Khum Gurung

MEMBRANE BIOREACTOR FOR THE REMOVAL OF EMERGING CONTAMINANTS FROM MUNICIPAL WASTEWATER AND ITS VIABILITY OF INTEGRATING ADVANCED OXIDATION PROCESSES
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Dissertation for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium of Mikkeli University Consortium (MUC), Mikkeli, Finland on the 1st of October 2019, at noon.

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Supervisors
Professor Mika Sillanpää
LUT School of Engineering Science
Lappeenranta-Lahti University of Technology LUT
Finland

Assistant Professor Mohamed Chaker Ncibi
LUT School of Engineering Science
Lappeenranta-Lahti University of Technology LUT
Finland

Reviewers
Professor Anastasios I. Zouboulis
Department of Chemistry
Aristotle University of Thessaloniki (AUTh)
Greece

Professor How Yong Ng
Department of Civil and Environmental Engineering
National University of Singapore (NUS)
Singapore

Opponent
Professor of Practice Anna Mikola
Department of Built Environment
School of Engineering
Aalto University
Finland

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Abstract

Khum Gurung
Membrane bioreactor for the removal of emerging contaminants from municipal wastewater and its viability of integrating advanced oxidation processes

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Water scarcity is undoubtedly a global concern due to exacerbated population growth, economic development, climate change, and rapid urbanization. This has necessitated the need for establishing more sustainable and well-functioning natural ecosystems by transforming current water industries based on smart technologies and management approaches. Municipal wastewater reclamation is one of the promising approaches to relieve growing pressure on global water resources. However, adequate and efficient treatment is always essential to achieve high quality reclaimed water, ensuring no potential risks to human health and aquatic environment due to the presence of emerging contaminants (ECs), for which legislations are being stricter with time. Since conventional wastewater treatment plants are not designed to remove ECs, the capabilities of advanced wastewater treatment technologies, for enhancing the removal of ECs before releasing the treated effluent into the environment or reclamation, such as membrane bioreactor (MBR) and its integration with advanced oxidation processes, are emerging topics of research worldwide.

This dissertation presents a comprehensive practical study on the applicability of the MBR system for treating municipal wastewater in terms of its performance on the removal of diverse ECs, such as pharmaceutically active compounds, steroid hormones, and endocrine disrupting compounds, under different operating conditions, including Nordic cold environment and varying solid retention times. Additionally, a potential viability of integrating MBR with two emerging advanced oxidation processes (AOP) technologies, such as electrochemical oxidation (ECO) and photocatalytic oxidation (PCO), were studied in batch modes to further enhancing the removal of ECs and to produce high quality reclaimed water.

A significant membrane fouling, accompanying with about 75% permeability drop, was observed when process temperature in MBR was below 10 °C, indicating high
deterioration of membrane performance. However, relatively consistent removal efficiency of human enteric viruses, such as norovirus GI, norovirus GII, and adenovirus, heavy metals, and selected ECs, was achieved. Similarly, the removal and fate of 23 diverse ECs was studied at varying solid retention times (60 and 21 days). It was observed that at long solid retention time, ECs removal majorly enhanced, while biopolymers concentrations decreased. Moreover, diverse removal efficiencies of the selected ECs were observed, which were explained based on their physicochemical properties and other process operating parameters. The electrochemical oxidation of carbamazepine, which is one of the highly recalcitrant EC, was studied in batch mode using Ti/Ta$_2$O$_5$-SnO$_2$ anode. The main operating parameters effecting the removal of carbamazepine, including current density, initial substrate concentration, pH, and temperature, were studied. A complete removal (>99.9%) of carbamazepine, with concentration close to environmental level (10 µg L$^{-1}$), in real MBR effluent was observed when electrolyzed under the optimized conditions (current density: 9 mA cm$^{-2}$, pH: 6, and temperature: 30 °C) in synthetic solutions. Subsequently, the removal of ECs (carbamazepine and diclofenac) was studied by heterogeneous photochemical oxidation using 5% Ag$_2$O/P-25 photocatalyst under UV irradiation. The matrix effect, i.e., ECs in deionized water and MBR effluent, was studied along with the catalyst dosage and initial ECs concentration. The optimal removal of carbamazepine and diclofenac reached 89.1% and 93.5%, respectively at catalyst dosage of 0.4 g L$^{-1}$ in deionized water matrix, and further revealed that optimal catalyst dosage for ECs removal in MBR effluent matrix increased by 1.5 to 2 fold to achieve the similar removal efficiency as deionized water matrix. High reusability of 5% Ag$_2$O/P-25 photocatalyst was observed for both ECs. Moreover, various intermediates of carbamazepine generated during photochemical oxidation were analyzed and identified, and a possible degradation pathway was proposed.

The current study has expanded the knowledge on the applicability and efficiency of MBR operation in unique Nordic environment and integration possibilities of MBR with selected innovative advanced oxidation processes. It has also revealed the need of many other important related topics for further investigations.

**Keywords:** Membrane bioreactor, municipal wastewater treatment, emerging contaminants, advanced oxidation processes, electrochemical oxidation, photochemical oxidation
Acknowledgements

I have always been fascinated by science and technology. As the life goes on, my interests and enthusiasm towards science have eventually led me to pursue PhD degree. Achieving PhD degree has always been my academic dream, although it was not a piece of cake. I should admit that it was full of challenges, hard work, and endurances. Now, I have accomplished nearly four years of my PhD study and I have a great opportunity to finally acknowledge many people who made this journey possible. In this occasion, I am feeling overwhelmed and would like to convey my sincere gratitude to all of them.

First of all, I would like to express my deepest gratitude to my supervisor, Prof. Mika Sillanpää for believing on me and providing me this opportunity to start and accomplish my PhD study under his commendable guidance. I am also grateful to Assistant Prof. Mohamed Chaker Ncibi for his valuable supports, suggestions and guidance throughout my PhD journey.

I would like to thank Department of Green Chemistry (DGC), where most of my research works for the doctoral dissertation was carried out, for facilitating incredible infrastructures and resources.

I am thankful to Prof. Anastasios I. Zouboulis and Prof. How Yong Ng for reviewing this dissertation and providing their valuable comments and suggestions that have enriched the content of the dissertation further.

Many thanks to Professor of Practice Anna Mikola for agreeing to act as the opponent for the public examination.

I would like to thank Business Finland Oy, which is the most prestigious public funding agency for promoting high quality research in Finland, for financially supporting this research work. The research project was granted with the title “Smart Effluents Project-New generation wastewater treatment solutions for requirements of 2050” and project decision number of 1043/31/2015. The project was started on October 2015 and ended by September 2018.

My sincere thanks go to Kenkäveronniemi wastewater treatment plant, Mikkeli, Finland, owned by Mikkeli water works (Mikkeli Vesilaitos), for being an active company partner to this project, allow us to install and operate our pilot MBR plant within their premise, and for providing technical supports during the project. I am grateful to Reijo Turkki (Director of Mikkeli Vesilaitos), Anne Bergman, Risto Repo, Jani Koski, Päivi and all other staffs of Kenkäveronniemi wastewater treatment plant, Mikkeli, for their tremendous support on operating the MBR pilot plant and some laboratory works.

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Khum Gurung

September 2019
Mikkeli, Finland
This doctoral dissertation is dedicated in memory of my late mother and father.
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Author’s contribution

Khum Gurung is the principal investigator, and corresponding author for all the publications I-IV.
Related publication


Other publications


### List of acronyms and symbols

**Acronyms**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdVs</td>
<td>Adenovirus</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>AOPs</td>
<td>Advanced oxidation processes</td>
</tr>
<tr>
<td>BDD</td>
<td>Boron-doped diamond</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BOD5</td>
<td>Biological oxygen demand of 5-days</td>
</tr>
<tr>
<td>CAS</td>
<td>Conventional activated sludge</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>CST</td>
<td>Capillary suction time</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>DSA</td>
<td>Dimensionally stable anodes</td>
</tr>
<tr>
<td>DW</td>
<td>Deionized water</td>
</tr>
<tr>
<td>ECs</td>
<td>Emerging contaminants</td>
</tr>
<tr>
<td>EDCs</td>
<td>Endocrine disrupting compounds</td>
</tr>
<tr>
<td>EDGs</td>
<td>Electron donating groups</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EPS</td>
<td>Extracellular polymeric substance</td>
</tr>
<tr>
<td>EWGs</td>
<td>Electron withdrawing groups</td>
</tr>
<tr>
<td>FOG</td>
<td>Fat-oil-grease</td>
</tr>
<tr>
<td>FS</td>
<td>Flat sheet</td>
</tr>
<tr>
<td>FT-ICR</td>
<td>Fourier-transform ion cyclotron resonance mass spectrometry</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HF</td>
<td>Hollow fibre</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of detection</td>
</tr>
<tr>
<td>LOQ</td>
<td>Limit of quantification</td>
</tr>
<tr>
<td>MBR</td>
<td>Membrane bioreactor</td>
</tr>
<tr>
<td>MBBR</td>
<td>Moving-bed biofilm reactor</td>
</tr>
<tr>
<td>MLSS</td>
<td>Mixed liquor suspended solid</td>
</tr>
<tr>
<td>MLVSS</td>
<td>Mixed liquor volatile suspended solid</td>
</tr>
<tr>
<td>MMO</td>
<td>Mixed metal oxide</td>
</tr>
<tr>
<td>MWCO</td>
<td>Molecular weight cut-off</td>
</tr>
<tr>
<td>NoV GI</td>
<td>Norovirus genome group I</td>
</tr>
<tr>
<td>NoV GII</td>
<td>Norovirus genome group II</td>
</tr>
<tr>
<td>OERs</td>
<td>Oxygen-evolution reactions</td>
</tr>
<tr>
<td>PCPs</td>
<td>Personal care products</td>
</tr>
</tbody>
</table>
List of acronyms and symbols

PE Polyethylene
PES Polyethylsulphone
PhACs Pharmaceutically active compounds
PP Polypropylene
PVDF Polyvinylidene difluoride
P-25 Aeroxide® Titania nanoparticles
RME Real MBR effluent
SAD<sub>mm</sub> Specific aeration demand per membrane surface area
SCE Saturated Calomel electrode
SEM Scanning electron microscope
SHE Standard Hydrogen electrode
SMP Soluble microbial product
SRT Solid retention time
SVI Sludge volume index
TMP Trans-membrane pressure
TP Total phosphorus
TSS Total suspended solid
WWTP Wastewater treatment plant

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>h</td>
<td>Planck constant (J.s)</td>
</tr>
<tr>
<td>θ</td>
<td>Frequency (Hz)</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-charge ratio</td>
</tr>
<tr>
<td>R&lt;sub&gt;t&lt;/sub&gt;</td>
<td>Total membrane filtration resistance (m&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>μ</td>
<td>Dynamic viscosity of water (Pa.s)</td>
</tr>
<tr>
<td>J</td>
<td>Membrane flux (Lm&lt;sup&gt;-2&lt;/sup&gt;h&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>log D</td>
<td>Distribution coefficient</td>
</tr>
<tr>
<td>log K&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Sludge-water distribution coefficient</td>
</tr>
<tr>
<td>E°</td>
<td>Standard redox potential (eV)</td>
</tr>
<tr>
<td>R&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>Adsorbed organic pollutants at anode surface</td>
</tr>
<tr>
<td>P&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>Oxidized adsorbed organic pollutants at anode surface</td>
</tr>
<tr>
<td>ΔE</td>
<td>Band gap energy (eV)</td>
</tr>
<tr>
<td>e&lt;sub&gt;cb-&lt;/sub&gt;</td>
<td>Excited electrons to conductance band</td>
</tr>
<tr>
<td>h&lt;sub&gt;vbs&lt;/sub&gt;</td>
<td>Photogenerated holes at valence band</td>
</tr>
</tbody>
</table>
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1 Introduction

1.1 Problem statement and research motivations

The global water demand has been increasing constantly due to exacerbated population growth, economic development, climatic change, intensive agricultural practices, changing consumption patterns and urbanization. Undoubtedly, combating water scarcity is a global issue (WHO, 2015a; UN GEMS, 2006). As a result, many of the natural water systems that preserve balanced and thriving ecosystems, have become severely stressed. The UN report in 2015 revealed that the global clean water scarcity will reach 40% by 2030 (WWAP, 2015). Indeed, water scarcity is not about having too little water, but it is the scarcity of having good water management practices, which severely endangers billions of people and the environment (World Water Council, 2019). Water scarcity afflicted many countries globally, leading poor access to clean potable water and sanitation (Cosgrove et al., 2014). Globally, about 1.1 billion people lack access to safe drinking water and 2.7 billion experience water crisis at least a month per year (WHO, 2015a; WWF, 2019). It is obvious that aquatic environments can no longer be perceived as constant water supply source, and rather these environments are complex matrices that need careful practices to ensure sustainable and well-functioning ecosystems in the future (UN GEMS, 2006). This enormous challenge requires a transformation of water industries based on smart integrated innovative technologies and effective management outlooks that protects and reuses water for many purposes (Cosgrove et al., 2014).

In these circumstances, municipal wastewater reclamation is one of the promising approaches to relieve increasing pressure on natural water resources. Nevertheless, adequate treatment is always required to achieve high quality reclaimed water for reuse and to ensure no potential threats to human health and aquatic environments (Ma et al., 2013). Especially, an active evaluation of possible risks of emerging contaminants (ECs) in the treated effluent of wastewater treatment streams has gained a great attention among the scientific community (Luo et al., 2014; Nassiri Koopaei and Abdollahi, 2017; Yang et al., 2017). Moreover, according to EU framework, ECs must be adequately removed before discharging wastewater or treated effluent to the aquatic environment due to their persistency, risk of bioaccumulation, and acute or chronic toxicity. Over the decades, EU water framework legislations are being more stringent day-by-day regarding the removal of many ECs found in the aquatic environment.

Conventional municipal wastewater treatment processes are mainly aimed for treating organic matters, suspended solids and nutrients, hence their poor efficiency to treat ECs. To ensure compliance with the stringent discharge limits for quality water reclamation, interests in the ability of membrane bioreactors (MBRs) in removing ECs from municipal wastewater has increased in recent decades (Judd, 2008). MBRs have emerged in the wastewater treatment sector as one of the most reliable alternatives to the conventional activated sludge (CAS) processes (Hai et al., 2014). Nevertheless, many ECs are not efficiently attenuated neither in CAS nor MBRs due to their refractory nature (Xiao et al.,...
Therefore, it is essential to develop a treatment system, in which, MBRs can be integrated with other advanced oxidation processes (AOPs), to enhance the removal of ECs before discharging the treated effluent is into the environment or reusing it. Nevertheless, the number of research studies on integrating MBR with AOPs are rather limited.

### 1.2 Research objectives

The current thesis investigates the feasibility of advanced wastewater treatment techniques to treat municipal wastewater containing traces of many ECs that are of emerging concern. The main research objectives can be divided into two principal aspects: (1) to assess the functional operation and performance of a conventional MBR unit in a unique Nordic environment (esp. low water temperature conditions) for treating real municipal wastewater, in which the pilot MBR unit was operated as an advanced secondary treatment process and its treatment efficiency, mainly the removal of ECs under varying operating conditions, such as varying temperatures and solid retention times (SRT) was assessed; (2) to investigate the possible integration of alternative advanced water treatment processes for enhancing the ECs removal efficiency of the conventional MBR with selected AOPs, such as electrochemical oxidation (ECO) and photocatalytic oxidation (PCO). The main objectives are summarized as follow:

- To study the performance of a conventional MBR to treat the real municipal wastewater in Nordic winter environment and under varying SRTs (Paper I and II)
- To study the removal of PhACs from MBR treated effluent by utilizing electrochemical oxidation on newly developed Ti/Ta$_2$O$_5$-SnO$_2$ anode (Paper III)
- To study the removal of PhACs from MBR treated effluent by photocatalytic oxidation with Ag$_2$O/P-25 photocatalyst (Paper IV)
2 Municipal wastewater

Municipal wastewater comprises of either sanitary sewage from households and commercial buildings or the mixture of sanitary sewage with industrial wastewater, stormwater and agricultural run-off (Metcalf & Eddy Inc., 2003). Combined sewers are designed to collect both sanitary sewage and stormwater run-off, while only sanitary sewage are allowed under separate sewers (US EPA, 2015a). In general, it is reported that about 70 - 130% of municipal fresh water consumption becomes wastewater (Qasim, 2017).

The characteristics of municipal wastewater varies from site to site depending on land uses, water consumption patterns, discharges of commercial and industrial wastewater, extent of separation between stormwater and sanitary sewage, and inclusive of both diurnal and seasonal fluctuations (Hung et al., 2012). The major constituent of municipal wastewater is approximately 99.9% of water and the rest fractions includes organics, inorganics, total suspended solids, together with traces of pharmaceuticals and other hazardous materials and microorganism (Sperling, 2007). It is difficult to achieve any effective wastewater management without the detailed understanding of wastewater characteristics. However, since water-consumption patterns of individuals can rise haphazardly, the composition and strength of wastewater generated from diverse standpoint sources fluctuates with time, thus impossible to quantify these fluctuations accurately. According to US EPA, municipal wastewater can be characterized in terms of physical, chemical and biological constituents (U.S. EPA, 1997). Table 1 shows the characteristics of typical municipal wastewater and possible sources.
# Municipal wastewater

Table 1. Characteristics of Municipal wastewater and their sources (Metcalf & Eddy Inc., 2003; U.S. EPA, 1997)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Sources</th>
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<tr>
<td><strong>a) Physical characteristics</strong></td>
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<tr>
<td>Color and Odor</td>
<td>Domestic and industrial wastewater, natural decay of organic matters</td>
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<td>Temperature</td>
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<td>Electrical conductivity</td>
<td>Domestic and industrial wastewater</td>
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<tr>
<td>Particle size distribution</td>
<td>Domestic and industrial wastewater, soil erosion</td>
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<tr>
<td><strong>b) Chemical characteristics</strong></td>
<td></td>
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<tr>
<td>Organics:</td>
<td></td>
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<tr>
<td>BOD₅/COD/TOC, Carbohydrates and proteins, Fats, oils and grease (FOG)</td>
<td>Domestic commercial and industrial wastewater</td>
</tr>
<tr>
<td>Refractory organics (Surfactants, pesticides, phenols, pharmaceuticals, PFCs etc.)</td>
<td>Domestic, industrial and agricultural wastewater</td>
</tr>
<tr>
<td>Inorganics:</td>
<td></td>
</tr>
<tr>
<td>Alkalinity, chlorides</td>
<td>Domestic water supply, domestic wastes, groundwater infiltration, water softener</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Domestic and agricultural wastewater</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>Domestic, commercial and industrial wastewater, storm water run-off</td>
</tr>
<tr>
<td>pH</td>
<td>Domestic, commercial and industrial wastewater</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>Industrial wastewater</td>
</tr>
<tr>
<td>Gases:</td>
<td></td>
</tr>
<tr>
<td>Methane, hydrogen sulfides, oxygen, nitrous oxides</td>
<td>Domestic water supply, decomposition of domestic wastewater, surface water infiltration</td>
</tr>
<tr>
<td><strong>c) Biological characteristics</strong></td>
<td></td>
</tr>
<tr>
<td>Bacteria, protozoa, algae, helminths</td>
<td>Wastewater treatment plants</td>
</tr>
<tr>
<td>Pathogens (coliorm, viruses)</td>
<td>Domestic wastewater</td>
</tr>
</tbody>
</table>
2.1 Occurrence of emerging contaminants in municipal wastewater

ECs are new chemicals with no associated regulatory standards, and whose effects on environment and human health are still largely unknown (Deblonde et al., 2011). Over the past few years, the occurrence of ECs, such as pharmaceutically active compounds (PhACs), personal care products (PCPs), stimulants, pesticides, steroid hormones, endocrine disrupting compounds (EDCs) and UV filters, has attained a great concern due to their ubiquitous presence in various compartments of the aquatic environment (e.g., water, sediment and biota) and their potential ecological threats (Barceló and Petrovic, 2008; Deblonde et al., 2011; Tran et al., 2018; Verlicchi and Zambello, 2015). ECs not only pose threat to aquatic life, but also their constant accumulation in aquatic environment could evolve antibiotic-resistant microbial strains (Ganiyu et al., 2015). Currently, more than 700 ECs and their active metabolites are identified in the EU aquatic environment (UN FAO, 2018). A large number of these ECs have been identified at source, in treated effluent, and wasted biomass of sewage treatment plants (Clara et al., 2005b; Trinh et al., 2016; Vieno et al., 2005). The significant spatial and temporal variations in the concentrations of ECs have been reported by many researchers due to number of factors, such as rate of production, specific sales and consumption practices, metabolism, and specific water consumptions (Luo et al., 2014). The physicochemical properties of some commonly identified ECs in municipal wastewater, most of which have used as model ECs in this thesis, are summarized in Table 2.

Many ECs are present at extremely low concentrations (µg L\(^{-1}\) to ng L\(^{-1}\)) in the environment, which make their identification and assessment even more challenging (Rodriguez-Narvaez et al., 2017; US EPA, 2015b). Most of the ECs found in wastewater and aquatic environment are of anthropogenic origin, which are generally introduced from various routes, including direct or treated discharge of wastewater from municipal, hospital, and industrial wastewater treatment plants (WWTPs), surface run-off from agricultural and veterinary sectors, landfill leachates, and sewer leakage or overflow (Luo et al., 2014; Tran et al., 2018). Of the many sources, occurrence of ECs at WWTPs are of main concern since they are frequently detected in both influent and treated effluent of WWTPs, and subsequently discharge ECs into the environment (Behera et al., 2011). The category and concentrations of ECs generally found in WWTPs depend on the socioeconomic composition of the population generating the municipal wastewater (Tran et al., 2018).
### Table 2. Physicochemical properties of some commonly identified ECs in municipal wastewater.

<table>
<thead>
<tr>
<th>Category</th>
<th>Compound</th>
<th>Molecular weight (g.mol⁻¹)</th>
<th>log D (at pH 7)</th>
<th>Dissociation constant (pKₐ)</th>
<th>Henry’s Law constant (at 25°C) (atm.m³.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PhACs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analgesics and anti-inflammatory agents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Paracetamol</td>
<td>151.16</td>
<td>0.47</td>
<td>9.86; 1.72</td>
<td>1.92 x 10⁻¹¹</td>
</tr>
<tr>
<td></td>
<td>Diclofenac</td>
<td>296.15</td>
<td>1.77</td>
<td>4.18; -2.26</td>
<td>2.69 x 10⁻¹¹</td>
</tr>
<tr>
<td></td>
<td>Ibuprofen</td>
<td>206.28</td>
<td>0.94</td>
<td>4.41</td>
<td>5.54 x 10⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>Ketoprofen</td>
<td>254.28</td>
<td>0.19</td>
<td>4.23</td>
<td>1.92 x 10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>230.26</td>
<td>0.73</td>
<td>4.84</td>
<td>6.08 x 10⁻¹²</td>
</tr>
<tr>
<td>Antiepileptics</td>
<td>Carbamazepine</td>
<td>236.27</td>
<td>1.89</td>
<td>13.94; -0.49</td>
<td>9.41 x 10⁻¹²</td>
</tr>
<tr>
<td>Antibiotics</td>
<td>Sulfamethoxazole</td>
<td>253.28</td>
<td>-0.22</td>
<td>5.81; 1.39</td>
<td>2.24 x 10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>Trimethoprim</td>
<td>290.32</td>
<td>0.27</td>
<td>7.04</td>
<td>1.37 x 10⁻¹⁴</td>
</tr>
<tr>
<td></td>
<td>Tetracycline</td>
<td>444.44</td>
<td>-2.06</td>
<td>4.50; 11.02</td>
<td>7.35 x 10⁻²⁹</td>
</tr>
<tr>
<td></td>
<td>Ciprofloxacin</td>
<td>331.35</td>
<td>-0.33</td>
<td>6.43; 8.68</td>
<td>2.10 x 10⁻¹⁷</td>
</tr>
<tr>
<td></td>
<td>Tylosin</td>
<td>916.11</td>
<td>0.15</td>
<td>13.06; 7.39</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>Ofloxacin</td>
<td>361.37</td>
<td>-0.20</td>
<td>5.19; 7.37</td>
<td>1.76 x 10⁻¹⁶</td>
</tr>
<tr>
<td></td>
<td>Norfloxacin</td>
<td>319.33</td>
<td>-0.65</td>
<td>0.16; 8.68</td>
<td>4.13 x 10⁻¹⁶</td>
</tr>
<tr>
<td></td>
<td>Oxytetracycline</td>
<td>460.43</td>
<td>-2.25</td>
<td>4.50; 10.80</td>
<td>1.33 x 10⁻³²</td>
</tr>
<tr>
<td></td>
<td>Metronidazole</td>
<td>171.15</td>
<td>-0.14</td>
<td>14.44; 2.58</td>
<td>2.01 x 10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>Doxycycline</td>
<td>444.44</td>
<td>-0.92</td>
<td>4.50; 10.84</td>
<td>3.20 x 10⁻²⁶</td>
</tr>
<tr>
<td>Lipid regulators</td>
<td>Clofibric acid</td>
<td>214.65</td>
<td>-1.06</td>
<td>3.18</td>
<td>2.91 x 10⁻¹¹</td>
</tr>
<tr>
<td></td>
<td>Gemfibrozil</td>
<td>250.34</td>
<td>2.07</td>
<td>4.75</td>
<td>1.92 x 10⁻¹¹</td>
</tr>
<tr>
<td></td>
<td>Bezafibrate</td>
<td>361.82</td>
<td>-0.93</td>
<td>3.29; -2.06</td>
<td>2.12 x 10⁻¹⁹</td>
</tr>
<tr>
<td></td>
<td>Simvastatin</td>
<td>418.57</td>
<td>4.72</td>
<td>13.49</td>
<td>4.93 x 10⁻¹⁶</td>
</tr>
<tr>
<td>β-Blocker</td>
<td>Bisoprolol</td>
<td>325.45</td>
<td>-0.54</td>
<td>9.42</td>
<td>4.54 x 10⁻¹⁵</td>
</tr>
<tr>
<td></td>
<td>Atenolol</td>
<td>266.34</td>
<td>-2.09</td>
<td>13.88; 9.43</td>
<td>1.34 x 10⁻¹⁷</td>
</tr>
<tr>
<td></td>
<td>Metoprolol</td>
<td>267.37</td>
<td>-0.81</td>
<td>13.89; 9.43</td>
<td>1.59 x 10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>Propranolol</td>
<td>259.35</td>
<td>0.45</td>
<td>13.84; 9.50</td>
<td>6.27 x 10⁻¹⁴</td>
</tr>
<tr>
<td></td>
<td>Sotalol</td>
<td>272.36</td>
<td>-2.01</td>
<td>8.28; 9.31</td>
<td>2.63 x 10⁻¹⁴</td>
</tr>
<tr>
<td>Diuretics</td>
<td>Furosemide</td>
<td>330.74</td>
<td>-0.79</td>
<td>3.04; -2.49</td>
<td>2.57 x 10⁻¹⁹</td>
</tr>
<tr>
<td></td>
<td>Hydrochlorothiazide</td>
<td>297.73</td>
<td>-0.03</td>
<td>8.95; -4.08</td>
<td>5.61 x 10⁻¹⁷</td>
</tr>
<tr>
<td></td>
<td>Enalapril</td>
<td>376.45</td>
<td>-0.14</td>
<td>3.15; 5.43</td>
<td>1.48 x 10⁻²⁰</td>
</tr>
<tr>
<td>Psychostimulants</td>
<td>Caffeine</td>
<td>194.19</td>
<td>-0.63</td>
<td>0.52</td>
<td>1.63 x 10⁻¹²</td>
</tr>
<tr>
<td>Category</td>
<td>Compound</td>
<td>Molecular weight (g.mol(^{-1}))</td>
<td>log D (at pH 7)</td>
<td>Dissociation constant (pK(_a))</td>
<td>Henry’s Law constant (at 25(^{\circ})C) (atm.m(^3).mol(^{-1}))</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------------------</td>
<td>----------------------------------</td>
<td>----------------</td>
<td>----------------------------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td><strong>Contrast media</strong></td>
<td>Iopamidol</td>
<td>777.09</td>
<td>-2.54</td>
<td>10.87; -2.85</td>
<td>6.67 × 10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>Iopromide</td>
<td>791.12</td>
<td>-2.66</td>
<td>10.62; -2.60</td>
<td>3.29 × 10(^{-5})</td>
</tr>
<tr>
<td><strong>Antidepressants</strong></td>
<td>Fluoxetine</td>
<td>309.33</td>
<td>1.15</td>
<td>10.05</td>
<td>2.25 × 10(^{-11})</td>
</tr>
<tr>
<td></td>
<td>Paroxetine</td>
<td>329.37</td>
<td>1.16</td>
<td>9.68</td>
<td>3.53 × 10(^{-12})</td>
</tr>
<tr>
<td><strong>Anticoagulants</strong></td>
<td>Warfarin</td>
<td>308.33</td>
<td>0.67</td>
<td>4.50</td>
<td>1.42 × 10(^{-13})</td>
</tr>
<tr>
<td><strong>Immunosuppressives</strong></td>
<td>Methylprednisolone</td>
<td>374.48</td>
<td>2.17</td>
<td>12.46</td>
<td>1.88 × 10(^{-17})</td>
</tr>
<tr>
<td></td>
<td>Methotrexate</td>
<td>454.45</td>
<td>-4.98</td>
<td>3.47; 5.56</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>Beclomethasone</td>
<td>408.92</td>
<td>2.44</td>
<td>12.17</td>
<td>2.22 × 10(^{-18})</td>
</tr>
<tr>
<td></td>
<td>Cyclophosphamide</td>
<td>261.08</td>
<td>0.73</td>
<td>2.84</td>
<td>9.46 × 10(^{-10})</td>
</tr>
<tr>
<td></td>
<td>Ifosfamide</td>
<td>261.08</td>
<td>0.76</td>
<td>1.44</td>
<td>9.46 × 10(^{-10})</td>
</tr>
<tr>
<td></td>
<td>Hydrocortisone</td>
<td>362.47</td>
<td>1.76</td>
<td>12.47</td>
<td>1.74 × 10(^{-17})</td>
</tr>
<tr>
<td><strong>Bronchodilators</strong></td>
<td>Terbutaline</td>
<td>225.28</td>
<td>-1.77</td>
<td>9.11; 9.65</td>
<td>3.59 × 10(^{-14})</td>
</tr>
<tr>
<td></td>
<td>Clenbuterol</td>
<td>277.19</td>
<td>0.24</td>
<td>13.29; 9.51</td>
<td>9.12 × 10(^{-13})</td>
</tr>
<tr>
<td></td>
<td>Salbutamol</td>
<td>239.31</td>
<td>-1.77</td>
<td>9.99; 9.62</td>
<td>8.75 × 10(^{-15})</td>
</tr>
<tr>
<td><strong>Antiparasitics</strong></td>
<td>Flubendazole</td>
<td>313.29</td>
<td>3.08</td>
<td>10.66; 4.45</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>Fenbendazole</td>
<td>299.35</td>
<td>2.35</td>
<td>10.80</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>Ketoconazole</td>
<td>531.43</td>
<td>3.80</td>
<td>6.88</td>
<td>2.18 × 10(^{-24})</td>
</tr>
<tr>
<td><strong>Contraceptives</strong></td>
<td>Norethindrone</td>
<td>298.43</td>
<td>2.86</td>
<td>13.09</td>
<td>9.5 × 10(^{-12})</td>
</tr>
<tr>
<td><strong>2. EDCs</strong></td>
<td>Plasticizer</td>
<td>Bisphenol A</td>
<td>228.29</td>
<td>3.64</td>
<td>10.29</td>
</tr>
<tr>
<td></td>
<td>Bisphenol A</td>
<td>228.29</td>
<td>3.64</td>
<td>10.29</td>
<td>1.92 × 10(^{-11})</td>
</tr>
<tr>
<td><strong>3. Steroid Hormones</strong></td>
<td>17β-Estradiol</td>
<td>272.38</td>
<td>4.15</td>
<td>10.27</td>
<td>1.17 × 10(^{-9})</td>
</tr>
<tr>
<td></td>
<td>17β-Estradiol</td>
<td>296.41</td>
<td>4.11</td>
<td>10.24</td>
<td>3.74 × 10(^{-10})</td>
</tr>
<tr>
<td></td>
<td>Estriol</td>
<td>288.39</td>
<td>2.53</td>
<td>10.25</td>
<td>1.75 × 10(^{-11})</td>
</tr>
<tr>
<td></td>
<td>Estrone</td>
<td>270.37</td>
<td>3.62</td>
<td>10.25</td>
<td>9.61 × 10(^{-10})</td>
</tr>
<tr>
<td></td>
<td>Progesterone</td>
<td>314.46</td>
<td>3.83</td>
<td>n.a.</td>
<td>1.51 × 10(^{-9})</td>
</tr>
<tr>
<td></td>
<td>Testosterone</td>
<td>288.43</td>
<td>3.18</td>
<td>15.06</td>
<td>4.89 × 10(^{-11})</td>
</tr>
<tr>
<td><strong>4. Industrial Surfactants</strong></td>
<td>Perfluoro-octanoic acid (PFOA)</td>
<td>414.07</td>
<td>2.69</td>
<td>0.50</td>
<td>1.13 × 10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>Perfluorooctane sulfonic acid (PFOS)</td>
<td>212.28</td>
<td>4.49</td>
<td>&lt;1.0</td>
<td>4.1 × 10(^{-4})</td>
</tr>
</tbody>
</table>

n.a. - data not available
(Data are extracted from SciFinder database
https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf)
2.2 Environmental intimidations of ECs

The major concern on environmental risk of ECs is evidenced only if they may adversely pose impact on aquatic life and human health. There are three major risk factors related to the ECs presence in the aquatic environment viz. persistency, bioaccumulation, and toxicity (Ebele et al., 2017). Persistency is mainly defined by the physicochemical properties of ECs, due to which many of them are difficult to remove by conventional means of treatment. Indeed, their incomplete removal could generate many active metabolites that could pose potential risks to aquatic life. Even though not all the detected ECs in environmental matrix are persistent, their continuous replenishment and release to the environment referred them as ‘‘pseudo-persistent’’ compounds, which pose higher persistence even when acted by environmental processes, such as photodegradation, biodegradation, and sorption into sediments (Bu et al., 2016; Ebele et al., 2017). Another risk is the bioaccumulation of ECs in aquatic biota. Generally, ECs are designed and used for specific target, but since many of ECs and their metabolites are biologically active, they can adversely affect non-targeted aquatic organisms (Rodríguez-Mozaz et al., 2016). Coogan et al reported an abundant bioaccumulation of ECs and their metabolites in algae samples of WWTPs (Coogan et al., 2007). On the other hand, toxicity is one of the major concern of ECs, which can emerge due to complex mixtures of ECs that leads to high synergetic effects. This means that the presence of ECs even at low concentrations could pose significant toxicity to aquatic microorganisms. Another risk related to the ECs in the environment is the possible emergence and spread of antibiotic resistant strains in natural bacterial populations, which is a very emerging topic in recent years. Antibiotic resistance is aggravated by the misuse and overuse of antibiotic that has continuously undermined many advances in health and medicine (WHO, 2015b).

2.3 Municipal wastewater treatment

The main objectives of wastewater treatment are to separate, convert, and eliminate objectionable and hazardous contaminants and infectious pathogenic organisms via a combination of physical, chemical and biological processes (EU, 1991). Wastewater produced from municipalities and communities must ultimately be returned to receiving waters or to land or reuse after the treatment. Wastewater treatment is a multi-step process, which typically involves primary, secondary and tertiary treatments, according to the treatment objectives, level of treatment efficiency, and environmental threats on the receiving water bodies (Sperling, 2007). The municipal wastewater reclamation is an important concept, in which the collected municipal wastewater is treated and reused for recharging fresh water sources and recovering value-added resources and energy (Metcalf & Eddy Inc., 2003).

The primary treatment mostly includes the physical treatment of wastewater in order to reduce to treatment load to the subsequent steps by selectively removing settleable organic and inorganic materials and floating (scums) materials via sedimentation. This
process can reduce about 25 – 50% of BOD₅, 50 – 70% TSS and 65% FOG loads (Aziz and Mojiri, 2014). However, advanced primary treatment or chemically enhanced primary treatment could be attained by the addition of coagulants (aluminium sulphate, ferric chloride or other polymers) to remove mainly phosphorus by precipitation (Sperling, 2007).

The secondary treatment is intended for the removal of organic pollutants (either suspended, particulate, or dissolved) and nutrients (nitrogen and phosphorus) (Punnia et al., 1998). Secondary treatment typically includes biological reactor, where pollutants are removed by bacteria metabolism, and followed by the secondary sedimentation tank to separate settleable solids and treated water. The biological treatment process can be suspended growth, attached growth, and their various combinations. The suspended growth system includes CAS process (with or without biological nitrogen and phosphorus removal), extended aeration, and sequencing batch reactors, in which microorganisms attached to the biomass are maintained in suspension. The biomass and microorganism assays develop in support medium in attached growth system, including trickling filter, rotating biological contractor, and submerged aerated biofilters. On the other hand, combined suspended attached growth system involves processes with internal and up-flow suspended packing for attached growth such as moving-bed biofilm reactor (MBBR) and fluidized-bed bioreactors (Metcalf & Eddy Inc., 2003).

2.4 EU legislation and removal of ECs from municipal wastewater

The main objective of EU framework is to protect natural water environment in Europe and to replenish every river, lake, groundwater, wetland and other surrounding water bodies (Buttiglieri and Knepper, 2008). Due to persistency, risk of bioaccumulation in biota, and high synergetic toxicity, ECs must be adequately removed before releasing with treated effluent to the environment. The EU Water Framework Directive 2000/06/CE announced a list of 33 priority substances or group of hazardous substances, including heavy metals, pesticides, and polyaromatic hydrocarbon (EU 2000). In December 2008, directive 2008/105/EC was introduced amending to directive 2000/06/CE for progressively reducing contamination of priority substances with environmental quality standards (EQS) (EU 2008). In 2013, the directive 2008/105/EC was further amended to 2013/60/EC by identifying additional 12 substances and a first watch list of chemicals, including diclofenac, 17-β -estradiol (E2) and 17- α -ethinylestradiol (EE2) (EU 2013), was established. The watch list of these substances was set out in Commission Implementing Decision (EU) 2015/495 according to Article 8h of directive 2013/60/EC that additionally includes 2,6-Ditert-butyl-4-methylphenol, 2-Ethylhexyl 4-methoxycinnamate, macrolide antibiotics, methiocarb, neonicotinoids, oxadiazon and tri-allate (EU 2015). In 2018, the Commission Implementing Decision (EU) 2015/495 was updated to EU 2018/840, in which the substances with adequately available high-quality monitoring data, such as diclofenac, 2,6-Ditert-butyl-4-methylphenol, 2-Ethylhexyl 4-methoxycinnamate, oxadiazon and tri-allate, were
Municipal wastewater removed from the watch list with inclusion of sensitive substances, including amoxicillin, metaflumizone and ciprofloxacin (EU 2018).

Since municipal WWTPs receive diverse type and concentrations of ECs originated from synthetic chemicals that have been used for many purposes, these WWTPs are the major sources of many environmental pollution. More than 100,000 tons of ECs are produced globally (Radjenović et al., 2008). As confirmed by many researchers, the conventional wastewater treatment methods, such as CAS processes, are not efficient enough to remove persistent ECs, and many of these ECs remain poorly degraded and subsequently discharged into receiving waterbodies with treated effluent (Clara et al., 2005; Vieno et al., 2007; Vieno and Sillanpää, 2014; Zorita et al., 2009). Polar ECs are mostly hydrophilic and highly persistent under activated sludge process conditions, which lead them easily detected even in the treated effluent (Buttiglieri and Knepper, 2008). Therefore, upgrading of WWTPs and implementation of more sustainable technologies could be the possible solutions to abate such ECs emissions and to achieve high-quality treated effluent for the safe reclamation (Radjenović et al., 2009). On this note, MBR is one of the advanced wastewater technologies that has gained increased interest over three decades (Xiao et al., 2019).
3 State-of-the-art of MBRs: advanced municipal wastewater treatment

3.1 Introduction to MBRs

MBRs couple biological treatment with membrane separation to produce clarified and highly disinfected effluent (Judd, 2016). MBR technology is based on suspended growth process that applies microporous membranes to allow solid/liquid separation (Radjenović et al., 2008). The combination of a biological reaction to membrane separation strengthens the biological process and replaces many other subsequent operations, such as secondary clarifiers (Coutte et al., 2017). MBRs have become a state-of-the-art technology in water management practices for wastewater treatment and reclamation due to their remarkable benefits such as high quality treated effluent, relatively small plant footprint, and less sludge production (Drews, 2010). The MBR enables to maintain a high MLSS concentration, which is important for slow growing microorganisms (Drews, 2010; Judd, 2008). MBRs can perform biological treatment and disinfection of the effluent simultaneously with the optimum control of biological degradation and greater stability and flexibility in operation (Radjenović et al., 2009).

There have been several historical milestones leading to the development of today’s MBRs. The combination of membrane solid/liquid separators in biological treatment system has been studied since 1960s (Visvanathan et al., 2000). The era between 1960s and 1980s is often known as a golden age on membrane science development (Hai et al., 2014). The first historical coupling of an activated sludge bioreactor with a cross flow membrane filtration looped side-stream MBRs, was developed by Dorr-Oliveir Inc. in 1969 (Smith et al., 1969). However, the first generation MBRs associated with poor economics due to higher membrane cost and higher energy consumption. The first breakthrough of the MBR application emerged in 1989 when Yamamoto et al. introduced the submerging membranes inside the bioreactor (Yamamoto et al., 1988). Currently, more than 800 commercial MBRs are implemented in Europe, with the compound annual global market growth rate up to 12% (Krzeminski et al., 2017). The global MBR market should grow from 1.9 billion USD in 2018 to reach 3.8 billion USD by 2023 (BCC Research, 2019). More than 60 super-large scale (capacity ≥ 100,000 m³ d⁻¹) MBR plants will be in use by 2026, with Tuas Water Reclamation Plant being largest MBR (1200,000 m³ d⁻¹) in the world (The MBR site, 2019).

Stricter legislations concerning the effluent discharge, demands for wastewater reuse, and dramatic reduction of membrane capital costs (~1/10) are the major drivers of rapid MBR growth worldwide (Park et al., 2015). For instance, EU Urban Wastewater Treatment Directive (91/271/EEC), amended directive 2006/7/EC for management of bathing water quality, and EPA Clean Water Protection Act (2009), are the important legal complies
3 State-of-the-art of MBRs: advanced municipal wastewater treatment on treated effluent discharge or reuse limits that expanded the MBR market growth (Krzeminski et al., 2017).

3.2 Membrane materials, configuration and operating principles of MBRs

Generally, pressure-driven membrane processes are comprised of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Of these membranes, including microfiltration (0.1 to 1 µm) and ultrafiltration membranes (0.05 to 0.1 µm), which are widely used to separate particulate materials from water and wastewater, are referred as low-pressure membranes (Yang et al., 2006). On the other hand, nanofiltration and reverse osmosis are high-pressure membranes, which are commonly used to separate more soluble matters (Bérubé, 2010). The commercial MBR membrane pore sizes are generally between 0.03 and 0.4 µm (Judd, 2016). The most widely used membrane materials are cellulose, polyamide, polysulphone, polymeric materials, including polyvinylidene difluoride (PVDF), polyethylysulphone (PES), polyethylene (PE), and polypropylene (PP). Among the commercial membranes, PVDF membranes are the most widely used membranes that account almost half of all the products both in flat sheet (FS) and hollow fibre (HF) configurations (Judd, 2016). Most of the polymeric membranes are resilient to chemical and physical reactions, but severely prone to fouling due to hydrophobic nature of these membranes and biopolymers. Therefore, often the surface of commercially available membrane modules are amended by chemical oxidation, metal organic framework, or plasma treatment to achieve more hydrophilic surface (Radjenović et al., 2008).

In general, there are two basic MBR configurations for the membrane module, depending on the membranes placed either inside or outside the bioreactor, such as immersed or submerged and side-stream or external MBR system as shown in Figure 1 (Gupta et al., 2008; Judd, 2008; Melin et al., 2006). Submerged or immersed MBRs are more often applied in municipal wastewater treatment due to their high compatibility with the activated sludge process, compactness in design, relatively low energy consumption, and easy wasting of excel sludge (Gupta et al., 2008). On contrary, external or side-stream MBRs are stand-alone systems, are generally used to treat industrial high strength wastewater with poor filterability and require relatively less membrane area than in submerged MBRs. As pumping and recirculation of activated sludge is the integrated part in external MBRs, high cost is required due to more energy dissipation (Judd, 2008).
There are three different modules of membranes commercially used in MBRs, such as tubular membranes, hollow fibre and flat sheet membranes (Figure 2). Tubular membranes are typically used in external MBRs, where membranes having internal diameter greater than 5 mm are grouped into modules containing multiple tubes. Hollow fiber and flat sheet membranes are used typically in submerged MBRs. Hollow fiber membranes generally have external diameter in the range of 1-3 mm and confined into modules of dozens to thousands of fibers (Bérubé, 2010).
3.3 Membrane fouling: a major shortcoming in MBRs

Despite the promising treatment technology, membrane fouling is an inevitable phenomenon in pressure-driven MBRs, which normally increases TMP and reduces permeate flux (Le-Clech et al., 2006). Membrane fouling is the possible deposition of sludge flocs, particulates, solutes, microorganisms, and cell debris in the membrane pores, and on the membrane surface (Burman and Sinha, 2018; Meng et al., 2009). However, due to its complex nature, membrane fouling in MBRs is not yet entirely understood (Meng et al., 2010).

The major fouling consequences in MBRs involve increase in TMP, rapid deterioration of permeate flux, and increase in filtration resistance, leading to frequent cleanings requirement, and high energy consumption for aeration (Drews, 2010). Moreover, membrane fouling also exacerbates feed pressure, reduces effluent quality, weakens membrane performance, and reduces membrane effective life (Burman and Sinha, 2018). The specific energy consumption in MBRs operation generally ranges from 0.6 – 2.3 kWh m⁻³ (Krzeminski et al., 2017), which is quite high in comparison to CAS processes (0.3 – 0.6 kWh m⁻³) (Dai et al., 2015). Even though, the membrane costs have dramatically reduced these days, which ultimately reduce capital investment cost in MBRs, the overall operating costs are still high mainly due to membrane aeration for fouling mitigation. Moreover, the use of aggressive chemicals for repeated membrane cleaning events can create additional environmental concerns (Drews, 2010).

Membrane fouling can be classified mainly into reversible and irreversible types. Reversible fouling during filtration mainly occurs due to external deposition of loosely bound materials on the membrane surface that causes cake layer formation. Reversible fouling can simply be controlled by physical techniques, which can involve back flushing or relaxation under crossflow conditions. Contrarily, irreversible fouling mainly occurs due to strongly attached materials and pore blocking of the membrane, which can only be removed by chemical cleaning (Burman and Sinha, 2018). Nevertheless, irrecoverable fouling, which is a subsequently left to be treated by chemical cleaning, is difficult to remove by any cleaning methods (Drews, 2010).

Furthermore, membrane fouling can be categorized as biofouling, inorganic fouling and organic fouling depending on the fouling components (Meng et al., 2009). Biofouling occurs because of biological growth, metabolism and its secretion, which ultimately accumulate on the membrane and its pores and leading to the formation of biofouling. Organic fouling is due to the organic substances contained in the biomass and organic by-products produced by microorganisms, which can easily be deposited on membrane surface. Colloidal initiate membrane pore clogging and biopolymers, such as protein, polysaccharides and humics can further propagate organic fouling. Whereas, inorganic fouling forms due to the chemical precipitation of inorganic ions (anions and cations), including Ca²⁺, Mg²⁺, Al³⁺, Fe³⁺, PO₄³⁻,SO₄²⁻ and OH⁻. Inorganic fouling mainly occurs
via two mechanisms, such as crystallization and particulate fouling. Of these three fouling, biofouling and organic fouling are dominant in MBRs (Burman and Sinha, 2018; Hai et al., 2014). Indeed, membrane fouling is a very complex mechanism that includes complicated inter-relationships between various factors, such as reactor design and operational conditions, wastewater composition, sludge rheology, ambient conditions (Zhang et al., 2014). Membrane fouling can be quantitatively determined according to the Darcy’s equation as follows (Meng and Yang, 2007):

\[
R_t = \frac{\text{TMP}}{\mu J}
\]

Where, \( R_t \) is the total membrane filtration resistance (m\(^{-1}\)); \( \text{TMP} \) is trans-membrane pressure (Pa); \( \mu \) dynamic permeate viscosity (Pa.s); and \( J \) is the membrane flux (L m\(^{-2}\) h\(^{-1}\)).

The water temperature greatly influences the efficiency of biological treatment processes (van den Brink et al., 2011). When temperature drops at about 15°C, methane-producing bacteria becomes essentially inactive, autotrophic bacteria practically cease functioning at about 5°C, and even chemoheterotrophic bacteria feeding on carbonaceous material becomes dormant at 2°C (Metcalf & Eddy Inc., 2003). In MBRs, temperature not only influences biological process but also effects on membrane performance. However, MBR process operation in low-temperature zones are comparatively less studied than under normal ambient conditions (Zhang et al., 2014).

At lower temperatures, MBR efficiency deteriorated mainly due to increased MLSS viscosity, releasing of more EPS due to increased sludge deflocculation, and reduced back transport velocity of particles from membrane surface (van den Brink et al., 2011). Arévalo et al. reported the loss in permeability and increased membrane flux resistance at temperatures < 15°C (Arévalo et al., 2014) in a full-scale MBR. Brink et al. showed that at low temperatures, membrane fouling is intensified due to the release of polysaccharides and submicron particles from sludge flocs (van den Brink et al., 2011).

The bulking of sludge has noticed with significant increase in the sludge volume index (SVI) at 13°C, which was accompanied by rapid membrane fouling and thereby two-fold increase in the membrane cleaning frequency (Zhang et al., 2014). The bulking sludge can cause severe cake fouling due to the accumulation of more irregular shaped sludge flocs, whereas deflocculated sludge can cause both cake fouling and pore blocking fouling by the deposition of colloidal particles and dissolved matter onto/into the membrane surface (Meng and Yang, 2007). Krzeminski et al. observed that the colloidal and soluble fraction (<1 µm) plays a major role in increasing the membrane resistance during winter period (Krzeminski et al., 2012). The possible fouling components in MBRs and their spatial and temporal distributions are schematically shown in Figure 3 (Meng et al., 2017).
The most common techniques of cleaning membranes in MBRs are physical and chemical methods. Physical cleaning includes backflushing or relaxation which is applied for 1-2 min in every 10-15 min, whereas alkaline (pH ~ 12) sodium hypochlorite often followed by acidic (pH ~3) citric (or oxalic) acid with concentration up to 1% are used as chemical cleaning (Judd, 2008). However, some innovative membrane cleaning protocols have been emerged over the traditional methods to emphasize improved efficiency and minimum energy expenditure. The emerging novel strategies involved the application of various additives (flux enhancers), biocarriers, sludge granulation, membrane surface modifications, and quorum quenching techniques (Drews, 2010).

3.4 Fate of ECs in MBRs: application of mass balance

The removal mechanism of ECs in MBRs is a complex phenomenon, which is characterized by following four major pathways: (i) biotransformation or biodegradation; (ii) sorption onto the sludge; (iii) volatilization; and (iv) physical retention via membrane size exclusion (Cirja et al., 2008a). However, the ECs removal via volatilization and physical retention by membrane is almost insignificant since Henry’s law constant (K_H) values of most of the ECs are absolutely low (< 10^{-6}) (Table 2) and the molecular weight cut-off (MWCO) of most of the pressure driven MF and UF membranes are above several
thousand Daltons compared to molecular weight of commonly found ECs i.e., 150 to 900 Da. Therefore, biotransformation and sorption onto the sludge are the major removal mechanisms of ECs in MBR treatments (Li et al., 2015; Luo et al., 2014).

The mass balance approach is useful to assess the fate of ECs considering their percentage shares of biotransformation/biodegradation, sorption and remained in the treated effluent. The mass loads (µg d⁻¹) of ECs in influent, effluent and sludge can be calculated by multiplying their measured concentrations (C_{Inf}, C_{Eff}, C_{Sludge}) with the equivalent flow data (Q_{Inf}, Q_{Eff}, Q_{Sludge}). Then, the relative distributions of ECs to the influent mass load can be estimated according to the following equations (2)-(5)(Joss et al., 2006):

Overall removal (%) = \( \frac{(C_{Inf} \times Q_{Inf} - C_{Eff} \times Q_{Eff})}{C_{Inf} \times Q_{Inf}} \times 100 \)  \hfill (2)

Removal via sorption onto sludge (%)
\[ = \frac{C_{Sludge} \times Q_{Sludge}}{C_{Inf} \times Q_{Inf}} \times 100 \]  \hfill (3)

Remain in effluent (%)
\[ = \frac{C_{Eff} \times Q_{Eff}}{C_{Inf} \times Q_{Inf}} \times 100 \]  \hfill (4)

Removal via biotransformation (%)
\[ = \text{Overall removal} (%) \]
\[ - \text{Removal via sorption onto sludge} (%) \]  \hfill (5)

where \( C_{Inf} \times Q_{Inf} ; C_{Eff} \times Q_{Eff} ; \text{ and } C_{Sludge} \times Q_{Sludge} \) are the mass load (µg d⁻¹) of ECs in influent, treated effluent and sludge, respectively.

The removal mechanism of ECs in MBRs is under the influence of mainly ‘internal factors’ and ‘external factors’(Luo et al., 2014). The internal factors are related to the physicochemical properties of ECs, including hydrophobicity, biodegradability, degree of ionization, and volatility (Cirja et al., 2008a; Li et al., 2015). In general, ECs with High log D value (\( \log D_{pH7} > 3.2 \)) are hydrophobic, poorly soluble and with high sorption affinity on organic constituents (Cirja et al., 2008a). The higher removal efficiency of hydrophobic compounds may be ascribed to the sorption of ECs onto sludge that assists for enhanced biotransformation. Contrarily, the removal of hydrophilic ECs (\( \log D_{pH7} < \))
The external factors are mainly WWTP-specific that involves process operating conditions, such as SRT, temperature and pH (Luo et al., 2014). SRT better controls the size and diversity of microorganism community. In general, the MBRs operated with extended SRTs can improve building up of slowly growing bacteria (e.g., nitrifying bacteria) and longer retention of sludge inside the bioreactor, which favors higher removal of ECs (Suárez et al., 2012). Nitrifying conditions can have positive effect on the removal of ECs via co-metabolism using ammonium monooxygenase enzyme. The SRTs above 10 days that allow nitrifying conditions can enhance the attenuation of many biodegradable compounds (Clara et al., 2005a). Nevertheless, there are many studies that revealed no enhanced elimination of ECs with wide variation of SRTs, indicating that high SRT does not necessarily mean enhanced removal of ECs (Luo et al., 2014). Likewise, pH value is another critical parameter influencing the removal of ECs in MBR treatment. Various protonation states of ECs can be expected depending on their pKa values. It is expected that at low pH, hydrophobicity of most of the ionizable ECs would increase that ultimately increases their adsorption onto sludge mass, which indeed favors increased time for biotransformation (Urase et al., 2005). Modest pH variation can also have significant effects on the removal of acidic ECs due to the activation of enzymes or enhanced affinity between sludge and ECs due to protonation phenomenon (Kimura et al., 2007). On contrary, at varying pH, no changes in the removal efficiency of non-ionizable compounds is noticed (Táheran et al., 2016).

On the other hand, seasonal variation of wastewater temperature can affect the removal of ECs in MBRs, which influence mostly biodegradation and partition mechanisms (Luo et al., 2014). In general, with increasing temperatures, adsorption equilibria are reached earlier, and microbial activities and biodegradation ECs are enhanced. However, Hai et al. reported the decreased removal of most hydrophobic ECs when process temperature reached 45 °C (Hai et al., 2011).
3.5 Fate of human enteric viruses and heavy metals in MBRs

The human enteric viruses, including noroviruses and adenoviruses, are most common pathogenic group associated with several waterborne diseases, such as epidemic gastroenteritis, conjunctivitis, and respiratory diseases (Kuo et al., 2010; Miura et al., 2015). Human enteric viruses are largely found in municipal wastewater, which are highly resistant to inactivation. Adequate reduction of viruses is of a prime regulatory focus from water reuse due to their acute impact on public health and hygiene (Chaudhry et al., 2015b). The inadequate WWTPs treatment efficiency often led to the insufficient removal of viruses from source waters, causing their outbreaks to the environment (Lodder and Husman, 2005).

MBRs offer absolute barrier to solids and microorganisms, despite MBRs are not significantly efficient retaining viruses via membrane size exclusion (Herath et al., 1999). Even though virus removal in MBRs are ascribed to their aggregation and adsorption to sludge and retention by the gel and cake layer formed on the membrane surface. On the other hand, formation of fouling layer on the membrane surface plays a vital role on controlling virus removal, yet current understanding of interactions between viruses and membrane surface, impact of membrane cleaning as well as membrane imperfections in MBRs is limited (Hai et al., 2014).

Miura et al. indicated that adsorption to sludge plays a major role in the removal of norovirus GII in the MBR, in which diverse adsorptive behavior of viruses to sludge influenced the overall removal efficiency (Miura et al., 2015). Kuo et al. reported the attachment of adenovirus to sludge and membrane-biofilm as a major mechanism for their removal in the MBR (Kuo et al., 2010). However, the biomass attachment removal mechanism is mostly dependent on the type of virus (Chaudhry et al., 2015a). In another study, Chaudhary et al. suggested the major removal contribution of viruses is majorly by backwashed membrane, inactivation by biomass due to predation or enzymes, the cake layer formation and attachment to solids (Chaudhry et al., 2015b).

Heavy metals refers to any metals with relatively high density (>5 g cm\(^{-3}\)) and atomic weights, which are most serious environmental threats due to their recalcitrance and persistence in the environment (Chipasa, 2003; Fu and Wang, 2011). The risks associated with the bioaccumulation in the food chains are the major environmental and human health concerns (Cantinho et al., 2016). The presence of heavy metals at certain concentrations not only pose environmental concerns but also strongly reduces microbial activity, leading to adverse effects on biological treatment processes (Chipasa, 2003). Trace quantities of many heavy metals are identified in municipal wastewater from various sources, mainly anthropogenic emissions. Of the many heavy metals, cadmium (Cd), lead (Pb), mercury (Hg) and nickel (Ni) are defined by EU directive 2013 as priority hazardous elements, which could pose acute to chronic health problems to human and aquatic life depending on their potency and time of exposure (EU, 2013).
Some studies have confirmed the potential of MBRs for enhanced removal of heavy metals from wastewater than conventional treatment methods (Di Fabio et al., 2013; Fatone et al., 2008; Katsou et al., 2011; Santos and Judd, 2010). There are several mechanisms involved in heavy metal removal by MBRs, such as surface adsorption and diffusion of metal ions in sludge flocs, adsorption and complexation formation of soluble metal ions in EPS matrix, and to some extent by chemical precipitation of metals due to alkaline nature of wastewater (Katsou et al., 2011). Di Fabio et al., who studied the removal and fate of heavy metals in a pilot-scale MBR revealed that the biosorption of heavy metals to fouling layer (esp. EPS matrix) is more evident than to sludge (Di Fabio et al., 2013). However, the pH of the medium greatly influences the number of EPS binding sites for heavy metals (Comte et al., 2008). Fatone et al. reported that operating MBRs at high SRTs is not effective strategy to enhance the removal of heavy metals at low concentrations (Fatone et al., 2008). Addition of vermiculite minerals could enhance the heavy metal removals due to increased sites for biofilm formation and microorganism growth, but can increase sludge concentration and membrane fouling (Katsou et al., 2011).
Advanced oxidation processes for wastewater treatment

Biological treatment is usually the most economic process to treat ‘readily degradable’ organic pollutants present in wastewater. However, if the wastewater is comprised of refractory (non-biodegradable) organic pollutants, such as several ECs, then it requires special type of treatment to meet the desired discharge limits (Comninellis, 1994). In this regard, advanced oxidation processes (AOPs), based on aqueous phase oxidation on the intermediacy of powerful reactive species, mainly hydroxyl radicals (’OH), leading to the nonselective degradation of the organic pollutants to their mineralization (Sirés et al., 2014).

AOP was first proposed by Glaze in 1980s for potable water treatment using ozone (Glaze, 1987). Since then AOPs are widely applied to treat wastewater as strong oxidants that can degrade recalcitrant ECs and simultaneously increase the biodegradability (Deng and Zhao, 2015). AOPs are promising, efficient and environmental-friendly approaches to treat wastewater contaminated with wide range of ECs, mainly by electrochemical, photochemical, ozonation, Fenton, or sonochemical reactions (Nidheesh et al., 2018; Oturan and Aaron, 2014). AOPs can be utilized either as pre- or post-biological treatment depending on the concentration of ECs in the wastewater influent stream. Pre-treatments using AOPs are more feasible when the concentrations of ECs are higher than the organic matters, whereas post-treatments are realistic when the concentrations of ECs are relatively lower than organic matters (Neoh et al., 2016).

The hydroxyl radical is the second most powerful oxidizing agent after fluorine with a redox potential of $E^\circ$ (’OH/H$_2$O) = 2.8 (V vs. SHE), and a life time of less than a second (Brillas and Martínez-Huitle, 2015). These in situ produced ’OH radicals then rapidly react with organic pollutants at high reaction rates mainly by the electron transfer or redox reactions, H atom abstraction (aliphatics), or the addition on an unsaturated bond (aromatics) to initiate a radical chain oxidation reaction (Nidheesh et al., 2018; Sirés et al., 2014).

4.1 Electrochemical oxidation (ECO) process

Electrochemical oxidation processes have gained great attention over the last decade for the decontamination of wastewater containing persistent organic pollutants and for disinfection purposes (Brillas et al., 2009; Särkkä et al., 2015). ECO processes are emerging as most appealing environmentally friendly and highly efficient electrochemical treatments (Martínez-Huitle and Brillas, 2009). The major benefit of electrochemical treatments is its ability to regulate and generate in situ ’OH radicals without adding chemicals or large amount of catalyst (Oturan and Aaron, 2014). Instead, ECO process can also benefits on the prevention and remediation of pollution issues since the electron is a clean reagent (Panizza and Cerisola, 2009). In ECO treatments, the organic pollutants can be removed by: (i) direct anodic oxidation (or direct electron
transfer between anode surface and pollutants), which usually yields relatively poor oxidation rates, and (ii) chemical reaction with electrogenerated reactive oxygen species at anode surface such as physisorbed or chemisorbed \( ^\cdot \text{OH} \) radicals, which leads to total or partial oxidation of pollutants, respectively (Martínez-Huitl and Brillas, 2009; Panizza and Cerisola, 2009).

In direct anodic oxidation, pollutants are oxidized at anode surface after adsorption solely due to the electron, without the involvement of any other substances. In this process, oxygen is transferred from water to the organic pollutant via electrical energy, which is called electrochemical oxygen transfer reaction as described by equation (6) (Panizza and Cerisola, 2009):

\[
R_{\text{ads}} - ne^- \rightarrow P_{\text{ads}} \tag{6}
\]

where, \( R_{\text{ads}} \) and \( P_{\text{ads}} \) are adsorbed and oxidized adsorbed organic pollutants at anode surface. Direct electro-oxidation can be possible at low potentials, but usually possesses low kinetics, depending on the electrocatalytic activity of anode materials. The use of low cell potentials avoiding oxygen evolution could frequently cause the loss of anodic activity. This is called poisoning effect and occurs due to the formation of polymer layer on the anode surface, which has limited their application in wastewater treatment practices (Martínez-Huitl and Brillas, 2009). The anode surface deactivation depends on, (i) adsorption properties of the anode surface, and (ii) nature and concentration of organic pollutants and their transformation products (Panizza and Cerisola, 2009).

On the other hand, electrochemical oxidation of organic pollutants can be obtained without the poisoning effect by electrolyzing the aqueous solution at high anodic voltages with the involvement of oxygen evolution reactions (OERs), which generates in situ \( ^\cdot \text{OH} \) radicals with no oxidation catalysts. A number of anodes favored partial and selective oxidation of organic pollutants (i.e., conversion method), whereas many others favored complete mineralization (i.e., combustion/incineration) to \( \text{CO}_2 \) (Brillas and Martínez-Huitl, 2015; Panizza and Cerisola, 2009). Comninellis found that the nature of anode material strongly affects both the selectivity and efficiency of the ECO process, and proposed a comprehensive model of organics oxidation in acidic medium including the competition with \( \text{O}_2 \) evolution reaction and heterogeneous \( ^\cdot \text{OH} \) radicals (Figure 4) (Comninellis, 1994). The model assumes that in the initial step of oxygen transfer reaction, water molecules split to form adsorbed \( ^\cdot \text{OH} \) radicals at anode oxide surface (MO₅) as equation (7):

\[
\text{MO}_x + \text{H}_2\text{O} \rightarrow \text{MO}_x (^\cdot \text{OH}) + \text{H}^+ + e^- \tag{7}
\]
Figure 4: Electrochemical oxidation scheme of organic pollutants on the metal oxide anode surface (Modified from (Comninellis, 1994)).

Then, the different behaviors of anodes in ECO process was described by considering two limiting cases of electrodes, defined as ‘active’ and ‘non-active’ anodes in the schematic model.

4.1.1 Active anodes

At active anodes, with low O$_2$-overpotentials (such as IrO$_2$, RuO$_2$, and Pt) (Martínez-Huitle and Brillas, 2009), a strong interaction occurs between the anode surface (MO$_x$) and ‘OH radicals (i.e., chemisorbed active oxygen in the lattice of metal oxide). The chemisorbed ‘OH radicals may interact with anode, forming so-called higher oxide (equation (8)). The surface redox couple MO$_{x+1}$/MO$_x$ can act as a mediator in the conversion of selective oxidation of organics (R with $m$ carbon atom and without heteroatoms) into short-chain carboxylic acids (equation (9)). Moreover, O$_2$ evolution as side reaction due to chemical decomposition of higher oxides is also involved in this reaction (equation (10))(Martínez-Huitle and Ferro, 2006; Panizza and Cerisola, 2009):

\[
\text{MO}_x(\cdot\text{OH}) \rightarrow \text{MO}_{x+1} + \text{H}^+ + \text{e}^-
\]  

(8)

\[
\text{MO}_{x+1} + R \rightarrow \text{MO}_x + \text{RO}
\]  

(9)
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\[
\alpha \text{MO}_x (\cdot \text{OH}) + \text{R} \rightarrow \alpha \text{MO}_x + \alpha \text{mCO}_2 + \alpha n\text{H}_2\text{O} + \alpha z\text{H}^+ + \alpha ze^- \quad (11)
\]

where, organic compound R needs \( \alpha = (2m+n) \) oxygen atoms for complete mineralization to \( \text{CO}_2 \). The oxidative reaction (9) is much more selective than mineralization reaction (6). Like in active anode behavior, reaction (11) also undergoes competitive side reaction, i.e. \( \text{O}_2 \) evolution reaction, resulting in decreased anodic oxidation performance, either direct oxidation to \( \text{O}_2 \) (equation (12)) or indirect consumption via dimerization to hydrogen peroxide (equation (13)).

\[
\text{MO}_x (\cdot \text{OH}) \rightarrow \text{MO}_x + (1/2) \text{O}_2 + \text{H}^+ + \text{e}^- \quad (12)
\]

\[
2 \text{MO}_x (\cdot \text{OH}) \rightarrow 2 \text{MO}_x + \text{H}_2\text{O}_2 \quad (13)
\]

According to the mechanisms, anodes with low \( \text{O}_2 \)-overpotentials (active anodes) (good catalysts for \( \text{O}_2 \) evolution) allow only partial oxidation of organics, whereas anodes with high \( \text{O}_2 \)-overpotentials (non-active) (poor catalysts for \( \text{O}_2 \) evolution) favor complete oxidation of organics to \( \text{CO}_2 \) (Panizza and Cerisola, 2009). Therefore, non-active anodes are ideal for wastewater purification. Nevertheless, since both organic oxidation and \( \text{O}_2 \) evolution reactions compete parallel, many anodes exhibit diverse behavior in practices (Nidheesh et al., 2018).

It is well confirmed that the type of anode material is the most important factor for determining the extent of organic pollutants degradation in ECO processes (Comninellis and Vercesi, 1991). There are wide variety of anode materials including doped and undoped \( \text{PbO}_2 \), mixed metal oxides of \( \text{Ti}, \text{Ru}, \text{Ir}, \text{Sn} \) and \( \text{Sb}, \text{Ti/Pt}, \text{carbon based anodes} \), and boron-doped diamond (BDD) thin films anodes (Brillas and Martínez-Huitle, 2015). The \( \text{PbO}_2 \) and BDD anodes, with high \( \text{O}_2 \)-overpotential, are the most commonly used anodes for the electrochemical degradation of organic pollutants. The \( \text{PbO}_2 \) anodes are inexpensive, easy to prepare, chemically stable, low electrical stability, and a large surface area (Martínez-Huitle and Brillas, 2009). Likewise, BDD anodes are made by depositing a thin diamond films on non-diamond materials, usually silicon, tungsten,
titanium, tantalum, or glassy carbon, by energy-assisted chemical vapor deposition. BDD anodes are very promising anode material for the electrochemical treatment of wastewater contaminated with organic pollutants. They exhibit a great chemical and electrochemical stability, a wide electrochemical working range (HER at -1.25 V vs SHE and OER at +2.3 V vs SHE), high inert surface with low adsorption, and a great mineralization efficiency compared to other anodes (Oturan and Aaron, 2014; Panizza and Cerisola, 2009). The behavior of PbO2 and BDD anodes during the electrooxidation of organic pollutant is well confirmed by Panizza and Cerisola (Panizza and Cerisola, 2009). Nevertheless, despite of the high O2-overpotential, PbO2 anodes show low durability by surface corrosion and leaching of highly toxic Pb2+ ions into to treated water (Brillas and Martínez-Huitle, 2015). Similarly, the major drawbacks of BDD anodes includes high material cost and difficulties in finding an appropriate substrate for thin diamond layer deposition (Panizza and Cerisola, 2009), which tend to compromise their applicability in large-scale applications.

Alternatively, MMO electrodes include a broad range of materials able to adsorb oxygen on their structure and more suitable for anodic oxidation of organic pollutants. Dimensionally stable anodes (DSA), are the commercial terms for MMO electrodes, due to their excellent ECO properties and structural integrity (Shestakova, 2016). DSAs usually constitutes a Ti substrates deposited by a thin semiconducting layer of metal oxide or mixed metal oxides, such as Ti/TiO2-RuO2, Ti/Ta2O5-IrO2, Ti/IrO2-RuO2, Ti/SnO2-Sb2O5, and Ti/Ir0.45O2-Ta2O5 (Brillas and Martínez-Huitle, 2015; Shestakova, 2016).

4.2 Photocatalytic oxidation (PCO)

Among other AOPs, heterogeneous photocatalysis is also a well-proven, efficient, and eco-friendly method for attenuating ambient concentrations of organic contaminants in aqueous or gas (air) phase (Guillard et al., 1999). Heterogeneous photocatalysis ascribes to the speeding of photoreaction in the presence of semiconductor catalyst and the light source. The major advantage of heterogeneous catalysis is the partial photocatalytic oxidation at beginning or complete mineralization of organic pollutants essentially to benign substances (Gaya and Abdullah, 2008). In early 70’s, Fujishima and Honda first unfolded the possibility of water splitting using titania (TiO2) photocatalyst in a photo-electrochemical solar cell, referred to as the “Honda-Fujishima effect” (Fujishima and Honda, 1972). Subsequently, the heterogeneous photocatalysis by titania photocatalyst became environmental frontiers (Gaya and Abdullah, 2008; Oturan and Aaron, 2014).

In heterogeneous photocatalysis process, organic pollutants are decontaminated in the presence of semiconductor photocatalysts, a light energy source, and reactive oxidizing species. When the irradiated photon energy is greater than the band gap energy (ΔE) of the semiconductor, electrons are excited to the conductance band (eCB) and positive holes is generated on the valence band (hVB) site vacated by electrons and electron-hole pairs (eCB/hVB) are formed (Joo et al., 2019). This chemistry of photo-generated electron-hole
pairs could form reactive oxidants such as $\cdot$OH radicals, and superoxide ($\cdot$O$_2^-$) radicals and adsorbed onto the semiconductor surface, and consequently organic pollutants are then non-selectively oxidized by both photo-generated holes and reactive oxidant species (Dong et al., 2015). However, the absorption of photons with lower energy than $\Delta E$ or shorter wavelengths causes energy loss in the forms of heat due to rapid recombination of charge carriers i.e., $e_\text{cb}/h_\text{vb}$' (Ahmed et al., 2011; Cavalcante et al., 2015). On this note, TiO$_2$ ($\Delta E = 3.2$ eV) assisted heterogeneous photocatalysis has been widely applied in recent years for photocatalytic oxidation of refractory organic pollutants present in wastewater. TiO$_2$ is easy to produce, inexpensive, chemically and biologically stable, and has an energy gap comparable to that of solar photons (Oturan and Aaron, 2014). The activation of TiO$_2$ by UV light irradiation and the photocatalytic degradation mechanism of organic pollutant can be represented by the following equations (14)-(17) (Ahmed et al., 2011):

$$\text{TiO}_2 \rightarrow e^- + h^+ \quad (14)$$

$$e^- + O_2 \rightarrow \cdot O_2^- \quad (15)$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (16)$$

$$h^+ / \cdot OH / \cdot O_2^- + R \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{inorganic ions} \quad (17)$$

In heterogeneous photocatalysis, TiO$_2$ catalyst can be utilized either as aqueous suspension or in thin film form (Murgolo et al., 2017). The dispersed TiO$_2$ form is easy to use, provide great surface area, and aerated suspensions prevents the recombining of $e_\text{cb}/h_\text{vb}$ to some extent, despite progressive formation of dark catalytic sludge could diminishes the efficiency of UV intensity. Contrarily, TiO$_2$ thin films do not need to separate the catalytic particles for reusability, but the catalytic layer should be very stable and active (Oturan and Aaron, 2014). There are a number of studies performed on heterogeneous UV/TiO$_2$ photocatalysis of many emerging contaminants (Benotti et al., 2009; De la Cruz et al., 2013; Doll and Frimmel, 2004; Ghaly et al., 2011; Hapeshi et al., 2010; Kanakaraju et al., 2014; Rizzo et al., 2009; Xue et al., 2011).

However, like other AOPs, major drawbacks associated with TiO$_2$-based heterogeneous photocatalysis, includes low quantum efficiency, low adsorption capacity for hydrophobic pollutants, post-recovery TiO$_2$ particles, and catalysts deactivation (Ahmed et al., 2011). To overcome these shortcomings, various countermeasures have been studied in order to enhance photocatalytic efficiency, complete destruction of organic pollutants, improve light adsorption range, increase stability and reproducibility, and to improve recycle and reuse capabilities of TiO$_2$ catalyst (Dong et al., 2015). Over the past few decades, transition metals (e.g., Fe, Ni, Cr, Ag, Au) or their oxides doped TiO$_2$ photocatalysts have been studied for enhancing the removal efficiency of various organic pollutants (Anpo, 2000; Ren et al., 2015; Khan et al., 2016; Chen et al., 2015; Zhou et al.,...
TiO$_2$ nanoparticles are modified by simply substitution reaction or intrinsic doping with different metal cations, which can then form metal oxides or a mixture of oxides. The transition metals doping improves trapping of excited electrons that inhibits rapid recombination of $e_{cb} / h_{vb}^+$. Therefore, metal nanoparticles act as an electron traps in storing and shuttling photogenerated electrons from the TiO$_2$ surface (Dong et al., 2015). In that context, Ag$_2$O with narrow energy band gap of 1.2 eV (Xu and Schoonen, 2000), which is a proven photocatalyst for organic pollutant degradation, can be doped on TiO$_2$ nanoparticles for increasing surface area, well-defined crystal structure and homogeneity in particles size for enhanced photocatalytic effect (Wang et al., 2011). Enhanced efficiency of dye removal via the heterogeneous photocatalysis using Ag$_2$O doped TiO$_2$ photocatalysts has been confirmed in many previous studies (Ren and Yang, 2017; Zhou et al., 2010).
4 Advanced oxidation processes for wastewater treatment
5 Integration potentials of MBR with AOPs

MBRs are established as environmental-friendly approaches for municipal wastewater treatment. However, the removal efficiency of many biologically persistent and hydrophilic ECs with biological treatment alone is not effective (Fatta-Kassinos et al., 2016). Moreover, although some MBRs can treat wastewater to meet the current guidelines and producing water for basic industrial reuses, the treated effluent still needs to be further decontaminated for high grade applications. Generally, single classical treatment techniques have been inadequate for the removal of persistent ECs, therefore it is necessary to integrate MBR with other green advanced treatment processes, such as AOPs, high retention membranes, MBBR, and granulation technology. Since usually MBR effluent is of high quality (i.e., low level of suspended solids and turbidity), MBRs offer great technical flexibility to be integrated with other technologies, and significant synergy can be achieved.

Of the many integration potentials, coupling MBR process with different AOPs have achieved a great deal of attention over the last decade. The ‘multi barrier approach’ integration of MBR with AOPs aims to enhance the quality of effluent, mitigate the fouling and to robust the process stability (Neoh et al., 2016). As a multi barrier approach, it is evidenced that the integrated approach can offer the recycling of oxidation products back to the biological system for further biodegradation (Laera et al., 2011). The general integration strategy of wastewater treatment using biological treatment and AOP can be illustrated by Figure 5. If the wastewater stream contains higher ECs load, then integration of AOP is beneficial as ‘pre-treatment’ of ECs, which converts recalcitrant ECs to more biodegradable and subsequently treated in MBR with high biodegradation efficiency. Whereas, integration of AOP as polishing step to MBR process could further improve the removal of residual fractions of ECs after MBR treatment. The integration approach not only benefits the synergy in the treatment performance, but also trade-off the shortcomings/ challenges of one another (Ganiyu et al., 2015).
Figure 5: Decision tree for potential integration approaches of MBR and AOP (Modified from (López et al., 2010)).

García-Gómez et al. showed an enhanced removal of carbamazepine in synthetic wastewater from about 6.5% to 99.99% (complete removal) when MBR system was coupled with ECO process using Ti/PbO2 anode (García-Gómez et al., 2016). While MBR was integrated with ozonation in the recirculation stream of the MBR effluent, residual concentration of anti-viral drug (acyclovir) in the MBR effluent was further removed by 99%. The major benefit of this integrated system was evident for the removal of specific ozonation transformation products of acyclovir, which was about 20-fold higher than MBR alone (Mascolo et al., 2010). Likewise, Pollice et al. reported the complete degradation of antibacterial (nalidixic acid) when treated with integrated MBR-ozonation process (Pollice et al., 2012). López et al. demonstrated that the integration of
MBR with solar photo-Fenton oxidation process could effectively treat wastewater polluted with pesticides, by enhancing biodegradability and lessening ecotoxicity of the treated effluent (López et al., 2010). A laboratory scale MBR system combined with nanofiltration or reverse osmosis membrane filtration by Alturki et al. reported more than 95% removal of 40 trace organic compounds (Alturki et al., 2010). More than 95% of carbamazepine removal efficiency was observed by Laera et al. when MBR was integrated with a lab-scale heterogeneous TiO$_2$-based annular slurry photoreactor (Laera et al., 2011).

The literature survey indicates that there have been very few studies acquired on the possibility of integrating MBR with AOPs to enhance the removal of ECs. Other than AOPs, physical treatment processes (e.g., nanofiltration and reverse osmosis) could possibly enhance the removal of persistent ECs, but ultimately ends-up in the concentrates or sludge, which may need to be treated further. Moreover, most of the NF or RO processes attenuate ECs based on their respective MWCO. On the other hand, AOPs such as ECO and PCO are eco-friendly processes that non-selectively degrade/combust highly persistent ECs via hydroxylation or dihydroxylation till their total mineralization or until they converted into non-toxic and biodegradable short-chained molecules (Ganiyu et al., 2015).
5 Integration potentials of MBR with AOPs
6 Materials and methods

6.2 Assessing the performance of MBR unit in different operating conditions

6.1.1 The Pilot-scale MBR set-up

A pilot scale submerged MBR unit (ARTAS Ltd. Turkey) was installed at full-scale Kenkäveronniemi WWTP, Mikkeli, Finland as depicted in Figure 6. The full-scale plant treats about 5 Million cubic meter of wastewater per year, majorly of municipal sewage with the influent load of about 63000 population equivalent. The treated wastewater is discharged into the Saimaa Lake, which is the largest in Finland and fourth largest freshwater lake in Europe.

The submerged flat-sheet membrane units (0.4 µm pore size), made of chlorinated polyethylene polymers, with total surface area of 16 m² (KUBOTA corporation, Japan), were used for the solid-liquid separation. The in-situ membrane fouling was controlled physically by providing crossflow scouring air via compressed air and adopting intermittent suction cycle for filtration. The clean-in-place (CIP) tank was connected with sodium hypochlorite (NaOCl) and Citric acid dosing tanks for the cleaning of membranes during fouling occasions. The pilot MBR was operated under different operating conditions depending on the purpose of studies (Paper I, II, III and IV) as described in Table 2.

![Figure 6: Schematic diagram of the pilot MBR unit at Kenkäveronniemi WWTP, Mikkeli, Finland.](image-url)
6 Materials and methods

Table 3. Different operating conditions of the MBR pilot plant depending on purpose of studies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Paper I</td>
</tr>
<tr>
<td>HRT</td>
<td>Hours</td>
<td>35</td>
</tr>
<tr>
<td>SRT</td>
<td>Days</td>
<td>25 - 30</td>
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<td>Avg. Flux</td>
<td>L m$^2$ h$^{-1}$</td>
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<tr>
<td>MLSS concentration</td>
<td>mg L$^{-1}$</td>
<td>5300 - 9800</td>
</tr>
<tr>
<td>F/M ratio</td>
<td>kg COD (kg MLSS. d$^{-1}$)</td>
<td>0.02 – 0.05</td>
</tr>
<tr>
<td>Aeration intensity (SAD$_{m}$)</td>
<td>m$^3$ m$^{-2}$ h$^{-1}$</td>
<td>0.4 – 0.6</td>
</tr>
<tr>
<td>Process temperature</td>
<td>°C</td>
<td>6.5 - 21</td>
</tr>
<tr>
<td>pH</td>
<td>Unitless</td>
<td>6.6 – 7.3</td>
</tr>
<tr>
<td>Suction cycle</td>
<td>Minutes</td>
<td>9-On/1-Off</td>
</tr>
</tbody>
</table>

6.2 Assessing integration approaches to MBR

For further polishing the treated effluent from the MBR treatment, two widely used AOPs, i.e., ECO and PCO processes were assessed for the removal of highly recalcitrant ECs, including carbamazepine and diclofenac, as model compounds. These AOP units were performed as ‘post-treatment’ to the residual concentrations of ECs from the MBR treated effluent.

6.2.1 Lab-scale set-up for batch ECO unit

The lab-scale set-up used for the electrochemical oxidation system is as shown in Figure 7. The experiment was carried out in a glass reactor with cooling jacket arrangement. The external electrical power was applied by using DC power supply. The inter-electrode gap of 10 mm was maintained between both anode and cathode electrodes. The aqueous solutions containing carbamazepine were electrolyzed under different operating conditions and its attenuation in the concentration was analyzed using UV-vis.
spectrophotometer. The newly developed Ti/Ta$_2$O$_5$-SnO$_2$ electrodes were synthesized by thermal decomposition method using precursor solution of tantalum (Ta) and tin (Sn) salts on titanium (Ti) plates. The as-prepared electrodes were then characterized for their microstructure, chemical analysis, and cyclic voltammetry (CV).

Figure 7: Experimental set-up for electrochemical oxidation.

6.2.2 Lab-scale set-up for PCO process

The photocatalytic experimental set-up using a self-made photocatalytic reactor is shown in Figure 8. The photocatalytic degradation of ECs (carbamazepine and diclofenac) in aqueous solutions (both in deionized water and real MBR effluent) was performed using 5% (w/w) Ag$_2$O/P-25 photocatalysts under UV irradiation. The sample aliquots of ECs were analyzed by using UV-vis spectrophotometer. The 5% (w/w) Ag$_2$O/P-25 photocatalysts were prepared by a simple pH-mediated chemical precipitation method and characterized for microstructure, morphology, elemental analysis, surface area, and energy band gap using different characterization instruments.
6.2.3 Analytical procedures

The common pollutants in wastewater, such as TSS, COD, NH$_4$-N and TP contained in influent and effluent of the MBR process, as well as MLSS and MLVSS concentrations were analyzed according to the Standard Methods (APHA, 1999) (Paper I-IV).

For human enteric viruses, including Adv and NoV (GI and GII) from liquid samples, pre-treated 500 mL samples (influent and effluent) were concentrated by two-phase separation method and viral nuclei acids were extracted using the High Pure Viral Nucleic Acid and High Pure Viral RNA Kit. For sludge samples, 500 mL of sample was centrifuged to 10 min at 1000g at 4°C. The supernatant was concentrated by two-phase separation process. For the solid fractions, 50 g of sludge pellet was mixed with 50 mL of 3% beef extract (pH 9.5) for 30 min at reverse transcriptase (RT) to elute viruses. After centrifugation for 20 min at 5000g at 4°C, the supernatant was recovered and adjusted to a pH 7.2. The supernatant samples were then mixed with polyethylene glycol 6000 (PEG 6000) and NaCl, and further rocked overnight at 4°C. After centrifugation for 30 min at 10000g, supernatant was discarded, and the PEG pellet was collected for nucleic acid extraction (U.S. EPA, 2003). The detection of Advs was carried out by performing the
real-time RT-PCR assays in a Rotor-GeneTM 3000 real-time rotary analyzer, whereas the real-time RT-PCR assays were carried out in one step for the detection of both NoVs using the QuantiTect Probe RT-PCR Kit. The possible effect of inhibitors in wastewater samples were assumed to be constant throughout the experimental period (Paper I). On the other hand, total number of bacteria indicators, such as E.coli and Enterococcus in the influent, sludge and permeate were enumerated using Colilert ® and Enterolert ® methods (Paper I).

For heavy metals analysis, liquid influent and effluent samples were acidified (pH<2) with HNO₃ acid, centrifuged at 4000 rpm for 20 min, and then supernatant was filtered with 0.20 µm cellulose syringe filters. The sludge samples were dried in oven at 105°C. About 0.5 g of dried sludge in 10 mL HNO₃: HCl (1:3) mixture was digested in a microwave digester. Finally, heavy metals were analyzed using inductively coupled plasma-optical emission spectrometer (ICP-OES, iCAP 6300, Thermo Electron Corporation, USA) from the pretreated samples (Fontmorin and Sillanpää, 2015) (Paper I & III).

The occurrence of diverse ECs from aqueous samples (influent and effluent) and solid samples (sludge) of the MBR treatment was carried out by standard solid phase extraction (SPE) followed by LC-MS/MS analysis (U.S. EPA, 2007) (Paper I & II). For SPE, typically, about 100 mL of effluent or 50 mL of influent or sludge samples were spiked with the mass-labelled surrogates, for example 13C-carbamazepine, 13C-bisphenol A, 2H-diclofenac, and so on. Additionally, mixing, ultrasonic extraction and centrifugation were repeatedly employed for sludge samples. The spiked samples were extracted, conditioned with the mixture of 20 mL methanol and 20 mL deionized water, washed with 10 mL of 5% methanol and eluted with 15 mL of methanol. The mixture was then evaporated to dryness under nitrogen flow and 0.5 mL of methanol and 0.5 mL of deionized water were added. The aliquots were then analyzed using LC-MS/MS (Waters Acquity UPLC and Xevo TQ, USA). The recovery correction during the calculation was made with respect to the mass-labelled surrogates. The measurement uncertainty (MU) was about 40%. The MU % was calculated according to the Nordest TR 537 that covered every step in the laboratory analysis. Moreover, the residual concentrations of ECs, such as carbamazepine and diclofenac were analyzed by UV-vis spectrophotometer (Lambda 45, USA) (Paper III & IV). The photocatalytically induced intermediates of carbamazepine were identified and quantified by using Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry (Bruker Daltonics, Germany) (Paper IV).

The fouling precursors, such as EPS and SMP from sludge were determined by centrifuging 25 mL of sludge samples at 4000 rpm at 4 °C for 30 min. The supernatant was filtered through a 0.45 µm glass filter and measured for SMP. The obtained pallets were resuspended by adding 0.05% NaCl, rapidly mixed with vortex mixture and the solution was kept in a water bath (~100 °C) for heat treatment for 60 min. Finally, the supernatant was filtered through a 0.45 µm glass filter and measured for total EPS. Both
SMP and EPS were analyzed using a TOC analyzer (TOC-V Series-CPN, Shimadzu, Japan) and expressed as mg of DOC g\(^{-1}\) MLVSS (Paper II).
7 Results and discussion

7.1 Assessing the performance of MBR at Nordic cold conditions (Paper I)

In order to investigate the performance of MBR at Nordic cold conditions, the MBR pilot unit was operated for more than 120 days in winter season of Finland (January to April 2016). This is the first comprehensive study on the performance of pilot MBR on treating the real municipal wastewater in the unique Nordic environment. The wastewater temperature inside the bioreactor varied from 7 to 20 °C. On this occasion, the effect of low sludge temperatures on membrane fouling was evaluated by monitoring TMP and deterioration of sludge settleability was measured by monitoring SVI. Moreover, the performance of MBR on removing organic, solids and nutrients loads in the incoming wastewater, reduction of common enteric viruses, and most importantly the attenuation of ECs, such as PhACs, EDCs and some toxic heavy metals, were assessed. The membrane fouling tendency under cold water conditions and adopted cleaning methods and frequencies are depicted in Figure 9.

While operating MBR in cold-water conditions, many consequences related to the process operation were observed. During the experimental period, the ambient air temperature was recorded, which was fluctuated between 0 and -33 °C for more than a week, which is very typical in winter seasons of Nordic regions. With the decreasing sludge temperature inside the bioreactor, increasing trend of TMP profile was observed (Figure 9). Two distinct stages of membrane fouling, which is well known tendency in MBRs (Park et al., 2015), such as slow and steady fouling and rapid (jump) fouling, were clearly observed. While the sludge temperature was recorded below 10 °C, two consecutive chemical cleanings for fouled membranes were adapted to reduce very frequent jumping of TMPs within a week. However, the cleaning cycle was extended to about two weeks when sludge temperature raised more than 10 °C. It was also noticed that other than cold water temperature, changing in the specific aeration demand per membrane surface area (SADm) could effect on membrane fouling behavior to some extent. The permeability of the membranes was dropped from about 345 L m⁻² bar⁻¹ to nearly 50 L m⁻² bar⁻¹ while temperature decreased from 20.5 ± 0.6 °C to below 10°C. About 75% of permeability drop was observed during the lowest sludge temperature period. After the final manual cleaning, the permeability was restored gradually and reached nearly to 300 L m⁻² bar⁻¹.

The results indicated that the cold-water conditions can deteriorate the hydraulic performance of MBR due to accelerated membrane fouling propensities. The sludge settleability was also highly deteriorated, as indicated by the SVI values being increased from 120 to 168 mL g⁻¹, during the coldest temperature events observed inside the bioreactor. On the other hand, despite of low temperature operation, relatively high quality of treated effluent was observed with the corresponding removal efficiencies of 100%, 92.8%, >99.8%, and 90.6% for TSS, COD, NH₄-N, and TP respectively.
Regarding the fate of human enteric viruses, such as Noroviruses (NoV GI and NoV GII) and adenovirus (AdVs), all three viruses were constantly detected in the influent samples during the experimental period as shown in Figure 10. NoV GI was detected in 85% of the influent samples with an average concentration of 95 GC mL$^{-1}$, whereas NoV GII and AdVs were positively detected in 100% with corresponding average concentrations of 896 and 124 GC mL$^{-1}$, respectively. The average log removal of 1.82, 3.02 and 1.94 log units were achieved during MBR treatment for NoV GI, NoV GII and AdVs, respectively. It was further confirmed that the virus removal efficiency was not correlated with the degree of membrane fouling. Moreover, none of the concentration of *Escherichia coli* and enterococci were detected in the MBR permeate over the experimental period, showing excellent retaining of these bacteria.
Similarly, the occurrences and removal efficiencies of four ECs, including PhACs, such as carbamazepine, bisoprolol, diclofenac, and EDC, i.e., bisphenol A, in the MBR treatment under cold weather conditions were investigated. All the selected ECs were frequently identified in the influent wastewater samples, but the relatively higher concentrations were observed from January up to the end of March, ascribing the high specific consumption of these ECs during cold season. The mean influent concentrations of carbamazepine, bisoprolol, diclofenac, and bisphenol A were 0.63, 1.84, 0.43 and 0.95 μg L$^{-1}$, respectively, where diclofenac was highly detected amongst other refractory compounds in cold season. In this study, the removal efficiency of individual ECs varied greatly under MBR treatment. The average removal efficiencies of bisoprolol and diclofenac were 65 ± 6% and 38 ± 7%, respectively (Figure 11). A decreasing trend in the removal rates of bisoprolol and diclofenac was observed from Jan-Feb to April, which might be partially due to the very low sludge temperature inside the bioreactor that might have affected the biodegradability of the ECs. Despite the low temperature MBR operation, the bisphenol A removal efficiency was substantially stable (> 97%) throughout the experimental period, which might be due to its high hydrophobicity that enhanced its adsorption to biomass and consequently biotransformed. On the other hand,
very poor removal efficiency of carbamazepine ranging from -89 to 28% (only for one occasion) was observed with highest negative removal efficiency during January to February (Figure 11).

On the other hand, inorganic micropollutants i.e. heavy metals including Zn, Ni, Co, Cu, As, Pb, Cd, and V, were also consistently detected in influent, permeate and sludge samples over the experimental period. The average concentration of trace metals in the incoming wastewater was found in the range of 0.1 to 80 µg L$^{-1}$, with their relative abundance in the order of Zn$>$ Ni $>$ Co $>$ Cu $>$ V $>$ Cr $>$ As $>$ Pb $>$ Cd. However, the removal efficiencies of the trace metals greatly varied from element to element in the MBR treatment. An average removal efficiency of $\geq 80\%$ was achieved for Cd, Pb, and V, while $\geq 60\%$ was observed for Zn and Co. Whereas, comparatively lower removal efficiencies (30 - 50%) were observed for Ni, Cu, As, and Cr under the identical operating conditions. In this study, chemical precipitation and biosorption mechanisms were expected to be dominant for the removal of trace metals in the MBR process. Moreover, metal complexation via metal-ligand co-ordinate bonding and the biofilm layer developed on the membrane surface could have contributed to the retention/adsorption of insoluble metal species to some extent other than solubility and stable or unstable forms of trace metals in the MBR treatment (Bolzonella et al., 2010).
Since trace metals are non-biodegradables, their incoming load in MBR process can either end up into the sludge or remains in the treated effluent. Therefore, it is crucial to assess the concentration of trace metals in both treated effluent and produced sludge, especially when they have some specific utilization. In this study, relatively abundant concentrations of trace metals were observed in MBR effluent and sludge samples, although their concentrations were observed below the allowable concentrations limit specified in the EU and US regulations.

### 7.2 Assessing the performance of MBR under varying solid retention times- fate and removal of ECs (Paper II)

Two different SRTs: 60 days and 21 days, were selected to mainly study the removal efficiency of 23 ECs, including PhACs (antibiotics, β-blockers, analgesics, diuretics, psychostimulants, antiepileptics, immunosuppressives, anticoagulants) and steroid hormones (testosterone, progesterone, estrone, and estroil), commonly detected in municipal wastewater. Overall, a consistently high removal efficiencies of conventional wastewater pollutants such as TSS, COD, NH$_4$-N, and TP were observed at both SRTs. Majority of ECs detected in influent wastewater during the testing SRT periods of 60 and 21 days revealed similar tendencies. Of the 23 ECs, compounds such as iopamidol, furosemide, caffeine, hydrochlorothiazide, paracetamol, naproxen, ibuprofen and diclofenac were detected in high levels, thus accounted for more than 50% of the total ECs. On the other hand, steroid hormones were observed at relatively low levels as compared to other PhACs.

The removal of selected ECs varied greatly during the MBR treatment process under the maintained operating conditions. However, the concentrations of many ECs in the treated effluent were below the limit of quantification (LOQ), which indicates their efficient removal under MBR treatment regardless of SRT variations. In this study, 17 ECs, including 13 PhACs (iopamidol, atenolol, tetracycline, caffeine, bisoprolol, ciprofloxacin, enalapril, ketoprofen, trimethoprim, paracetamol, naproxen, ibuprofen, and hydrocortisone) and four steroid hormones (estriol, testosterone, estrone, progesterone) showed the median removal efficiency of more than 90% (90 to ≥ 99.7%). Three PhACs including metoprolol, furosemide and propranolol showed median removal efficiencies in the range of 50 – 87%, diclofenac showed poor removal of 39 – 46%, and two PhACs (carbamazepine and hydrochlorothiazide) were very poorly removed (-8 to 10%). The fate of anti-coagulant (iopamidol) and immunosuppressive (hydrocortisone) was studied for the first time in the MBR treatment. Out of four β-blockers, the removal rates of metoprolol and propranolol were slightly higher at longer SRT of 60 days (82 - 84%) than in shorter SRT of 21 days (50 - 60%). Even though the attenuation of hydrochlorothiazide was very low, its median removal efficiency improved from -1 % at SRT of 21 days to 10% at SRT of 60 days. Similarly, the median removal efficiency of carbamazepine enhanced to 2% from - 8% while SRT varied from 21 to 60 days. In most of the occasions, concentrations of hydrochlorothiazide and carbamazepine in the treated
Results and discussion

effluent were higher than in the influent, therefore showing negative removal efficiency. The major reason for the phenomenon of ‘negative removal’ was ascribed to the transformation of metabolites, such as glucuronide-conjugates back to the parent compounds during the biological process, and eventually released with higher concentrations in the treated effluent (Jelic et al., 2011).

Furthermore, to understand the pathway of ECs removal, mass-balance study was carried out as described by equations (2)-(5). The shared proportions of ECs relative to the influent load based on biotransformation, sorption onto sludge and remained in the treated effluent are elucidated in Figure 12. The dominant mechanism for ECs removal was presumably via biosorption and biotransformation. The ECs, including atenolol, caffeine, paracetamol, naproxen, ibuprofen, esteriol and progesterone were removed significantly with biotransformation rate of 83 to ≥ 99.9%. High biotransformation rate of 58 - 92% was assigned for iopamidol, furosemide and trimethoprim. Slightly enhanced biotransformation of metoprolol, hydrochlorothiazide and propranolol was observed at SRT of 60 days than at SRT of 21 days. On the other hand, some of the ECs were found to have been removed via sorption onto the biomass (sludge). More than 90% removal rate was accounted for ciprofloxacin, which could pose serious risk if the excess sludge has multiple utilization. Some other ECs, such as propranolol, carbamazepine and testosterone, showed about 10 - 50% sorption efficiency, whereas most of the ECs posed a very weak sorption affinity to the biomass with the sorption efficiency ranging from 0 - 21%. The physicochemical properties of individual ECs, such as hydrophobicity (hydrophilic or hydrophobic, characterized by log D values), degree of ionization (pKa), sorption coefficient (log Kd), could have additionally influenced their removal in MBR treatment (Cirja et al., 2008b).

The calculated values of log Kd revealed that the selected ECs in MBR treatment were removed either predominantly via sorption process or via simultaneous biodegradation followed by partitioning onto sludge (Guerra et al., 2014). However, it was observed that the calculated sorption coefficients were not correlated with the degree of biotransformation for many ECs, which indicates that log Kd values of ECs may vary plant-to-plant depending on different operating conditions (Kim et al., 2014). Furthermore, noticeable changes in the concentrations of biopolymers such as SMP and EPS were observed while changing the SRTs. The SMP concentration increased from 5.6 to 15.5 mg (g MLVSS)^-1 (about 3 times) and EPS concentration increased from 51 to 103 mg (g MLVSS)^-1 while SRT changed from 60 to 21 days, respectively. Similarly, it was revealed that the dewaterability (measured in terms of CST) of the MBR sludge correlates well with the SRT values. The sludge with high CST values possesses difficulty in dewatering due to the presence of more cell bound water.
7.3 Assessing the AOPs as integration alternatives to MBR to enhance the removal of ECs.

It was clear from the above studies that the removal of many ECs was not optimal although they meet most of the recent limit standards. This indicates that the MBR treatment itself is not the ultimate solution to remediate those highly recalcitrant ECs, which advocates the need of highly efficient techniques to meet the future discharge limits. In recent years, developing a more robust treatment processes to ensure high quality reclaimed effluent from municipal wastewater, especially with the focus on the removal of ECs has gained increasing interests. In this context, we studied the potential integration options of two AOP based green technologies: ECO and PCO processes, to further enhance the removal of ECs from MBR effluent.
7 Results and discussion

7.3.1 Study of ECO process for carbamazepine removal using Ti/Ta₂O₅-SnO₂ electrode (Paper III)

In this study, for the first time, the removal efficiency of one of the highly recalcitrant PhACs, carbamazepine, in synthetic solutions and the real MBR effluent was assessed via ECO process using newly developed Ti/Ta₂O₅-SnO₂ electrode. The characterization of Ti/Ta₂O₅-SnO₂ electrode revealed that the electrocatalytic activity was enhanced due to doped metallic impurities on the Ti substrate, roughness factor of 12.5 as compared to smooth surface oxide, and high-overvoltage potentials (appeared between 1.7 and 2 V vs. SCE) that endorsed the generation of powerful •OH radicals and subsequent oxidation of carbamazepine. It was also observed that carbamazepine molecules oxidized at the potential of 1.45 V vs. SCE with distinct anodic current peak. Moreover, the influence of four major operating parameters, such as current density, initial concentration of carbamazepine, initial pH of solution and reaction temperature, were also studied.

The current densities of 1, 5, 7, 9, 15 and 17 mA cm⁻² were tested to electrolyze carbamazepine (20 mg L⁻¹) with supporting 0.1 M Na₂SO₄ electrolyte for 8 h (Figure 13a). With the increasing current density from 1 to 9 mA cm⁻², carbamazepine removals reached about 53 - 71.7%. However, beyond the current density of 9 mA cm⁻², no significant increase in either removal efficiency or kinetics was observed. The reasons might be attributed to the parasitic reactions of •OH radicals to O₂ gas evolution and mass transfer rate of pollutants towards electrode surface (Song et al., 2010). Furthermore, the electrical energy consumption to treat one cubic meter of water contaminated with carbamazepine by electrochemical treatment for 8 h using Ti/Ta₂O₅-SnO₂ was observed in the range of 3.2 - 172.7 kWh m⁻³, when current densities varied from 1 - 17 mA cm⁻². The energy consumption was increased from 3.2 - 60.3 kWh m⁻³ to achieve the carbamazepine removal efficiency of 53 - 71.7 % with corresponding current density applied from 1 to 9 mA cm⁻². Beyond the current density of 9 mA cm⁻², it was noticed that the energy consumption increased by a factor of more than 2 for achieving the comparable degree of carbamazepine removal efficiency. Therefore, 9 mA cm⁻² was selected as an optimal current density due to comparably high degree of carbamazepine removal efficiency and less energy consumption. The reaction kinetics fitted both pseudo-first order and pseudo-second order model, but latter described better electro-degradation of carbamazepine with slightly higher regression coefficients (R²). To study the effect of initial concentration of carbamazepine on the electrochemical treatment, four different batches of carbamazepine solutions, such as 2, 10, 20 and 30 mg L⁻¹ were electrolyzed under the optimized current density (9 mA cm⁻²) (Figure 13b). After the 8 h of electrolysis, the removal efficiency reached about 80.3%, 73.3%, 71.8% and 70.2% at initial concentrations of 2, 10, 20 and 30 mg L⁻¹, respectively. The results indicated that at low initial concentration of substrates, the electrochemical treatment is more efficient. This might be due to the reason that at low initial concentrations of pollutants, electrochemical oxidation of organic molecules can be faster than the diffusion of side-products (Dai et al., 2014).
Similarly, to assess the effect of initial solution pH on the electrochemical treatment of carbamazepine, acidic to alkaline conditions with the pH values of 2, 4, 8 and 10, were studied (Figure 13c). The results showed that initial pH conditions do not have that significant effect on the removal efficiency of carbamazepine under electrochemical treatment. Nevertheless, optimal removal efficiency of 75.2% was achieved at pH 6, which is very relevant since MBR effluent normally observed at the pH of 6 - 7. On the other hand, effect of temperature was assessed by electrolyzing carbamazepine solution at different temperature conditions ranging from 10 - 30°C (Figure 13d). The carbamazepine removal efficiency of 71.7%, 74.1% and 75.5% were achieved at 10, 20 and 30°C, respectively under the electrochemical treatment for 8 h, indicating the slightly enhanced trend of treatment efficiency with the increasing solution temperature. Furthermore, under the optimal current density of 9 mA cm\(^{-2}\) and pH of 6.0, the TOC removal of carbamazepine were 61.2%, 69.8% and 71.1% at solution temperature of 10 °C, 20 °C and 30 °C, respectively. Since the solution temperature during this work was about 11 °C, the average degree of mineralization was expected about 61%. In order to study the effect of electrode type, the carbamazepine removal efficiency of as-prepared Ti/Ta\(_2\)O\(_5\)-SnO\(_2\) and commercially available Ti/PbO\(_2\) (Magneto, Netherland) was compared. After the 8 h of electrolysis, the carbamazepine removal efficiency at Ti/Ta\(_2\)O\(_5\)-SnO\(_2\) and Ti/PbO\(_2\) anodes reached 71.7% and 77.9%, respectively, showing relatively high removal efficiency of commercial electrode. However, a significant leaching of PbO\(_2\) was observed when extending electrolysis to 16 h and 24 h, releasing Pb concentrations of 37.3 and 25.8 μg L\(^{-1}\), respectively, which is higher than the maximum allowable concentration of Pb (14 μg L\(^{-1}\)) in inland and other surface water (EU, 2013). On the other hand, leaching of Sn, Ti and Ta was observed in the range of 145.7 - 407.3 μg L\(^{-1}\), 53.6 - 92.9 μg L\(^{-1}\) and 2 - 14 μg L\(^{-1}\), respectively while electrolyzing for 24 h. The high dissolution of Sn to bulk solution was followed respectively by Ti and Ta, yet there are no specific regulations on these compounds in surface water sources. Since the removal efficiencies of either electrodes are quite comparable, the as-prepared Ti/Ta\(_2\)O\(_5\)-SnO\(_2\) is eco-friendly with no heavy metal leaching into the treated water.
7 Results and discussion

Figure 13: Effect of operating conditions (a) applied current densities; (b) initial carbamazepine concentrations; (c) initial solution pH; and (d) temperature on the electrochemical oxidation of carbamazepine.

Furthermore, the optimal conditions (current density= 9 mA cm\(^{-2}\); pH= 6; T= 11 ± 1 °C; at Ti/Ta\(_2\)O\(_5\)-SnO\(_2\) electrodes) for the removal of carbamazepine from synthetic solution were applied to treat the real MBR effluent spiked with carbamazepine (10.75 μg L\(^{-1}\)). A complete carbamazepine removal efficiency of >99.9% was achieved after the 4h of electrolysis, which required lowest energy consumption of about 57 kWh m\(^{-3}\). The results revealed that the ECO process based on the use of newly developed Ti/Ta\(_2\)O\(_5\)-SnO\(_2\) semiconducting electrode is a reliable process to remediate carbamazepine from contaminated water streams, with promising potential to be integrated with MBR technology.

7.3.2 Study of PCO process for PhACs removal using Ag\(_2\)O/P-25 photocatalyst (Paper IV)

This study advocates the photocatalytic removal of commonly detected PhACs in municipal wastewater, such as carbamazepine and diclofenac, using newly developed UV light driven 5% Ag\(_2\)O/P-25 photocatalyst for the first time ever. Two different water
matrices, including deionized water (DW) and real MBR effluent (RME) contaminated with selected PhACs, were tested. For the preliminary screening experiments 0.4 g L⁻¹ of four different photocatalysts including Ag₂O/P-25, Sn₃O₇/P-25, PdO/P-25 and NiO/P-25 were dispersed into 50 mg L⁻¹ of carbamazepine and diclofenac and the extent of adsorption under dark conditions, UV-photolysis and UV irradiated photocatalysis were studied. In any case, the removal of carbamazepine and diclofenac via adsorption alone was only about 2 – 9%. Similarly, UV-photolysis for 180 min showed the carbamazepine and diclofenac degradation rates of nearly 13% and 25%, respectively. Whereas, photocatalytic degradation under UV irradiation for 180 min using four as prepared photocatalysts showed significant attenuation of carbamazepine and diclofenac. Since 5% Ag₂O/P-25 revealed a comparatively higher removal efficiency of the selected PhACs than other photocatalysts, hence it was selected for the subsequent experiments.

The characterization of 5% Ag₂O/P-25 by SEM and EDX showed the agglomeration and homogenous dispersion of Ag⁺ nanoparticles on the surface of P-25. The FTIR analysis showed the main absorption peaks at 3000, 1533.67, 1420, 1050 and 433.33 cm⁻¹, supporting the presence of chemical bonds (O-H stretching vibration, stretching of C=O group or O-H bending and M-O stretching vibration, respectively) in the bulk compositions (Figure 14a). The BET analysis indicated that the surface area of P-25 increased slightly by the deposition of Ag₂O nanoparticles from 47.27 to 54.1 m² g⁻¹. The energy band gap estimated based on the reflectance spectra of 5% Ag₂O/P-25 was about 2.96 eV, which revealed the high possibility of harnessing absorption spectra in UV-vis range (Figure 14b).

![Figure 14: FTIR spectrum (a) and plots of (F (R∞) h𝑣)¹/² vs (h𝑣) for the approximation of the optical band gap (b) of 5% Ag₂O/P-25.](image-url)
In this study, operating parameters involved in the photocatalytic removal of selected PhACs using 5% Ag₂O/P-25, such as solution matrix, catalyst dosage, and initial PhACs concentration were experimented as shown in Figure 15. The removal of carbamazepine and diclofenac in two solution matrices (DW and RME) was assessed at the catalyst dosage ranging from 0.2 to 1.0 g L⁻¹. In DW matrix (Figure 15 a-d), carbamazepine and diclofenac removal efficiencies reached 80.4 - 89.1% and 87.5 - 93.5% at catalyst dosage ranging from 0.2 - 0.4 g L⁻¹, respectively. Since the removal efficiency of both carbamazepine and diclofenac did not improve significantly beyond the catalyst dose of 0.4 g L⁻¹, so this value was considered as optimal dose for the photocatalytic removal of both PhACs in DW matrix. For RME matrix, the removal efficiency of carbamazepine reached 89.74% from 76.6% while increasing catalyst dosage from 0.4 - 0.8 g L⁻¹, but no significant improvement was observed beyond 0.8 g L⁻¹. Whereas, optimal diclofenac removal efficiency of 90.7% was achieved at catalyst dose of 0.6 g L⁻¹. Therefore, the optimal dosage of 5% Ag₂O/P-25 in RME matrix to achieve comparable extent of carbamazepine and diclofenac removal efficiency as in DW matrix, was increased nearly by 2 and 1.5-fold, respectively. Furthermore, the effect of initial concentration on the photocatalytic removal of PhACs by 5% Ag₂O/P-25 was studied in RME matrix (Figure 15 e-f). The decreasing tendency in the removal efficiency of carbamazepine and diclofenac was observed while gradually increasing their initial concentrations. The removal efficiency of carbamazepine and diclofenac decreased about 38% and 23% while initial concentrations were increased from 20 to 50 mg L⁻¹. Moreover, the photocatalytic degradation kinetics of PhACs at 20 min of initial reaction fitted the Langmuir-Hinshelwood kinetics model very well with regression coefficients of the linear fitting ≥ 98% for both carbamazepine and diclofenac. The mineralization efficiencies of about 68% and 65% were observed during the photocatalytic degradation of carbamazepine in DW and RME matrices, respectively, whereas slightly lower mineralization efficiencies of diclofenac i.e., 60% and 55% were accounted in DW and RME matrices, respectively.
Figure 15: Effect of catalyst dosage in different water matrices on photocatalytic removal of (a & b) carbamazepine in DW and RME; (c & d) diclofenac in DW and RME; and effect of initial PhACs concentration (e) carbamazepine in RME; (f) diclofenac in RME.
Results and discussion

The quenching experiments indicated that the addition of ethylenediaminetetraacetic acid (EDTA) and methanol (for suppressing $h^+$ and $'OH$), the photocatalytic degradation of carbamazepine was substantially reduced nearly by 70% and 90% in 60 min, respectively, whereas only about 18% reduction was observed with the $O_2$-purging (suppressing $'O_2'$). On the other hand, diclofenac removal was substantially decreased to 62% in the presence of EDTA, but no significant effect in removal efficiency ($\approx$ 7%) was observed due to methanol and $O_2$-purging. The results indicated that the induced $h^+$ and $'OH$ are the dominant reactive oxidation species during the photocatalytic degradation of carbamazepine, whereas $h^+$ mainly attributed to diclofenac degradation.

Similarly, to assess the reusability of 5% Ag$_2$O/P-25, cyclic photocatalytic experiments were conducted for both the PhACs (Figure 16). The 5% Ag$_2$O/P-25 did not show any significant loss in the photocatalytic degradation efficiency of carbamazepine until five repetitive cycles, exhibiting a remarkable reusability. Whereas, gradually decreased photocatalytic removal efficiency (dropped by about 35% until 5$^{th}$ cycle) of diclofenac was observed during cyclic reuse of 5% Ag$_2$O/P-25. Nonetheless, since the inhibition rate of the photocatalytic activity was almost stable after 2$^{nd}$ cycle, it can be concluded that the as-prepared 5% Ag$_2$O/P-25 is moderately stable for the attenuation of diclofenac and could be useful for the long-term industrial application. Moreover, in either cases, the recovery of photocatalyst was achieved by centrifuging the solution just for 15 min, which is probably the more cost efficient than high filtration costs associated with TiO$_2$ nanoparticles.

![Figure 16](image_url)
The intermediate identification study on the photocatalytic degradation of carbamazepine (one of the selected PhACs) using high-resolution FT-ICR mass spectrometry detected the common transformation products of carbamazepine, such as 10,11-dihydro-carbamazepine-10,11-epoxide (m/z 253), acridine-9-carboxaldehyde (m/z 208), and hydroxyacridine-9-carboxaldehyde (m/z 224). The identification of many intermediate products indicated the complexities involved during the photocatalysis of carbamazepine. Moreover, a possible multi-step carbamazepine photodegradation path was proposed based on the unambiguously identified intermediate products in this study and suggested in the other literatures as shown in Figure 17.
Figure 17: Photogenerated intermediates and proposed photodegradation pathway of carbamazepine by 5% Ag$_2$O/P-25 photocatalyst under UV irradiation.
8 Conclusions and further research

MBRs are very potential technology for municipal wastewater treatment and reclamation. However, the depth of understandings on their performance and operational consequences in the regions where low temperature conditions remain for longer period of the year are very limited. For this aim, the pilot scale MBR plant was operated under varying operating conditions to study the membrane fouling and efficiency of MBR on removing ECs. It is noticed that severe membrane fouling is associated with MBR operation during cold water conditions. However, MBR showed excellent removal of ECs, heavy metals and human enteric viruses even under extreme cold water conditions including other common pollutants. Diverse removal efficiencies of ECs were observed during the MBR treatment and several influencing factors were evaluated. Biotransformation and sorption to sludge were found to be the predominating reasons of the removal of ECs, although metal complexation, retention by membrane fouling layer and membrane material have also attributed on the attenuation of heavy metals and viruses. Moreover, physicochemical properties of ECs and operational conditions had also contributed on removal by MBR treatment. Overall, a very good quality of treated effluent was achieved by MBR treatment despite of varying operating conditions, even though the removal efficiencies of many ECs were not optimal.

This indicated that the MBR treatment is not the ultimate solution to remediate many of highly recalcitrant ECs. Therefore, integration possibilities of MBR with some AOPs, viz. ECO and PCO to ensure high quality reclaimed effluent with emphasizing the removal efficiency of ECs from municipal wastewater treatment, were explored. In ECO, a newly developed Ti/Ta₂O₅-SnO₂ electrode was used for the electrochemical degradation of carbamazepine. The optimal removal of carbamazepine in aqueous solution was reached 75.5% when electrolyzed under the current density of 9 mA cm⁻², pH of 6, 30 °C for 8 hrs. A complete removal of carbamazepine in real MBR effluent was observed when electrolyzed under the optimized conditions in aqueous solutions. On the other hand, in PCO, heterogenous 5% Ag₂O/P₂5 photocatalyst was used for the photocatalytic degradation of carbamazepine and diclofenac from aqueous solutions and real MBR effluent matrices. About 89.1% and 93.5% removal of carbamazepine and diclofenac was achieved using 5% Ag₂O/P-25 at catalyst dosage of 0.4 g L⁻¹ under UV irradiation for 180 min. However, to achieve the same degree of attenuation, the optimal catalyst dosages for both carbamazepine and diclofenac were increased by the factor of 2 and 1.5, respectively. The photo-induced holes and *OH were the primary oxidation species involved in the photocatalytic reactions. Moreover, some important degradation by-products of carbamazepine were identified and quantified, and multi-step degradation pathway was proposed. Therefore, the batch experiments on ECO and PCO systems revealed the enhanced removal of selected ECs than in the MBR treatment alone, which indicated their potentials of integrating with MBR technology to improve effluent quality and the better stability of the treatment process.
This dissertation has expanded the knowledge on the applicability and efficiency of MBR operation at rather low water temperature conditions in Nordic environment and integration possibilities of MBR with selected AOPs. However, it has also unfolded the need of many other important topics for further investigations. Of the many research topics related to the current work, some of them are briefly described below.

As substantial membrane fouling was observed in MBR during winter periods, more research could be focused on finding fouling mitigation strategies. On this note, feasibility of integrating MBR with electrocoagulation can be studied, which is expected to simultaneously destroy major organic fouling fractions (e.g. EPS and SMP), enhance ECs removal efficiency, and generate less sludge. Similarly, the ability of low-cost adsorbents, such as biochars derived from wasted sludge, could be studied as subsequent fouling mitigation approach. On the other side, scaling-up of integrated MBR-AOPs options could be studied in a pilot-scale. Further, optimizing the operation of pilot-scale integrated system, regeneration of electrodes and photocatalysts, and overall cost evaluation of the system should be investigated. Similarly, toxicity associated with the treated effluent after AOPs could be a challenge due to the generation of more toxic transformation by-products. Therefore, further studies should be focused on detail identification of the generated by-products of parent ECs and their relative toxicities in the treated effluent.
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Publication I

Khum Gurung, Mohamed Chaker Ncibi, Mika Sillanpää
Assessing membrane fouling and the performance of pilot-scale membrane bioreactor (MBR) to treat real municipal wastewater during winter season in Nordic regions

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Assessing membrane fouling and the performance of pilot-scale membrane bioreactor (MBR) to treat real municipal wastewater during winter season in Nordic regions

Khum Gurunga,⁎, Mohamed Chaker Ncibib, Mika Sillanpääa,b

a Laboratory of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland
b Department of Civil and Environmental Engineering, Florida International University, Miami FL-33174, USA

HIGHLIGHTS

• Performance of a pilot-scale MBR was studied at low temperatures in Nordic region.
• Substantial membrane fouling was observed at low temperatures (below 10 °C).
• About 75% of the permeability drop was observed due to fouling.
• High removal rates were achieved for pathogens.
• High removal rates for the emerging micropollutants were observed.

GRAPHICAL ABSTRACT

In this study, the performance of a pilot-scale membrane bioreactor (MBR) to treat real municipal wastewater was assessed at low temperatures (7 to 20 °C) in Nordic regions. First, the effect of low temperatures on membrane fouling was evaluated by monitoring trans-membrane pressure. A significant membrane fouling was observed when the sludge temperature inside the MBR unit was below 10 °C with a 75% permeability drop, thus indicating high deterioration of the membrane performance at low temperatures. Moreover, increasing values of sludge volume index (SVI) during low temperatures showed high deterioration of sludge settleability. As for the pollution removal, MBR achieved high performances primarily for pathogens and emerging micropollutants. The average log reductions of 1.82, 3.02, and 1.94 log units were achieved for norovirus GI, norovirus GII, and adenoviruses, respectively. Among the four trace organic compounds (TrOCs), the average removal efficiencies of bisoprolol, diclofenac and bisphenol A were 65%, 38%, and 97%, respectively. However, carbamazepine was not efficiently removed (−89% to 28%). Regarding trace metals, an average removal of 80% was achieved for Cd, Pb, and V. For the rest of the metals, the removal capacities were between 30 and 60%.

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Keywords: Membrane bioreactor Membrane fouling Low temperature Municipal wastewater Pathogens Emerging micropollutants

⁎ Corresponding author.
E-mail addresses: khungrg@yahoo.com (K. Gurung), mika.sillanpaa@lut.fi (M. Sillanpää).

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1. Introduction

Temperature influences the performance of biological treatment in conventional activated sludge processes (Arvela et al., 2014; Metcalf and Eddy Inc., 2003). Moreover, in MBRs, temperature not only affects the bioconversion process but also influences microbial community, fouling rate and sludge morphology (Zhang et al., 2014). The biological activity of the activated sludge tends to decrease in winter periods. Indeed, when temperature drops to about 15 °C, methano-producing bacteria become essentially dormant, and at about 0 °C, the autotrophic bacteria practically cease functioning. Even the chemoheterotrophic bacteria performing on carbonaceous material becomes inactive at 2 °C (Metcalf and Eddy Inc., 2003). Moreover, in MBRs, temperature not only affects the bioconversion process but also in MBRs, temperature not only affects the bioconversion process but also affects the performance of membrane bioreactors. In this context, it was reported that the low temperatures can cause rapid membrane fouling as compared to mesophilic temperature under which proteins are the dominant foulants (Gao et al., 2014). There has been many previous studies on membrane fouling (Drew, 2010; van den Brink et al., 2011; Zhang et al., 2014). Membrane fouling at low temperatures are also found to induce changes in the cake layer thickness and/or porosity of the membranes (van den Brink et al., 2011). Moreover, other factors attributed to the membrane fouling at low temperature include increased viscosity, reduced sludge stabilization, reduced particle size of sludge and reduced mass transfer efficiency (Zhang et al., 2014).

The fate of human enteric viruses such as noroviruses and adenoviruses are of major interest because they are common causes of waterborne outbreaks. In MBR system, the removal mechanisms of pathogens can be either via attachment to biomass developed on the membrane surface or adsorption in/on the biomass flocs and to some extent via retention by micro-membranes (Nisra et al., 2015).

The active evaluation of possible risk of emerging organic micropollutants or eDOMs such as pharmaceutically active compounds (PhACs) and endocrine disrupting chemicals (EDCs) in treated effluents of wastewater treatment systems has become a great concern (Treu et al., 2012). In winter seasons in cold regions, higher concentrations of emerging micropollutants are detected due to the decrease in bacterial biodegradation activities under low temperature (Kruglova et al., 2016), in addition to the increasing consumption of pharmaceutical drugs, especially antibiotics, in winters (Suda et al., 2014). In Finland, carbamazepine (CBZ), diclofenac (DFC), and bisoprolol (BIS) are three commonly used PhACs (FiMIA, 2015). The toxicity of these PhACs on fish, algae, and bacteria in concentrations < 1 mg L\(^{-1}\) have been recently reported (Kruglova et al., 2016).

On the other hand, trace metals are recalcitrance and persistence inorganic micropollutants (Fu and Wang, 2011) that could cause acute and chronic toxicity (Kavvases et al., 2003). Moreover, their presence at certain concentrations is not only of environmental concern but also strongly reduces microbial activity, thus resulting adverse effects on biological wastewater treatment processes (Ichipasa, 2003). In MBRs, the removal of trace metals is highly enhanced primarily due to the reduction in suspended solids from effluents (D.Fabio et al., 2013).

In this context, the present research aims at studying the performance of a submerged pilot MBR to treat real municipal wastewater under the low temperature conditions during winter season in Finland. The investigation mainly focused on assessing the membrane fouling, pathogen removal and fate of emerging micropollutants (organic and inorganic). To the best of our knowledge, this is the first detailed study on MBR treating real municipal wastewater under low temperature periods in Nordic environment.

2. Materials and Methods

2.1. The pilot scale MBR plant and operating conditions

In this research, a pilot-scale MBR was employed to treat a real municipal wastewater in Mikkeli, Finland. The detailed experimental set-up arrangement of the MBR plant was explained elsewhere (Gurung et al., 2016). The capacity of the MBR pilot plant was designed to treat 3 m\(^3\) of wastewater per day. The MBR unit used flat sheet microfiltration membranes having pore size of 0.4 µm and effective surface area of 16 m\(^2\). The MBR unit was fed with primary clarified wastewater of the full-scale Kenkäveronniemi WWTP. The stabilized sludge was wasted from the membrane compartment daily to maintain designated solids retention time (SRT). The treated permeate water and wasted sludge were collected in the permeate and sludge tanks, respectively and then discharged to the WWTP sewer.

The MBR pilot unit was operated for > 120 days from January to April 2016, coinciding with the winter season in Finland (temperature of influent wastewater around 7–10 °C). The water level in the membrane tank was maintained constant (< 5% change in water volume during the study). No backwashing was performed, however, the chemical washings of membranes were carried out whenever the TMP reached a level of ≥20 kPa by using sodium hypochlorite followed by citric acid. The pH of the biological reactors was adjusted using NaOH solution.

During the manual cleaning, membrane cartridges were taken out of the bioreactor and then accumulated cake layer was cleaned by using brush and water jet. The operating conditions of pilot operation is summarized in Table 1.

The major pollutants in wastewaters such as total suspended solids (TSS), chemical oxygen demand (COD), ammonium nitrogen (NH\(_4\)-N), and total phosphorus (TP) in influent and permeate were determined according to the Standard Methods (American Public Health Association et al., 1999). Liquid samples were collected for 24 h using automatic composite samplers in weekly basis. The SVI was determined weekly from mixed liquor grab samples according to the previously described method (Fontmorin and Sillanpää, 2015). The mixed liquor suspended solids (MLSS) concentrations of mixed liquor from both aerobic and membrane bioreactors were determined once a week according to Standard Methods (American Public Health Association et al., 1999).

Membrane fouling was quantified as a progressing phenomenon by monitoring trans-membrane pressure (TMP), while the permeate flux was maintained almost constant over the experimental period. Membrane performance was assessed according to the following equation (Park et al., 2015):

\[
L_p = \frac{J}{\Delta P_{\text{TMP}}} - \frac{1}{\mu_k} \frac{1}{R_e} \mu_k \mu_r
\]

where \(L_p\) is membrane permeability (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)); \(J\) is membrane flux (L m\(^{-2}\) h\(^{-1}\)); \(\Delta P_{\text{TMP}}\) is trans-membrane pressure (Pa); \(\mu_k\) is permeate viscosity (Pa⋅s); and \(R_e\) is total filtration resistance (m\(^{-1}\)).

The analysis of noroviruses (GI and GB) and adenoviruses were performed from influent, permeate and mixed liquor according to the methods described elsewhere (Miura et al., 2015; Simmons et al., 2016).
Moreover, the concentrations of *E. coli* and Enterococcus in the influent, sludge and permeate were enumerated by using Colilert® and Enterolert® methods. The occurrence of TrOCs both in liquid and solid phases were analyzed from influent, permeate and sludge, respectively using standard solid phase extraction (SPE) and LC-MS/MS methods (EPA, 2007). The analysis of heavy metals in the influent, permeate and sludge samples was conducted with an inductively coupled plasma-optical emission spectrometer (ICP-OES, iCAP 6300, Thermo Electron Corporation, USA) from the pretreated samples (Fontmorin and Sillanpää, 2015).

3. Results and discussion

3.1. MBR operation and membrane fouling at low temperatures

Fig. 1 shows the variations in sludge temperature, TMP profile and aeration intensity during MBR operation. At the beginning of this experiment, the average sludge temperature was 11 ± 1.5 °C, the specific aeration demand per membrane surface (SADm) was fixed at about 0.6 m³ h⁻¹ m⁻² and the TMP was about 2 kPa until 9th February. However, two weeks later, the atmospheric temperature began to drop sharply. The outside air temperature was varying between 0 °C and −33 °C for more than a week, which is the typical Nordic weather phenomenon during winter seasons. Due to this sudden temperature drop, some pumps and connecting pipes were frozen and severely clogged. Thus, the system malfunctioned and stopped for more than a week (18th to 25th January). Heating cables were installed to the stretch of pipes from feed point to the pilot plant inlet. The broken pumps were changed with new ones and the clogged pipes were cleaned with hot water. Additionally, three heaters (25 W capacity each): two inside the pilot plant and one at the influent pumping station were installed and the process resumed again. The average temperature of mixed liquor reached 20.5 ± 0.6 °C immediately after the process restarted until 8th February, which was expected due to the heating effects of air mass flow along with heaters and heating cables. Thus, the SADm was reduced and maintained at 0.4 m³ h⁻¹ m⁻² from 9th February to 6th April in order to ensure the lowest possible temperature inside the bioreactors. As a consequence, the sludge temperature started decreasing gradually from 10th February and reached nearly 10 °C by 18th March. In addition, the decreasing temperature of the sludge was also attributed to the incoming flow of melted ice to the municipal wastewater. Occasionally, heaters and heating cables were intermittently used depending on outside air temperature in order to prevent serious damages related to freezing.

The first TMP jump occurred between 23rd February and 18th March. The temperature shock was evident when temperature dropped to about 10 °C, which is consistent with the results of Gao et al. (Gao et al., 2014). As the membrane fouling accelerated rapidly and the TMP reached nearly to 17 kPa (1st peak), first chemical washing of membranes was performed. After the washing TMP dropped to about 6 kPa, but increased rapidly and finally reached nearly to 12 kPa (2nd peak) within a week from the 1st peak. Yet, the sludge temperature was measured to be 7.7 ± 1.2 °C during the 2nd peak and the propensity of the membrane fouling was very rapid. Therefore, it was concluded that the rapid increase in the TMP was highly attributed to the low temperature of sludge. Besides, due to the Easter holidays, the second in situ washing of membranes was performed during the 2nd fouling peak (a bit early when compared to the 1st peak). Again, the TMP increased gradually and reached nearly to 13 kPa within 12 days from the 2nd peak. The sludge temperature was increased to about 8–12 °C and stayed almost stable after second chemical washing. The membrane fouling occurrence between the 1st peak and 2nd peak was within a week. However, it extended to nearly two weeks between 2nd and 3rd

![Fig. 1. Membrane fouling behavior and cleaning measures. (Note: SADm is not in scale).](image-url)
peak. The extended time between the fouling peaks can be attributed to the increased sludge temperature. The results showed that membrane fouling was important during low temperature periods, which is in agreement with other studies (Gao et al., 2014; van den Brink et al., 2011; Zhang et al., 2014). As the sludge temperature stayed at about 12 °C (after 2nd fouling peak) for two consecutive weeks, maintaining low temperatures in this point was no more possible as the weather started to gradually warm up. Therefore, after 2nd fouling peak, the SADm was increased back to 0.6 m³h⁻¹m⁻². This increase helped reducing the TMP by approximately 2.5 kPa within a week. Thus, the fouling phenomena occurring during the MBR operation were not only attributed to the low temperature conditions but also to some extent, related to the reduction in aeration intensity. During the chemical washing the TMP dropped nearly to 6 kPa and then raised rapidly, illustrating that this cleaning procedure is not so effective. As for the manual washing of membranes, it reduced the TMP to nearly 3 kPa. Moreover, the mixed liquor viscosity increases, resulting in the rapid building of fouling resistance, leading to the rise of TMP (van den Brink et al., 2011; Zhang et al., 2014). Membrane fouling at low temperatures can also be accelerated due to the reduced shear stress proclaimed by coarse air bubbling, low particle back transport velocity and high hydrophobicity of the mixed liquor (Zhang et al., 2014). In addition, the pore size can shrink in the low temperatures due to intrinsic characteristics of membranes. At low temperatures, a higher amount of submicron particles are found in the mixed liquor composition, which enhances the rapid fouling by pore blocking or narrowing of the membrane pores, however, cake layer formation becomes dominant after the initial fouling (van den Brink et al., 2011).

At the beginning, the permeability was about 345 Lm⁻²h⁻¹bar⁻¹, and the correlation with temperature was not so clear. During the 1st peak of fouling, the permeability dropped to 50 L m⁻²h⁻¹bar⁻¹. After the 1st membrane cleaning, the permeability increased back to 130 L m⁻²h⁻¹bar⁻¹, but rapidly declined to 75 L m⁻²h⁻¹bar⁻¹ until the 2nd peak of fouling. About 75% of permeability drop was observed during the period with the lowest temperatures (from 9th March to 11th April), as compared to the initial permeability. About 50% of permeability differences were reported between summer and winter periods in the full scale MBRs (van den Brink et al., 2011). After the manual cleaning of membranes, the permeability was restored gradually and reached nearly to 300 L m⁻²h⁻¹bar⁻¹, though unable to regain the initial value. The results showed that the accelerated membrane fouling due to low temperature deteriorated the hydraulic performance (permeability) of membranes. Therefore, extra membranes are recommended to be installed for the colder periods in order to ensure constant membrane permeability, especially in countries where long low temperature periods exists throughout a year. Membrane fluxes can be lowered using extra membranes, resulting in a slower propensity of membrane fouling due to the distribution of trans-membrane pressures. This leads to maintain relatively high and constant permeability.

Fig. 2 shows the variations of the MLSS concentrations and SVI of mixed liquor. The average SVI was found to be increasing from 120 mLg⁻¹ to 168 mLg⁻¹ when the average sludge temperature varied between 15 and 10 °C. The higher SVI values at low operating temperature indicates that the compressibility and settleability of sludge are highly deteriorated (Zhang et al., 2014). More fine particles, colloids or polymers are released when operating at low temperatures due to low density morphology of mixed liquor, leading to high tendency of membrane fouling (Drews, 2010). More irregular shaped sludge flocs might be produced due to bulky sludge which facilitates the development of highly dense cake layer on the membrane surface, thus resulting in a more significantly fouling phenomena (Zhang et al., 2014). On the other hand, the MLSS concentration was found to be reduced from about 9800 mg L⁻¹ at the beginning to 5600 mg L⁻¹ when the sludge temperature dropped by approximately 10 °C (from 20 °C to 10 °C). However, the MLSS concentration remained almost stable when the sludge temperature was about 8 °C to 12 °C. The results are consistent with previous study where reduced biomass concentrations is reported during low temperature operations (Zhang et al., 2014). Under the low temperatures less energy is released from the oxidation of organic matter, which lowers the rate of cell synthesis and thus deteriorate the sludge yield (Zhang et al., 2014). Similar observations reported by Krzeminski et al. (2012) revealed that sludge concentrations are highly reduced in winter than in summer in a full-scale MBR plant. The treated water quality regarding the removal of TSS, organic matter and inorganic nutrients (NH₄-N and TP) is shown in Table 2. Despite of low temperature operation, high quality treated water was achieved. 100% removal of TSS was accomplished, thus revealing an excellent retention capability from inert suspended solids by the micro-filtration (MF) membranes. About 95% of COD removal was achieved with the effluent concentration of 18.7 ± 2.9 mg L⁻¹. The present work is in good agreement with a previous study (Avéla et al., 2014), in which no significant effect was observed on the removal of COD under a wide temperature variation (9–33 °C), when full-scale MBR was operated at SRT and HRT of 35 days and 35 h, respectively. High removal rate of NH₄-N (nearly 100%) during the experimental period indicated an efficient nitrification process in the MBR system, regardless of low temperature conditions. Higher nitrification under low temperature operation was expected due to the relatively longer SRT maintained during the experimental period. Maximum growth and accumulation of nitrifying bacteria (nitrifiers) are achieved when MBR is operated at relatively longer SRT of 35 days which offsets slow growth of nitrifiers due to low temperature, thus leading to excellent nitrification (Avéla et al., 2014). Furthermore, the average removal rate of TP reached nearly 91% with the concentration of 0.43 mg L⁻¹ in permeate, even though no chemical coagulants were added to the MBR system. Therefore, enhanced biological phosphorus removal process is expected at longer SRT during MBR operation due to the enrichment of some phosphate-accumulating organisms (PAOs).

3.2. Removal of human viruses: Noroviruses (NoV GI and NoV GII), and Adenoviruses (AdVs)

NoVs GI and GII, and AdVs were consistently detected in all the influent samples, and their occurrences are elucidated in Fig. 3. The detection rates varied depending on the samples and behaviors of different viruses types (Miura et al., 2015). In the present work, the detected but not quantified virus concentrations were assigned as positive results.
for viruses, except those under the limit of detection (i.e. ND: not detected).

NoV GI was detected in 85% of the influent samples with an average concentration of 95 GC mL\(^{-1}\) and high positive results during February and March. NoV GI in the mixed liquor samples were below the limit of quantification with an average concentration of 48 ± 28 GC mL\(^{-1}\). NoV GI was detected only in two permeate samples, during February and April. The log removal of NoV GI was ranging from −0.67 to −2.73 (1.82 ± 0.46) log units. Similarly, NoV GII was constantly detected in 100% of the influent samples with an average concentration of 896 GC mL\(^{-1}\) having gradually increasing trend during January to March, and then declining tendency during April. NoV GII in the mixed liquor samples were mostly below limit of quantification with an average concentration of 25 ± 44 GC mL\(^{-1}\). The log removal of NoV GII was achieved in the range of −2.1 to −3.62 (3.02 ± 0.5) log units. On the other hand, AdVs were detected in 100% of the influent samples with an average concentration of 28 ± 37 GC mL\(^{-1}\). The log removal of AdVs varied consistently throughout the low temperature period. AdVs were highly detected in the mixed liquor with an average concentration of 196 GC mL\(^{-1}\). Interestingly, only one positive sample was detected for AdVs (on 23rd March) from the permeate sample. The log removal of AdVs ranged from −0.76 to −2.76 (1.94 ± 0.7) log units.

The tendency of variations monitored for NoVs and AdVs in the influent wastewater during winter period is consistent to the previous studies (Xiao et al., 2010; Miura et al., 2015; Simmons et al., 2011). In this study, the overall removal efficiencies of NoV GI (−0.67 to −2.73 log unit), NoV GII (−2.1 to −3.62 log units), and AdVs (−0.76 to −2.76 log units) were achieved. Miura et al. (2015) reported the log reductions of −0.2 to −1.4 log units for NoV GI. Ottosson et al. (2008) reported mean log reduction of 1.0 to 1.1 log units for NoVs in pilot-scale MBR with a 0.45 μm pore size membranes. Sima et al. (2011) reported the log removal of 0.9 to 0.8 log units for NoV GI in full-scale MBR treatment. Similarly, in the full-scale MBR with nominal pore size (0.04 μm) membranes, Simmons et al. (Simmons et al., 2011) reported the average log removals of 3.0 and 4.7 log units for AdVs and NoV GI, respectively.

Viruses adsorption to mixed liquor plays an important role in the removal of viruses by MBR process (Miura et al., 2015; Ottosson et al., 2006; Simmons et al., 2011). In this study, NoV GI was detected under limit of detection in the mixed liquor, whereas NoV GII was observed at very low concentrations. The log removal of NoV GI and NoV GII was about 0.5 log units and 1.7 log units, respectively in the mixed liquor. One reason might be attributed to the presence of inhibitors in the samples, which may affect the sensitivity of the analytical method or even cause false-negative results (Schrader et al., 2012). In this study, the influent to the MBR was fed from primary settling tank of the main process (where returned sludge was recycled periodically), which might have traces of calcium ions (inorganic inhibitors). The presence of organic inhibitors such as polysaccharides, humic acids, proteins (Schrader et al., 2012), which are highly available during cold temperature (Zhang et al., 2014), might have effects on PCR. On the other hand, AdVs were significantly higher in the mixed liquor samples than in the influent, showing their high adsorption affinity towards mixed liquor (Kuo et al., 2010). However, as the surface characteristics of viruses varies greatly, therefore their adsorption to the complex biomasses may vary too (Miura et al., 2015). It is likely that viruses which are adsorbed to sludge more efficiently removed at waste sludge in the MBR pilot process (Miura et al., 2015). This indicates that even under the low temperature conditions, appropriate control of MLSS concentration in MBR process can enhance efficient virus removal. Furthermore, differences in the log removal efficiencies related to the morphology of viruses was not clearly observed. The removal of NoV GII (27–40 nm) was found to be higher than the AdVs (90–100 nm). This result is contradictory with the findings of Simmons et al. (2011), where higher removal of human adenoviruses was achieved compared to NoV GII in MBR process. This tendency could be explained by the variations in influent concentrations in the one hand, and that of the limits of detection on the other hand. The combination of those variations might lead to higher or lower removal efficiency of viruses during the calculation (Simmons et al., 2011).

In the present study, NoV GI, NoV GII, and AdVs were detected in the MBR permeate, though the occurrence was not consistent, which confirms that MBR is not an absolute barrier for retaining virus passage (Simmons et al., 2011). During this research work, variations in the membrane fouling degree were observed with the TMP ranging from 2 to 18 kPa. Despite the cleaning of membranes, the overall removal efficiency of viruses in the MBR process did not change. Moreover, passage of all three viruses were observed in the permeate samples before or after the membrane fouling peaks. These results suggested that the virus removal efficiency was not related to the degree of membrane fouling, which is in good agreement with the previous study (Miura et al., 2015). Further research would be needed for hourly or daily samples before and after the cleaning of membranes to determine the precise correlation between fouling and virus removal. Furthermore, the average concentrations of the Escherichia coli and enterococci were observed in the influent wastewater in the range of 4.8 × 10\(^5\) MPN 100 mL\(^{-1}\) and 1.9 × 10\(^5\) to 4.8 × 10\(^5\) MPN

### Table 2

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<th>Parameter</th>
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<th>Effluent concentration</th>
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<td>90.0 ± 2.4</td>
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</table>

### Fig. 3

Concentrations of NoV GI, NoV GII, and AdVs. Black triangles – influent; grey diamonds – mixed liquor; white squares – permeate; dashed line – Limit of Quantification; ND – below Limit of Detection.
100 mL−1, respectively. However, none of them were detected in the MBR permeate over the experimental period. Nonetheless, the high concentrations of Escherichia coli (1.6 × 10^10 to 8.05 × 10^10 MPN 100 mL−1) and enterococci (1.07 × 10^10 to 4.3 × 10^10 MPN 100 mL−1) were detected in the sludge supernatant. The average bacteria removal efficiency of the MBR process during low temperature period was >9.5 log units, which is in the good agreement with other study (Ottoson et al., 2006).

### 3.3 Fate of organic micropollutants: TrOCs

The occurrence and removal efficiencies of CBZ, BIS, DCF, and BPA in the MBR process are shown in Fig. 4a-b. All the selected TrOCs were detected in the influents throughout the experimental period, although the relatively higher concentrations were measured from January up to the end of March as shown in Fig. 4a. The mean influent concentrations of CBZ, BIS and BPA were 0.63, 0.43, and 0.95 μg L−1, respectively. Similarly, for DCF, the concentration was 1.84 ± 0.4 μg L−1, which was the highest among the other refractory compounds during cold season.

The mean concentrations of CBZ, BIS, DCF and BPA in the MBR permeate were 0.77, 0.14, 1.12, and −0.05 μg L−1, respectively. Most of the TrOCs were found comparatively low in the permeate than in the influent (excluding CBZ), indicating the enhanced efficiency of the MBR process to remove many emerging TrOCs from the real wastewaters. TrOCs removal efficiency differ from plant to plant and even country to country as it highly depends on wastewater characteristics and specific operating procedures implemented by particular treatment processes (Tambosi et al., 2010). The overall removal rates in this study varied largely among the individual TrOCs. The mean removal efficiencies of CBZ, BIS, DCF and BPA achieved during low temperatures (interpreted as monthly average) are shown in Fig. 4b. Negative removal efficiencies of CBZ were mostly observed, except a relatively low efficiency of about 9% and 28% during last two weeks of March. CBZ removal rates varied from −89 to 28% (average of −23%) with the highest negative efficiency during January–February. The average removal efficiencies of BIS and DCF were 65 ± 6% and 38 ± 7%, respectively. Decreasing tendencies of the removal rates were observed both for BIS and DCF from Jan–Feb to April. On the other hand, BPA concentrations in the permeate were significantly below −0.05 μg L−1 (LOQ) regardless of low temperature operation, thus substantially stable BPA removal efficiency of >97% (−95 to >98%) was achieved.

A mass balance of TrOCs in MBR was performed (Table 3) according to the method described by Kimura et al. (2007), where quantity of the TrOCs adsorbed on mixed liquor solids are measured and compared with the eliminated quantity estimated by considering the influent minus the permeate concentrations. The presented mass balances must be interpreted as rough estimates as they were calculated from the averaged values considering a completely mixed and steady state. Table 3 clearly elucidates great variations between the overall elimination and the elimination due to sorption regardless of the compounds. For all the selected TrOCs, a very weak removal via biomass sorption was observed. Thus, the removal mechanism for BIS, DCF and BPA was attributed primarily due to the biotransformation of TrOCs in the MBR process. Similar studies on MBR demonstrated that sorption is not the dominant mechanism, but biotransformation is crucial in the elimination of TrOCs regardless of the treatment conditions (Clara et al., 2005; Kimura et al., 2007; Tambosi et al., 2010). The biological elimination of TrOCs could be due to the direct metabolism or by co-metabolization where bacteria use TrOCs as direct carbon source, or just break them down via specific enzymes which have potential to degrade or transform trace organic molecules (Vieira and Sillanpää, 2014).

![Fig. 4. Concentrations of CBZ, BIS, DCF and BPA in influents during low-temperature periods (a); removal efficiencies achieved for selected TrOCs (monthly average) (b).](image-url)
enzymanic cleavage in the activated sludge process in MBRs (Vierno et al., 2007). The small percentage of CBZ removal during the MBR process is associated with retention by the sludge and elimination during sludge wasting (González-Pérez et al., 2016). In addition, large concentrations of CBZ found in mixed liquors and permeate suggested the recalcitrant behavior of CBZ to the biological transformation or biodegradation (González-Pérez et al., 2016). The poor removal of CBZ is partly due to its hydrophilic characteristics (Log Kow < 2.5) and chemical stability (González-Pérez et al., 2016).

3.3.2. DCF removal

The average influent concentration of DCF (1.12 μg L⁻¹) was higher than the values (0.23 to 1.1 μg L⁻¹) reported by other researchers in municipal sewage treatment plants. In this study, the partial removal efficiency of dichloroanilin varied from 13% to 89% (average 38%), which is similar to the results in the previous studies performed during the winter season (Clara et al., 2005; Trinh et al., 2016). In lab-scale MBR under SRTs of 30–90 days at varying temperatures (8 to 12 °C), Kruglova et al. (2016) reported substantially slow biological degradation of DCF. Likewise, the elimination of DCF was higher in Jan–Feb than March–April. One reason might be the mixed liquor temperature being higher around 15 °C during Jan–Feb. The other reason could be the high MLSS concentrations (approximately 8,000 mg L⁻¹) in the MBR process. In March, the process temperature was even below 10 °C for more than a week. Longer SRTs allow high microbial population and biomass concentrations and thus would enhance the biological interactions with the structurally-complex pharmaceuticals (Kimura et al., 2007). Majority of the studies reported in the literature revealed higher removal performance of DCF with longer SRTs in MBR processes. However, it is worth noticed that some contradictory results with no correlation between the elimination of DCF and SRT were also reported (Verno and Sillanpää, 2014).

3.3.3. BIS removal

The present work is probably the only study performed so far on BIS removal in MBR operations at low temperature conditions. The removal efficiency of BIS varied over the investigation period with higher removal rates observed during Jan–Feb (73%) than in March (64%) and April (55%), during which sludge temperature varied approximately from 20°C to 12 °C. The explanation for the higher removal of BIS in MBR process might be attributed to the higher biodegradability at higher temperature and vice-versa.

3.3.4. BPA removal

Relatively higher and stable removal of BPA (~97%) was achieved as compared to other compounds regardless of low temperature conditions. The average BPA removal efficiency of ~90% was documented by (Clara et al., 2005; Trinh et al., 2016) in the MBR processes during cold periods of the year, which is consistent with our result. Due to its high hydrophobicity (Log D = 3), BPA might have a tendency to sorb on suspended solids of mixed liquor matrix and subsequently be removed with the withdrawal of excess sludge (Cirja et al., 2008). However, about 95% of BPA was found to be eliminated via biotransformation, relative to influent load in this study. Thus, biotransformation is the dominant pathway of BPA removal. One reason for the slow elimination of BPA via sorption process in MBR process might be due to its very polar nature (Cirja et al., 2008). Biotransformation was also reported as the main pathway for BPA removal by other researchers (Trinh et al., 2016).

3.4. Fate of inorganic micropollutants: trace metals

3.4.1. Concentrations of trace metals and removal efficiencies

Concentrations of the selected trace metals in the influent and permeate, corresponding removal efficiencies, and the maximum allowable concentrations (MAC) according to Water Quality Guidelines or Standards set by international organizations are shown in Table 4. All the trace metals were detected in the collected samples with an occurrence frequency of 100%. Concentrations of trace metals in the influent were in the range of 0.1 to 80 μg L⁻¹ (only dissolved fractions), which are consistent with the range of trace metal concentrations documented by other researchers (Di Fabio et al., 2013). With an average concentration of 75 μg L⁻¹, Zn was the most dominant, whereas Cd was the lowest (0.1 μg L⁻¹) detected among other trace metals. On the other hand, metal concentrations of Cr, Pb and Cd in influent wastewater explained that no industrial or mining wastewaters are channeled with the municipal wastewater. The relative abundance of trace metals in infiltrate and permeate samples followed the general order of Zn > Ni > Cu > Cd > V > Cr > As > Pb > Cd. Similar order of abundances of trace metals have been reported by other researchers in common municipal wastewaters (Chippas, 2003; Karvelas et al., 2003). The concentrations of Zn, Ni, Cu, and Co were highly fluctuating in the permeate samples, whereas the concentrations of V, Cr, As, Pb, and Cd were almost stable.

The removal efficiencies of trace metals in MBR process varied with respect to each element. An average removal of ~98% was achieved for Cd, Pb, and V, whereas about 60% removal was registered for Zn and Co. On the other hand, between 30% and 50% of Ni, Cu, As, and Cr were removed under the same operating conditions. Similar results are reported by other researchers (Bolzonella et al., 2010). In fact, the removal efficiencies are largely dependent on the initial concentrations of metals. In the present work, since the feeding source of wastewater was the effluent from primary clarifiers of WWTP, the removal of some metals is expected to start before reaching MBR system. When a raw wastewater undergoes clarification, a portion of trace metals is abated by adsorption onto solid particles (Chippas, 2003; Di Fabio et al., 2013). Moreover, the concentrations of trace metals in permeate were found to be far lower than the maximum allowable concentrations reported in the water quality guidelines.

Trace metals removal in MBRs can occur via various processes including precipitation of metals inside bioreactor, biosorption of metal ions on sludge or bacterial flocs, and reoxidation of some metals. In the present study, the pH inside the biological reactors was maintained at 6.6–7, therefore, both precipitation and biosorption mechanisms were expected for the removal of trace metals. Katsoy et al. (2011) reported an average removal of 80%–98% for Cu and Pb and to a lower extent 50%–77% for Ni and Zn by precipitation at pH 7–9. Malamis et al. (2011) has reported that beyond pH 6 the sludge biosorption rate is decreasing and chemical precipitation becomes dominant mechanism for metal removal. The gradual increase in pH generates more OH⁻ ions in the mixture which form complex precipitates with metals (Fu and Wang, 2011). A significant metals removal via biosorption can be suggested for the present work, since the precipitation mechanism should be dominant (and much faster than biosorption) in the pH of range 8–11 (Fu and Wang, 2011). Comte et al. (Comte et al., 2008) reported more favorable biosorption of metals at pH range of 6–9, in which activated sludge is negatively charged and provides potential sorption sites for metals. However, dominant metals removal mechanism via biosorption is observed at pH 4 for Pb and 6 for Cd, Cu and Zn when sludge is employed as sorbent (Hammani et al., 2007; Malamis et al., 2011).

Higher concentrations of Zn and Ni spotted in permeate might be attributed to the metal ions penetrated through the membranes due to their high solubility at aforementioned pH, which is consistent with the observation reported previously (Katsoy et al., 2011). However, in addition to the solubilization, these observations can be partially attributed to the unstable forms of Zn and Ni. On the other hand, removal of Cr, Pb, As, Cd, As, and Co remained relatively high which was possibly
due to the low pH required for solubilizing and their availability in stable form within the given pH. Enhanced removal of trace metals is reported with the increasing MLSS concentration as more sites are available for the sorption of soluble metal ions (Katsou et al., 2011; Malamis et al. 2011). On the contrary, Hammaini et al. (2007) reported relatively steady or reduced metal sorption capacity with the increase in MLSS concentration due to the screen effect between cells. Promising removal efficiencies of trace metals by different types of membranes such as ultra-filtration, reverse osmosis, nanofiltration and electrodialysis have been reported (Fu and Wang, 2011; Katsou et al., 2011). However, the higher removal efficiencies of most of the metals in the present study was attributed to the complete retention of TSS via MF membranes, which is in agreement with a previous study (Bolzonella et al., 2010). Furthermore, a substantial removal of trace metals is reported by a research study (Malamis et al., 2011), in which MF membrane was combined with activated sludge. On the other hand, an enhanced biofouling of trace metals on the problematic biofilm developed on membrane surface (fouling layer) than to the sludge flocs is reported in pilot-scale MBR (Di Fabio et al., 2013). Even though fouling has negative influence on membrane permeability, a fraction of metal removal could be originating from membrane fouling.

3.4.2. Trace metals in sludge (mixed liquor)

Average trace metal concentrations in activated sludge of MBR process are summarized in Table 5. To assess the toxicity of excess sludge from MBR process, it is very important to monitor trace metal accumulation in the bioreactor for the long term functioning (Bolzonella et al., 2010). Trace metals in sludge are present in several forms including metal precipitates in the sludge flocs, soluble metal ions, complexes of soluble metals and accumulated soluble metal in the microbial cells (Chipaia, 2003). Trace metals are non-biodegradable compounds, thus the total trace metal loading of feed wastewater will either end up in the sludge or remain in the treated effluent. In fact, trace metals released via excess sludge is more crucial than through treated effluent to the point-source of discharges (Karvelas et al., 2003). The frequency of occurrence of all trace metals in the sludge samples was 100% and same for the liquid samples. From the analytical results, Zn was the most abundant metal in sludge, whereas Cd exhibited the lowest abundance. However, the concentrations of Zn, Ni, Cu, Pb, and Cd were found to be under the allowable concentrations specified in the EU standard. As no limits are set for Ca, Cr, As by EU so far, their concentrations were compared with US regulations and also found under the MAC (the concentration threshold for V was not mentioned).

4. Conclusion

In this study, the performance of pilot-scale MBR unit, operated at low temperature conditions in Nordic regions, was investigated for the treatment of real municipal wastewater. An accelerated membrane fouling was observed during low temperature periods and while maintaining aeration intensity below the normal value. This resulted in a substantial decrease in membrane permeability (about 75%), leading to an increased frequency of membrane cleaning. The average reductions of 1.82, 3.02, and 1.94 log units were achieved for norovirus GI, norovirus GII, and enteroviruses, respectively. Removal efficiencies of V was not mentioned). The average removal efficiencies of BIS, DCF and BPA were 65%, 38%, and -97%, respectively. However, the MBR pilot did not show efficient removal of carbamazepine.

Overall, and based on European and American regulations, high quality permeate was achieved, demonstrating the aptitude of MBR system to perform satisfactory wastewater treatment during the winter season in Nordic regions and reclaim treated water and sludge for the agricultural and industrial sectors.

Acknowledgements

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<th>Metal</th>
<th>Influent concentration (average) [μg L⁻¹]</th>
<th>Permeate concentration (average) [μg L⁻¹]</th>
<th>Removal efficiency (Average) [%]</th>
<th>Maximum allowable concentration [μg L⁻¹]</th>
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<td>Ni</td>
<td>1433 ± 39</td>
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<td>Cu</td>
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Table 5: Average trace metal concentrations in sludge with maximum allowable concentrations as per International Standards.
Publication II

Khum Gurung, Mohamed Chaker Ncibi, Mika Sillanpää

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Removal and fate of emerging organic micropollutants (EOMs) in municipal wastewater by a pilot-scale membrane bioreactor (MBR) treatment under varying solid retention times

Khum Gurung⁎, Mohamed Chaker Ncibi, Mika Sillanpää

Department of Green Chemistry, School of Engineering Science, Lappeenranta-Lahti University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland

HIGHLIGHTS
• Fate of 23 EOMs in pilot MBR treatment at varying SRT was studied.
• At long SRT, EOMs removal majorly enhanced while SMP and EPS concentration lessened.
• Hormones and antibiotics were highly removed than diuretics and anti-epileptics.
• Iopamidol and hydrocortisone (~90% removal) were studied for the first time in MBR.
• MBR effluent fulfilled the water quality requirements for reuse.

GRAPHICAL ABSTRACT

This study investigates the removal and fate of 23 emerging organic micropollutants (EOMs) including a wide range of pharmaceuticals (antibiotics, β-blockers, analgesics, diuretics, psychostimulants, antiepileptics, immunosuppressives, anticoagulants), and steroid hormones detected in municipal wastewater by a pilot-scale membrane bioreactor (MBR) plant at two different solid retention times (SRTs) of 60 and 21 days. Different removal efficiencies of the selected EOMs were observed and explained based on their physicochemical properties (such as distribution coefficient, log D; dissociation constant, pKa; solid-water distribution coefficients, and Kd) along with process operating parameters. The dominant removal mechanisms of EOMs were biotransformation and sorption onto the sludge, which were confirmed by the mass balance study. Moreover, changes in the sludge properties, as a consequence of different SRTs, were evaluated based on variations in soluble microbial products (SMP), extracellular polymeric substances (EPS), and capillary suction time (CST). Finally, the quality of the MBR effluent was compared with some established guidelines, which confirmed the fulfillment of water quality requirements for reuse purposes.

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Keywords: Municipal wastewater treatment, Membrane bioreactor, Emerging organic micropollutants, Biotransformation/biodegradation, Solid retention times

1. Introduction

In recent decades, the occurrence of emerging organic micropollutants (EOMs) in the aquatic environment has received a global attention because of its possible environmental intimidations. Globally, a large number of EOMs have been frequently detected at source, and in treated...
efficient and wasted sludge at wastewater treatment plants (WWTPs) (Clara et al., 2005b; Trinh et al., 2012, 2016). Moreover, the occurrence of EOMs could endanger the reuse of reclaimed wastewater in achieving sustainable water management within the WWTPs (Behera et al., 2011). Most of the EOMs found in wastewater are of anthropogenic origin from various sources such as households, hospitals, veterinary surgeries, farms and pharmaceutical manufacturing (FOMs, which eventually end up at WWTPs (Clara et al., 2005b). Since conventional WWTPs are not specifically designed to eliminate EOMs, many of these EOMs pass through WWTPs and are thus eventually discharged into the environment (Behera et al., 2011; Jelic et al., 2011; Miège et al., 2009; Sim et al., 2010; Viero et al., 2005; Yang et al., 2011; Yung et al., 2009). Some countries such as Australia and Switzerland have adopted discharge guidelines for some EOMs (NHMRC/EPHC/NRMMC, 2008; countries such as Australia and Switzerland have adopted discharge guidelines for some EOMs (NHMRC/EPHC/NRMMC, 2008; Schröder et al., 2012; Tambosi et al., 2010), but the majority of other EOMs have not yet been addressed. However, recent amendment in directive 2013/39/EU has introduced more watch list substances, in which diclofenac has removed while malicidate antibiotics, methiocarb, niclosamide, metamizol, amoxicillin and ciprofloxacin have been added (EU, 2018).

To ensure compliance with future discharge requirements, interest in the ability of MBRs in the removal of EOMs from municipal wastewater has increased in recent decades. MBRs are becoming a mature technology in water management practices for wastewater reclamation and reuse due to their ability to produce superior-quality effluent, a relatively small footprint and little sludge (Judd, 2008; Meng et al., 2009). The removal mechanisms of EOMs involved in MBR treatment are complex and include biotransformation/biodegradation, adsorption to sludge, volatilisation, and physical retention by the membrane (Cirja et al., 2008). However, biotransformation and adsorption to biomass are often reported to be the dominant mechanisms for the removal of EOMs in the MBR process (Clara et al., 2005b; Kim et al., 2014; Radjenović et al., 2009). On that note, physicochemical properties such as distribution coefficient, log D, dissociation constant, pKₐ, solid-water distribution coefficients, and Kᵣ and functional groups associated with EOMs showed notable effects on their removal (Li et al., 2015; Tadkaew et al., 2011). At the pH above pKₐ, phenolic hydroxyl groups of some hormones dissociates that leads to the charge repulsion between the negatively charged hormone and negatively charged membrane (Schäfer et al., 2011). Naproxen and diclofenac (pKₐ values of 3.2 and 3.1, respectively) depolarised at a pH 7.8 and rejected by negatively charged membrane surface, whereas carbamazepine (pKₐ = 13.9) showed no ionisation at same pH level, hence attained a poor removal (Röhricht et al., 2009). At pH 6–7, tetracyclines (pKₐ = 3–4.5) are not charged, hence removed only via adsorption to sludge (Kim et al., 2005). The sorption onto sludge can be considered to be insignificant for EOMs with log Kᵣ ≤ 2.48 (Joss et al., 2000). The overall removal efficiencies of most of hydrophilic pharmaceuticals (log D < 3.2) were above 92% in the MBR (Trinh et al., 2016).

Often previous studies on the removal of EOMs by MBROs focused on the aqueous phase (Bo et al., 2009; Radjenović et al., 2009; Schröder et al., 2012; Trinh et al., 2012) and their mass load adsorbed in the solid phase was often neglected, which restricts the differentiation between the removal mechanisms via adsorption onto sludge and biotransformation. There is limited literature investigating the fate of EOMs in MBROs when treating real municipal wastewater (Kim et al., 2014; Radjenović et al., 2009; Trinh et al., 2016). Some researchers have estimated the contributions of the adsorption and biotransformation of EOMs based on values of Kᵣ from literature or by direct batch experiments (Clara et al., 2005a; Kimura et al., 2007). Additionally, previous studies on the fate of EOMs in MBR either mainly focused on pharmaceuticals and personal care products (PPCPs) (Radjenović et al., 2009; Suárez et al., 2012; Tambosi et al., 2010; Trinh et al., 2016) or are based on lab-scale batch experiments (Hai et al., 2018; Phan et al., 2014; Tadkaew et al., 2011; Wijpkoon et al., 2013). The influence of solid retention times (SRTs) on the removal mechanisms of PPCPs by MBROs has been studied by a few researchers (Clara et al., 2005b; Schröder et al., 2012; Tambosi et al., 2010), but these studies counted either estimated values of Kᵣ or negligible amounts of adsorbed fractions of PPCPs onto sludge, as well as a spiking of PPCPs in the MBRO system.

Based on the above identified research gaps, the current study investigates the removal dynamics of 23 frequently detected EOMs in the treatment of real municipal wastewater at an MBR pilot plant operated at two different SRTs. To the best of our knowledge, the removal and fate of EOMs such as isepamicin, hydrocortisone, furasemide, ciprofloxacin, tetracycline, and enalapril have rarely (if not) been studied in the past by MBR processes. A mass balance study was assessed to further confirm the removal mechanisms associated with different EOMs. Besides, the influence of physicochemical properties on the removal of EOMs was discussed. Additionally, the influence of SRTs on sludge characteristics including dewaterability, major foulants such as soluble microbial products (SMPs), and extracellular polymeric substances (EPS) was discussed. Finally, the quality of MBR-treated effluent in terms of EOMs was compared with some established guidelines.

2. Materials and methods

2.1. MBR system, operational protocol, selected EOMs and sample collection

A pilot-scale MBR system was employed in this study. The schematic diagram indicating major components of the MBR pilot plant is shown in Fig. 1. The key features of the MBR pilot plant is described in our previous work (Garung et al., 2016). Typically, the submerged flat-sheet membrane units (0.4 μm pore size) with membrane surface area of 16 m² (KUBOTA Co., Japan) were used for solid-liquid separation. A peristaltic pump (Thomas, Germany) was used to draw water in an intermittent suction mode. For in-situ cleaning of membranes, the clean-in-place (CIP) tank was also installed and connected with Sodium hypochlorite and Citric acid dosing tanks. Scouring air was supplied to maintain biological activities and to mitigate membrane fouling. The feed to the MBR pilot plant was taken continuously from the outlet of the primary clarifier at the Kenkäveronniemi WWTP, Mikkeli, Finland. This plant treats about 15,000 m³ of wastewater per day.

In this study, the pilot plant was operated in two different SRTs of 60 days and 21 days in order to investigate MBR performance in treating the pollution load of nutrients, organics, solids and, preferably, the removal of EOMs. Table 1 summarises the in-depth operational conditions of the MBR pilot plant for this study. The pilot plant was operated a protocol similar to that reported by other researchers (Van den Broeck et al., 2012). The SRT of 60 days was adapted ~10 weeks before the actual sampling periods in order to stabilize the activated sludge. However, relatively less adaption period of sludge (about a week) was maintained for SRT of 21 days by wasting required amount of sludge out of the system. Each of the two different SRTs were maintained for stable sludge period of 4 weeks. During the investigation, the permeate flow rate and the transmembrane pressure (TMP) were nearly constant (4–5 kPa), so no in-situ cleaning of membranes was necessary.

A set of 55 EOMs representing a wide range of pharmaceuticals, pesticide and steroid hormones with diverse physicochemical properties were selected. The study of these EOMs was made based on their increasing annual consumption, potential adverse impacts on health of human and aquatic animals, and stringent future regulations in the EU Water Framework Directive (EU, 2013) on pharmaceuticals and hormones. The physicochemical properties of studied EOMs were summarised in Table S1 (Supplementary Information). Weekly 24-h composite aqueous samples of influent (1 L), MBR permeate (1 L) and grab samples of sludge (0.5 L) were collected for 8 weeks (4 samples of each SRT). The sum total of samples included 8 influent, 8 effluent
and 8 sludge samples. All the collected samples including liquid and sludge phases were stored in dark and cold conditions (~$-18 ^\circ C$) before the analysis.

2.2. Mass balance calculation

To assess quantitatively the fate of the EOMs, the percentage shares of biotransformation/degradation, sorption and remaining in effluent were estimated using a mass balance approach (Jelic et al., 2011). The mass flow rates of EOMs in the influent, effluent and sludge were calculated by multiplying measured concentrations in given streams by the corresponding flow data. Then, mass load lost per unit of time ($\mu g/d$) due to all the processes that possibly occur during the MBR process and their relative distributions to the influent mass load were calculated according to the following Eqs. (1)–(4).

\[
\text{Overall removal (\%)} = \frac{Q_{\text{influent}} \times C_{\text{influent}} - Q_{\text{effluent}} \times C_{\text{effluent}} - Q_{\text{sludge}} \times C_{\text{sludge}}}{Q_{\text{influent}} \times C_{\text{influent}}} \times 100
\]  

(1)

Removal via sorption onto sludge (\%) = \frac{Q_{\text{sludge}} \times C_{\text{sludge}}}{Q_{\text{influent}} \times C_{\text{influent}}} \times 100
\]  

(2)

Remain in effluent (\%) = \frac{Q_{\text{effluent}} \times C_{\text{effluent}}}{Q_{\text{influent}} \times C_{\text{influent}}} \times 100
\]  

(3)

Removal via biotransformation (\%) = \text{Overall removal (\%)} - \text{Removal via sorption onto sludge (\%)}
\]  

(4)

where $Q_{\text{influent}}, Q_{\text{effluent}}, Q_{\text{sludge}},$ and $Q_{\text{excess sludge}}$ are the mass flow rate ($\mu g/d$) of influent, treated effluent and sludge, respectively.

2.3. Analytical methods

Chemical oxygen demand (COD), total suspended solids (TSS), ammonium nitrogen (NH$_4$-N), total nitrogen (TN), total phosphorus (TP), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were determined according to Standard Methods for the Examination of Water and Wastewater (APHA, 1999). The CST of sludge was measured using a capillary suction timer (Type 304 M, Triton, UK). The concentrations of EPS and SMP of the sludge were determined by previously described methods (Ramesh et al., 2006). At first, 25 mL of sludge sample was centrifuged at 4000 rpm at 4 $^\circ C$ for 30 min. The supernatant was filtered through a 0.45 $\mu m$ glass filter and measured for SMP. The obtained pallet was resuspended by adding 0.05% NaCl, mixed with vortex mixture and the solution was kept in a water bath (~100 $^\circ C$) for heat treatment for 60 min. Finally, the supernatant was filtered through a 0.45 $\mu m$ glass filter and measured for total EPS. Both SMP and EPS were analysed in term of dissolved organic carbon (DOC) using a TOC analyser (TOC-VSeries-CPN, Shimadzu, Japan).

The concentrations of EOMs in influent, permeate and sludge samples were analysed using standard solid phase extraction (SPE) followed by UPLC-MS/MS (modified EPA 1694 and modified EPA 539). The measurement uncertainty (MU) was 40%. The MU was calculated according to the Noreast TR 537 that covered every step in the laboratory analysis.

3. Results and discussion

3.1. Basic performance of MBR

As real municipal wastewater was fed into the MBR, the influent composition varies over time, and does the pollution removal efficiency.
Table 2 summarises the composition of influent wastewater during each period of SRT and the treatment efficiency of the MBR on conventional pollutants such as COD, NH₄-N, TN, and TP. The fluctuations on influent composition were not significant (Table 2). The pH of the effluent was around 7. The removal efficiencies of TSS, COD and NH₄-N were consistently high (>95%–99.5% respectively) at both SRTs. For two SRTs, the suspended solids in the effluent (L⁻¹), furrow below the 771 mg L⁻¹, caffeine (140.43 ± 6453 ng L⁻¹), hydrochlorothiazide (2035 ± 757 ng L⁻¹), paracetamol (93.60 ± 3384 ng L⁻¹), naproxen (1395 ± 276 ng L⁻¹), ibuprofen (41400 ± 565 ng L⁻¹), and diclofenac (1620 ± 194 ng L⁻¹), respectively were observed at the highest levels during the testing periods. 50% of the total EOMs in the influent was accounted for these eight compounds. The high concentrations of caffeine, naproxen and ibuprofen are consistent with previous papers (Kim et al., 2014; Trinh et al., 2012, 2016). An effective attenuation of caffeine (99.7%). These results are in agreement with many previous works (Kim et al., 2014; Trinh et al., 2012, 2016). An effective attenuation of caffeine via MBR was reported in some other studies (Maeng et al., 2013). Moreover, EOMs including anti-coagulant (opiodopil) and immunosuppressant (hydrosorcisine), whose fate was studied for the first time in the MBR process, were efficiently removed in the range of 96–99.6%. Regarding β-blockers, atenolol and bisoprolol were attenuated at consistently high removal efficiency (92–97%) at both SRTs, whereas two other β-blockers (metoprolol and propranolol) were attenuated slightly higher at a longer SRT of 60 days (82–84%) than in shorter SRT days of 21 (50–60%). Very high removal efficiencies of analogues (para- cetamol, ibuprofen, ketoprofen, naproxen) were observed ranging from 96 to 99.9%. The higher removal of paracetamol is due to its structure that allows unrestricted access of bacteria and enzymes to the sterically unprotected molecule that is then subsequently modified (Tambosi et al., 2010). Moreover, the removal of ibuprofen, ketoprofen and naproxen is partially accompanied by the heterotrophic bacteria community, which is highly favourable in extended SRTs, and less so by slow-growing ammonia-oxidising bacteria (Falas et al., 2012). The higher removal efficiencies of analogues are in agreement with those reported by many researchers (Kim et al., 2014; Radjenović et al., 2009; Schröder et al., 2012; Tambosi et al., 2010). On the other hand, diclofenac (analogic) was attenuated at relatively low efficiency compared to other analogues with median removal efficiencies of 38% and 45% at SRTs of 60 days and 21 days, respectively. A great discrepancy in the removal efficiency of diclofenac via MBR was reported in some
Fig. 2. Occurrences of EOMs in MBR process at two different SRTs (60 days and 21 days) arranged according to their Log D(at pH7) values. EOMs with concentration lower than LOQ are not included.

Fig. 3. Median removal efficiencies of EOMs in MBR process at different SRTs. The removal efficiencies of EOMs with their detection in influent - LOQ are not presented. The LOQ values of EOMs in the effluent are used to calculate % removal whenever measured concentrations are below LOQ. Error bar represents the standard deviation calculated from the duplicate samples taken once in a week.
The diuretics (furosemide and enalapril), which were rarely studied in MBRs, were highly attenuated at both the SRTs with median removal efficiencies of 87% and 96%, respectively. These results are consistent with the previous study (Kim et al., 2014). On the other hand, the attenuation of diuretics (hydrochlorothiazide) was very low or hardly removed at all in this study. During SRT of 21 days, the removal efficiency ranged from ~52% to 13% (median ~15%), which was slightly enhanced at SRT of 60 days achieving removal efficiency between ~19% and 41% (median 10%). The comparably poor removal of hydrochlorothiazide (~5%) is reported by other researchers when treating municipal wastewater with full-scale MBR (Radjenović et al., 2009). The increased concentrations of hydrochlorothiazide in treated effluent, more than the influent levels (i.e. negative removal efficiency), might be due to the transformation of metabolites such as unmeasured products of the human metabolism and/or metabolites that could be converted back to their parent compounds during the biological treatment process. This phenomenon of “negative removal” was also reported in other studies (Jelic et al., 2011).

The attenuation of an anti-epileptic drug (carbamazepine) was very low and frequently not removed, regardless of varying SRTs. At an SRT of 60 days, the median removal efficiency of carbamazepine was close to 2% (not removed in two samples out of four), whereas non-removal was observed (median ~8%) at an SRT of 21 days. This means that, in most of the events, effluent concentrations of MBR were greater than influent levels. The major metabolite of carbamazepine in humans is 10,11 epoxy-carbamazepine, which is excreted principally as glucuronide-conjugates (Korpi et al., 2013). These glucuronide-conjugates can presumably be excreted effectively by the MBR, achieving steady removal efficiency of 99.9% (median 99%) for atenolol, caffeine, paracetamol, naproxen, ibuprofen, estradiol and progesterone. Similarly, high biotransformation rate was accounted to iopamidol, furosemide and trimethoprim (58–92%, median 86%). Moderate biotransformation was observed for diclofenac (median 33%). Enhanced biotransformation of metoprolol, hydrochlorothiazide, and propranolol were achieved at SRT of 60 days (78%, 27% and 51%) compared to SRT of 21 days (37%, 0% and 0%, respectively). On the other hand, carbamazepine showed high resistance to biotransformation, so was highly detected in the effluent. The biotransformation proportions observed for naproxen, ibuprofen, trimethoprim, enalapril, atenolol, metoprolol and furosemide are consistent with previous studies (Jelic et al., 2011; Joss et al., 2008; Kim et al., 2014).

On the other hand, some of the EOMs were observed to be removed via sorption to sludge as indicated in Fig. 4. EOMs can be sorbed to sludge and subsequently removed while wasting the excess sludge from the bioreactor. The mechanism of sorption occurs via adsorption and desorption (Li et al., 2015). Sorption occurs due to the hydrophobic interactions of the aliphatic and aromatic groups of EOMs with the lipophilic cell membrane of some microorganisms and the fat fractions of sludge, whereas adsorption involves the electrostatic interactions of the positively charged (e.g., amino groups) to negatively charged surface of microorganisms (Jelic et al., 2008). Most of the EOMs were frequently detected in the sludge under LOQ (10 to 500 ng L\(^{-1}\)), median 100 ng g\(^{-1}\)) (Fig. S1). Other EOMs were detected in the range of 38–3750 ng g\(^{-1}\) (median 275 ng g\(^{-1}\)) at which ciprofloxacin followed by hydrochlorothiazide were the highest detected in the sludge. This result is in agreement with a previous study, where ciprofloxacin was most frequently detected in MBR sludge, although the concentration level was considerably higher (~10⁴ ng g\(^{-1}\)) (Kim et al., 2014). From the results, ciprofloxacin posed a serious challenge due to very strong affinity to the sludge with a sorption fraction of ~90%. Relatively higher sorption of ciprofloxacin is reported by many researchers (Kim et al., 2014). Biosorption as a dominant mechanism for the removal of ciprofloxacin is explained by many authors (Githini et al., 2011; Guerra et al., 2014). Similarly, propranolol, carbamazepine and testosterone showed moderate sorption efficiency to the sludge (10–50%, median 32%), whilst weak sorption affinities were observed for rest of the EOMs (0–21%, median 6%).

In order to better understand the fate of EOMs due to sorption to the sludge, sludge-water distribution coefficients or sorption coefficients (\(K_d\)) for high sorption fractions of ~90% and moderate fraction (10–50%) were 3.0 to 4.9 (Fig. 4), demonstrating their removal by strong sorption to sludge. These results are comparable with the findings of other researchers (Kim et al., 2014). Nevertheless, many compounds which showed a high degree of removal via biotransformation (e.g. tetracycline, bisoprolol, enalapril, ketoprofen, ibuprofen, hydrocortisone, estradiol and progesterone) accounted for the high log \(K_d\) values (3.9 to 4.3), indicating that these EOMs are attenuated simultaneously by biodegradation and partitioning onto biosolids (Guerra et al., 2014). On the other hand, the relatively low value of log \(K_d\) (2.6)
to 3.0) was calculated for diclofenac, carbamazepine and hydrochlorothiazide, indicating their poor removal efficiencies via sorption. In general, the higher biotransformation of EOMs was followed by lower sorption potential, which was not in accordance with the calculated log Ka. These results suggest that log Ka values may vary plant-to-plant depending on operating conditions and the extent of removal efficiencies (Kim et al., 2014). Indeed, the biotransformation of EOMs is enhanced by the sorption process due to the longer retention time of solids in the MBR process (Tadkaew et al., 2011).

3.5. Other factors influencing the removal of EOMs in MBR

Hyrophobic interaction is also one of the key mechanisms controlling biosorption of EOMs, hence the removal efficiencies in MBR processes (Cirja et al., 2008). Most of the EOMs quantified in the influent load at both testing periods were hydrophobic (log DpH < 3.2) (Hai et al., 2018; Tadkaew et al., 2011; Wijekoon et al., 2013) ranging from pharmaceuticals to steroid hormones. Of the four hormones, only testosterone, estrone and progesterone are hydrophobic (log DpH > 3.2) (Fig. 3). Hydrophobicity can be defined by log Kow for non-ionic and log D for ionic compounds (Taheran et al., 2016). All three hydrophobic EOMs showed consistently high removal efficiencies of 96–99% (median 97%). Similar results have been reported in other studies (Suárez et al., 2012). The higher removal efficiency of hydrophobic compounds might be due to: (i) the dominating mechanism of sorption to the sludge that facilitates enhanced biological degradation, and (ii) possessing only e-donating groups (EDGs) that enhance better oxidation (Tadkaew et al., 2011). High log D is characteristic of hydrophobic EOMs, poor hydrosolubility and high sorption tendency on organic constituents of sludge matrix (Cirja et al., 2008). Moreover, the calculated log Ka values of these EOMs were above 4, indicating substantially high sorption affinity to the sludge.

On the other hand, the removal of hydrophilic EOMs (log DpH < 3.2) varied from 'limited removal' (carbamazepine and hydrochlorothiazide) to almost complete removal (paracetamol, caffeine and ibuprofen). It is very obvious that the removal of hydrophilic EOMs varies significantly since they have diverse molecular structures and functional groups (Table S1). Varying removal efficiencies accounted for in hydrophilic EOMs can be explained based on the qualitative framework by Tadkaew et al. (Tadkaew et al., 2011) as: (i) compounds possessing only EDGs (slightly hydrophobic such as estriol) could achieve high removal (>99%); (ii) compounds possessing both EDGs and e-withdrawing (EWGs) such as amide and chloride in their molecular structure (Tadkaew et al., 2011; Wijekoon et al., 2013) including paracetamol, ibuprofen, diclofenac, hydrocortisone, naproxen, propranolol, romemprin, ciprofloxacin, bisoprolol, caffeine, furosemide, metoprolol, tetracycline, atenolol and isopamidol with varying removal efficiencies ranging from 37 to 99.9%; (iii) compounds possessing only strong EWGs such as hydrochlorothiazide and carbamazepine (0–10%). Therefore, the dominating removal mechanism of hydrophobic compounds is strongly influenced by their intrinsic biodegradability as sorption to sludge is less significant (Tadkaew et al., 2011).

Another aspect may be the degree of ionisation (pKa) of the selected EOMs, which controls their ionisation state as a consequence of pH variation in the solution. For EOMs including ibuprofen, diclofenac, naproxen, ketoprofen, enalapril, caffeine, furosemide, tetracycline and ciprofloxacin possessing a pKa of between 0.52 and 6.43 (Table S1), removal efficiencies varied from 38 to 99%. The results are partially consistent with the previous work, where acidic EOMs showed low removal efficiency in neutral pH condition. This might be related to the fact that these EOMs are negatively charged at neutral pH due to the presence of carboxyl functional group in their structures (Urase et al., 2005). Likewise, EOMs with pKa values of 7 to 15 (Table S1) showed varied removal efficiencies ranging from ‘non-removal’ to -97%, with the
lowest being carbamazepine and hydrochlorothiazide and the highest being paracetamol. Carbamazepine and hydrochlorothiazide both have a basic amine functional group, which may be protonated to gain a positive charge under neutral pH (Ngihm and Khan, 2007; Utase et al., 2005). This phenomenon may have increased their hydrophlicity which was confirmed by their noticeably higher concentrations in the MBR effluents (Fig. 5).

The molecular weights (MWs) of the selected EOMs varied from 151 g mol$^{-1}$ (paracetamol) to 777 g mol$^{-1}$ (iopamidol) in this study (Table S1). However, the removal tendencies of EOMs in relation to MWs were not clear. For example, paracetamol and caffeine were almost completely removed although their MWs were the lowest on the list (151 and 194 g mol$^{-1}$), whereas the removal efficiencies of other EOMs with MWs ranging from 206 to 777 g mol$^{-1}$ varied from non-removal to 99.6%. EOMs with higher MW may provide more branches that allow microbes to selectively cleave certain target sites and subsequently initiate degradation (Tadkaew et al., 2011).

Furthermore, the average MLSS concentrations inside the reactor were 8.5 ± 0.8 g L$^{-1}$ (paracetamol) to 77.7 g L$^{-1}$ (iopamidol) in this study (Fig. 5). However, the removal tendencies of EOMs in relation to MWs were not clear. For example, paracetamol and caffeine were almost completely removed although their MWs were the lowest on the list (151 and 194 g mol$^{-1}$), whereas the removal efficiencies of other EOMs with MWs ranging from 206 to 777 g mol$^{-1}$ varied from non-removal to 99.6%. EOMs with higher MW may provide more branches that allow microbes to selectively cleave certain target sites and subsequently initiate degradation (Tadkaew et al., 2011).

Furthermore, the average MLSS concentrations inside the reactor were 8.5 ± 0.8 g L$^{-1}$ and 3.7 ± 1.1 g L$^{-1}$ at SRTs of 60 days and 21 days, respectively. Results showed that the removal of metoprolol, hydrochlorothiazide, propanolol and carbamazepine was enhanced while operating the MBR at high SRT (i.e. high MLSS concentration) (Fig. 3). At increasing SRTs, the amount of sludge wasted from the bio-reactor decreases, which allows longer retention and subsequent degradation of less polar EOMs in the system. The higher specific area provided by increasing MLSS concentration enables more enzymatic activities (Cirja et al., 2008).

3.6. Influence of SRTs on sludge characteristics

Fig. 5 shows the variations in SMP and EPS during the MBR treatment at two different SRTs. Although the TMP profile of the MBR system was quite stable during the testing periods of both the SRTs, noticeable differences in the concentrations of SMP and EPS were observed. SMP concentration increased from 5.6 to 15.5 mg gMLVSS$^{-1}$ during the testing periods of both the SRTs, noticeable increase in viscosity that demands high scouring air involved in the pilot operation. Many researchers reported that the release of SMP and EPS concentration decreases as the sludge stays longer in the bioreactor, and increases when lowering the SRT (Grelier et al., 2006; Meng et al., 2009). The presence of EOMs in MBR may affect microbial activities and the structure community of microorganisms in activated sludge, which increases the endogenous respiration rates and subsequently releases EPS (Avella et al., 2010).

However, studying the extent of EOM influence on releasing SMP and EPS was out of the scope of this study.

Furthermore, the dewaterability of MBR sludge was also assessed at both SRTs in terms of their corresponding CST values (Fig. 5). The average CST of the sludge operated at an SRT of 60 days (31 s) was about twice as high as at an SRT of 21 days (15 s). An increasing trend of sludge CST with increasing SRT is reported by other researchers, which indicates that the sludge with high CST is difficult to dewater due to the high content of bound water (Ng et al., 2006). Also, increasing SMP and EPS concentrations indicated the decreasing CST of sludge due to increased fractions of fine and colloidal particles, and vice versa (Grelier et al., 2006).

3.7. MBR effluent quality in compliance with Australian and Swiss guidelines

To evaluate the quality of MBR-treated effluent in terms of EOMs concentrations, the observed concentrations of EOMs were studied in compliance with the Australian (NHMRC/EHC/ NRMMC, 2008) and Swiss guideline values (Oekotoxzentrum Centre Ecotox, 2016) (Table 3). Nevertheless, no guidelines or standards have yet been proposed for EOMs selected by the EU. A wider range of pharmaceuticals and steroid hormones was established in the Australian guidelines than in the Swiss guidelines. Most of the studied EOMs were observed well below the guideline values of both the standards (Table 3). No steroid hormones were detected above their LOQs, which were lower than both the guidelines. Among diuretics, enalapril was detected below the LOQ (10 ng L$^{-1}$), whereas hydrochlorothiazide and furosemide were frequently detected in the range of 185–1700 ng L$^{-1}$ in treated sludge. Similarly, immunosuppressive (hydrocortisone) was not detected above its LOQ, but no guidelines for diuretics and immunosuppressives are available or have been proposed so far. Caffeine was detected at a concentration of 60–328 ng L$^{-1}$, which was lower than the guideline value of 350 ng L$^{-1}$. However, it showed excellent removal efficiency of 99% in MBR treatment since the influent concentration was very high (140,427 ± 6453 ng L$^{-1}$). Regarding poorly removed carbamazepine, the observed concentration of 480–665 ng L$^{-1}$ was lower than both guidelines. Overall, the results indicated that the quality of effluent by MBR treatment fulfilled the water quality requirements for reuse purposes, regardless of varying SRTs.

4. Conclusion

The removal and fate of selected EOMs by the MBR pilot plant at varying SRTs were studied. Only 23 EOMs were detected in the influent wastewater during the testing periods above their LOQs. Diverse removal dynamics for selected EOMs were observed. The application of mass balance assessment proved that biotransformation and sorption onto sludge were the dominant mechanisms associated with the removal of EOMs. Even though the EOMs removal efficiencies were not that significant at SRTs of 21 and 60 days, enhanced removal of the majority of EOMs were observed at longer SRT. Therefore, SRT of 60 days would be preferred to be implemented, which would additionally help in releasing less concentrations of SMP and EPS. This study has expanded the understanding of the removal and fate of the EOMs (some
Table 3
Comparison of median concentrations of EDCs in MBR effluent with Australian and Swiss guidelines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (ng L⁻¹)</th>
<th>Australian guideline</th>
<th>Swiss guideline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MBR Effluent - values</td>
<td>SRT 60</td>
<td>SRT 21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(NHMRC/EPHC/NRMMC)</td>
<td>(Osokosentrum Centre Ecosia, 2010)</td>
</tr>
<tr>
<td>Ipratropium</td>
<td>200 (250)</td>
<td>400 × 10³</td>
<td>n.p.</td>
</tr>
<tr>
<td>Tetraclorine</td>
<td>10 (10)</td>
<td>105 × 10³</td>
<td>n.p.</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>100 (350)</td>
<td>25 × 10⁵</td>
<td>750 × 10³</td>
</tr>
<tr>
<td>Caffeine</td>
<td>328 (305)</td>
<td>350</td>
<td>n.p.</td>
</tr>
<tr>
<td>Bisoprolol</td>
<td>11 (15.5)</td>
<td>630 × 10³</td>
<td>n.p.</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>50 (51.5)</td>
<td>250 × 10³</td>
<td>380</td>
</tr>
<tr>
<td>Enalapril</td>
<td>70 × 10³</td>
<td>210 × 10³</td>
<td>10 (10)</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>1350</td>
<td>n.a.</td>
<td>n.p.</td>
</tr>
<tr>
<td>Hydrocortisone</td>
<td>1700</td>
<td>n.a.</td>
<td>n.p.</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>5 (5)</td>
<td>3.5 × 10³</td>
<td>n.p.</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>28.5 (42)</td>
<td>70 × 10³</td>
<td>210 × 10³</td>
</tr>
<tr>
<td>Propranolol</td>
<td>31 (31.5)</td>
<td>40 × 10³</td>
<td>12 × 10⁵</td>
</tr>
<tr>
<td>Paracetamol</td>
<td>325 (90)</td>
<td>175 × 10³</td>
<td>n.p.</td>
</tr>
<tr>
<td>Naproxen</td>
<td>19.5 (84)</td>
<td>220 × 10³</td>
<td>800 × 10³</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>59 (56)</td>
<td>400 × 10³</td>
<td>1700 × 10³</td>
</tr>
<tr>
<td>Doxiflucin</td>
<td>760 (1050)</td>
<td>180 × 10¹</td>
<td>n.p.</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>480 (405)</td>
<td>100 × 10³</td>
<td>2000 × 10³</td>
</tr>
<tr>
<td>Estradiol</td>
<td>&gt;5 (10)</td>
<td>7 × 10⁵</td>
<td>n.p.</td>
</tr>
<tr>
<td>Progesterone</td>
<td>&gt;5 (10)</td>
<td>105 × 10³</td>
<td>n.p.</td>
</tr>
<tr>
<td>n.a. values not available; n.p. not proposed; &quot; denotes below LOQ.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of which were never or rarely studied before in MBR) via MBR treatments under different operating conditions (i.e., SRTs), which certainly helps in achieving more sustainable water management.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.02.308.

References
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Removal of carbamazepine from MBR effluent by electrochemical oxidation (EO) using a Ti/Ta2O5-SnO2 electrode

Khum Gurung*, Mohamed Chaker Neibi†, Marina Shestakova†, Mika Sillanpää‡,§

* Laboratory of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Savonkatu 12, FI-50130, Mikkeli, Finland
† Department of Civil and Environmental Engineering, Florida International University, Miami, FL, 33174, USA
‡ Laboratory of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Savonkatu 12, FI-50130, Mikkeli, Finland
§ Department of Civil and Environmental Engineering, Florida International University, Miami, FL, 33174, USA

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ABSTRACT

This study aims at investigating the electrochemical oxidation (EO) of carbamazepine (CBZ) synthetic solutions and real membrane bioreactor (MBR) effluent using newly developed Ti/Ta2O5-SnO2 electrodes to enhance CBZ removal. The characterization of the prepared Ti/Ta2O5-SnO2 electrodes was performed by using scanning electron microscope, energy dispersive X-ray spectroscopy, atomic force microscope, and cyclic voltammetry analyses. The main operating parameters influencing the CBZ removal efficiency in synthetic solutions using Ti/Ta2O5-SnO2 electrodes were evaluated including the applied current density, initial CBZ concentration, pH, and temperature. The optimum removal of CBZ (20 mg L−1) and TOC reached 75.5% and 71.1%, respectively, after 8 h of electrolysis, under current density of 9 mA cm−2, pH 6, temperature of 30 °C, and using 0.1 M Na2SO4 as supporting electrolyte. Increasing current density and temperature influenced the CBZ removal, unlike pH which did not have significant influence on CBZ removal. The performance of Ti/Ta2O5-SnO2 electrode was compared with conventional Ti/PbO2 electrode in terms of CBZ removal efficiencies and stability of the electrodes. The results showed that under the same operating conditions, the CBZ removal efficiency of Ti/PbO2 electrode was slightly higher than of Ti/Ta2O5-SnO2 (77.9 and 71.7%, respectively). Nonetheless, the use of this newly developed electrode is more energy-efficient as it required the lowest energy consumption of 60.3 kWh m−3 to achieve optimum CBZ removal, in addition to fact that no heavy metals were leached (unlike the PbO2 electrode). Furthermore, a complete degradative removal of real MBR effluents spiked with CBZ was achieved when electrolyzed under the optimized conditions of CBZ synthtic solutions. Overall, the EO based on the use of Ti/Ta2O5-SnO2 electrode was found to be a reliable approach to remove CBZ from contaminated waters, with promising potential for integration with MBR technology to remediate CBZ.

1. Introduction

Pharmaceutically active compounds (PhACs) have gained a great deal of attention among researchers in recent years as emerging micropollutants with long-term potential threats to aquatic environment and human health [1–4]. These PhACs are introduced to aquatic ecosystems primarily from the effluents of wastewater treatment plants (WWTPs). In addition, direct and unsafe discharge of untreated wastewaters from agriculture, industries and hospitals are also reported to contribute to the release of PhACs into the aquatic ecosystems [2,3,5–7].

Carbamazepine, which is used for the treatment of epilepsy, depression, trigeminal neuralgia and wide variety of mental disorders, is one of the frequently identified PhAC in various aquatic environments [2,3,5]. The world-scale annual consumption of CBZ is more than 1000 tons and about 28% of it ends up in WWTPs as unmetabolized forms. [3,5]. In Finland, the annual consumption of CBZ is around 3.3 tons, with comparatively more concentrations in winter seasons than in summer at WWTP effluents [8]. CBZ is highly recalcitrant to biodegradation in conventional activated sludge processes and photo-degradation (more than 100 days) [2]. In fact, many researchers have documented difficulties in removing CBZ, with biodegradation removal of only less than 10% [3,4,6,8]. Thus, it is crucial to apply highly efficient degradation technologies for the removal of CBZ in order to achieve the highest mineralization or generate non (or less) toxic intermediates.

In this context, MBRs have been studied for the removal of various PhACs including CBZ by many researchers [9–11]. However, a relatively low removal (0–28%) of CBZ was reported in MBR processes when treating synthetic and real wastewaters [2,9,11]. Thus, biodegradation and membrane filtration alone are not efficient enough for the removal of CBZ. Therefore, in order to meet the future legislations...
MO environment, formation of polymer
vation of electrodes, related either to the poor mass transfer, corrosive
intermediate step of higher oxide formation (Eqs.(2) and (3)) [14, 16].
thus allow only selective oxidation of organics (R), which involves in-
H2O + MOx + H+ + e– (OH) generated from water oxidation (Eq. (1)) [13, 14]. Hy-
droxy radicals are extremely reactive oxidants (2.8 V (vs. SHE)) with
the life time of less than a second, which makes their detection very
challenging [15]. The subsequent oxidation mechanism of organic
compounds depends on the behavior of anodes, which are divided as
“non-active” and “active” [13–16]. In both cases, firstly, water mole-
cules splitted and leading to the formation of OH at the anode oxide
surface (MOx) (Eq. (1)) [17].

\[ \text{H}_2\text{O} + \text{MO} + \text{MO}_{\text{ac}} + \text{H}^+ + e^- \]  
\[ (\text{OH}) \]  
\[ (\text{Eq. (1))}] [17]. 

At ‘active’ anodes, OH radicals are chemisorbed (strongly adsorbed),
thus allow only selective oxidation of organics (R), which involves in-
termediate step of higher oxide formation (Eqs. (2) and (3)) [14, 16].

\[ \text{MO}_{\text{ac}} + \text{R} + \text{MO} + \text{EO} \]  
\[ (\text{Eq. (2))}] [14, 16]. 

On the other hand, at ‘non-active’ anodes, the formation of higher
oxide is excluded and OH radicals are physisorbed without interaction
on the anode surface [14, 16]. Moreover, ‘non-active’ anodes with high
O2 overpotential towards water oxidation exhibit high electrochemical
stability and can generate many strong (OH) radicals predominantly
leading to the complete combustion of organics (Eqs. (4)) [15–17].

\[ \text{MO}_{\text{ac}} + \text{H}^+ + \text{e}^- \rightarrow \text{MO} + \text{H}_2\text{O} \]  
\[ (\text{Eq. (4))}] [15–17]. 

The major problems of EO process are the polarization and passi-
vation of anodes, hence reducing the rate of electrochemical reaction
in real wastewater. To overcome these, noble metal oxide interlayers due
to the considerable porosity in supported catalyst
films. [14, 15, 16]. In any cases, those phenomena result in the at-
tenuation of the efficiency and service life of electrodes.

Various anodes such as PbO2 and more recently, boron-doped
diamond (BDD) have shown an interesting electro-degradation effi-
ciency for CBZ [2, 3, 6]. Nevertheless, the higher cost of BDD electrodes
and the possible leaching of lead (Pb) from PbO2-coated electrodes tend
to remove the surface impurities and deformations, and then oven
dried at 105 °C. Thus, the precursor material deposited only one side
of Ti substrates had surface area of 50 cm² and the deposited material
was equal to 1.10 mg cm⁻² ± 5%.

2. Materials and methods

2.1 Reagents and materials

All the reagents and materials used were of analytical grade. CBZ
(meets USP testing specifications), Titanium foil (99.7% trace metal
basis, 2 mm thick), SnO2/C2H4O (≥ 99.99% trace metal basis), NaOH (≥ 99.99% trace metal basis), Na2SO4 (99.9% anhydrous), H4P2O7 (85%),
Na2SO4 (~ 99% anhydrous) were purchased from Sigma-Aldrich, USA.

Commercial Ti/PbO2 electrodes (5 cm × 10 cm × 2 mm) were sup-
plied by Magneto, Netherlands.

A synthetic stock solution containing CBZ (20 mg L⁻¹) was pre-
pared using Milli-Q water (18.2 MΩ cm), stirred at 500 rpm for 24 h at
room temperature [5]. Then, 0.1 M (14.2 mg L⁻¹) of Na2SO4 (better
supporting electrolyte than NaCl regarding economical, effectiveness
and environmental aspects) was added to increase conductivity of the
solution. In this regard, the possible formation of organic chloride
products is also limiting the use of NaCl in electrochemical processes
[5]. Finally, the synthetic stock solution was stirred in the refrigerator at
4 °C for further use.

2.2 Preparation of Ti/Ta2O5-SnO2 electrodes

Ti/Ta2O5-SnO2 electrodes were prepared by thermal decomposition of
precursor solutions on Ti substrates [25]. For the preparation of the electrodes, the methodology is detailed in a previous study conducted in
our laboratory [26]. The optimized nominal composition of Ta (7.5 at.%) and Sn (92.5 at.%) were used to prepare precursor solutions by
dissolving SnCl2·2H2O and TaCl5 salts in absolute alcohol (pro analysis,
Panreac), where total concentration of metal ions was kept constant
(0.04 M). At first, Ti substrate plates (5 cm × 10 cm × 2 mm) were
pre-treated by mechanical polishing and followed by degreasing in
10 wt.% NaOH for 10 min and etching in boiled 18 wt.% HCl (pro analysis,
Fluka) for 30 min, and finally rinsed carefully using Milli-Q water. Secondly, the precursor solution was applied only one side
of the pre-treated Ti substrates by drop casting method. The precursor
solution of 1 mL volume was dropped on to the Ti substrate, uniformly
distributed using the tip of a Pasteur glass pipette, dried in oven at 80 °C
for 5 min, and then annealed in muffle furnace at 550 °C for 5 min. The process
was repeated until 8 layers of ultrathin film deposition of the precursor
solution, which attributed highest electro-catalytic properties
of the electrodes [26]. After the final layer, electrodes were additionally
annealed at 550 °C for 10 h to enhance the formation of composite
oxide of Ta and Sn on the electrode surface via thermal-decomposition.
The final composite oxides on Ti substrate gave the wide band gap n-
type SnO2 semi-conductor extrinsically doped with TaOx. After 10 h,
electrodes were cooled down and kept in an ultrasonic bath for 5 min in
order to remove the surface impurities and deformations, and then oven
dried at 105 °C. Thus, the precursor material deposited only one side
of Ti substrates had surface area of 50 cm²
and the deposited material
was equal to 1.10 mg cm⁻² ± 5%.

2.3 Physicochemical and electrochemical characterization of the electrodes

Microstructure of the Ti/Ta2O5-SnO2 electrodes was analyzed by
using scanning electron microscope (SEM) (Hitachi, SU3500, Japan)
using 5 kV of acceleration voltage. The chemical analysis of selected
areas of the electrode surface was performed with energy-dispersive X-
ray spectroscopy (UltraDry™ Compact EDS Detector, Thermo Fisher,
USA). The AFM images were taken by using atomic force microscope
(AFM) (NX10, Park, Korea) using the non-contact mode.

The electrochemical characterization of the Ti/Ta2O5-SnO2 elec-
trode was performed by conducting cyclic voltammetry (CV) mea-
surements using an Autolab (PGSTAT 12 Potentiostat/Galvanostat,
Metrohm, Switzerland) connected with GPES software (Eco Chemie, Netherlands). All the CV measurements were performed in a three electrode cell (100 mL). A coiled platinum wire was used as counter electrode and saturated calomel electrode (SCE) as reference electrode, whereas Ti/Ta2O5-SnO2 electrode (1 cm × 1 cm) was used as working electrode. First, the voltammograms were recorded at different scan rates from 20 to 100 mV s⁻¹ in 0.1 M Na₂SO₄ aqueous solution between 0.6 and 0.8 V (vs. SCE), where only double-layer currents (non-faradic) were observed for estimating the relative roughness factor. Second, the voltammograms were plotted between the anodic currents against electrical voltage between 0.2–2.5 V (vs. SCE) at scan rate of 100 mV s⁻¹ with or without CBZ in 0.1 M Na₂SO₄ aqueous solution. In each of the assays, aqueous solution inside the CV cell was deoxygenated by argon bubbling prior to the measurements.

2.4. Electrochemical degradation assays

The experimental set-up for the electrochemical degradation system is shown in Fig. S1. The CBZ-containing solutions were electrolyzed using an open glass reactor of 500 mL capacity with cooling jacket for the circulation of thermostated water, under a 500 rpm stirring. The reaction temperature was maintained at 11 ± 1 °C. The electrochemical unit consisted of Ti/Ta2O5-SnO2 electrode as anode and pure Ti plate (same area) as cathode, with an inter-electrode gap of 10 mm. The electrical power was applied via DC power supply (EX752M-Multimode PSU, TTI, UK) with maximum current and potential rating of 4A and 150 V, respectively. All the electrochemical degradation assays were performed under galvanostatic conditions. Each experiment was run for 8 h with sampling every hour.

2.5. Analytical methods

2.5.1. CBZ measurements

The removal of CBZ was analyzed by UV–vis spectrophotometer (Lambda 45, Perkin Elmer, USA) by measuring the absorbance of UV light by CBZ at 210 nm. A calibration curve was created by scanning different concentrations of CBZ from 1 to 30 mg L⁻¹ (Fig. S1, Supplementary data) in order to calculate the residual CBZ concentration and thus the removal efficiency. As for the real MBR effluent, since the spiked samples have low concentration of CBZ (10 μg L⁻¹), they were analyzed with LC-MS/MS (Acquity UPLC/Xevo TQMS, USA) using 5 cm C18 column (Acquity UPLC BEH, USA).

2.5.2. Other measurements

Non-Purgeable Organic Carbon (NPOC) was measured with TOC-analyzer (TOC-V Series-CPN, Shimadzu, Japan) to evaluate the mineralization efficiency. The pH was measured using pH meter (pH 110, VWR). The electrical conductivity was monitored by using conductivity meter (Eurocan Con 6, EUTECH, USA).

The energy consumption (EC) needed for the electrochemical treatment per volume of working solution was calculated based on Eq. (5) [15].

\[
EC \ (\text{KWh} \ \text{m}^{-3}) = \frac{U_{\text{cell}} \cdot I \cdot t}{V_s} \tag{5}
\]

where \(U_{\text{cell}}\) is the average potential difference of the cell (in V), \(I\) is the applied current (in A), \(t\) is the electrolysis time (in h), and \(V_s\) is the working solution volume (in dm³).

3. Results and discussion

3.1. Microstructural characterization

SEM and AFM micrographs of Ti/Ta₂O₅-SnO₂ electrode before and after the 8 h of electrolysis (Fig. 1a–f) showed foam-like porous microstructure with large numbers of relatively homogenous agglomerates mainly related to the density of Ta₂O₅ crystals, which can partially increase the surface roughness. In fact, the porosity and relative surface roughness depend on the active oxide layers. When the electrode was subjected to electrolysis for 8 h, the surface exhibited structural changes in the surface showing heterogeneously-distributed porous network and more rough structure as shown in Fig. 1d–e.
Likewise, the AFM analysis before electrolysis shows a more even topography of the electrode surface as shown in Fig. 1c. Whereas, the surface structure of the electrode after the 8 h of electrolysis depicts more deformed surface with visible deep and extended valley (dark spots in Fig. 1f). The depth of undulations was noted to be ± 1.5 μm and ± 4 μm on the electrode surface before and after the electrolysis, respectively.

3.2. Elemental characterization

The EDX elemental microanalysis was conducted to determine the bulk composition of metal oxide thin films on Ti/Ta₂O₅-SnO₂ electrode. The EDX elemental mappings on the surface of Ti/Ta₂O₅-SnO₂ electrode under the current density of 9 mA cm⁻², before and after the 8 h of electrolysis, are as shown in Fig. 2a–c and d–f, respectively. The atomic molar percentages of the precursor metals from EDX were found to be Sn-91.7 at.% and Ta-8.3 at.% before and Sn-91.5 at.% and Ta-8.5 at.% after the electrolysis. The elemental composition of metals showed reasonable agreement with the nominal mixture used [26]. Moreover, the atomic ratio of Sn/Ta from EDX (10.9) was more closed to the nominal ratio (12.33). This suggests that the Ti substrate is covered more uniformly with Sn, whereas Ta deposition is more dispersed. Overall, the metal fractions did not change noticeably before and after the electrolysis, though morphological changes existed.

3.3. Electrochemical characterization

The electrocatalytic activity of any electrode depends mostly on factors such as relative roughness factor of the electrode surface and the voltammetric currents associated with the degree of electroactive sites [27]. For the roughness factor, the current values for different sweep rates were measured at E = 0.7 V (vs. SCE), where an approximate symmetry for anodic and cathodic currents was recorded as shown in Fig. 3a. By plotting the anodic currents with respect to the scanning rates, a regression equation is deduced (shown in Fig. 3a, inset) as:

\[ i (A) = 0.0001 v(Vs^{-1}) + 2.6 \times 10^{-8}, R^2 = 0.9977 \]  

Fig. 2. EDX mappings of Ti/Ta₂O₅-SnO₂ electrodes before (a–c) and after 8 h of electrolysis (d–f) under current density of 9 mA cm⁻².

Fig. 3. Cyclic voltammograms of Ti/Ta₂O₅-SnO₂ in (a) double-layer region (0.6–0.8 V) at scan rates from 20 to 100 mV s⁻¹ in 0.1 M Na₂SO₄ solution. Inset: Linear regression of i versus v measured at E = 0.7 V; (b) CBZ (30 mg L⁻¹, pH 5.7) with supporting electrolyte 0.1 M Na₂SO₄ scanned between 0.2–2.5 V at scan rate of 100 mV s⁻¹.
The linear relationship between electric current and sweep rate shows that the Faradic current in this region is negligible, thus only the electric double-layer current is measured [27]. The double-layer charging current is much related to the double-layer capacitance of the electrode/solution interface as conductive layer was made of metal oxides [28]. So, the normalized capacitance of 0.0001 F cm$^{-2}$ was calculated by dividing the slope value of Eq. (6) with the geometric surface area of the electrode. Further, the capacitance of the electrode surface was compared with that of a smooth surface oxide layer, with the capacitance of 8 F cm$^{-2}$ [27], which gave a relative roughness factor of 1.25. Therefore, the roughness of electrode surface has slightly improved by Ta doping over SnO$_2$ layer, which in turn have attributed a good electrocatalytic activity to the Ti/Ta$_2$O$_5$-SnO$_2$ electrodes. However, roughness factors of metal oxide films might vary by factor of several thousands with high discrepancy in magnitude between them [28].

Furthermore, CV tests were again performed to investigate the electrochemical property of CBZ molecule at Ti/Ta$_2$O$_5$-SnO$_2$ electrode, as shown in Fig. 3b. The oxygen evolution reactions (OERs) appeared between 1.7 and 2 V (vs. SCE) in both the solutions. In the presence of CBZ, a small anodic current peak was noticed at potential of 1.45 V (vs. SCE) in the voltammogram (Fig. 3b). The absent of more distinct peaks for CBZ oxidation might probably be due to the CBZ oxidation at a potential close to OER region. Furthermore, it can be noticed that there was no reduction peak recorded in the voltammogram during reverse scanning, which might be due to the irreversible characteristics of CBZ [29].

### 3.4. Effects of operating parameters on the removal of CBZ

#### 3.4.1. Effect of current density

In electrochemistry, applied current density is the most important parameter which controls electron transfer and the generation of reactive oxidants [30], thus directly influences the removal rates of pollutants. Such major influencing role of current densities during the electrochemical removal of CBZ has been reported in many studies [5,6,20,23,31]. In this study, different current densities ranging from 1 to 17 mA cm$^{-2}$ were applied in order to select an optimum current density with higher rate of CBZ removal as shown in Fig. 4.

It was observed that after the 8 h of electrolysis, the CBZ removal reached 53.0%, 67.0%, 68.5%, and 71.7% with corresponding current densities of 1, 5, 7, and 9 mA cm$^{-2}$, respectively. This trend is in accordance with the fact that increasing current density increases the organic pollution removal efficiency by the generation of more reactive oxygen species (esp. -OH radicals) [37,23]. The generated powerful -OH radicals then attack CBZ molecules and destruct it. Likewise, the CBZ removal rates were 73.8% and 72% at current densities of 15 and 17 mA cm$^{-2}$, respectively. Thus, beyond current density of 9 mA cm$^{-2}$, neither removal rate nor the kinetics increased noticeably. Two possible reasons might have associated with this phenomenon. First, the undesirable parasitic reactions of -OH radicals to O$_2$ gas or dimerization to weak oxidants such as -OH$_2$ radicals, which could compete the main oxidation reaction (via -OH radicals), and can reduce the oxidation efficiency of the targeted pollutants [6,14,23,32]. Second, as anodic oxidation takes place heterogeneously with physio-adsorbed -OH radicals at electrode surface, electrochemical degradation rate after reaching the limiting current density might be directly proportional to the mass transfer rate of pollutants towards the electrode surface [23].

The current density of 9 mA cm$^{-2}$ was selected as optimum current density for further study to ensure both an improved removal efficiency and a low energy consumption.

Furthermore, in order to evaluate the degradation kinetics of CBZ, the kinetic data were analyzed by using different kinetic models: pseudo-first order kinetic model and pseudo-second order kinetic model. The following Eqs. (7) and (8) were used for the pseudo-first order and pseudo-second order kinetic models,

$$
\ln \left( \frac{C_i}{C_f} \right) = kt
$$

$$
\frac{1}{C_i} - \frac{1}{C_f} = k_2 t
$$

where $C_i$ is the initial concentration of CBZ, $C_f$ is the concentration of CBZ at time t; $t$ is the reaction time; $k_1$ is the pseudo-first order rate constant (s$^{-1}$), and $k_2$ is the pseudo-second order rate constant (L mol$^{-1}$ s$^{-1}$). The regression coefficients ($R^2$) for both pseudo-first order and pseudo-second order kinetics were compared corresponding to the different current densities as indicated in Table 1. The calculated values of $R^2$ from the pseudo-first order kinetic model were slightly lower than the value obtained from the pseudo-second order kinetic model. These results indicated that the pseudo-second order model better describes the degradation of CBZ by EIO process. This is in

<table>
<thead>
<tr>
<th>Current density (mA cm$^{-2}$)</th>
<th>1</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>15</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CBZ removal</td>
<td>53.0</td>
<td>67.0</td>
<td>68.5</td>
<td>71.7</td>
<td>73.9</td>
<td>72.1</td>
</tr>
<tr>
<td>Pseudo-first order model, $R^2$</td>
<td>0.999</td>
<td>0.971</td>
<td>0.990</td>
<td>0.971</td>
<td>0.970</td>
<td>0.952</td>
</tr>
<tr>
<td>Pseudo-Second order model, $R^2$</td>
<td>0.997</td>
<td>0.996</td>
<td>0.993</td>
<td>0.993</td>
<td>0.991</td>
<td>0.983</td>
</tr>
<tr>
<td>$k_2$ (L mol$^{-1}$ s$^{-1}$)</td>
<td>0.47</td>
<td>0.91</td>
<td>1.12</td>
<td>1.42</td>
<td>1.57</td>
<td>1.46</td>
</tr>
<tr>
<td>Half-life (h)</td>
<td>6.9</td>
<td>3.6</td>
<td>2.9</td>
<td>2.3</td>
<td>2.1</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Fig. 4. Effect of applied current density on the removal of CBZ during electrolysis (CBZ, 20 mg L$^{-1}$; Ta$_2$O$_5$-SnO$_2$, pH-5.7; $T = 11 ± 1 ^\circ$C) on Ti/Ta$_2$O$_5$-SnO$_2$ anodes. Inset: fitting of the different current densities to a pseudo-second order kinetic model.

Table 1


---
agreement with the previous work by J. D. García-Espinoza et al. [6], who also reported that the second-order was the best model to fit the kinetics in the electrochemical removal of CBZ with Ti/PbO2 anodes. However, the pseudo-first order kinetic model for CBZ removal using an EO process have also been reported in other works [5,34,35]. In the present work, since k2 values for both the models are comparable, the pseudo-first order model is also valid to describe the reaction kinetics of CBZ degradation. In this regard, it is worth noting that within 8 h of the reaction time, the formation of intermediate compounds could slightly disturb the kinetic analysis.

The tendency of the enhanced CBZ removal efficiencies corresponding to the increased current densities are further supported with the results of pseudo-second order rate constant values, k2 (Table 1). The increasing trend in the values of k2 as a function of applied current densities indicates that amplified OERs are associated with increased current densities. With the increasing O2 gas evolution, the mass transport phenomena increases indicatively leading to the enhanced diffusion flux of CBZ molecules towards anode surface, which subsequently increases k values [20]. From Table 1, at optimum current density of 9 mA cm\(^{-2}\), the value of k2 was 1.42 L mol\(^{-1}\) s\(^{-1}\) and the half-life was found to be 2.3 h. It indicates that 50% of the CBZ removal was reached within 2.3 h of electrolysis under the current density of 9 mA cm\(^{-2}\).

3.4.2. Effect of initial CBZ concentration

It is obvious that the concentrations of CBZ fluctuates periodically or seasonally at wastewater treatment plants [89,96]. Therefore, it is more significant to investigate the effect of the initial concentration of CBZ on the removal efficiency of electrochemical treatment process. In this context, different concentrations of CBZ ranging from 2 to 30 mg L\(^{-1}\) were electrolyzed under the constant current density of 9 mA cm\(^{-2}\) for 8 h, in order to evaluate the influence of initial concentrations of CBZ on the removal efficiency, as shown in Fig. 5.

The removal rates of about 80.6%, 73.3%, 71.8%, and 69.2% were achieved after the 8 h of electrolysis when initial concentrations of CBZ were 2, 10, 20, and 30 mg L\(^{-1}\) respectively (Fig. 5, inset). The removal rate was much faster during the initial 2 h of operation in all of the four different assays, however, decreased from 80.6% to 70.2%, when the initial CBZ concentrations increased from 2 to 30 mg L\(^{-1}\). About 70% of CBZ removal was achieved within 3.5 h of electrolysis for 2 mg L\(^{-1}\) of initial CBZ concentration, whereas 8 h were needed to achieve the same CBZ removal for initial CBZ concentration of 30 mg L\(^{-1}\). These results are consistent with other works in which electrochemical degradation gave better results at low initial concentration [21,23,31].

At higher initial concentrations, the mass transfer of organic substances increases, which ultimately inhibits the interaction between the targeted pollutant and anode active sites [21,23]. This can generate more intermediate products, which in turn competes with CBZ in the reaction with -OH radicals and can reduce the CBZ removal efficiency [21]. So, while increasing the initial concentration of CBZ under identical current densities, the oxidation process can be limited by the formation of -OH radicals [20]. Further, the electrode surface might be mediated with passivation (diffusion layer) due to the generation of more reaction products. On the other hand, at lower concentrations, the higher CBZ removal rate was achieved, which indicates that the greater amount of CBZ molecules are attacked by the -OH radicals. This result can be explained by the phenomena that at low initial concentrations, electrochemical degradation rates of organic molecules can be faster than the diffusion of side-products [21].

3.4.3. Effect of pH

pH values can have a significant influence on the electrochemical treatment processes [19]. To assess the effect of pH on the removal efficiency of CBZ at Ti/Ta2O5-SnO2 anode, different initial pH conditions ranging from acidic to basic media (2–10) were investigated. Fig. 6 depicts the degradation kinetics of CBZ (20 mg L\(^{-1}\)) when electrolyzed for 8 h under the current density of 9 mA cm\(^{-2}\) with supporting electrolyte of 0.1 M NaOH. In Fig. 6 (inset), the residual concentrations of CBZ after the 8 h electrolysis are found to be decreasing from about 6.3, 5.7, and 5.0 mg L\(^{-1}\) at initial pH values of 2, 4, and 6, respectively. However, the residual concentrations are in increasing trend in basic media ranging from 5.7 to 6.0 mg L\(^{-1}\) at corresponding pH values of 8 and 10, respectively. Under the identical conditions, the optimum removal of 75.2% was achieved at pH value of 6. Whereas, the removal efficiencies were 68.8%, 71.2%, 71.5%, and 70.1% at the pH values of 2, 4, 8, and 10, respectively. Thus, these results indicate that the influence of pH was not significant for electrochemical removal of CBZ, which is in agreement with other studies [3,6,23]. The reason might be the high acid-dissociation constant (pKa) of CBZ (13.94), for which no significant dissociation is generally reported, either in acidic or basic conditions [6]. In practice, this tendency will be useful in real treatment cases since MBR processes are normally operated at pH of 6.7 [9]. On the other hand, the decreasing trend of the CBZ removal efficiency with increasing pH values might be attributed to the significant shift of OER onset potential to less positive values (low O2 overvoltage), which favors more oxygen formation than pollutant oxidation [37]. It was also noticed that the solution pH did not change significantly in acidic assays over the 8 h of time. Nevertheless, the solution pH was found to be changing into a more acidic character (pH 8–10) when performed in alkaline media (pH 8–10 initially), which might be due to the formation of weak acid products such as carboxylic acids [32,38].

![Figure 5](image-url)
3.4.4 Effect of temperature

The reaction rate constants are exponentially dependent on the temperature of the medium following the Arrhenius law. The similar principle can be expected in the electrochemical processes. Therefore, to investigate the effect of temperature on the electro-oxidation, 20 mg L$^{-1}$ of CBZ solution was electrolyzed on Ti/Ta$_2$O$_5$-SnO$_2$ anode under the current density of 9 mA cm$^{-2}$ at three different temperatures ranging from 10 to 30 °C. Fig. 7 shows the effect of different temperatures on the CBZ degradation kinetics during 8 h of electrolysis. The removal efficiencies of 71.7%, 74.1%, and 75.5% were achieved when corresponding operating temperatures were maintained at 10 °C, 20 °C, and 30 °C (Fig. 7, inset). Thus, increasing the temperature had a slight positive influence on the kinetic rates. One possible reason might be a better mass transfer of pollutants towards the anode surface at higher temperature, due to high molecular agitation which could enhance the oxidation efficiency [39]. Another reason might be the indirect oxidation reaction of organics in the bulk solution by electrogenerated oxidants peroxodisulphates (S$_2$O$_8^{2-}$), which is one of the powerful oxidizing species, from the oxidation of electrolyte (Na$_2$SO$_4$). Indeed, it was reported that the rate of oxidation of organic pollutants via peroxodisulphates increases with positive increments in the solution temperature [31]. In terms of hydrodynamics of the bulk solution, viscosity decreases with increasing solution temperature, which enhances mass transfer rate of organic species towards electrode surface thus contributes higher oxidation efficiency [20].

Moreover, the degree of mineralization was also analyzed at this stage under the optimum operating conditions. Using current density of 9 mA cm$^{-2}$, pH of 6.0 and initial CBZ concentration of 20 mg L$^{-1}$, optimum removal of TOC were 61.2%, 69.8% and 71.1% under the solution temperatures of 10 °C, 20 °C, and 30 °C, respectively (Fig. 7, inset). Therefore, the average rate of mineralization during this work was about 61%, as the operating temperature was maintained at about 11 ± 1 °C. It can be concluded that increase in the temperature has positive effect on the degree of mineralization too. Nevertheless, the mineralization efficiency was always lower than that of CBZ (71.1% and 75.5%, respectively). The most possible reason might be attributed to the fact that carboxylic acids are highly recalcitrant, thus they degrade slower than parent compounds [32].

3.5 Comparison between Ti/Ta$_2$O$_5$-SnO$_2$ and Ti/PbO$_2$ electrodes

In order to evaluate the effect of different electrode materials on the CBZ removal efficiencies, Ti/Ta$_2$O$_5$-SnO$_2$ and Ti/PbO$_2$ electrodes were compared. The stability of both electrodes were also compared by performing leaching tests. Fig. 8 shows the removal kinetics of 20 mg L$^{-1}$ CBZ in aqueous 0.1 M Na$_2$SO$_4$ solution, pH 6.0, T = 10 °C, and using current density of 9 mA cm$^{-2}$. The removal trends of both Ti/Ta$_2$O$_5$-SnO$_2$ and Ti/PbO$_2$ electrodes were almost identical until 2 h of electrolysis. However, after 8 h of electrolysis, the CBZ removal efficiency reached 71.7% and 77.9% on Ti/Ta$_2$O$_5$-SnO$_2$ and Ti/PbO$_2$ electrodes.
and electrodes, respectively (Fig. 8). From the results, it can be concluded that under the identical operating conditions, the Ti/PbO2 electrode is more effective on CBZ removal. This tendency could be explained by the fact that the Ti/PbO2 anodes have greater electrocatalytic activity than Ti/Ta2O5-SnO2 anodes due to their higher relative roughness factor [41]. The increase in surface roughness can produce larger amount of physically adsorbed OH radicals under the identical current density [21], which could react rapidly with all organic species at the vicinity of anode surface [31]. Furthermore, stability of both the electrodes was examined in terms of the leaching of Ta, Sn, Ti and Pb, by monitoring their ion concentrations in the bulk solution. Each electrodes were electrolyzed for 24 h by reusing the same electrodes but over three days (8 h per day with fresh solutions each run), as mentioned in Fig. 9a,b. The electrical energy consumed to treat specific volumes polluted solutions is the prime concern to assess the viability of any electro-chemical degradation processes. The EC evolved during the electro-chemical degradation of CBZ at varying current densities (Cf. Section 3.4.1) are shown in Fig. 10. It indicates that the minimum electrical energy consumption of 3.2 kWh m\(^{-2}\) was required to reach 53% of CBZ removal while using the current density of 1 mA cm\(^{-2}\). The EC increased from 26.3 to 60.3 kWh m\(^{-2}\) when current densities increased from 5 to 9 mA cm\(^{-2}\). Beyond the current density of 9 mA cm\(^{-2}\) until 17 mA cm\(^{-2}\), the EC increased from 60.3 kWh m\(^{-2}\) and reached to 172.7 kWh m\(^{-2}\), even though the removal efficiencies were not improved significantly. For the optimum current density of 9 mA cm\(^{-2}\), the energy required to degrade 71.7% of CBZ was 60.3 kWh m\(^{-2}\). It has been observed that the current densities higher than the limiting one (9 mA cm\(^{-2}\) in the present study) can be associated with high energy consumption. The reason can be that a large mass of OH radicals might be evolved to O\(_2\) due to parasitic reactions, then a large cell voltage is often used mostly for O\(_2\) generation, which does not help further in oxidizing the organic pollutant [31].

3.6. The energy consumption

The electrical energy consumed to treat specific volumes polluted solutions is the prime concern to assess the viability of any electro-chemical degradation processes. The EC evolved during the electro-chemical degradation of CBZ at varying current densities (Cf. Section 3.4.1) are shown in Fig. 10. It indicates that the minimum electrical energy consumption of 3.2 kWh m\(^{-2}\) was required to reach 53% of CBZ removal while using the current density of 1 mA cm\(^{-2}\). The EC increased from 26.3 to 60.3 kWh m\(^{-2}\) when current densities increased from 5 to 9 mA cm\(^{-2}\). Beyond the current density of 9 mA cm\(^{-2}\) until 17 mA cm\(^{-2}\), the EC increased from 60.3 kWh m\(^{-2}\) and reached to 172.7 kWh m\(^{-2}\), even though the removal efficiencies were not improved significantly. For the optimum current density of 9 mA cm\(^{-2}\), the energy required to degrade 71.7% of CBZ was 60.3 kWh m\(^{-2}\). It has been observed that the current densities higher than the limiting one (9 mA cm\(^{-2}\) in the present study) can be associated with high energy consumption. The reason can be that a large mass of OH radicals might be evolved to O\(_2\) due to parasitic reactions, then a large cell voltage is often used mostly for O\(_2\) generation, which does not help further in oxidizing the organic pollutant [31].
3.7. Applicability of EO process in real MBR effluent for CBZ removal

In practice, the optimum operating conditions during the removal of CBZ from synthetic solution were applied for the treatment of CBZ in the real MBR effluents, collected from a local MBR pilot. The characteristics of the MBR effluent, detailed specifications and operating conditions of the MBR pilot plant are described in previous study [9]. The MBR effluent samples were then spiked with a precise amount of CBZ to have an initial concentration of 10 μg L⁻¹. Moreover, two different working solutions, with or without supporting electrolyte, were prepared and experimented. The details of experimental conditions and results are presented in Table 2.

From Table 2, it can be noticed that the EO method, which was operated under optimal conditions, has shown an excellent CBZ removal efficiencies in the real MBR permeate, independent of the influence of supporting electrolyte. About 90% removal of CBZ was attained after 2 h of electrolysis, which further reached 99.99% within 4 h of electrolysis, for both assays (data not shown). These results are consistent with the findings of García-Gómez et al. [2], where low concentrations of CBZ spiked into the synthetic wastewater was electrolyzed by using EO method. Nevertheless, the energy consumption was higher when no supporting electrolyte was used as compared to the use of it (Table 2). High salinity of effluent wastewater could increase the conductivity and thus can lower the energy consumption [1]. Nonetheless, the conductivity of the MBR effluent in this work was reported to be 600 μS cm⁻¹, which was not enough to maintain a constant electrical pressure during the redox reactions. On the other aspect, the cost of using supporting electrolyte (approx. US$ 70 per metric ton) is much cheaper than the consumption of electricity (approx. US$ 0.05 per kWh).

4. Conclusion

The electrochemical oxidation of CBZ from synthetic solutions and real MBR effluents using a newly developed Ti/Ta₂O₅-SnO₂ electrodes was investigated under galvanostatic conditions. The characterization of the Ti/Ta₂O₅-SnO₂ electrodes were performed by using SEM, EDX, AFM, and cyclic voltammetry analyses. The main operating parameters influencing the CBZ removal efficiency in synthetic solutions on the tested anodes were evaluated as a function of applied current density, initial CBZ concentration, pH, and temperature. The results showed that the maximum removal of CBZ (20 mg L⁻¹) and TOC reached 75.9%, and 71.1%, respectively, after 8 h of electrolysis, current density of 9 mA cm⁻², solution pH 6, temperature of 30 °C, and using 0.1 M Na₂SO₄ as supporting electrolyte. The performance of Ti/Ta₂O₅-SnO₂ electrode was compared with Ti/PbO₂ electrode in terms of CBZ removal efficiencies and stability. The results showed that, under the same conditions, the CBZ removal efficiency of Ti/PbO₂ electrode was slightly higher when compared with the investigated electrode, but the latter was more environmentally friendly. Besides, achieving an optimal CBZ removal efficiency of 71.7% required the lowest energy consumption of 60.3 kWh m⁻³.

Furthermore, the complete degradative removal of CBZ was achieved in spiked real MBR effluents, under the optimal operating conditions. Overall, the EO based on the use of novel Ti/Ta₂O₅-SnO₂ electrode was found to be a reliable process to remove CBZ from contaminated waters, with promising potential for integration with MBR technology to remediate CBZ.

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<table>
<thead>
<tr>
<th>Parameter (μg L⁻¹)</th>
<th>Initial concentration in MBR effluent</th>
<th>Final concentration after 8 h of electrolysis</th>
<th>Electrolyte</th>
<th>Removal (%)</th>
<th>EC (kWh m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.75 ± 0.35</td>
<td>0.07 (LOD)</td>
<td>No electrolyte</td>
<td>99.99</td>
<td>100.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.07 (LOD)</td>
<td>0.1 M Na₂SO₄</td>
<td>99.99</td>
<td>57.2</td>
<td></td>
</tr>
</tbody>
</table>

* (LOD) Limit of detection.
Publication IV

Khum Gurung, Mohamed Chaker Ncibi, Senthil K. Thangaraj, Janne Jänis, Mahdi Seyedsalehi, Mika Sillanpää

**Removal of pharmaceutically active compounds (PhACs) from real membrane bioreactor (MBR) effluents by photocatalytic degradation using composite Ag$_2$O/P-25 photocatalyst**

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Removal of pharmaceutically active compounds (PhACs) from real membrane bioreactor (MBR) effluents by photocatalytic degradation using composite Ag$_2$O/P-25 photocatalyst

Khum Gurunga,⁎, Mohamed Chaker Ncibia, Senthil K. Thangarajb, Janne Jänisb, Mahdi Seyedsalehc, Mika Sillanpääa

a Department of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland
b Department of Chemistry, University of Eastern Finland, Yliopistonkatu 7, FI-80101 Joensuu, Finland
c School of Environment, Tsinghua University, Beijing 100084, China

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ABSTRACT

Pharmaceutically active compounds (PhACs) are emerging pollutants causing serious challenges to wastewater treatment plants due to poor biodegradability. In this study, the enhanced removal of highly recalcitrant and commonly monitored PhACs, carbamazepine (CBZ) and diclofenac (DCF) by heterogeneous photocatalysis was investigated using 5% Ag$_2$O/P-25 photocatalyst. The photocatalyst was characterized by scanning electron microscope (SEM-EDX), Brunauer-Emmett-Teller (BET), Fourier transfer infrared spectroscopy (FTIR) and UV–vis diffuse reflectance spectra (UV-DRS). The effects of catalyst dose, initial pollutants concentration, and mineralization during the photocatalytic degradation of PhACs were investigated. The matrix effect was assessed in deionized water (DW) and real membrane bioreactor effluent (RME). Optimal CBZ and DCF removals of 89.10% and 93.5%, respectively for 180 min of UV irradiation were achieved at catalyst dosage of 0.4 g L$^{-1}$ in DW matrix. However, the optimal catalyst dosages for CBZ and DCF in RME matrix were increased by factor 2 and 1.5, respectively, to achieve the same degree of removal. Declining trends of removal rate were observed when initial concentrations of both the PhACs were increased under optimal catalyst dosages, and kinetics seem to fit the Langmuir-Hinshelwood model. Photo-induced holes and *OH were the dominant oxidation species involved in the photocatalytic degradation of the PhACs. A plausible reusability of 5% Ag$_2$O/P-25 photocatalyst was observed for both the PhACs. Moreover, various aromatic/aliphatic intermediates generated during the photodegradation CBZ were identified using fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry, and a possible multi-step degradation pathway was proposed. Overall, the removal of PhACs using 5% Ag$_2$O/P-25 photocatalyst showed promising results in real wastewater.

1. Introduction

Pharmaceutically active compounds are used for the prevention, diagnosis, and treatment of several diseases in humans and animals. The global annual average per capita consumption of pharmaceuticals is estimated at about 15 g, whereas industrialized countries accounted between 50 and 150 g [1]. The annual per capita expenditures on pharmaceuticals ranged from US$ 7.61 in low-income countries to US$ 431.6 in high-income countries [2]. As most of the PhACs are non-volatile and highly charged molecules composed of diverse moieties, these emerging pollutants are highly recalcitrant and not entirely degraded after the medical use, hence the excretion of unchanged (parent) compounds and metabolites and their channeling to the aquatic environment [3]. In recent years, the fate of the PhACs and their metabolites has received a great deal of interest from the scientific community. Though PhACs are normally detected in the concentration range of ng L$^{-1}$ or µg L$^{-1}$, they can pose serious issues due to their potential adverse effects on human health and ecosystem [4,5]. However, other factors such as increased persistence, time of exposure, biotransformation, and degradation mechanisms can also influence the impacts of PhACs, other than their concentration alone [5]. Among the large number of PhACs, CBZ and DCF are the most frequently identified in aquatic environments [1]. CBZ is an antiepileptic drug often used to treat epilepsy and seizures, whereas DCF is a non-steroidal anti-inflammatory drug (NSAID) commonly used as analgesic, anti-rheumatic, and antiarthritic [6,7].
CBZ has been proposed as an anthropogenic indicator in water bodies [8]. Moreover, DCF is included in the watch list of priority substances as emerging pollutants in EU directive that needs careful environmental monitoring in its member states [9]. The wastewater treatment plants (WWTPs) are the primary receptor of PhACs via direct and unsafe discharge of untreated wastewaters from domestic, households, industries, agriculture lands, and hospitals [10,11]. PhACs have been found in the effluents of municipal WWTPs because of their incomplete removal [5]. It is well known that conventional WWTPs are not fully efficient in treating most of the PhACs [1,12,13]. Even Membrane bioreactors (MBRs), which are regarded as having superior capabilities in terms of performance and flexibility [14], are not effective in the removal of certain PhACs [8,15]. In this regard, many researchers have recommended the development of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of treatment systems where biological degradation is integrated with advanced oxidation processes (AOPs) as a pre-treatment of
at 50 Hz, (EDTA) as a hole (photocatalytic processes, including ethylenediaminetetraacetic acid P-25. In practice, several chemical compounds were tested during the photocatalytic degradation of CBZ and DCF using 5% Ag2O/P-25. In a preliminary stage, photocatalytic degradation efficiencies of aqueous solution (20 mg L−1) and reaction was started as in photodegradation experiment for 180 min. Samples were collected at the interval of 60 min, 120 min, and 180 min. After the first run, suspension was centrifuged at 3550 rpm for 30 min, washed thoroughly with deionized water, and again dispersed into the another fresh CBZ solution to start the second run. Similarly, the experiment was repeated five times.

2.4. Characterisation of photocatalysts

Microstructure and morphology of the synthesized photocatalysts were examined by scanning electron microscope (SEM) (Hitachi, SU3500, Japan) using acceleration voltage of 5 kV. The elemental analysis of photocatalyst was performed using energy-dispersive X-ray spectroscopy (Thermo Fisher, USA). The Brunauer-Emmett-Teller (BET) surface area (SBET) was determined by using Tristar II Plus. The UV–vis diffuse reflectance spectra were measured in the range of 250–800 nm using Agilent Cary 5000 spectrophotometer with DRA2500 integrating sphere. The Fourier transfer infrared spectroscopy (FTIR) was performed using Bruker Platinum ATR VERTEX 70.

2.5. Photodegradation experiments

The photocatalytic degradation experiments were performed in a self-made continuous stirred photochemical reactor as shown in Fig. S1 (Supplementary information). The photocatalytic reaction chamber consists of a UV lamp (rated power is 14 W, rated voltage is 216 V) and a quartz tube with one end closed, magnetic stirrer, rotor, and a reaction vessel with double-jacketed cooling system. The model solution (300 mL) was dispersed into the solution and magnetically stirred in dark for 30 min to achieve adsorption equilibrium. Upon the irradiation, an aliquot of 3 mL reaction solution was sampled at given time intervals. The reaction solution aliquots were then filtered through 0.45 μm membranes prior to analysis. No buffer was used and the pH values ranged from 5 to 7 (before and after) during all set of the experiments.

2.6. Trap experiments

The radicals and holes trapping experiments were designed to elucidate the types and roles of reactive species, and mechanisms involved during the photocatalytic degradation of CBZ and DCF using 5% Ag2O/P-25. In practice, several chemical compounds were tested during the photocatalytic processes, including ethylenediaminetetraacetic acid (EDTA) as a hole (h+) scavenger [28], methanol (MeOH) as hydroxyl radical (·OH) scavenger [36], and O2-purging (·O2− scavenger) via N2 [37].

2.7. Reusability experiments

Cyclic experiments were performed to check the reusability of the investigated photocatalyst over the degradation of CBZ and DCF. Typically, 0.24 g of 5% Ag2O/P-25 was dispersed into 0.3 L CBZ solution (20 mg L−1) and reaction was started as in photodegradation experiment for 180 min. Samples were collected at the interval of 60 min, 120 min, and 180 min. After the first run, suspension was centrifuged at 3550 rpm for 30 min, washed thoroughly with deionized water, and again dispersed into the another fresh CBZ solution to start the second run. Similarly, the experiment was repeated five times.

2.8. Analytical procedures

The changes in the concentration of CBZ and DCF during photocatalytic reaction were analyzed using a UV–Vis spectrophotometer (Lambda 45, Perkin Elmer, USA). The absorbance was measured at 285 nm and 276 nm for CBZ and DCF, respectively, since these wavelengths correspond to the characteristic peaks of these drugs in the UV spectrum. Moreover, it should be noted that the absorbance measurements of the treated solutions might not indicate the absolute concentration of parent CBZ or DCF as some of the treated intermediate products may also absorb at similar wavelengths, thus contributing to increased absorbance. Therefore, the reported concentrations used to calculate percentage removal may account both residual parent pollutants and some of the related reaction by-products, which could underestimate the actual degradation efficiency of the parent compounds. Dissolved organic carbon (DOC) was also measured using TOC analyzer (Shimadzu, Japan) to assess the extent of mineralization.

The degradation products of CBZ were analyzed by 12-T Bruker solariXTM XR hybrid Qb-Fourier Transform Ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, Bremen, Germany) coupled with an electrospray ionization (ESI) source (Apollo-II), operated in the positive-ion mode. The photocatalytic degradation products of CBZ (10 μL) were prepared in methanol (diluted 10.200 v/v). Acetic acid (1 v-%) was added to the samples to aid protonation. The samples were directly infused into the ion source at a flow rate of 2 μL min−1. The ion accumulation time in the hexapole was 0.8 s and the time of flight from the collision cell to the ICR cell was set at 0.260 ms. Dry nitrogen was used as drying (4.0 L min−1) and nebulizing gas (80 °C, 1.0 bar). For each spectrum, 200 time-domain transients (4 MWord each) were co-added and full-sine apodized. The mass spectra were externally calibrated using an ES tuning mix (Agilent Technology). Bruker FTMS Control™ 2.1 software was used for the instrument control and data acquisition. The mass spectra were further processed and analyzed by using Bruker DataAnalysis 4.4 software.

3. Results and discussion

3.1. Screening of photocatalysts: dark adsorption, UV-photolysis, and UV photocatalysis

In a preliminary stage, photocatalytic degradation efficiencies of
was made because of the comparable e
both the model pollutants. 
the cases. At the catalyst dose of 0.4 g L
experiments were run for several 
to evaluate the extent of adsorption and UV-photolysis of target pol-
target pollutants were slightly converted under UV-photolysis. 
Moreover, the selection of Ag2O/P-25 over PdO/P-25 and NiO/P-25 
photocatalytic activity either in case of CBZ or DCF, therefore selected 

four different photocatalysts including Ag2O/P-25, SnO2/P-25, PdO/P- 
and NIO/P-25 were tested on the selected pollutants. First, in order 
evaluate the extent of adsorption and UV-photolysis of target pol-
to ensure the highest absorption of photons, without gen-

The BET surface area, pore size, and pure volume of 5% Ag2O/P-25 
were estimated as reported in Table S2 (Supplementary information). 
The 5% of pure TiO2 (P-25) increased slightly from 47.27 m² g⁻¹ to 54.1 m² g⁻¹ due to the deposition of Ag2O nanoparticles over P-25 surface. Likewise, the average pore size and pore volume of P-25 were increased from 8.25 to 9.27 nm and 0.10 to 0.13 cm³ g⁻¹, respectively. However, this observation indicated that the contribution of the Ag2O particles to the specific surface area of P-25 was relatively low. The increased surface area, pore size and pore volume showed that Ag2O particles were well dispersed over P-25 surface with limited interference with the existing pores. Similar trends in the characteristic modifications of P-25 after doping with Ag2O have been reported in other studies [44].

For the energy band gap (Eg) determination of semiconductors, the reflectance spectra of photocatalysts were converted to the absorbance spectra using the Kubelka-Munk functions [45] and then Eg evaluated by using Tauc plot [44-46]. The undoped P-25 showed a band gap of 3.2 eV with the absorption peak at ~395 nm. After doping with Ag2O, the wavelength threshold of the absorption peak of P-25 was between 400 and 500 nm, with the corresponding energy band gap at 2.96 eV as shown in Fig. S2-b (supplementary information). The decreased band gap energy inferred the chemical interactions between P-25 and Ag2O nanoparticles. Therefore, lower energy transitions are possible in Ag2O/P-25 semiconductors as Ag2O could create localized energy levels in the P-25 bandgap, which evidently increases the absorption spectra in UV-vis range [44].

3.3. Effect of catalyst dose, solution matrix, and initial substrate concentration on the removal of selected PhACs

In order to ensure the highest absorption of photons, without gener-

The major characteristics of as-prepared 5% Ag2O/P-25 photocatalyst such as surface chemical compositions and morphology were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) analysis in the previous work [34,35]. However, we further characterized the as-prepared photocatalyst by other analytical techniques such as SEM, EDX, BET, FTIR, and UV-reflectance spectra. The morphology and elemental microanalysis of the selected 5% Ag2O/P-25 photocatalyst were investigated by SEM and EDX. The SEM micrographs with different magnifications are as shown in Fig. 2. The surface of P-25 nanoparticles acts as underlying substrate to absorb Ag2O nanoparticles and an average diameter of 4.4–20 nm could evenly disperse on the surface of P-25 during pH-mediated precipitation process [36,34]. Presence of Ag nanoparticles on the surface of P-25 photocatalyst was confirmed by the EDX elemental analysis, which reveals the bulk compositions of Ti, O, C, and Ag elements (Fig. 2). The TiO2 nanoparticles provide numerous nucleation sites, which could be responsible for the homogeneous dispersion of Ag2O nanoparticles on the surface of TiO2 nanoparticles [36]. Furthermore, elemental mappings of 5% Ag2O/P-25 confirms the homogenous dispersion of Ag⁺ particles on P-25 as depicted by Fig. 3(d-h).

To further confirm the chemical composition of 5% Ag2O/P-25 photocatalyst, FTIR spectroscopy was performed as depicted in Fig. S2-a. The main absorption peaks were observed at 3000, 1533, 1428, 1050 and 433.3 cm⁻¹. The peak located at 433.3 cm⁻¹ could be assigned to M=O (i.e. either Ti–O or Ag–O) stretching vibration [41,42]. The broad absorption band at about 2976.75 cm⁻¹ is characteristic of O–H stretching vibration of the Ti=OH. The vibrational peaks at 1558.38, 1419.43 and 1052.3 cm⁻¹ are due to stretching of C=O group, O–H bending and stretching of C–O bond, respectively [42,43].
and DCF was determined for two different solution matrices (i.e. DW and RME) as shown in Fig. 3. The catalyst dose of 0.2–1.0 g L\(^{-1}\) was assessed for DW matrix, whereas 0.4–1.2 g L\(^{-1}\) was used in the case of RME matrix. Since organic matter in RME could inhibit the degradation of organic pollutants, higher amount of catalyst dose is essential to achieve enhanced removal efficiencies [4]. Therefore, a higher range of catalyst dosing was selected to assess the influence of organic matter contained in the RME matrix. Table 2 shows the collective removal of target pollutants and the extent of mineralization in two solution matrices under different operating conditions.

The photocatalytic degradation kinetics of CBZ in DW and RME matrices are shown in Fig. 3a and b, respectively. In DW matrix, and after an irradiation time of 180 min, the removal of CBZ reached from 80.4% to 89.10% while increasing the catalyst dosing from 0.2 to 0.4 g L\(^{-1}\). Likewise, for the case of DCF, the removal rate increased from 87.5% to 93.5% in DW matrix for the similar range of catalyst. The higher removal rate of DCF compared to CBZ in identical operating conditions exhibited greater affinity of DCF molecules towards photocatalytic degradation by 5% Ag\(_2\)O/P-25. From Fig. 3 and Table 2, it is clear that the photocatalytic degradation of both CBZ and DCF beyond the 0.4 g L\(^{-1}\) of catalyst dose remained constant. Therefore, 0.4 g L\(^{-1}\) of 5% Ag\(_2\)O/P-25 was concluded to be the optimum catalyst dose for the removal of both PhACs in DW matrix. Similar tendencies have been reported in earlier studies [4,47]. The limiting value 0.4 g L\(^{-1}\) might be attributed to fact that photocatalytic rate increases with catalyst dosing at the beginning and then decreases (or saturates) at higher doses due to unfavorable phenomenon, such as light scattering due to enhanced reflectance and increased opacity of the suspension [48,49]. Also, the agglomeration of solid particles due to excess dose may result in a reduction of active surface sites available for photon absorption, which eventually reduces photocatalytic efficiency [33]. Even though the number of active sites increases with more catalyst dosing, the penetration of light is to be compromised because of the shielding effect [33,48]. The trade-off between these two divergent phenomena results in an optimal catalyst dosing for photocatalytic processes [33]. The shielding by TiO\(_2\) particles may occur due to deactivation phenomenon of activated TiO\(_2\) molecules by collision with ground state molecules [48,50]. Nevertheless, the optimal catalyst dosing is highly dependent on the concentration and source/type of the pollutant and the operating conditions as well [33]. Therefore, the optimal catalyst dose of 0.4 g L\(^{-1}\) achieved for both CBZ and DCF in DW matrix might be different for other conditions.

On the other hand, relatively slow kinetics was observed in the experiments performed with RME matrices of both CBZ and DCF (Fig. 3b and d). In Table 2, an increasing trend of CBZ removal rate was clearly observed from 76.6 to 93.9% when the catalyst dose was increased from 0.4 to 0.8 g L\(^{-1}\). However, the removal rate decreased by nearly 3% when catalyst dose was subsequently increased beyond 0.8 g L\(^{-1}\). On the other hand, DCF removal rate was improved greatly when the catalyst dose was increased from 0.4 g L\(^{-1}\) to just 0.6 g L\(^{-1}\), though no further remarkable enhancement was observed beyond 0.6 g L\(^{-1}\) of catalyst dose. Therefore, different optimal catalyst dose for
CBZ (i.e. 0.8 g L\(^{-1}\)) and DCF (i.e. 0.6 g L\(^{-1}\)) were established in RME matrix.

As clearly seen in Table 2, there is an obvious deviation in the optimum catalyst dose of DW and RME matrices. The need for optimal catalyst dose in RME matrix, in order to achieve approximately the same level of removal efficiency in DW matrix, is increased by factor of 2 and 1.5 for CBZ and DCF, respectively. Therefore, the competition between organic matter and the PhAGs on the surface of catalyst was evidently observed in the RME matrix during the photocatalytic process. This may be attributed to either the organic carbon content of RME samples, or the presence of various species that may act as natural scavengers and other reactive moieties [12]. The organic matter in real effluent not only competes for the active species generated in the process but could also be adsorbed on the surface of photocatalysts, which inhibits the photocatalytic activity [4]. Additionally, a possible interference of inorganic ions on catalyst surface deactivation, and a competition for UV absorption should also be taken into consideration [51].

Subsequently, the optimized catalyst doses for CBZ and DCF removal in RME matrix were used to study the influence of initial substrate concentration in photocatalytic degradation kinetics, as depicted in Fig. 4. The initial substrate concentration was varied in the range of 20–50 mg L\(^{-1}\) at optimal catalyst doses of 0.8 g L\(^{-1}\) and 0.6 g L\(^{-1}\) for CBZ and DCF, respectively. In Fig. 4a and b, decreasing trends in the removal of CBZ and DCF were observed when initial substrate concentrations were gradually increased. The removal efficiency of CBZ was decreased by 38%, when the concentration was increased from 20 to 50 mg L\(^{-1}\) (Fig. 4a, inset). Whereas, only 23% reduction was observed in the DCF removal efficiency with the same range of concentration increments (Fig. 4b, inset). These trends may be attributed to the increasing occupied sites of the catalyst due to more pollutant molecules adsorbed on the surface of catalyst, which inhibits the generation of reactive species [12]. On the other hand, high pollutants concentrations can lead to a decreasing penetration of photons into the bulk solution and hence the solutions become more impermeable to UV irradiation due to an induced inner filtering effect. Thus, the photoexcitation of catalyst particles by photon energy will be reduced leading to a diminished photodegradation efficacy [52].
fit the Langmuir-Hinshelwood (L-H) kinetic model as shown in Eq. (1) [12,53]:

\[ \frac{C_{eq}}{r_0} = \frac{C_{eq}}{r_0} + \frac{1}{k_r K} \]  

(1)

where \( r_0 \) is the initial reaction rate, \( C_{eq} \) is the equilibrium concentration of substrate in solution after the completion of dark experiments, \( k_r \) is the reaction rate constant at maximum coverage, and \( K \) is equilibrium constant for adsorption of the substrate onto the catalyst surface.

In order to check if the investigated photocatalytic degradation follows the L-H kinetic model, the experimental data with initial concentrations of target pollutants (20–50 mg L\(^{-1}\)) in RME matrix (Fig. 5) were assessed and the initial rates were calculated at 20 min of initial reaction. A graphical plot of Eq. (1) for runs at various initial substrate concentrations is shown in Fig. 5, which indicates that the photocatalytic degradation well fitted the Langmuir-Hinshelwood kinetic model.

Moreover, the degradation kinetics beyond 20 min of irradiation were observed to follow a curve rather than a straight line when modelled with pseudo-first order (PFO) kinetic for both CBZ and DCF compounds. The possible formation of aromatic organic intermediates, which can be detected at the similar wavelengths of parent compounds, could affect the corresponding final absorbance values and consequently the reaction kinetics [54].

3.4. Mineralization of PhACs

In order to characterize the mineralization extent of CBZ and DCF in different solution matrices, the DOC measurements were carried out during photocatalytic treatment. The optimal catalyst doses were adopted for different solution matrices and target pollutants. Fig. 6a and b shows the normalized DOC removals during the photocatalytic treatment of CBZ and DCF, respectively. About 60% of mineralization rate was observed when the CBZ removal was 90% in DW matrix,
whereas the mineralization rate was reduced to 65% when CBZ removal was 94% in RME matrix (Table 2). Moreover, results showed that the mineralization rates of both target compounds were inhibited to some extent in RME matrix as compared to DW matrix. This fact evidently confirms the influence of organic matter (cf. Table S1) present in the RME matrix.

3.5. Role of reactive oxygen species and mechanism involved in the photocatalytic degradation

The influence of reactive species (h+, OH, O2−) involved during the photocatalytic degradation of CBZ and DCF using 5% Ag2O/P-25 is shown in Fig. 7. In Fig. 7a, the photocatalytic degradation of CBZ under UV irradiation for 60 min was substantially suppressed with the addition of EDTA and MeOH by nearly 70% and 90%, respectively, as compared to the control test. However, the degradation percentage decreased slightly (18%) when O2-purging test was performed. The results indicated that trapped holes and hydroxyl radicals adsorbed on the surface of the 5% Ag2O/P-25 were the dominant oxidative species during the photocatalytic degradation of CBZ molecules. Similarly, the degradation rate of DCF in the presence of EDTA was substantially decreased to 62% as compared to the control test (Fig. 7b). However, the effect of either MeOH or O2-purging was not significant (~7%), which suggests that the trapped holes were the main oxidative species prompted due to UV irradiation of 5% Ag2O/P-25, and thus accountable for the photocatalytic degradation of DCF. Interestingly, the conversion of DCF was not influenced due to the addition of MeOH. To confirm this result, other scavengers such as isopropyl alcohol and tert-butanol were also tested, however similar effects were observed (data not shown). This might be due to the higher affinity of photo-generated ROS with DCF molecules, compared to the added scavengers. Moreover, the major role of photogenerated holes during the photocatalytic oxidation of TiO2 based photocatalyst has been reported [55]. In addition, the organic pollutants could also absorb actinic photons from UV irradiation and transfer energy or electrons to produce reactive oxidation species, which in turn degrade the organic pollutants. This phenomenon is referred to as self-sensitized photooxidation of pollutants [56].

On the basis of above results, a possible photocatalytic mechanism scheme of the heterojunction 5% Ag2O/P-25 photocatalyst was proposed as shown in Fig. S3 (Supplementary information). When composite Ag2O/P-25 was irradiated by UV, both e− and h+ were excited in the conduction band (CB) and valence band (VB), respectively according to Eqs. (2) and (3). In normal case, most of e−−h+ pairs recombine rapidly to produce heat. As ECB (TiO2, −0.4 eV vs. SHE) is lower than E0/2(CB, −0.04 eV vs. SHE), O2 can produce from dissolved O2 [57,58]. However, the ECAg2O (Ag2O, +0.2 eV vs. SHE) was higher than E0/2(CB, −0.04 eV vs. SHE). Thus unable to produce O2− from dissolved O2 [58,59]. The electrons produced on CB of TiO2 can transfer easily to Ag2O as ECAg2O of TiO2 is positioned above that of Ag2O [57]. Subsequently, the partial lattice Ag+ in Ag2O nanoparticles on the surface of TiO2 reacts with photons-induced electrons and reduced to metallic Ag (Eq. (4)). Further, the metallic Ag acted as an electron pool and transferred the produced electrons to combine with O2. The Ag2O as electron absorber inhibits the recombination of the photogenerated e−−h+ pairs, which allows the holes to effectively oxidize organic pollutants, and thus the photocatalytic activity is highly improved [30]. Meanwhile, the generated electrons are trapped by dissolved O2 to produce O2−, and transformed to reactive oxygen species OH by multistep reductions (Eq. (5)-(8)). Moreover, the ECAg2O of TiO2 (2.8 eV vs. SHE) was higher than the E0/2(OH/H2O) (+2.68 eV vs. SHE) [57,59], indicating that the photogenerated holes at VB of TiO2 could oxidize H2O to OH according to Eq. (9). Subsequently, photoinuced holes in the VB of TiO2 can easily move and accumulate at the VB of Ag2O since ECAg2O (Ag2O, +1.6 eV vs. SHE) is less positive than that of TiO2. As a result, the recombination potential of e−−h+ pairs was largely reduced, thus greatly enhancing quantum efficiency [28]. Moreover, photoinduced holes transferred and accumulated in the VB of Ag2O could directly oxidize the target pollutants to a great extent. The photogenerated reactive species (h+, OH, O2−) could degrade CBZ or DCF molecules into intermediates and finally to mineralization (Eq. (10)).
3.6. Reusability of 5% Ag₂O/P-25 catalyst on PhACs removal

The reusability of any catalyst during photocatalytic process is an important factor to evaluate its performance in practical applications. For this aim, cyclic photocatalytic experiments were performed for both target pollutants on 5% Ag₂O/P-25, as shown in Fig. 8. After, five consecutive cycles of photocatalytic degradation of CBZ, the catalyst did not exhibit any significant loss of its activity (Fig. 8a). The results are indicative of the potential practical application of Ag₂O/P-25 catalyst based on its remarkable reusability for CBZ degradation. The plausible photocatalytic activity of the selected catalyst might be attributed to the self-stability exhibited by Ag₂O nanoparticles once the complex structure of Ag₆₄O₆ is formed during the photocatalytic process [60]. Moreover, the separation of catalyst from aqueous solution was achieved in all the cycles with just 15 min of centrifugation, which leads to the conclusion that the complex catalyst synthesized can easily be recovered without high filtration costs, as normally associated with TiO₂ nanoparticles [22].

On the other hand, the photocatalytic removal efficiency of DCF inhibited gradually during cyclic reuse of composite catalyst (Fig. 8b). The removal percentage of DCF dropped by 35% up to 5th cycle as compared to 1st cycle. Nevertheless, as the inhibition rate of the photocatalytic activity was acceptable and remained almost stable after 2nd cycle, the synthesized 5% Ag₂O/P-25 demonstrated a moderately stable activity towards DCF degradation, and thus could be recommended for the long-term application. However, the inhibitory mechanism observed during the photocatalytic process of DCF under the identical working conditions of CBZ was not clear. This might be due to the possible de-activation of catalyst by surface blockage, irreversible adsorption on active sites, and aggregation of catalyst particles [47]. A clear transformation in a physical appearance of 5% Ag₂O/P-25 was observed before and after the reaction (Fig. 5a). Infrared spectra of the mixture of Ag₂O/P-25 and CBZ were compared with the spectra of CBZ. The vibration bands at 1630 and 1600 cm⁻¹ could be ascribed to the aromatic ring of CBZ, which forms intermediate 1 via route b. The intermediate 1 can further be transformed into intermediate 6 (oxcarbamazepine). Alternatively, intermediate 2 (epoxide-CBZ) and intermediate 5 (2-carboxyphenylamino-5-hydroxybenzoic acid) form via route a due to short-lived reaction intermediate, hydroxy-CBZ. The reaction of intermediate 2 with OH radicals can form other degradation products, such as intermediate 3 (acridine-9-carboxaldehyde). The ring cleavage in the intermediate 3 is followed by the loss of amide group, which leads to an undetected intermediate, which further reacts with OH to form intermediate 4 (hydroxyacridine-9-carboxaldehyde). Due to ring cleavage, intermediate 5 can further be transformed into other intermediates 6 (anthranilic/salicylic acid) and 7 (cathelic). Finally, the complex hydroxylated intermediates and low molecular mass compounds can be oxidized through ring-reacting reactions to aliphatic compounds and further oxidation to mineralization (CO₂ and H₂O).

3.7. CBZ intermediates identification and possible degradation pathway

Of the selected PhACs, transformation products formed during the photocatalytic degradation of CBZ (as an illustrative) using Ag₂O/P-25 under UV irradiation were analyzed using high-resolution FT-ICR mass spectrometry and detected based on their accurate masses and deduced elemental formulae (Table S3, supplementary information). The common transformation products of CBZ such as 10,11-dihydropyrimidinone (m/z 253), acridine-9-carboxaldehyde (m/z 208), hydroxycarbazole (m/z 224) [38,39,50,62] were detected. The photocatalysis transforms CBZ to degradation products showing other ecological properties [60]. The large number of compounds formed during the photocatalytic degradation evidences the complexity involved in the photocatalysis of CBZ, thus indicating the possible occurrence of multi-step degradation routes and interconnected pathways [16].

A photocatalytic degradation mechanism of CBZ shown in Fig. 9 was proposed based on the degradation products unambiguously identified photoproducts in this study and proposals of the previous literatures [38,39,62,50]. The short-lived proposed intermediates are in the brackets, while stable intermediates are inside the parentheses. Since substituents could appear in different positions in the aromatic rings, they have been represented as crossing the parenthesis marks. As verified by the quenching experiments, the major reactive species involved in photocatalytic degradation of CBZ in aqueous Ag₂O/P-25 suspensions were photogenerated h⁺ and ‘OH radicals.

In photocatalytic process, hydroxylation of aromatic rings by ‘OH radicals promotes the sequential ring cleavage reactions [7]. There might be two different routes (a, and b) when photogenerated ‘OH radicals react with CBZ to form hydroxy-CBZ. First, ‘OH radical attacks the aromatic ring of CBZ, which forms intermediate 1 via route b. The intermediate 1 can further be transformed into intermediate 6 (oxcarbamazepine). Alternatively, intermediate 2 (epoxide-CBZ) and intermediate 5 (2-carboxyphenylamino-5-hydroxybenzoic acid) form via route a due to short-lived reaction intermediate, hydroxy-CBZ. The reaction of intermediate 2 with ‘OH radicals can form other degradation products, such as intermediate 3 (acridine-9-carboxaldehyde). The ring cleavage in the intermediate 3 is followed by the loss of amide group, which leads to an undetected intermediate, which further reacts with ‘OH to form intermediate 4 (hydroxyacridine-9-carboxaldehyde). Due to ring cleavage, intermediate 5 can further be transformed into other intermediates 6 (anthranilic/salicylic acid) and 7 (cathelic). Finally, the complex hydroxylated intermediates and low molecular mass compounds can be oxidized through ring-reacting reactions to aliphatic compounds and further oxidation to mineralization (CO₂ and H₂O).

4. Conclusion

A heterojunction 5% Ag₂O/P-25 was selected as an efficient photocatalyst by a screening assessment of four different photocatalysts.
Dark adsorption, UV photolysis and photocatalytic kinetics of target pollutants were investigated as preliminary tests. The selected 5% Ag₂O/P-25 catalyst was prepared and characterized by SEM, EDX, BET, and UV–vis diffuse reflectance spectra. The effects of catalyst dose, initial pollutants concentration, and mineralization during the photocatalytic degradation of CBZ and DCF were investigated in both DW and RME solution matrices. The optimal CBZ and DCF removals of 89.10% and 93.5%, respectively for 180 min of UV irradiation were observed at Fig. 9. Proposed photodegradation pathway of CBZ by Ag₂O/P-25 under UV light irradiation. [CBZ]₀ = 20 mg L⁻¹, Catalyst dosage = 0.4 g L⁻¹.
catalyst dose of 0.4 g L⁻¹ in DW matrix. However, the optimal catalyst doses for CBZ and DCF in RME matrix were respectively increased by factor 2 and 1.5, to achieve the same level of removal, which may be due to the influence of organic matters and natural scavengers in the real effluents. A noticeable decreasing trends in removal rates were ob-
served with the increased initial concentration of both PhACs, and ki-
netics seems to fit the Langmuir-Hinshelwood model. A substantial im-
provement in mineralization was also achieved. The results showed that photoinduced holes and •OH were the dominant oxidation species in the photocatalytic degradation of PhACs. A possible reaction me-
chanism and energy band matching of complex 5% Ag/0.7-25 was also demonstrated. Good reusability was exhibited by the selected photo-
catalyst during photocatalytic degradation of target PhACs, ensuring its aptitude for practical applications. Moreover, multiple routes of the CBZ transformation and various intermediates formed during pho-
catalytic degradation were studied and a possible multi-step degrada-
tion path was proposed.

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