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Ozonation mechanism of carbamazepine and ketoprofen in RO concentrate from municipal wastewater treatment: Kinetic regimes, removal efficiency and matrix effect

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HIGHLIGHTS

- Chemical reactions occurred at a fast rate during the first 60 min ozonation, and then transitioned to a moderate regime.
- A satisfactory removal of micropollutants by ozonation was achieved before initial ozone demand was fulfilled.
- Ozonation was less effective to eliminate ozone-refractory KET than ozone-reactive CBZ.
- The presence of organic matters and alkalinity in RO concentrate exhibited strong impacts on KET decomposition by ozonation.
- Transformation of organic compounds was a dominated step instead of mineralization.

GRAPHICAL ABSTRACT

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ABSTRACT

A relatively important disadvantage of reverse osmosis (RO) application to municipal wastewater reclamation is related to management of a concentrated waste stream containing high levels of organic contaminants. The present study investigated ozonation performance of RO concentrate from municipal wastewater treatment in a stirred semi-batch reactor. In this work, carbamazepine (CBZ, as a representative of ozone-reactive micropollutants) and ketoprofen (KET, one of ozone-resistant organic chemicals) were selected as target micropollutants. The absence of dissolved ozone within the first 60 min corresponding to initial ozone demand (IOD) complement suggested that chemical reactions took place quite fast, and ozone mass transfer was considered as a limiting step. A complete elimination of CBZ and an excellent removal of KET were observed in this period, indicating that molecular ozone was a dominated oxidant responsible for the decomposition of the target micropollutants in RO concentrate containing initial dissolved organic carbon (DOC_0 , $\sim 50.8 \text{ mg L}^{-1}$). >90% of ozone-reactive CBZ was eliminated at a low ozone dose of 0.33 g consumed ozone per g DOC_0 . More ozone dose requirement for an equivalent removal of KET was ascribed to its low ozone kinetic rate constant below $10 \text{ L mol}^{-1} \text{ s}^{-1}$. In addition, the presence of high contents of organic matters and alkalinity in RO concentrate exhibited pronounced effects on the degradation of KET because of a competition with oxidants. Overall, ozonation appeared to be a promising alternative for disposal of RO concentrate in terms of micropollutant removal. However, additional technologies should be followed to further enhance the degradation rate of organic matters for a zero liquid discharge treatment scheme.

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Nomenclature

AOPs	Advanced oxidation process
BOD ₅	5-day biological oxygen demand, mg L ⁻¹
BQM	1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one
BQD	1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione
BaQD	1-(2-benzoic acid)-(1H,3H)-quinazoline-2,4-dione
BaQM	1-(2-benzoic acid)-4-hydro-(1H,3H)-quinazoline-2-one
CBZ	Carbamazepine
COD	Chemical oxygen demand, mg L ⁻¹
DIC	Dissolved inorganic carbon, mg L ⁻¹
DOC	Dissolved organic carbon, mg L ⁻¹
DOM	Dissolved organic matters
E	Enhancement factor
EfOM	Effluent organic matters
IOD	Initial ozone demand, mg L ⁻¹
m	Ozone solubility parameter
MWWTPs	Municipal wastewater treatment plants
KET	Ketoprofen
k _{O3}	Ozone rate constant, L mol ⁻¹ s ⁻¹
k _{OH}	Hydroxyl radical rate constant, L mol ⁻¹ s ⁻¹
k _{La}	Volumetric mass transfer coefficient
pKa	Disassociation constant
Q _{gas}	Ozone gas flowrate, L h ⁻¹
RO	Reverse osmosis
t	Reaction time, h
V _{liq}	Liquid volume, L
VRF	Volumetric reduction factor
·OH	Hydroxyl radicals
O ₃ applied	Applied ozone dose (AOD)
O ₃ transferred	Transferred ozone dose (TOD)
O ₃ consumed	Consumed ozone dose
[O ₃] _{gas-in}	Ozone gas concentration inlet, mg L ⁻¹
[O ₃] _{gas-out}	Ozone gas concentration outlet, mg L ⁻¹
[O ₃] _{liq}	Dissolved ozone concentration in liquid phase, mg L ⁻¹
[O ₃] _{liq} *	Dissolved ozone concentration at the equilibrium, mg L ⁻¹

1. Introduction

Even though municipal wastewater is one of the largest pollution sources, reclamation of effluents from municipal wastewater plants (MWWTPs) has been considered as an economically feasible solution to cope with water scarcity problems (Xu et al., 2010). However, the presence of trace micropollutants (including pharmaceuticals, personal care products, etc.) in MWWTPs effluents at a concentration range of ng L⁻¹ - µg L⁻¹, which might have adverse effects on the ecosystem and human health, does not allow a direct reuse of MWWTPs effluents (Dolar et al., 2012; Gomes et al., 2017; Guillosoy et al., 2019; Jiang et al., 2013; Luo et al., 2014). Therefore, advanced technologies, such as reverse osmosis (RO) process, should be followed to produce excellent quality water by removing these trace micropollutants from municipal secondary effluents. During the past two decades, RO process, as a tertiary treatment for municipal wastewater reuse, has been well-established in rejecting emerging micropollutants mainly through size exclusion (steric hindrance), electrostatic interactions, and hydrophobic interactions between solutes, solvent and membrane (Alturki et al., 2010; Dolar et al., 2012; Jacob et al., 2012; Mamo et al., 2018; Tam et al., 2007).

However, one significant disadvantage of RO process for municipal wastewater reclamation is linked to the disposal of a concentrated

waste stream (termed as RO concentrate) usually representing 10% - 50% of feed water (Azaïs et al., 2016; Bagastyo et al., 2011; Hurwitz et al., 2014; Miralles-Cuevas et al., 2017; Pérez et al., 2010). Municipal RO concentrate is typically characterized by a pH range of 6.9–8.8, high levels of conductivity (1.7–23.5 mS cm⁻¹), persistent organic matters (DOC: 14–68 mg L⁻¹) and a broad range of emerging organic contaminants (Bagastyo et al., 2011; Deng, 2020; Pérez et al., 2010; Pradhan et al., 2015; Zhou et al., 2011). The concentration of micropollutants in RO concentrate usually multiplies by a factor of 2–7 as compared to RO feed water (Bagastyo et al., 2011; Pérez-González et al., 2012). Since the compositions of RO concentrate are more complicated than that of municipal wastewater effluents (as RO feed), RO concentrate seems to be more toxic to the aquatic organism. In fact, genotoxicity of RO concentrate is much larger than that of RO feed (Tang et al., 2013). Zhou et al. (2011) observe that the municipal RO concentrate appears to be toxic to the tested organism, with 62% inhibition to bacteria *V. fischeri*. In addition, municipal RO concentrate has a relatively low biodegradability, with a ratio of 5-day biological oxygen demand (BOD₅) to COD (BOD₅/COD) of 0.02–0.06 (Deng, 2020; Justo et al., 2013; Vendramel et al., 2013; Zhou et al., 2011), demonstrating recalcitrantly biodegradable organic matter content. Direct or indirect discharge of municipal concentrate into the aquatic environment could lead to pollution to ecosystem. To reduce the content of toxic organic compounds and to improve biodegradability level, therefore, it is of importance to develop cost-effective technologies prior to the direct discharge of RO concentrate to surface water.

Ozonation is an attractive technology in the elimination of a wide range of micropollutants from wastewater due to a combination of molecular ozone and by-product radicals from ozone self-decomposition or from the reactions of ozone with organic matrix (El-taliawy et al., 2017; Javier Benitez et al., 2009). Since reactions via both molecular ozone and ·OH radicals can take place in real aqueous medium, ozonation itself is often recognized as an advanced oxidation process (AOP) or AOP-like process (Miklos et al., 2018). A highly efficient degradation for trace organic contaminants by ozonation have been presented in some reviews (Gomes et al., 2017; Oller et al., 2011). It should be pointed out that, nonetheless, a low mineralization level achieved after ozonation indicates that oxidation intermediates with toxic feature might be accumulated. Therefore, the integration between ozonation and other AOPs (such as UV/H₂O₂, electrochemical oxidation, etc.) or biological treatment is proposed to improve the mineralization level of treated wastewater. Over the past decade, there are some studies to report the ozonation effectiveness of municipal RO concentrate, but their focuses are mainly on the degradation of organic matters and the improvement of biodegradability (Jeirani et al., 2015; Justo et al., 2015; Lee et al., 2009; Vendramel et al., 2013; Zhou et al., 2011). An early study conducted by Benner et al. (2008) investigate the ozonation behaviour of four common beta blockers including acebutolol, atenolol, metoprolol and propranolol. Applied ozone dose of 5–10 mg L⁻¹ is proved to be sufficient to eliminate all the tested micropollutants efficiently from RO concentrate. In recent 10 years, several studies have been done to remove trace micropollutants from RO concentrate by ozonation. Joss et al. (2011) and Woo et al. (2019) apply ozonation as pre-treatment to attenuate organic content before recycling back into a biological system. Their results emphasize that micropollutant load can be abated significantly from RO concentrate after ozonation. Justo et al. (2013) compare the performance of ozone alone and UV plus H₂O₂ for decontamination of municipal RO concentrate. Even though UV/H₂O₂ is expected to be more effective in removing the target micropollutants due to reactions of organic chemicals with non-selective ·OH radicals, >80% removal for most of micropollutants can be achieved at ozone consumption of 0.82 g O₃ per g TOC₀. In addition, several studies have also focused on the application of ozonation for the treatment of municipal nanofiltration concentrate (Acero et al., 2016; Azaïs et al., 2017, 2016; Miralles-Cuevas et al., 2017). The main goal of these published studies is to evaluate ozonation performance in removing micropollutants and

organic matters from membrane concentrate. Nonetheless, additional studies related to ozonation kinetic regimes should therefore be considered for a better understanding of the ozonation mechanism of micropollutants present in municipal NF/RO concentrate.

On the other hand, an ozone dose requirement for a good elimination of micropollutants from wastewater strongly depends on their reactivity towards molecular ozone and the wastewater matrix (including organic matters and inorganic salts). As compared to municipal secondary effluents, RO concentrate contains higher concentrated inorganic ions, especially Cl^- , HCO_3^- and SO_4^{2-} , with the concentration above 100 mg L^{-1} , even up to 1000 mg L^{-1} (Justo et al., 2015; Pérez et al., 2010; Shanmuganathan et al., 2017; Zhou et al., 2011). Such ions could directly or indirectly compete for oxidants (Beltrán, 2004). Therefore, a hypothesis can be made that the ozonation mechanism of micropollutants might be more complex in a complicated matrix (such as RO concentrate). Besides micropollutant removal rate, more researches concerning kinetic regimes and matrix effects during the ozonation of RO concentrate from municipal wastewater treatment still need to be extended.

The main objective of this present paper was to understand the ozonation mechanism of micropollutant present in a complicated water matrix (such as RO concentrate). For this purpose, the ozonation of RO concentrate containing micropollutants was conducted in a semi-batch reactor. Ozone-reactive carbamazepine (CBZ) and ozone-refractory ketoprofen (KET) were used as the target micropollutants. To the best of my knowledge, information on ozonation behaviour of KET in membrane concentrate was still in scarcity. In this work, the kinetic regimes were explicitly evaluated by measuring gaseous and liquid ozone, calculating initial ozone demand (IOD) and enhancement factor. The ozonation efficiency of both CBZ and KET was then assessed. Matrix effects and the formation of oxidation transformation products were also discussed simply.

2. Materials and methods

2.1. Target micropollutants

Carbamazepine (CBZ) and ketoprofen (KET) with a purity higher than 99% were purchased from Sigma-Aldrich and used as received. Table 1 shows the chemical structure of the selected micropollutants and their expected ozone attacking site. These two micropollutants were selected specifically according to their significantly different kinetic rate constant with ozone.

2.2. RO performance and characteristics of RO concentrate

Prior to ozonation, a dead-end mode RO cell, where municipal secondary effluents were used as RO feed, was conducted at a working pressure of 8 bar to produce RO concentrate. Volumetric reduction factor (VRF, volume ratio of RO feed to RO concentrate) was set as 3, which corresponded to 67% water recovery. In this work, CBZ and KET were not detected in MWWTPs effluents. To examine the fate of micropollutants in an integrated system consisting of RO process and ozonation, CBZ and KET with a high concentration of $\sim 10 \text{ mg L}^{-1}$ were spiked into municipal secondary effluents as RO feed. Note that, solvent (methanol or ethanol) was not utilized to prepare the stock solution of target micropollutants in consideration of its impact on ozone consumption. Indeed, the presence of ethanol (0.05%, v/v) exhibited a significant inhibition on ozonation efficiency of CBZ and KET, especially for KET, as implied in Fig. S1 (See Supplementary Information).

Table 2 displays the most important results of RO performance for municipal secondary effluents treatment. At water recovery of 67% (VRF: 3), RO membrane was effective in rejecting constituents from

secondary effluents, with an observed retention (expressed as $((C_{\text{concentrate}} - C_{\text{permeate}}) / C_{\text{concentrate}}) \times 100$) ranging from 59% of NO_3^- to 94% of chemical oxygen demand (COD). The concentration of most of inorganic ions and organic constituents in RO concentrate increased by a factor of 2.0–2.5 in comparison with RO feed. A higher DOC content in RO concentrate was attributed to the addition of CBZ and KET as compared to $\sim 8.0 \text{ mg L}^{-1}$ in RO concentrate without micropollutants. RO concentrate obtained was stored at 4°C and brought to room temperature before analysis and ozonation experiments.

2.3. Ozonation set-up

Ozonation experiments were performed at a lab scale in a stirred and thermostatic semi-batch reactor with a useful volume of 2 L, as depicted in Fig. 1. Ozone as a feed gas at a desired concentration around 10 mg L^{-1} , generated from pure oxygen by using an ozone generator with a power of around 1.5 (BMT Messtechnik GmbH 802 N, Germany), was introduced continuously at the bottom of the reactor through a porous gas diffuser at a constant gas flow rate of 30 L h^{-1} . In order to examine if the production of the ozone generator maintained constant during the experiment, the concentration of ozone gas-in was again measured at the end of the ozonation experiment where gaseous ozone directly passed through an ozone analyser by changing Valve 1 and Valve 2 position, as shown in Fig. 1. The concentration of ozone at the inlet and outlet gas stream was measured by a BMT 964 ozone analyser (BMT Messtechnik GmbH, Germany). A complete and continuous mixing of the bulk liquid phase could be achieved by using a turbine with 6-blades at a rate of 470 rpm. An online ozone analyser (Orbisphere Laboratories model 410, Germany), mounted on the recirculation loop, was utilized to detect the concentration of dissolved ozone. A circulation rate of 500 rpm adjusted by a peristaltic pump (Masterflex, USA) was required to assure the solution containing dissolved ozone pass through polarographic membrane. Both excess gas and gas-out flows were forced into an ozone destruction unit before releasing into the atmosphere. During the ozonation experiment, the solution in the reactor was kept at a constant temperature by circulating water from a thermostatic bath through the reactor jacket. The solution pH was monitored by a pH analyser (Consort R305, Belgium). The values corresponding to the concentration of ozone gas-in, gas-out and dissolved ozone, solution pH and temperature are recorded continuously by a software in PC.

Experiments of RO concentrate ozonation were conducted without pH adjustment, and lasted 3 h at a constant temperature of $20 \pm 1^\circ\text{C}$. Over the entire ozonation process, several samples were withdrawn from the reactor at desired intervals and were analysed quickly. Experiments of RO concentrate ozonation were conducted in triplicate.

Ozone balance was evaluated by recording continuously ozone concentration in the both gaseous and liquid phase. Three parameters for ozone consumption: i.e., applied ozone dose, transferred ozone dose, and consumed ozone dose, can be calculated based on ozone mass balance. Applied ozone dose (mg) reflected the total amount of gaseous ozone injected over the entire experiment, as expressed in Eq. (1). Transferred ozone dose (mg) referred to the accumulated amount of ozone transferred effectively from the gaseous phase to the liquid phase (Eq. (2)). Consumed ozone dose (mg) was described as the amount of ozone required to finish chemical reactions (Eq. (3)). In this work, ozone consumption referred to consumed ozone dose. Ozone transfer yield represented as a ratio of transferred ozone dose to applied ozone dose, as shown in Eq. (4).

$$O_3 \text{ applied} = \int_0^t [O_3]_{\text{gas-in}} Q_{\text{gas}} dt \quad (1)$$

$$O_3 \text{ transferred} = \int_0^t [O_3]_{\text{gas-in}} Q_{\text{gas}} dt - \int_0^t [O_3]_{\text{gas-out}} Q_{\text{gas}} dt \quad (2)$$

Table 1
Relevant properties and the expected ozone attacking site of target micropollutants.

Micropollutant	Carbamazepine	Ketoprofen
Use	Anti-epileptic	Anti-inflammatory
Formula	C ₁₅ H ₁₂ N ₂ O	C ₁₆ H ₁₄ O ₃
Molar mass (g mol ⁻¹)	236.3	254.3
pKa ^a	2.3, 13.9 ^b	4.5 ^b
Speciation at neutral or slightly basic pH	Neutral	Anion
Expected attacking site by ozone
Kinetic rate constant with ozone at pH 7 (L mol ⁻¹ s ⁻¹)	~3 × 10 ⁵ c	0.4 ^d
Kinetic rate constant with ·OH radicals at pH 7 (L mol ⁻¹ s ⁻¹)	8.8 × 10 ⁹ c	8.4 × 10 ⁹ d

(a) pKa: the acid dissociation constant at a logarithmic scale. (b) from Moffat et al. (2011). (c) from Huber et al. (2003). (d) from Real et al. (2009).

factor describes an increase in the rate of ozone mass transfer caused by the chemical reactions (Beltrán, 2004). The enhancement factor from experimental results (E_{exp}) can be calculated based on Eq. (5) (Triger, 2012).

$$E_{exp} = \frac{Q_{gas} ([O_3]_{gas-in} - [O_3]_{gas-out})}{k_L a V_{liq} ([O_3]_{liq}^* - [O_3]_{liq})} \quad (5)$$

$$[O_3]_{liq}^* = m [O_3]_{gas-out} \quad (6)$$

where $k_L a$ represents the volumetric mass transfer coefficient (s⁻¹), which is equal to 0.0052 s⁻¹ based on the result in pure water. $[O_3]_{liq}^*$ is the concentration of dissolved ozone at the equilibrium (mg L⁻¹). m is the solubility parameter of ozone in water solution, which takes a value of 0.31 from the findings of López-López et al. (2007).

2.4. Chemical analysis

COD was determined following HACH COD analysis procedure. Briefly, 2 mL of samples were added to a COD test vial (HACH) with a clean pipet, which was then digested in a preheated reactor (HACH Co., USA) at 150 °C for 2 h. COD of samples after heating was determined with a direct reading UV spectrophotometer (DR/2000, HACH Co., USA) at a wavelength of 420 nm. The measurement of both DOC and DIC were conducted with a TOC analyser (VCSH-TOC, Shimadzu, Japan) after samples passed through a 0.45 µm PES filter to remove bigger particles. Concentrations of anions (Cl⁻, N-NO₂⁻, N-NO₃⁻, SO₄²⁻ and P-PO₄³⁻) and cations (Na⁺, K⁺, N-NH₄⁺, Mg²⁺ and Ca²⁺) were analysed with ionic chromatography (IC) system (IC 25 and ICS-2000, Dionex, USA). Before ionic analysis, samples should be passed through a 0.2 µm PES filter.

The analytical determination of CBZ and KET in the aqueous solution was performed using reverse phase-HPLC (Agilent LC 1200, USA) equipped with UV diode-array detector. Separation was carried out with ZORBAX Eclipse XDB-C 18 column (4.6 × 150 mm, 5 µm) in the isocratic mode with ethanol of 55% and water of 45% (v/v). The injection volume and the flow rate were set as 20 µL and 1 mL min⁻¹, respectively. The system was operating at 40 °C. The analytical limit of detection (LOD) was 5 µg L⁻¹ for CBZ and 10 µg L⁻¹ for KET. The analytical limit of quantification (LOQ) was 17 µg L⁻¹ for CBZ and 33 µg L⁻¹ for KET.

$$O_3 \text{ consumed} = \left(\int_0^t [O_3]_{gas-in} Q_{gas} dt - \int_0^t [O_3]_{gas-out} Q_{gas} dt \right) - [O_3]_{liq(t)} V_{liq} \quad (3)$$

$$\text{Transfer yield (\%)} = \frac{\text{transferred ozone dose}}{\text{applied ozone dose}} \times 100 \quad (4)$$

where the unit of applied, transferred and consumed ozone dose is mg. $[O_3]_{gas-in}$, $[O_3]_{gas-out}$ and $[O_3]_{liq}$ are the concentration of ozone gas-in, -out and dissolved ozone at the reaction time t (mg L⁻¹), respectively. Q_{gas} and V_{liq} are the gas flow rate (Lh⁻¹) and the liquid volume (L), respectively.

In order to compare the ozonation efficiency of micropollutants with results obtained from other studies, a specific ozone consumption dose (g consumed O₃ per g DOC₀) was employed in this work, which can be obtained from consumed ozone dose normalized to the initial DOC amount of RO concentrate.

During the ozonation process, dimensionless Hatta number and enhancement factor were known to be two relatively important parameters to evaluate ozonation kinetic regimes. Taking account of the complexity of organic matters in real wastewater, it was not possible to discuss reaction regime in terms of Hatta number. Enhancement

Table 2
Characteristics of RO concentrate and RO observed retention of the selected parameters.

Parameter	Unit	RO feed	RO permeate	RO concentrate	Observed retention (%)	C _{concentrate} / C _{feed}
pH	-	7.9	7.8	8.2	-	-
Conductivity	mS cm ⁻¹	1.2 ± 0.1	0.3 ± 0.1	2.6 ± 0.1	72	3.0
DOC	mg L ⁻¹	20.3 ± 0.4	3.9 ± 0.1	50.8 ± 1.0	81	2.5
DIC	mg L ⁻¹	44.2 ± 0.9	8.5 ± 0.2	82.5 ± 1.7	81	1.9
COD	mg L ⁻¹	64.0 ± 2	4.0 ± 2	143 ± 10	94	2.2
Cl ⁻	mg L ⁻¹	232 ± 23	66.9 ± 6.7	536 ± 54	71	2.3
N-NO ₂ ⁻	mg L ⁻¹	0.5 ± 0.1	0.2 ± 0.1	1.29 ± 0.13	66	2.4
N-NO ₃ ⁻	mg L ⁻¹	7.8 ± 0.8	3.2 ± 0.3	0.37 ± 0.04	59	2.5
SO ₄ ²⁻	mg L ⁻¹	18.5 ± 1.9	3.3 ± 0.3	39.0 ± 3.9	81	2.3
P-PO ₄ ³⁻	mg L ⁻¹	2.2 ± 0.2	0.4 ± 0.1	2.5 ± 0.3	80	1.1
Na ⁺	mg L ⁻¹	120 ± 12	46.0 ± 4.6	286 ± 29	62	2.4
N-NH ₄ ⁺	mg L ⁻¹	nd	nd	nd	-	-
K ⁺	mg L ⁻¹	10.9 ± 1.1	3.4 ± 0.3	27.0 ± 2.7	69	2.5
Mg ²⁺	mg L ⁻¹	4.0 ± 0.4	1.0 ± 0.1	10.5 ± 1.1	74	2.6
Ca ²⁺	mg L ⁻¹	115 ± 12	27.7 ± 2.8	241 ± 24	76	2.1
CBZ	µg L ⁻¹	10.7 ± 0.2	2.2 ± 0.1	25.13 ± 0.50	80	2.3
KET	µg L ⁻¹	10.6 ± 0.2	1.5 ± 0.1	26.56 ± 0.53	86	2.5

Observed retention of a species (%) = ((C_{concentrate} - C_{permeate}) / C_{concentrate}) × 100, from Liu et al. (2014).

DOC: dissolved organic carbon. DIC: dissolved inorganic carbon. COD: chemical oxygen demand. nd: not detected.

Fig. 1. Ozonation pilot with a semi-batch reactor.

3. Results and discussions

3.1. Profile of ozone concentration and reaction kinetic regimes

Experimental plots of ozone concentration either in gaseous or liquid phase as a function of reaction time during the ozonation of RO concentrate are displayed in Fig. 2a. With respect to ozone gas-out, two stages, i.e., a rapid rise and a gradual increase, can be clearly identified. The first one took place during the first 15 min of ozonation, where the concentration of ozone gas-out elevated rapidly to 4.8 mg L^{-1} . During the following ozonation, the concentration of ozone gas-out increased slowly and gradually closed to that of ozone gas-in with a value of 10 mg L^{-1} . The gap between ozone gas-in and -out curve became narrower with ozonation, indicating chemical reactions enhancing the gas-liquid ozone transfer diminished along reaction time (Domenjoud et al., 2011).

As can be seen from dissolved ozone curve, two distinct kinetic regimes were undergone over the entire ozonation process, namely, a fast reaction kinetic regime and a kinetic regime at a moderate rate. No dissolved ozone was found during the first 60 min of ozonation, which meant that all the transferred ozone was consumed at the interface or in the film layer. The absence of dissolved ozone at the early stage of ozonation has been reported by several authors for the disposal of membrane concentrate by ozonation (Acero et al., 2016; Azaïs et al., 2016; Van Geluwe et al., 2011). It was assumed that chemical reactions of compounds with oxidants occurred relatively fast in this stage, and mass transfer of ozone was considered as a major limitation step. At the beginning of ozonation, a high enhancement factor (E_{exp}) from experimental results, with a value around 21, also provided evidence that ozonation kinetics was controlled by ozone mass transfer. Based on the double film theory equation, when the concentration of dissolved ozone was equal to 0 mg L^{-1} , the driving force of ozone absorption (dissolved ozone concentration at the interface - that in the liquid phase) was maximum (Beltrán, 2004; Marce et al., 2016), and a fast kinetic regime was undergone in the liquid film closed to gas-liquid interface because of fast chemical reactions (Aguinaco et al., 2012). In this work, no dissolved ozone detection at the beginning of ozonation was mainly related to the consumption of molecular ozone by ozone-reactive organic compounds like CBZ possessing olefin moiety. Indeed, dissolved ozone was found after 5 min ozonation of RO concentrate without micropollutants, as implied in Fig. S2 (See Supplementary Information). With the continuous ozonation, a rapid increase in dissolved ozone concentration was followed, and the concentration reached around 3 mg L^{-1} at the end of 180 min ozonation. The detection of dissolved ozone in this period suggested that chemical reactions transitioned from a fast kinetic regime to a moderate regime, and both mass transfer of ozone and chemical reactions were limiting steps. At the end of 180 min reaction time, a plateau was not achieved for dissolved ozone, which was not consistent with the observations from

ozonation of RO concentrate without CBZ and KET (See Fig. S2), implying chemical reactions of organic compounds with molecular ozone were not finished but quite slow. The nature and pollutants load of wastewater were responsible for the evolution of ozone gas-out and dissolved ozone curve (Marce et al., 2016).

Ozone consumption amount during the initial stage of ozonation can be represented by instantaneous (initial) ozone demand (IOD, mg L^{-1}) (Cho et al., 2010; Park et al., 2001). In a semi-batch reactor, IOD is defined as the transferred ozone dose before dissolved ozone was monitored (Marce et al., 2016). To determine IOD during the ozonation of RO concentrate, dissolved ozone concentration was plotted against transferred ozone dose (mg L^{-1}), as exhibited in Fig. 2b. As observed in this figure, transferred ozone dose at a concentration of 80.4 mg L^{-1} (in the first 60 min) was required to satisfy IOD, which was much higher than the one obtained from RO concentrate without micropollutants ($\sim 7 \text{ mg L}^{-1}$, see Fig. S2). This was not surprising taking account of a great contribution of highly concentrated micropollutants in RO concentrate to ozone consumption, as discussed later. In addition, this value was also larger than that from pure water containing similar levels of CBZ and KET ($\sim 10 \text{ mg L}^{-1}$ for IOD, see Fig. S3 in Supplementary Information), which was mainly related to the complexity nature of municipal RO concentrate including slightly basic condition and the presence of effluent organic matters. Justo et al. (2013) reported that transferred ozone of 90.3 mg L^{-1} was required when IOD was fulfilled for RO concentrate disposal. However, at a lower transferred ozone of $6.7\text{--}23 \text{ mg L}^{-1}$, IOD was satisfied during the ozonation of municipal nanofiltration concentrate treatment (Azaïs et al., 2016). IOD complement was strongly depending on load of organic matters in wastewater, especially for organic compounds containing the reactive moieties such as olefin, phenol and amine (Azaïs et al., 2016). Indeed, IOD of tertiary effluents (DOC: $6.5\text{--}13.2 \text{ mg L}^{-1}$) was in a range of $5\text{--}10 \text{ mg L}^{-1}$, whereas $64\text{--}348 \text{ mg L}^{-1}$ for primary effluents (DOC: $60\text{--}110 \text{ mg L}^{-1}$) (Marce et al., 2016). Once IOD was satisfied, dissolved ozone began to accumulate until a plateau achieved, as mentioned above.

Fig. 2c represents the evolution of applied ozone dose, transferred ozone dose and consumed ozone dose and ozone transfer yield as a function of reaction time. During the first 30 min of ozonation, a strong depletion in the ozone transfer yield, ranging from 100% to 58%, was noticed. After that, a linear reduction was followed with ozonation. At the end of 180 min ozonation, the yield reached around 40%, which was higher than 20% obtained during the ozonation of RO concentrate without target micropollutants (see Fig. S2). This also highlighted that chemical reactions were not finished completely after 180 min ozonation of RO concentrate.

3.2. Micropollutant removal

Fig. 3a plots the removal rate of two target micropollutants and dissolved ozone concentration as a function of cumulated consumed ozone dose during the ozonation of RO concentrate. Once ozonation was started, the concentration of both CBZ and KET decreased. A complete degradation of CBZ and a satisfactory removal of KET were achieved during the IOD complement stage (no dissolved ozone detected within 60 min), indicating that the degradation of these two micropollutants was mainly governed by the direct reaction with molecular ozone during the ozonation of RO concentrate. According to Wert et al. (2009), the oxidation of organic compounds via $\cdot\text{OH}$ radicals became less available before IOD was satisfied. Indeed, the presence of $\cdot\text{OH}$ radical scavengers including effluent organic matters (EfOM) and alkalinity inhibited chain reactions responsible for the generation of $\cdot\text{OH}$ radical from ozone decomposition. The $\cdot\text{OH}$ radical scavenging rate was linked to the consumption of radicals by each scavenger species, which was estimated by considering the concentration of scavengers ($[i]$) and their corresponding rate constant with $\cdot\text{OH}$ radicals ($k_{\text{OH}\cdot i}$). At present, dissolved organic matters (DOM) and alkalinity, acted as two main $\cdot\text{OH}$ radical scavengers, have been widely reported in the previous studies (Azaïs

Fig. 2. Ozonation behaviour of municipal RO concentrate. (a) Profile of gaseous and dissolved ozone concentration as a function of reaction time. (b) Determination of initial ozone demand. (c) Ozone mass transfer yield. The unit of IOD is often expressed as mg L⁻¹ in previous studies, so the unit of transferred ozone dose is also set as mg L⁻¹ in Fig. 2b. Initial DOC: 50.8 mg L⁻¹. Initial pH: 8.2. The liquid volume: 2 L. The gas flow rate: 30 L h⁻¹.

et al., 2016; Beltrán, 2004; Miralles-Cuevas et al., 2017). Their values of $k_{OH\cdot} \times [i]$ as a criterion for radical scavenging rate are listed in Table 3. DOM exhibited a higher scavenging contribution than alkalinity during the ozonation of RO concentrate, which was in well agreement with the results described by Nöthe et al. (2009) and Suarez et al. (2007) for wastewater ozonation.

As observed in Fig. 3a, with respect to CBZ, its load dropped quickly with ozonation. At an ozone dose of 0.33 g consumed ozone per g DOC₀ corresponding to 10 min reaction time, >90% of CBZ was disappeared. A similar observation was also found during the ozonation of RO concentrate containing a lower concentration of micropollutants (at µg L⁻¹ range), where an ozone dose of 0.31 g consumed ozone per g DOC₀ could remove ~85% of CBZ from RO concentrate (see Fig. S4 in Supplementary Information). However, this dose for >90% removal of CBZ was different with the one reported in the previous literature. Joss et al. (2011) observed that more ozone dose (0.85 g consumed ozone per g DOC₀) was consumed to remove >90% of CBZ from RO concentrate. In another study, a similar level of ozone consumption (0.82 g consumed ozone per g DOC₀) only eliminated around 60% of CBZ (Justo et al., 2013). The difference in ozone consumption for >90% removal of CBZ was linked to the nature of the tested RO concentrate. Inorganic constituents and organic substances present in wastewater were able to be in competition with molecular ozone and ·OH radicals oxidants. To address this point, ozonation of CBZ and KET with a similar

concentration (~25 mg L⁻¹) was performed in pure water under the same operating conditions, and the results are depicted in Fig. 3b. The initial ~25 mg L⁻¹ of CBZ was reduced to the limit of detection at a low ozone consumption of 30 mg corresponding to 10 min reaction time. This finding evidenced the reaction of constituents in RO concentrate with oxidants.

When an excellent disappearance for CBZ was achieved in the first 10 min of contact time, only 5% of KET was eliminated at the same reaction time. After CBZ was degraded completely, the concentration of KET was abated quickly. >160 mg consumed ozone (>1.58 g consumed ozone per g DOC₀) was required to degrade KET to below the limit of detection, which was around 2.3 times higher than that in pure water with consumed ozone dose of around 70 mg. This significant difference in ozone consumption for a satisfactory removal of KET between RO concentrate and pure water supported that the presence of organic constituents and inorganic ions in wastewater exhibited pronounced effects on the degradation of KET by ozonation. At present, literature on ozonation efficiency of KET in RO concentrate was not available. However, ozonation efficiency of KET in municipal secondary effluents was widely reported. Ozone consumption of 1.2 g applied ozone per g DOC₀ was sufficient to eliminate 90% of KET (Hübner et al., 2013). 79%–86% of KET was reduced from municipal secondary effluents at an ozone dose of 0.72 g transfer ozone per g DOC₀ (Singh et al., 2015). An ozone dose of 0.4 g transferred ozone per g DOC₀ only achieved 70% elimination

Fig. 3. Removal of CBZ and KET as a function of cumulated consumed ozone dose in RO concentrate (a) and pure water (b). The initial pH: 8.2 for RO concentrate and 4.6 for pure water. The liquid volume: 2 L. The gas flow rate: 30 L h⁻¹.

for KET during the ozonation of municipal wastewater (Penru et al., 2016). These observations underlined a fact that a large ozone dose was required for an excellent degradation of KET in municipal wastewater.

Regardless of water matrix (RO concentrate or pure water), at the same ozone consumption, a higher elimination rate for CBZ than KET was noticed, as indicated in Fig. 3. The reason for this was associated with their different reactivity towards molecular ozone. When CBZ and KET co-existed in the solution, molecular ozone preferred to attack CBZ instead of KET. Indeed, ozone was selective to react with organic compounds containing electron-rich functional groups, including unsaturated carbon bonds ($\text{C}=\text{C}$), activated aromatic system, phenol, and non-protonated amine (De Vera et al., 2015; Derco et al., 2015; Hoigné and Bader, 1976; Lee and von Gunten, 2016). The most reactive site in CBZ structure was carbon double bond at the central heterocyclic ring, which was commonly attacked by ozone as electrophilic agent, with a second-order rate constant with molecular ozone (k_{O_3}) of $\sim 3 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ (Huber et al., 2003). Nonetheless, KET has a relatively low reactivity towards ozone and about $0.4 \text{ L mol}^{-1} \text{ s}^{-1}$ of ozone kinetic rate constant was already reported by Real et al. (2009).

Based on the discussion above, it can be concluded that ozonation was effective in removing CBZ and KET from RO concentrate. Since high contents of organic species and inorganic constituents were present in RO concentrate, more ozone consumption was required for a satisfactory elimination of KET.

3.3. Transformation of micropollutants

During the ozonation process of micropollutants in wastewater, intermediates and by-products were formed (Bourgin et al., 2015; Knopp et al., 2016). Identification of main transformation products of micropollutants by ozonation was mainly performed with ultrapure water containing individually each pollutant based on the reported

literature. At present, regarding CBZ, its oxidation pathway has been proposed frequently in the literature (Alharbi et al., 2016; Azaïs et al., 2017; Hübner et al., 2014; McDowell et al., 2005; Tootchi et al., 2013), and four main ozonation by-products, including 1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one (BQM), 1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione (BQD), 1-(2-benzoic acid)-(1H,3H)-quinazoline-2,4-dione (BaQD) and 1-(2-benzoic acid)-4-hydro-(1H,3H)-quinazoline-2-one (BaQM), have been previously described. However, information on transformation products of ketoprofen by ozonation was still limited. Only Illés et al. (2014) proposed four major aromatic intermediates. To date, there was little information concerning oxidation by-products of micropollutants in municipal RO concentrate.

Fig. 4 displays evolution of area of peak observed in HPLC-UV spectrum during the ozonation of RO concentrate. Once ozonation reaction started, a fast decline in CBZ concentration was undergone, whereas a peak at the retention time of about 2.3 min occurred quickly and its area achieved the maximum during the first 5 min of ozonation. This intermediate was likely to be BQM as a primary intermediate of CBZ based on the reported literature. With the continuous ozonation, the area of this peak decreased along ozonation and disappeared completely within the first 30–60 min ozonation. BQM with ozone kinetic rate constant of $\sim 7 \text{ L mol}^{-1} \text{ s}^{-1}$ was higher than that of KET (Hübner et al., 2014), demonstrating that molecular ozone preferred to attack BQM when BQM and KET co-existed. Therefore, the presence of Peak-2 with a maximum concentration in the first 30–60 min of ozonation was mainly due to further reactions of BQM with molecular ozone. Similar peaks were also observed during the ozonation of a mixture containing CBZ and KET in pure water (See Fig. S5 in Supplementary Information). It should be pointed out that, in pure water, the area of Peak-1 and Peak-2 reached the maximum in the first 3–6 min and 10–20 min reaction time, respectively. This finding also confirmed that constituents present in municipal RO concentrate consumed oxidants to some extent.

Alharbi et al. (2016) and Hübner et al. (2014) observed that 40%–60% of CBZ was oxidized to primary transformation product BQM, and then the reactions of BQM with molecular ozone can produce either BQD or BaQM. However, their kinetic rate constants with molecular ozone were relatively low, with values $< 10 \text{ L mol}^{-1} \text{ s}^{-1}$. McDowell et al. (2005) reported that the total amount of BQM and BQD produced during the ozonation surface water accounted for around 80% of CBZ.

Given that relatively low reactivity of KET with molecular ozone and limitation of HPLC-UV analysis for transformation products, there was

Table 3
·OH radicals scavenging rate of main scavengers at the beginning of ozonation of RO concentrate.

Scavenger	[i] ₀ (mg L ⁻¹)	k_{OH-i} (L mol ⁻¹ s ⁻¹)	Scavenging rate (s ⁻¹)
DOC	50.8	$4.41 \times 10^4 ((\text{mgC/L})^{-1} \cdot \text{s}^{-1})^a$	2.2×10^6
HCO ₃ ⁻	416.8	$8.5 \times 10^6^b$	5.8×10^4

(a): from Azaïs et al. (2016). (b) from Beltrán (2004).

no significant peak for oxidation by-products of KET. The mechanism for formation of transformation products from the ozonation of CBZ and KET in RO concentrate was quite complex and would not be discussed in this work.

3.4. Organic matters degradation

The evolution of residual COD and DOC and dissolved ozone concentration versus consumed ozone dose is represented in Fig. 5. The concentration of both COD and DOC reduced almost linearly with ozonation. When extending ozonation time to 180 min (a complete removal for the target micropollutants), 64% reduction in COD was noted. Ozonation process was not able to degrade organic matters to a significant level, only with 33% mineralization in terms of DOC removal, which mainly resulted from the formation of intermediates and by-products. Such organic chemicals have been proven to be refractory to further ozonation process (Martins and Quinta-Ferreira, 2014). Low reduction of DOC and moderate elimination of COD suggested that transformation step played a predominant role in ozonation process of RO concentrate instead of mineralization. In this work, the main objectives were to investigate the kinetic regimes and micropollutant removal from municipal RO concentrate, thus, it was not necessary to prolong ozonation time to achieve a significant removal for organic matters.

On the other hand, the concentration of the tested cations and anions remained almost constant throughout the experiment. Since the contents of NO_2^- and NH_3 in RO concentrate were relatively low or below the limit of detection, ozonation did not exhibit significant impacts on their concentration. The pH decreased from the initial 8.1 to 7.6 at the end of 180 min ozonation.

It should be noted that, it was possible that ozone-treated effluents were more toxic and hazardous than the untreated one (Beltrán et al., 2009; Illés et al., 2014). Taking account of biodegradability improvement of ozone-treated effluents, therefore, other subsequent treatment system such as biological unit was recommended to enhance mineralization of organic matters (Acero et al., 2016; Azaïs et al., 2016; Justo et al., 2015).

4. Conclusions

The following conclusions were obtained from the present work investigating the kinetic regimes and ozonation efficiency of micropollutants in RO concentrate produced from RO treatment of municipal wastewater.

Fig. 4. Evolution of peaks during the ozonation of CBZ and KET in RO concentrate.

- No detection of dissolved ozone during the first 60 min and a relatively high enhancement factor at the initial ozonation stage indicated that chemical reactions took place at a fast rate, and ozone mass transfer was a limiting step. With the continuous ozonation, the fast kinetic regime transitioned to a moderate regime.
- Direct reaction via molecular ozone was a main oxidation pathway being responsible for degradation of carbamazepine (CBZ) and ketoprofen (KET) in RO concentrate. Indeed, a complete elimination of CBZ and a satisfactory degradation of KET were observed in the absence of dissolved ozone.
- Ozonation was more effective in removing CBZ than KET, which was related to a higher reactivity of CBZ (containing olefin moiety) towards molecular ozone.
- During the ozonation of RO concentrate, transformation step was predominant instead of mineralization.
- Overall, ozonation process was a feasible technology for disposal of municipal RO concentrate in terms of micropollutant removal.

To achieve zero discharge of micropollutants from municipal secondary effluents, further studies, such as relationship between ozonation intermediates and potential toxicity, performance of biological process for ozone-treated effluents, need to be extended.

Declaration of competing interest

The author reports no conflicts of interest. The author alone is responsible for the content and writing of this article.

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Supplementary data

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Fig. 5. Variation of DOC and COD as a function of cumulated consumed ozone during the ozonation of RO concentrate.

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