Removal of trace organics by MBR treatment: The role of molecular properties

Nichanan Tadkaew [a], Faisal I. Hai [a], James A. McDonald [b], Stuart J. Khan [b], Long D. Nghiem [a],*

[a] The Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, The University of Wollongong, NSW 2522, Australia
[b] Water Research Centre, The University of New South Wales, NSW 2552, Australia

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ABSTRACT

This study examined the relationship between specific molecular features of trace organic contaminants and their removal efficiencies by a laboratory scale membrane bioreactor (MBR). Removal efficiencies of 40 trace organic compounds were assessed under stable operating conditions. The reported results demonstrate an apparent correlation between chemical structures and the removal of trace organic contaminants by the laboratory scale MBR system. The removal of all 14 very hydrophobic (Log $D > 3.2$) trace organic compounds selected in this study was consistently high and was above 85%. The occurrence and types of electron withdrawing or donating functional groups appear to be important factors governing their removal by MBR treatment. In this study, all hydrophilic and moderately hydrophobic (Log $D < 3.2$) compounds possessing strong electron withdrawing functional groups showed removal efficiency of less than 20%. In contrast, high removal efficiencies were observed with most compounds bearing electron donating functional groups such as hydroxyl and primary amine groups. A qualitative framework for the assessment of trace organic removal by MBR treatment was proposed to provide further insights into the removal mechanisms.

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1. Introduction

Major driving forces towards water recycling today are the growing demand for water from an increasing population, changing lifestyle patterns, urbanisation, and diminishing natural water resources. In addition, better public awareness about environmental protection has resulted in progressively more stringent wastewater quality discharge regulations. Despite the growing interest in water recycling, our predictive capacity regarding the ability of treatment technologies to remove specific trace organic contaminants remains very limited. This is reflected by the public reluctance to accept reclaimed water for potable reuse and the fact that most water recycling applications are currently still restricted to non-potable purposes.

Membrane bioreactors (MBRs) have recently emerged as an important technology for water recycling, capable of transforming wastewater to high quality effluent suitable for various water recycling applications (Atkinson, 2006). Becoming commercially available only around two decades ago, MBR technology has already been well proven and can provide a superior rating for most bulk water quality indicators such as pathogens, suspended solids and nutrient removal compared to conventional activated sludge (CAS) treatment processes (Melin et al., 2006; Visvanathan et al., 2000). However, the efficiency of MBR technology as a barrier for a range of trace organic

contaminants such as endocrine disrupting chemicals (EDCs), pesticides, and pharmaceutically active compounds (PhACs), as well as the specific removal mechanisms involved remain unclear (Clara et al., 2005; De Wever et al., 2007; Kimura et al., 2005; Qu et al., 2009; Visvanathan et al., 2005; Wintgens et al., 2004). Previous studies have indicated significant variation in the removal of trace organics by MBRs, ranging from near complete removal for some compounds (e.g. ibuprofen and bezafibrate) to almost no removal for several others (e.g. carbamazepine and diclofenac) (Clara et al., 2005; Kimura et al., 2005; Tadkaew et al., 2010; Urase et al., 2005). The reasons for such variation are not yet fully understood.

Physicochemical properties of trace organics have been reported to significantly govern their removal efficiency by MBR treatment. Biosorption of trace contaminants, driven primarily by hydrophobic interaction, appears to be one of the key mechanisms controlling removal efficiency during MBR treatment. For instance, apparent improvement in removal efficiency of certain acidic trace organics such as ibuprofen, ketoprofen, and diclofenac has been observed when MBRs are operated under acidic conditions rather than neutral conditions (Tadkaew et al., 2010; Urase et al., 2005). This phenomenon was explained by the speciation of the compounds from hydrophilic ionic forms to much more hydrophobic forms at pH lower than their acid dissociation (pK_a) values.

A limited number of studies has shed some light on the effect of chemical structures on the removal efficiency of trace chemicals during biological treatment processes. For example, Kimura et al. (2005) attributed the poor removal of clofibric acid, diclofenac, and dichloprop to the presence of chlorine in their molecular structure or their relatively complicated aromatic rings. Several studies have utilised the US-EPA-developed Biodegradation Probability Program for Windows (BIOWIN) software package commissioned by the US-EPA which is one of the most widely used computer-based quantitative structure biodegradability relationship (QSBR) programs to estimate the biodegradability of organic compounds under aerobic conditions. Lapertot and Pulgarin (2006) investigated the biodegradability of 17 priority hazardous substances and suggested that the primary and ultimate BIOWIN models were generally suitable for removal assessment of these compounds in industrial wastewater treatment processes. On the other hand, Yu et al. (2006) reported some inconsistency between the likelihood of biodegradability predicted by BIOWIN and experimental data when they investigated the removal efficiency of 18 pharmaceutical and personal care products at a conventional municipal wastewater treatment plant.

Although the connection between chemical structure and removal efficiency seems highly plausible, studies to develop a capacity to predict the removal efficiency of trace organic contaminants by MBR treatment processes based on a range of molecular parameters are still limited. Because of the involvement of many diverse and complex functional groups, the connection between chemical structure and removal efficiency has not yet been thoroughly examined in the literature. In fact, several previous attempts to identify a definitive relationship between the structures of trace organic contaminants and their removal efficiencies during CAS and MBR treatment have identified significant challenges (Joss et al., 2005; Radjenovic et al., 2007).

This study aimed to elucidate the connection between specific molecular features of trace organic contaminants and their removal efficiencies by a laboratory scale MBR. The MBR system was operated under stable conditions for an extended period to allow for a systematic examination of the removal of 40 trace organic contaminants at environmentally relevant concentrations. Hydrophobicity and molecular structures of the selected trace organic compounds were carefully delineated and correlated to their removal efficiencies. Key factors governing the removal efficiencies of trace organic contaminants were identified and reported.

2. Materials and methods

2.1. Laboratory scale MBR system

A laboratory scale MBR system was used in this study. Detailed description of this MBR system is available elsewhere (Tadkaew et al., 2010). The system consisted of a glass reactor, a continuous mixer, two air pumps, a pressure sensor, and influent and effluent pumps. Two ZeeWeed-1 (ZW-1) submerged hollow fibre ultrafiltration membrane modules supplied by Zenon Environmental (Ontario, Canada) were used in this set-up. The membrane has a nominal pore size of 0.04 μm. Each module has an effective membrane surface area of 0.047 m². A chiller (Neslab RTE 7) equipped with a stainless steel heat exchanging coil was used to maintain a constant temperature in the MBR. A personal computer was used to control the permeate peristaltic pump to operate on a 14 min suction and 1 min off cycle to provide relaxation time to the membrane modules. Flow rate of the influent pump was matched with that of the permeate pump to maintain a constant reactor volume. A mixer was continuously used to ensure homogeneous conditions of the mixed liquor and to prevent the settling of biomass.

2.2. Synthetic wastewater

A synthetic wastewater simulating municipal sewage was used to ensure a stable feeding rate throughout the experiment. Concentrated stock solution was prepared and stored in a refrigerator at 4 °C. It was then diluted with MilliQ water on a daily basis to make up a feed solution containing glucose (400 mg/L), peptone (75 mg/L), KH_2PO_4 (17.5 mg/L), $MgSO_4$ (17.5 mg/L), $FeSO_4$ (10 mg/L), and sodium acetate (225 mg/L). This composition was based on a previous study (Zhang et al., 2006).

2.3. Trace organic compounds

In this study, 40 organic compounds were selected to represent four major trace organic groups of concern in water reuse applications – namely pesticides, pharmaceutically active compounds, steroid hormones, and other endocrine disrupting chemicals. The selection of these model trace organic compounds was also based on their widespread occurrence in domestic sewage and their diverse physicochemical properties (e.g. hydrophobicity and molecular weight). The effective hydrophobicity of these compounds varies significantly as reflected by their Log D values at pH 8 (see Supplementary data)

which is typical of an activated sludge reactor (Wells, 2006). The most hydrophilic compound is enalapril with Log D at pH 8 of -1.21 and the most hydrophobic compound is nonylphenol with Log D at pH 8 of 6.19. All selected trace organic compounds were of analytical grade. A combined stock solution was prepared in pure acetonitrile. The trace organic stock solution was kept in a freezer and was used within less than a month.

2.4. Analytical techniques

The analysis of the model trace organics was based on a previously reported method (Tadkaew et al., 2010; Vanderford and Snyder, 2006). Analytes were extracted using 5 mL, 500 mg solid phase extraction hydrophilic/lipophilic balance (HLB) cartridges (Waters, Millford, MA, USA). Samples were spiked with a solution containing 50 ng of an isotopically labelled version of each analyte. The sample was then loaded onto the cartridges at 15 mL/min, after which the cartridges were rinsed with 5 mL of reagent water and dried with a stream of nitrogen for 30 min. Loaded cartridges were stored at $-4\,°C$ in sealed bags until elution and analysis.

Analytes were separated using an Agilent (Palo Alto, CA, USA) 1200 series high performance liquid chromatography (HPLC) system equipped with a 150×4.6 mm, 5 μm particle size, Luna C18 (2) column (Phenomenex, Torrence, CA, USA). Mass spectrometry was performed using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with a turbo-V ion source employed in both positive and negative electro-spray ionisation modes. Steroid hormones were analysed using an atmospheric pressure chemical ionisation method and all other compounds were analysed using an electro-spray ionisation method. For each analyte and internal standard a precursor ion and two product ions were monitored for reliable confirmation. Relative retention times of the analyte and isotopically labelled internal standard were also monitored to ensure correct identification.

Standard solutions of all analytes were prepared at 1, 5, 10, 50, 100, 500 and 1000 ng/mL. A relative response ratio of analyte/internal standard over a 1–1000 ng concentration range was generated enabling quantification with correction for losses due to ion suppression and incomplete SPE recovery. All calibration curves had a correlation coefficient of 0.99 or better. The limit of reporting was determined using an s/n ratio of greater than 10.

Conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity metre. Total organic carbon (TOC) and total nitrogen (TN) were analysed using a Shimadzu TOC/TN-V$_{CSH}$ analyser. TOC analysis was conducted in non-purgeable organic carbon (NPOC) mode. Samples were kept at 4 °C until analysed and calibrations were performed in the range between 0 and 1000 mg/L and 0–100 mg/L for TOC and TN, respectively. Mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) contents in the MBR were measured in accordance to the Standard Methods for the Examination of Water and Wastewater (Eaton et al., 2005).

2.5. MBR experimental protocol

The MBR was seeded with activated sludge from the Wollongong sewage treatment plant, NSW, Australia. After the initial start-up process, which lasted about 2 months, a small amount of sludge was regularly extracted from the reactor to keep the sludge age at approximately 70 days. The hydraulic retention time was set at 24 h, corresponding to a permeate flux of 4.3 L/m^2 h. The MBR temperature and dissolved oxygen content were kept constant at $20.0 \pm 0.1\,°C$ and 2 ± 1 mg/L, respectively. Performance of the MBR system with regard to basic water quality parameters was then monitored for an extended period of more than four weeks.

Once stable operation had been achieved, trace organic contaminants were continuously introduced into the feed solution to make up a concentration of approximately 2 μg/L of each selected compound. The investigation with trace organics was conducted over a period of four weeks during which no sludge was withdrawn from the reactor. The feed solution was kept in a stainless steel reservoir at controlled room temperature ($20 \pm 2\,°C$). Feed and permeate samples were taken twice a week in duplicate and solid phase extraction was conducted immediately for subsequent trace organic analysis. Removal efficiency was calculated as $R = 100 \times (1 - C_{Eff}/C_{Inf})$, where C_{Eff} and C_{Inf} are effluent (permeate) and influent concentrations (ng/L) of the trace organic compound, respectively. It is noted that complete degradation of an organic compound may follow different pathways and undergo several steps. Therefore, the term removal here does not necessarily indicate complete degradation of the trace organics, but rather a loss of the specific trace chemical molecule. In many cases, stable intermediates or 'metabolites' may be produced, but detailed consideration of these intermediates is beyond the scope of this study.

3. Results and discussion

3.1. Performance stability of the MBR

In this study, synthetic feed solution was used to ensure a consistent influent composition. The MBR showed stable and good performance with respect to all key water quality parameters. The stable performance continued even following the introduction of the trace organic contaminants to the feed solution. A notable exception, however, was a significant decline in the removal of total nitrogen (TN) immediately after the introduction of the trace organic contaminants from almost complete removal to as low as 60%. The decrease in TN removal can be explained by the introduction of acetonitrile, the solvent used to introduce the trace organics, to the influent. The MBR system used in this study was operated under aerobic conditions and therefore is not expected to have any biological denitrification capacity. The original synthetic feed solution was deficient in nitrogen, and therefore, the initial high TN removal observed here could be attributed to the conversion of dissolved organic nitrogen to biomass, which would then be retained by the membrane. Because acetonitrile was used as a carrying solvent for the introduction of trace organic contaminant cocktail into the feed solution, the introduction of trace organic contaminants into the feed solution resulted in a significant increase in TN in the influent from 12 mg/L to approximately 49.5 mg/L. This was assumed to be the main reason for the observed decrease

in TN removal. The increase in nitrogen content of the feed water did not exert any discernible impact on any other biological performance indicators of the MBR system. There was a slight increase in the MLSS content in the reactor from 8.6 g/L to 10.0 g/L over the duration of the experiment of approximately one month while the MLVSS/MLSS ratio remained constant at approximately 0.9. Other basic performance parameters including TOC removal efficiency (98%), pH of the MLSS (7.5 ± 0.1), effluent conductivity (559 ± 19 μS/cm) were also relatively stable during the entire experiment. In addition, no abnormal transmembrane pressure increase was observed following the introduction of trace contaminants to the feed solution (data not shown).

Stable performance of the MBR system could also be observed with respect to the removal of trace organic contaminants (Fig. 1). It is noted that the error bars shown in Fig. 1 represent the standard deviations of eight influent and effluent samples, regularly collected in duplicate throughout the experiment. It is also notable that the removal efficiencies of the 40 compounds investigated in this study vary significantly ranging from negligible removal (e.g. atrazine,

carbamazepine, dilatin, and trimethoprim) to removal to below the analytical detection limit (e.g. 17β-oestradiol, testosterone, and triclocarban), indicating a removal of at least 98%. The observed significant variation in the removal efficiency of the trace organic contaminants by MBR treatment indicates that improved understanding of the key factors that govern the elimination of specific chemicals is required to enable prediction of MBR treatment performance for any particular chemical or class of chemicals.

3.2. Removal of trace organic contaminants

A logical approach to qualitatively predict the effectiveness of MBR treatment for the removal of a wide range of trace organic contaminants is to evaluate their removal efficiency according to the intended applications or origins of these compounds. Accordingly, Table 1 summarises the removal efficiencies of the 40 compounds selected in this study. Data previously reported in other studies, whenever available, are also included for comparison purposes. With caffeine being the only noteworthy exception, results reported here are in
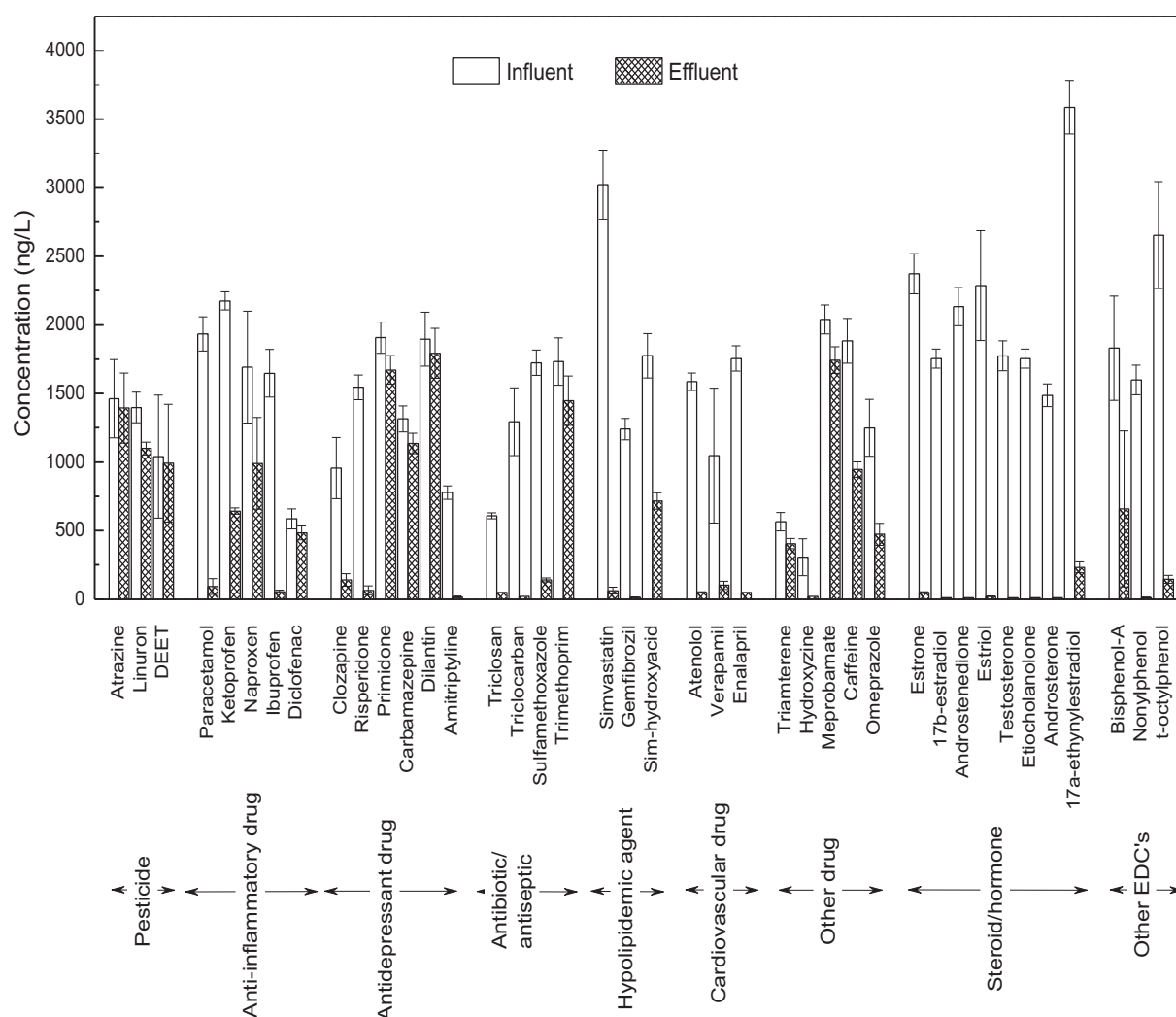

Fig. 1 − Influent and effluent concentrations of the selected trace organic contaminants. Samples were collected twice a week and in duplicate for four weeks. Error bars represent the standard deviation of 16 measurements.

Table 1 – Removal efficiencies of the selected trace organic contaminants (*n* = 16) obtained in this investigation and corresponding values recorded in the literature.

Class	Compound	This study (%) (Average ± Std)	Literature (%) (min–max)	References
Pesticides	Atrazine	4.4 ± 3.7	9–40	Bernhard et al. (2006), Bouju et al. (2008)
	Linuron	21.1 ± 4.1	Not available	
	DEET	4.6 ± 2.4	0–78	Bernhard et al. (2006), Kim et al. (2007), Snyder et al. (2007)
Non-steroidal anti-inflammatory	Paracetamol	95.1 ± 3.4	≥99	Kim et al. (2007), Radjenovic et al. (2007, 2009), Joss et al. (2005)
	Ketoprofen	70.5 ± 0.8	43.9–95	Radjenovic et al. (2007, 2009), Kimura et al. (2005), Quintana et al. (2005)
	Naproxen	40.1 ± 2.8	36–91.6	Kim et al. (2007), Radjenovic et al. (2007, 2009), Joss et al. (2005), Quintana et al. (2005), Urase et al. (2005)
	Ibuprofen	96.7 ± 0.7	≥90	Bernhard et al. (2006), Kim et al. (2007), Radjenovic et al. (2007, 2009), Joss et al. (2005), Quintana et al. (2005), Reif et al. (2008), Kreuzinger et al. (2004), Clara et al. (2005), Smook et al. (2008)
	Diclofenac	17.3 ± 4.2	0–87.4	Bernhard et al. (2006), Kim et al. (2007), Radjenovic et al. (2007, 2009), Quintana et al. (2005), Kreuzinger et al. (2004), Clara et al. (2005), Gonzalez et al. (2006), Abegglen et al. (2009)
Anti-depressants & mood stabilisers	Clozapine	84.8 ± 5.4	Not available	
	Risperidone	95.8 ± 2.2	Not available	
	Primidone	12.4 ± 4.3	Not available	
	Carbamazepine	13.4 ± 4.3	0–13	Bernhard et al. (2006), Radjenovic et al. (2007), Joss et al. (2005), Reif et al. (2008), Clara et al. (2004, 2005)
	Dilantin	5.4 ± 3.6	0–12	Snyder et al. (2007)
	Amitriptyline	97.8 ± 0.8	Not available	
Antibiotic & antiseptic	Triclosan	>91.8	61–95	Kim et al. (2007), Snyder et al. (2007)
	Triclocarban	>98.4	Not available	
	Sulfamethoxazole	91.9 ± 0.6	52–80.8	Kim et al. (2007), Radjenovic et al. (2007, 2009), Reif et al. (2008), Kreuzinger et al. (2004), Clara et al. (2005), Göbel et al. (2007)
	Trimethoprim	16.6 ± 3.7	0–90	Kim et al. (2007), Radjenovic et al. (2009), Reif et al. (2008), Göbel et al. (2007)
Hypolipidemic agents	Simvastatin	97.9 ± 0.9	Not available	
	Gemfibrozil	98.95 ± 0.1	32.5–90	Radjenovic et al. (2007, 2009), Reif et al. (2008)
	Sim-hydroxyacid	59.6 ± 2.8	Not available	
Cardiovascular drugs	Atenolol	96.9 ± 0.2	70	Radjenovic et al. (2007), Reif et al. (2008), Quintana et al. (2005)
	Verapamil	88.4 ± 6.1	Not available	
	Enalapril	97.1 ± 0.1	Not available	
Other drugs	Triamterene	27.9 ± 6.3	Not available	
	Hydroxyzine	>92.2	Not available	
	Meprobamate	14.5 ± 3.3	Not available	
	Caffeine	49.6 ± 4.1	98–99	Kim et al. (2007), Snyder et al. (2007)
	Omeprazole	62.1 ± 3.5	Not available	
Steroid hormones	Oestrone	98.0 ± 0.2	96.3	Clara et al. (2005), Lyko et al. (2005)
	17β-estradiol	>99.4	100	Clara et al. (2005), Lyko et al. (2005)
	Androstenedione	>99.5	Not available	
	Oestriol	98.2 ± 1.9	>99	Clara et al. (2005)
	Testosterone	>99.4	Not available	
	Etiocholanolone	>99.4	Not available	
	Androsterone	>99.3	Not available	
	17α-ethynylestradiol	93.5 ± 1.2	81.9–93.6	Lyko et al. (2005)
Other EDCs	Bisphenol A	90.4 ± 3.1	68.9–99.0	Urase et al. (2005), Kreuzinger et al. (2004), Clara et al. (2005), Lyko et al. (2005), Chen et al. (2008)
	Nonyphenol	99.3 ± 0.2	0–88	Kreuzinger et al. (2004), Clara et al. (2005), Cirja et al. (2006), Hu et al. (2007)
	t-octylphenol	94.5 ± 1.1	44.9–99.0	Clara et al. (2005)

good agreement with the literature data. The mean removal efficiency of caffeine observed in our study is 49.6%, which is substantially lower than the previously reported values (Kim et al., 2007; Snyder et al., 2007). In a recent study, Santos et al. (2009) examined the performance of four CAS waste-water treatment plants in Seville city (Spain). They reported a highly variable caffeine removal efficiency among these four treatment plants with the mean value ranging from as low as 44% up to 75% (Santos et al., 2009). Given the similarity between MBR and CAS treatment, it is possible that this discrepancy can be explained by the differences in operating conditions. The literature data presented in Table 1 are from a range of sources with different operating conditions and system arrangements. The reported experimental results confirm that the MBR system used in this study behaved well within the range of typical performance data from other systems. Therefore, the results presented in this study and the conclusions drawn from them would be broadly applicable and generalisable to most typical MBR systems. In fact, data presented in Table 1 suggest that some generalisation can be made about certain groups of compounds.

All the three pesticides investigated in this study showed very low removal efficiencies. Atrazine, a chloro-triazine herbicide, was removed at a rate of less than 5%. It has been reported to be poorly removed both in CAS and MBR (Bernhard et al., 2006) and that a major removal mechanism was sorption onto withdrawn sludge (Bouju et al., 2008). Linuron is a dichloro-phenylurea herbicide. Despite being a widely used herbicide, no reports on the removal of Linuron in CAS or MBR could be found. However, its slow natural attenuation rate in various soils and the evolution of more toxic and persistent chloroaniline intermediates in the process have been reported (Dejonghe et al., 2003). A mean removal of 21% of linuron as achieved in our MBR, therefore, appears to be consistent with the reported recalcitrance of this compound. DEET is a toluamide compound and is the most common active ingredient in insect repellants. In this study, a mean removal of 4.6% of DEET was recorded during MBR treatment. This removal efficiency is at the lower end of range reported in other published studies. Bernhard et al. (2006) reported nil to over 50% removal of DEET by MBR treatment and suggested that DEET removal efficiency was dependent on the sludge retention time (SRT). Kim et al. (2007) reported no removal of DEET in their study; however, no information about the SRT was provided. The highest removal efficiency of DEET of 78% was reported by Snyder et al. (2007) calculated from a one off sampling event at a pilot scale treatment facility.

Near complete removal or removal to below the analytical limit of all eight steroid hormones and three other EDCs selected for investigation (bisphenol A, nonylphenol, and t-octylphenol) were observed in this study. These results are consistent with other published studies (Table 1). It is noteworthy that all of these compounds possess significant hydrophobicity and bear similar molecular backbone structures; which may, in part, explain the similarities of their removal efficiencies.

No generalistion can be inferred for any of the six therapeutic classes of pharmaceuticals investigated in this study (Table 1). Their removal efficiencies by MBR treatment vary widely even within the same class of compounds. The removal efficiencies of the five non-steroidal anti-inflammatory drugs (NSAIDs) differ remarkably from one another. For example, ibuprofen registers a removal efficiency of 97% whereas the removal efficiency of diclofenac is only 17%. Unlike the other NSAIDs, diclofenac is a chlorinated compound, which can possibly explain its recalcitrant behaviour during MBR treatment. Significant variation in the removal efficiency can also be observed among compounds used as anti-depressants and mood stabilisers. Dilantin, primidone and carbamazepine were poorly removed, whereas the removal efficiencies of clozapine, risperidone, and amitriptyline were 85% and higher. Given the considerable dissimilarity in the molecular structure among these anti-depressants and mood stabilisers, differences in their removal efficiencies can be expected. Further analysis of the molecular structures of these compounds is presented in Section 3.3.2. Significant variation in removal efficiency was observed among the other pharmaceutical groups (cardiovascular and other drugs) and can again be attributed to their diverse molecular structures (Table 1 and Supplementary data 1). Among the hypolipidemic agents (lipid lowering drugs) investigated in this study, simvastatin is a hydrophobic compound with Log D (at pH 8) of 4.41 and the compound registers a removal efficiency of 98% (Table 1). Simvastatin hydroxyacid shares the same molecular backbone structure with that of simvastatin. However, the 3, 5-dihydroxy-heptanoic acid functional group of simvastatin hydroxyacid renders the compound much more hydrophilic (Log D at pH 8 of 0.64). Consequently, simvastatin hydroxyacid shows a much lower removal efficiency of 60% in comparison to that of the related compound simvastatin.

Results reported in Table 1 suggest that the classification of trace organics according to their intended use or origin can only be used to qualitatively predict the removal efficiencies of compounds of similar molecular structure, having similar molecular features or physicochemical properties. In fact, certain molecular features and physicochemical properties of the trace organic contaminants appear to be the underlying factors governing their rate of removal during MBR treatment.

3.3.   Role of molecular features

Attempts to fit the removal efficiency data obtained in our study and the corresponding available biodegradability scores from BIOWIN model did not result in any meaningful correlations (data not shown). Although this result is somewhat surprising, it does not necessarily invalidate the model. BIOWIN is essentially a statistical model and the discrepancies may have arisen to some extent due to the fact that the BIOWIN scores were derived from batch tests, which cannot effectively replicate the biological conditions of an MBR. It is also noteworthy that only three out of 40 compounds investigated in this study were included in the database which has been used for the development of BIOWIN. Furthermore, BIOWIN would not account for the adsorption of trace organics to biosolids which can be an important removal mechanism along with biodegradation. Given the poor correlation between the removal efficiencies experimentally obtained in this study and the BIOWIN biodegradability scores, it is necessary to further examine the key

physicochemical properties and molecular features that can govern the removal efficiency of trace organic compounds.

3.3.1. Effects of hydrophobicity

The removal of trace organic contaminants by an activated sludge treatment process is a complex function of both sorption and biological degradation. In a CAS treatment process, the sludge-bound contaminants can be subsequently removed via sludge withdrawal. In addition, sorption of trace organic contaminants to biosolids results in a longer residence time in the reactor, which may lead to further removal via biodegradation. Because the MLSS content and sludge retention time of typical MBR processes are much higher than those of CAS treatment, sorption has been suggested as a major removal mechanism for the removal of trace organic contaminants by MBR treatment. In a systematic survey of the literature data, Wells suggested that the sorption of a trace organic contaminant to the activated sludge could be assessed by considering the Log D value of the compound at a given pH (Wells, 2006). Experimental results presented in Fig. 2 indicate that this finding can be extended to MBR treatment. There appears to be a 'removal envelop' that can be defined by the hydrophobicity of the trace organic contaminants (Fig. 2). Removal of the very hydrophobic (Log D > 3.2) compounds is probably dominated by sorption to the activated sludge facilitating enhanced biological degradation in some cases. Therefore, these compounds consistently showed high removal efficiency (above 85%). As the Log D value of the compounds decreased to below 3.2, sorption of these trace organic contaminants onto the activated sludge was no longer a dominating removal mechanism and the removal efficiency of these compounds was much more strongly influenced by their intrinsic biodegradability. As a result, the removal efficiency of trace organics with low Log D values (at pH 8) varies significantly from less than 20% to removal to below the analytical detection limit (corresponding to a removal of at least 98%). Of particular note in Fig. 2 is a cluster of five compounds that show very low removal efficiencies despite their moderately high hydrophobicity (Log D in the rage from 2 to 3.2). It is also noteworthy that these five compounds possess one or several electron withdrawing functional

groups, such as a chlorine atom or amide group. Results reported here suggest that individual molecular features can also be an important factor governing the removal efficiency of trace organics during MBR treatment.

3.3.2. Effects of molecular weight

The molecular weights of the trace organics studied here ranged from 151 g/mol (paracetamol) to 455 g/mol (verapamil). There appears to be a weak but nevertheless discernible correlation between the removal efficiency of these trace organics and their molecular weights (Fig. 3). Compounds with molecular weight of more than 300 g/mol were relatively well removed (>60%), while the removal efficiencies of those with molecular weight of less than 300 g/mol varied from almost no removal to more than 98% (removal beyond the analytical detection limit). A plausible explanation for this observation could be the relative hydrophobicity (Log D at pH 8 in the range from 2.03 to 5.74, see Supplementary data) of the compounds having molecular weight of more than 300 g/mol. In addition, in this study, removal efficiency does not necessarily represent a complete mineralisation of the compound. Compounds with higher molecular weight may have more branches, which would offer more opportunities for the microbes to selectively cleave a certain target site and initiate degradation.

3.3.3. Effect of chemical structure

Experimental results obtained in this study confirm the possible role of molecular functional groups in governing the removal of moderately hydrophobic and hydrophilic trace organic compounds by MBR treatment. The 40 trace organic compounds investigated in this study can be systematically categorised into three groups. Group A consists of compounds with Log D at pH 8 of above 3.2. As discussed above, sorption was a dominant removal mechanism for these hydrophobic compounds and the removal efficiencies of all compounds of group A were above 85% (Fig. 2). To further elucidate the role of different molecular features, the rest of the compounds can be categorised in terms of ring structure (heterocyclic/non-heterocyclic, mono or polynuclear) and functional groups (electron withdrawing/donating moieties). Fig. 4 shows the removal efficiency as a function of ring structure, whereas
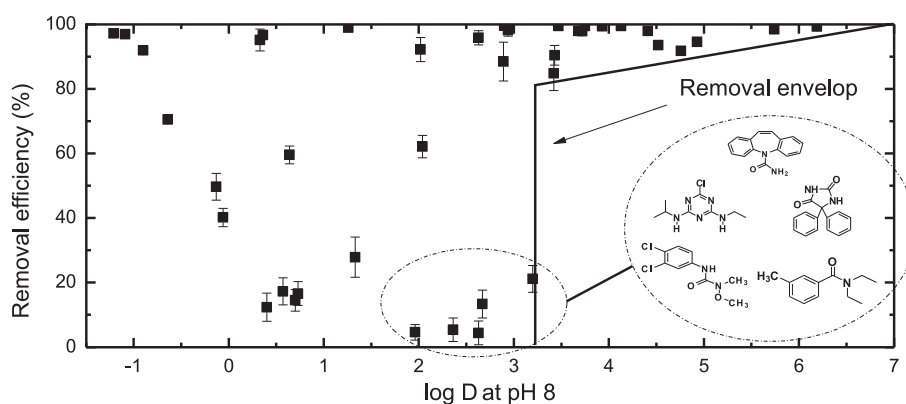
Fig. 2 – The relationship of removal of trace organic compounds with effective hydrophobicity (Log D). The MLSS pH during the experiment was 7.5 ± 0.1. Log D values were obtained from the SciFinder Scholar (ACS) database. Error bars represent the standard deviation of 16 measurements.
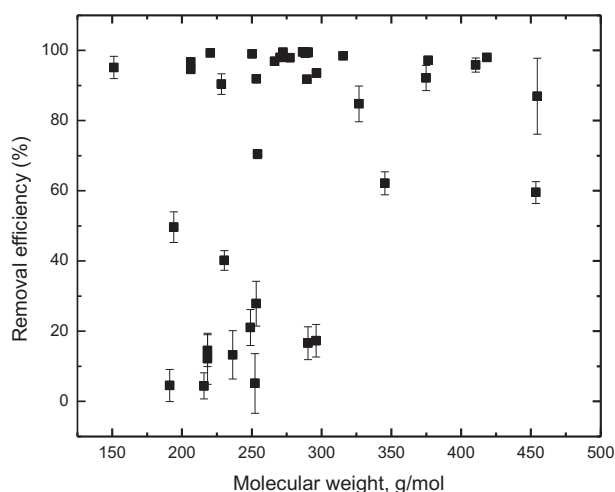
Fig. 3 − Removal efficiency of trace organic compounds as a function of their molecular weight. Error bars represent the standard deviation of 16 measurements.

Fig. 5 presents the compounds under three distinct categories (B, C and C*) based on the presence and types of electron withdrawing or donating functional groups.

No clear distinction between heterocyclic or non-heterocyclic compounds removal could be observed in this study (Fig. 4). Similarly, no discernible trend in terms of mononuclear or polynuclear compounds could be observed. It is generally considered that simple aliphatic and monocyclic aromatic compounds are readily degradable, while polycyclic structures may be more persistent (Jones et al., 2005). However, irrespective of the mono or polynuclear structure, degradation may be initiated by the mere cleavage of a side chain structure and then further mineralisation may depend on the complexity of the nucleus. In this study, removal indicates the loss of the parent structure, and not complete

mineralisation. Therefore, the absence of any discernible correlation between the removal efficiency and ring structure is not entirely unexpected.

As shown in Fig. 7, the compounds containing strong electron withdrawing groups (B) consistently showed very low (<20%) removal efficiency. According to Knackmuss (1996), the initial electrophilic attack by oxygenases of aerobic bacteria is often a rate-limiting step and the first of a chain of reactions responsible for the biodegradation of many organic compounds. As a result, the presence of electron withdrawing functional groups generates an electron deficiency and thus renders the compounds less susceptible to oxidative catabolism. Electron donating functional groups, on the other hand, render the molecules more prone to electrophilic attack by oxygenases of aerobic bacteria. Consequently, the removal efficiencies of organic compounds bearing strong electron donating functional groups were, in most cases, much higher than those of group B in Fig. 7. The compounds containing both electron withdrawing and donating groups however showing less than 70% removal have been placed in group C*.

The elucidation of the overall influence of these functional groups and particularly their opposing effects on the biodegradability of trace organic compounds is a complex task and would generally require extensive exercise involving simultaneous application of quantitative structure activity relationship and biochemical interpretation, as demonstrated for a particular compound class (N-heterocycles) by Philipp et al. (2007). Because a large number of diverse compound classes were studied here, such a rigorous approach falls beyond the scope of this paper. Nevertheless some general inferences, can be drawn from the results in the light of metabolic pathway information retrieved from the sparse literature and also from biodegradation prediction tools such as UM-BBD PPS (Wackett and Ellis, 1999).

The biodegradation of amide-only compounds needs to proceed from conversion of the amide group to primary amine (Hart and Orr, 1975). As suggested by the low removal of
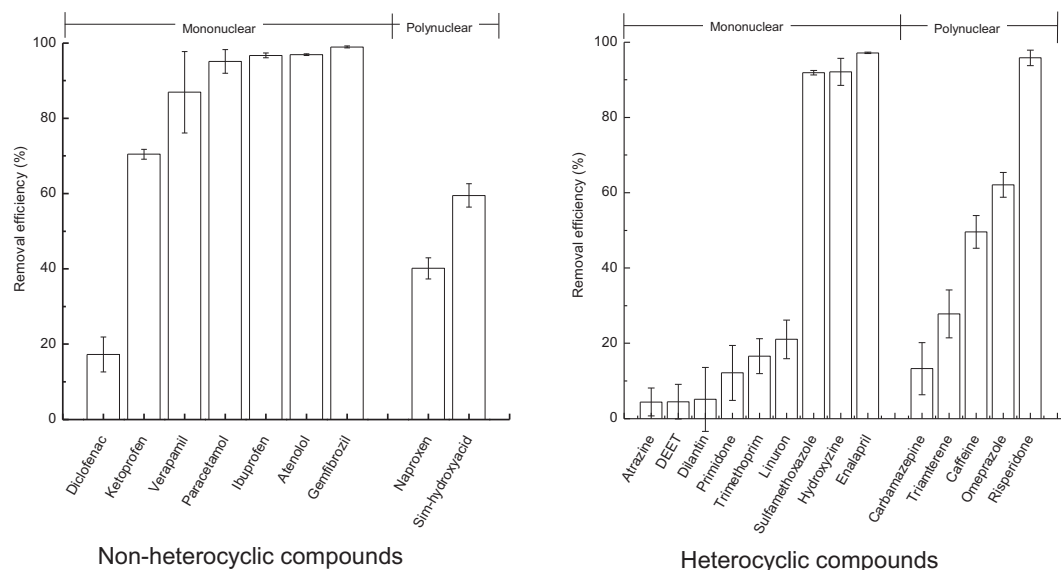
Fig. 4 − Removal efficiency as a function of ring structure. Error bars represent the standard deviation of 16 measurements.
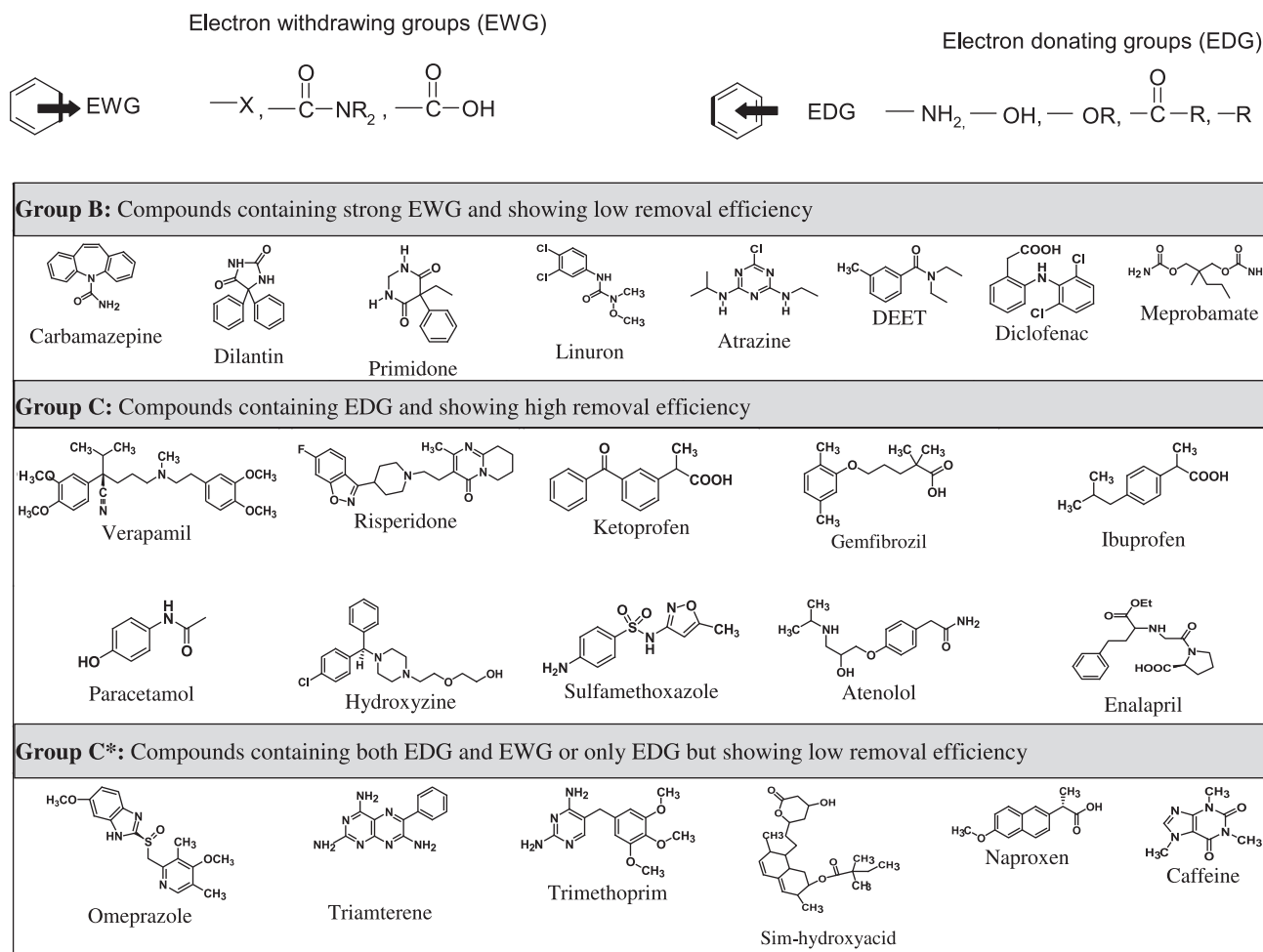
Fig. 5 – **Compound classification according to the presence of electron donating or withdrawing functional groups.**

carbamazepine and dilantin, this pathway appears to be extraordinarily recalcitrant. All the tested compounds possessing only methyl (weak electron donor) and amide (strong electron withdrawing) groups including primidone, DEET and meprobamate were very poorly removed. The presence of methyl groups means that the degradation could initiate from conversion of the methyl group to alcohol (Shaw and Harayama, 1992), bypassing the recalcitrant amide conversion. However, methyl and other aliphatic groups have very weak electron donating capacity, and thus in presence of a strong electron withdrawing group they may have limited activating effect.

All three compounds (i.e. atenolol, enalapril and caffeine) containing both the amine (strong electron donating) and the amide (strong electron withdrawing) functional groups were quite well removed (50–97%). Degradation of compounds with one or more amine groups may proceed by converting the existing amine to a less substituted form of amine and aldehyde/ketone (Hakil et al., 1998). Comparing the performance of these three compounds (containing amide and amine groups) with that of primidone, DEET and meprobamate (containing amide and methyl groups), it appears that the coexistence of the amine, and not the methyl group, with the

amide group may make these compounds more amenable to biodegradation. The excellent removal of another amide-containing compound paracetamol can be attributed to the presence of the hydroxyl group which is also a strong electron donating functional group. In this context, it is noteworthy that the entire set of hydroxyl group-containing compounds tested in this study showed high removal. Such positive impact of hydroxyl group on biodegradation is in line with previous literature reports (Tunkel et al., 2000).

Halogenated organics comprise a superset which has many antimicrobial as well as human toxic and carcinogenic industrial chemicals as members (Häggblom and Bossert, 2004). Linuron contains both halogen and amide groups and accordingly demonstrated low removal. Interestingly, of the halogenated compounds with amine groups, risperidone (containing amine, methyl and amide) and hydroxyzine (containing amine and hydroxyl) showed good removal while diclofenac (containing amine and carboxylic) and atrazine (containing amine and methyl) showed poor removal. Literature review regarding the metabolic pathways of these compounds provided further insights but could not resolve the paradox. It is suggested in the literature that the metabolism of hydroxyzine can proceed simultaneously through the
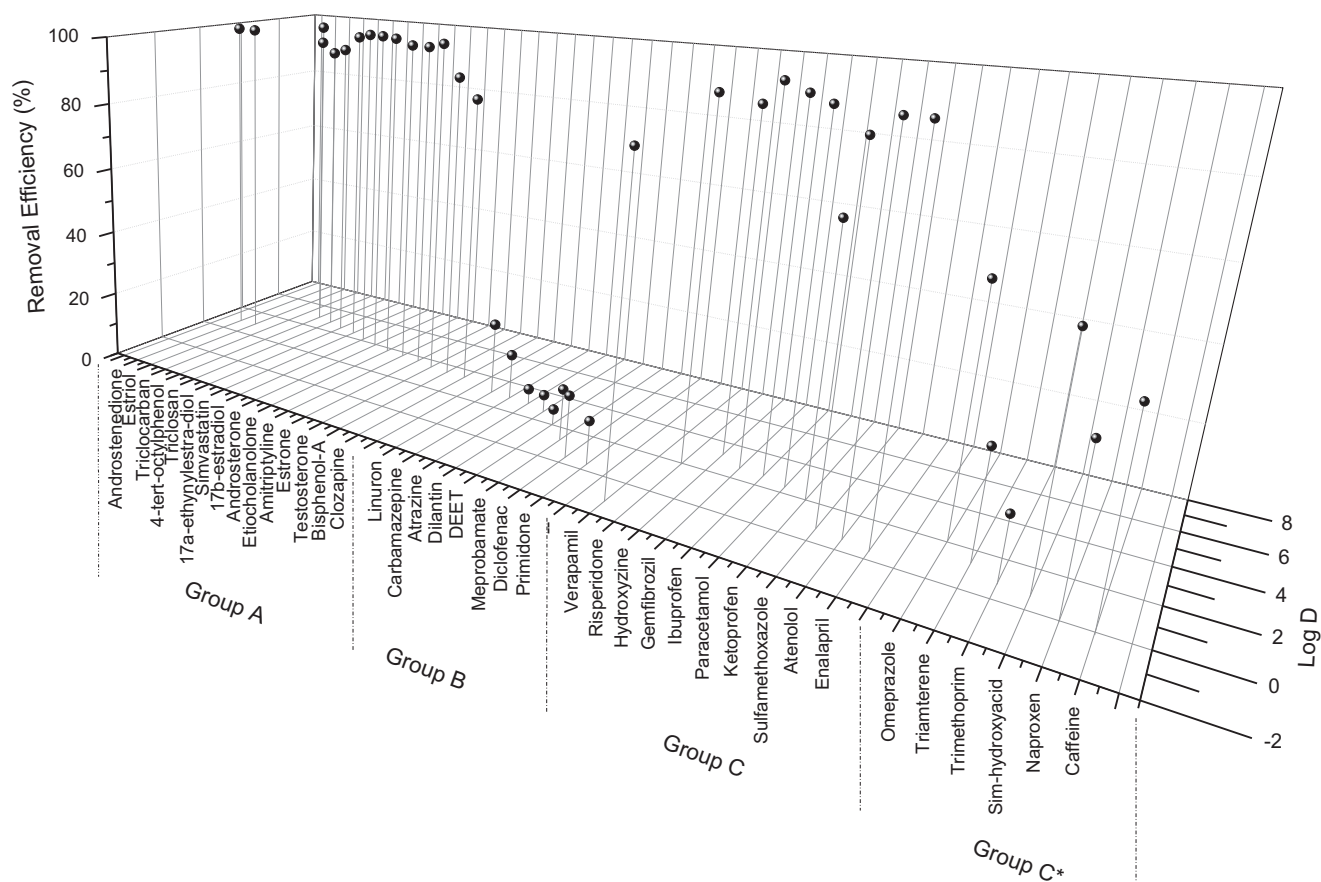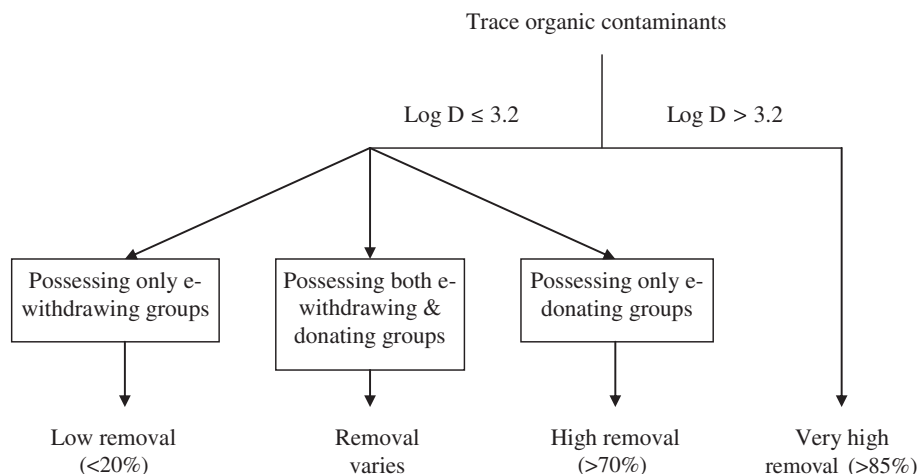
Fig. 6 – The combined effects of functional group and hydrophobicity on the removal of trace organic compounds by the MBR. Error bars represent the standard deviation of 16 measurements. Group A: all compounds with Log D > 3.2 (at pH 8). Groups B, C, and C* are defined in Fig. 5.

conversion of amine to aldehyde/ketone and/or through oxidation of the alcohol moiety to a carboxylic acid (Campoli-Richards et al., 1990). In the case of risperidone the degradation may initiate via 9-hydroxylation and/or via N-dealkylation at the piperadine nitrogen (Mannens et al., 1993). Diclofenac has been suggested to be degraded by hydroxylation of the 1-amino-2-unsubstituted aromatic fragment (Marco-Urrea et al., 2010). The degradation of atrazine, on the other hand, has been reported to be initiated through N-monodealkylation, hydroxylation of the isopropyl or tert-butyl moiety (Lang et al., 1996) or in the rare case via oxidation of the s-triazine ring to hydroxy-s-triazine (De Souza et al., 1995). While it is certain that the aerobic oxidation of the halogenated compounds is initiated from the co-existing electron withdrawing groups and not via dehalogentaion, it is not clear why, despite seemingly similar metabolic pathways (e.g. hydroxylation, dealkylation), the compounds exhibit different extents of recalcitrance.

Hydroxylation of the vicinal unsubstituted aromatic fragment and the mono-carbon-substituted benzenoid are the predominant initial degradation pathways (Quintana et al., 2005) for the well removed compounds ibuprofen (97%) and ketoprofen (70%), respectively. It is, however, not clear why despite possessing a suitable structure for the similar

metabolic pathway as ketoprofen, triamterene registered a rather low removal of 28%. The absence of any literature data regarding triamterene removal by CAS or MBR restricts further clarification regarding this matter. The only possible distinction that can be offered at this stage is that triamterene is a heterocyclic compound.

It is known that the degradation of compounds with an aromatic-aliphatic ether fragment can proceed by ether cleavage, producing a phenol derivative and an aldehyde (Bernhardt et al., 1988). Of the tested compounds that fit into this category, gemfibrozil (98%) and verapamil (87%) were well removed while omeprazol (62%) and naproxen (40%) demonstrated moderate removal, and trimethoprim was poorly removed (16%). The predominant biodegradation route of naproxen and trimethoprim appears to be via ether cleavage (Quintana et al., 2005); however, the degradation can potentially proceed via conversion of a tertiary/secondary aliphatic group to the corresponding alcohol. On the other hand, in addition to the ether cleavage verapamil may be degraded by N-demethylation (Unadkat et al., 2008). The degradation of omeprazole can also initiate from the conversion of di-[C,O]-substituted sulfoxide to sulfone (Kanazawa et al., 2003), and gemfibrozil can be degraded also through conversion of an aromatic methyl to primary alcohol (Hermening et al., 2000).

Trace organic contaminants

Log D ≤ 3.2   Log D > 3.2

| Possessing only e-withdrawing groups | Possessing both e-withdrawing & donating groups | Possessing only e-donating groups |

Low removal (<20%)   Removal varies   High removal (>70%)   Very high removal (>85%)

Fig. 7 − A qualitative framework for the prediction of trace organic removal by MBR treatment.

The discrepancy in the removal efficiencies of these compounds may, therefore, be attributed to the distinct alternate routes of biodegradation, which may govern the overall removal.

The combined effect of functional groups and hydrophobicity on the removal of trace organic compounds by the MBR is shown in Fig. 6. It is evident from the above discussion that all the aspects of chemical structure i.e. aromatic moiety, ring composition, substituent groups, side chain and associated metabolic pathway need to be taken into account in conjunction with physical parameters namely hydrophobicity and molecular weight to explain observed variabilities in trace organic removal by MBR.

As noted earlier, in an MBR, adsorption and biodegradation may simultaneously play important roles. However, for the compounds with low hydrophobicity, properties such as molecular weight, ring structure and functional groups may influence the biodegradability and consequently govern the overall removal. Although some similarities can be expected, the purpose of this section is clearly not to describe the biodegradability of trace organics in biological wastewater treatment in general. The comprehensive discussion on biodegradability and metabolic pathway as furnished here serves the important purpose of explaining the removal of compounds with low hydrophobicity in the MBR.

3.4. A framework to predict removal efficiency

Notwithstanding a few exceptions which will be subjected to further investigation, results reported in this study indicate a clear link between molecular features and the removal of trace organic compounds by MBR treatment. Fig. 7, based on the data presented in this study, outlines a qualitative and schematic framework for the prediction of the removal efficiency of any given compound by an aerobic MBR treatment process. Given the similarities between CAS and MBR treatment, the framework proposed here may also be applicable to CAS treatment processes to some extent. However, differences in operational conditions between MBR and CAS must be

carefully considered. For example, because MBR usually operates at a much longer sludge retention time and can offer complete retention of the biomass, hydrophobicity of the trace organic compounds would have a more profound impact on their removal efficiency by MBR than that by CAS. For the compounds with low hydrophobicity, where biodegradability is likely to govern the overall removal, the performance of CAS operated under the same loading and sludge retention time may be comparable to MBR (Clara et al., 2005). However it also needs to be noted that MBR may facilitate growth and maintenance of special degrading microbes (Hai et al., 2010) which may contribute to enhanced removal of compounds with low hydrophobicity. To derive further insight into this matter, long-term performance of CAS and MBR will need to be compared with the same set of compounds. That, however, is beyond the scope of this study. It is prudent to note that this proposed framework has been based on a limited set of data of only 40 compounds. Nevertheless, this framework has the potential to provide significant insights to the removal of trace organic contaminants by MBR treatment. With ongoing scientific and dedicated efforts in this field, the framework can be a foundation for a future quantitative model for the prediction of trace organic removal by MBR and CAS treatment.

4. Conclusion

Results reported in this study indicate an apparent correlation between molecular features and the removal of trace organic contaminants by a laboratory scale MBR system. The removal efficiencies of all 14 very hydrophobic trace organic compounds (Log D at pH 8 > 3.2) selected in this study consistently showed removal efficiencies in the range between 85% to removal below the analytical detection limit, indicating a removal of at least 98%. The occurrence of electron withdrawing or electron donating functional groups appears to be another important factor governing their removal by MBR treatment. All hydrophilic and moderately hydrophobic (Log D < 3.2) compounds possessing strong

electron withdrawing functional groups consistently showed removal efficiency of well below 20%. In contrast, high removal efficiency was observed with most compounds bearing electron donating functional groups such as hydroxyl groups and primary amine groups. Nevertheless, further analysis also revealed several exceptions which remained unexplainable given the current lack of biochemical data about these compounds of interest. Based on the reported data, a qualitative framework for the assessment of trace organics removal by MBR treatment was presented.

Acknowledgements

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.watres.2011.01.023.

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