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Complete oxidation of organic waste under mild supercritical water oxidation by combining effluent recirculation and membrane filtration

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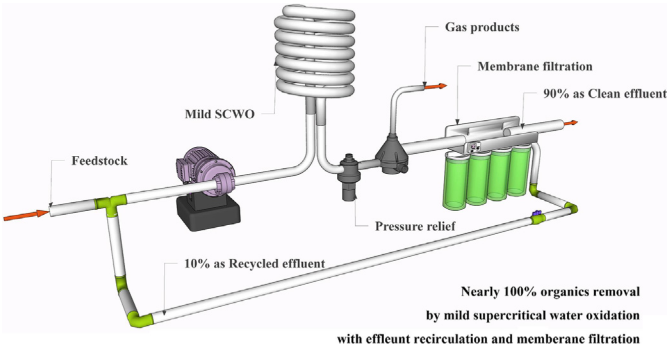
HIGHLIGHTS

- Effluent recirculation was applied to modify SCWO.
- A combination of SCWO and membrane filtration process was proposed.
- The membrane retained the majority of incompletely oxidized organics for recycling.
- Mild SCWO with recirculation of retentate achieved high oxidation of organics.

GRAPHICAL ABSTRACT



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ABSTRACT

Supercritical water oxidation (SCWO) is a technology that can oxidize various organic (wet) wastes into CO_2. Complete oxidation of specific organics with SCWO goes in tandem with tailored conditions, typically involving elevated operating temperatures, long residence times, high oxidizer-to-waste ratios, or a combination of those, which promote difficulties, *e.g.*, corrosion. These challenges hamper the practical implementation of SCWO, albeit SCWO offers excellent oxidation efficiencies. This work proposes a novel process combining mild supercritical water oxidation (SCWO) with membrane filtration to enhance the oxidation of organics. The modified SCWO works at mild reaction conditions (*i.e.*, 380 °C, 25 MPa and oxidizer equivalence ratios as low as 1.5) to potentially decrease the risks. The membrane filtration discards clean effluent and recycles the retentate (containing incomplete oxidized organics) back to the mild SCWO process for further oxidation, thereafter resulting in near-complete removal of organics. Fresh feed is continuously added, as in the conventional process, along with recycled retentate to guarantee the throughput of the modified SCWO process. A mixture of SCWO-resistant volatile fatty acids (TOC = 4000 $mg\cdot L^{-1}$) was studied to validate the proposed process. The proposed process in this study enhances the organic decomposition from 43.2% to 100% at mild conditions with only 10% capacity loss. CO_2 was the dominant gas product with traces of CO and H_2. Carbon output in the gas products increased with recirculation and got close to the carbon input of the freshly added feed ultimately. The results indicated that the proposed process maximized the benefits of both technologies, which allows the development of a technological process for supercritical water oxidation, as well as a new stratagem for waste treatment.

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Nomenclature

CB	carbon balance, %
CB_{mf}	carbon balance in membrane filtration, %
CB_{SCWO}	carbon balance in SCWO process, %
C_{effl}	the carbon concentration in the aqueous effluent, $g \cdot g^{-1}$
C_{feed}	the carbon concentration of the feed solution the current run, $g \cdot g^{-1}$
C_{gas}	the concentration of carbon in the gaseous products, $g \cdot m^{-3}$
C_{p-i}	concentration of carbon in the permeate$_i$, $g \cdot g^{-1}$
$C_{recycled}$	the carbon concentration of the recycled effluent of the previous run in the influent of the current run, $g \cdot g^{-1}$
C_{rete-i}	concentration of carbon in the retentate$_i$, $g \cdot g^{-1}$
CSTR	continuous stirred tank reactor
ER-SCWO	effluent recirculation in supercritical water oxidation
F_{effl}	mass flow rate of the aqueous effluent, $g \cdot s^{-1}$
F_{gas}	the gas volumetric flow rate, $m^3 \cdot s^{-1}$
F_{infl}	mass flow rate of the aqueous influent, $g \cdot s^{-1}$
M_f	mass of the f initial membrane feed solutions, g
M_{p-i}	mass of the permeate$_i$, g
M_{rete-i}	mass of the retentate$_i$, g
OE	oxidation efficiency, %
OER	oxidant equivalence ratio
SCWO	supercritical water oxidation
TOC	total organic carbon, $g \cdot g^{-1}$
VFAs	volatile fatty acids

1. Introduction

Supercritical water oxidation (SCWO) is a green technology and able to oxidize many types of organic wastes to harmless gas products in seconds at a typical temperature between 374 and 800 °C with pressures between 22 and 40 MPa (Brunner, 2014a; Brunner, 2014b; Vadillo et al., 2014). Gas products from SCWO are generally composed of carbon dioxide and, to a lesser extent, carbon monoxide and methane. Minor gas species (*e.g.,* CH_4 and CO) could be easily converted to carbon dioxide which is a greenhouse gas but can be used in downstream applications (*e.g.,* in plant growth in greenhouses or as a chemical feedstock in synthesis), and is safer to dispose of than potentially toxic and oxidation-resistant organics that are present in the waste to be processed. Air, O_2, and H_2O_2 are commonly used oxidizers. Higher temperatures, longer residence times and higher oxidizer loads have been proven to result in higher degrees of oxidation but along with higher risks (Bermejo and Cocero, 2006). The harsh reaction conditions (*i.e.,* high pressure and temperature) require a special setup design (Marrone, 2013). A higher extent of corrosion caused by the high oxidizer load is also a problem (Cocero and Martínez, 2004; Li and Xu, 2015). Longer residence times need a larger reactor or lead to lower throughput capacity per unit time (Chen et al., 2015). Moreover, each organic waste stream has its individual optimized reaction conditions (Kritzer and Dinjus, 2001; Li et al., 2020). SCWO has to meet several criteria with respect to process conditions to satisfy the oxidation of different organics effectively (Al-Atta et al., 2018; Rice and Steeper, 1998). Therefore, one of the most popular research topics in SCWO is to investigate the optimized operational parameters for a variety of organics waste streams at the lowest costs and risks (Yang et al., 2018; Zhang et al., 2016).

Mild temperatures and low oxidizer addition generally are ineffective at completely oxidizing organics (Zhang et al., 2019). However, longer residence times are assumed to be positive to improve organic oxidation (Zhang et al., 2018). Inspired by chemical engineering, an effluent recirculation process is proposed in this study to prolong the residence time while operating SCWO at milder conditions to decrease the risks. The residence time in a recirculation process could be theoretically infinite for any carbon-containing intermediates that do not partition to the gas phase. Organic intermediates keep recirculating until they are fully oxidized to gas. As a result, most organics could potentially be fully oxidized at a constant temperature and pressure within only one setup (Zhao et al., 2020). Hence, the reaction parameter optimization studies to treat different organic wastes within a given setup can be avoided. Moreover, mild reaction conditions could potentially reduce corrosion, especially if the longer residence time provided by the recirculation allows a lower oxidizer dosing and lower temperature. Additionally, the milder conditions avoid the evolution of NO_x from N-species in the organic waste which would otherwise occur at high temperatures (Clauwaert et al., 2017; Cocero, 2001). Therefore, effluent recirculation in supercritical water oxidation (ER-SCWO) is proposed. The scenario is that the fresh feed is continuously fed and oxidized as in the conventional SCWO process. Incomplete oxidation products are recycled till fully oxidized and the produced gas, mostly consisting of CO_2, is released. The ER-SCWO enables maximum oxidation of different organics with one setup at constantly milder conditions and suffering fewer risks. The concept of recirculating effluent to increase reaction efficiency is commonly used in chemical engineering (Chen et al., 2018; Khalil et al., 2018). Only a few researchers have tried to apply this concept to supercritical water processes. It succeeded in improving the gas yield of supercritical water gasification (Jin et al., 2017). With regard to the SCWO process, effluent recirculation was only recently reported for the first time as a means to improve oxidation (Zhang et al., 2020).

Though the benefits mentioned above, the application of effluent recirculation in SCWO has one potential drawback. SCWO technology frequently handles wet wastes, oxidizers dissolved in water (*e.g.,* H_2O_2) and generates chemical water, resulting in a large amount of additional water in the effluent. The recirculation of the effluent will recycle both incomplete oxidation products and additional water back to the system. The latter is considered useless for the SCWO process and basically adds cost as an ever-increasing volume of water needs to be processed. It is essential to recycle incomplete oxidation products within an as small volume as possible and remove the water within the effluent as much as possible. Membrane filtration technology has the potential to achieve the separation of incomplete oxidation products from water (Abdel-Fatah, 2018). Specifically, pressure-driven membrane separation (*i.e.,* nanofiltration and reverse osmosis) is used to retain solutes from various aqueous solutions and has been widely applied in the field of industrial wastewater treatment (food industry, petroleum industry, pharmaceuticals and chemical processing industry, *etc.,*) (Yang et al., 2019). However, membrane filtration technology cannot degrade the concentrated products without a combination with other methods. Moreover, the external pressure (*i.e.,* energy) required to retain organics in the retentate and produce clean water has been one of the major costs of pressure-driven membrane separation processes (Abdel-Fatah, 2018). In the proposed process, SCWO is an inherent high pressure (> 22 MPa) system and as such, the existing outlet pressure of the effluent (with a partial reduction thereof) can be used to drive the filtration, which can reduce the major cost of membrane filtration implementation. The improved conceptual process combines the benefits of membrane filtration technology and SCWO.

This work is to validate whether effluent recirculation could near completely oxidize organic wastes at mild SCWO conditions. A mixture of fatty acids was tested as the feedstock with two sets of oxidizer equivalence ratios ($OER = 1.5$ and 3.0) at a fixed temperature of 380 °C, a pressure of 25 MPa, and a single-pass residence time of 24.6 s. This work also verifies whether a membrane filtration process is suitable to discharge water from the reactor effluent in order to guarantee process capacity. The combination of SCWO and membrane filtration technology were studied in a semi continuous manner. The effluent from SCWO was concentrated by a membrane process, then recycled into the SCWO system with fresh feed at a constant ratio. The filtration efficiency of the membrane filtration process has been obtained. The composition of gas and aqueous effluent were analyzed. Further, perspectives and subsequent works to be conducted in the development and application of ER-SCWO will be recommended.

2. Materials and method

2.1. Input feedstock

The feedstock solution was prepared by mixing acetic acid, butyric acid, valeric acid, caproic acid, propionic acid (analytical reagent grade, VWR Belgium), and distilled water. Each acid contributes 800 $mg \cdot L^{-1}$ of organic carbon to the solution, resulting in 4000 $mg \cdot L^{-1}$ of total organic carbon or 0.78 *wt%* (dry basis) of dissolved matter in the feedstock solution. These five volatile fatty acids were chosen because they were major components of a specific anaerobic fermentation filtrate as a waste stream for which the ER-SCWO was proposed, and these volatile fatty acids were proven to be highly resistant to oxidation under the tested conditions (Zhang et al., 2019). Additionally, acetic acid is known to be one of the most recalcitrant intermediates in SCWO of organic wastes. This solution of fatty acids was assumed to be capable of properly assessing the enhanced oxidation of organics by means of effluent recirculation.

Hydrogen peroxide (33 *wt%*, VWR, Belgium) was used as the oxidizer. The 33 *wt%* stock solution of hydrogen peroxide was diluted with demineralized water to 10.85 *wt%* and 5.43 *wt%* to obtain OER's of 3.0 and 1.5 with respect to carbon in the fresh feedstock solution, respectively.

2.2. ER-SCWO operation

Fig. 1 represents the schematic workflow of the effluent recirculation SCWO process. The first and second runs are presented here. The following runs are the same as the second one. At the initial run, distilled water mixed with the feedstock solution at a constant weight ratio of 1:9, constituted the influent stream prior to entering the reactor. After the reaction, the gas effluent was released, and the aqueous effluent was seperated by a membrane filtration setup to discharge 90% of the effluent as permeate. The retentate was recycled as *recycled effluent*. The retentate was mixed again with adequate fresh feedstock solution at a constant weight ratio of 1:9, becoming the influent stream for the second run. The following runs are the same as in the procedure mentioned above.

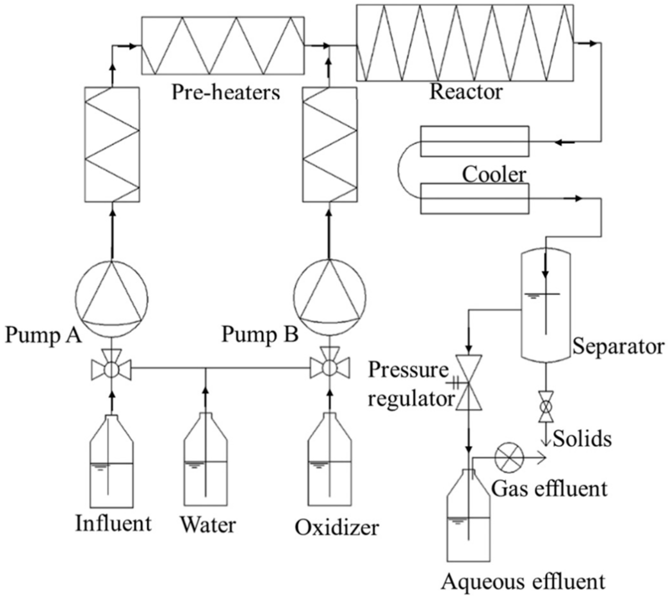

Fig. 2. Schematic diagram of the experimental apparatus.

2.3. SCWO setup and operation

A coiled tubular continuous reactor system (as shown in Fig. 2) was used to carry out the SCWO experiments. The system, with a total volume of 1300 mL, has two membrane diaphragm metering pumps (A and B), a feed preheater coil, an oxidizer preheater coil, a tubular reactor of 100 mL, a cooler, a separator, and a spring-loaded backpressure valve. The room-temperature feedstock stream took <120 s to reach a temperature around 200 °C to 220 °C in the preheater before mixing with oxidizer which took around <90 s in the preheater to reach a temperature around 200 °C to 220 °C. The feedstock was verified to have no TOC removal during preheating. The H_2O_2 was verified to be completely decomposed to water and oxygen gas during preheating. The cooler, reactor and preheaters were made of Inconel 600 alloy (ID: 3.09 mm, OD: 6.35 mm). Other pressurized parts were made of stainless steel 316 L (ID: 3.05 mm, OD: 6.35 mm).

During start-up, pure water was pumped into the system through pump A and B. After the pressure and temperature of the system were stable at 25 ± 0.5 MPa and 380 ± 0.5 °C, pure water for pump A and B were switched to influent and oxidizer stream, respectively. Pump A and B were fixed at a flow rate of 1.17 $g \cdot s^{-1}$ and 0.66 $g \cdot s^{-1}$,

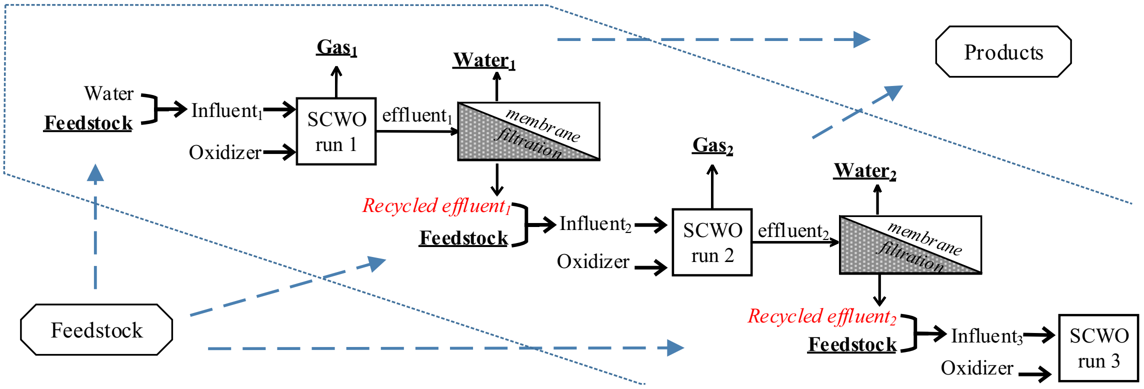

Fig. 1. Schematic workflow of the experiments in a batch manner; feedstock are the tested organics (fatty acids); gas effluent is the product mostly consisting of CO_2; clean water is discarded.

respectively. As such, the residence time in the reactor was 24.6 s at the tested conditions. The reaction temperature was chosen because it is a low/mild temperature compared to most supercritical water oxidation studies (Veriansyah and Kim, 2007; Zhang et al., 2016).

2.4. Membrane filtration setup and operation

The membrane filtration configuration was made up of several constituents: an electric pump, a membrane module unit operated in the crossflow mode and three collecting vessels (feed, retentate/concentrate and permeate). The NF-90 membrane (Dow Chemical Company, USA) was inserted between two halves of the module unit to separate the feed and permeate solution. The module has an inner width of 5 cm, a length of 25 cm (resulting in a membrane surface area of 125 cm^2) and a channel depth of 0.1 cm. The operational crossflow during the membrane tests was 16.7 $mL\cdot s^{-1}$ with a pressure of 2 ± 0.1 MPa. The flux of permeate was in the range of 48– 72 $L\cdot h^{-1}\cdot m^{-2}$.

The aqueous effluent from any SCWO run was collected and cooled down to room temperature. Afterwards, the aqueous effluent was separated by nanofiltration into a retentate and a permeate. The quantity of the retentate (containing incomplete oxidation products) was carefully controlled to be equal to the recycled effluent entering the previous SCWO process by weighting the permeate. The weight ratio of retentate and permeate was designed to be 1:9. As a result, a volume of water comparable to that of the non-recycled portion in the SCWO process (*i.e.,* water in which the fresh acids and peroxide were dissolved, as well as the chemical water being formed in the dissociation of hydrogen peroxide and in the oxidation of organic compounds) was fully discarded as permeate.

However, the membrane process cannot reject solutes (organics) completely. The discarded permeate after one filtration process may contain some incomplete oxidation products. To maximize the rejection of organic solutes in the membrane filtration process, the permeate was filtered by the membrane again (Fig. 3) to simulate double-pass nanofiltration and get a second retentate and permeate, at a weight ratio of 2:8. Subsequently, $permeate_2$ was further treated with the same procedure to get $retentate_3$ and $permeate_3$. Consequently, the aqueous effluent was separated into four portions being $retentate_1$, $retentate_2$, $retentate_3$ and $permeate_3$ with a weight ratio of 10:18:14.4:57.6, respectively. $Retentate_2$ and $retentate_3$ were reserved and $permeate_3$ was discarded. $Retentate_1$ was the recycled effluent as in Fig. 1. The reflux ratio of the SCWO effluent was 0.1. For the sake of maximal recovery of incomplete oxidation products, $retentate_3$ and $retentate_2$ were also reused in this work. $Retentate_2$ and $retentate_3$ were taken as two individual portions containing incomplete oxidation products and water, and were mixed with a concentrated input feedstock solution. The latter's weight was equal to $permeate_3$ for preparing the feedstock for any non-initial runs (Fig. 3). The concentrated feedstock solution had the same ingredients as the fresh feedstock solution designed in Section 2.1, but contained 1.5625 times higher concentration of each component. Therefore, the mixture would have the same acid composition as the fresh feedstock solution and also contained incomplete oxidation products, resulting in a mixture of fresh feedstock and incomplete oxidation products. Next, this prepared feedstock was mixed with $retentate_1$, becoming the influent for the subsequent SCWO run. More specifically, the influent equaled to a mixture of fresh feedstock (90 *wt%*) and all retentate (10 *wt%*) which contained the majority of rejected incomplete oxidation products. The above mentioned treatment was to maximize the recycling of incomplete oxidation products in order to understand their further oxidation during recirculation.

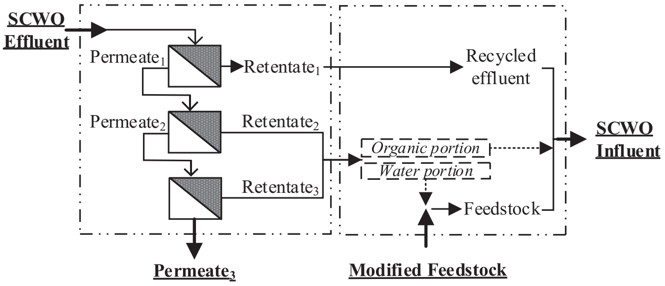

Fig. 3. Membrane filtration process and noninitial influent preparation (several membranes were drawn to describe the procedure, only one membrane module was applied in reality).

2.5. Analytical techniques and calculations

2.5.1. Gas composition

Gas samples were collected with 60 mL plastic syringes during the experiments. A micro-GC (Varian 4900) was used to measure H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and C_4H_{10}. The volume percentages of these gases were measured. The gas effluent flow rate was recorded by a gas flow meter (Omega FLR 1005). Combining the volumetric carbon concentration with the volumetric gas flow rate, the mass flow rate of carbon in the gas was obtained.

2.5.2. Liquid composition

The total organic carbon (TOC) in the liquid (*i.e.,* feedstock, recycled effluent, influent, effluent, retentate solution, permeate solution) was measured using a TOC-VCPN analyzer combined with ASI-V autosampler (Shimadzu, Japan).

Quantitative analysis of the volatile fatty acids (C_2-C_8 fatty acids (including isoforms C_4-C_6)) in the liquid effluent were measured in triplicate by gas chromatography (GC-2014, Shimadzu®, The Netherlands). The GC was equipped with a DB-FFAP 123–3232 column (30 m × 0.32 mm × 0.25 μm, $L \times ID \times df$; Agilent, Belgium) operated at 140 °C and a flame ionization detector (FID) at 250 °C. The detection limits (lower, upper in $mg\cdot L^{-1}$) were as follows: C2 (40, 600), C3/C4 (7900) and C5/C6 (8, 1000). Liquid (reactor effluent) samples were conditioned with sulfuric acid and sodium chloride, and 2-methyl hexanoic acid was added as the internal standard for quantification. The extraction of the volatile fatty acids was performed with diethyl ether (Zhang et al., 2019).

2.5.3. Carbon mass flow and carbon balance

All the data are expressed as mass flows of carbon (incoming: feedstock and recycled effluent; outgoing: gas effluent and aqueous effluent; filtration: retentate solution and permeate solution). Solid products were not detected in all the studied cases. The carbon balance closure (CB, %) of the SCWO process was calculated as:

$$CB_{Scwo}\,(\%) = \frac{C_{gas}[g\cdot m^{-3}] \times F_{gas}[m^3\cdot s^{-1}] + C_{effl}[g\cdot g^{-1}] \times F_{effl}[g\cdot s^{-1}]}{(C_{feed}[g\cdot g^{-1}] + C_{recycled}[g\cdot g^{-1}]) \times F_{infl}[g\cdot s^{-1}]} \times 100, \tag{1}$$

where, $C_{gas}[g\cdot m^{-3}]$ represents the concentration of carbon in the gaseous products; $C_{effl}[g\cdot g^{-1}]$ represents the carbon concentration in the aqueous effluent; $C_{feed}[g\cdot g^{-1}]$ and $C_{recycled}[g\cdot g^{-1}]$ represent the carbon concentration of the feed solution and the recycled effluent of the previous run in the influent of the current run, respectively; $F_{gas}[m^3\cdot s^{-1}]$ represents the gas volumetric flow rate; $F_{effl}[g\cdot s^{-1}]$ and $F_{infl}[g\cdot s^{-1}]$ represents the mass flow rate of the aqueous effluent and the influent entering the reactor, respectively.

The carbon balance closure (CB, %) of the membrane filtration process was calculated as:

$$CB_{mf}\ (\%) = \frac{\sum_{i=1}^{3}\left(C_{rete-i}\left[g\cdot g^{-1}\right]\times M_{rete-i}[g]\right)+C_{p-3}\left[g\cdot g^{-1}\right]\times M_{p-3}[g]}{C_f\left[g\cdot g^{-1}\right]\times M_f[g]}\times 100, \tag{2}$$

where, $C_{rete-i}[g\cdot g^{-1}]$, $C_{p-3}[g\cdot g^{-1}]$ and C_f represent the concentration of carbon in the retentate$_i$, permeate$_3$ and initial membrane feed solution during the membrane filtration process, respectively; $M_{rete-i}[g]$, $M_{p-3}[g]$ and $M_f[g]$ represent mass of the retentate$_i$, permeate$_3$ and initial membrane feed solutions during the membrane filtration process, respectively.

2.5.4. Equivalent TOC removal

The equivalent TOC removal efficiency (TRE, %) is a parameter indicating the removal of organics in each ER-SCWO run, by taking the entire ER-SCWO system as a black box. It is calculated from the carbon mass flow rates of fresh feedstock solution and produced aqueous effluent:

$$TRE\ (\%) = \frac{C_{effl}\left[g\cdot g^{-1}\right]\times F_{effl}\left[g\cdot s^{-1}\right]-C_{recycled}\left[g\cdot g^{-1}\right]\times F_{infl}\left[g\cdot s^{-1}\right]}{C_{feed}\left[g\cdot g^{-1}\right]\times F_{infl}\left[g\cdot s^{-1}\right]}\times 100, \tag{3}$$

2.5.5. Solute rejection

The solute/organic rejection (%) of the membrane process was used to indicate the performance of the membrane and calculated by:

$$Rejection\ (\%) = \left(1-\frac{C_p\left[g\cdot g^{-1}\right]}{C_f\left[g\cdot g^{-1}\right]}\right)\times 100, \tag{4}$$

where, $C_p[g\cdot g^{-1}]$ and $C_f[g\cdot g^{-1}]$ represent the concentration of carbon in permeate and feed solution, respectively.

2.5.6. Solute preservation of the membrane

Except for solute rejection to evaluate the membrane performance, the organic preservation (%) is more important as it demonstrates how much of the solute remained after the membrane process. The solute preservation is the most important function of the membrane process in ER-SCWO. It was calculated by:

$$Preservation\ (\%) = \left(\frac{\sum_{i=1}^{3}\left(C_{rete-i}\left[g\cdot g^{-1}\right]\times M_{rete-i}[g]\right)}{C_f\left[g\cdot g^{-1}\right]\times M_f[g]}\right)\times 100. \tag{5}$$

3. Results and discussion

3.1. Organic solute filtration by the membrane filtration process

The membrane process did not obtain excellent organic rejection for single-stage nanofiltration. Table 1 demonstrates that the first-time filtration only achieved around 80% of carbon rejection for all SCWO runs, resulting in smaller organic components being more present in the permeate and requiring a further nanofiltration step for separation. Organics rejection of the second filtration is lower, and the third filtration is even lower, as shown in Table 1. Importantly, nanofiltration was capable of retaining most of the carbon in the retentate for recirculation. The final permeate contained 30– 100 $mg\cdot L^{-1}$ organic carbon, and acetic acid was observed to be the major component. The discharge of the final permeate will be discussed later. Unfortunately, it is difficult to compare the membrane rejection among different filtration steps because the effluent was a complex mixture with various organics and each filtration step handles different and complex organics.

Table 1 demonstrates the preservation of organics after the membrane filtration process. Though single-pass nanofiltration cannot reach high carbon preservation, consecutively filtering three times would obtain an organic preservation >95%, indicating that the membrane filtration process is capable of separating water from the effluent and preserve organics in the retentate for recirculation in subsequent SCWO runs. Since carbon preservation was close to 100%, it is assumed that the susceptibility to oxidation performance of recycled carbon would be the same as if it was fully recycled. This assumption is used in the following discussion of supercritical water oxidation.

3.2. Carbon conversion within effluent recirculation SCWO

Table 2 presents the carbon mass flow from SCWO experiments with one initial run and six recirculation runs at two OER sets. The carbon in the influent entering the SCWO reactor stemmed from fresh feed and recycled aqueous effluent from the previous run, while carbon in the influent during the initial run only stemmed from feedstock carbon. Carbon yield in the gas effluent initially increases successively with each recirculation run. The same trend is also observed for the carbon in the aqueous effluent. With a near constant mass flow rate of carbon in the freshly added feedstock, the carbon concentration in the gas effluent should remain constant in the absence of effluent recirculation. As a result, the increase in carbon concentration in the gas effluent is most probably due to the recycled carbon (from the previous run) being further degraded and oxidized in the current run.

As demonstrated in Table 2, SCWO experiments at OER = 3.0 achieve a quasi-steady situation after five times of recirculation where the carbon mass flow rate in the gas effluent fluctuates and gets close to the carbon mass flow rate in the freshly added feedstock. Hence, it can be assumed that full decomposition of the initially added organic compounds in the feed (prior to run 0) is obtained after six SCWO runs. The equivalent TOC removal of the whole system is calculated by the outgoing and incoming carbon flows using Eq. (3). The results are displayed in Fig. 4. TOC removal in the initial run is only 43.2% and increases to 64.8% after the 1st recirculation of the effluent. Organic residuals from the initial run are not fully oxidized during the 1st recirculation and are further recycled and oxidized to result in an equivalent TOC removal of 77.9% in the 2nd recirculation run. With recirculation operation, most organic residuals from previous runs accumulate to the subsequent run and get further oxidized to boost the equivalent overall TOC removal. At the 5th recirculation run, the equivalent TOC removal reaches 99.2%, indicating a near dynamic equilibrium of incoming (feedstock) carbon and outgoing (gas-phase) carbon.

It is important to state that OER has a significant influence on the recirculation experiments by comparing the experiments at OER = 1.5 and 3.0. Higher OER is superior in decomposing and oxidizing organics resulting in fewer recirculation times before attaining a quasi-steady situation. A maximum equivalent TOC removal of 94.0% is obtained after six recirculation runs at OER = 1.5, as shown in Fig. 4. More recirculation runs are necessary for a lower OER to reach same equivalent TOC removal. Moreover, less oxidizer is used at low OER which is a benefit for SCWO operations, resulting in less oxidizer cost and less corrosion by avoiding high oxidizer load (Bermejo and Cocero, 2006). Nevertheless, a higher carbon concentration in the recycled effluent is observed as shown in Table 2. The high carbon containing effluent is not a problem in the studied case as the tested feedstock (*i.e.,* volatile fatty acids) only generates soluble intermediates. In more general cases, the high carbon concentration in the effluent at very low OER would probably generate solid intermediates/products (Zhang et al., 2018), resulting in a critical issue of undecomposed solid products in either the membrane filtration process or the high pressure SCWO system. Further study on a proper OER is suggested.

Table 1
Performance of the membrane filtration as a function of the SCWO recirculation run number at OER 3.0 and 1.5.

OER	Recirculation SCWO runs	TOC of the effluent ($mg•L^{-1}$)	First rejection (%)	Permeate flux of first filtration ($L•h^{-1}•m^{-2}$)	Second rejection (%)	Third rejection (%)	Carbon preservation (%)
3.0	0	1024	83.4	72.5	69.4	57.7	97.6
	1	1590	84.7	63.4	70.1	54.9	98.3
	2	1959	84.3	55.2	70.8	55.4	98.4
	3	2154	83.2	49.0	73.1	59.9	98.5
	4	2169	81.5	47.3	76.8	65.6	98.9
	5	2135	84.0	48.5	73.3	63.2	98.7
	6*	2091	/	/	/	/	/
1.5	0	1172	76.3	72.5	63.7	55.4	95.3
	1	2072	82.2	58.1	72.5	68.3	98.3
	2	2762	81.9	46.1	73.5	68.4	98.3
	3	3212	80.4	41.8	75.5	75.4	98.7
	4	3432	77.9	40.3	70.8	68.0	98.2
	5	3524	77.0	38.9	68.3	69.2	97.9
	6*	3491	/	/	/	/	/

* The effluent of run 6 was no longer treated with membrane filtration process as it was the final run.

Table 2
Carbon mass flow rates in each SCWO run with effluent recycling, as a function of OER 3.0 and 1.5.

OER	Recirculation SCWO runs	Carbon in the influent ($mg \cdot s^{-1}$)		Carbon in the effluent ($mg \cdot s^{-1}$)		Carbon balance (%)
		Fresh	Recycled	Aqueous	Gas	
3.0	0	4.196	0.000	2.400	1.735	98.6
	1	4.110	2.349	3.797	2.560	98.4
	2	4.192	3.745	4.668	3.168	98.7
	3	4.139	4.609	5.230	3.390	98.5
	4	4.224	5.168	5.368	3.891	98.6
	5	4.242	5.334	5.369	4.036	98.2
	6	4.346	5.318	5.276	4.269	98.8
1.5	0	4.078	0.000	2.713	1.302	98.5
	1	4.254	2.604	4.898	1.893	99.0
	2	4.217	4.841	6.513	2.426	98.7
	3	4.247	6.483	7.717	2.912	99.1
	4	4.100	7.648	8.334	3.264	98.7
	5	4.199	8.215	8.636	3.635	98.8
	6	4.205	8.495	8.746	3.785	98.7

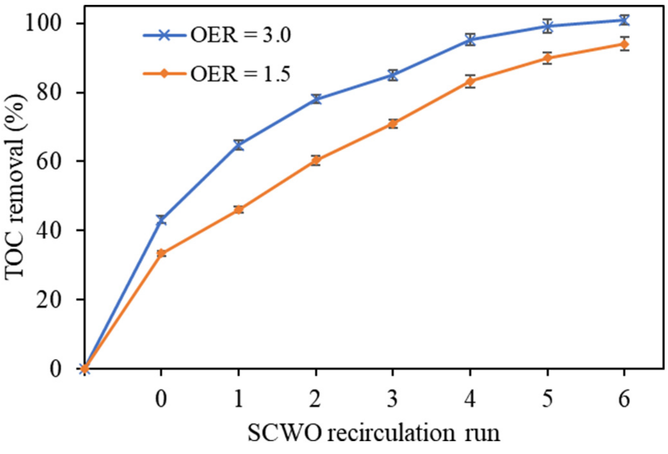

Fig. 4. TOC removal during different SCWO recirculation runs at OER 3.0 and 1.5.

3.3. Gas products

The gas product yields in ER-SCWO experiments are shown in Fig. 5. CO_2 is the primary product as expected. At OER = 3.0, the production in CO_2 increases with recirculation, from 2.87 $mL \cdot s^{-1}$ at the initial run to 7.03 $mL \cdot s^{-1}$ after six times recirculation. The yield in byproducts (*i.e.*, CO and H_2) also increases along with recirculation. The gain in gas yield is explained by the enhanced organic decomposition resulting from the recirculated effluent. It is also observed that the growth rate in byproducts yield is more significant than that of the CO_2 yield, and the biggest difference happens between non-recycling and recycling runs. We suspected this is caused by the decrease in the actual ratio of oxidizer to carbon in the influent during recirculation, since more incomplete organics are recycled (thus there is a higher concentration of carbon in the feed) while the addition of oxidizer is constant irrespective of recirculation. The concentration of carbon in the influent increases significantly during several previous runs and attains a steady high value from the 3rd recirculation. Since the oxidizer addition, as set by the OER, is only based on the carbon stemming from the fresh feedstock going into the process, and subsequently higher amounts of carbon are added from the recirculation effluent, a significant decrease in the actual ratio of oxidizer to carbon appears at this and any subsequent run. The yield in CO and H_2 increases in inverse proportion to the change in actual OER. This agrees with previous researches that carbon monoxide and hydrogen gas appear at lower OER (Guo et al., 2010). This assumption is also confirmed by the experiments at OER = 1.5, as shown in Fig. 5 (b). The yield in carbon monoxide and hydrogen gas is higher at OER = 1.5 compared to OER = 3.0, though the total gas yield is less.

For the purpose of organic removal to harmless products using SCWO technology, CO_2 should be the only gas product. Whereas the production of CO and H_2 are inevitable and more likely to be generated at lower OER during this recirculation process. As such, a downstream method of disposing CO and H_2 should be considered. Catalytic gas oxidation could be an alternative solution to get end products free from CO and H_2 (Mahapatra et al., 2019). On the other hand, a byproduct of concentrated CO and H_2 as fuel would also be possible if CO_2 is separated as a commercial product from SCWO as recommended by Cocero (Cocero, 2018).

3.4. Aqueous effluent

The organic constituent concentrations in the SCWO effluent are illustrated in Table 3. All of the fed VFAs were detected in large concentrations, together occupying >70% of the total organic carbon. Acetic acid is the primary compound, which agrees with literature (Savage, 1999; Schmieder and Abeln, 1999) that acetic acid is one of the major and refractory intermediates in supercritical water oxidation. Besides, oxidation and degradation of other acids used in this study's feedstock is likely to generate acetic acid as well (Day et al., 1973; Sánchez-Oneto et al., 2006), resulting in acetic acid accumulating in the effluent. This also explains the increasing percentage of acetic acid in the effluent in later recirculation runs (Table 3). The concentration of the other four acids decrease with recirculation at different rates, though the concentration of all acids in the effluent increase with recirculation, resulting

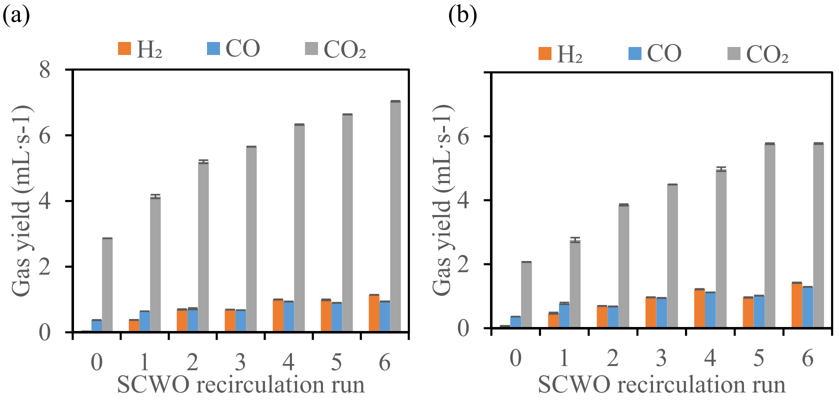

Fig. 5. Gas yield during different recirculation runs at (a) OER = 3.0 and (b) OER = 1.5.

from the incomplete oxidation of the fed acids. Organics that are easier to be oxidized would reach the quasi-steady situation earlier, and contribute less to the effluent-TOC.

In addition to the acids that were in the feedstock, some extra organic compounds were also present in the effluent (Table 3). They are assumed to be intermediates from acid oxidation. Compared to acetic acid, those intermediates should be easier to oxidize and contribute to the gaseous end products. In a typical SCWO process, degradation (*e.g.*, hydrolysis) and oxidation reactions happen simultaneously (as shown in Fig. 6). Both the organics from the feedstock and their intermediates could remain in the effluent from incomplete oxidation processes. With the recirculation process, the intermediates get further oxidized and contribute to the gaseous end product, which agrees well with the increment in gas yield.

Due to the incomplete rejection of organics from the membrane filtration process, small intermediates such as acetic acid are also discarded in the permeate to a certain extent. The loss in carbon would decrease the yield in gas products (CO_2) as well as necessitate a potential post-treatment of the aqueous effluent (*e.g.*, biological aerobic treatment after membrane filtration). However, it could also be considered a benefit from another perspective. The oxidation of acetic acid was reported to be a rate-limiting step in SCWO (Brunner, 2014a). The discharge of acetic acid might shift the oxidation reaction towards end products.

3.5. Discussion and perspectives

3.5.1. Benefits compared with conventional SCWO systems

A conventional SCWO system could achieve the equivalent organic removal of 43.2% at 380 °C, OER = 3.0 and a single-pass residence time of 24.6 s given the feedstock used in this study. By applying the proposed ER-SCWO, the equivalent organic removal increases gradually and reaches near 100% after five times of recirculation. During recirculation, the organic concentration in the influent, gas effluent and aqueous effluent all increase and finally reach a dynamic equilibrium. Time (being five times the recirculation time in this case) used to reach the steady state is negligible for a long-term running system. Compared with a conventional system, the proposed system has only slightly lower capacity but much higher organic removal efficiency. As demonstrated in Fig. 7, the proposed system has a feedstock flow rate of 10% less than a single-pass conventional system (provided equal flow rate in the reactor), indicating that the process with recirculation would consume around 11% more energy if feeding same amount of fresh feedstocks. However, the oxidation efficiency of the proposed system could reach nearly 100%, significantly higher than 43.2% of a conventional, single-pass system.

What's more, the proposed system is capable of reaching 100% decomposition in one setup regardless of the organic waste type which is being fed (it basically has near-infinite residence time for organics). To reach the same level of oxidation efficiency, a conventional setup would need a much longer reactor or a combination of higher temperatures and more oxidizer. Moreover, a conventional setup will likely require re-optimizing the process parameters when switching to other types of waste feed. Corrosion caused by higher oxidizer usage or higher temperature is inevitable, but in all likelihood, less prevalent in the recirculation setup which operates at milder conditions.

Table 3
Constituents of the effluent after each recirculation run at OER = 3.0.

Recirculation SCWO runs	Acetic acid (%)	Propionic acid (%)	Butyric acid (%)	Valeric acid (%)	Caproic acid (%)	Extra organics (%)
0	30.1	15.0	11.9	8.1	6.3	28.6
1	33.4	13.0	8.0	5.7	4.0	35.8
2	35.4	11.6	6.4	4.6	3.2	38.9
3	37.1	10.5	5.6	4.0	2.8	40.0
4	39.4	10.2	4.8	3.9	2.8	39.0
5	40.6	9.9	5.1	3.9	2.8	37.6
6	42.3	9.9	5.4	4.0	2.9	35.5

3.5.2. The use of membrane filtration process

The effluent from SCWO process contains water originating from (i) the water within the wet waste feedstock, (ii) the generation of chemical water from hydrogen oxidation present in the organic feedstock and (iii) the H_2O_2 solution itself. The effluent recirculation (*i.e.*, without membrane separation) would recycle the excess water along with incomplete oxidized organics, resulting in the buildup of influent volume for the subsequent run. The membrane filtration process is used to discard water and recycle incomplete decomposed organics and hence, keep the volume of recirculated effluent constant. One of

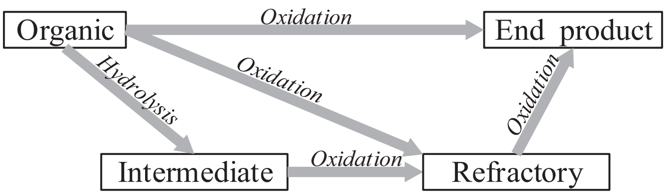

Fig. 6. Reactions pathway, modified from (Brunner, 2014a; Bermejo and Cocero, 2006).

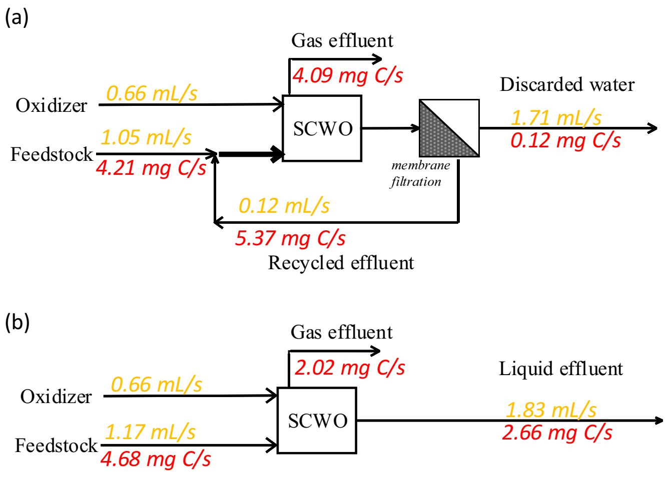

Fig. 7. Diagram of the aqueous and carbon mass flow in (a) combination system and (b) single-pass conventional system (numerical value are modified from experimental results of this work).

the major costs of applying membrane processes is the requirement to pressurize the feed solution. SCWO is an inherent high pressure system and as such, the existing outlet pressure of the effluent (with a partial reduction thereof) can be used to drive the process.

The choice of membrane type is important as this study aimed to retain all organics for further oxidation. A NF-90 membrane was used to carry out the experiments. NF was not considered the best membrane for its (relative) 'large pore' size resulting in some loss of organics to the permeate, while it could achieve a higher flux compared to RO membranes (Mohammad et al., 2015). Several methods were applied to minimize this loss in organics. Interestingly, it is supposed that full rejection of solute/organics might not be the optimal way for SCWO as some organic intermediates (*e.g.*, acetic acid) might have low reactivity in SCWO but are fairly easy to process in biological water treatment (Aymonier et al., 2001). If the feedstock contains salts, they will accumulate in the SCWO system resulting from membrane separation and recirculation. Salts accumulation was not an issue in this study, yet deserves further research in treating wastes with high inorganic concentration (Xu et al., 2015).

3.5.3. Open questions

This work was conducted within a semi continuous manner. SCWO and membrane filtration processes were performed separately and not yet integrated. The filtration took much longer time than SCWO, probably resulting from the small membrane configuration. A retentate buffer tank could be a valid solution. An integrated system however should match the mass flow rates of the two processes. Meanwhile, the adjustment of pressure from SCWO outlet to drive the membrane filtration process should be carefully studied.

Proper single-pass residence time, OER and feedstock concentration should be investigated to guarantee solids-free effluent for the sake of recirculation. Reaction temperature should be further studied to avoid corrosion near the critical point as well as the corrosion at high temperature (Bermejo and Cocero, 2006). Gas products from the combined ER-SCWO system need a proper posttreatment since the formation of CO and H_2 are considerable, especially when relatively low OER's are being used.

3.5.4. Expected application of ER-SCWO

The recirculation method has the potential to improve the application of SCWO technology. The recirculation method allows: (1) the residence time is not fixed and is basically infinite which allows complete break-down of refractory compounds. Reactors without recirculation (*i.e.*, present CSTR's or tubular reactors) have a residence time determined by design, hence they are custom designed to handle a particular waste stream in mind. A single SCWO setup/strategy with recirculation is versatile in dealing with different organic compounds, (2) the ER-SCWO reactor could be more compact with a much smaller reactor volume compared to a standard single-pass SCWO reactor, (3) a reactor design with recirculation has the potential to operate at less harsh process conditions (in terms of temperature, pressure and oxidizer) and thus putting less stringent requirements on reactor material selection. The proposed process is capable of being developed into a mobile and compact setup with smaller reactor dimensions and being more versatile in treating various organic wastes, especially toxic ones.

4. Conclusion

The ER-SCWO process proposed in this study enhances the organic decomposition from 43.2% to near 100%. The membrane filtration process discards relatively clean water. The proposed ER-SCWO process is capable of guaranteeing only a 10% loss in feedstock throughput when compared to the conventional, single-pass SCWO processes operating at the same reactor flow rate. The reaction conditions of the ER-SCWO process are milder than in most previous researches, indicating a potentially lower corrosive environment. The ER-SCWO process could provide a universal strategy allowing the decomposition of different organic wastes within one setup under the same reaction conditions.

CRediT authorship contribution statement

Dongdong Zhang: Conceptualization, Methodology, Software, Investigation, Data curation, Formal analysis, Writing - original draft, Writing - review & editing.**Qi Niu:**Conceptualization, Investigation, Writing - original draft, Writing - review & editing.**Lingshan Ma:**Investigation, Writing - original draft, Writing - review & editing.**Sebastiaan Derese:**Writing - original draft, Writing - review & editing.**Arne Verliefde:**Writing - original draft, Writing - review & editing.**Frederik Ronsse:**Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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