Supercritical water oxidation of recalcitrant organic pollutants present in retentates from RO desalination of secondary effluents

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ABSTRACT

This work focuses on applying supercritical water oxidation (SCWO) for eliminating residues of pharmaceutical, endocrine-disruptor and pesticide species from the reject of reverse-osmosis-treated secondary municipal wastewater. SCWO, a well-known treatment method for organic sludge and highly concentrated wastewaters, has not yet been investigated with reverse osmosis (RO) retentates of municipal secondary effluents. The results shown here, focusing on batch SCWO of municipal effluent RO retentate spiked with emerging pollutants, demonstrate the potential of utilizing this single advanced-oxidation generic treatment to fully-mineralize the vast variety of organic species encountered in municipal wastewater effluents, while at the same time lowering its total organic carbon concentration by up to 99%. The chosen model pollutants (carbamazepine and 17β-Estradiol both in synthetic solution and within a real effluent RO retentate matrix) and the effluent's background organic matter, started to degrade already at subcritical conditions, however near-complete mineralization of the full matrix (including transformation products) was invariably attained only at fully-established supercritical conditions (450°C–540°C). The extreme hydrothermal oxidation conditions applied in this work allowed for simultaneous oxidation of target molecules and background organic species throughout the applied temperature range, while the phenomenon known as "radicals scavenging" by the background organic matter, was not observed. A new technique is introduced in this work for controlling the pressure within semi-batch SCWO experiments.

Keywords: SCWO; Effluent RO retentate; Carbamazepine; 17β-Estradiol

1. Introduction

Modern societies utilize a wide variety of organic chemicals for medical, cosmetic, industrial and agricultural purposes. Many of these chemicals are eventually found at the μg/L to ng/L scale in reclaimed water sources and groundwater [1–3]. Meanwhile, rapidly expanding population, escalating water consumption and dwindling water resources have severely aggravated the water shortage problem on a global scale, particularly in arid and water-stressed countries, making wastewater reuse a viable approach for meeting current and future water demands in many parts of the world [4–8]. Among various reclaimed water sources, secondary/tertiary effluents from wastewater treatment plants (WWTPs), that is, biologically treated municipal wastewater, represent a stable, non-seasonal source. Israel is a global leader in the reclamation of treated wastewater; 40% of the Israeli agricultural water allocation originates from reclaimed wastewater. Challenges, however, have remained to develop extensive, successful and safe reuse schemes [9]. Secondary effluent is a complex wastewater matrix consisting of traditional pollutants such as high total dissolved solids (TDS) content (typically > 1,500 mg/L), effluent organic

matter (EfOM), and pathogens [6,10–12] along with emerging contaminants (e.g. pharmaceuticals, hormones, personal care products, etc.) [13].

The occurrence of forty emerging pollutants in the influent and effluents of WWTP in China, South Korea, and various European countries was reviewed [14]. The reported accumulated concentrations were 200–300 µg/L, which accounted for 2%–3% of the effluent total organic carbon (TOC) or 2%–5% of the dissolved organic carbon [9]. Obviously, without appropriate treatment, certain wastewater-derived pollutants of ecological and health concern would remain in the reclaimed water and/or accumulate in the soil [14–22], invariably infiltrating thereafter into the food chain [23,24]. In most countries, there is no environmental regulation focusing on emerging pollutants. However, in 2015, the European Union issued a "watch list" of ten major pharmaceutical and endocrine-disrupting chemicals (EDC) [25]. In 2016 Switzerland was the first and thus far the only country to issue a formal regulation [26], enforcing WWTPs to install, over the next twenty years, the required facilities for the removal of twelve indicator emerging pollutants, at a minimal overall efficiency of 80%. The environmental cost of five selected pharmaceutical pollutants was evaluated [27] by calculating the shadow prices for different ecosystems. The environmental benefit of the removal of these micropollutants was estimated at 0.1–128 €/mg for various pollutants and ecosystems. Accordingly, even a very conservative estimate of an average shadow cost of 2.0 €/mg translates into huge environmental cost of 400 Euros for each m³ of WWTP effluent.

Traditional methods for environmental remediation of non-biodegradable pollutants involve pretreatment by different physical-chemical processes such as oxidation, photo-catalysis, photo-Fenton reactions, adsorption, filtration, advanced biological treatment and precipitation [28–32]. Careful consideration of the application of these methods as a pretreatment for secondary municipal effluents RO desalination process [33] or as post-treatment for raw municipal wastewater [34] reveals specific drawbacks that limit their application. Activated carbon adsorption is limited by high cost and difficulty of regeneration. Advanced oxidation processes (AOPs) are generally very energy-intensive and often do not result in full mineralization. Hydroxyl radicals unselectively react with target pollutants and co-existing species, resulting in low efficiency. Ozone is limited by its low solubility, high cost, safety concerns, and the production of disinfection byproducts (e.g. bromate), some of which are more toxic than their mother molecule [35]. Second, the presence of multiple contaminants in secondary effluent requires a treatment train comprising of several treatment unit operations, each targeting specific contaminants, making the design and operation cumbersome and costly, with a large physical footprint. Innovative, technically sound, simple to operate, and cost-effective technologies are thus in high demand to address these multiple contaminants for water reuse, applied as post-treatment for RO desalination retentate. The coupling of membrane filtration and AOP was recently reviewed [34]. Several AOPs [28,31,36] (e.g. ozonation, peroxone, photo-Fenton, photocatalysis and electrochemical AOP) were successfully integrated as a pretreatment or a post-treatment for RO desalination and as a combined process. However, all these AOPs suffer from the abovementioned drawbacks. The inevitable conclusion is that the RO retentate, emanating from desalination of partially treated effluents at 10%–15% of the original flow rate, and containing a large fraction of the original organic contaminants at varying oxidation states, should be further treated using a fiercer method, on the one hand, but also a more generic one, on the other.

The purpose of this work was to assess the applicability of supercritical water oxidation (SCWO) as a new treatment method for the removal (complete mineralization) of emerging pollutants encountered in secondary effluents, and particularly in RO retentate emanating from their desalination.

In its supercritical state ($T > 374°C$, $P > 220.6$ bar), water has very low dielectric constant, which enables much faster oxidation of organics [37], and possible desalination capabilities, that in some cases can minimize concentrated retentate discharge to an almost zero liquid discharge (ZLD) operational conditions [38]. SCWO is a known thermal AOP treatment method which is to-date only considered in special cases of concentrated organic wastewater and sludge or highly toxic wastes with limited applicability, due to the high operation and installation costs involved [39,40]. At supercritical water environment, organic pollutants can be oxidized completely to CO_2 at efficiencies exceeding 99.99% at a short residence time, extending from few seconds to few minutes ([41] and others).

RO retentate emanating from secondary effluent desalination typically contains a much lower concentration of pollutants, as compared to the "common" SCWO feed streams, in terms of both organic components and TDS. It appears hence more suited to continuous operation at milder temperature and pressure, by using lower oxidant concentrations, thereby resulting in less corrosion and plugging problems than those experienced with SCWO applications addressing the more concentrated brines [40]. Operation at such milder conditions may also enable efficient heat and pressure exchange, resulting in reduced operating costs. Successful implementation of SCWO for the proposed application can establish a single solution tool for the full mineralization of emerging pollutants in secondary WWTP effluents. Future coupling with salts separation in a nearly ZLD manner should enable safe recovery of all municipal wastewater, with minimum environmental and toxicological effects.

The aim of the semi-batch SCWO experiments presented in this work was to provide insight into the possible implementation of a continuous SCWO system treating RO retentate of municipal secondary effluents. The paper reports on 35 semi-batch SCWO experiments that examined the degradation efficiency of carbamazepine (CBZ) and 17β-Estradiol (E2) and some of their known transformation products, both within synthetic solutions and as part of a municipal effluent RO retentate matrix. In some of the trials, retentate solutions spiked with CBZ and E2 were tested in the presence of isopropyl alcohol (IPA) as a co-fuel.

2. Materials and methods

2.1. Model emerging pollutants

As briefly mentioned, trace pharmaceutical contaminants in municipal wastewater are modeled in this research

by CBZ (Fig. 1), and EDCs by 17β-Estradiol (E2) (Fig. 2). CBZ is a synthetic drug used as an anticonvulsant medication, primarily in the treatment of epilepsy and neuropathic pain. CBZ and E2 are emerging pollutants commonly found in secondary municipal effluents. E2 is included in the 2015 European community watch list [25] while CBZ appears in the 2016 Switzerland emerging pollutants treatment act [26], as one of the 12 refractory pollutants indicators for effective removal. Both model pollutants represent the wide range of occurrence of the dozens of thousands of emerging pollutants that exist in secondary effluents. CBZ typically appears in the µg/L range and Estradiol in the ng/L range [3,14,15,42].

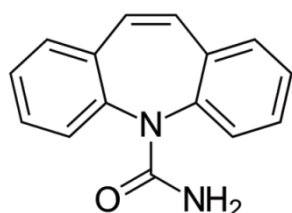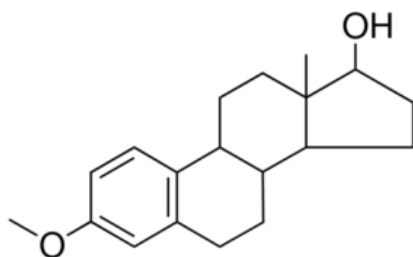The occurrence, toxicity and possible treatment methods of CBZ and E2 had been addressed in numerous works in the last 20 years. Table 1 reviews some of the recent published works and lists possible treatment methods for CBZ and E2 in wastewater and aquatic systems.

To the best of the authors' knowledge, results from SCWO of CBZ, E2 and secondary municipal effluent RO retentate, have not been reported before.

2.2. Preparation of tested synthetic solutions

Synthetic solutions were prepared using analytical grade chemicals Sigma-Aldrich (Saint Louis, USA), Table 2.

Both CBZ and E2 are sparingly soluble in water [44,59–62]. To overcome CBZ's low solubility, a synthetic solution comprising 25 mg CBZ was dissolved in 50 mL mixture of 80% methanol and 20% water. However, since the presence of methanol disallows CBZ mineralization analysis and may also act as a co-fuel [63], this solution was used only for the calibration of analytical instruments and for preliminary CBZ SCWO experiments. For other experiments, a saturated aqueous solutions of CBZ and E2 were prepared by over-dosing of solid CBZ or E2 (separately), keeping the solid particles in the master solution flask's bottom, for ensuring solid/water equilibrium. For all synthetic oxidation runs involving CBZ or E2, such saturated master solutions were prepared.

Fig. 1. Carbamazepine (CBZ) [43].

Fig. 2. 17β-Estradiol (E2) [44].

2.3. Effluent desalination and retentate composition

Two different sources of secondary effluents RO retentates were tested. The first was taken from a secondary-effluent RO desalination-pilot plant, fed from a commercial activated-sludge WWTP (Nir Etzion, Israel). The second source was secondary effluents obtained from a domestic WWTP (Haifa, Israel).

The latter secondary effluents were acidified to pH6, ultra-filtrated and desalinated through a Dupont Filmtec 2540 XLE (Edina, MN, USA) brackish RO membrane at recovery ratio of 86% and TOC rejection of 96.5%, following the procedure in [64]. Characteristic compositions of both RO retentates that were used in this study are listed in Table 3.

Table 1
Recent investigations and reviews for treatment processes for CBZ and E2

Pollutant	Treatment	Removal efficiency	Reference
CBZ	Gamma radiation and ferrate oxidation	CBZ 21.5%–100%, TOC 18.3%–60.6%	[45]
	Photo-Fenton	CBZ 40%–100%	[46]
	Electro-chemical degradation by chlorine or persulfate	CBZ 73%–95.5%, TOC 14.9%–50%	[47]
	Hydrodynamic cavitation combined with various AOPs	CBZ 38.7%–100%	[48]
E2	Catalytic activated persulfate degradation	E2 40%–100%, TOC 62.5%–71.4%	[49]
	Biotransformation by algae	E2 100%	[50]
	Fe^{+3} saturated montmorillonite	E2 40%–80%	[51]
EDCs	Granular activated carbon, UV photolysis, UV photocatalysis, ozonation	100%, 100%, 45%–80%, 95%, respectively	[52]
	Review of elimination methods		[53]
Pharmaceutical wastewater	Sub and supercritical water oxidation	CBZ 90.27%–98%	[54]
	Sub and supercritical water oxidation	CBZ – partial, TOC 97.8%	[55]

Table 2
Analytical grade chemicals used for synthetic solutions preparation, and for the spiking of real effluents

Chemical	CAS #	Formula	MW [g/mol]	Represent
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.27	Carbamazepine
Acridine	260-94-6	$C_{13}H_9N$	179.22	One of the Carbamazepine degradation products [56]
17β-Estradiol	50-28-2	$C_{18}H_{24}O_2$	272.38	17β-Estradiol
Estrone VETRANAL	53-16-7	$C_{18}H_{22}O_2$	270.37	Estradiol degradation product (E1) [57,58]
Starch	9005-84-9	$(C_6H_{10}O_5)_n$	342.3	Soluble microbial products (SMP), as 80% of the effluent organic material (EfOM) [36]
Humic acid sodium salt	68131-04-4	$C_9H_8Na_2O_4$	226.14	Natural organic matter (NOM), as 20% of the effluent organic material (EfOM) [36]

Table 3
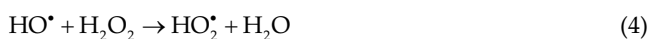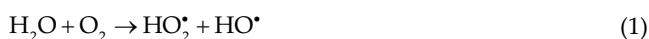Characteristics of secondary effluents and their RO retentate

Parameter	Nir Eztion's effluents' RO retentate	2nd effluents from Haifa's WWTP	Haifa's secondary effluents' RO retentate
pH	7.7	8.4	5.9
TOC (mg/L)	81.3 ± 6.1^b	17.18 ± 0.14	54.03 ± 1.37
COD (mg/L)	414.4 ± 48.6	127.2 ± 2.4	724.6
Alkalinity (mg/L as $CaCO_3$)	448.1 ± 157.9^b	229.48 ± 0.59	8.57 ± 0.65^a
Ca^{2+} (mg/L)	598.2 ± 1.1	38.2 ± 0.9	236.5 ± 3.4
K^+ (mg/L)	285.8 ± 0.3	18.7 ± 0.3	97.1 ± 2.6
Mg^{2+} (mg/L)	167.9 ± 0.3	9.7 ± 0.1	58.0 ± 0.1
Na^+ (mg/L)	$1{,}242.6 \pm 1.5$	107.4 ± 2.9	603.4 ± 7.0
P (mg/L)	72.3 ± 0.2	4.9 ± 1.3	10.6 ± 2.2
SO_4^{2-} (mg/L)	$1{,}057 \pm 1.3$	30.6 ± 0.7	158.5 ± 0.7
Cl^- (mg/L)	$1{,}467.5 \pm 12.0$	159.6 ± 2.3	$1{,}892.7 \pm 29.7$

Values represent average and standard deviation of 3 replicates.
[a]Acidified, [b][65].

2.4. Oxidizing agent

Three externally-added oxidants have been commonly used within SCWO: compressed oxygen, compressed air and hydrogen peroxide solution [40,66]. As reported by others [67,68], hydrogen peroxide, water and oxygen are involved in a set of loop homolysis and redox free radical side reactions which are greatly favored at SCW conditions [69,70], enabling inter-changeable use of oxygen and hydrogen peroxide (Eqs. (1)–(4) and Fig. 3).

$$H_2O + O_2 \rightarrow HO_2^{\bullet} + HO^{\bullet} \tag{1}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \tag{2}$$

$$H_2O_2 \rightarrow HO^{\bullet} + HO^{\bullet} \tag{3}$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{4}$$

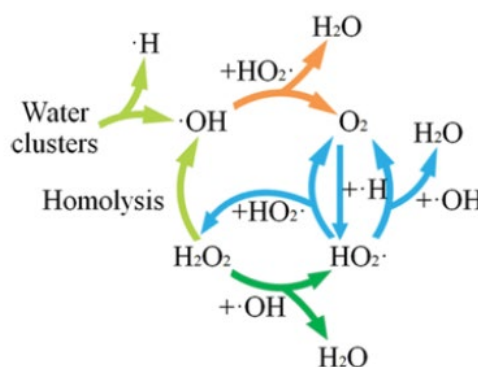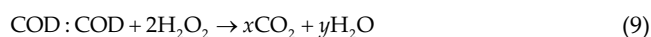For convenience reasons, hydrogen peroxide 30% solution was used in all the experiments in this work. Additionally,
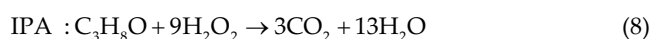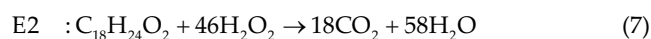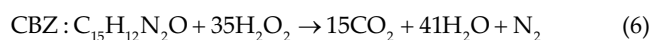

Fig. 3. Sources of active radicals in the SCWO process [71].

as proposed and demonstrated by others, for example, [63,72,73], the addition of IPA, methanol or ethanol as co-fuels and co-oxidants, increases the oxidation rate of the organic matter in solution by producing organic radicals. Hence, in this research, IPA was added in some of the experiments at a molar IPA to TOC ratio proposed by others [74], for the

oxidation of dimethyl formaldehyde. The basic H_2O_2 oxidation stoichiometric reactions for CBZ, E2, chemical oxygen demand (COD) and IPA are:

$$H_2O : 2H_2O_2 \rightarrow 2H_2O + O_2 \tag{5}$$

$$CBZ : C_{15}H_{12}N_2O + 35H_2O_2 \rightarrow 15CO_2 + 41H_2O + N_2 \tag{6}$$

$$E2 \quad : C_{18}H_{24}O_2 + 46H_2O_2 \rightarrow 18CO_2 + 58H_2O \tag{7}$$

$$IPA \quad : C_3H_8O + 9H_2O_2 \rightarrow 3CO_2 + 13H_2O \tag{8}$$

$$COD : COD + 2H_2O_2 \rightarrow xCO_2 + yH_2O \tag{9}$$

The required oxidant dose for the synthetic solutions experiments was calculated according to the feed composition and factored according to the oxidation stoichiometry. Oxidant dose for the effluent experiments was calculated according to the measured COD and the concentration of the added IPA.

2.5. SCWO reactor

Batch non-mixed oxidation experiments were performed in a 3/4″ stainless steel spool (Wall thickness = 3 mm), connected to a pressure transmitter, thermocouple and the required piping, as schematically shown in Fig. 4. All piping parts were purchased from Sitec High-Pressure Technology AG, Switzerland. The reaction spool was placed in a horizontal 2″ Carbolite (Carbolite Gero, Hope Valley, UK) pipe furnace.

Temperatures and pressures were recorded continuously throughout the experiments. The 200 mm spool was filled with 23 ml of feed reaction solution, connected to an outside pipe filled with deionized water. Two-needle valves were used for solution purging and sampling.

As the temperature increased, 1–2 ml samples were drained, enabling the control of system pressure and monitoring reactor composition with time. To our knowledge, such technique has not been used before for semi-batch monitoring of SCWO experiments. The reactor was heated to temperatures of 350°C–600°C and reached pressures of up to 400 bar. All temperature and pressure measurements were recorded using a LabVIEW interface with a sampling rate of 2 s.

2.6. Description of oxidation experiments

The experiments were divided into five groups, to examine the behavior and capabilities of the experimental system and to investigate the hydrothermal oxidation of different solution matrices, ranging from relatively simple cases (synthetic single-contaminant solutions) to actual secondary RO-retentate matrices. The first section comprised of four runs aimed at verifying the hydraulic behavior of the system and serve as feasibility tests for the oxidation of CBZ and NOM + SMP solutions.

The second group of experiments consisted of ten runs of synthetic CBZ solutions at the mg/L through µg/L concentration range, conducted at the highest/lowest temperatures and pressures within the supercritical water region, and with varied oxidant to pollutant stoichiometric ratios (OC). The third group of experiments consisted of eight E2 synthetic-solution oxidation runs conducted throughout the subcritical and supercritical water region, at different OCs. The fourth and fifth groups consisted of seven and six oxidation runs, respectively, with the RO retentates from Nir Eztion and Haifa secondary effluents, in three experimental combinations, to examine the pollutants degradation and TOC mineralization in real effluent matrices. In all the experiments, the oxidant and the co-fuel were premixed with the sample before it was fed to the reactor.

The removal efficiency in the case of specific pollutant or the mineralization efficiency in the case of TOC, were calculated according to Eq. (10), where C_i is the relevant concentration, and C_0 is the feed concentration.

$$\eta = 1 - \frac{C_i}{C_0} \tag{10}$$

2.7. Analyses

Samples taken from Valve 2 (Fig. 4), were used for composition, and TOC measurements. The small volume of the samples dictated measuring techniques that do not require large sample volumes, (e.g. within the LCMS quantification limits for any of the target molecules).

2.7.1. Quantification of model pollutants

Analysis of model pollutants and selected transformation products was performed by a LC–ESI–MS–MS
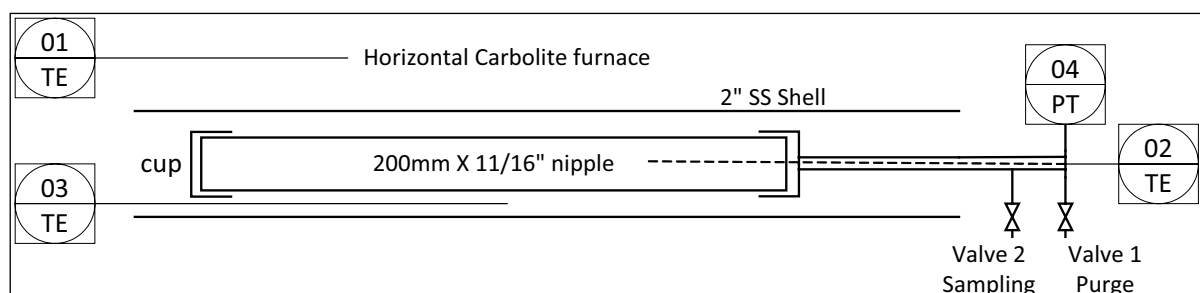

Fig. 4. Semi batch supercritical oxidation apparatus. TE01 = oven temperature, TE02 = reactor temperature, TE03 = shell temperature, PT04 = reactor pressure.

(LCMS) system composed of Agilant 1100 HPLC (Agilant Technologies, Waldbronn, Germany) equipped with quaternary Pump, degasser, column oven, auto-sampler and coupled to an Applied Biosystems Sciex API 3200 triple-quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with electrospray ionization (ESI). The CBZ concentration oxidation experiments were analyzed using a calibration curve in the range 0.05–50 µg/L, to allow for a clear signal of the CBZ in the used LCMS protocol. All samples were subjected to 0.2 µm filtration and were thereafter diluted with deionized water to the LCMS calibration range. A detailed description of LCMS analytical procedures appears in the Supplementary File.

2.7.2. Total organic carbon measurement

TOC was measured by a Sievers M5310C (Suez Water Technologies, Boulder Co, USA) TOC Analyzer with a detection range of 0.04–50 mg/L. All samples were filtered in an Eppendorf high-speed centrifuge and diluted with deionized water to the instrument's allowed conductivity range and a minimum volume of 11 ml, enabling at least 4 repetitions. Blank TOC of all sampling procedures were measured and accounted for in the TOC balance.

2.7.3. Further analytical methods

The COD of the effluent solution was measured by the ASTM method 5220 [75]. Effluent inorganic characterization was performed by Thermo Fisher Scientific ICP-AES (Thermo Fisher Scientific, Cambridge, UK), to determine the Na, Mg, S, P, Fe, Ca, K dissolved concentrations. The chloride concentration was measured by the argentometric method, according to the Standard Methods 4500-Cl [75]. The effluent alkalinity was measured by the Gran titration method [75]. Hydrogen peroxide concentration was analyzed by permanganate titration method, as detailed in [76].

3. Results and discussion

The major observation that can be drawn from Table 4, which lists the operational parameters and removal efficiencies in all the executed experiments, is that both CBZ and E2 can be almost fully degraded (above 98.6% for CBZ and 99.9% for E2) under the applied experimental conditions, also when they appear in the presence of a very high (orders of magnitude higher than the target pollutants themselves) and diverse organic matter background, emanating from the actual WWTP effluents. No such findings appear in the literature addressing CBZ and E2 within SCWO, nor in the context of municipal effluents RO retentates, underlining the novel nature of this study. The following sections discuss the applied operational conditions and the results obtained in the individual experiments.

The batch treatment system applied in this work cannot be used to infer on oxidation kinetics, nor can it be used to learn on the steady-state results that can be attained at the various temperatures on the way to the maximal temperature that was applied in each test. The only result that can be considered valid at steady state is the one recorded at the final T/P condition, that is, the ultimate experiment supercritical conditions. Nevertheless, we report here on the results that

were attained in the various T/P points on the way, because they contribute information on species that can break down also at subcritical conditions. The reader is however advised to consider these intermediate results only as qualitative, and only the ultimate result as a quantitative one. Having said this, a previous comparison between batch and continuous SCWO of pesticide-containing wastewater [77], reported on differences of only a few percent in the recorded degradations between slow-heating batch oxidation conditions and continuous SCWO experiments, applied at the same operating conditions.

3.1. System pressure/temperature profile

The physical behavior of the semi-batch reaction system was examined in a preliminary experiment in which the reactor and piping were filled with deionized water. Fig. 5 shows the typical behavior of both the pressure and the temperature in the semi-batch reactor. As the temperature increased, the density of the water was reduced, and the vapor pressure increased. As a result vapor phase formed to attain equilibrium with the liquid water at the given conditions.

Every few minutes, a sharp increase in the system pressure was observed, which was attributed to the diminishing vapor phase volume and the subsequent compression of the subcooled liquid phase. Immediately after purging (valve 1) and sampling (valve 2), the vapor phase was reformed, and the pressure dropped to the value expected based on equilibrium with the temperature inside the reactor. From this behavior, it is clear that increasing the sample size would not have resulted in a lower pressure since T and P equilibrium is reached between the phases. This routine was repeated each time the pressure had sharply increased during the elevation of the temperature up to the water supercritical point. The volume of the water inside the reactor was calculated by deducting the samples' mass.

After arriving at the supercritical region, the reactor content stabilized at a single supercritical phase, where the reactor pressure and temperature were related by the system's fixed volume. However, measuring the temperature inside the vial constituted a technical challenge in this system, because of the high temperatures involved and the high mass of steel, compared to the small mass of water inside the reactor. To overcome this, the inside temperature was calculated, as shown in Table 5 for two sampling points in the subcritical and supercritical regions.

In the subcritical zone, the tabulated temperature is the water saturation temperature at the measured pressure after extracting the samples, while at the supercritical region the reactor temperature was calculated according to Duan's equation of state, which is valid for SCW up to 1,000°C and 3,500 bar, within 2% accuracy [78].

$$Z = \sum a_{ij} T_r^{-i} V_r'^{-j} + b_1 T_r^{-3} V_r'^{-2} \left(b_2 + b_3 V_r'^{-2} \right) \exp\left(-b_3 V_r'^{-2} \right) \tag{11}$$

where $V_r' = V P_C / R T_C$.

As shown in Table 5, the differences between the calculated and measured temperature values inside the reactor were small, with a maximum of about 15°C difference in the supercritical region, which is well within the accuracy of

Table 4
SCWO experiments parameters and results

Experiments group	#Run	Solution composition	T_{max} (°C)	P_{max} [Barg]	OC	Removal efficiency	Remarks
1. Preliminary	1	Water	416	299			
	2	NOM + SMP: 20 mg/L HA + 80 mgL starch	405	279	1.9	98.36% TOC	
	3	48.5 µg/L CBZ + MeOH	389	253	0	99.67% CBZ	No additional oxidant
	4	16mg/L CBZ + MeOH	409	282	0	98.73% CBZ	No additional oxidant
2. CBZ synthetic solutions	5	35 mg/L CBZ	402	274	2.0	99.59% CBZ	
	6	35 mg/L CBZ	403	274	3.0	99.84% CBZ	
	7	90 µg/L CBZ	395	278	37	98.63% CBZ	No additional oxidant
	8	90 µg/L CBZ	402	268	39	99.01% CBZ	No additional oxidant
	9	35 mg/L CBZ	418	269	3.6	100% CBZ, 99.72% ACR	
	10	35 mg/L CBZ	426	273	3.6	100% CBZ, 99.87% ACR	
	11	90 µg/L CBZ	411	290	32	99.35% CBZ, 65.28% ACR	No additional oxidant
	12	90 µg/L CBZ	415	272	32	99.84% CBZ, 49.16% ACR	No additional oxidant
	13	124 mg/L CBZ	519	398	1	96.9% TOC, 99.99% CBZ, 98.9% ACR	
	14	141 mg/L CBZ	547	421	4	98.8% TOC, 99.99% CBZ, 99.98% ACR	
3. E2 synthetic solutions	15	4.6 mg/L E2	407	286	8.3	>99.99% E2	
	16	4.6 mg/L E2	406	291	9.1	>99.99% E2	
	17	1.5 mg/L E2	334	137	17.7	99.98% E2, 99.95% E1	Subcritical conditions
	18	1.5 mg/L E2	331	130	27.4	99.98% E2, >99.75% E1	Subcritical conditions
	19	1.2 mg/L E2	397	260	2.5	99.91% E2, >99.49% E1	No additional oxidant
	20	1.2 mg/L E2	394	250	2.5	99.93% E2, >99.49% E1	No additional oxidant
	21	1.5 mg/L E2	467	418	55.0	79.2% TOC, >99.986% E2, >96.3% E1	
	22	2.4 mg/L E2	440	428	34.0	61% TOC, >99.99% E2, >99.2% E1	

(continued)

Table 4 Continued

Experiments group	#Run	Solution composition	T_{max} (°C)	P_{max} (Barg)	OC	Removal efficiency	Remarks
4. Nir Etzion effluent RO retentate	23	Effluent retentate	452	365	3.4	84.7% TOC	
	24	Effluent retentate	503	281	3.4	81.7% TOC	
	25	Effluent retentate	510	298	3.4	84.2% TOC	
	26	Effluent + 640 µg/L CBZ, 19 µg/L E2	511	316	3.6	95.6% TOC, 100% CBZ, >93% ACR, >99% E2 & E1	
	27	Effluent + 640 µg/L CBZ, 19 µg/L E2	511	317	3.6	92.6% TOC, 100% CBZ, >93% ACR, >99% E2, E1 n.d.	
	28	Effluent + 640 µg/L CBZ, 19 µg/L E2, 340 mg/L IPA	511	396	4.4	99.4% TOC-IPA (1), 98.1% TOC-Eff (2), >99.8% CBZ, >92.5% ACR, >99% E2, E1 n.d.	
	29	Effluent + 640 µg/L CBZ, 19 µg/L E2, 340 mg/L IPA	516	384	4.9	99.7% TOC-IPA (1), 99.1% TOC-Eff (2), >99.8% CBZ, >92.1% ACR, >99% E2, E1 n.d.	
5. Haifa effluent RO retentate	30	Effluent retentate	502	425	1.5	93.0% TOC, 96.6% CBZ, 92.7% ACR	
	31	Effluent retentate	539	380	5.0	99.0% TOC, 99.2% CBZ, 95.2% ACR	
	32	Effluent + 2,430 µg/L CBZ, 22 µg/L E2	485	404	5.0	97.1% TOC, >99.9 CBZ, 96.6% ACR, >99% E2, E1 n.d.	
	33	Effluent + 1,940 µg/L CBZ, 18 µg/L E2	505	422	1.8	89.8% TOC, >99.9% CBZ, 42.1% ACR, >98.6% E2, E1 n.d.	
	34	Effluent + 2,300 µg/L CBZ, 21 µg/L E2, 300 g/L IPA	494	449	5.0	99.4% TOC-IPA (1), 97.7% TOC-eff (2), 99.98% CBZ, >90.6% ACR, >98.8% E2, E1 n.d.	
	35	Effluent + 2,400 µg/L CBZ, 7 g/L E2, 300 mg/L IPA	449	426	5.0	99.1% TOC-IPA (1), 97.1% TOC-eff (2), >99.99% CBZ, >89.3% ACR, >96.2% E2, E1 n.d.	

(1) TOC removal including added IPA.
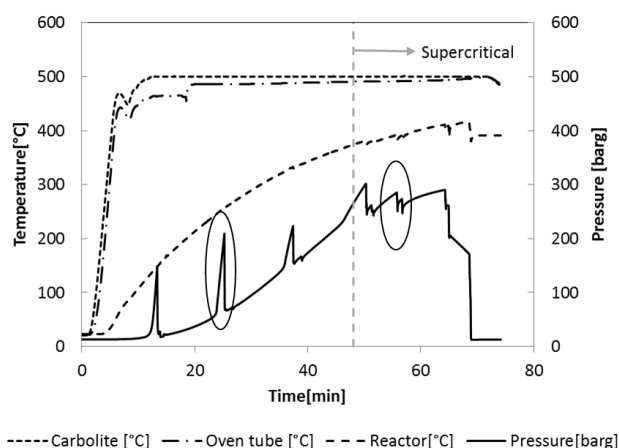(2) TOC removal calculated without the added IPA.

Fig. 5. Typical pressure and temperature profile developing in the reactor during a batch oxidation experiment. Circled areas represent examples of temperature calculations, as specified in Table 5.

Table 5
Comparison between measured and calculated temperature values inside the reactor

Time (min)	25.2	55.8
Reactor inside water mass (g)	20.41	9.42
Reactor measured temperature (°C)	265	390
Reactor calculated temperature (°C)	268	394
Pressure before sampling (barg)	208.8	285.4
Pressure after sampling (barg)	54.5	251.1

Duan's EoS. Accordingly, the reactor temperature which is presented in all the figures in this paper is the measured value.

3.2. Supercritical oxidation of samples containing natural organic matter plus soluble microbial products

Secondary EfOM consists mainly of natural organic matter (NOM) and soluble microbial products (SMP) [2,36]. The emerging pollutant concentration amounts typically to single-digit percentages (0.2–0.3 mg/L in TOC units) out of the overall EfOM concentration. Hence, mineralization of the emerging pollutant concentration inevitably requires the mineralization of the full NOM + SMP fraction in the EfOM. To test the feasibility of complete oxidation of this fraction at SCWO conditions, a 100 mg/L synthetic solution consisting of 20% humic acids (NOM) and 80% starch (SMP) was prepared and used as feed solution in Run #2. Fig. 6 describes the temperature, pressure and remaining TOC along Run #2. As shown in Fig. 6, the TOC concentration decreased very quickly already at the subcritical conditions, with a final TOC removal efficiency of 98.4%. The maximum temperature during this oxidation batch was just above 400°C and the oxidation stoichiometric coefficient (OC) was 1.9.

Contrary to what was found in a UVA/TiO$_2$ oxidation of similar target molecules [36], the current results suggest that the oxidation of the NOM and SMP probably takes place
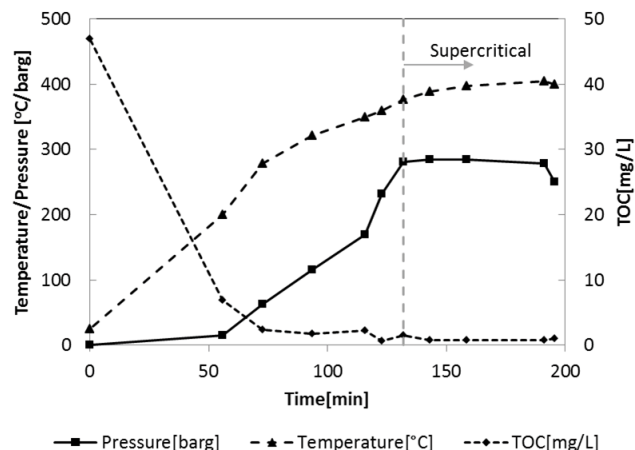

Fig. 6. Change in the TOC concentration during SCWO of a synthetic solution containing NOM + SMP (Run #2 in Table 4).

before the water reaches supercritical conditions, hence it did not interfere with the oxidation of the emerging pollutants.

3.3. Hydrothermal decomposition of synthetic solutions of CBZ and methanol

Figs. 7 and 8 show the temperature, pressure and CBZ concentration along oxidation Runs #3 and #4 (CBZ concentrations of 48.5 μg/L and 13 mg/L, respectively).

Both Runs #3 and #4 were processed without the addition of oxidant (other than the naturally existing dissolved oxygen in the feed water), however with a very high molar ratio between methanol and CBZ (9,400 to 1). Both runs exhibited CBZ decomposition from the onset, at subcritical conditions, with an earlier decomposition of the CBZ at $T < 250$°C in Run#3, that is, when the initial CBZ concentration was at the mg/L range, which may be attributed to the higher proportional amount of the dissolved oxygen in the water. Runs #3 and #4 show that CBZ decomposes already at subcritical conditions in the presence of a high methanol concentration. However, to verify the conditions at which CBZ mineralizes, further experiments were conducted using CBZ solutions which did not contain methanol as a solvent.

3.4. CBZ degradation in the absence of methanol

The oxidation efficiencies of synthetic solutions with varying concentrations of CBZ, various oxidant coefficient values (OC) and maximum temperature and pressure, were examined in Runs #5–14. As shown in Table 4, the CBZ removal efficiencies in all of these experiments were very high, ranging between 98.63% and 100%. TOC removal efficiency was examined in Runs #13–14 and yielded 96.9%–98.8%. As expected, high TOC removal efficiencies were attained at higher temperatures and longer retention times than those required for equivalent CBZ removal efficiencies.

In addition to the CBZ and TOC concentration, the concentration of acridine (ACR) (one of CBZ's transformation products at low-temperature, free radicals based AOPs [79]) was also analyzed. The possible formation of ACR as a transformation product in SCWO is of interest because it is a
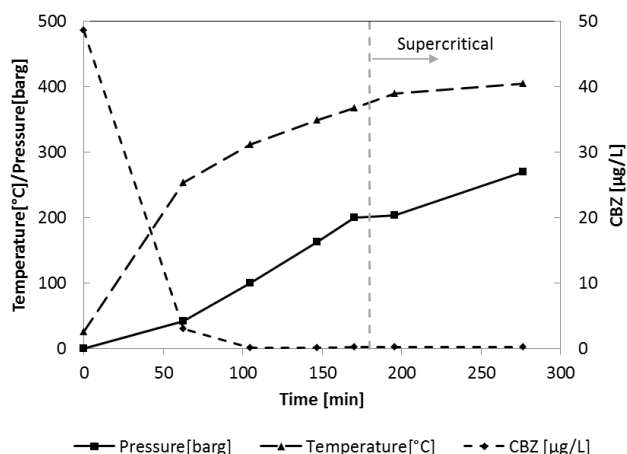
Fig. 7. Change in CBZ concentration with time in Run #3 ([CBZ]i = 48.5 µg/L; presence of MeOH).

Fig. 9. Removal efficiencies of CBZ, TOC and ACR in Run #14, as a function of time and temperature. Initial CBZ concentration = 141 mg/L.
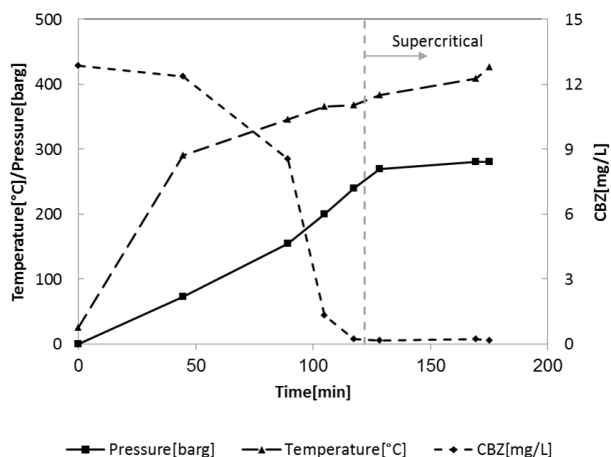

Fig. 8. Change in CBZ concentration with time in Run #4 ([CBZ]i = 13.0 mg/L; presence of MeOH).

three-ring nitrogen heterocycle and a pyridine (PYR) based molecule, which may exhibit pyridine or quinoline SCWO degradation characteristics [80,81].

For example, [80–82] reported that PYR and quinoline required temperatures of 527°C and 575°C, respectively, for complete decomposition, and complete mineralization of quinoline was attained only at 650°C. In the context of current work, it is important to note the toxicity of ACR and its transformation products towards aqueous fauna, reported in [83], which emphasizes the importance of complete mineralization of both parent pollutants and their transformation products.

Fig. 9 shows the CBZ and TOC removal efficiencies and ACR concentrations recorded in Run #14. As shown before, the transformation compound ACR was formed already at subcritical conditions and decomposed as the temperature (and pressure) increased. Similar trends were observed also in Runs #9 through #13. The reported removal efficiencies of ACR were calculated with respect to the measured maximum and minimum concentrations, in each of these oxidation runs.
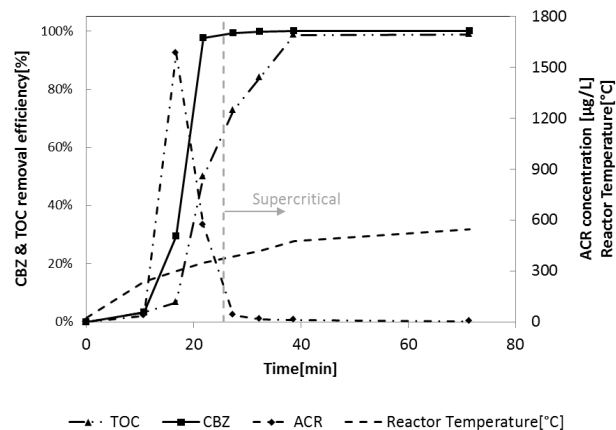
As shown in Table 4, ACR removal efficiencies in Runs #11 and #12 (relatively low temperature and low CBZ feed concentration) were in the range of 50%–60%, while the ACR removal efficiencies in Runs #9,#10,#13,#14 (high CBZ feed concentration) were above 98.9%, regardless of the high OC (=32) in Runs #11 and #12 (no additional oxidant was added). The results seem to indicate that other oxygen-consuming processes, for example, the interaction of oxygen and iron under supercritical water conditions [84], which possibly consumed the small amount of dissolved oxygen available in Runs #11 and #12, bringing the ACR oxidation reaction to oxygen deficiency, thereby resulting in partial decomposition of the ACR, which is not dissimilar to previous observations [80] of pyridine's minimal degradation at thermal degradation conditions.

3.5. Synthetic 17β-Estradiol (E2) solution degradation

Synthetic solutions of E2 at the feed concentration range of 1,200–4,700 µg/L were treated at different temperatures and OC in Runs #15–#22, as detailed in Table 4. Runs #15 and #16 were conducted at up to a temperature slightly above 400°C and resulted in complete degradation of the E2, already at temperature as low as 150°C. Following that, Runs #17 and #18 were conducted at subcritical conditions (maximum of 330°C and 137 bar) and as expected, the estradiol decomposed completely already at 200°C–250°C. In these runs, Estrone (E1) was also analyzed. E1, an endocrine disruptor on its own [85,86], has been reported as an E2 transformation product forming in low-temperature degradation processes [57,58]. E1 was found in these runs' samples (Fig. 10), as well as in samples from all other runs that contained E2 in the feed solution.

Runs #19 and #20 were performed without additional oxidant (apart from the dissolved oxygen in the feed solution) and resulted in complete breakdown of the estrogens, emphasizing the sensitivity of ACR decomposition to the amount of oxidant in the system.

Fig. 10 shows the concentrations of E2, E1, and TOC concentrations in Run #21 along with the reactor temperature profile.
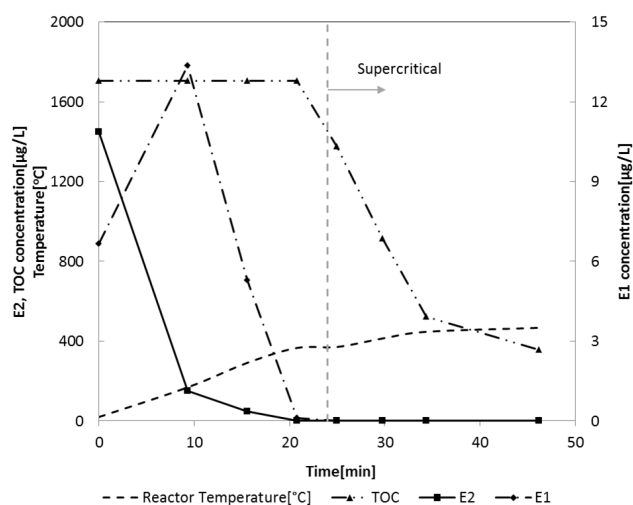
Fig. 10. TOC, E2 and E1 concentration profiles in Run #21 as a function of time and temperature.
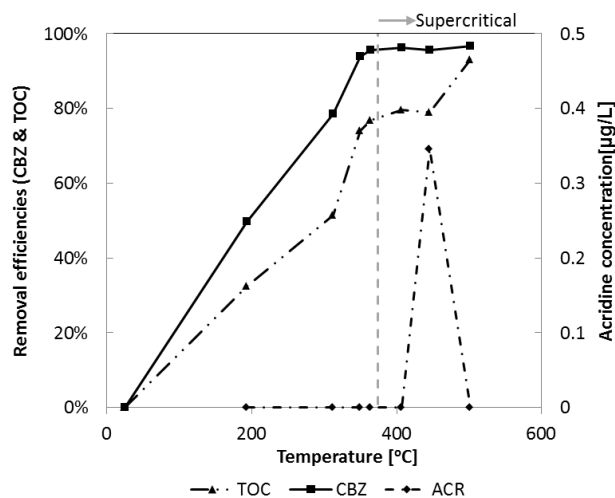

Fig. 11. Removal efficiencies of CBZ and TOC, and ACR concentrations in Run #30 (actual effluent RO retentate solution), as a function of the temperature. CBZ and TOC feed concentrations were 19.8 and 55,200 µg/l, respectively.

Fig. 10 shows that E1 was formed in Run #21 while E2 quickly degraded. However, full mineralization of both E2 and E1 was more difficult to achieve (TOC removal was only partial in Runs #21 and #22, that is, 60%–80%), and was recorded only at fully developed supercritical conditions. Table 4 also shows that high excess of oxidant was not required for the removal of estrogens, and did not seem to enhance, under the tested experimental conditions, their full mineralization. Operational conditions leading to higher mineralization efficiencies of estrogens were outside the scope of this work.

3.6. SCWO of actual effluent RO retentate solutions

SCWO Runs #23–#35 focused on the oxidation of effluent RO retentates. Runs #23–#25, #30 and #31 aimed at oxidizing raw RO retentates at OC values of 2.4–17 and temperatures of 450°C–539°C. According to the TOC removal efficiencies shown in Table 4, as expected, the degree of mineralization increased as the temperature and OC were increased. Fig. 11 shows removal efficiencies of CBZ and TOC, and the ACR concentration profile from an experiment executed on a retentate solution from Haifa's WWTP (Run #30). No estrogens were detected under the applied analytical procedure in the 1–2 mL samples that were drawn. Similar results were obtained in all five effluent RO retentate experiments, implying that the background effluent composition was not significant.

As shown in Fig. 11, a small concentration of ACR was formed in Run #30 as the CBZ degraded. It can be assumed that ACR was not the first CBZ transformation product, because it appeared only after CBZ had been almost fully degraded. Furthermore, 93% mineralization was attained only at above 500°C, that is, long after the CBZ had decomposed (96.9% removal of CBZ). Moreover, the final stage of TOC removal, 80%–93% (equivalent to about 7 mg/L TOC) at temperatures of 450°C–500°C, suggests that the final NOM + SMP mineralization occurred simultaneously to the emerging pollutants' mineralization. Run #31 was oxidized

with an OC value of 5 and resulted in 97.7% mineralization already at 404°C, indicating the importance of excess oxidant in the complete mineralization of real-life matrix solutions.

3.7. SCWO of effluent RO retentates spiked with CBZ and E2

SCWO Runs #26, #27, #32 and #33 focused on RO retentates originating from both WWTPs, which were also spiked by CBZ and E2. The purpose of the spiking was to examine the degradation of both model pollutants as part of a real effluent matrix environment. The maximum operating temperature, pressures and the feed OC factor, as well as the removal efficiencies, are listed in Table 4. TOC removal efficiencies increased as the OC was increased from 1.8 to 3.6 and 5.0, reaching 97.1% already at a temperature of 485°C. CBZ and estrogens were almost fully removed, while ACR removal, as expected, was sensitive to the OC value. Fig. 12 shows the removal efficiencies of TOC, CBZ and ACR and Fig. 13 the removal efficiencies of TOC, E2 and E1, both figures relating to Run #32.

There was no apparent difference between the results obtained from the oxidation runs of the two different wastewater sources. The last two samples of SCWO Runs #24-#27, #30 and #31 had a typical hydrogen sulfide odor at reactor temperatures above 500°C, suggesting that organic sulfur molecules reached the final step of decomposition, as suggested for the decomposition of penicillin [71]. However, the last two samples of SCWO Runs #32 and #33 did not release such odor, possibly due to the lower maximum temperature of Run # 32 and the lower OC value applied in Run #33.

The possible release of hydrogen sulfide at the end of the SCWO run and the possible means to treat it should be further addressed in continuous SCWO experiments. The results presented in both Figs. 12 and 13 show the importance of supercritical conditions for attaining nearly complete TOC mineralization, as compared to the full decomposition of
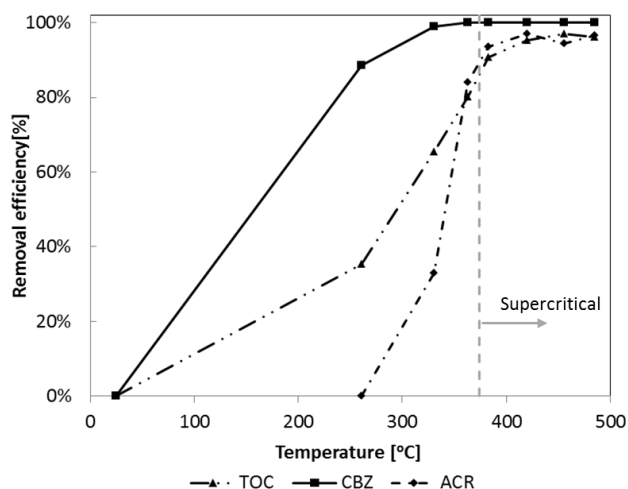
Fig. 12. Removal efficiencies of CBZ, ACR and TOC in Run #32 (spiked effluent RO retentate solution). Initial CBZ and TOC feed concentrations were 2,430 and 51,330 µg/L, respectively.

Fig. 14. Removal efficiencies and temperature profile in Run #35 (spiked Haifa WWTP RO retentate + IPA). Feed concentrations of TOC, CBZ and E2 were 185 mg/L, 2.4 mg/L, and 7 µg/L, respectively.
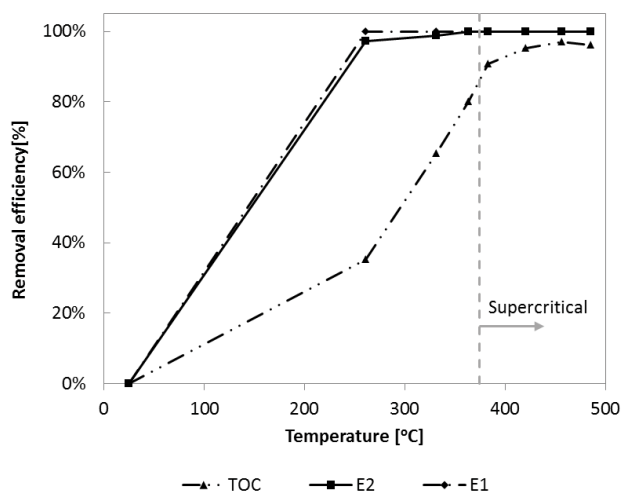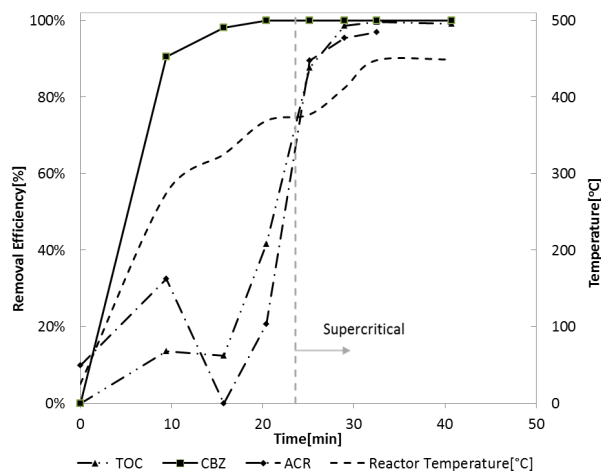

Fig. 13. Removal efficiencies of E2, E1 and TOC in Run #32 (spiked effluent RO retentate solution). Initial E2 and TOC feed concentrations were 22.6 and 51,330 µg/L, respectively.

both the CBZ and the estrogens, which was attained in these runs at milder (subcritical) conditions.

3.8. SCWO of spiked RO retentate with the addition of IPA

SCWO Runs #28, #29, #34 and #35 involved RO retentates from both WWTP sources which were both spiked with the model contaminents and to which IPA was added at a molar ratio of $n_{TOC}/n_{IPA} = 0.9$–1.2, as suggested by others [74].

Fig. 14 shows the removal efficiencies and temperature profile recorded in Run #35. In this case, both estrogens concentrations dropped below the LCMS detection limit (0.25 µg/L), already at temperatures lower than 270°C.

As shown in Fig. 14, the SCWO run profile in this experiment was similar to those obtained in the synthetic solution runs, with an important difference that the removal of the

contaminants was achieved at lower temperatures, with a maximum reactor temperature of 450°C and OC value of 8. In oxidation Runs #28 and #29, processed with OC = 5, full mineralization was attained at 511°C and 516°C, respectively. Interestingly, all oxidation runs that included IPA as a co-fuel, did not yield $H_2S_{(g)}$ odor, although the maximum operating temperature in these runs was above 500°C.

As shown in Table 4, the TOC removal efficiency of the IPA-dosed runs, based on the spiked sample TOC, was higher by 1%–6% than the TOC removal efficiency of the spiked runs to which IPA was not added, suggesting that IPA has the capacity to increase the oxidation efficiency of the SCW in municipal effluent RO retentate matrixes, as previously reported [72] for 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).

4. Conclusions and future work

This research demonstrates for the first time a SCWO-based technique for the complete removal of emerging pollutants from municipal effluent RO retentates. The results support the notion of utilizing a single AOP generic treatment to fully mineralize the vast variety of organic matter found in municipal wastewater effluents, resulting, in reduction of the TOC concentration by two orders of magnitude. The results show that the model pollutants (CBZ and 17β-Estradiol) both in synthetic solution and as part of a real effluent RO retentate matrix, started degrading already at subcritical conditions. ACR (a CBZ transformation product) was detected at small concentrations throughout the runs and fully decomposed only at temperatures above 500°C. The addition of IPA at a molar ratio of about 1:1 TOC/IPA, increased the mineralization of the spiked RO retentates and enabled near-complete decomposition of ACR already at ~450°C. However, nearly complete mineralization of a solution simulating real effluent RO retentate matrix was attained only at condition characterized by a very high concentration of free radicals, that is, at fully established supercritical conditions. The paper shows, for the first time, that

supercritical oxidation conditions enable full degradation of all the background organic material that accumulates in the retentates from RO treated secondary effluents, as well as the transformation products of the tested emerging pollutants, thereby enhancing the motivation for developing a feasible continuous process to be implemented at large scale for preventing the accumulation of species of emerging concern in the environment.

The operation and capital costs of SCWO plants applied for the treatment of concentrated industrial wastes and sludge have been reported by others, for example, [37,87–91]. The operating costs range from 100 to $600/ton of dry sludge (DS), the latter figure equivalent to $24/ton feed of 4% (w/w) sludge. This rough cost estimation, in our case, leads to only 0.25% of the average emerging pollutant's shadow price, that was mentioned in the Introduction section [27]. Put bluntly, the cost of treating these recalcitrant and toxic substances is not expected to be low, however, the cost of not treating them, in the long run, can be expected to be significantly higher. In large scale operations, the operating costs can be further reduced by recovering heat and pressure (70% and 40% recovery, respectively), as previously estimated by [37,88].

Future experiments of municipal effluent RO retentate SCWO should focus on improving mineralization efficiencies at lower oxidant coefficient (OC) values, comparing the effects of other co-fuels (e.g. methanol and ethanol) with IPA, and examining the elimination and mineralization of municipal effluents emerging pollutants in a heterogeneous-catalyzed SCWO system, aimed to reduce real-life operational costs.

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Supplementary information

The analysis of model pollutants and selected transformation products was performed by LC–ESI–MS–MS (LCMS) system composed of Agilant 1200 HPLC (Agilant Technologies, Waldbronn, Germany) equipped with quaternary pump, degasser, column oven, auto-sampler and coupled to an Applied Biosystems Sciex API 3200 triple-quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with electrospray ionization. All compounds were separated on Purospher STAR RP-18 end-capped column, 3 mm × 125 mm, particle size 5 μm Purosphere STAR RP-18 (Merck, Darmstadt, Germany), the temperature was adjusted to 30°C ± 2°C. The flow rate was 0.4 mL/min and the injection volumes 20 μL.

S1. Carbamazepine and acridine

LCMS separation of carbamazepine (CBZ) and acridine (ACR) was conducted by using a mixture of methanol (MeOH) and 1% (V/V) formic acid (FA) solution as mobile phase. The gradient program was as follows: constant 5% MeOH and 95% FA solution for 2 min, then changes of 5%–100% MeOH, 95%–0% FA solution were taken during 2–7 min. 100% content of MeOH was kept until 11 min and then restored to 5% at 13 min. Constant 5% MeOH and 95% FA solution was kept for 6 min (13–19 min.).

Electrospray mass data were acquired in the positive mode with a spray voltage of 5.5 kV. The source temperature was 550°C. Nitrogen was used as the curtain gas (setting 30), IonSource gas 1 (GS1 gas setting 50) and IonSource gas 2 (GS2 gas setting 60). MS/MS was performed using nitrogen as collision gas (CAD gas setting 10). Other specific operating conditions of MS/MS of CBZ and ACR are shown in Table S1.

S2. Estrogen derivatives

LC separation of estrogen derivatives (E2 and E1) was conducted by using a mixture of methanol (MeOH) and 0.625 mmol/L ammonium acetate solution as a mobile phase. The gradient program was as follows: constant 5% MeOH and 95% ammonium acetate solution for 3 min, then changes

Table S1
Optimized LC-MS/MS parameters for each compound

	Carbamazepine (CBZ)[a]	Carbamazepine (CBZ)[b]	Acridine (ACR)[a]	Acridine (ACR)[b]
[M+1]/Fragment ion (m/z)	237.1/194.1	237.1/193.1	180.0/152.0	180.0/127.0
Declustering potential DP (V)	40	40	70	70
Entrance potential EP (V)	10.5	10.5	10.5	10.5
Collision energy CE (rel. units)	25	25	50	56
Collision cell exit potential CXP (V)	4	4	1.3	2.5
Retention time RT (min)	10.5	10.5	9.9	9.9

[a]for quantitation.
[b]for qualitative identification.

Table S2
Optimized LC-MS/MS parameters of each compound

	E2[a]	E2[b]	E1[a]	E1[b]
[M+1]/Fragment ion (m/z)	271.2/145.2	271.2/183.2	269.2/145.2	269.2/143.2
Declustering potential DP (V)	–120	–120	–50	–50
Entrance potential EP (V)	–9.0	–9.0	–9.0	–9.0
Collision energy CE (rel. units)	–60	–57	–50	–74
Collision cell exit potential CXP (V)	–4	–5	–4	–4

[a]for quantitation.
[b]for qualitative identification.

of 5%–100% MeOH, 95%–0% ammonium acetate solution were taken in 3–6 min. 100% content of MeOH was kept until 16 min and then restored to 5% at 18 min. Constant 5% MeOH and 95% ammonium acetate solution was kept for 7 min (18–25 min).

Electrospray mass data were acquired in the negative mode with a spray voltage of –4.5 kV. The source temperature was 450°C. Nitrogen was used as the curtain gas (setting 10), IonSource gas 1 (GS1 gas setting 50) and IonSource gas 2 (GS2 gas setting 60). MS/MS was performed using nitrogen as collision gas (CAD gas setting 10). Other specific operating conditions of MS/MS of estrogen derivatives are shown in Table S2.

The data were acquired with Sciex Analyst software, version 1.5.1 (Applied Biosystems, Foster City, CA, USA).