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# Coal chemical industry membrane concentrates: characterisation and treatment by ozonation and catalytic ozonation processes

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**Environmental context.** Reverse osmosis (RO) is widely used for the treatment of hazardous wastewaters produced from the coal chemical industry (CCI) to achieve zero liquid discharge however the use of RO inevitably results in accumulation of refractory organic matter in the RO membrane concentrate, the treatment of which is challenging. This work provides useful insights into the organic composition of RO concentrates obtained from a range of real CCI wastewaters. The efficacy of treatment of these concentrates by ozonation processes is assessed as is the cost effectiveness of such treatment.

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## ABSTRACT

**Rationale.** The enactment of increasingly stringent regulations has prompted the implementation of membrane technologies such as reverse osmosis (RO) in the management of coal chemical industry (CCI) wastewaters with the goal of achieving zero liquid discharge (ZLD). However, this practice inevitably results in the production of high salinity concentrates containing refractory organic matter. **Methodology.** In this study, we characterised the organic composition of RO concentrates obtained from the CCI using a variety of methods including liquid chromatography–organic carbon/nitrogen detection (LC-OCND) and investigated the degradability of organic compounds present in these concentrates by ozonation and catalytic ozonation processes. **Results and discussion.** Organic analysis using LC-OCND revealed that humic-like substances and low molecular weight neutral compounds were the dominant constituents in the CCI concentrates examined. Measurement of degradability of the CCI concentrate by a pure ozonation process showed low treatment efficiency (~20% dissolved organic carbon (DOC) removal) as a result of the refractory nature of the organic compounds present in the wastewater. The degradation of these organics by a catalytic ozonation process employing a commercially available Fe-oxide based catalyst was higher than that observed by pure ozonation although the extent of organics removal (DOC removal ~47%) is still low due to the refractory nature of the organics as well as the influence of salts on the catalyst performance. Techno-economic analysis of the pure ozonation and catalytic ozonation processes indicated that the total cost of implementation of the ozonation processes (homogeneous or heterogeneous) for CCI concentrate treatment is negligible compared with the overall cost of the complete ZLD process.

**Keywords:** catalytic ozonation, coal chemical wastewaters, liquid chromatography–organic carbon/nitrogen detection, low molecular weight neutrals, refractory organics, RO concentrate, technoeconomic assessment, zero liquid discharge.

## Introduction

We are pleased to include this article in the Special Edition of *Environmental Chemistry* dedicated to Dr Graeme Batley. One of the hallmarks of Graeme's career has been the application of analytical chemistry to the understanding and, where possible, solution of real-world problems. In this article, we use a variety of analytical methods to characterise membrane concentrates produced in the coal chemical industry (CCI) and, based on the

results obtained, assess the viability of the increasingly widely used treatment technology of ozonation, both conventional and catalytic, to the removal of recalcitrant organic compounds from these troublesome wastewaters. Particular attention is given to the increasingly popular method of liquid chromatography–organic carbon/nitrogen detection (LC-OCND) as a relatively simple means of separating compounds in these complex mixtures into different groups based on their size, charge and hydrophobicity. We then assess the ability of ozonation to degrade these various groupings. Graeme's work has been particularly impactful because of his use of analytical tools to find pragmatic solutions to environmental problems, an approach we believe is embodied in the work presented here.

The CCI plays an important role in the supply of a variety of high-value chemicals such as synthetic natural gas, methanol and ammonia (Zhang *et al.* 2019). However, CCI is also a leading contributor to wastewater discharge with treatment of CCI wastewater particularly challenging due to the presence of toxic and hazardous compounds such as polycyclic aromatic hydrocarbons and nitrogen heterocyclic compounds (Zhao and Liu 2016). Extensive effort has therefore been devoted to the research and development of various processes (including biological processes, coagulation processes and advanced oxidation processes (AOPs)) for the removal of organic matter (and other contaminants such as ammonia and fluoride) from CCI wastewaters. Membrane technologies are also becoming increasingly popular as a treatment option to polish the effluent from biological and/or coagulation processes to meet rigorous discharge standards and, in some instances, zero liquid discharge (ZLD) requirements (Jin *et al.* 2013; Li *et al.* 2016). Both low- and high-pressure driven membrane processes (e.g. ultrafiltration (UF) and reverse osmosis (RO)) have been used in the management of CCI wastewaters (Ji *et al.* 2016; Wang *et al.* 2019; Li *et al.* 2020). While UF membranes are typically integrated with coagulation, activated carbon adsorption and biological processes to enhance the removal of colloidal particles, the high-pressure technologies such as RO have smaller molecular weight cut-offs (MWCO) and produce desalinated effluents suitable for reuse in coal production and/or for cooling purposes. However, the use of RO inevitably results in the accumulation of refractory organic matter in the RO membrane concentrate, the treatment of which has been recognised as one of the critical challenges in the management of CCI wastewater and achievement of ZLD (Xiong and Wei 2017; Shi *et al.* 2021).

Recently, implementation of AOPs in the treatment of RO concentrates from industrial wastewater reclamation plants has gained interest (Cai *et al.* 2020). However, there is limited understanding of the nature of the refractory organic compounds present in the RO concentrate produced following treatment of CCI wastewaters and how this might influence the overall degradability and treatment efficiency. In this study, we characterised the organic matter present in

a variety of RO concentrates from full-scale plants treating CCI wastewaters (referred as CCI concentrates from hereon) and investigated the treatment of one of these concentrates by pure ozonation and catalytic ozonation processes (Miklos *et al.* 2018; Du *et al.* 2020; Zheng *et al.* 2022). We used liquid chromatography–organic carbon/nitrogen detection (LC-OCND) (Huber *et al.* 2011) to fractionate the organic matter present in the concentrate into different groups and subsequently assessed the treatability of these various groups by pure ozonation and catalytic ozonation. We also characterised the changes in the excitation–emission fluorescence (EEM) spectra of the CCI concentrate following treatment by pure ozonation and catalytic ozonation processes although it should be noted that this technique only depicts the fraction of organic matter that exhibits fluorescence (Yang *et al.* 2013; Yu *et al.* 2016; Li *et al.* 2019). We have also performed a detailed technical economic analysis of the pure ozonation and catalytic ozonation processes to determine the economic viability of these to achieve ZLD. This is one of very few studies that have performed detailed analysis of the organic nature of CCI concentrates from various coal chemical processes to provide insights into the organic composition of CCI concentrates and the treatability of these concentrates using ozonation processes.

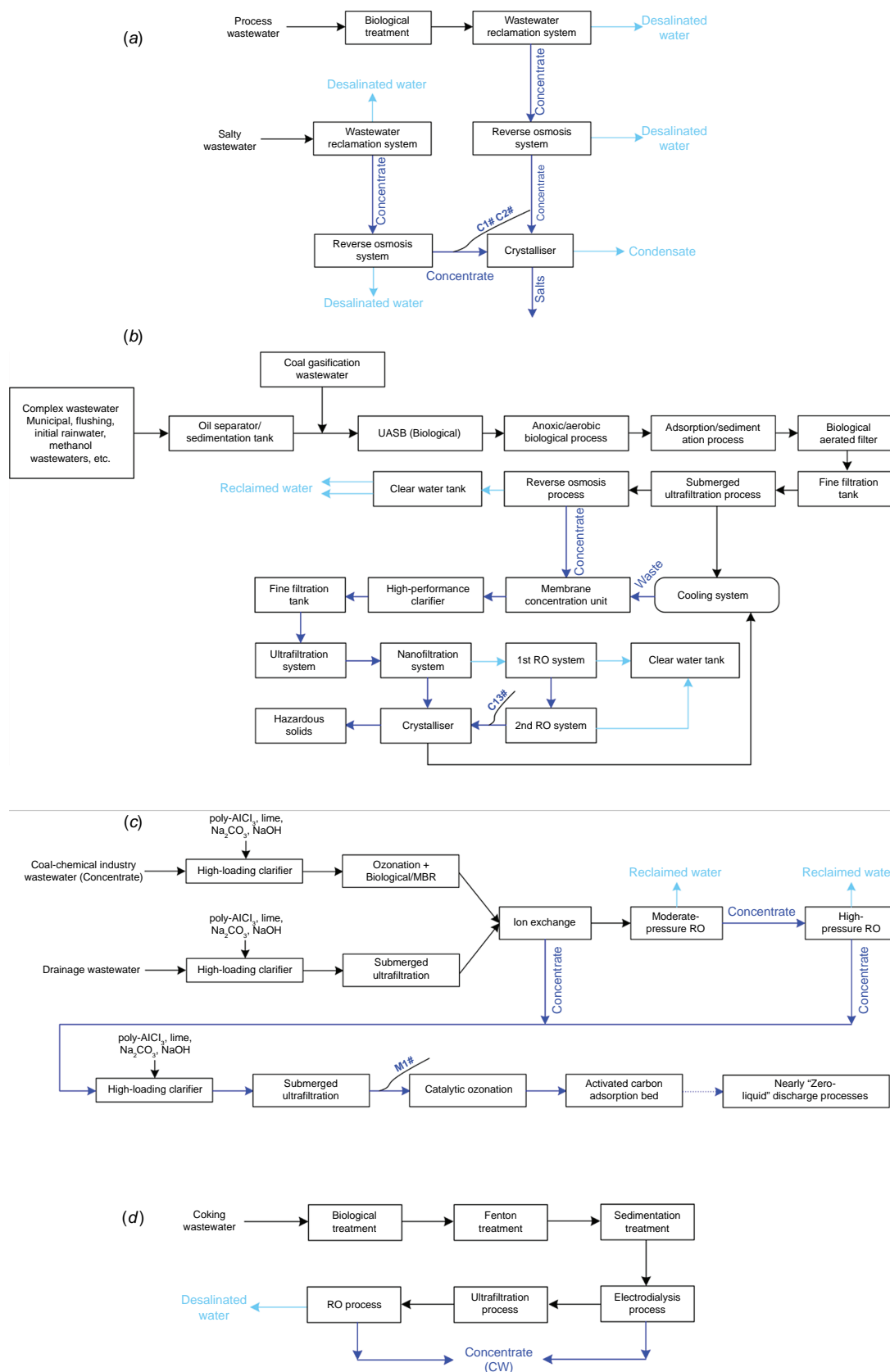
## Experimental

### CCI concentrate sampling

Five CCI concentrate samples (i.e. C1#, C2#, C13#, M1# and CW1#) were collected from four wastewater treatment plants. C1# and C2# are essentially duplicate samples taken on the same day of an RO concentrate from a coal gasification wastewater treatment plant (Xintian) with the location from which these samples were taken shown in the flow diagram of the treatment unit in Fig. 1a. C13# represents an RO concentrate sample from another treatment facility for coal gasification wastewater (Fig. 1b). M1# represents a combined stream of concentrates from the ion exchange and RO units, used for treatment of methanol synthesis wastewater (Zhongmei Yuanxing), which was further polished by coagulation and ultrafiltration prior to collection (Fig. 1c). CW1# represents a sample of mixed concentrates from RO and electrodialysis processes from a coking wastewater treatment plant in Qian-an (Fig. 1d). The concentrate used in this study has undergone multistage ultrafiltration prior to the RO process and hence contains no particulate organic carbon (>0.22  $\mu\text{m}$ ).

### Reagents

All chemicals (NaCl, Na<sub>2</sub>SO<sub>4</sub>, *tert*-butyl alcohol (TBA, SKU 360538) and humic acid (HA, SKU 53680)) used in this work were of analytical grade and purchased from Sigma–Aldrich unless stated otherwise. All solutions were



**Fig. 1.** Flow diagram of the treatment process and the sampling point of C1# and C2# (a), C13# (b), M1# (c) and CW1# (d).

prepared in Milli-Q (MQ) ultrapure water with a resistivity of  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  (Millipore). To avoid contamination by trace metals, all glassware was soaked in 5% v/v nitric acid prior to use. A  $1.0 \text{ g C L}^{-1}$  stock solution of HA (Aldrich) was prepared in MQ and filtered using  $0.22 \text{ }\mu\text{m}$  PVDF filters (Millipore) prior to use. Gas phase ozone was produced from an ozone generator (Yuan *et al.* 2020) (T4000,  $5.0 \text{ g L}^{-1}$ , Oxyzone Pty Ltd, Australia) with pure oxygen used as the gas source.

### Catalyst description and characterisation

The Fe-loaded  $\text{Al}_2\text{O}_3$  catalyst used for the catalytic ozonation study was provided by the Coal Chemical Research Institute (CCRI, China). Upon receipt, the catalyst was prewashed with MQ water until the supernatant was clear and then dried at  $60^\circ\text{C}$  prior to use. Detailed characterisation of the surface properties and composition of the catalyst was performed in our earlier work (Yuan *et al.* 2022) and showed that the major constituents of the catalyst were hematite (01-084-9870),  $\text{Al}_2\text{O}_3$  (00-046-1131) and  $\text{MnO}_2$  (04-009-8106). The  $\text{pH}_{\text{zpc}}$  of the catalyst was around 8.4 suggesting that the catalyst surface will be positive under the pH conditions investigated in this study (pH 7.5–7.6).

### CCI concentrate analysis

Methods used for analysis of CCI concentrate samples are summarised in Supplementary Table S1. The concentration of organics present in the CCI concentrates was quantified using dissolved organic carbon (DOC) and chemical oxygen demand (COD) measurements. DOC and COD were measured using a Shimadzu TOC analyser and Hach COD reactor respectively. COD measurements were corrected for the presence of high  $\text{Cl}^-$  concentrations in the CCI concentrates by subtracting the COD contributed from  $\text{Cl}^-$  ( $\text{COD}_{\text{Cl}^-}$ ) from the measured sample COD values. For calculation of  $\text{COD}_{\text{Cl}^-}$ , the  $\text{Cl}^-$  concentration in the samples was measured using ion chromatography (IC) and then converted into  $\text{COD}_{\text{Cl}^-}$  values using the calibration curve developed by measuring the COD value of pure NaCl solutions. Fractionation of the organic matter present in the CCI concentrates was conducted using a LC-OCND size-exclusion chromatography system (DOC-LABOR) according to the standard protocols for this instrument (Huber 2017). The signals of the principal components including biopolymers (BP, molecular weight (MW)  $> 20\,000 \text{ Da}$ ), humic substances (HS, MW of  $500\text{--}10\,000 \text{ Da}$ ), building blocks (BB, MW of  $300\text{--}500 \text{ Da}$ ), low molecular weight (LMW) acids (MW  $< 350 \text{ Da}$ ), LMW uncharged species (or 'neutrals'; MW  $< 350 \text{ Da}$ ) and hydrophobic organic carbon were integrated using the proprietary software ChromCalc (DOC-LABOR, Karlsruhe, Germany) (Huber *et al.* 2011). Note that the NaCl concentrations in the concentrate were much lower than the salt concentrations (i.e.  $35 \text{ g L}^{-1}$ ) at which LC-OCND analysis may be impacted due to formation of hypochlorite on UV irradiation. The similarity in total DOC

concentrations determined by TOC analysis and LC-OCND analysis further supports the conclusion that the influence of salts on LC-OCND measurements was negligible.

We also used EEM fluorescence spectroscopy to investigate the transformation of organic compounds in CCI concentrate CW1# (Yang *et al.* 2013; Yu *et al.* 2016; Li *et al.* 2019) following treatment by pure ozonation and catalytic ozonation. All EEM spectra were measured using a fluorescence spectrometer (Cary Eclipse) with scanning emission spectra from 250 to 600 nm at a data interval of 5 nm and excitation wavelength from 200 to 450 nm at an increment of 5 nm. Both the excitation and emission slits were set at 5 nm and the scan speed was set at  $600 \text{ nm min}^{-1}$ . The spectrum of Milli-Q water was used as the baseline. Note that the concentrate samples were diluted 1000 times to enable analysis by EEM fluorescence spectroscopy, but some degree of inner filter effects remained due to matrix complexity. Classification of EEM signals into categories of humic acid-like and fulvic acid-like substances was performed according to the method documented elsewhere (Chen *et al.* 2003; Li *et al.* 2019).

### Ozonation and catalytic ozonation setup

Investigation of the degradability of the organic compounds in the concentrate obtained from the Qian-an treatment plant (CW1#) by pure ozonation and catalytic ozonation processes was carried out in a semi-batch system (Supplementary Fig. S1). The volume of the concentrate was fixed at 150 mL and the initial pH of the concentrate was adjusted to 7.5–7.6 using 1 M HCl or 1 M NaOH solutions. The initial DOC and total dissolved solids contents of the concentrate were  $\sim 30 \text{ mg L}^{-1}$  and  $9 \pm 1 \text{ g L}^{-1}$ , respectively. In these studies,  $\text{O}_3$  gas was sparged into the wastewater at a controlled flow rate of  $600 \text{ mL min}^{-1}$  using a gas-phase ozone concentration of  $51 \text{ mg L}^{-1}$ . For catalytic ozonation,  $33.3 \text{ g L}^{-1}$  of the catalyst was added to the reactor. At predetermined time intervals (i.e. 10, 20, 30, 40, 60 and 120 min), 5 mL of sample was withdrawn from the reactor. Following sparging with  $\text{N}_2$  gas for 1 min, the samples were filtered using  $0.22 \text{ }\mu\text{m}$  PVDF filters (Millipore) and the COD value, DOC concentration and LC-OCND and EEM spectra were measured according to the aforementioned methods.

## Results and discussion

### Composition of CCI concentrates

The composition of the various CCI concentrate samples is provided in Table 1. The accuracy of major ion measurements was evaluated by checking the charge balance using Visual MINTEQ with the results of these analyses given in Supplementary Table S2. As shown, the charge balance errors are between 5 and 20% for these samples with this error considered acceptable.

**Table 1.** Chemical compositions of CCl concentrate samples.

Item	Unit	C1#	C2#	C13#	MI#	CWI#
pH		5.7–6.9	5.8–7.0	7.9–8.4	7.7–8.0	7.91
Total suspended solids	g L <sup>-1</sup>	0.31	0.24	0.61	0.12	0.034
Total dissolved solids	mg L <sup>-1</sup>	16 102	16 126	22 604	61 686	4958
Conductivity	μs cm <sup>-1</sup>	32 300	32 600	45 400	101 000	8813
Soluble COD	mg L <sup>-1</sup>	574	691	2040	23	67.44
DOC	mg L <sup>-1</sup>	427.5	409.5	1346.7	109.2	30.0
BOD <sub>5</sub>	mg L <sup>-1</sup>	23.5	21.5	84.2	0.6	10.1
Hardness (CaCO <sub>3</sub> )	mg L <sup>-1</sup>	751	731	470	26	756
Alkalinity (CaCO <sub>3</sub> )	mg L <sup>-1</sup>	227	205	6817	795	183
CO <sub>3</sub> <sup>2-</sup>	mM	n.d. <sup>A</sup>	n.d.	9.6	1.0	0.085
HCO <sub>3</sub> <sup>-</sup>	mM	4.5	4.1	116.9	13.9	3.5
Turbidity	NTU	5.8	4.4	6.4	1.0	1.7
Colloidal Si	mg L <sup>-1</sup>	0.49	0.86	2.38	0.25	1.49
Total phosphorous (as P)	mg L <sup>-1</sup>	0.79	0.85	2.17	0.71	0.072
Total dissolved phosphorous (as P)	mg L <sup>-1</sup>	0.69	0.71	1.99	0.61	0.03
NH <sub>4</sub> -N	mg L <sup>-1</sup> as N	41.9	43.0	459	2.60	2.9 ± 3.2
Na <sup>+</sup>	mg L <sup>-1</sup>	4610	4330	6110	18 300	2138 ± 788
K <sup>+</sup>	mg L <sup>-1</sup>	47.0	46.7	133.0	208.0	11.8 ± 0.4
Ca <sup>2+</sup>	mg L <sup>-1</sup>	3.67	8.72	63.8	5.16	106.0 ± 7.8
Mg <sup>2+</sup>	mg L <sup>-1</sup>	173	164	67.8	0.573	83.1 ± 0.6
Total Fe <sup>A</sup>	mg L <sup>-1</sup>	1.29	0.082	12.0	0.289	0.68 ± 0.10
Total Al	μg L <sup>-1</sup>	42.7	13.1	1030	4.40	86.9 ± 34.1
Total Mn <sup>B</sup>	μg L <sup>-1</sup>	328	274	103	3.66	1023 ± 95
Cl <sup>-</sup>	mg L <sup>-1</sup>	6730	6890	8240	2850	1640 ± 338
NO <sub>3</sub> -N	mg L <sup>-1</sup> as N	119	90.2	362	126	553.5 ± 41.7
SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	2270	2250	507	41 400	4455 ± 1190
F <sup>-</sup>	mg L <sup>-1</sup>	52.8	47.6	68.2	7.57	153.5 ± 2.1
S <sup>2-</sup>	mg L <sup>-1</sup>	n.d.	n.d.	n.d.	n.d.	n.d.

<sup>A</sup>Fe is present as Fe<sup>III</sup> (most likely as Fe<sup>III</sup> organic complexes).

<sup>B</sup>Mn is present as Mn<sup>II</sup>. Note: The concentrate used in this study has undergone multistage ultrafiltration prior to the RO process and hence contains no particulate organic carbon (>0.22 μm). Hence the total organic carbon is same as the dissolved organic carbon measured here.

n.d.: not detectable.

It can be seen from Table 1 that the composition of C1# and C2# are quite comparable, reflecting the accuracy of these analysis results given the source similarity of these samples. The sum of cation and anion concentrations (>14 000 mg L<sup>-1</sup>) is largely equal to the total dissolved solid concentrations for each sample. The high hardness value of these concentrates is due to the presence of Mg ions. Other multivalent elements including Fe, Al and Mn are present at relatively low concentrations. Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are the dominant anions in C1# and C2# samples. The high concentration of Cl<sup>-</sup> (~200 mM) may potentially create

challenges in application of ozonation and catalytic ozonation processes. As shown in our recent work (Yuan *et al.* 2022), scavenging of ·OH by chloride ions (particularly in the case of the catalytic ozonation process) as well as transformation of humic-like moieties to a more compact hydrophobic form in the presence of cations (such as Na<sup>+</sup>/Ca<sup>2+</sup>) affects the removal of organics by both pure ozonation and catalytic ozonation processes. Since the presence of divalent cations results in more charge shielding between adjacent functional groups in humic compounds compared to that induced by monovalent ions (Baalousha *et al.* 2006), we

expect the transformation of humics to a hydrophobic form to be pronounced in the case of C1# and C2# due to the high hardness of these wastewaters.

As in the case of C1# and C2#,  $\text{Na}^+$  (~250 mM) and  $\text{Cl}^-$  (~250 mM) are the dominant ionic species in the C13# sample although COD is present at a much higher concentration and  $\text{SO}_4^{2-}$  at a much lower concentration (~5 mM) compared to other CCI concentrates. These results are generally in accord with the use of nanofiltration prior to the RO unit (Fig. 1b). In addition, bicarbonate and ammonia are present at much higher concentrations in C13# than in the other samples. Since ammonia can react with ozone (Haag *et al.* 1984; Khuntia *et al.* 2012) and bicarbonate ions scavenge  $\cdot\text{OH}$  (Ruffino and Zanetti 2019), matrix effects are likely to be more prominent in the case of C13# compared to other CCI concentrates. As in the case of C1# and C2#, humic-like moieties in this concentrate (if any) are likely to be present in compact hydrophobic form due to the high hardness of these waters which will affect the removal of these moieties by both pure ozonation and catalytic ozonation processes.

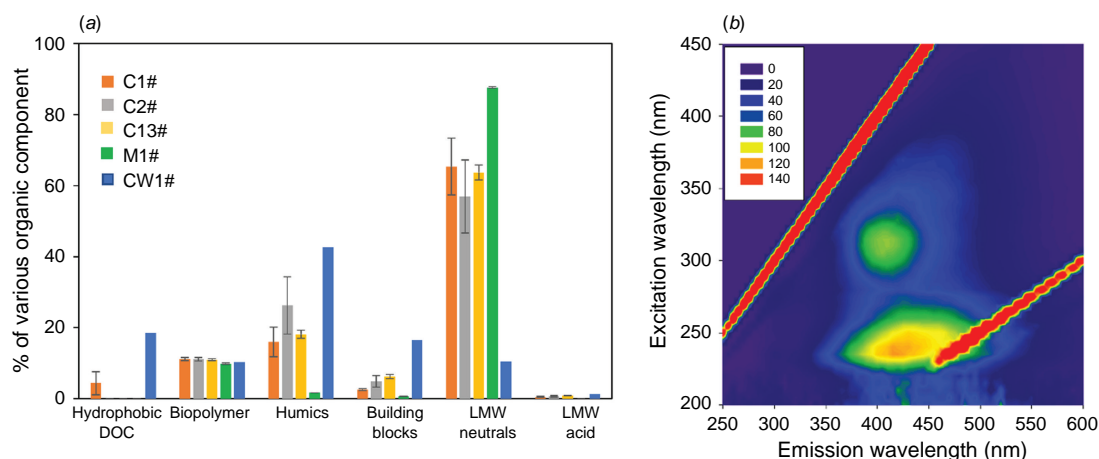
In contrast to C1#, C2# and C13#, M1# represents a combined concentrate stream of the waste from the ion exchange process and the concentrate of the second stage RO in a facility treating methanol synthesis wastewater (Fig. 1c). The low hardness in this sample is not surprising as a result of the pre-treatment by a high-loading clarifier with the addition of poly- $\text{AlCl}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ .  $\text{SO}_4^{2-}$  is the dominant anion in M1# due to inclusion of ion exchange waste in M1# (Fig. 1c). In summary, the COD concentration of M1# is relatively low and further mineralisation using AOPs may not be required prior to the thermal treatment of the concentrate (although the catalytic ozonation process has been installed on site).

CW1# represents a mixed RO and electrodialysis concentrate from a coking wastewater treatment facility

(Qian-an, Fig. 1d). The COD and salt concentrations of these concentrate samples were relatively low (i.e.  $\text{COD} < 120 \text{ mg L}^{-1}$ ,  $\text{TDS} < 10 \text{ g L}^{-1}$ ). The high hardness of these concentrates is due to the presence of Ca and Mg ions. Other multivalent elements including Fe, Al and Mn are present at relatively low concentrations. Similar to the cases of C1# and C2#,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are the dominant anions in the CW1# sample as well. The high concentration of  $\text{Cl}^-$  (~50 mM) and high hardness of these samples may potentially create challenges in the application of ozonation and catalytic ozonation processes (Yuan *et al.* 2022). Since the impact of  $\text{Ca}^{2+}$  on the transformation of humic substances and the strength of aggregates formed is more pronounced compared to that observed in the presence of  $\text{Mg}^{2+}$  (Hakim *et al.* 2019), the degradability of humic-like moieties is expected to be lower for this concentrate sample compared to C1# and C2#. Our results also show that  $\text{F}^-$  is present at fairly high concentrations in these concentrate samples although its treatment is beyond the scope of this study.

### Fractionation of the organic matter by LC-OCND

Fig. 2a indicates that for CCI concentrate samples C1#, C2#, C13# and M1#, LMW neutrals including alcohols, aldehydes, ketones, amino acids and sugars are the major components (57–88% of the DOC) followed by humic substances and biopolymers. In coking wastewater samples (CW1#), humic substances are the major component (~45%) with hydrophobic organics, building blocks and LMW neutrals present at lower concentrations. While there is no LC-OCND investigation of CCI concentrates reported in the literature, a comparable study on petroleum industrial wastewater treatment in Singapore (Cai *et al.* 2020) also showed the presence of ‘humic substances’ as the dominant organic fraction in the



**Fig. 2.** (a) Percentage of various organic constituents present in CCI concentrate samples measured using LC-OCND analysis. Panel (b) shows the EEM spectra of CCI concentrate sample CW1#.  $N \geq 2$ .

RO concentrate collected from a water reclamation facility in which the biologically treated effluents were further polished by an MF-RO system.

A typical EEM spectrum of the Qian-an CCI concentrate is shown in Fig. 2b with two peaks (i.e. 36.4 and 26.7 AU ( $\text{mg C L}^{-1}$ ) $^{-1}$ ) identified at Ex/Em = 235/415 nm and 310/410 nm respectively related to fulvic-like and humic-like substances in Regions III and V of the EEM spectra (Chen *et al.* 2003; Li *et al.* 2019). Signals of aromatic proteins I and II in the EEM spectrum were very low with the fluorescence properties generally in good agreement with the LC-OCND results.

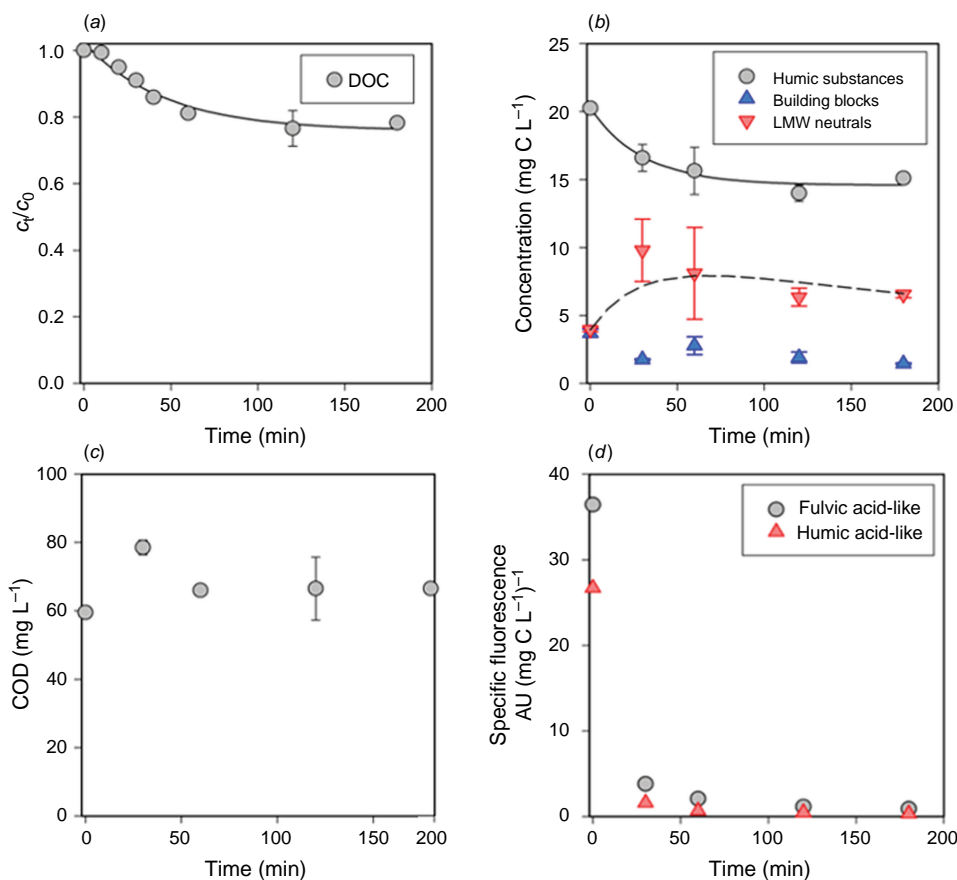
### Degradability of the refractory organic matter in concentrates by pure ozonation

In this section, we investigate the degradability of the CCI concentrate by pure ozonation. Since only the concentrate from the Qian-an plant (i.e. CW1#) could be regularly collected for further analysis, only treatment of this concentrate stream was performed. Fig. 3 summarises the changes in DOC concentration, LC-OCND components, COD concentration and EEM components as a function of ozonation duration. It can be seen from Fig. 3a that the removal of DOC (~20%) is largely completed in the first 1 h of reaction with the ongoing bubbling of ozone resulting in a minimal

increase in the removal efficiency. We classified the DOC based on its reactivity with ozone (Eqn 1):

$$\begin{aligned}
 [\text{DOC}]_t &= [\text{DOC}]_{\text{O}_3, \text{resistant}, 0} e^{-k_1 t} \\
 &+ [\text{DOC}]_{\text{O}_3, \text{reactive}, 0} e^{-k_2 t} \\
 &\approx [\text{DOC}]_{\text{O}_3, \text{resistant}, 0} + [\text{DOC}]_{\text{O}_3, \text{reactive}, 0} e^{-k_2 t}
 \end{aligned}
 \quad (1)$$

where  $k_1$  and  $k_2$  represent the apparent pseudo first order rate constants for degradation of  $\text{O}_3$ -resistant DOC and  $\text{O}_3$ -reactive DOC, respectively, with  $k_1 \ll k_2$ . Fitting Eqn 1 to the results in Fig. 3a, we find that ~76% of the DOC in the Qian-an CCI concentrate is resistant to  $\text{O}_3$  attack with the pseudo first order degradation rate constant of the reactive component equal to  $0.021 \text{ min}^{-1}$ . LC-OCND results provided more information on the temporal variations of the different components quantified by this technique (i.e. humic substances, building blocks and LMW neutrals; Fig. 3b). The concentrations of humic substances varied in a similar manner to the total DOC (Fig. 3a) with the  $\text{O}_3$ -resistant component representing 72% of the total humic substances and the  $\text{O}_3$ -reactive humic substances exhibiting a slightly higher pseudo first order degradation rate constant ( $k_2' = 0.033 \text{ min}^{-1}$ , Eqn 2) than that of the DOC. It is worthwhile noting that the oxidation of humic substances led to the formation of LMW neutrals rather than



**Fig. 3.** Time-resolved concentration (or intensity) of (a) DOC, (b) LC-OCND components (c) COD and (d) EEM components during ozonation of Qian-an concentrate. Lines in panels (a) and (b) represent pseudo-first order modeling results. The specific fluorescence in panel (d) was calculated by normalising the peak intensities (AU) of fulvic acid-like and humic acid-like substances to the DOC concentrations of the samples.  $[\text{pH}]_0 = 7.5\text{--}7.6$ ,  $[\text{pH}]_{\text{final}} = 7.0\text{--}7.3$ .



building blocks although this fraction has a molecular weight range between humic substances and LMW neutrals (Huber *et al.* 2011). An accumulation of LMW neutrals was noted in the first 30 min followed by a decrease through the ongoing process. Since the decrease in humic substance concentration and the initial increase in LMW neutral concentration were similar, it is plausible to conclude that the native LMW neutrals present in the Qian-an concentrate were not O<sub>3</sub> reactive. The LMW neutral concentration as a function of time was therefore calculated according to Eqns 2 and 3. The pseudo first order rate constant of degradation of LMW neutrals formed on oxidation of humics (i.e.  $k'_3$ ) was calculated to be 0.005 min<sup>-1</sup> indicating that the intermediate products of humics oxidation are more refractory to ozonation. In contrast to the DOC and LC-OCND results, the COD concentration firstly increased with the transformation of humic substances to LMW neutrals and then decreased with the ozonation of LMW neutrals (Fig. 3c). It seems that part of the native humics in the CCI concentrate could not be oxidised by the COD<sub>Cr</sub> reagents but, once these moieties are oxidised on ozonation, the product(s) formed are oxidised by COD<sub>Cr</sub> reagents initially resulting in an increase in the COD value followed by a small decrease on further breakdown of these oxidised products.

$$[\text{HS}]_t \approx [\text{HS}]_{\text{O}_3, \text{ resistant}, 0} + [\text{HS}]_{\text{O}_3, \text{ reactive}, 0} e^{-k'_2 t} \quad (2)$$

$$[\text{LMW} - \text{N}]_t \approx [\text{LMW} - \text{N}]_{\text{O}_3, \text{ resistant}, 0} + [\text{HS}]_{\text{O}_3, \text{ reactive}, 0} \frac{k'_2}{k'_3 - k'_2} (e^{-k'_2 t} - e^{-k'_3 t}) \quad (3)$$

The removal of fluorescence signals has been widely used as an indicator of treatability of refractory organic matter from coking wastewaters and concentrates (Yang *et al.* 2013; Yu *et al.* 2016; Li *et al.* 2019). Results shown in Fig. 3d confirm that the fluorescent compounds present in CCI concentrates are readily oxidised by the ozonation process with the specific fluorescence significantly decreasing within 30 min of reaction. The complete EEM spectra of the CCI concentrate at various reaction times is shown in Supplementary Fig. S2. These results agree with a recent study which showed that ozonation caused a significant reduction in aromaticity of humic substances resulting in a decrease in the fluorescence intensity of the local peaks measured using synchronous scanning fluorescence spectroscopy (Sadrnourmohammadi *et al.* 2020). However, the use of EEM spectroscopy to depict the removal of the refractory organic matter from CCI concentrates is questionable since the results shown in Fig. 3 confirm that the fluorescent compounds likely account for only a small portion of the total humic substances present. While the fulvic acid-like and humic acid-like substances shown in the EEM spectra are likely O<sub>3</sub> reactive, the O<sub>3</sub>-resistant fraction is non fluorescent and is the dominant fraction of organics present in the CCI

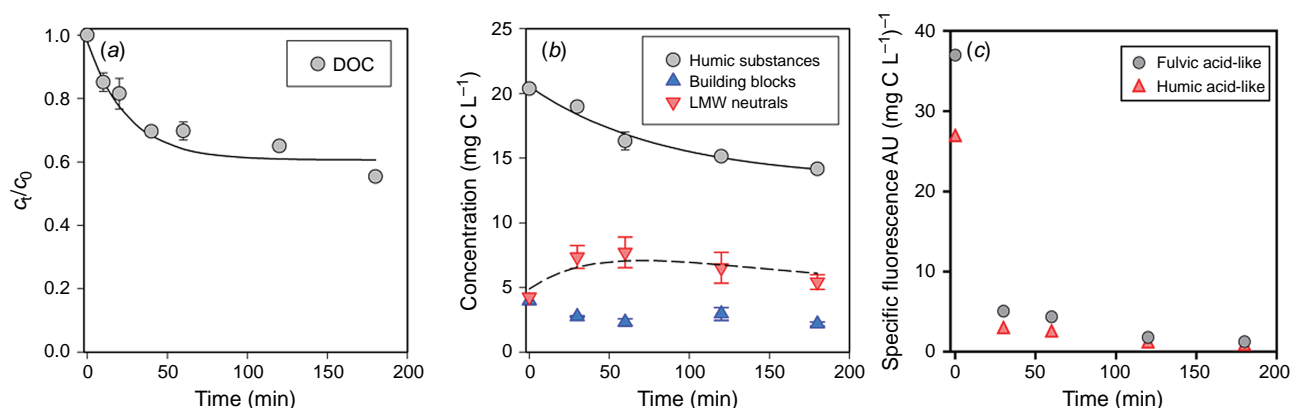
concentrate (Fig. 3b). As such, it is clear that the LC-OCND technique provides more insight into the organic composition and degradability of CCI concentrates compared to fluorescence spectroscopy.

The low degradability of DOC in the CCI concentrate by the pure ozonation process is possibly related to the high salinity and/or refractory nature of the organics. Measurement of the degradation of synthetic wastewaters containing humic acid (Aldrich) at a salinity similar to that of the CCI concentrates showed that ~46% of the DOC of HA was removed after 1 h of ozonation (Supplementary Fig. S3a). The COD of the HA solution decreased significantly with only 10% COD remaining after 1 h of treatment (Supplementary Fig. S3b). LC-OCND analysis of treated samples clearly show that the humic substances (i.e. HA) had been largely transformed to LMW neutrals despite the high salinity of the solution matrix (Supplementary Fig. S3c). These results thus suggest that matrix effects are not the primary reason for the low removal of humic substances from the Qian-an concentrate by the ozonation process. The low degradability of the CCI concentrate organic constituents is related more to the refractory nature of the organics. As such, further understanding of the structure and properties of the O<sub>3</sub>-resistance humic substances present in these concentrates would benefit the design of treatment processes for removal of these refractory organic compounds from the wastewater concentrate.

### Degradability of the refractory organic matter in concentrates by catalytic ozonation

Results from pure ozonation studies indicated that the organic matter in the CCI concentrates is not readily oxidised by O<sub>3</sub> but may possibly degrade under stronger oxidant (e.g. 'OH) attack. Thus, we investigated the degradation of CCI concentrate by catalytic ozonation employing an Fe-oxide@Al<sub>2</sub>O<sub>3</sub> catalyst. In our earlier work (Yuan *et al.* 2022), we investigated the mechanism of the catalytic ozonation process using Fe-oxide@Al<sub>2</sub>O<sub>3</sub> and showed that O<sub>3</sub> decays on the Fe-oxide@Al<sub>2</sub>O<sub>3</sub> surface to form surface-located 'OH which then diffuse away from the surface and interact with organic compounds present in the interfacial boundary layer and/or bulk solution. The formation of surface-located 'OH on catalyst-O<sub>3</sub> interaction was confirmed in our earlier work (Yuan *et al.* 2022) using fluorescence microscopy imaging analysis.

As shown in Fig. 4, treatment of the CCI concentrate by catalytic ozonation results in higher DOC removal (47%) compared to that observed by pure ozonation (20%). Fitting Eqn 1 to the results shown in Fig. 4a, we find that ~60% of the DOC in the Qian-an CCI concentrate is resistant to degradation by catalytic ozonation with the pseudo first order degradation rate constant of the reactive component equal to 0.040 min<sup>-1</sup>; a value nearly two-fold higher than the rate constant determined in the pure ozonation studies. LC-OCND results show that the concentration of humic



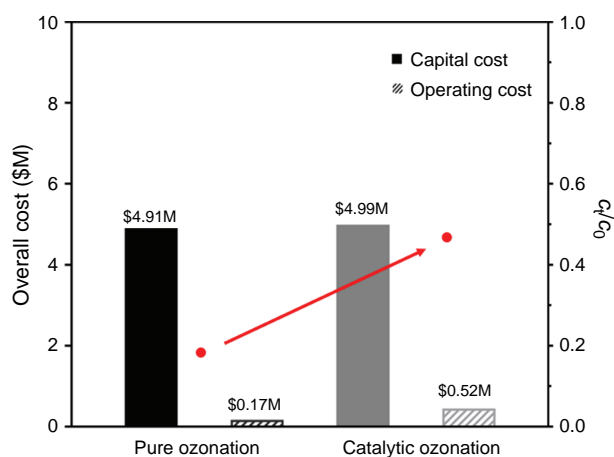
**Fig. 4.** Time-resolved concentration (or intensity) of (a) DOC, (b) LC-OCND components and (c) EEM components during catalytic ozonation of Qian-an concentrate. Lines in panels (a) and (b) represent pseudo-first order modeling results. The specific fluorescence in panel (c) was calculated by normalising the peak intensities (AU) of fulvic acid-like and humic acid-like substances to the DOC concentrations of the samples.  $[\text{pH}]_0 = 7.5\text{--}7.6$ ,  $[\text{pH}]_{\text{final}} = 7.0\text{--}7.3$ .

substances (Fig. 4b) varied in a similar manner to the total DOC concentration (Fig. 4a) with the  $\text{O}_3$ -resistant component representing 64% of the total humic substances and the  $\text{O}_3$ -reactive humic substances exhibiting a slightly lower pseudo first order degradation rate constant ( $k_2' = 0.012 \text{ min}^{-1}$ , Eqn 2) than that of the DOC. This is in contrast with the results obtained from pure ozonation studies wherein  $k_2' > k_1$ . This observation suggests that catalytic ozonation is more effective in oxidising other organic components (i.e. LMW neutral and/or building block) while humic substances are more readily degraded by direct  $\text{O}_3$  attack. Fitting Eqns 2 and 3 to the LMW neutral concentration, we obtain a pseudo first order degradation rate constant of  $0.017 \text{ min}^{-1}$  which is much higher than the value determined for the pure ozonation process ( $0.005 \text{ min}^{-1}$ ). This result supports the conclusion that the intermediate products of humics oxidation are more readily oxidised by the oxidants generated on catalytic ozonation compared to pure ozonation. As observed in the case of pure ozonation, specific fluorescence of the CCI concentrate significantly decreased within 30 min of treatment (Fig. 4c) confirming that the fluorescent compounds present in CCI concentrates are readily oxidised by ozone with no further enhancement in the rate of removal of these fluorescent compounds by the catalytic ozonation process. Our earlier results indicated that the accumulation of chloride ions in the electrical double layer near the catalyst surface, particularly when  $\text{pH} < \text{pH}_{\text{pzc}}$ , results in significant scavenging of surface associated  $\cdot\text{OH}$ . As such, the influence of salts present in CCI concentrate on the performance of this catalyst will be significant. Use of a halide-resistant catalyst is thus expected to further enhance the performance of the catalytic ozonation process. Furthermore, employing a two-stage process involving pure ozonation (to degrade humic-like substances) followed by catalytic ozonation (to degrade oxidation products of these substances) may be more effective than use of catalytic ozonation alone.

Overall, our results show that the catalytic ozonation process is effective in degrading CCI concentrate. With improved understanding of the nature of the refractory organics and use of a halide-resistant catalyst, the treatment efficiency of CCI concentrates by a catalytic ozonation process may be further increased.

## Techno-economic analysis

In order to explore the viability of use of ozonation processes at an industrial scale, we also performed a detailed technical-economic analysis of the ozonation and catalytic ozonation processes for a treatment capacity of  $5000 \text{ m}^3 \text{ day}^{-1}$  and water quality the same as that of the concentrate from the Qian-an plant (i.e.  $\text{COD}_{\text{feed}} = 150 \text{ mg L}^{-1}$ ). For the technical-economic analysis, we calculated total capital investment and operating costs for both the pure and catalytic ozonation processes. For total capital investment, we included the cost of procuring and installing all process equipment (referred to as the inside investment cost (ISBL)), offsite investment cost (OSBL), design and engineering cost, contingency cost and working capital (Kinney and Gauche 2006). For the operating cost calculation, we included the costs of raw materials, transportation, utilities use and waste disposal. Detailed descriptions of the calculation of total capital investment and operation costs are provided in Section S3 in the Supplementary material. The breakdown of the various components of the total capital investment and operation costs are shown in Supplementary Figs S5, S6 respectively. As shown in Fig. 5, compared to the pure ozonation process, the overall capital cost and operating cost (annual) of the catalytic ozonation process is only slightly higher ( $\sim \$0.08$  and  $\sim \$0.35 \text{ M}$ , respectively), while the DOC removal (%) improved significantly from  $\sim 20$  to 47% with this result demonstrating that application of catalytic ozonation rather than pure ozonation alone is justified for the treatment of CCI concentrates. The cost difference between



**Fig. 5.** Cost (bars) and DOC removal (circles) of CCI concentrate by pure ozonation and catalytic ozonation processes. Note that the DOC removal is shown on the y-axis (right side) as  $c_t/c_0$  where  $c_t$  represents the DOC removed and  $c_0$  represents the initial DOC of CCI concentrate.

the pure ozonation and catalytic ozonation processes is mainly due to the cost of raw material, catalyst delivery and the extra process of catalyst regeneration. The daily operating cost of the catalytic ozonation process, which mainly constitutes the raw material cost and electricity cost for process equipment, is estimated to be only  $\$0.22 \text{ m}^{-3}$ . The overall cost of installation and operation of the catalytic ozonation process is much less than the cost of a complete ZLD process ( $\sim \$200 \text{ M}$ ) (Tong and Elimelech 2016) suggesting that the use of the catalytic ozonation process for concentrate treatment is economically viable.

## Conclusions

The integration of membrane technologies has gained increasing popularity in ZLD management of CCI wastewaters with this practice generating high-salinity concentrates containing refractory organic matter. Results of this study indicate that the pH of CCI concentrates were largely circumneutral with NaCl and/or  $\text{Na}_2\text{SO}_4$  being the dominant salts present although other cations/anions (e.g.  $\text{Ca}^{2+}/\text{Mg}^{2+}$ ) were present at significant concentrations in some cases. LC-OCND results showed that humic substances and LMW neutrals were the dominant components in all CCI concentrates. Degradation of the organic matter in CCI concentrate from the Qian-an treatment plant by ozonation and catalytic ozonation processes showed that nearly 20 and 47% of the DOC could be removed following 1 h of treatment in the absence and presence of catalyst, respectively. The low removal of DOC by the pure ozonation process from Qian-an concentrate was mainly ascribed to the refractory nature of the humics and LMW neutrals present in the CCI concentrate with salinity effects (i.e. scavenging of  $\text{O}_3$  and  $\text{OH}$  by chloride ions) having no significant influence on the

pure ozonation performance. The refractory nature of the humics is potentially due to the presence of a high concentration of  $\text{Ca}^{2+}$  in these samples which is known to transform humics to compact and unreactive forms (Baalousha et al. 2006; Yuan et al. 2022). Catalytic ozonation showed better removal of DOC (47%) with the generation of stronger oxidants (particularly  $\text{OH}$ ) presumably facilitating the degradation of LMW neutrals formed on oxidation of humic-like substances. Cost analysis of the catalytic ozonation process indicated that the total cost of this process is negligible compared with the cost of the complete ZLD process, suggesting that the use of catalytic ozonation represents a viable method for the degradation of the refractory organics in CCI concentrates. It should be noted however that CCI membrane concentrates are likely to vary widely in composition with any one technology (such as catalytic ozonation) unlikely to be effective in treating all types of concentrate with the efficacy of catalytic ozonation and, indeed, other oxidation technologies expected to be dependent on the particular contaminants present.

## Supplementary material

Supplementary material is available online.

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**Data availability.** The data that support this study will be shared upon reasonable request to the corresponding author.

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