-1}}$ for both DMP and DEP and $0.003\,\mathrm{g\,L^{-1}}$ for DEHP, in accordance with their respective solubilities. The reactor was thermostated at 20°C by a cryothermostat and mechanically stirred. For the O_3/AC and the adsorption experiments, a weight of 2.0 g of AC was added. O_3, produced from pure oxygen by a BMT 803N O_3 generator, was introduced through a porous diffuser at the bottom of the reactor. The gas flow rate was $0.040\,\mathrm{Nm^3\,h^{-1}}$ and the O_3 concentration in the inlet gas was fixed at $50\,\mathrm{g\,Nm^{-3}}$ (measured by a BMT 964 ozone analyser). The unconverted ozone in the outlet gas was removed by an ozone catalytic destructor (Wedecco). During the experiments, 2 mL of samples were collected at suitable intervals of time. A volume of 100 μL of sulphite solution (0.1 M) was introduced in each sample to remove dissolved O_3 and filtration through a 0.45 μm membrane filter was performed to remove AC from the solution.

2.3. Analysis

2.3.1. Determination of the phthalate concentration

The DMP and DEP concentrations in samples were quantified by HPLC (Kontron 325 system) equipped with a Hypersil C18 column (250 mm long × 4.6 mm i.d, Thermo Scientific) and a Spectra Physics 200 UV detector (228 nm). The mobile phase was a mixture of acetronitrile/water (70:30, v:v) delivered at a flow rate of 1 mL min^{-1}. The detection limit of each phthalate was 1 mg L^{-1} and, in these experimental conditions, the retention times of DMP and DEP were, respectively, 3.9 and 5.0 min.

The DEHP concentration was monitored by HPLC (Nucleodur C18 column) equipped with a mass spectrometer as detector. The mobile phase was a mixture of acetronitrile/water (93:7, v:v) delivered at a flow rate of 0.3 mL min^{-1}. Mass-spectrometric detection was performed on a 1,100 MSD Agilent equipped with electrospray ionisation. The molecular ion $[M+H]^+$ corresponding to DEHP was characterised by the m/z ratio = 391. The detection limit of DEHP was 0.01 μg L^{-1}.

2.3.2. Matrices

The main characteristics (inorganic carbon [IC] concentration, chemical oxygen demand [COD] and pH) of the different matrices used were determined. The IC was estimated with a total organic carbon analyzer (Shimadzu). The COD was determined by a colorimetric method recommended by the Standard Method for Examination of Water and Wastewater [21,22]. To determine the COD, dichromate reagent was used as chemical oxidant. A volume of 2.0 mL of the sample solution was added to a vial, and then refluxed during 2 h at 148˚C. The value of COD was then measured by UV spectrometry. The initial phthalates concentration in each matrix was determined before use. A sample was collected, filtered through a membrane filter (0.45 μm) and analysed by HPLC. It appeared that the matrices used were free of the phthalates used in this study.

2.4. Kinetic model

Phthalate degradation kinetics by O_3/AC coupling was modelled by a global pseudo-first-order model, presented in a previous study [1], based on the sum of the effects occurring during the treatment process. It was assumed that the dissolved ozone and the hydroxyl radical concentrations remained constant throughout the experiments [23]. This assumption was verified by measuring the dissolved O_3 concentration during the experiments by the carmine indigo method. It was also assumed that no O_3 diffusion limitation occurs. Based on these assumptions, the phthalate degradation kinetics can be written as in Eq. (1):

$$-\frac{d[P]}{dt} = k_{\text{global}} \times [P] \tag{1}$$

where $[P]$ is the phthalate concentration within the mix (mol L^{-1}), t is the time (s) and k_{global} is the kinetic constant of the phthalate degradation during the O_3/AC process (s^{-1}). This constant can be obtained from the slope of $\ln[P] = f(t)$ obtained during removal of the phthalates by O_3/AC coupling. According to the previous assumptions, k_{global} is the sum of the homogeneous and heterogeneous contributions:

$$k_{\text{global}} = k_{\text{homo}} + k_{\text{hetero}} \tag{2}$$

where k_{homo} is the kinetic constant of the reactions occurring in the bulk liquid (s^{-1}) and k_{hetero} is the kinetic constant of the reactions occurring with AC (s^{-1}). k_{homo} can be obtained from the experiments performed with O_3 only. k_{hetero} is deducted from the values of k_{global} and k_{homo}.

According to the previous equations, the kinetic contribution of heterogeneous reactions to phthalate degradation, δ^{hetero} (%), can be obtained from Eq. (3):

$$\delta^{\text{hetero}} = \frac{k_{\text{global}} - k_{\text{homo}}}{k_{\text{global}}} \times 100 \tag{3}$$

3. Results and discussion

3.1. AC properties

The characterisation of the ACs is presented in Table 1 and was reported in previous work [1]. L27 has an acid surface (1.57 meq g^{-1} of total acid functions) and X17 has a basic surface (0.85 meq g^{-1}of basic functions). The results obtained by the Boehm method were in agreement with the pH_{pzc} values. The

Table 1
Chemical and porous properties of the ACs L27 and X17

AC	L27	X17
S_{tot}, m^2 g^{-1}	1,060	514
S_{ext}, m^2 g^{-1}	444	130
S_{micro}, m^2 g^{-1}	616	384
W_0, cm^3 g^{-1}	0.57	0.29
L_o, Å	18.5	15.1
Acidity, meq g^{-1}	1.57	0.20
Basicity, meq g^{-1}	0.18	0.85
pH_{pzc}	3.0	8.2

Table 2
Characterisation of the different matrices

	COD (mg L^{-1})	IC (mg L^{-1})	pH
Tap water	32	<5.0	6.9
Loire River	<26	21.63	7.6
WWTP outflow	42	49.65	7.2

two ACs also have different porous properties. The N_2 adsorption–desorption isotherms (not shown here) showed that L27 has the most fully developed porous properties: the specific external surface (S_{ext}) and total surface (S_{tot}) are, respectively, 444 and 1,060 m^2 g^{-1} for L27, and 130 and 514 m^2 g^{-1} for X17. Moreover, L27 presents a microporous volume two times higher than that of X17.

3.2. Matrix properties

The characterisation of the different matrices used is presented in Table 2. The results obtained show that

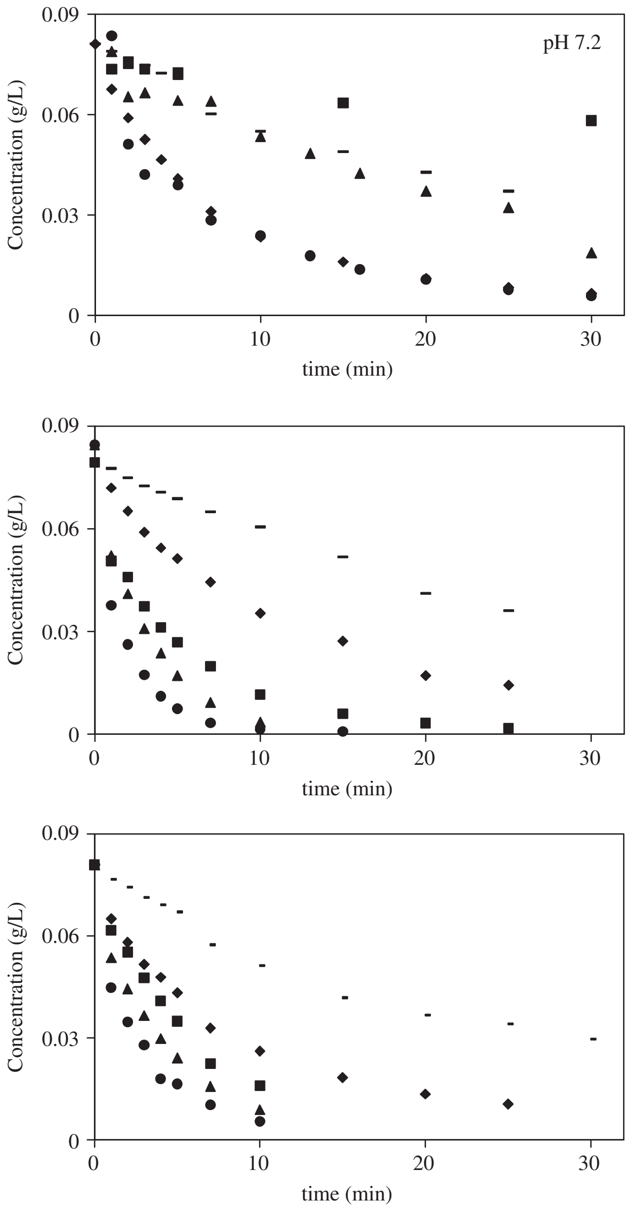

Fig. 1. DMP degradation in deionised water by O_3/L27 coupling (●), O_3/X17 coupling (▲), ozonation (■), adsorption on L27 (◆) and adsorption on X17 (–) at different pH values.

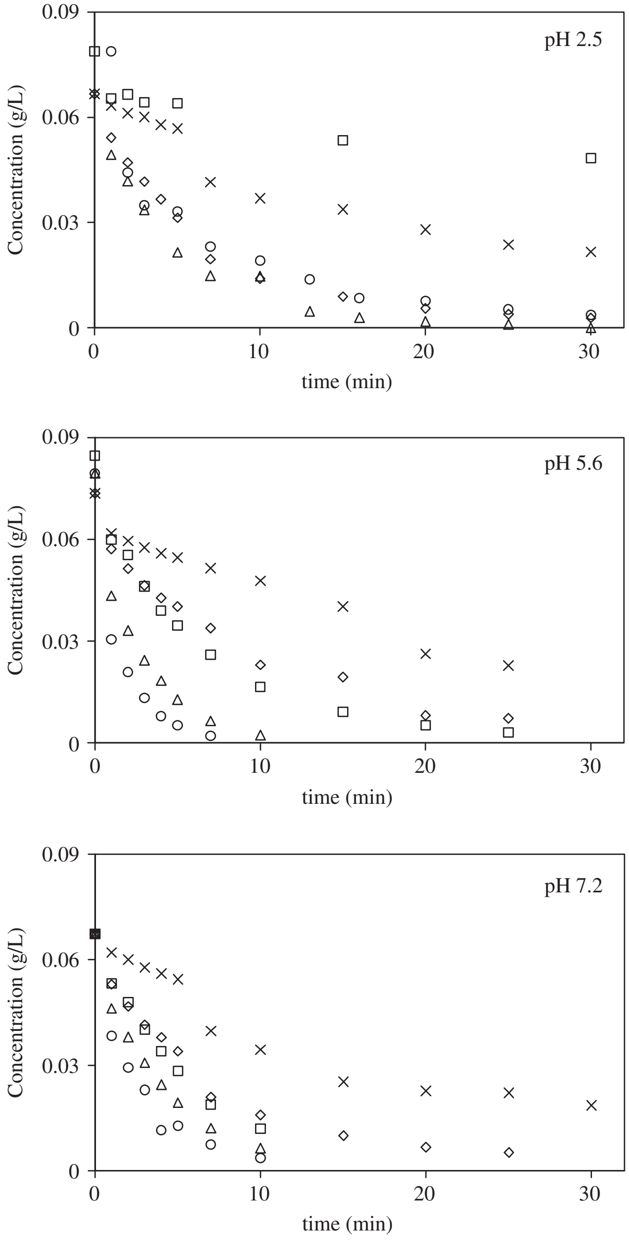

Fig. 2. DEP degradation in deionised water by O_3/L27 coupling (○), O_3/X17 coupling (Δ), ozonation (□), adsorption on L27 (◇) and adsorption on X17 (×) at different pH values.

the WWTP outflow had the highest pollution load (COD = 42 mg L^{-1}). Furthermore, the values of IC obtained were 49.65 mg L^{-1} for the WWTP outflow, against 21.63 mg L^{-1} for the Loire River and less than 5.0 mg L^{-1} for tap water. This IC can be attributed to carbonate and hydrogenocarbonate ions present in water. The values of pH vary from 6.9 (tap water) to 7.6 (Loire River).

3.3. Phthalate degradation kinetics

3.3.1. Influence of pH on phthalate degradation

Phthalate degradation was performed at different pH values (2.5, 5.6 and 7.2) in deionised water. The evolution of DMP and DEP concentration during the treatment by O_3/AC coupling, ozonation and adsorption is shown in Figs. 1 and 2. The modelling of the degradation kinetics of each phthalate within the mix is presented on Table 3. DMP and DEP degradation kinetics were correctly described by the pseudo-first-order model used. From the first sample collected, the DEHP concentration (not shown here) was below the quantification limit, except during the adsorption process, where significant DEHP concentrations were observed. It was not possible to model the DEHP degradation kinetics because of the very low initial concentration of this compound (due to its low solubility in water).

Results show that DMP and DEP can be completely removed by O_3/AC coupling and that this process is much more efficient than conventional methods in all the experimental conditions used. For example, at pH = 2.5, k_{DEP} varied from 0.010 min^{-1} (ozonation) to 0.173 min^{-1} (O_3/L27 coupling). Degradation kinetics depends strongly on the pH value for both O_3/AC coupling and the ozonation process. This phenomenon is due to the enhancement of hydroxyl radical generation by interaction between O_3 and hydroxyl ions when pH rises. Moreover, for O_3/AC coupling, some studies report that radical reactions can be initiated and promoted by interaction between O_3 and deprotonated surface oxygen groups [2]. This could explain why, for O_3/L27 coupling (pH_{PZC} = 3.0 for L27), the degradation kinetic constants were higher when the pH increased: for example, k_{DMP} rose from 0.173 to 0.501 min^{-1} when the pH value increased from 2.5 to 7.2.

Comparison of the results obtained with the ACs show that L27 was more efficient (when used in the coupling and as adsorbent) than X17. For example, k_{DMP} varied from 0.087 to 0.296 min^{-1} with O_3/X17 and from 0.157 to 0.397 min^{-1} with O_3/L27. According to several studies, X17, which presents a high amount of basic functions, should be the most efficient since it has been shown that interaction between O_3 and basic functions initiates and promotes radical species [1,5]. The results obtained in this study confirm that the textural properties also influence the coupling efficiency: L27 has a higher external and microporous surface than X17, which could favour the interaction between the micropollutants and the oxidative species and hence favour the reaction site role of this AC.

During the treatment by O_3/AC coupling, the evolution of DEP and DMP concentrations was very similar and the kinetic constants obtained were very close. Moreover, DEHP was rapidly and completely

Table 3
Degradation kinetics of DMP and DEP present in deionised water

pH	Method	k_{DMP} (min^{-1})	R^2	k_{DEP} (min^{-1})	R^2
2.5	Ozonation	0.010	0.990	0.013	0.980
	Adsorption X17	0.039	0.956	0.031	0.984
	Adsorption L27	0.059	0.908	0.075	0.902
	O_3/X17	0.087	0.986	0.103	0.989
	O_3/L27	0.157	0.982	0.173	0.978
5.6	Ozonation	0.130	0.992	0.146	0.989
	Adsorption X17	0.024	0.984	0.033	0.982
	Adsorption L27	0.049	0.952	0.134	0.962
	O_3/X17	0.202	0.996	0.238	0.986
	O_3/L27	0.235	0.970	0.266	0.950
7.2	Ozonation	0.165	0.988	0.182	0.988
	Adsorption X17	0.029	0.974	0.104	0.969
	Adsorption L27	0.079	0.974	0.104	0.969
	O_3/X17	0.296	0.998	0.341	0.995
	O_3/L27	0.397	0.981	0.501	0.986

Table 4
Influence of the pH on the kinetic contribution of heterogeneous reactions to phthalate removal, δ^{hetero} (%)

	δ^{hetero} (%) DMP		δ^{hetero} (%) DEP	
	X17	L27	X17	L27
2.5	88.5	93.6	87.4	92.5
5.6	35.6	44.7	38.7	35.4
7.2	44.3	58.4	46.6	46.6

removed within the first few minutes of treatment. This means that this process provides an efficient treatment for the different phthalates and could be successfully used to remove these micropollutants. Our previous results established that the pollutant degradation mainly occurs by radical reactions [1]. The hydroxyl radicals generated are highly reactive species which are able to remove different pollutants with less selectivity than O_3.

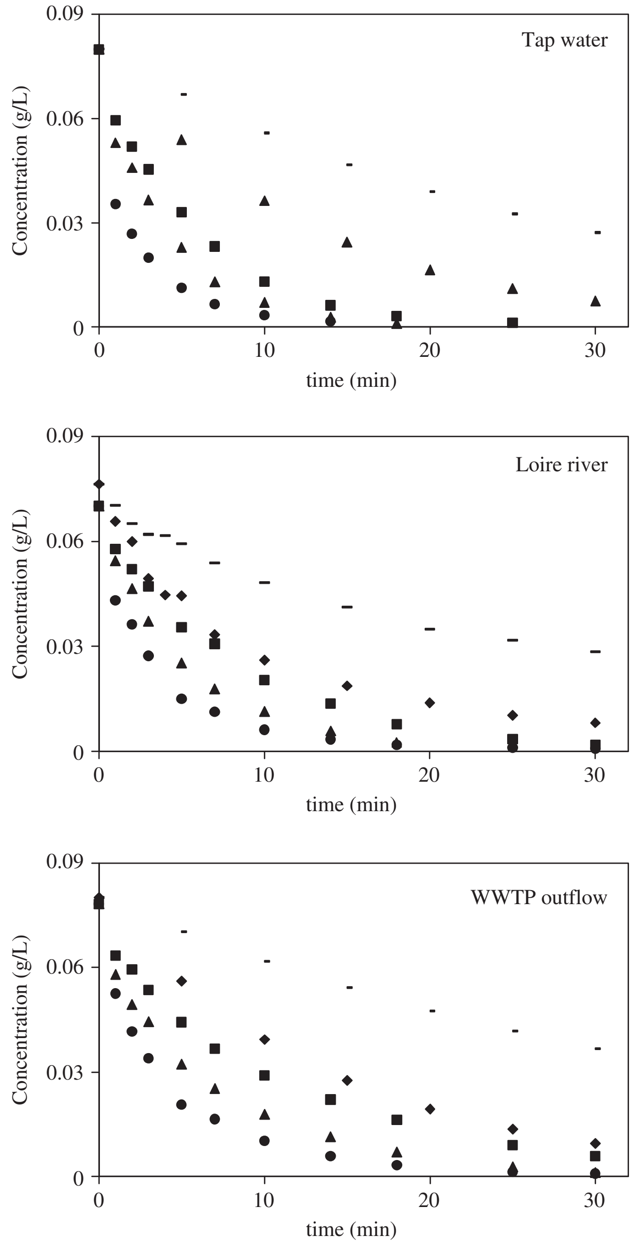

Fig. 3. Degradation of DMP present in different matrices by O_3/L27 coupling (●), O_3/X17 coupling (▲), ozonation (■), adsorption on L27 (◆) and adsorption on X17 (–).

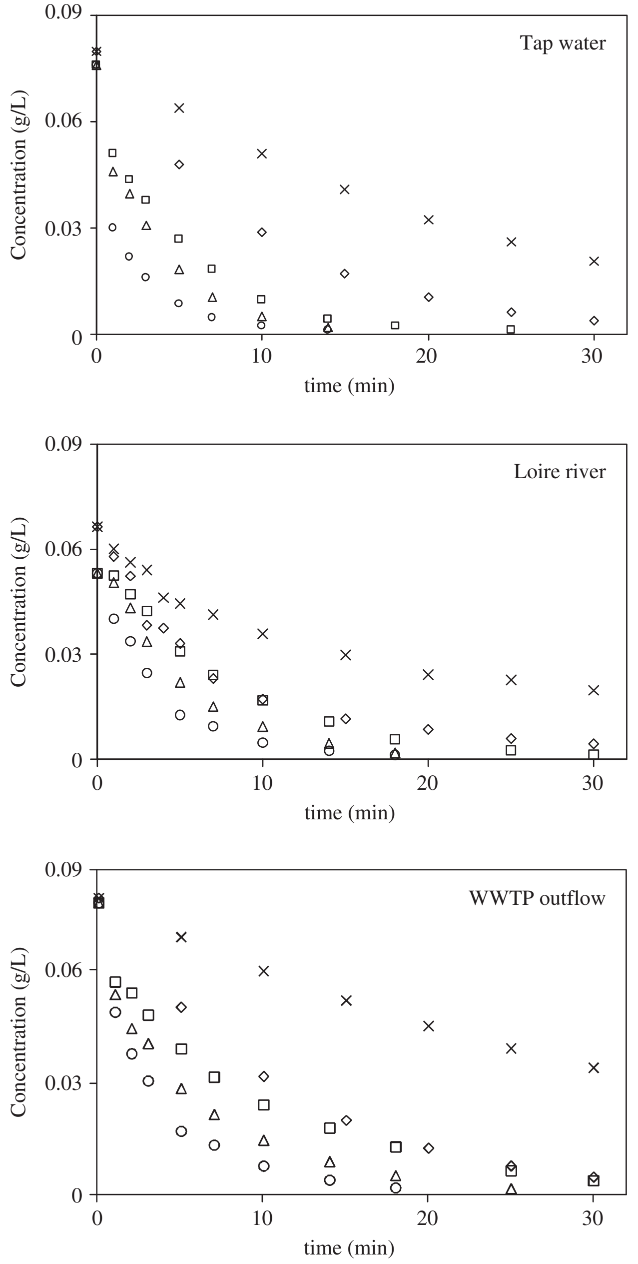

Fig. 4. Degradation of DEP present in different matrices by O_3/L27 coupling (○), O_3/X17 coupling (Δ), ozonation (□), adsorption on L27 (◇) and adsorption on X17 (×).

The determination of the kinetic contribution of heterogeneous reactions to phthalates, presented in Table 4, confirms that the presence of AC significantly enhances the micropollutant removal efficiency comparing to the single ozonation process. Moreover, it appeared that this influence is highest at low pH ($\delta^{\text{hetero}} = 93.6\%$ for DMP and $\delta^{\text{hetero}} = 92.5\%$ for DEP at pH = 2.5 with AC L27). In these acidic conditions, the ozonation reaction in bulk liquid is slow and the O_3/AC coupling makes it possible to maintain high degradation efficiency. Thus, O_3/AC coupling appeared to be an efficient process to remove these micropollutants, especially in operational conditions which disfavour the ozonation process.

3.3.2. *Influence of the matrix*

Phthalate removal was studied by introducing DEP, DMP and DEHP into different matrices: tap water, surface water (Loire River) and WWTP outflow. During all the experiments, the evolution of the pH was measured during the treatment process. No significant evolution of this parameter was observed.

Figs. 3 and 4 show the evolution of phthalate concentrations during the treatment by O_3/AC coupling, ozonation and adsorption. It can be seen that, with all the matrices used, the fastest phthalate degradation was obtained with O_3/AC coupling, while phthalate removal appeared to be slow with the adsorption process. Moreover, the evolution of DEP and DMP was very similar throughout the treatment.

For both ozonation and O_3/AC coupling, the degradation kinetics were correctly modelled by the global pseudo-first-order model (Table 5). For the adsorption process, the modelling does not perfectly fit the experimental points: in this study, in order to simplify the equations, it was assumed that adsorption could be modelled by a chemical pseudo-first-order model, but, in a previous study, it was shown that a pseudo-second-order adsorption model is more appropriate to describe this kinetic [17]. Nevertheless, with this simplified model, the R^2 values remain high and the result was usable. The DEP degradation kinetics at pH = 7.2 was previously estimated in deionised water with O_3 ($k_{\text{DEP}} = 0.613\,\text{min}^{-1}$), O_3/X17 coupling ($k_{\text{DEP}} = 0.721\,\text{min}^{-1}$) and O_3/L27 coupling ($k_{\text{DEP}} = 0.866\,\text{min}^{-1}$) [1]. With the matrix used, a significant decrease in the degradation kinetics was observed. For example, with O_3/L27 coupling, k_{DEP} varied from $0.148\,\text{min}^{-1}$ (WWTP outflow) to $0.262\,\text{min}^{-1}$ (tap water). Similar results were obtained for DMP degradation. This phenomenon could be due to the presence of other organic compounds in the solution, leading to competitive reactions. Experiments performed in a previous study with *t*-BuOH as radical scavenger showed that O_3/AC coupling acts mainly by radical reactions: on the grounds of their high reactivity, the hydroxyl radicals generated are not selective species [1]. The decrease in degradation kinetics can also be due to the presence of radical scavengers in the effluent: with O_3/AC coupling, the phthalate degradation kinetics decreases when IC rises. This IC corresponds to the presence of carbonate and hydrogenocarbonate ions, which are well-known natural radical scavengers. Nevertheless, even with the most loaded matrix, O_3/AC coupling gave the best results.

Table 5
Degradation kinetics of DMP and DEP introduced into different matrices

Matrix	Method	k_{DMP} (min^{-1})	R^2	k_{DEP} (min^{-1})	R^2
Tap water	Ozonation	0.177	0.998	0.194	0.997
	Adsorption X17	0.036	0.988	0.045	0.976
	Adsorption L27	0.079	0.958	0.102	0.954
	O_3/X17	0.235	0.998	0.256	0.997
	O_3/L27	0.262	0.970	0.292	0.970
Loire river	Ozonation	0.118	0.999	0.126	0.998
	Adsorption X17	0.023	0.979	0.029	0.983
	Adsorption L27	0.056	0.940	0.090	0.968
	O_3/X17	0.171	0.997	0.187	0.997
	O_3/L27	0.190	0.978	0.208	0.990
WWTP outflow	Ozonation	0.083	0.995	0.089	0.998
	Adsorption X17	0.026	0.973	0.028	0.963
	Adsorption L27	0.071	0.976	0.091	0.953
	O_3/X17	0.131	0.996	0.133	0.998
	O_3/L27	0.148	0.990	0.179	0.991

Table 6
Influence of the matrix on the kinetic contribution of heterogeneous reactions to phthalate removal, δ^{hetero} (%)

	δ^{hetero} (%) DMP		δ^{hetero} (%) DEP	
	X17	L27	X17	L27
Tap water	24.7	32.7	24.2	33.6
Loire river	31.0	37.9	32.6	39.4
WWTP outflow	36.6	43.9	33.1	50.3

The determination of δ^{hetero} from the phthalate degradation kinetic constant for both DMP and DEP, presented in Table 6, confirms that the O_3/AC coupling presents a great potential in operational conditions which disfavour the classical processes. For example, for the O_3/L27 process the kinetic contribution of heterogeneous reactions to DMP degradation was 43.9% with the WWTP outflow (presenting the highest pollution load and IC concentration), while it was only 32.7% with the tap water. The results presented in Table 6 also show that δ^{hetero} was significantly higher with L27 than with X17, confirming that textural properties influence the process efficiency: a higher external and microporous surface can enhance the reaction site role of the AC. Nevertheless, the comparison of the results obtained with deionised water and natural matrices (Tables 4 and 6) show that δ^{hetero} is slightly lower with the latter. This can be attributed to the presence of radical scavengers and other compounds, leading to a slight decrease in the treatment process efficiency.

4. Conclusion

The aim of this work was to study the efficiency of O_3/AC coupling to remove phthalates from different matrices. The great potential of the coupling to remove a mix of these micropollutants has been demonstrated. The main results obtained in this study were:

- This process can be successfully applied to the treatment of different phthalates without any variation in performance: in this study, the evolution of DEP and DMP throughout the O_3/AC treatment process was very similar and DEHP was rapidly removed.
- The O_3/AC coupling was proven to be more efficient than conventional processes in every experimental conditions used.
- The O_3/AC coupling permits to ensure a very efficient phthalate removal, even with complex matrices. Nevertheless, compared to the results obtained with deionised water, a significant decrease in the kinetics constant was observed. This could be due to competitive reactions with other compounds present in the water and to the presence of radical scavengers (since O_3/AC coupling mainly acts by radical reactions).

This coupling therefore appears to be an efficient way to remove phthalates, especially in operating conditions limiting the efficiency of the conventional process. Nevertheless, before using this process to remove phthalates present in real industrial wastewater, it would be necessary to perform preliminary experiments to ensure the efficiency of this process with the matrices to be treated.

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