Understanding the mechanisms of trace organic contaminant removal by high retention membrane bioreactors: a critical review

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Abstract
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**Abstract:**
High retention membrane bioreactors (HR-MBR) combine a high retention membrane separation process such as membrane distillation, forward osmosis or nanofiltration with a conventional activated sludge (CAS) process. Depending on the physicochemical properties of the trace organic contaminants (TrOCs) as well as the selected high retention membrane process, HR-MBR can achieve effective removal (80-99%) of a broad spectrum of TrOCs. An in-depth assessment of the available literature on HR-MBR performance suggests that compared to CAS and conventional MBRs (using micro- or ultrafiltration membrane), aqueous phase removal of TrOCs in HR-MBR is significantly better. Conceptually, longer retention time may significantly improve TrOC biodegradation, but there are insufficient data in the literature to evaluate the extent of TrOC biodegradation-improvement by HR-MBR. The accumulation of hardly biodegradable TrOCs within the bioreactor of an HR-MBR system may complicate further treatment and beneficial reuse of sludge. In addition to TrOCs, accumulation of salts gradually increases the salinity in bioreactor and can adversely affect microbial activities. Strategies to mitigate these limitations are discussed. A qualitative framework is proposed to predict the contribution of the different key mechanisms of TrOC removal (i.e., membrane retention, biodegradation and sorption) in HR-MBR.

**Keywords:** High retention membrane bioreactors; trace organic contaminants; removal mechanisms; predictive framework; membrane distillation (MD), forward osmosis (FO); nanofiltration (NF)
Introduction

Wastewater treatment and reuse are important strategies to mitigate pollution and water scarcity (Tang et al. 2018). For safe water reuse applications, effective removal of a wide range of pollutants including bulk organics, salts, nutrients and trace organic contaminants (TrOCs) is essential. Among these pollutants, the effective removal of TrOCs such as pharmaceuticals, pesticides, steroid hormones, industrial chemicals and ingredients of personal care products is one of the most challenging aspects of wastewater treatment and reuse as conventional activated sludge (CAS) based wastewater treatment plants were not designed for their removal (Hai et al. 2014b, Radjenović et al. 2009). Since TrOCs are potentially harmful to the aquatic ecosystems and human health (Alexander et al. 2012, Asif et al. 2018c, Hai et al. 2018, Schwarzenbach et al. 2006), development of a wastewater treatment process for effective removal of TrOCs has gained significant interest in the recent years.

Membrane bioreactors (MBR) have been extensively studied over the last decade due to their potential of producing high quality effluent that may be suitable for water reuse applications (Bouju et al. 2008, Hai et al. 2014a, Hai et al. 2014c, Melin et al. 2006). In conventional MBR, activated sludge is responsible for the degradation of the pollutants such as bulk organics, nutrients and TrOCs, while micro- or ultrafiltration (MF/UF) based membrane separation process effectively retains the activated sludge within the bioreactor (Hai et al. 2011b, Jegatheesan & Visvanathan 2014, Reif et al. 2008). Conventional MBR can achieve efficient aqueous phase removal of bulk organics from wastewater (Judd 2014, Judd 2016, Radjenović et al. 2008a). However, the ineffectiveness of conventional MBRs for the removal of certain groups of TrOCs is a significant concern. For effective removal of TrOCs, high retention membrane separation processes such as nanofiltration (NF)/reverse osmosis (Alturki et al. 2010, Wang et al. 2015) and membrane distillation (Jacob et al. 2015, Song et al. 2018a, Wijekoon et al. 2014a) have been combined with conventional MBRs as a post-treatment step. To avoid an additional high retention membrane separation process, the high retention (HR)-MBRs have been developed which can achieve TrOC retention by
membrane and subsequent biodegradation in a single step for the production of high quality effluent suitable for water reuse applications (Luo et al. 2014).

HR-MBR combines the high retention membranes such as nanofiltration (NF), forward osmosis (FO) or membrane distillation (MD) with an activated sludge process. Available studies report that HR-MBR provides effective removal of a wide range of TrOCs and can produce high quality TrOC-free effluent stream (Luo et al. 2017b, Wijekoon et al. 2014b). One of the underlying rationales for the development of HR-MBR was that the effective retention of pollutants within the bioreactor may facilitate biodegradation due to the prolonged contact time between the activated sludge and TrOCs. Despite the effective TrOC retention by the high retention membranes (Luo et al. 2017b, Wang 2013), degradation of TrOCs by activated sludge within the bioreactor has not been reported to consistently improve (Luo et al. 2017b, Wijekoon et al. 2014b). This is because the degradation of TrOCs by the activated sludge depends on their intrinsic biodegradability that is governed by their physicochemical properties such as chemical structure and hydrophobicity (Hai et al. 2014b).

A few excellent reviews on the main features, overall performance and technological constraints of HR-MBR have been published recently (Blandin et al. 2018, Luo et al. 2014, Song et al. 2018b, Yeo et al. 2015). However, removal of TrOCs by HR-MBR and factors affecting the removal of TrOCs by the activated sludge in HR-MBR have not been critically reviewed and discussed. This review aims to critically analyze the removal of TrOCs by the high retention membranes and activated sludge in HR-MBR. In addition, mechanisms of TrOC removal by HR-MBR are systematically elucidated. Based on the contribution of each mechanism of TrOC removal, a qualitative predictive framework is proposed. Finally, future research directions are identified and discussed.
HR-MBR configurations

In addition to the use of high retention membranes that allows effective retention of pollutants including TrOCs, HR-MBRs may have different features compared to the conventional MBR configuration (Figure 1a). Three configurations of HR-MBR, namely membrane distillation (MD)-MBR (Figure 1b), forward osmosis (FO)-MBR (Figure 1c) and nanofiltration (NF)-MBR (Figure 1d) have been investigated to-date (Luo et al. 2017b, Phan et al. 2016b, Wijekoon et al. 2014b).

Mechanisms of TrOC removal by HR-MBR include: (i) membrane retention; (ii) biodegradation; (iii) sorption; (iv) air stripping/volatilization; and (v) photolysis (Hai et al. 2014b, Pomiès et al. 2013, Verlicchi et al. 2012). Removal of TrOCs by volatilization depends on the Henry’s constant (H), which is the ratio of the concentration of a target pollutant in air to its concentration in wastewater. It has been reported that the removal of target pollutants via volatilization can be significant (5-10%) if their H values are higher than 0.005 (Joss et al. 2006, Park et al. 2017, Stevens-Garmon et al. 2011). Since the values of H for TrOCs generally fall in the range of $10^{-6}$ to $10^{-10}$, TrOC removal in HR-MBR via volatilization is insignificant. Similarly, contribution of photolysis is negligible due to the high mixed liquor suspended solids (MLSS) concentration in the bioreactor (Trinh et al. 2016, Wijekoon et al. 2014b). Hence, biodegradation, sorption and membrane retention mechanisms primarily contribute in varying extent for TrOC removal by HR-MBR as discussed in the following sub-sections.

Mechanisms of TrOC removal by high retention membranes

Retention by high retention membrane appears to be the most dominant mechanism for removal of TrOCs that are resistant to degradation by the activated sludge. Therefore, understanding the mechanisms of TrOC removal by MD, NF and FO membranes is vital. TrOC retention/removal by high retention membranes depends on: (i) the type of high retention membrane; (ii) influent characteristics; and (iii) operating conditions (Table 1). TrOC retention by NF and FO membranes has been reported to be influenced by a
number of factors (Table 1) such as physicochemical properties (e.g., hydrophobicity, charge and molecular weight) of TrOCs, operating parameters and membrane properties as explained below (Bellona et al. 2004, Hau et al. 2014, Nghiem & Coleman 2008, Nghiem et al. 2005). On the other hand, TrOC retention by MD membranes depends on the volatility ($p_K_H$) and hydrophobicity ($\log D$) of pollutants (Luo et al. 2014, Wijekoon et al. 2014a), thereby making TrOC retention by MD membrane simpler as compared to NF and FO membranes. In a stand-alone MD process, ‘$p_K_H$/log D’ ratio of less than 2.5 corresponds to ineffective TrOCs retention (50-70%), while TrOCs with a high $p_K_H$/log D ratio (>2.5) are effectively retained (90-99%) by MD membranes (Wijekoon et al. 2014a).

(Table 1)

Mechanisms of TrOC retention by NF and FO membrane consist of: (i) the net sorption of a solute on the membrane surface; (ii) the transport of solute inside the membrane; and (iii) the sieving property of the membrane (Coday et al. 2014, Luo et al. 2014, Nghiem et al. 2006). Influence of other factors including hydrophobicity and charge repulsion on sorption and solute transport has also been observed (Agenson et al. 2003, Taheran et al. 2016). In general, size exclusion mechanism is responsible for the retention of non-ionic and hydrophilic (log D <3) TrOCs, and the extent of retention depends on the molecular weight cut-off (MWCO) of membranes. For example, a tight NF membrane (MWCO <200 g/mole) achieved 97% retention of carbamazepine (log D = 1.89) from a filtered lake water containing a mixture of 22 TrOCs, while only 50% removal was observed by a loose NF membrane (MWCO >300 g/mole) (Comerton et al. 2008). In another study by Xie et al. (2012b), retention of carbamazepine by a cellulose triacetate FO membrane remained in between 80 and 90% at different pH values (i.e., 3.5-7.5). Similarly, carbamazepine retention by cellulose triacetate and thin film composite polyamide FO membranes was reported to be 90-95% (Jin et al. 2012). Effective retention (80-99%) of other hydrophilic TrOCs such as metronidazole (log D = -0.14), clofibrac acid (log D = -1.06) and N, N-Diethyl-meta-toluamide (DEET, log D = 2.42) by NF and FO membranes has been reported (Alturki et al. 2010, Cath et al. 2010, Linares et al. 2011, Valladares et al. 2011, Verliefde et al. 2009). Hydrophobic TrOCs (log D >3) such as steroid hormones, bisphenol A
and 4-tert-octylphenol have also been reported to be effectively retained (>80%) by both NF and FO membranes (Alturki et al. 2013, Nghiem & Coleman 2008, Verliefde et al. 2009). Notably, hydrophobicity of TrOCs can influence their retention because hydrophobic TrOCs can adsorb onto the membrane surface, thus initially resulting in their effective retention. However, as the filtration continues, their retention may reduce due to their subsequent diffusion into the permeate (Nghiem & Coleman 2008, Verliefde et al. 2009).

Compared to hydrophilic TrOCs, hydrophobic TrOCs, regardless of their size, can diffuse into the permeate to attain an equilibrium between the concentration of hydrophobic TrOCs on/near the membrane surface and the permeate. This gradually reduces the extent of TrOC retention by the NF and the FO membranes (Hu et al. 2007, Verliefde et al. 2007, Xie et al. 2012a). Once an equilibrium between the concentration of TrOCs on/near membrane surface and permeate is established, the role of adsorption in TrOC retention diminishes, and charge repulsion and size exclusion mechanisms govern the retention of TrOCs by NF and FO membranes (Coday et al. 2014, Yoon et al. 2006).

NF and FO membranes are negatively charged at pH=7 owing to the protonation of their functional groups (Coday et al. 2014, Comerton et al. 2008). Hence, membrane surface charge and its interaction with charged TrOCs such as diclofenac, naproxen and ibuprofen will govern the extent of their retention. Poor rejection of positively charged hydrophobic TrOCs such as steroid hormones by NF/FO membrane can be attributed to the attraction between positively charged TrOCs and negatively charged membrane surface. This consequently increases the concentration of solute at the surface of membrane, thus increasing their diffusion into permeate. On the other hand, effective retention of negatively charged hydrophilic TrOCs is due to the charge repulsion mechanism, which keeps TrOCs away from the membrane surface (Kimura et al. 2004, Radjenović et al. 2008b, Verliefde et al. 2007). Notably, the transformation of neutral TrOCs to negatively charged TrOCs at pH>pK_a can improve their retention by NF and the FO membranes. For example, an increase of 50 and 65% in the retention of sulfamethoxazole (pK_a = 5.6) and ibuprofen (pK_a = 4.47), respectively, by a thin film composite NF membrane was observed when the feed pH was changed from 5 to 10 (Nghiem et al. 2006). In another study, retention of ibuprofen (pK_a = 4.47) and naproxen (pK_a
4.2) by an FO membrane was observed to be increased by 10-15% due to the increase in the pH of feed from 6 to 8 (i.e., pH>pKₐ) (Jin et al. 2012). Based on the discussion regarding the factors affecting the retention of TrOCs by NF and FO membrane, a qualitative predictive framework is presented in Figure 2.

[Figure 2]

**Aqueous phase removal of TrOCs by HR-MBR**

As mentioned before, three configurations of HR-MBR, namely membrane distillation bioreactor (MDBR), forward osmosis (FO-MBR) and nanofiltration (NF-MBR) have been investigated to-date (Fernandez-Fontaina et al. 2012, Luo et al. 2017b, Phan et al. 2016b, Wijekoon et al. 2014b). Depending on the physicochemical properties of TrOCs and the type of HR-MBR configuration, removal of TrOCs by HR-MBRs can range between 90-99% (Table 2).

[Table 2]

The advantage of an integrated biodegradation and membrane separation process is that HR-MBR can achieve better TrOC removal as compared to the standalone HR-membrane. For instance, Wijekoon et al. (2014a) studied the rejection of a mixture of 30 TrOCs by a standalone MD process, and observed partial retention (50-70%) of a few volatile TrOCs (pKₐ<9) such as 4-tert-octylphenol (pKₐ= 5.06), benzophenone (pKₐ= 5.88) and amitriptyline (pKₐ= 8.18). On other hand, when the performance of MDBR was studied for the removal of a mixture of 30 TrOCs, effective removal (95-99%) was achieved by MDBR for all the selected 30 TrOCs including those partially removed by the standalone MD process (Wijekoon et al. 2014a, Wijekoon et al. 2014b).

Compared to ineffective or unstable removal of a few hydrophobic TrOCs such as bisphenol A (40-80%), oxybenzone (70-75%), estrone (80%), and 17α – ethynylestradiol (70-90%) by a standalone FO process (Coday et al. 2014), FO-MBR has been reported to achieve above 99% removal for hydrophobic TrOCs (Luo et al. 2015b, Luo et al. 2017b). Better performance of MDBR and FO-MBR for TrOC removal as compared to the standalone MD and FO process can be attributed to the efficient degradation of volatile
and hydrophobic TrOCs such as 4-tert-octylphenol, benzophenone, triclosan, bisphenol A and oxybenzone by the activated sludge (Holloway et al. 2014, Luo et al. 2015b, Wijekoon et al. 2014b).

Both MDBR and FO-MBR was reported to achieve effective removal of a range of TrOCs (Table 2) (Li et al. 2018, Luo et al. 2014). Indeed, a comparison of the aqueous phase removal of TrOCs by CAS, conventional MBR and HR-MBR reveals that median TrOC removal by HR-MBR is almost 90%, while median values for CAS and MBR are approximately 60 and 65%, respectively (Figure 3).

[Figure 3]

**Factors affecting TrOC removal by activated sludge in HR-MBR**

*Effect of TrOC molecular structure*

Degradation of TrOCs by activated sludge depends on their intrinsic biodegradability and sorption potential. The extent of TrOC degradation can vary depending on the chemical structure of the target compound (Luo et al. 2015b, Tadkaew et al. 2011). In general, simple structured TrOCs without branched/multi chain alkyl groups are readily biodegraded compared to structurally complex TrOCs due to their resistance to microbial degradation. Similar to conventional MBR, TrOCs containing strong electron withdrawing functional groups (EWG) such as carboxyl, halogen and amide are resistant to biodegradation, and their degradation is also poor and/or unstable in HR-MBR (Phan et al. 2016b, Wijekoon et al. 2014b). For instance, atrazine, carbamazepine and diclofenac are resistant to biodegradation due to the presence of EWGs (*i.e.*, halogen and amide) in their structures (Nguyen et al. 2013a, Tadkaew et al. 2011).

Based on their biodegradation, TrOCs can be divided into three categories: (i) low or unstable removal (5-30%) for TrOCs containing strong EWGs such as atrazine, carbamazepine and primidone; (ii) consistently high removal (80-90%) of hydrophobic TrOCs containing electron donating groups (EDGs) such as steroid hormones; and (iii) poor to moderate removal (30-80%) of hydrophilic TrOC containing both EWGs and EDGs (Luo et al. 2017a, Phan et al. 2016b, Wijekoon et al. 2014b). Limited degradation of some TrOCs by the activated sludge highlights the significance of high retention membranes in effective TrOC removal.
for producing a high quality effluent. Specific groups of TrOCs that are poorly degraded by the activated sludge accumulate within the bioreactor of HR-MBR.

**Effect of TrOC sorption on activated sludge**

Hydrophobic TrOCs (log D>3) can adsorb onto the activated sludge by following mechanisms: (i) chemical binding to bacterial proteins and nucleic acids; (ii) sorption onto polysaccharide structures outside the bacterial cell; (iii) adsorption onto bacterial lipid structure (Semblante et al. 2015). With a few exceptions, HR-MBR can achieve as high as 99% removal of hydrophobic TrOCs via biodegradation and sorption (Holloway et al. 2014, Wijekoon et al. 2014b). Additionally, non-hydrophobic interactions such as hydrogen bonding, electrostatic interactions and ion exchange can also instigate sorption of hydrophilic TrOCs onto activated sludge. For instance, Wijekoon et al. (2014b) observed that sorption significantly contributed to the removal of a hydrophilic TrOC salicylic acid (log D = -1.22).

Sorption on activated sludge contributes to improvement of overall aqueous phase removal of TrOCs in conventional MBRs (Lay et al. 2012, Mascolo et al. 2010, Phan et al. 2015a, Phan et al. 2015b, Stevens-Garmon et al. 2011). For instance, halogenated TrOCs are widely reported to be persistent to microbial degradation. However, the increase in halogen-content increases the hydrophobicity of halogenated TrOCs (Hai et al. 2011a). Thus efficient removal of halogenated TrOCs, particularly of triclosan, have been reported to be achieved by even conventional MBRs due to its sorption onto activated sludge (Hai et al. 2014b, Tadkaew et al. 2011, Wijekoon et al. 2013). Although sorption also contributes to the removal of TrOCs within the bioreactor of HR-MBRs, the overall TrOC removal by HR-MBR is less dependent on sorption because of the high retention membranes which can retain even the TrOCs demonstrating low sorption on sludge.

Following sorption onto the activated sludge, the extent of TrOCs degradation depends on their intrinsic biodegradability (Hai et al. 2014b). For instance, Wijekoon et al. (2014b) observed higher concentrations of two highly hydrophobic TrOCs, namely triclosan and octocrylene in the sludge samples of an MDBR as compared to other hydrophobic TrOCs such as bisphenol A and steroid hormones. This is because of the
presence of strong EWGs in the molecular structure of triclosan and octocrylene i.e., halogen and carbonyl, respectively (Hai et al. 2014b, Tadkaew et al. 2011).

**Effect of mixed liquor suspended solids concentration**

Conceptually, mixed liquor suspended solid (MLSS) concentration may affect the removal of TrOCs in a biological process by influencing the rate of biodegradation. However, biodegradation also depends on TrOC physicochemical properties and diversity of microbial communities (Phan et al. 2014, Phan et al. 2016a, Trinh et al. 2012). Indeed biodegradation of TrOCs containing EDGs in their molecular structure (i.e., easily biodegradable) has been reported to be 80-99% in conventional MBRs at the tested MLSS concentrations ranging from 2-15 g/L (He et al. 2013, Sui et al. 2011, Tadkaew et al. 2010, Tambosi et al. 2010). Similarly, effective degradation (90-99%) of TrOCs containing EDGs such as naproxen, ketoprofen, bisphenol A and t-octylphenol has been achieved in NF-MBR, FO-MBR and MDBR over MLSS concentrations of 2-5 g/L (Luo et al. 2017b, Phan et al. 2016b, Wijekoon et al. 2014b). Holloway et al. (2014) also achieved 95-99% degradation of TrOCs containing strong EDGs such as naproxen, oxybenzone, ibuprofen and caffeine by operating an FO-MBR at a MLSS concentration of 3-4 g/L.

Degradation of hydrophilic TrOCs containing EWGs in conventional MBR has been reported to be poor irrespective of operating MLSS concentrations (Clara et al. 2005, Kim et al. 2007, Li et al. 2011, Trinh et al. 2012, Xue et al. 2010). Similarly, poor and unstable degradation (15-40%) by the activated sludge in HR-MBR has been reported for hydrophilic TrOCs containing EWGs such as carbamazepine, DEET and atrazine (Luo et al. 2015b, Phan et al. 2016b).

**Effect of solids retention time**

Solids retention time (SRT) governs the microbial makeup of a bioreactor. Conceptually, long SRT may improve the extent of TrOC removal by providing adequate time for the development of special TrOC degrading microbial communities (Feki et al. 2009, Maeng et al. 2013, Phan et al. 2014). Indeed, biodegradation of a few resistant TrOCs such as sulfamethoxazole, diclofenac, mefenamic acid and
carbamazepine improved significantly following an increase in the SRT of conventional MBR (Figure 4). The biodegradation of resistant TrOCs containing strong EWGs varied depending on the type of HR-MBR configuration. For instance, FO-MBR (SRT = 20 days) achieved better degradation of carbamazepine, atrazine, clofibrac acid, fenoprop and diclofenac as compared to MDBR (SRT = 88 days) (Luo et al. 2017b, Phan et al. 2016b, Wijekoon et al. 2014b). Disrupted metabolic activities associated with the treatment in thermophilic conditions may have resulted in less effective degradation of resistant TrOCs by MDBR (Tran et al. 2013, Wijekoon et al. 2014b). However, a systematic study is necessary to determine the actual reasons of these observations.

As expected, no improvement was observed in the degradation of easily biodegradable TrOCs containing EDGs such as naproxen, ketoprofen and ibuprofen by increasing the SRT of a conventional MBR beyond 15 days (Kimura et al. 2007, Radjenovic et al. 2007, Tambosi et al. 2010, Wijekoon et al. 2013). Similarly, no observable effect of SRT on the degradation of TrOCs such as naproxen, ketoprofen, ibuprofen, bisphenol A and 4-tert-octylphenol has been reported in HR-MBRs over a wide range of SRTs (Holloway et al. 2014, Lay et al. 2010, Phan et al. 2016b, Wijekoon et al. 2014b).

[Figure 4]

**Effect of operating temperature**

To date lab-scale FO- and NF-MBRs have been operated at the room temperature *i.e.*, 18-21 °C, while the operating temperature of MDBR falls in the thermophilic range *i.e.*, 40-60 °C (Goh et al. 2013, Holloway et al. 2015, Phan et al. 2016b, Wijekoon et al. 2014b). As noted in the previous section, relatively less degradation of a few hydrophilic TrOCs such as carbamazepine, atrazine, clofibrac acid, fenoprop and diclofenac has been observed in MDBR as compared to FO-MBR (Luo et al. 2017b, Wijekoon et al. 2014b). This can be attributed to the higher operating temperature of MDBR which can disrupt microbial activities. Particularly, high operating temperature (>35 °C) can affect TrOC degradation by reducing the abundance of nitrifying bacteria (Gao et al. 2013, Shore et al. 2012, Zhang et al. 2009). In conventional MBR, improvement in TrOC removal has been reported to concur with the achievement of efficient nitrification
(Estrada-Arriaga & Mijaylova 2011). To provide further insight into this aspect, the effect of thermophilic conditions on the microbial diversity and TrOC removal in various formats of HR-MBR should be further investigated.

**Fate of TrOCs in HR-MBR**

Effective retention of TrOCs (90-99%) within the bioreactor of HR-MBR by the high retention membranes may facilitate their biodegradation due to the prolonged contact time between the activated sludge and TrOCs. Indeed, comparing data from independent studies, degradation of some TrOCs seems to be more stable in HR-MBR as compared to conventional MBR and CAS (Figure 5). The degradation improvement for these TrOCs in HR-MBR is discernible, however, not very high. An assessment of the relative contribution of different mechanisms of TrOC removal suggests that membrane retention and biodegradation govern the effectiveness of treatment by HR-MBR (Figure 6). According to the available literature, TrOC removal in HR-MBR via sorption onto activated sludge ranges between 1-10% and 2-30% for hydrophilic and hydrophobic TrOCs, respectively.

[Figure 5]

[Figure 6]

The fate of TrOCs during wastewater treatment by HR-MBR is governed by the TrOC physicochemical properties (e.g., chemical structure and hydrophobicity), which influence their biodegradation. The hardly biodegradable TrOCs will not appear in the treated effluent because of the extra barrier provided by the high retention membranes. However, when not subsequently biodegraded, their accumulation on sludge would complicate sludge disposal and reuse. Based on the contribution of each mechanism of TrOC removal, a qualitative framework for the removal of TrOCs in HR-MBR is proposed in Figure 7.

[Figure 7]

**Effect of salt and TrOC accumulation**
HR-MBRs produce high quality effluent by retaining organic and inorganic impurities (Luo et al. 2017b, Wijekoon et al. 2014b). Complete retention of inorganic impurities results in the accumulation of salts within the bioreactor. In addition, reverse salt flux in FO-MBR also contributes to salinity buildup. The effect of salinity build-up in bioreactor has been investigated in FO-MBR (Wang et al. 2014, Zhang et al. 2017). Salinity build-up affects physical and biochemical characteristics of the biomass. For instance, increase in the concentration of extracellular polymeric substances (EPS) and soluble microbial products (SMP) has been observed following an increase in salt concentration (Luo et al. 2015a, Qiu & Ting 2013). Moreover, increase in SMP and EPS concentration can instigate membrane fouling that can affect TrOC removal by high retention membranes (Cody et al. 2014, Lay et al. 2010).

In a recent study, Luo et al. (2017b) observed a reduction in mixed liquor volatile suspended solid (MLVSS) concentration during the first two weeks of FO-MBR operation during the treatment of synthetic wastewater containing a mixture of 30 TrOCs. In addition, they reported reduced bacterial diversity during the first 20 days of FO-MBR operation (Luo et al. 2017b). They attributed the reduction in MLVSS concentration and bacterial diversity to salinity buildup in the bioreactor. Despite the adverse effects of salinity build-up on microbial activity, no effect on overall TrOC removal was observed because the high retention membrane effectively retained TrOCs within the bioreactor (Luo et al. 2015b, Wijekoon et al. 2014b).

Delgado et al. (2010) observed an increase in the endogenous respiration rates of the activated sludge collected from a conventional MBR following its exposure to carbamazepine at a concentration of 1 µg/L, probably because microbes require more maintenance energy in order to acclimatize to the stress induced by a chemical. Similarly, specific oxygen uptake rate of the activated sludge in a bioreactor was reduced by 19, 39 and 40%, when exposed to carbamazepine, ketoprofen and naproxen each at 10 µM concentration (Wang et al. 2008). Accumulation of resistant TrOCs in the bioreactor can adversely affect microbial activity, and, hence TrOC removal. However, these aspects are yet to be systematically studied.

The problem of TrOC and salt accumulation can be solved by integrating an additional ultrafiltration (UF) or microfiltration (MF) membrane with the bioreactor of HR-MBR and periodically purging liquid media
through the UF/MF membrane. In a study by Holloway et al. (2015), performance of FO-MBR with and without an additional UF membrane was studied. They observed that the flux of an integrated UF+FO-MBR system remained almost constant at ~7 L/m² h for 4 months, while the flux of the FO-MBR without UF membrane reduced from 6 to less than 2 L/m² h within two months (Holloway et al. 2015). In another study, a stable operation (flux and MLSS concentration) of an FO-MBR following the integration of MF membrane was achieved for two months, but the performance was not compared to a ‘control’ FO-MBR (Luo et al. 2015b). The issue of reverse salt flux in FO-MBR can be solved by using organic draw solutes instead of low molecular weight inorganic salts. Organic draw solutes are biodegradable, and hence will not cause salinity buildup in FO-MBR (Bowden et al. 2012, Hau et al. 2014, Nawaz et al. 2013).

**Future research**

All available HR-MBR studies presented in this review employed synthetic wastewater. Real wastewater is complex and contains a wide range of pollutants that can potentially interfere with the TrOC removal performance of HR-MBR. For instance, Mascolo et al. (2010) observed during the biological treatment of pharmaceutical wastewater that the extent of biodegradation of a target compound can vary in presence of different pollutants such as wastewater derived solvents or even the co-existence of other biodegradable compounds in wastewater (Mascolo et al. 2010). Hence, it is important to evaluate the performance of HR-MBR for the treatment of real wastewater.

To improve the degradation of TrOCs in HR-MBR, other microbes with better TrOC degradation capacity than conventional activated sludge can be introduced. In this context, white-rot fungi and their extracellular enzymes (Hai et al. 2006) are worth-noting. White-rot fungi and their enzymes have been reported to achieve effective degradation of TrOCs that are resistant to activated sludge based treatment process (Asif et al. 2017a, Asif et al. 2018b, Yang et al. 2013). In a study by Nguyen et al. (2013b), addition of whole-cell white-rot fungi in conventional bacteria-dominated MBR significantly improved the degradation of three pharmaceuticals and three pesticides. Furthermore, coupling of an MD system to an enzymatic bioreactor achieved better TrOC degradation as compared to a previously developed ultrafiltration based
enzymatic membrane bioreactor (Asif et al. 2018a, Asif et al. 2018b, Asif et al. 2017b, Nguyen et al. 2015, Nguyen et al. 2014), indicating the benefit of combining white-rot fungal enzyme system with high retention membranes.

The metabolites formed during treatment of TrOCs by advanced oxidation processes (AOPs) may be more amenable to degradation by activated sludge (Prado et al. 2017, Reungoat et al. 2010, Wang & Wang 2017). Thus AOPs such as ozonation and photocatalysis can be integrated with the bioreactor of HR-MBR for improving TrOC degradation. Laera et al. (2011) studied the performance of an integrated conventional MBR-UV/TiO₂ system for the treatment of pharmaceutical industry wastewater. Carbamazepine is highly resistant to degradation by the conventional activated sludge (Laera et al. 2011, Wijekoon et al. 2014b), but Laera et al. (2011) achieved above 95% removal of carbamazepine with this combination. In another study, an integrated CAS-gamma radiation system was reported to achieve up to 80% removal of carbamazepine from municipal wastewater (Wang & Wang 2017). Improved biodegradation is important as it can simplify the sludge treatment process. However, the cost associated with the application of AOPs needs to be carefully considered.

Size exclusion, diffusion and charge repulsion govern the retention of TrOCs in NF and FO based HR-MBR. Since TrOC properties (e.g. steric hindrance and polarity) depends on pH and feed characteristics, it is critical to investigate the effect of different feed characteristics on the retention of TrOCs by high retention membranes (Agenson & Urase 2007, Chon et al. 2012, Coday et al. 2014, Valladares et al. 2011). There is also a need to develop a technique to categorize different wastewater streams based on the type of TrOCs in order to facilitate the understanding of membrane retention mechanisms. TrOC retention by the high retention membranes needs to be assessed for longer operating period because short term operation with small bioreactor size may result in inaccurate estimation of TrOC retention.

High strength wastewater with elevated concentrations of soluble microbial product and extracellular polymeric substance can cause rapid membrane fouling. Membrane fouling can affect TrOC retention by high retention membranes (Coday et al. 2014, Taheran et al. 2016). Due to the interaction with the
carboxylic and hydroxyl functional groups of the organic matter in wastewater, the negative charge on the surface of FO and NF membranes can increase following the formation of a fouling layer, consequently improving the retention of negatively charged TrOCs such as naproxen, ketoprofen and diclofenac via charge repulsion (Murray et al. 2010, Valladares et al. 2011, Xie et al. 2013). On the other hand, fouling layer may increase the effective MWCO size of the membranes, resulting in slightly poor retention (5-10%) of hydrophilic nonionic TrOCs, e.g. carbamazepine, clofibric acid and sulfamethoxazole, and hydrophobic TrOCs, e.g. oxybenzone and bisphenol A (Coday et al. 2014, Valladares et al. 2011). Hence, the impact of membrane fouling on TrOC retention in HR-MBRs needs to be investigated. Finally, HR-MBRs can produce high quality effluent by providing complete retention of TrOCs and salts. Sludge produced by HR-MBR is saline and potentially toxic. Hence, it is vital to assess further treatment and reuse of sludge withdrawn from HR-MBRs.

Performance of pilot- and full-scale nanofiltration/reverse osmosis, membrane distillation or forward osmosis systems has been assessed for desalination (Guillen-Burrieza et al. 2014, Hancock et al. 2013), resource recovery (Dow et al. 2016, Martinetti et al. 2009, Wang et al. 2016) and wastewater treatment (Altaee & Hilal 2014, Campagna et al. 2013, Ong et al. 2014). However, a few technological challenges such as salinity build-up, membrane stability and low permeate flux should be addressed for the scale up and commercial applications of HR-MBR for wastewater treatment. These challenges have been reviewed comprehensively by Luo et al. (2014) and Blandin et al. (2018).

**Conclusion**

Trace organic contaminants (TrOCs) such as pharmaceuticals, pesticides, industrial chemicals and steroid hormones are commonly detected in wastewater and wastewater-impacted water bodies. Ineffective removal of TrOCs by the wastewater treatment processes such as conventional activated sludge (CAS) and membrane bioreactors (MBR) triggered the development of high retention MBR (HR-MBR). HR-MBR couples a high retention membrane separation process (e.g., membrane distillation, forward osmosis or nanofiltration) to an activated sludge bioreactor. In lab-scale studies, HR-MBRs have demonstrated
promising results with more effective TrOC removal (80-99%) compared to CAS and MBR. TrOC biodegradation by activated sludge depends on a number of factors. Comparing data from independent studies, degradation of some TrOCs seems to be more stable in HR-MBR as compared to conventional MBR and CAS. The degradation-improvement for these TrOCs in HR-MBR is discernible, however, not very high. The hardly biodegradable TrOCs do not appear in the effluent of HR-MBR because of the extra barrier provided by the high retention membranes. However, when not subsequently biodegraded, their accumulation on sludge might complicate sludge disposal and reuse. In this context, bioaugmentation of activated sludge with white-rot fungi that have demonstrated better TrOC degradation capability as compared to activated sludge can be further explored.

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Figure captions

**Figure 1.** Schematics of (a) Conventional membrane bioreactor (MBR); (b) membrane distillation bioreactor (MDBR); (c); forward osmosis- membrane bioreactor (FO-MBR); and (d) nanofiltration-membrane bioreactor (NF-MBR)

**Figure 2.** Qualitative predictive framework for the retention of TrOCs by NF or FO membrane. Modified from (Bellona et al. 2004, Taheran et al. 2016)

**Figure 3.** Aqueous phase removal of TrOCs by CAS, MBR and HR-MBR. Box-and-whisker plot is showing information about: the interquartile range; median (horizontal line in the box); min and max (whiskers); and average (block square in the box). Complete data set for MBR and CAS is given in Supplementary Data Table S1 and S2, respectively. Data source for HR-MBR: Wijekoon et al. (2014b); Alturki et al. (2012); Holloway et al. (2014); Luo et al. (2015b); and Luo et al. (2017b); Phan et al. (2016b); and Wang (2013).

**Figure 4.** Effect of SRT on the aqueous phase removal of selected TrOCs by conventional MBR. (a) Significant SRT dependent improvement in TrOC removal; and (b) insignificant dependence of TrOC removal on SRT. Data source: Alturki et al. (2010); Bouju et al. (2008); Clara et al. (2005); Kimura et al. (2007); Maeng et al. (2013); Radjenovic et al. (2007); Radjenović et al. (2009); Reif et al. (2008); Alturki et al. (2010); Tambosi et al. (2010); and Wijekoon et al. (2013)

**Figure 5.** Variations in the biodegradation of TrOCs in CAS (a), MBR (b) and HR-MBR (c). Box-and-whisker plot is showing information about: the interquartile range; median (horizontal line in the box); min and max (whiskers); and average (block square in the box). Numbers in the parenthesis on the x-axis represent the no. of data points (no. of data points: HR-MBR+MBR+CAS). Complete data set for MBR and CAS is given in Supplementary Data Table S1 and S2, respectively. Data source for HR-MBR: Wijekoon et al. (2014b); Alturki et al. (2012); Holloway et al. (2014); Luo et al. (2015b); and Luo et al. (2017b); Phan et al. (2016b); and Wang (2013).

**Figure 6.** Contribution of different mechanisms for TrOC removal in HR-MBR and conventional MBR. HR-MBR data source: Alturki et al. (2012); Holloway et al. (2014); Luo et al. (2015b); Luo et al. (2017b); and Wijekoon et al. (2014b). Conventional MBR data source: Wijekoon et al. (2013) and Radjenović et al. (2009)

**Figure 7.** A qualitative framework to predict the contribution of different mechanisms of TrOC removal in HR-MBR categorized based on their physicochemical properties.
Figure 1: Schematics of (a) Conventional membrane bioreactor (MBR); (b) membrane distillation bioreactor (MDBR); (c) forward osmosis- membrane bioreactor (FO-MBR); and (d) nanofiltration- membrane bioreactor (NF-MBR)
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4. Effect of SRT on the aqueous phase removal of selected TrOCs by conventional MBR. (a) Significant SRT dependent improvement in TrOC removal; and (b) insignificant dependence of TrOC removal on SRT. Data source: Alturki et al. (2010); Bouju et al. (2008); Clara et al. (2005); Kimura et al. (2007); Maeng et al. (2013); Radjenovic et al. (2007); Radjenović et al. (2009); Reif et al. (2008); Tadkaew et al. (2010); Tambosi et al. (2010); and Wijekoon et al. (2013)
Figure 5. Variations in the biodegradation of TrOCs in CAS (a), MBR (b) and HR-MBR (c). Box-and-whisker plot is showing information about: the interquartile range; median (horizontal line in the box); min and max (whiskers); and average (block square in the box). Numbers in the parenthesis on the x-axis represent the no. of data points (no. of data points: HR-MBR+MBR+CAS). Complete data set for MBR and CAS is given in Supplementary Data Table S1 and S2, respectively. Data source for HR-MBR: Wijekoon et al. (2014b); Alturki et al. (2012); Holloway et al. (2014); Luo et al. (2015b); and Luo et al. (2017b); Phan et al. (2016); and Wang (2013).
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Figure 7. A qualitative framework to predict the contribution of different mechanisms of TrOC removal in HR-MBR categorized based on their physicochemical properties.
**List of Tables**

Table 1. Factors affecting the retention of TrOCs by high retention membranes

<table>
<thead>
<tr>
<th>Factors</th>
<th>MD membrane</th>
<th>FO membrane</th>
<th>NF membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fouling</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Diffusion of solute</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Hydrophobicity</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Membrane MWCO</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Charge on TrOCs</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Membrane surface charge</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Polarity</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Molecular width</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Volatility of TrOCs</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Temperature and pH</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
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</table>

“-” : no effect according to available reports
<table>
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<tr>
<th>TrOCs</th>
<th>Chemical formula a</th>
<th>Molecular Weight a</th>
<th>Dissociation coefficient (pKₐ) a</th>
<th>Henry constant (H) b</th>
<th>pKₐ b</th>
<th>Log D at pH=7 a</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>g/mole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FO-MBR c</td>
</tr>
<tr>
<td>Primidone</td>
<td>C₆H₁₂N₃O</td>
<td>218.25</td>
<td>12.26 ± 0.40</td>
<td>1.164E-14</td>
<td>13.93</td>
<td>0.83</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>C₁₆H₁₄O₃</td>
<td>254.28</td>
<td>4.23 ± 0.10</td>
<td>2.005E-14</td>
<td>13.70</td>
<td>0.19</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Naproxen</td>
<td>C₁₄H₁₄O₃</td>
<td>230.26</td>
<td>4.84 ± 0.30</td>
<td>2.096E-13</td>
<td>12.68</td>
<td>0.73</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>C₁₈H₂₂O₃</td>
<td>250.33</td>
<td>4.75</td>
<td>7.677E-13</td>
<td>12.11</td>
<td>2.07</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Metronidazole</td>
<td>C₂₀H₂₁N₂O</td>
<td>171.15</td>
<td>14.44 ± 0.10</td>
<td>2.073E-12</td>
<td>11.68</td>
<td>-0.14</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>C₁₄H₁₁Cl₃NO₂</td>
<td>296.15</td>
<td>4.18 ± 0.10</td>
<td>3.098E-12</td>
<td>11.51</td>
<td>1.77</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Fenoprofen</td>
<td>C₈H₇Cl₂O₃</td>
<td>269.51</td>
<td>2.93</td>
<td>3.284E-12</td>
<td>11.48</td>
<td>-0.13</td>
<td>83-99</td>
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<td>Ibuprofen</td>
<td>C₁₃H₁₂O₂</td>
<td>206.28</td>
<td>4.41 ± 0.10</td>
<td>4.066E-11</td>
<td>10.39</td>
<td>0.94</td>
<td>&gt;99</td>
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<tr>
<td>Ametryn</td>
<td>C₃H₇N₅O</td>
<td>27.33</td>
<td>3.71±0.41</td>
<td>4.418E-10</td>
<td>9.35</td>
<td>2.97</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>C₁₀H₁₁ClO₃</td>
<td>214.65</td>
<td>3.18 ± 0.10</td>
<td>2.909E-10</td>
<td>9.54</td>
<td>-1.06</td>
<td>&gt;99</td>
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<tr>
<td>Carbamazepine</td>
<td>C₁₄H₁₂N₂O</td>
<td>236.27</td>
<td>13.94 ± 0.20</td>
<td>8.168E-10</td>
<td>9.09</td>
<td>1.89</td>
<td>50-99</td>
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<tr>
<td>Octocylene</td>
<td>C₂₄H₂₃N</td>
<td>361.48</td>
<td>-</td>
<td>3.382E-09</td>
<td>8.47</td>
<td>6.89</td>
<td>80-90</td>
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<tr>
<td>Amitriptyline</td>
<td>C₂₃H₂₁N</td>
<td>277.40</td>
<td>9.18 ± 0.28</td>
<td>6.596E-09</td>
<td>8.18</td>
<td>2.28</td>
<td>&gt;99</td>
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<tr>
<td>Atrazine</td>
<td>C₈H₁₂ClN₃</td>
<td>215.68</td>
<td>2.27 ± 0.10</td>
<td>5.223E-08</td>
<td>7.28</td>
<td>2.64</td>
<td>75-90</td>
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<tr>
<td>Propranolol</td>
<td>C₁₃H₁₅NO</td>
<td>209.24</td>
<td>1.49 ± 0.70</td>
<td>5.265E-07</td>
<td>6.28</td>
<td>1.54</td>
<td>&gt;99</td>
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<tr>
<td>Benzophenone</td>
<td>C₁₃H₁₇O₂</td>
<td>182.22</td>
<td>-</td>
<td>1.316E-06</td>
<td>5.88</td>
<td>3.21</td>
<td>&gt;99</td>
</tr>
<tr>
<td>N, N-Diethyl-meta-toluamide (DEET)</td>
<td>C₂₀H₁₇NO</td>
<td>191.13</td>
<td>-</td>
<td>1.410E-06</td>
<td>5.85</td>
<td>2.42</td>
<td>40-90</td>
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<td>Estradiol</td>
<td>C₁₈H₂₃O₂</td>
<td>298.33</td>
<td>10.25 ± 0.70</td>
<td>1.644E-11</td>
<td>10.78</td>
<td>1.89</td>
<td>&gt;99</td>
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<tr>
<td>17α – Ethynylestradiol</td>
<td>C₂₀H₂₅O₂</td>
<td>269.40</td>
<td>10.24 ± 0.60</td>
<td>3.399E-10</td>
<td>9.47</td>
<td>4.11</td>
<td>&gt;99</td>
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<tr>
<td>Oxybenzone</td>
<td>C₁₇H₁₄O₂</td>
<td>228.24</td>
<td>7.56±0.35</td>
<td>5.851E-10</td>
<td>9.23</td>
<td>3.89</td>
<td>&gt;99</td>
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<td>Estrone</td>
<td>C₁₈H₂₅O₂</td>
<td>270.37</td>
<td>10.25 ± 0.40</td>
<td>9.286E-10</td>
<td>9.03</td>
<td>3.62</td>
<td>&gt;99</td>
</tr>
<tr>
<td>17β – Estradiol</td>
<td>C₁₈H₂₃O₂</td>
<td>272.38</td>
<td>10.27</td>
<td>1.173E-09</td>
<td>8.93</td>
<td>4.15</td>
<td>&gt;99</td>
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<tr>
<td>17β – Estradiol-17-acetate</td>
<td>C₂₀H₃₀O₃</td>
<td>314.42</td>
<td>10.26 ± 0.60</td>
<td>2.151E-09</td>
<td>8.67</td>
<td>5.11</td>
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<tr>
<td>Bisphenol A</td>
<td>C₁₈H₁₆O₂</td>
<td>228.29</td>
<td>10.29 ± 0.10</td>
<td>2.197E-09</td>
<td>8.66</td>
<td>3.64</td>
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<td>Salicylic acid</td>
<td>C₇H₆O₃</td>
<td>138.12</td>
<td>3.01 ± 0.10</td>
<td>6.653E-09</td>
<td>8.18</td>
<td>-1.13</td>
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<td>Triclosan</td>
<td>C₁₂H₁₇Cl₂O₆</td>
<td>289.54</td>
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<td>6.537E-07</td>
<td>6.18</td>
<td>5.28</td>
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<td>4-tert-Butylphenol</td>
<td>C₁₀H₁₄O</td>
<td>150.22</td>
<td>10.13 ± 0.13</td>
<td>7.136E-06</td>
<td>5.15</td>
<td>3.40</td>
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<td>4-tert-Octylphenol</td>
<td>C₁₄H₂₂O</td>
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<td>8.670E-06</td>
<td>5.06</td>
<td>5.18</td>
<td>&gt;99</td>
</tr>
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</table>

a Data extracted from SciFinder Scholar;

b Henry’s law constant (H) = Vapour pressure × molecular weight/water solubility; and pKₐ = - log₁₀ H.

c Wijekoon et al. (2014)

d Altkir et al. (2012); Holloway et al. (2014); Lay et al. (2012) Luo et al. (2015); and Luo et al. (2017).

*Phan et al. (2016); and Wang (2013)