Characterization and fate of EfOM during ozonation applied for effective abatement of recalcitrant micropollutants

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ABSTRACT

Alterations occurring in the effluent organic matter (EfOM) during ozonation could be detrimental depending on the final application of the treated effluent. In this work, the fate of EfOM in different ozonized wastewaters was assessed through the monitoring of general water quality parameters and organic fractions determined through size-exclusion chromatography combined with organic carbon detection (SEC-OCD) analysis. These different components of EfOM were distinguished based on relative molecular weights and assigned to fractions named as biopolymers, humic substances, building blocks and low molecular weight neutrals and acids. The significant abatement (60-90%) of an ozone-refractory micropollutant (MP) was employed as reference to simulate potential scenarios in which also the presence of these species is wanted to be attenuated. Ultraviolet absorbance at 254 nm (UVA_{254}) and chemical oxygen demand (COD) reductions ranged from 40 to 80% and from 10 to 45%, respectively, for ozone doses between 0.6 and 1.0 mM, depending on the organic matter content (both dissolved and suspended) and alkalinity of the effluents. Dissolved organic carbon (DOC) analysis showed 21-27% reductions in Membrane bioreactor (MBR) effluents, whereas for conventional activated sludge (CAS) samples this value increased (6-35%) during the oxidative treatment. This was attributed to the continuous solubilization of humic substances, according to SEC-OCD results. Moreover, accumulation of lower molecular weight fractions such as building blocks or acids was observed in all the tested effluents, and attributed to the breakdown of largest EfOM fractions, mainly humic substances. Relationships proposed in this work between humic substances evolution, water quality (UVA_{254}) and process parameters (immediate ozone demand (IOD), IOD-normalized hydroxyl radical exposure ($\int[\bullet OH]\mathrm{d}t$/IOD) and transferred ozone dose (TOD)) might be useful for EfOM variations estimations along ozonation.

KEYWORDS

Wastewater ozonation, micropollutants oxidation, EfOM fractions, SEC-OCD, humic substances

1. Introduction

In a time in which water scarcity increasingly constitutes one of the most serious threats for human and environmental safety, enhanced wastewater treatment and reclamation consolidates as the strategy to follow if sustainability regarding this vital resource is wanted to be preserved [1–3]. Advanced treatment of effluents released into freshwater bodies minimizes the negative impacts (*i.e.*, pollution of the receiving aqueous compartments) derived from this practice. On the other hand, reclaimed wastewater can be employed for a variety of non-potable uses, including agricultural and municipal irrigation, environmental applications, recreational activities or industrial processes [3,4]. By means of these practices, significant volumes of freshwater are saved. However, the use of this alternative water source in applications implying further human or animal exposure is limited by the presence –among others– of organic micropollutants (MPs) which, although in general not regulated, pose potential risks for living species [1]. Considering this particular issue, ozonation and activated carbon are nowadays one of the most recognized advanced treatment technologies for enhanced wastewater treatment and reclamation purposes [5–11].

So far, most studies dealing with ozonation of wastewater effluents mainly focus on the fate of ozone-sensitive micropollutants and harmful oxidation byproducts – such as bromate [12–14] – under such operational conditions (*i.e.*, low ozone doses). Higher oxidant doses such as those required for ozone-resistant MPs abatement are in general not considered in full-scale ozonation steps, although several organic compounds typically present in wastewater effluents are recalcitrant to ozone and present toxic properties which should encourage their effective abatement. On their part, changes in effluent organic matter (EfOM) are traditionally set aside or studied, at most, through the variation of general related parameters such as total and dissolved organic carbon (TOC and DOC, respectively), chemical oxygen demand (COD) or ultraviolet absorbance at 254 nm (UVA_{254}) [15–20]. There is still, however, a lack of knowledge regarding the fate of the different organic fractions during municipal wastewater ozonation. Deeper information can be obtained by means of size-exclusion chromatography in combination with organic carbon detection, SEC-OCD [21], which is able to separate and quantify different EfOM fractions according to their relative molecular weights and additional measurements such as UVA_{254} or organic nitrogen content.

There are several publications in literature describing the impact of wastewater effluent ozonation on EfOM fractions [22–31]. However, in some of these works the employed ozone doses were either not properly quantified [22,23] or too high to be considered for practical applications [24]. Moreover, changes in EfOM fractions are often available in a very qualitatively way [25–27], or expressed as variations in the average molecular size but not quantified in terms of organic carbon concentrations [28,29]. In other few works, changes in EfOM fractions were not related to or discussed together with micropollutants oxidation or the reduction of any other general parameters typically monitored in wastewater treatment [30,31]. None of these studies discuss the fate of EfOM for various wastewater sources presenting different water qualities.

EfOM contained in reclaimed wastewater treated by ozonation can cause some technical and environmental problems if further treatments are planned next. For instance, residual organic matter (OM) could contribute to the formation of harmful disinfection by-products in a subsequent disinfection step, or be partly responsible for membrane fouling in a filtration unit [32,33]. Also, EfOM can compete with target pollutants for adsorption sites in activated carbon systems or avoid the separation of these chemicals from the water matrix if these are bound to the organic matter surface [32,33]. Moreover, since prior to be used this water need to be redirected to its final destination, EfOM – especially its lower molecular weight fractions – can be a perfect substrate for bacterial growth in distribution systems, or cause eutrophication in receiving water compartments if the final use is related to surface or groundwater recharge [32].

This work aimed to contribute to the – still – scarce knowledge regarding the variation of EfOM fractions during ozonation of wastewater effluents. Concretely, the objective of the study was to assess changes taking place when ozone doses required for the effective abatement of micropollutants are applied, including the elimination of ozone-resistant species. Thus, a potentially realistic scenario was explored in this study. To do so, ozonation experiments in semi-continuous mode where performed for six different wastewater effluents presenting a wide range of water qualities and spiked with an ozone-resistant organic micropollutant as internal reference. The evolution of distinguishable dissolved EfOM fractions was then followed by means of the SEC-OCD technique, together with variations observed for other parameters typically discussed in practice, such as UVA_{254}, COD and DOC. Finally, some relationships between EfOM changes and some effluent quality and ozonation parameters were discussed.

2. Materials and methods

2.1. Wastewater effluents

Six different wastewater effluents coming from five wastewater treatment plants (WWTPs) in the province of Barcelona (Spain) were employed in this work. All of them treat municipal wastewater. Technical details of WWTPs from which they were collected are gathered in Table 1. All effluents samples were filtered through 25 µm filter paper to remove coarse particles not belonging to the effluent (*e.g.*, dragged from the sample collection system) and avoid technical problems with the equipment used during ozonation experiments (*e.g.*, ozone sensor). All the effluent samples were kept at 4 ºC until they were used.

Table 1. List of wastewater effluent samples used in this work and technical details of WWTPs from which they were collected. (PC: primary clarification; MBR: membrane bioreactor; UF: ultrafiltration membrane; NR: nutrient removal; CAS: conventional activated sludge; IFAS: Integrated fixed-film activated sludge; SC: secondary clarification).

Sample ID	WWTP location	Population equivalent [PE]	Design flow [$m^3\ d^{-1}$]	Type of treatment
M1	Vacarisses	5280	1320	PC + MBR (UF) with NR
M2	Vallvidrera	5500	1100	PC + MBR (UF) with NR
M3	Gavà	192000	32000	PC + MBR (UF) with NR
C1	El Prat	2275000	420000	PC + CAS with NR + SC
C2	Gavà	192000	32000	PC + IFAS with NR + SC
C3	La Llagosta	358333	43000	PC + CAS + SC

2.2. Ozonation experiments

Wastewater ozonation experiments were performed in a 750 mL semi-batch reactor, at a temperature of 20 ºC and without pH adjustment. Ozone was generated by using a 301.19 lab ozonizer (Sander, Germany) and introduced into the reactor through a porous diffuser. A mechanical stirrer was used to provide a proper contact between liquid and gas phases. The gas flow rate and the ozone inlet concentration were maintained at 0.1 L min^{-1} and 0.63 mmol L^{-1}, respectively. The transferred ozone dose (TOD), which represents the ozone consumption, was determined through continuous evaluation of the O_3 mass balance in the gas phase [34]. Inlet and outlet ozone concentrations were measured by two BMT 964 ozone analyzers (BMT Messtechnik, Germany). The residual concentration of ozone in the aqueous phase was monitored by means of a Q45H/64 dissolved O_3 sensor (Analytical Technology, USA).

Each wastewater effluent was spiked with 0.45 µM of the pesticide acetamiprid (ACMP), here employed as reference micropollutant because of its resistance to molecular ozone attack during ozonation, and then ozonized for 30 min under the mentioned operational conditions. Samples were withdrawn at known time intervals and kept at room conditions until complete consumption of dissolved ozone was achieved. Then, analyses for ACMP, typical physicochemical parameters (namely UVA_{254}, DOC and COD) and EfOM fractions were conducted.

Immediate ozone demand (IOD) of each wastewater sample was estimated in this work as the minimum TOD required to detect dissolved ozone in the reaction medium [38]. The initial hydroxyl radical (•OH) consumption rates, which provide information about the amount of •OH available in the reaction medium for micropollutant oxidation [39], were here estimated considering the sum of contributions by dissolved EfOM and alkalinity. For EfOM contribution, a mean rate constant value between dissolved EfOM and •OH of $2.1 \cdot 10^{5}$ (mg C L)$^{-1}$s^{-1} was used according to the work by Lee et al. [10], together with the DOC values determined for each effluent sample (see Table 3). Consumption rate due to alkalinity was calculated according to the known rate constant of bicarbonate ion reaction with •OH ($8.5 \cdot 10^{6}$ M^{-1}s^{-1} [40]) and the IC values determined for each effluent sample (see Table 3). Thus, calculations were performed according to the expression $\bullet OH_{\text{scavenging rate}} = 2.1\cdot10^5\cdot DOC + 8.5\cdot10^6\cdot IC$.

2.3. *Analytical methods*

ACMP concentration was determined through HPLC-UV. Samples were previously filtered through 0.45 µm polytetrafluoroethylene (PTFE) filters. The mobile phase consisted of 70:30 volumetric mixtures of acetonitrile and ultrapure water at pH 3 (achieved by addition of H_3PO_4). Separation was achieved by means of a 25x0.46 cm (5 µm size packing) Sea18 column (Teknokroma, Spain). The flow rate and injection volume were set at 1 mL min^{-1} and 100 µL, respectively. Detection was performed at 254 nm. UV absorbance at 254 nm was measured by means of a DR6000 UV Vis spectrophotometer (Hach, USA) employing a quartz cuvette (path length: 1 cm). TOC, DOC and inorganic carbon (IC) were measured by means of a Shimadzu TOC-VCSN analyzer. COD was determined according to Standard Methods procedure 5220D [36]. Nitrite (NO_2^-) concentration was determined by means of ion-exchange chromatography with UV detection. For DOC, IC, UVA_{254} and nitrite analyses, samples were previously filtered through 0.45 µm PTFE filters. In order to characterize EfOM fractions after applying particular ozone doses, the SEC-OCD technique from DOC-Labor was employed. Detailed information regarding this technique can be found elsewhere [21,37]. In summary, samples were previously filtered through 0.45 µm PTFE filters. The mobile phase was a phosphate buffer (0.01 M, pH 7) containing 0.1 M of NaCl. Separation of EfOM fractions by molecular weight was achieved by using a 25x2.2 cm column filled with HW-50 resin purchased from Sigma-Aldrich (Germany). Operation flow-rate and injection volume were 1 mL min^{-1} and 1 mL, respectively. As mentioned, the SEC-OCD procedure consists of size exclusion chromatography (SEC) followed by organic carbon detection. For calibration of humic substances molecular weights, Suwannee River standard humic and fulvic acids were employed. Both were acquired from the International Humic Substances Society. Based on the good agreement between the chromatographic behavior of these standards and that of effluent samples, as well as to additional UVA_{254} measurements, the name humic substances (HS) was assigned to one of the observed EfOM fractions. The nominal average molecular weights of fulvic and humic acid standards (711 and 1066, respectively) could be used to determine the molecular weight distribution of HS. The fraction with the highest molecular size (thus, eluting first and before HS) received the name biopolymers (BP). The fraction observed after HS elution was named as building blocks (BB), and was related to products coming from the breakdown of humic substances. The names low molecular weight acids and neutrals (LMWA and LMWN, respectively) were assigned to those fractions eluting last. The slightly more hydrophobic character of LMWN compared to LMWA allowed distinction between both fractions. A summary of the different fraction assignments can be found in Table 2. It has to be noted that fraction assignments in this work were made using the same fraction names firstly proposed by Huber and coworkers for characterization of organic matter in natural waters [21,37], and then adopted by other researchers for description of other types of water samples, including wastewater effluents [39].

Table 2. Properties of dissolved EfOM fractions distinguished in SEC-OCD analyses.

Dissolved EfOM fraction assignment	Molecular weight	Description

Biopolymers (BP)	> 20000	Associated to amino sugars, polypeptides and proteins. Do not absorb UV radiation.
Humic substances (HS)	~1000	Mix of hydrophobic humic substances and humic/fulvic acids, in varying concentrations
Building blocks (BB)	300 - 450	Degradation intermediates of humic substances
Low molecular weight neutrals (LMWN)	< 300	Short chain, non-acidic degradation products: alcohols, aldehydes, ketones…
Low molecular weight acids (LMWA)	< 300	Final degradation products of organics

3. Results and discussion

3.1. *Effluent characteristics*

The main physicochemical characteristics of all effluent samples are gathered in Table 3. Differences observed in the main quality parameters of tested effluents were attributed to particular WWTPs technologies and operational conditions, especially those regarding biological processes and subsequent separation steps. They covered a relatively broad range of effluent qualities and therefore represented the diverse range of wastewaters that currently can be found in practice.

Table 3. Effluent quality parameters. M and C stands for MBR and CAS effluents, respectively. All measurements were performed per triplicate (n=3). Discrepancies between replicates were in all cases lower than 5%.

Sample ID	**WWTP location**	**pH**	**UVA$_{254}$ * [m^{-1}]**	**TOC [mg C L^{-1}]**	**DOC * [mg C L^{-1}]**	**COD [mg O$_2$ L^{-1}]**	**Turbidity [NTU]**	**IC * [mg C L^{-1}]**	**NO$_2^-$ * [mg N L^{-1}]**

M1	Vacarisses	7.9	17.9	6.7	6.6	14.9	0.6	87.4	0.9
M2	Vallvidrera	7.4	16.3	10.5	10.3	20.7	0.9	42.7	< 0.1
M3	Gavà	7.7	14.9	12.4	12.1	16.6	0.3	53.0	0.1
C1	El Prat	7.5	22.9	14.0	13.6	29.7	1.1	63.6	0.1
C2	Gavà	7.8	67.2	42.1	27.6	93.5	28.6	114.7	0.1
C3	La Llagosta	7.7	66.4	25.6	21.3	53.0	20.1	98.3	< 0.1

* Samples were filtered through 0.45 µm PTFE filters for the measurement of these parameters.

3.2. Ozone demand, radical scavenging and removal of the reference compound ACMP

Estimated values of IOD and •OH consumption rates are presented in Table 4.

Table 4. Estimated IOD and •OH consumption rates of tested effluent samples. EfOM contributions in samples C2 and C3 may have been underestimated, as only dissolved EfOM was taken into account.

Effluent sample ID	**M1**	**M2**	**M3**	**C1**	**C2**	**C3**
IOD [mmol O_3 L^{-1}]	0.29	0.19	0.23	0.3	0.6	0.4
•OH consumption rate [s^{-1}]	$2.0\cdot10^5$	$2.5\cdot10^5$	$2.9\cdot10^5$	$3.3\cdot10^5$	$6.6\cdot10^5$	$5.2\cdot10^5$

Although relatively low O_3 doses (*e.g.*, 0.1-0.3 mmol L^{-1} or 5-15 mg L^{-1}) should be enough to meet the removal of organic compounds with medium or high reactivity to ozone [10,11,14,41], this criteria could get gradually stricter as is likely to occur in view of the increasing water scarcity and concern on micropollutants presence in water resources. Then, the abatement of even those MPs recalcitrant to ozone may be also required in a near future. In this study, we selected ACMP as reference compound on the basis of this hypothesis. ACMP reacts very slowly with ozone [35], and therefore only hydroxyl radicals generated through O_3 decay contribute to its degradation during ozonation. If ozone-resistant MPs such as this pesticide are significantly removed from wastewater effluents, a higher abatement of any other compound with higher sensitivity towards ozone attack would be guaranteed. Furthermore, O_3 doses necessary for disinfection purposes are generally lower than that for micropollutant oxidation [9,42].

Measurements of the reference compound ACMP ($[ACMP]_0$: 0.45 µM) at regular reaction times allowed the obtaining of the degradation profiles presented in Fig. 1. Ozone doses required to reach 80% abatement of ACMP differed significantly between samples. These were approximately between 0.4 and 0.8 mM (~19-38 mg L^{-1}) for effluents M1-M3 and C1, whereas for effluents C2 and C3 such doses were about 1 mM (48 mg L^{-1}) or even higher. For an abatement level of 50%, doses between 0.3 and 0.5 mM (14-24 mg L^{-1}) would instead be required for the less polluted effluents and between 0.6 and 0.8 Mm (29-38 mg L^{-1}) for samples C2 and C3.

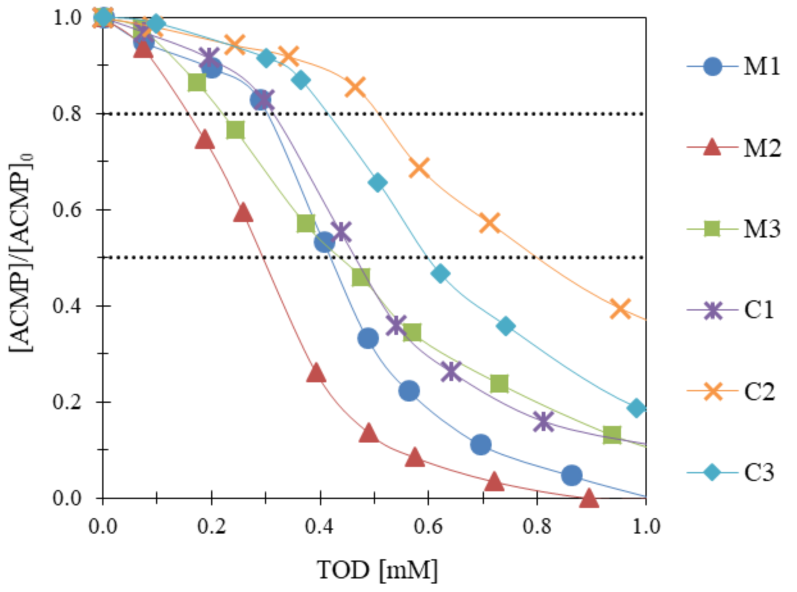

Figure 1. Abatement of the reference compound ACMP during semi-batch ozonation experiments with different wastewater effluent samples.

The feasibility of ozonation steps implementation for MPs abatement (including ozone-resistant compounds) should be individually assessed for each wastewater source by means of more comprehensive procedures [43], especially for those effluents presenting a higher O_3 demand and •OH scavenging rate (*e.g.*, C2 and C3). In any case, in this study we considered maximum ozone doses of about 1 mM as potentially practical for ozone applications to enhanced wastewater treatment and reclamation goals, and explored the fate of EfOM when subjected to these treatment conditions.

3.3. Changes of general EfOM descriptors (UVA_{254}, COD and DOC) during ozonation

Changes in UV absorbance at 254 nm (UVA_{254}) during ozonation experiments are shown in Fig. 2. Ozone typically reacts with electron-rich moieties of EfOM [39], resulting this in a sustained decrease of the wastewater UV absorption along the process. Differences observed between effluents regarding UVA_{254} decrease can be related to their respective water characteristics, which led to different availabilities of oxidants in the reaction medium (see estimated IOD and •OH consumption rate values in Table 4). Thus, for C2 and C3 effluents, both containing important amounts of O_3-consuming [20] particulate and colloidal matter (see the difference between TOC and DOC values as well as turbidity, Table 3) and alkalinity (IC), the UVA_{254} decrease at 30 min (TOD: 0.9-1.0 mM) ranged between 40 and 50%, whereas for MBR effluents (M1-M3) this value was determined to be considerably higher (70-80%) for a lower ozone consumption. In the particular case of C1, its lower content in solid and colloidal matter (difference between TOC and DOC values: 0.4 mg C L^{-1}; turbidity: 1.1 NTU) compared with C2 and C3 allowed a larger aromaticity reduction, more similar to that accounted for membrane bioreactor effluents. Other organic matter descriptors such as COD, DOC, TOC (addressed in the following paragraphs) and turbidity varied along the oxidative treatment displaying a similar dependence with effluent characteristics. For instance, turbidity measurements at the end of treatment (*i.e.*, after 30 min of ozonation, which corresponded to the highest applied ozone dose), reductions of 70-80% for effluents M1-M3, 60% for C1 and about 30-40% in the case of samples C2 and C3 were registered.

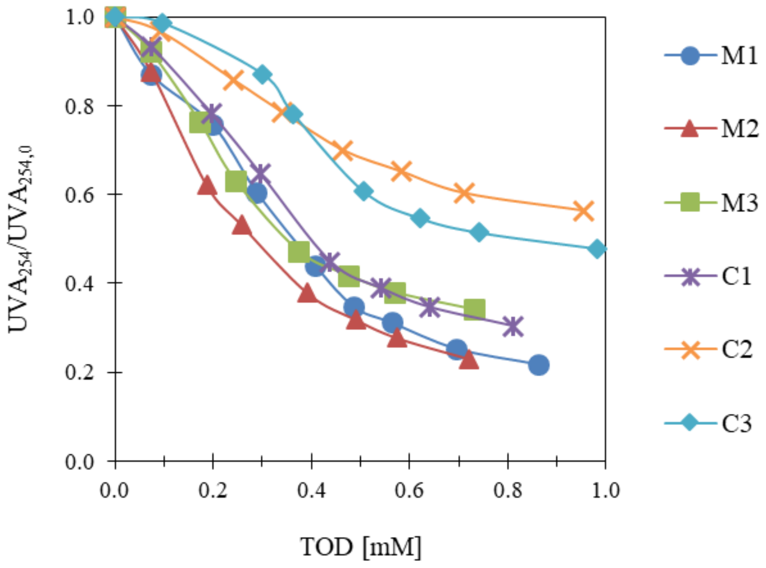

Figure 2. UV absorbance (at 254 nm) evolution during ozonation of wastewater effluents.

Fig. 3 shows the COD/COD$_0$ profiles obtained for each water source, as a function of the TOD. COD removals at the end of the treatment (TOD: 0.6-1.0 mM) ranged from 10 to 45%, depending on the tested sample. Again, clear differences were observed between effluents, together with a consistent trend for this bulk parameter with respect to the UVA$_{254}$ evolution, previously described. According to this, for instance, the M2 effluent – with relatively low content in organic matter and the lowest alkalinity among the studied wastewaters – was the one for which the largest COD removal was observed, whereas C2 and C3 samples (highest content in both organic and inorganic carbon as well as in colloidal and particulate matter) exhibited the lowest –and also the slowest– reduction for this parameter.

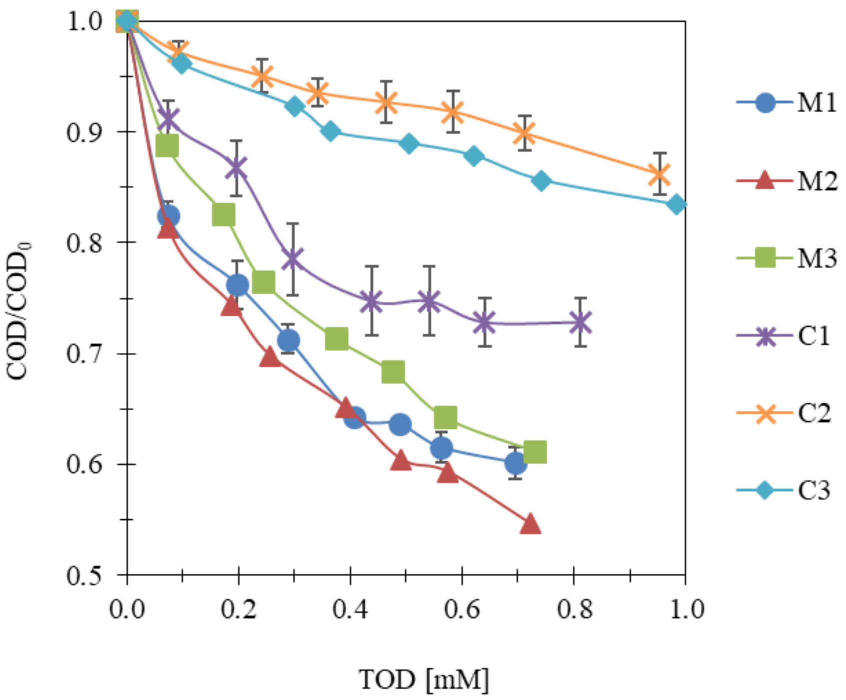

Figure 3. COD removal versus transferred ozone dose during semi-batch effluent ozonation experiments.

In general, lower overall reductions of COD (max. 45%) in comparison to UVA_{254} (up to 80%) were observed. It seems that the provided oxidation conditions were not strong enough in order to achieve comparable levels of organic matter transformation in terms aromaticity depletion and COD reduction.

Fig. 4 shows the percentage of DOC removal during effluent ozonation experiments, determined at three different ozone doses (TOD values of 0.2-0.3, 0.3-0.5 and 0.6-1.0 mM). For effluents M1, M2 and M3, all of them coming from MBR systems, the DOC concentrations after 30 min of treatment (TOD: 0.6-0.7 mM) were reduced by 27%, 22% and 21%, respectively. TOC measurements of the same samples (data not shown) revealed almost identical removal values, which is logical given the fact that nearly all of the organic matter was in dissolved form. In any case, organic carbon removals were in comparison lower than those reached for COD or UVA_{254} at the same consumed ozone doses. In wastewater ozonation, the degree of mineralization is typically low, and other water quality parameters related to the organic content – such as COD and UVA_{254} – are in general more affected during the process. This is reasonable, as DOC concentration only is reduced when decarboxylation reactions are produced, that is, when the maximum possible level of organic matter oxidation takes place [39].

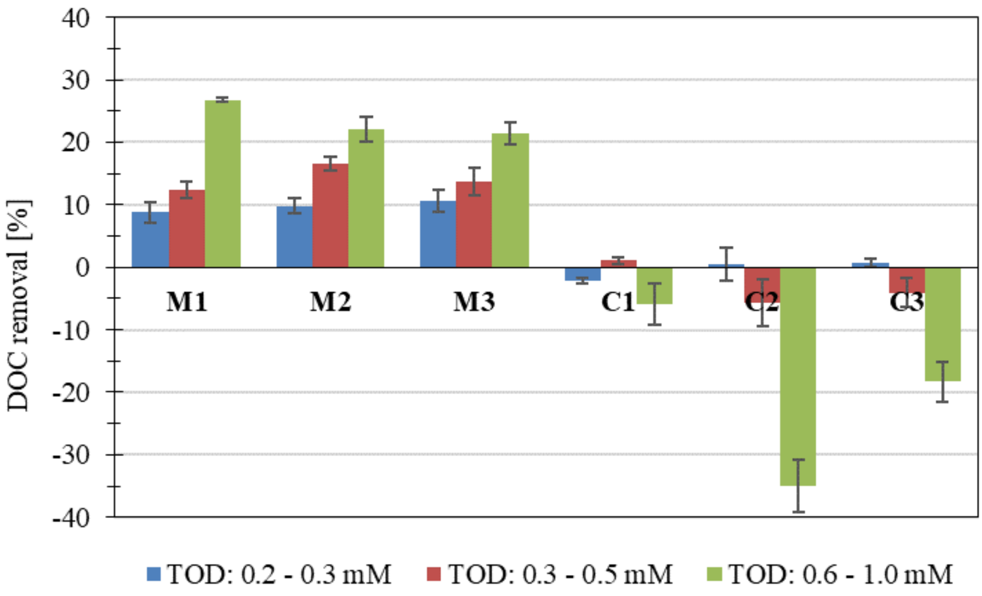

Figure 4. DOC concentration removal in wastewater ozonation experiments at various transferred ozone doses (TOD).

Concerning effluents C1, C2 and C3, the observed DOC removals at the end of ozonation experiments were negative in all cases. Water effluents coming from CAS systems usually contain residual amounts of suspended solids and colloids (see TOC, DOC and turbidity values of Table 3). Therefore, and in agreement with literature [44,45], it is possible that part of this non-dissolved material could be solubilized upon oxidation. For the CAS effluents tested in the present study, this phenomenon was observed after consumption of relatively high ozone doses (*i.e.*, 0.7-1.0 mM), rather than at low TOD values. In fact, at O_3 doses between 0.2 and 0.5 mM only small changes in the DOC concentration where registered, which could be indicative of a simultaneous oxidation-solubilization of, respectively, the dissolved and undissolved EfOM. An indicative of this competition between degradation and solubilization may be the TOC removals measured at the end of treatment, which were insignificant for samples C2 and C3 and only about 10% in the case of C1.

3.4. Evolution of EfOM fractions

Figs. 5 and 6 show the evolution of (dissolved) EfOM fractions and their relative contribution to DOC during ozonation of wastewater effluents. At this point it has to be recalled that EfOM fractions referred to in the following lines are due to fraction assignments based on the chromatographic behavior of organic matter components in wastewater effluent samples, according to the methods described for SEC-OCD analyses in section 2.3. Samples coming from CAS processes presented larger percentages of biopolymers than MBR effluents (7-25% vs 1-2%, respectively), which was already expected given that ultrafiltration membranes employed in MBR units are able to retain extracellular polymeric substances (EPSs). Differences were also observed in the humic substances concentration (2697-3319 and 3335-5217 μg C L^{-1} for MBR and CAS, respectively) which, in agreement with previous related studies concerning membrane fouling in MBR units, suggests that a part of the largest constituents of this EfOM fraction could also be retained during the separation process [24,46].

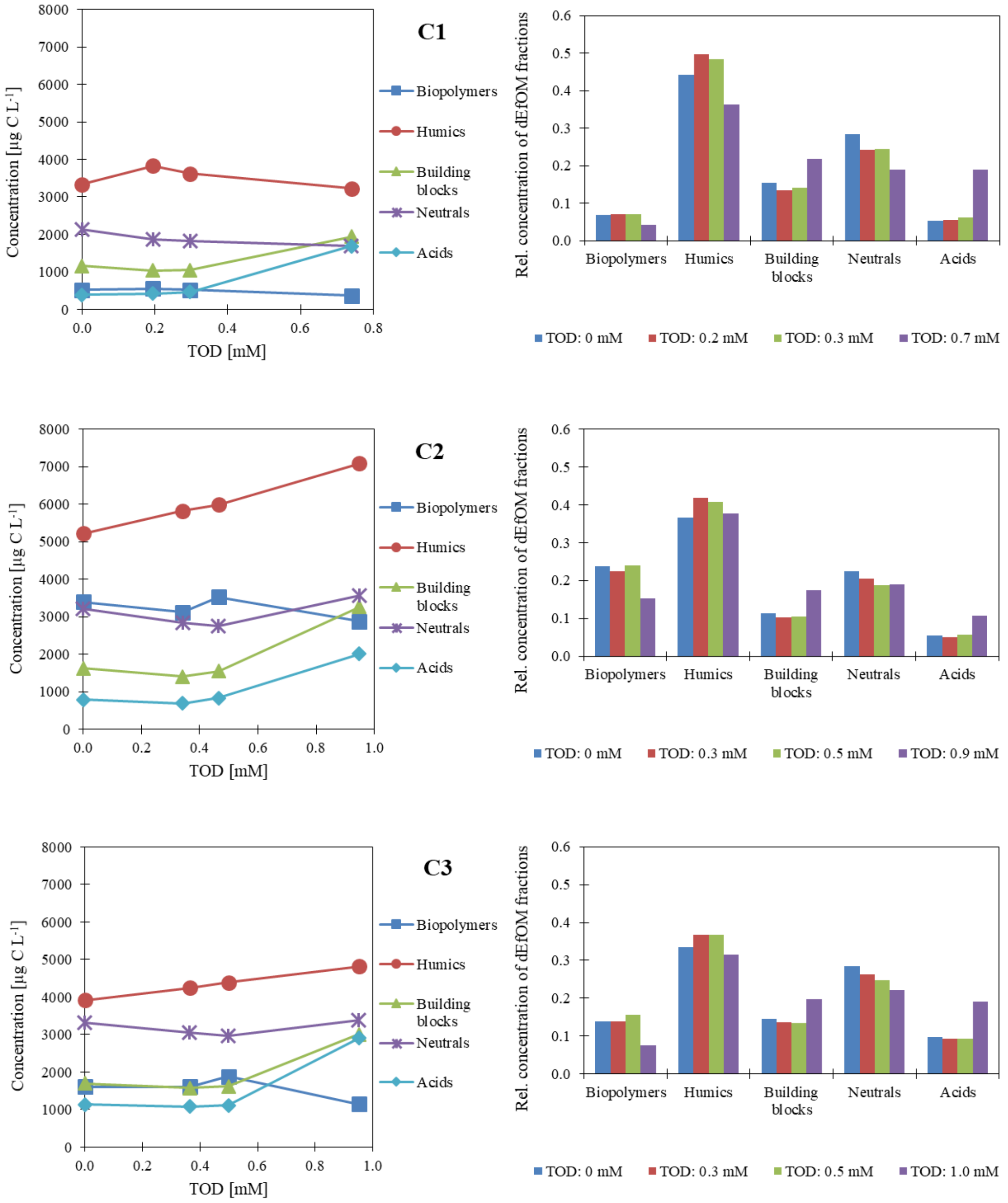

Figure 5. Evolution of dissolved EfOM fractions (left) and contribution to DOC (right) for ozonized CAS effluents. Relative concentration of EfOM fractions in right column plots (y-axis) refer to DOC of considered fraction divided by total DOC.

Regarding CAS effluents (Fig. 5), biopolymers were not significantly removed until higher doses of ozone were consumed [from 7 to 4% (C1), from 24 to 15% (C2) and from 14 to 8% (C3) of dissolved EfOM content for O_3 doses of 0.7-1.0 mM]. Especially remarkable is the case of humic substances, which noticeably increased from the beginning of the treatment, especially for C2 and C3 samples. The observed accumulation of humic substances during the entire C2 and C3 ozonation time, together with the fact that these two waters contain the highest fraction of suspended solids among all the studied effluents may be linked. Thus, the non-soluble fraction of humic substances could be solubilized when oxidized [24,37]. This affirmation would be experimentally supported by the DOC measurements made at different ozone doses and early seen in this study, which revealed significant increases in this parameter (35% and 18% for C2 and C3 samples, respectively) for consumed ozone doses of 0.9-1.0 mM. Significantly higher doses applied in related works for effluents containing suspended EfOM [24] could have hinder a possible initial increase of this fraction followed by subsequent depletion for higher oxidant dosages. This was in fact observed for sample C1, a CAS effluent containing a lesser amount of suspended solids. Moreover, the continuous solubilization of humic substances would provide an additional explanation to the low rates of UVA_{254} depletion found for C2 and C3 waters. BB remained almost unaltered until higher ozone doses were applied, which means that humic substances were not being destroyed at those oxidation extents. Only at O_3 doses of 0.7-1.0 mM, an enrichment in the BB contents [from 15 to 22% (C1), from 11 to 17% (C2) and from 15 to 20% (C3)] was noticeable in all EfOMs. Regarding LMWN, the concentration of this fraction increased at the end of the treatment (*i.e.*, for ozone doses of 0.7-1.0 mM) for samples C2 and C3, but only after an initial – and also slight – reduction at the first stages of the process took place. On the contrary, for effluent C1 a slightly decrease in this fraction concentration was observed during the entire ozonation time. Again, differences between effluents C2 and C3, on one hand, and effluent C1, on the other, appear to be well explained by the solubilization process taking place in the first ones: the continuous introduction of humic substances to the system would hypothetically lead to an accumulation of degradation intermediates (*i.e.*, LMWN), contrarily to what typically happens in water matrices in which this re-dissolution of OM does not significantly take place (*e.g.*, MBR effluents and also sample C1). Despite the increase in LMWN observed for C2 and C3, a gradual impoverishment and accumulation of this fraction in all the tested CAS effluents was registered [overall changes in EfOM composition for consumed O_3 doses of 0.7-1.0 mM: from 28 to 19% (C1), from 23 to 19% (C2), from 28 to 22% (C3)]. Finally, a significant accumulation of LMWA was observed for all three samples at ozone doses of 0.7-1.0 mM, leading to the enrichment in this component of the corresponding EfOM compositions [from 5 to 19% (C1), from 6 to 11% (C2) and from 10 to 19% (C3)]. This evolution was predictable, as carboxylic acids present low reactivity towards ozone and the contribution of hydroxyl radical oxidation in complex water matrices is usually expected to be low [39,47].

The evolution of EfOM fractions during ozonation of MBR effluents is shown in Fig. 6. With no biopolymers nor suspended solids present in wastewater matrices, ozone primarily attacked humic substances and LMWN, leading this to the gradual accumulation of BB but particularly LMWA (from 4 to 18% (M1), from 3 to 20% (M2) and from 5 to 8% (M3), for consumed ozone doses of 0.6-0.7 mM). The overall increase of humic substances concentration observed for the M3 dissolved EfOM was the result of the small changes that took place in the rest of fractions, together with a DOC reduction of *ca.* 21% at the end of the treatment.

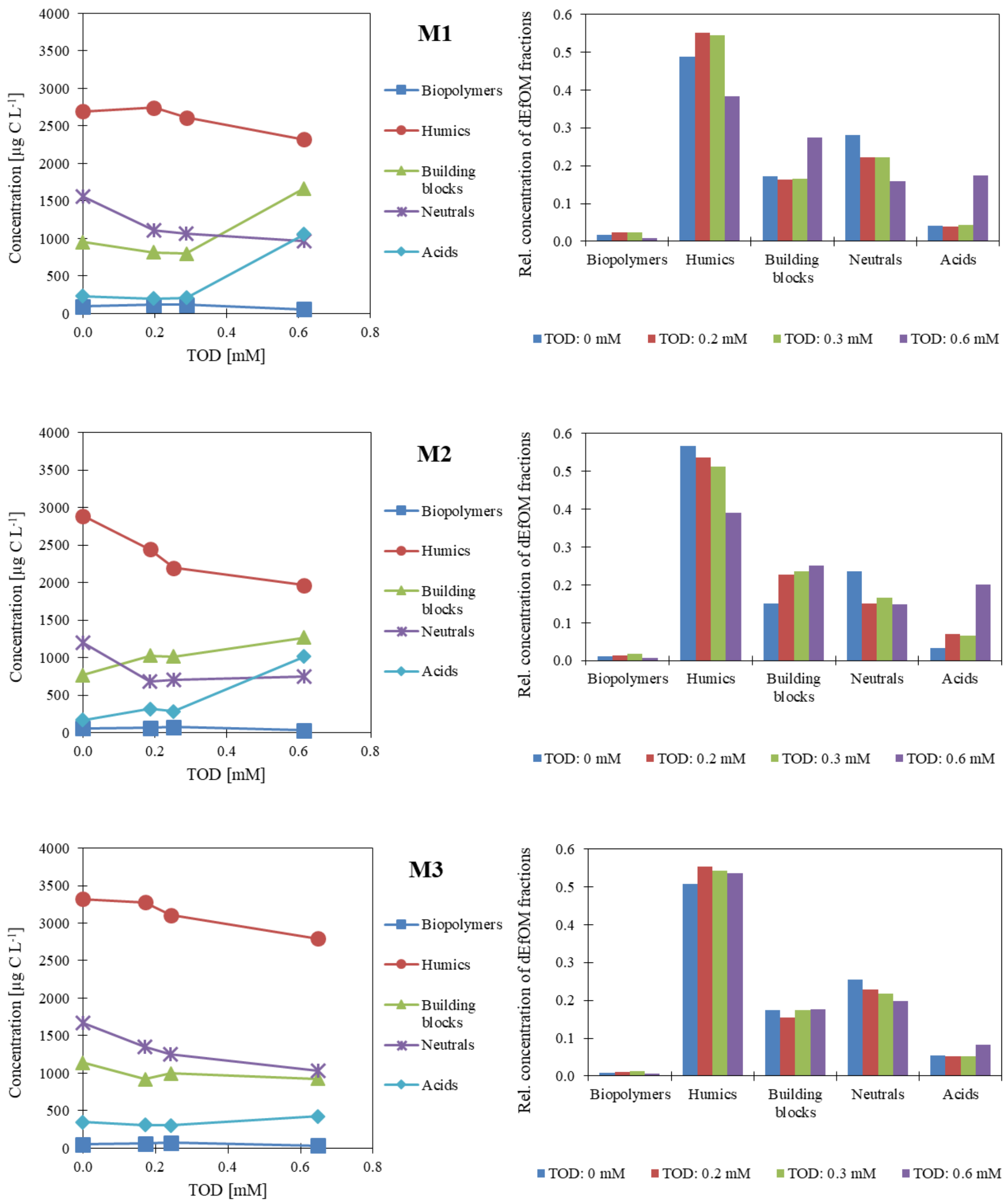

Figure 6. Evolution of dissolved EfOM fractions (left) and contribution to DOC (right) for ozonized MBR effluents. Relative concentration of EfOM fractions in right column plots (y-axis) refer to DOC of considered fraction divided by total DOC.

In view of the above results, it is clear that applying ozonation can change EfOM along the treatment. These changes in turn, could cause negative impacts that require especial mention: in first place, the cleavage of macromolecules and medium-size structures to yield LMWA, which are not effectively mineralized by ozone, is known for leading to the enhancement of water biodegradability [20,48]. Although this could be interesting if a final biological treatment step is planned (*e.g.*, biological activated carbon), it could be also detrimental if this water is discharged or directly reused instead: biodegradable EfOM is a perfect substrate for bacterial growth in pipes, membranes or receiving water compartments [49]. Regarding the biopolymers fraction, the observed reduction during the process was in any of the cases higher than *ca.* 45%. For CAS effluents, containing a significantly higher concentration of these components, the reduction percentage was still lower. This means that the greatest part of biopolymers, partly responsible for membrane fouling, for instance, remained unaltered in the water matrix. With respect to particulate matter solubilization during the treatment, ozonizing secondary effluents containing suspended solids seems to be not recommended. Finally, increasing DOC in an already treated wastewater would be in first place inefficient for obvious reasons. In addition, this detrimental effect could lead to other problems such as increased generation of disinfection by-products in hypothetical post-treatment.

3.5. Relationship between process parameters and EfOM changes

Although UVA_{254} is typically used as an estimate of the content in humic substances of EfOM [19,50–53], a strict correlation between these two factors has not been observed during ozonation experiments. Oxidation of humic substances initially occurs at the external part of the coil formed by these molecules, which in turn prevents its inner part to be destroyed by ozone and hydroxyl radicals [54]. According to the aromaticity model for humic substances proposed by Del Vecchio and Blough [55], the attack on the peripheral part of chemical structures of humic substances potentially leads to the oxidation of electron-donating or -accepting subunits responsible for charge transfer transitions. As charge transfer transitions between these structures are responsible for UV absorption, this would be enough to reduce the sample UVA_{254}. Similar observations reported by studies employing chlorine as oxidizing agent [56], instead of ozone, support this hypothesis. Likewise, the observed mismatch between COD and UVA_{254} reduction during ozonation experiments (see Figs. 1 and 2) could be partly related to the mentioned steric impediment caused by the spatial configuration of humic substances.

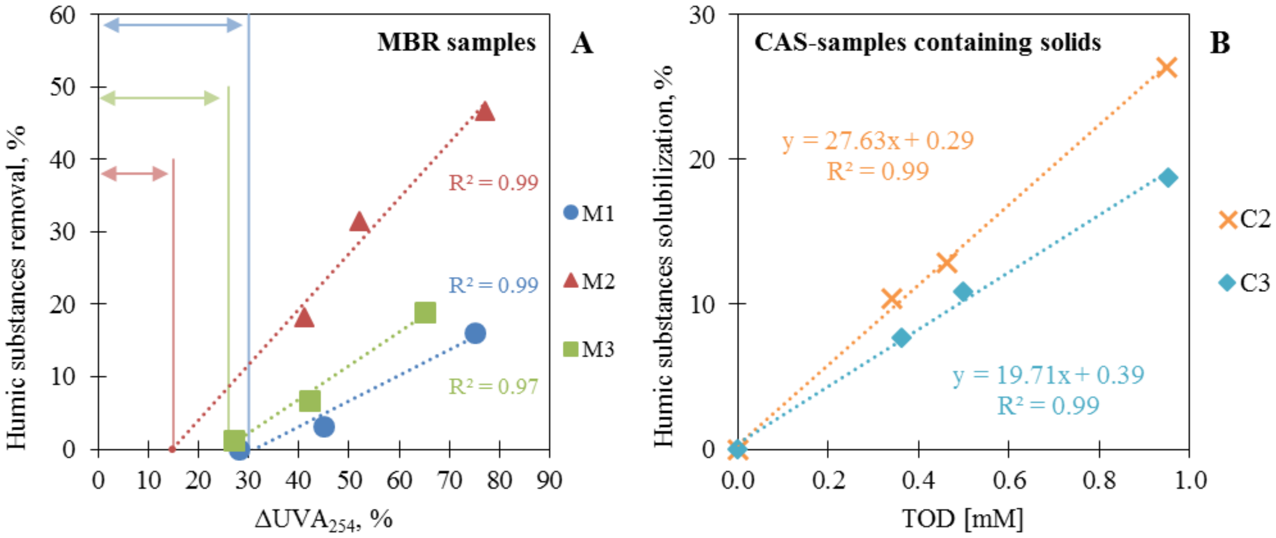

Figure 7. Relationship between effluent quality and process parameters with humic substances concentration in wastewater effluents ozonation. A) Humic substances removal in MBR effluent samples versus % UVA_{254} reduction; B) Humic substances solubilization versus transferred ozone dose in CAS effluent samples containing significant amounts of suspended organic matter.

Recent works have shown how the measurement of spectroscopic parameters (UVA and fluorescence removal) could be potentially used as on-line proxies for biodegradable DOC generation during ozonation and other advanced tertiary treatments [49,57]. This biodegradable fraction of EfOM corresponds to the presence of medium-weight BB, as well as to LMWN and LMWA. Since all these species have their origin in the cleavage of larger molecules of humic substances, it seems logical to put the focus on the relationship between this fraction and some common effluent quality and process parameters in order to anticipate potential changes during ozonation.

Fig. 7A shows a plot of the percentage of humic substances removal versus the UVA_{254} depletion, for samples coming from MBR units. As seen, a good relationship between them appears to be possible after an initial lag stage in which any abatement of humic substances is observed. In other words, a degree of UV absorbance reduction is observed before measuring any depletion in the concentration of humic substances. This is also indicated in Fig. 7A. The magnitude of this lag can be related with the oxidizing conditions of the media, since a higher availability of oxidant species favors a more severe oxidation of humic substances. As known, O_3 and •OH availability during ozonation will depend on the effluent characteristics, which is mainly given by the contents in organic and inorganic matter that readily consume these oxidants. Interestingly, the observed trend for IOD (*i.e.*, 0.29, 0.19 and 0.23 mmol O_3 L^{-1} for samples M1, M2 and M3, respectively) agreed well with the trend observed for the lag values represented in Fig. 7A, which resulted to be: M2 > M3 > M1 (corresponding to 14.5, 25.5 and 31.1 % of UVA_{254} depletion, respectively). The slope of the humic substances-UVA_{254} removal correlation for these waters, which would give an idea about the process kinetics, also followed the same trend (0.35, 0.76 and 0.47 for M1, M2 and M3, respectively).

Contrarily, the agreement between humic substances-UVA254 removal and IOD, on one hand, and the observed lag phase and IOD, on the other, was not observed with the initial •OH consumption rate values estimated for MBR effluents. In fact, the presence of •OH in the reaction medium not only depends on the consumption rate of these species by the water matrix but also on the capacity of consumed ozone to generate them. Therefore, a better indicator of •OH availability to react with humic substances during the first stages of ozonation process should also consider ozone consumption. A good option can be the use of the ratio between •OH exposure (*i.e.*, $\int [\bullet [OH]\mathrm{d}t$) and IOD. Hydroxyl radical exposure for an ozone consumption corresponding to the IOD value could be estimated in this work through ACMP degradation data presented in Fig. 1, according to the calculation procedure described elsewhere [34] and based on the use of an ozone-resistant compound as •OH probe. The obtained $\int [\bullet [OH]\mathrm{d}t/\mathrm{IOD}$ values were $3.1\cdot10^{-7}$, $7.3\cdot10^{-7}$ and $4.9\cdot10^{-7}$ s for samples M1, M2 and M3, respectively. As can be checked, the trend followed by these values now match with the lag and slope values in Fig. 7A: the higher the amount of hydroxyl radicals available per ozone dose, the stronger the oxidation conditions, thus allowing a more significant (and faster) degradation of humic substances by •OH during the initial stages of ozonation.

Finally, if it was the case that ozonation was applied to a CAS effluent containing significant amounts of suspended matter, the percentage of humic substances solubilization in the water matrix seems to be well correlated with the transferred ozone dose (TOD). This is shown in Fig. 7B: the higher the oxidation extent, the higher the number of hydrophilic moieties generated in the non-soluble fractions of EfOM, which can then be solubilized into the water matrix. In addition, larger concentrations of solid matter, which also contribute to a higher IOD value, seem to favor faster solubilization kinetics, as shown in the correlation parameters obtained in experiments with samples C2 and C3.

Conclusions

Ozone application for the effective removal of micropollutants including ozone-resistant species, which can be a potentially realistic situation in wastewater treatment in a near future, from wastewater produced significant changes in EfOM concentration and quality in all effluents tested. The extent of COD and UVA_{254} reduction agreed well with the water quality of each effluent, being the most influencing factors the concentration of both dissolved and particulate/colloidal matter and alkalinity. For CAS samples containing relatively large amounts of suspended solids, an increase in the DOC concentration was observed. This was attributed to the solubilization of non-dissolved humic substances. The continuous introduction of this fraction (humic substances) in the reaction medium resulted in the net accumulation of this component. Only for samples coming from MBR systems, the sequential reduction of the largest fractions leading to an accumulation of some of the lightest components, namely BB and LMWA, could be clearly observed. Also for these waters, a net level of OM mineralization took place. In general, an accumulation of low molecular weight acids at the end of the treatment was registered. Correlations between some observed changes (variation in humic substances concentration), water quality (UVA_{254}) and process parameters (IOD, $\int [\bullet [OH] \mathrm{d}t$/IOD, TOD) were established. Changes in organic matter concentration and characteristics derived from ozone application could be detrimental for water reuse purposes, depending on the final application of the treated water. Thus, accumulation of lower weight fractions could lead to bacterial growth or eutrophication, and the increase in humic substances concentration upon oxidation of particular/colloidal matter is in any case detrimental because of the general increase in the DOC content. Thus, a careful consideration of this factor together with the water properties of the effluent to treat and the quality requirements to achieve throughout the process (*e.g.*, micropollutants removal) should be properly assessed during the planning stage of an ozonation unit.

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