

オゾン/過酸化水素促進酸化による
生物学的二次処理水中有機物の分解過程

Characterization and removal of organic compounds in Effluent from Sewage Biological Treatment
by O₃/H₂O₂ Advanced Oxidation Process

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Abstract

Even though O₃/H₂O₂ based advanced oxidation process (AOP) has been proven to be an effective polishing treatment for sewage effluent, some of organic compounds were still found after treatment as the TOC value of treated sample was around 1 mg/L. In pursue of identifying these remaining substances, High Performance Size Exclusion Chromatography with Organic Carbon Detector (HPSEC-OCD) was used to determine range of apparent molecular weight (AMW) of the remaining substances. In this study, four HPSEC-OCD results were observed and compared: (a) sewage effluent before AOP, (b) after ozone only treatment, (c) after ozonation with hydrogen peroxide addition in the beginning, (d) after ozonation with hydrogen peroxide continuously added. HPSEC-OCD chromatograms show that biopolymer in AMW range of 30,000 Da and low-molecular weight (LMW) neutrals in AMW range of 500 Da were removed in all cases. However, humic substances and building blocks in AMW range of 2,700 and 2,000 Da are only removed in presence of hydrogen peroxide. LMW acids in which has AMW range of 1,100-1,200 Da were found irremovable. Furthermore, concentration in this AMW range increased after all treatment. The increase was hypothesized to be by-products of AOP reactions with larger molecules.

Keywords: Sewage Treatment, Advance Oxidation Process (AOP), HPSEC-OCD

1. Introduction

O₃/H₂O₂ based advanced oxidation process (O₃/H₂O₂ AOP) has been proven to be an effective polishing process for treating refractory organic compounds from biological sewage treatment¹⁾. However, previous study²⁾ shows that not all organic compounds can be removed by O₃/H₂O₂ AOP as some of organic compounds were still found in treated sample, indicated by TOC value around 1 mg/L. It is important to identify these irremovable substances as they will accumulate in nature over time and may pose risk to human and environment in the upcoming future. In pursue of identifying these untreatable substances, High Performance Size Exclusion Chromatography with Organic Carbon Detector (HPSEC-OCD) is used extensively in this study to roughly determine apparent molecular weight (AMW) range and concentration of such irremovable organic substances.

2. Methodology

2.1 Sample collection

The sewage effluent used in this study was collected from final settling basin at a sewage treatment plant in Kansai area, where anaerobic-anoxic-aerobic method with nitrified liquor recirculation is

utilized. Sampled water was then vacuum-filtered with glass fiber filter (GA-100, ADVANTEC) to remove any remaining suspended solid. Sample was then stored under refrigeration to minimize degradation.

2.2 O₃/H₂O₂ advanced oxidation process setup

Semi-batch type reactor from the previous studies²⁾ was used. The setup consisted of ozone generator (SGA-01A-PSA4, Sumitomo Precision Products), flow meter (RK-1350V, KOFLOC), three 1L glass bottles, each for: backflow prevention, NO_x trap (filled with water), and moisture trap respectively, 1L glass reactor (internal dimensions: \varnothing 8.2 cm x 19 cm) with bottom gas diffuser (\varnothing 100-200 μ m pores), sampling tap, and H₂O₂ inlet connected to peristaltic pump discharge. The ozone transfer capacity of the reactor was previously tested at 0.27 L/min. The gas outlet of the reactor was connected to ozone monitor (EG-60, Ebara Jitsugyo) for monitoring ozone concentration after the reactor. A data logger was used to record reading from ozone monitor to obtain ozone concentration profile during experiment. Sewage effluent used in the experiment was taken out of refrigerator and left to room temperature prior to the experiment. The water was treated by AOP in 3 conditions: (a) Ozonation with ozone-rich gas, ozone concentration 50 mg/L, at flow rate 0.5 L/min for 30 minutes; (b) Ozonation same as (a) with 30 mg/L hydrogen peroxide solution added to water right before ozonation; (c) Ozonation same as (a) with hydrogen peroxide continuously added into reactor at 1.0 mg/L/min. The ozone concentration of ozone-rich gas generated by the ozone generator was confirmed prior to each experiment by iodine titration method³⁾. The reading of ozone monitor was then linearly offset to match the value obtained by iodine titration to ensure accurate reading.

2.3 Water Quality Analysis

Samples were collected from reactor every 5 minutes. For each collection, the followings were performed: (1) dissolved ozone concentration measurement by the indigo colorimetric method⁴⁾, immediately after collection; (2) hydrogen peroxide concentration measurement by DMP method⁵⁾, immediately after collection; (3) Non-purgeable total organic carbon (NPOC) measurement (TOC-VCSH, Shimadzu, Japan); (4) HPSEC-OCD analysis. Except for dissolved ozone concentration measurement, samples were purged with nitrogen before measurement to get rid of remaining ozone in order to stop further reaction.

2.4 HPSEC-OCD Analysis

HPSEC-OCD was used to determine AMW of dissolved organic compounds contained in each sample. The system consists of high-performance liquid chromatography unit (LaChrom Elite w/ L-2130 pump, Hitachi), custom-made chromatographic column (21.5 (ID) \times 200 (L) mm, Tosoh) packed with hydroxylated methacrylic polymer chromatographic resin with a pore size of 12.5 nm and particle size of 30 μ m (Toyoparl HW-50S, Tosoh). The column temperature was kept constant at 25°C, using thermostat-equipped ribbon heater. The column was periodically flushed with purified water to ensure contamination-free. An OCD (Modified Sievers M9, Suez Water Technologies & Solutions) was connected downstream to measure TOC of column outlet stream. The measurement was in 4-second interval (Turbo mode) with 5.0 μ L/min acid flow rate and 2.0 μ L/min oxidant flow rate. The eluent used in analysis was phosphate buffer (2.4 mM NaH₂PO₄ + 1.6 mM Na₂HPO₄) in 25 mM

sodium sulphate solution to achieve ionic strength 100 mM which is recommended by manufacturer to minimize unwanted interaction between elutes and resin. Slight amount of 0.1M NaOH was added to adjust pH of eluent to 6.8. The eluent flow rate was 1 mL/min. Prior to injection, the samples were syringe-driven through a 0.2- μ m filter (Millex-LG, Merck Millipore) to ensure particle-free. Sample was then introduced into system via manual injector with 5ml loop (7725i, Rheodyne). Data from OCD were streamed and recorded to PC via ethernet port and communication software (PuTTY, open-source). The streaming started in synchrony with sample injection and marked a start of chromatogram. Chromatograms were plotted and analyzed in MS Excel spreadsheet, in which area and retention time of each peak were calculated. Polyethylene glycol (PEG) with molecular weight ranging from 200 to 20,000 Da were used to make semi-log calibration curve for AMW calculation (figure 2). PEG was selected as standard as it was reported to have low undesirable interactions with Toyopearl HW resin⁶). Relationships between TOC value from NPOC analysis and sums of chromatogram peak areas for each experiment were plotted (figure 3). The concentration of each peak in chromatogram was then estimated from these graphs.

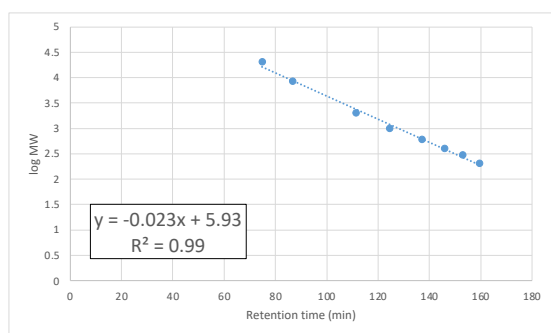


Figure 2: Semi-log calibration curve from PEG measurement

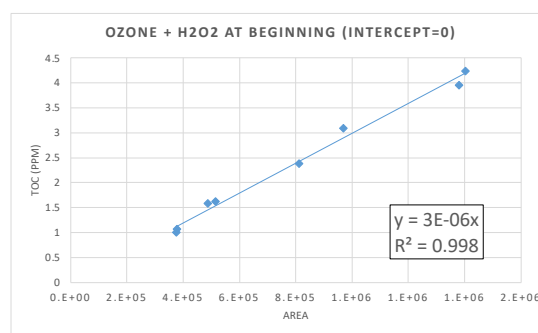


Figure 3: Example of relationships between total peak Area and TOC

3. Results and Discussion

According to literature⁷), SEC-OCD chromatograms can be generally classified by the descending retention time into biopolymers, humic substances (HS), building blocks which are low molecular weight HS-like materials resulted from degradation of HS, low-molecular weight (LMW) acids, and LMW neutrals (alcohols, aldehydes, ketones, and amino acids). From figure 4, five peaks can be classified in chromatogram of untreated sewage effluent: biopolymer at 30,000 Da, HS and building blocks at 2,700 and 2,000 Da, LMW acids at 1,100 Da, and LMW neutrals at 500 Da range. After treatment, biopolymers and LMW neutrals were completely removed in all cases. However, HS and building blocks were only removed in presence of hydrogen peroxide. In all cases, peaks of LMW acids are observed to be higher than initial concentration before treatment.

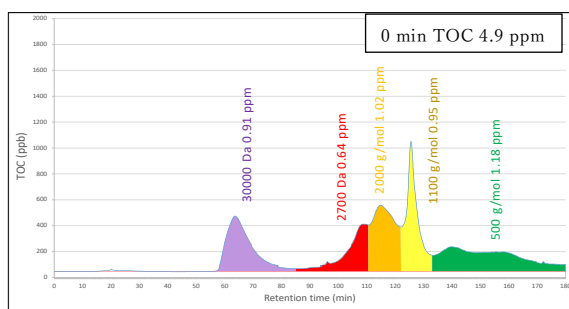


Figure 4 (top-left): Chromatogram, untreated sewage effluent (0 min)

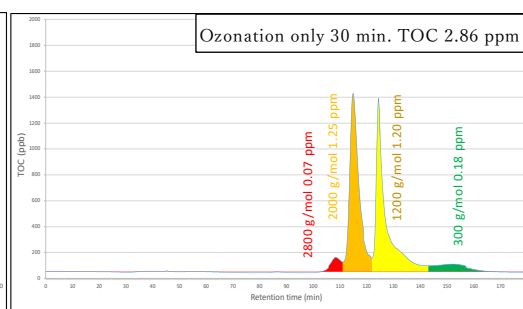


Figure 5 (top-right): Chromatogram, 30 min after ozonation only.

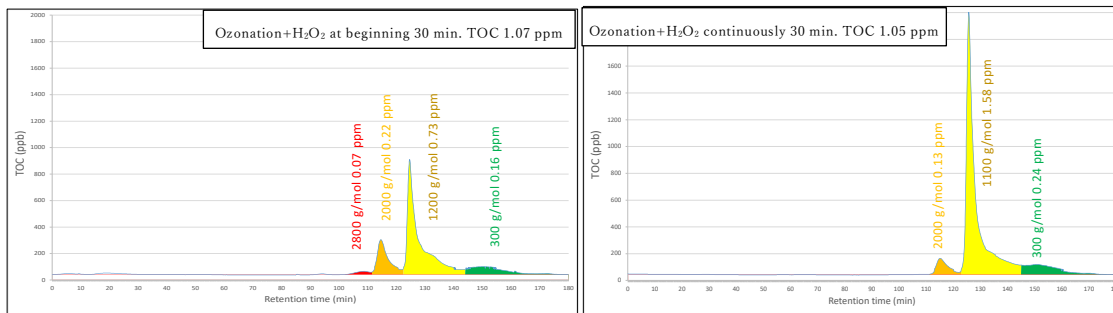


Figure 6 (bottom-left): Chromatogram, 30 min after ozonation and H₂O₂ added at the beginning.

Figure 7 (bottom-right): Chromatogram, 30 min after ozonation and H₂O₂ continuously added.

4. Conclusion

TOC values and SEC-OCD chromatograms of samples after AOP both confirm that ozone-hydrogen peroxide AOP treatment yield better result than ozonation alone. In all cases, LMW acids with AMW range of 1,100-1,200 Da were found irremovable. Furthermore, its concentration increased in all cases. This is supposably due to conversion of larger molecules into smaller molecules as per AOP. At this stage, it is difficult to determine if this LMW acids peak are solely AOP by-product or irremovable organic compounds from biological process or both combined. Thus, next challenge is to identify compositions as well as origins of these organic compounds in order to deepen understanding of O₃/H₂O₂ AOP capability.

5. References

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