



Determination of organic pollutants in municipal reverse osmosis concentrate by electrospray ionization–quadrupole time-of-flight tandem mass spectrometry and photocatalytic degradation methods

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HIGHLIGHTS

- A combination of multiple techniques to determine organics in ROC
- Deduced structures for 63 fluoro surfactants and 9 pharmaceuticals by ESI–QToF
- Estimated quantity of NOM, fluoro surfactants and pharmaceuticals

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ABSTRACT

Recently UV/TiO₂ photocatalytic treatment for municipal reverse osmosis concentrate (ROC) has drawn increasing attention due to its high efficiency and low cost. We determined the organics in ROC samples by a combination of multiple analytical techniques: i.e. electrospray ionization–quadrupole time of flight (ESI–QToF), photocatalytic degradation method, total organic carbon (TOC) analysis, fluorescence spectroscopy, ultraviolet–visible (UV–Vis) spectroscopy and gas chromatography/mass spectrometry (GC/MS). By these multiple techniques we were able to determine the total dissolved organic carbon (DOC) to be 24.50 ppm, which was composed of high molecular weight (MW) (>2000 Da) natural organic matter (NOM) of 23.36 ppm (95.35wt.) and low MW (<2000 Da) fluorosurfactants of 1.08 ppm (4.41%), and pharmaceuticals & other organic compounds of 0.06 ppm (0.24%). Using ESI–QToF tandem mass spectrometry, molecular structures of 5 series of fluorosurfactants (63 compounds) and 9 pharmaceuticals were elucidated. Conjugated compounds and sample color were monitored by UV–Vis spectroscopy. No volatile organic compounds (VOCs) were detected in the ROC samples by GC/MS. A combination of these 6 techniques provided a comprehensive method to depict the overall constituents of various organics in ROC. Quantitative estimation of organic compounds and structural determination of surfactants and pharmaceuticals in ROC were also investigated.

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1. Introduction

Reverse osmosis (RO) membrane technology has been widely applied in wastewater recovery processes. However, currently only 75–85% clean product water can be achieved by utilizing reverse osmosis for wastewater recovery. The remaining 15–25% RO concentrate (ROC) is brackish waste, causing higher power consumption and is potentially harmful to the environment due to its high organic content [1,2]. The organic contaminants in ROC may include natural organic matter (NOM), refractory chemicals added by the public into wastewater (e.g., detergents,

pesticides, personal care products, pharmaceutical products, endocrine disruptors), residuals from wastewater treatment processes (e.g., soluble microbial products, partially biodegraded organics, anti-scaling chemicals), and biological materials (i.e., bacteria, viruses, oocysts, and cell fragments) [2]. Currently ROC is not classified as hazardous waste, and hence is usually disposed to surface water, oceans, and underground water, thus posing potential risk to ecology systems [3,4]. Recent attention on ROC focuses on evaluation of various advanced organic processes (AOPs) for ROC treatment: UV/TiO₂, UV/TiO₂/sand filter, FeCl₃/UV/TiO₂, UV/TiO₂/O₃, UV/H₂O₂, electrochemical treatment, sonolysis, etc. [1,2,5–12]. During wastewater treatment, researchers found that there were close relationships between the chemical properties of wastewater constituents and their reactivities biologically or chemically. Westerhoff et al. [2] found that some pharmaceuticals (such

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as carbamazepine and meprobamate) were photodegradable (while π electrons play an important role) by UV/TiO₂ through carboxylic intermediates (i.e. formate, acetate, etc.) and finally to CO₂. They also disclosed the reactivity of natural organic matters (NOM) with chlorine, bromine, and O₃. Sedlak et al. [13] discovered the formation of *n*-nitrosodimethylamine from dimethylamine during chlorination and studied the transformation of odorants [14,15] by ozonation and UV/H₂O₂. Rosario-Ortiz et al. [16] established reactivity of effluent organic matter (EfOM) with OH• as a function of MW, evaluated oxidation of pharmaceuticals by UV/H₂O₂ and dibutylphthalate (DBP) formation during ozonation, and characterized polarity of NOM. Although phenolic surfactants [17–20] (e.g. nonylphenolics, NP; octylphenolethoxylates, OPE; dodecylbenzenesulfonate, DBS; and benzenesulfonate, DB) could be photodegraded, other surfactants without aromatic ring and double bonds, such as fluoro surfactants FC-143 [21], are stable under UV/TiO₂. Instead they formed micelles which could assist the degradation of polychlorinated biphenyls (PCBs) and pesticide permethrin [22]. However, the overall organic constituents and their percentages in ROC have not been determined to date. The information would be beneficial to the development of treatment methods and processes.

In this report we investigated the overall organic constituents and their percentages in ROC samples. Due to the complexity of real ROC samples from wastewater treatment plant, it was difficult to comprehensively characterize all the organics in ROC by a single technique. We made use of TOC analysis to measure the dissolved organic carbon, which included larger (MW >2000 Da) and smaller (MW <2000 Da) molecules. Smaller molecules (e.g. surfactants, pharmaceuticals, etc.) could be monitored by HPLC–ESI–QToF and GC/MS, while larger ones (e.g. NOM) required other techniques such as fluorescence spectroscopy for their determination. Since real ROC samples contained various organic matters, there were difficulties to obtain appropriate standards to quantify accurately each category of organics. Therefore, we utilized photocatalytic degradation reaction of ROC for sufficiently long UV irradiation time under efficient TiO₂ photocatalyst to assist the quantitative estimation of each category of organic constituents. In addition, conjugated compounds and ROC sample color could be monitored by UV–Vis spectroscopy qualitatively to confirm the results obtained by the other 5 techniques. Structures of small molecules were elucidated by ESI–QToF tandem mass spectrometry.

2. Materials and methods

HPLC grade methanol was obtained from Sigma-Aldrich. ROC was obtained from Singapore Public Utilities Board water treatment plant. The sample was stored in a refrigerator at 4 °C and the sample bottle was wrapped with an aluminum foil to protect it from any possible photodegradation. The characteristics of the ROC are listed in Table 1. The TiO₂ photocatalyst [23,24] was prepared by the sol–gel method from the hydrolysis of TiOSO₄·xH₂O at 90 ± 2 °C for 6 h, followed by rinsing with DI water and calcination at 400 °C for 1 h. The prepared TiO₂ powder photocatalyst was characterized to be nanocrystalline anatase with an average particle size of 6.4 nm, a surface area of 146.9 m²/g, and an indirect allowed bandgap of 3.26 eV as determined by XRD, N₂ sorption, and UV–Vis diffuse reflectance spectroscopy (DRS) (Fig. S1, S2, S3). Photocatalytic reactions of ROC were conducted under monochromatic UV 365 nm irradiation (18 mW/cm²; 6.467 × 10¹⁵ photons/s mL) over prepared titanium dioxide (0.1%wt. loading) described above in a quartz reactor with temperature control at 25 ± 0.2 °C (reaction setup shown in Fig. S4). Besides the consideration to minimize the possible adsorption effect by the photocatalyst, 0.1%wt. loading was chosen because it was much faster than 0.05 and 0.00% loading but only slightly slower than 0.2% (Fig. S5). 100 mL ROC sample was placed into the quartz reactor and then 0.10 g of the prepared TiO₂ anatase powder was added into the 100 mL ROC sample with magnetic stirring (120 rpm), under the described UV condition. Reaction was carried out for up to 24 h. The ROC samples after reaction were labelled as

Table 1
Characteristics of the reverse osmosis concentrate (ROC).

Parameters	Values
DOC (mg/L)	25.0 ± 2.0
TKN (mg/L)	10 ± 3
COD (mg/L)	60.0 ± 5
pH value	6.9 ± 0.2
Color (Pt-Co) ^a	144 ± 10
Turbidity (ntu)	3.2 ± 0.4
TDS (mg/L)	1129 ± 40
Conductivity (μS/cm)	1705 ± 21
Cations (mg/L)	
Na ⁺	203 ± 10
Mg ²⁺	7 ± 0.1
K ⁺	62 ± 5
Ca ²⁺	65 ± 8
Anions (mg/L)	
Cl [−]	256 ± 16
SO ₄ ^{2−}	217 ± 4
NO ₃ [−]	91 ± 4
NO ₂ [−]	2 ± 1
PO ₄ ^{3−}	39 ± 7

^a Color was measured in Pt–Co units according to ASTM D1209 “standard test methods for color of clear liquids (platinum–cobalt scale)”.

ROC0hr, ROC2hr, ROC6hr, ROC12hr, ROC18hr and ROC24hr, respectively, according to different reaction time periods. The difference between ROC and ROC0hr was that ROC was not contacted with the catalyst while ROC0hr was contacted with the catalyst for 5 min without irradiation (adsorption was expected to occur during contact).

A liquid chromatography–quadrupole time-of-flight (LC–QToF) tandem mass spectrometry consisting of an AB Sciex QTOF 5600 MS/MS system and a Dionex ULTIMATE 3000 HPLC system was used for the separation and identification of the organic contaminants in the ROC concentrate. The LC column used was a Waters XTerra MS C18 column (5.0 μm, 3.9 mm × 150 mm). Mobile phase A was 0.1% formic acid in DI water. Mobile phase B was 0.1% formic acid in methanol. A typical gradient was: 0 min, 30% B; 4 min, 70% B; and 6 min, 30% B. The flow rate was 300 μL/min. MS analysis was performed in positive (+) mode. For ROC sample preparation, 2 mL ROC sample was filtered through 0.20 μm Minisart filter. DI water was used as blank sample. All samples and blank were filtered. A total of 7 samples and 1 blank were analyzed: i.e. ROC, ROC0hr, ROC2hr, ROC6hr, ROC12hr, ROC18hr, ROC24hr, and DI water. QToF was calibrated to be within 0.5 ppm mass accuracy prior to analysis. A Shimadzu TOC–VWS Total Organic Carbon Analyzer was used to analyze DOC concentration. Inorganic carbon was removed in the TOC analyzer system before analysis. Samples were filtered through 0.45 μm Minisart filters prior to analysis. DOC included larger (MW >2000 Da) and smaller (MW <2000 Da) molecules. Since ESI–QToF could only analyze smaller molecules, fluorescence spectroscopy was applied to monitor larger molecules (mainly NOM including humic substances, aromatic protein, soluble microbial products, etc.). A Gilden Photonics FluoroSENS fluorescence spectrometer was used for fluorescence analysis: excitation wavelength was 349 nm, and emission wavelength scanning range was 370–800 nm. To investigate any possible VOC contents, a Shimadzu GCMS–QP2100 plus mass detector was used. For GC–MS sample preparation, solid phase extraction (SPE) was performed with C18 cartridges (500 mg/6 mL) using standard SPE procedure. The standard SPE C18 procedure used was as the following: 1. condition with 5 mL HPLC grade methanol; 2. equilibrate with 5 mL de-ionized water; 3. load 1 mL ROC sample with a flowrate of 1 to 2 mL/min; 4. wash with 5 mL de-ionized water; 5. elute with 5 mL methanol, and then 2.5 mL isopropyl alcohol; and 6. evaporate to dryness, and reconstitute to 1 mL in methanol. For GC–MS, the control blank was the methanol that went through the same standard SPE procedure but without using the ROC sample. This served to eliminate any contaminants from the SPE procedure. The UV–Visible spectrum was recorded on a

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