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# Development of a predictive framework to assess the removal of trace organic chemicals by anaerobic membrane bioreactor

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## HIGHLIGHTS

- The fate of TrOCs in AnMBR depends on their hydrophobicity & molecular structure.
- Biodegradation accounted for most of the removal of TrOCs by AnMBR.
- Hydrophobic TrOCs were well removed by AnMBR regardless of their molecular features.
- Hydrophilic TrOCs with electron donating functional groups were also well removed.
- Accumulation in sludge was observed with several persistent & hydrophobic TrOCs.

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## ABSTRACT

This study aims to develop a predictive framework to assess the removal and fate of trace organic chemicals (TrOCs) during wastewater treatment by anaerobic membrane bioreactor (AnMBR). The fate of 27 TrOCs in both the liquid and sludge phases during AnMBR treatment was systematically investigated. The results demonstrate a relationship between hydrophobicity and specific molecular features of TrOCs and their removal efficiency. These molecular features include the presence of electron withdrawing groups (EWGs) or donating groups (EDGs), especially those containing nitrogen and sulphur. All seven hydrophobic contaminants were well removed (>70%) by AnMBR treatment. Most hydrophilic TrOCs containing EDGs were also well removed (>70%). In contrast, hydrophilic TrOCs containing EWGs were mostly poorly removed and could accumulate in the sludge phase. The removal of several nitrogen/sulphur bearing TrOCs (e.g., linuron and caffeine) by AnMBR was higher than that by aerobic treatment, possibly due to nitrogen or sulphur reducing bacteria.



## 1. Introduction

Aerobic and anaerobic processes are widely used for wastewater treatment. Both processes can be integrated with membrane filtration to form an aerobic or anaerobic membrane bioreactor (MBR). MBR processes have attracted significant scientific and industry attention over the last few decades. In particular, given their ability to treat concentrated wastewater and simultaneously produce biogas, which is an important renewable fuel, the number of scientific studies, as well as practical application of anaerobic membrane bioreactors (AnMBRs), have increased significantly (Liao et al., 2006; Shoener et al., 2014; Visvanathan and Abeynayaka, 2012).

Of significant interest during wastewater treatment is the removal of trace organic chemicals (TrOCs) for environmental protection as well as water reuse application requirements. A large number of TrOCs have been detected in raw sewage and sewage-impacted water bodies around the world. These include steroid hormones, pharmaceuticals, personal care products, surfactants, pesticides, and disinfection by-products (Alidina et al., 2014; Brack et al., 2015; Luo et al., 2014; Osorio et al., 2012; Tran et al., 2013, 2014; Hai et al., 2014). Their occurrence in the aquatic environment is of concern to public health and the environment because many of them are known or suspected to have an adverse impact on living organisms including human beings (Schwarzenbach et al., 2006).

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The removal of TrOCs by MBR has been intensively studied for the last 20 years. However, previous studies have focussed almost exclusively on the aerobic MBR process rather than its AnMBR counterpart. Indeed, previous studies have allowed us to develop a comprehensive understanding of the fate and removal of TrOCs during aerobic MBR treatment. By contrast, there is a dearth of information regarding the removal of TrOCs by AnMBR. Monsalvo et al. (2014) appears to be the only study that has addressed the removal of TrOCs by AnMBR.

Numerous studies have investigated the removal and removal mechanisms of TrOCs by aerobic MBR treatment (Clara et al., 2005; Reif et al., 2008; Navaratna et al., 2012; Tadkaew et al., 2011; Wijekoon et al., 2013). It is well established that both biodegradation and adsorption can govern the removal of TrOCs from the aqueous phase during aerobic MBR treatment. In addition, molecular structure is an important factor for aerobic biodegradation of TrOCs. Tadkaew et al. (2011) developed a qualitative framework for assessing the removal of TrOCs by aerobic MBR treatment based on their hydrophobicity and the presence of electron donating groups (EDGs) or electron withdrawing groups (EWGs). Data reported by Tadkaew et al. (2011) demonstrated that TrOCs with EDGs (e.g., hydroxyl and amine) are effectively removed whereas TrOCs with EWGs (e.g., chloro and amide) in their structure are poorly removed by an aerobic MBR. In a subsequent study, Wijekoon et al. (2013) successfully extended this framework to elucidate the fate of TrOCs in the aqueous and sludge phases during aerobic MBR treatment. According to Wijekoon et al. (2013), recalcitrant and hydrophobic/hydrophilic contaminants are mainly removed via adsorption to sludge while readily biodegradable and hydrophobic/hydrophilic TrOC are mainly removed via biodegradation/transformation. Previous work also suggests that low dissolved oxygen conditions could favour the removal of some TrOCs (e.g., carbamazepine (Hai et al., 2011)) that are otherwise persistent to aerobic treatment. Similarly, there is evidence that nitrifying bacteria may enhance the removal of some TrOCs (Vader et al., 2000; Wijekoon et al., 2013).

Current knowledge on TrOC removal by AnMBR is still limited (Abargues et al., 2012; Monsalvo et al., 2014). Abargues et al. (2012) and Czajka and Londry (2006) reported that anaerobic removal of octylphenols, nonylphenols and 17α–ethinylestradiol is negligible. On the other hand, Monsalvo et al. (2014) reported considerably higher removal (20%) of 17α–ethinylestradiol. This discrepancy in the current literature can be attributed to the fact that anaerobic biodegradation of TrOCs can take place in diverse microbial cultures. Anaerobic biodegradation of TrOCs can be carried out not only by the methanogenic archaea, but also sulphate reducing, iron reducing and nitrate reducing bacteria that act as the final electron acceptors (Czajka and Londry, 2006; Dionisi et al., 2006; Zeng et al., 2009). For example, in the presence of nitrate, 17α–ethinylestradiol can be effectively removed by biodegradation while in the absence of nitrate, removal of 17α–ethinylestradiol adsorption to biosolids was the main removal mechanism (Zeng et al., 2009). In contrast, Czajka and Londry (2006), reported no biodegradation of 17α–ethinylestradiol over 3 years of incubation period in isolated methanogenic, sulphate reducing, nitrate reducing or ion reducing conditions. Halogenated TrOCs (e.g., polyaromatic hydrocarbons) could be effectively biodegraded under anaerobic condition (Dionisi et al., 2006). Anaerobic reductive dehalogenation seems to be the main biodegradation mechanism for halogenated compounds – these compounds can be used as final electron acceptors by a number of anaerobic microorganisms (Dionisi et al., 2006) but the process is typically slow and requires the addition of an electron donor such as hydrogen release compounds.

This study aims to provide insight into the removal and fate of TrOCs during AnMBR treatment. The removal of several groups of TrOCs from both the aqueous and sludge phases was determined and related to the compound hydrophobicity and molecular characteristics in order to elucidate their removal mechanisms. A generalized framework for predicting the removal of TrOCs by AnMBR treatment was proposed based on the results obtained.

## 2. Methods

### 2.1. AnMBR experimental setup

An AnMBR system consisting of a conical shaped 30 L stainless steel reactor and an external ceramic membrane module (NGK, Japan) as shown in Supplementary Data Fig. S1 was used. Hot water was circulated through a plastic tube wrapped around the reactor. The temperature of the circulated hot water was regulated by a PID controlled heater (Neslab RTE7, Thermo Scientific, USA). Mixed liquor was circulated at 42 L/h using a peristaltic pump (DULCOFlex, Prominent, Australia) to ensure complete mixing. A conductive level controller (Omron, Japan) connected to the feed pump was used to maintain the reactor working volume at 20 L. The membrane module had a nominal pore size and effective surface area of 1 μm and 0.09 $m^2$, respectively. Peristaltic pumps (Masterflex L/S, USA) were used for feeding, recirculation and permeate extraction. Effluent from the AnMBR was circulated to the ceramic membrane on a cycle of 14 min on and 1 min off. The reactor and all pipework used in the AnMBR system were covered with insulation foam to minimize heat loss. Biogas production rate was monitored using a custom made gas counter. Biogas was collected via a Tedlar sampling bag prior to gas composition analysis.

### 2.2. Experimental protocol

The AnMBR was inoculated with anaerobic sludge from the Wollongong Wastewater Treatment Plant (Wollongong, Australia). A synthetic wastewater was used to simulate high strength domestic wastewater and to maintain stable operating conditions. The synthetic wastewater was prepared daily by diluting a concentrated stock solution with Milli-Q water to obtain 4000 mg/L glucose, 750 mg/L peptone, 175 mg/L $KH_2PO_4$, 175 mg/L $MgCl_2$, 2250 mg/L $CH_3COONa$ and 175 mg/L urea (Alturki et al., 2012). Micronutrients, namely, $FeCl_2$ (45 mg/L), $NiCl_2$ (10 mg/L), $CoCl_2$ (6 mg/L), and $(NH_4)_6Mo_7O_{24}$ (4 mg/L) were added (Khanal, 2008). The concentrated stock solutions were prepared every week and kept at 4 °C. Sodium bicarbonate was used to maintain the reactor pH at 7. Prior to the addition of the TrOCs to the influent, the MBR system was operated for approximately 4 months for acclimatisation.

Biomass characteristics including mixed liquor suspended solids (MLSS), volatile suspended solids (MLVSS), pH, conductivity, oxidation reduction potential (ORP), alkalinity; organic removal efficiency in terms of chemical oxygen demand (COD) and total nitrogen (TN); and biogas production were monitored approximately twice a week. The digester temperature was set at 35 ± 1 °C. Hydraulic retention time, permeate flux, and organic loading rate of bioreactor were 4 days, 1.8 L/$m^2$ h and 1.3 gCOD/L d, respectively. Excess sludge was withdrawn every 3–4 days to maintain the MLSS concentration in the reactor at 10 g/L, resulting in a sludge retention time (SRT) of approximately 180 days.

The mixed liquor was collected weekly and then centrifuged at 3270×*g* for 10 min (Alleegra X-12R, Beckman Coulter, USA) to obtain sludge pellets for analysis of TrOCs in sludge. Feed and permeate samples were also collected for TrOC analysis on a weekly basis. The mass balance of each compound was conducted based on the compound concentration in the feed, permeate, and sludge.

TrOC removal by AnMBR was defined as:

$$R = 100 \times \left(1 - \frac{C_p}{C_F}\right) \quad (1)$$