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Faisal I. Hai
University of Wollongong, faisal@uow.edu.au

Nichanan Tadkaew
University of Wollongong, nt84@uow.edu.au

James A. McDonald
University of New South Wales

Stuart J. Khan
University of New South Wales

Long Nghiem
University of Wollongong, longn@uow.edu.au

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Is halogen content the most important factor in removal of halogenated trace organics by MBR treatment?

Faisal I. Hai [1,]* , Nichanan Tadkaew [1], James A. McDonald [2], Stuart J. Khan [2], and Long D. Nghiem [1]

[1] School of Civil Mining and Environmental Engineering

The University of Wollongong, NSW 2522, Australia

[2] Water Research Centre

The University of New South Wales, NSW 2552, Australia

* Corresponding author: Faisal Ibney Hai, Email: faisal@uow.edu.au; Ph +61 2 4221 3177

Abstract

This study investigated the relationship between physicochemical properties (namely halogen content and hydrophobicity) of halogenated trace organics and their removal efficiencies by a laboratory scale membrane bioreactor (MBR) under stable operating conditions. The reported results demonstrated a combined effect of halogen content and hydrophobicity on the removal. Compounds with high halogen content (> 0.3) were well removed (> 85%) when they possessed high hydrophobicity (Log D > 3.2), while those with lower Log D values were also well removed if they had low halogen content (< 0.1). General indices such as the BIOWIN index (which is based on only biodegradation) or a more specific index such as the halogen content (which captures a chemical aspect) appeared insufficient to predict the removal efficiency of halogenated compounds in MBR. Experimental data confirmed that the ratio of halogen content and Log D, which incorporates two important physico-chemical properties, is comparatively more suitable.

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Keywords: biodegradation, chemical structure, halogenated trace organics, hydrophobicity, membrane bioreactor (MBR).

1 Introduction

The growing demand for potable water in many parts of the world is a matter of significant concern. This crisis has accelerated the use of alternative water sources, especially wastewater reclamation (Shannon et al., 2008). A range of trace organics, which are suspected to have an impact on humans and wildlife, have been widely detected in sewage and sewage-impacted surface waters all over the world (Halling-Sørensen et al., 1998). Most of these compounds are of anthropogenic origin. Because of their incomplete elimination during wastewater treatment, wastewater treatment plant effluents are important point sources responsible for their introduction to the aquatic environment. The occurrence of these trace organics in secondary treated effluent is of significant ecological health concern, particularly with regard to water reuse practices.

Membrane bioreactor (MBR) has been developed in the recent decades as a potential technique for wastewater reclamation (Hai and Yamamoto, 2011). Although the effluent quality of MBR is generally better than that of conventional activated sludge (CAS) processes, evidence shows that certain trace organics are not completely removed by MBR treatment (Clara et al., 2005). Currently fundamental understanding to elucidate the underlying reasons and improve the treatment performance is incomplete.

Biosorption of trace contaminants driven primarily by hydrophobic interaction appears to be one of the key mechanisms controlling removal efficiency in MBR (Tadkaew et al., 2010; Urase et al., 2005). Studies elucidating the effect of chemical structures on the

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removal efficiency of trace organics during biological treatment processes remain very limited. Kimura et al. (2005) attributed the low removal clofibric acid, diclofenac, and dichloprop to the presence of chlorine in their molecular structure or their relatively complicated aromatic rings. Since then similar statements underscoring the importance of presence of chlorine in the compound structure on its removal potential in MBR have appeared in the literature. Negligible to intermediate removal (< 50 %) of certain halogenated pesticides (Bernhard et al., 2006) as well as pharmaceuticals such as hydrochlorothiazide, indometacin and loratidine (Radjenovic et al., 2009), iopromide (Clara et al., 2005), fenofibric acid (Rosal et al., 2010) has been reported. Halogenated organics comprise a superset which has many antimicrobial, human toxic, and carcinogenic industrial chemicals (Häggblom and Bossert, 2004). Many of them can also accumulate in biological organisms. In this context, the recalcitrance of halogenated trace organics appears to be highly plausible. However, a comprehensive literature review covering studies which simultaneously investigated halogenated as well as non-halogenated compounds has revealed reports contradictory to the general notion that all halogenated trace organics are recalcitrant to MBR treatment. Excellent removal of several halogenated pharmaceuticals/pesticide such as ofloxacin, fluoxetine and gibenclamide (Radjenovic et al., 2009), dichlorobenzoic acid (Bernhard et al., 2006), triclocarban (Kim et al., 2007), triclosan (Halden and Paull, 2005), pentachlorophenol (Visvanathan et al., 2005) by MBR treatment has been reported in the literature.

Although many individual studies have reported varying removal rates of halogenated trace organics in MBR or CAS, none has made a systematic effort to verify the mode of impact of halogenation on the removal performance of halogenated compounds. The

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underlying hypothesis of the present study was that although the aromatic nature and high halogen content of a compound may impart significant resistance to biodegradation, incorporation of halogen atoms can also increase the hydrophobicity of the compound. Therefore, both halogen content and hydrophobicity must be taken into account for the prediction of removal efficiency. This hypothesis cannot be verified based on the sparse literature data as the operational parameters can vary from study to study. To address this important knowledge gap, the removal of a set of halogenated trace organics possessing varying halogen content and hydrophobicity was studied to ascertain the above mentioned governing factors.

2 Materials and methods

2.1. Trace organic compounds and synthetic wastewater

Eight halogenated trace organic compounds including two pesticides (atrazine and linuron), four pharmaceuticals (diclofenac, clozapine, risperidone and hydroxyzine) and two antiseptic products (triclosan and triclocarban) were selected based on their widespread occurrence in domestic sewage and their diverse physicochemical properties (e.g. molecular weight, halogen content, hydrophobicity) (Supplementary Data Table 1). Their molecular weight ranges from 215.7 g/mol (atrazine) to 410.5 g/mol (risperidone). Their halogen content (weight ratio) ranges from 0.05 (risperidone) to 0.37 (triclosan). The effective hydrophobicity of these compounds varies significantly as reflected by their Log D values at pH 8 which is typical of an activated sludge reactor (Wells, 2006). At pH 8, diclofenac is the most hydrophilic compound with a Log D of 0.57 and the most hydrophobic compound is triclocarban with a Log D of 5.74.

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A synthetic wastewater (Tadkaew et al., 2010) simulating municipal sewage was used to ensure a stable feeding rate throughout the experiment. Trace organic contaminants were continuously introduced into the feed solution to make up a concentration of approximately 2 μg/L of each selected compound.

2.2. Laboratory scale MBR system

Detailed description of the laboratory scale MBR system used in this study is available elsewhere (Tadkaew et al., 2010). Two ZeeWeed-1 (ZW-1) submerged hollow fibre ultrafiltration membrane modules (total effective surface area = 0.094 m^2) supplied by Zenon Environmental (Ontario, Canada) were used in this set-up. The membranes were operated on a 14 minute suction and 1 minute off cycle resulting in an average permeate flux of 4.3 L/m^2h and a hydraulic retention time of 24 hours.

The MBR was seeded with activated sludge from the Wollongong sewage treatment plant, NSW, Australia. The MBR temperature and dissolved oxygen content were kept constant at 20.0 ± 0.1 ^oC and 2 ± 1 mg/L, respectively. Performance of the MBR system with regard to basic water quality parameters was then monitored throughout three months of start-up period. The addition of trace organics into the synthetic wastewater was initiated once stable operation had been achieved. This part of the examination lasted for four weeks and no sludge was wasted during this period (theoretically meaning infinite sludge retention time).

2.3. Analytical techniques

The collected effluent was kept in a dark room at 4 ^oC and analyzed within less than 48 hours. Removal efficiency was calculated as $R = 100 \times (1 - C_{Eff} / C_{Inf})$, where C_{Eff} and C_{Inf} are

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effluent (permeate) and influent concentrations (ng/L) of the trace organic compound, respectively. It is noteworthy that the term removal here does not necessarily indicate complete mineralization of the trace organics to carbon dioxide and water. The analysis of the model trace organics was performed using a high performance liquid chromatography (HPLC) with a tandem mass spectrometry (MS/MS) detector based on a previously reported method (Tadkaew et al., 2010). Total organic carbon (TOC) was analyzed using a Shimadzu TOC/TN-V_{CSH} analyzer. MLSS and MVLSS contents in the MBR were measured in accordance to the Standard Methods for the Examination of Water and Wastewater (Eaton et al., 2005).

3 Results and discussion

3.1. Performance stability of the MBR

In order to confirm that the trace organics removal efficiencies used in analyses were obtained under stable biological activity in the MBR the basic water quality parameters (such as TOC) and the key operational parameters (such as pH, MLSS, TMP) were continuously monitored. The basic performance parameters including TOC removal efficiency, MLSS concentration, pH of the MLSS, effluent conductivity were relatively stable during the entire experiment (Supplementary Data Table 2). In addition, no abnormal transmembrane pressure increase was observed following the introduction of the trace contaminants to the feed solution.

3.2. Removal of trace organic contaminants

Stable removal of all trace organics can be confirmed by the small standard deviation obtained from total 16 measurements conducted four times a week over the four weeks period of this study (Figure 1).

[FIGURE 1]

The two 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). Despite being a widely used dichloro-phenylurea 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 the current study, therefore, appears to be consistent with the reported recalcitrance of this compound (Dejonghe et al., 2003).

The studied anti-depressants and mood stabilizer drugs (risperidone and clozapine) were consistently well removed (< 85%). Risperidone contains a fluorinated benzisoxazole, piperidine groups and a diazabicylco (or pyrimidone) moiety as structural fragments. In addition to the fluorine atom it contains an amide group which is known to cause resistance to biodegradation (Hollender et al., 2009). However, a stable 96% removal of this compound was observed in the MBR. On the other hand, the core chemical structure of the antipsychotic drug clozapine features a dibenzodiazepine functionalized with a piperazine group. One of

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the benzene rings in its molecule contains a chlorine atom. A stable around 85% removal of this compound was observed. No relevant data on the removal of these compounds in CAS or MBR could be found for comparison purpose.

In accordance with the literature data, a moderate 17% removal of the non-steroidal anti-inflammatory drug diclofenac was observed. Depending on the SRT, negligible (Kim et al., 2007) to above 50% (Clara et al., 2005) removal of diclofenac by MBR treatment has been reported. However, the removal rates reported in different studies even under similar SRT vary considerably. Such variation may be attributed to the inherent recalcitrant nature of diclofenac as confirmed by batch tests by other authors (Radjenovic et al., 2009).

Hydroxyzine is an antihistamine of diphenylmethane and piperazine class. Besse and Garric (2008) classified hydroxyzine and its intermediate cetirizine as potentially hazardous compound however could not reach to a definitive conclusion owing to scarce ecotoxicological data. A stable removal of 92% of hydroxyzine was achieved in the current study. No other data regarding removal of hydroxyzine in CAS or MBR could be found in the open literature.

Triclocarban and triclosan are antimicrobial additives in personal care products. The diaryl urea compound triclocarban and the diaryl ether triclosan share a number of similarities including two aromatic benzene rings carrying three chlorine substituents. Excellent removal (> 90%) of these two compounds was observed. Reported removal rates of triclosan in MBR range from 61 to 95% depending on the influent concentration (Kim et al., 2007). On the other hand, Halden and Paul (2005) reported more than 98% removal of triclocarban by CAS treatment. The results reported in this study are, therefore, in good agreement with the literature data.

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It is notable that the removal efficiencies of the eight compounds investigated in this study varied significantly ranging from negligible removal (e.g.: atrazine) to removal to below the analytical detection limit (e.g.: triclocarban), indicating a removal of at least 98%. The observed significant variation in the removal efficiency of the selected halogenated trace organic contaminants by MBR treatment indicated 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.

3.3. Factors governing removal efficiency

3.3.1 Qualitative structure-biodegradability relationship

The biodegradability index in the widely used US-EPA developed BIOWIN model is based primarily on the presence or absence of specific structural fragments with known or suspected substantial impact on biodegradation, namely functional groups, halogen substitution, bonding types, and steric structures. However, contradictory reports on the applicability of BIOWIN model in predicting biodegradability of priority hazardous substances in wastewater treatment plants exist (Nghiem et al., 2009). All the compounds in the current study possessed BIOWIN index of around 3 or less, corresponding to a primary biodegradation timeframe of several weeks (Supplementary Data Figure 1). While this was consistent with the low removal of atrazine, linuron and diclofenac, the high removal (> 85 %) of the other five compounds could not be explained by their BIOWIN index. BIOWIN is essentially a statistical model and the discrepancies may have had arisen to some extent due to the fact that the BIOWIN indices were derived from batch tests, which could not effectively replicate the biological conditions of the MBR (adsorption and biodegradation).

3.3.2 Effect of halogen content

In contrary to the special emphasis in the available literature about the effect of halogen group on compound removal, in this study the MBR removal efficiency did not show any meaningful correlation with the halogen content (Figure 2a). In fact the two most halogenated compounds (triclocarban and triclosan) showed much higher removal (> 90%) than the three other compounds with intermediate halogen content (atrazine, linuron and diclofenac). The limited removal of the monochlorinated aromatic compound atrazine in comparison to the high removal of the polychlorinated compounds triclosan and triclocarban indicated that the removal of halogenated aromatic trace organics cannot be predicted only on the basis of the halogen content. As noted in section 3.2, high removal (up to 90%) of a few heavily chlorinated compounds such as triclosan and triclocarban have been reported previously in either CAS or MBR (Halden and Paull, 2005; Kim et al., 2007). However, the present study is the first systematic demonstration of the fact that halogen content is not the only governing factor of the removal of halogenated compounds by MBR treatment. Seven chlorinated and one fluorinated compound was tested in this study. Because of the difference of the molecular weight of chlorine and fluorine one may wonder whether it is appropriate to define halogen content in weight ratio. It can, however, be confirmed that the observed trend remains unchanged even when halogen content is expressed in terms the ratio of number of halogen and total atoms (data not shown).

[FIGURE 2]

3.3.3 Effect of hydrophobicity

With the characteristic high MLSS content and long sludge retention time of MBR, sorption of trace organic contaminants to sludge results in their extended residence time in

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the reactor, which may lead to further removal via biodegradation. In a systematic survey of the literature data, Wells (2006) suggested that the sorption of trace organic contaminants to the activated sludge could be assessed by considering the Log D value of the compound at a given pH. Rosal et al. (2010) demonstrated good correlation of removal efficiency by CAS treatment with Log D of a set of compounds including some halogenated compounds such as chlorofibric acid, triclosan, and triclocarban. As shown in Figure 2b, in this study all the compounds with Log D > 3.2 (i.e., clozapine, triclosan and triclocarban) were well removed (> 85%). A careful comparison of Figures 2a and 2b revealed that compounds with high halogen content (> 0.3) were well removed when they possessed high hydrophobicity (e.g., triclosan and triclocarban with log D > 3.2). Similarly, risperidone and hydroxyzine were well removed despite their low Log D values as they possessed low halogen content (< 0.1). It is noteworthy that the effect of Log D value on removal efficiency was somewhat inconsistent in case of compounds with Log D values equal or lower than 3.2 (e.g., atrazine and linuron versus hydroxyzine and risperidone). Nevertheless the above comparison of the trends in Figures 2a and 2b indicated a combined effect of halogen content and hydrophobicity on their removal efficiency by MBR treatment.

3.3.4 Combined effect of halogen content and hydrophobicity

In an effort to capture the combined effects of halogen content and hydrophobicity, the removal efficiency was plotted against the ratio of halogen content and Log D (Figure 2c). The removal efficiency of all the tested compounds, except atrazine and linuron, could be well explained with this plot. This observation highlighted the fact that while halogen content may govern the chemical stability of a certain compound the extent of its removal in MBR depends simultaneously on its hydrophobicity. It appeared that general indices such as the

BIOWIN index (which is based on only biodegradation) or more specific indices such as the halogen content (which captures a chemical aspect) are not sufficient to predict the removal efficiency of halogenated compounds by MBR treatment. In this context, the ratio of halogen content and Log D, which incorporates two important physico-chemical properties, appeared to be a more appropriate index. The non-compliance of atrazine and linuron removal to the above-mentioned trend can be explained by the presence of other fragments in their chemical structure which, along with the halogen group, may form substantial resistance against microbial degradation. For instance, linuron contains amide group which is considered to impart high recalcitrance to structure (Hollender et al., 2009). Again, due to the highly oxidized carbons in the triazine ring atrazine is less amenable to microbial degradation (Bernhard et al., 2006). For certain halogenated compounds, however, the removal rate in MBR may be well explained by the proposed halogen content/Log D index despite the co-existence of other recalcitrant fragments in the structure (e.g., amide group in risperidone). The overall influence of all the electron withdrawing and donating functional groups on the removal of halogenated trace organic compounds remains unknown at this stage.

4 Conclusion

In line with the operation mode of MBR (adsorption and biodegradation), the ratio of halogen content and Log D was demonstrated as an appropriate index to predict trace organics removal efficiency by MBR. This is the first systematic demonstration of the fact that halogen content is not the only governing factor of the removal of halogenated compounds by MBR treatment. Future studies will attempt to ascertain the overall influence of all the electron withdrawing and donating functional groups on the removal of halogenated trace organic compounds.

5 Acknowledgements

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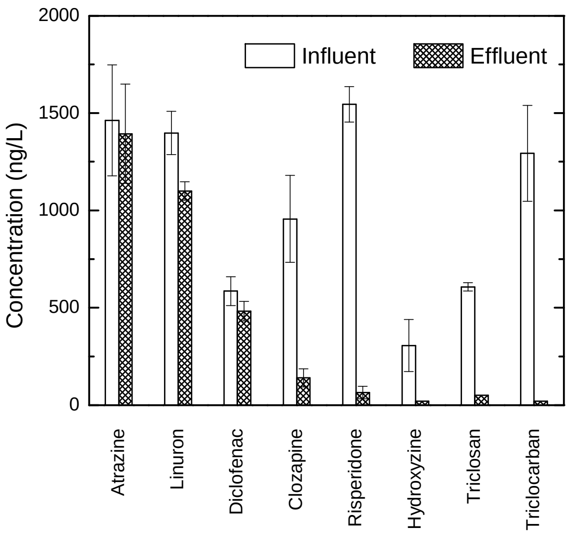
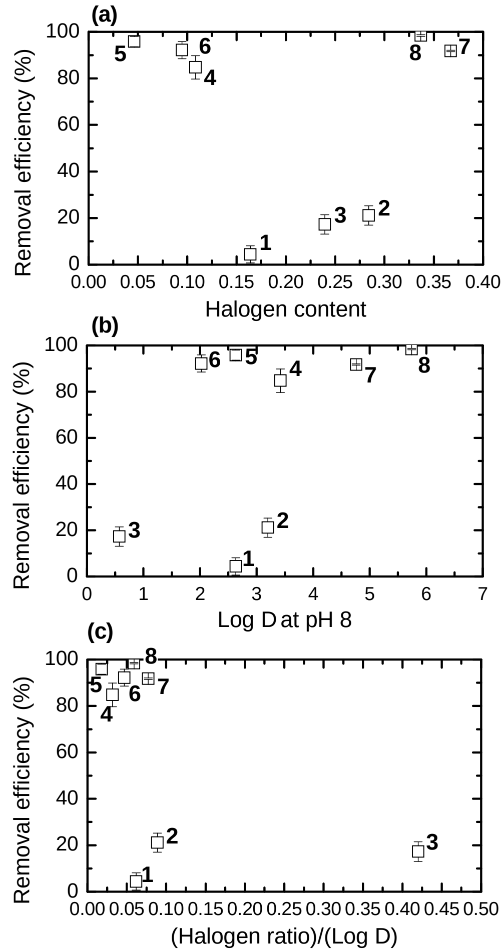


Figure 1: Influent and effluent concentration of the selected halogenated trace organic contaminants. Samples were collected twice a week and in duplicate for four weeks. Error bars represent the standard deviation of 16 measurements.



(**Compounds**: 1. atrazine, 2. linuron, 3. diclofenac, 4. clozapine, 5. risperidone, 6. hydroxyzine, 7. triclosan, 8. triclocarban)

Figure 2: Relationship of removal efficiency of trace organics with (a) halogen content (by weight), (b) effective hydrophobicity (Log D) and (c) the ratio of halogen content and Log D. (The pH of MBR MLSS 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.)

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Supplementary Data

Faisal I. Hai [1,*], Nichanan Tadkaew [1], James A. McDonald [2], Stuart J. Khan [2], and Long D. Nghiem [1]

[1] School of Civil Mining and Environmental Engineering

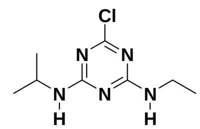
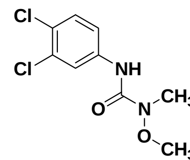
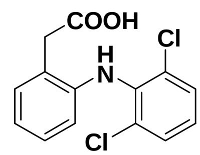
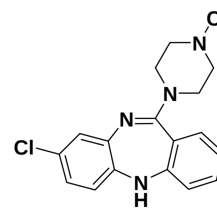
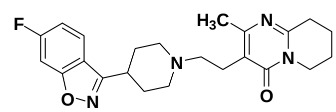
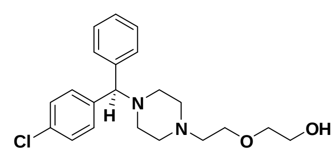
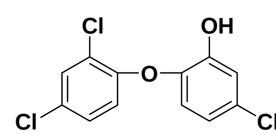
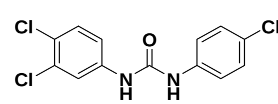
The University of Wollongong, NSW 2522, Australia

[2] Water Research Centre

The University of New South Wales, NSW 2552, Australia

* Corresponding author: Faisal Ibney Hai, Email: faisal@uow.edu.au; Ph +61 2 4221 3054

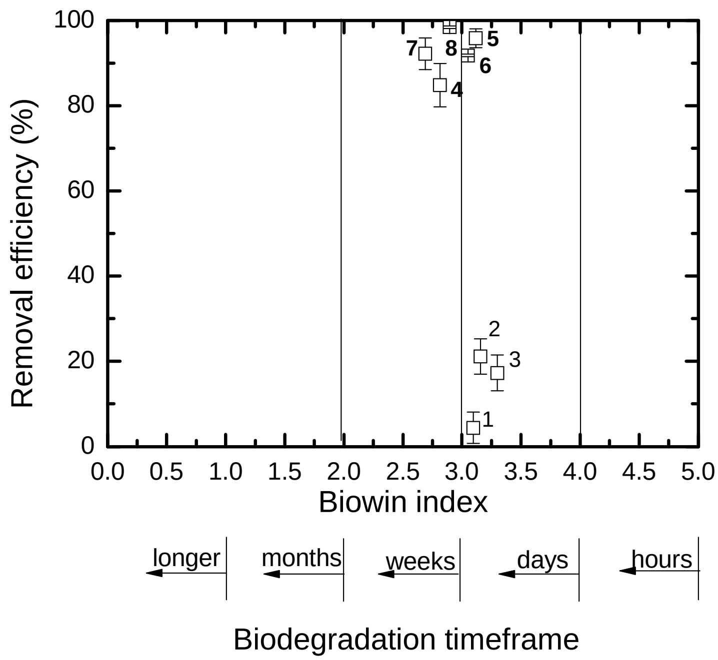
Table 1: Physicochemical properties of the selected trace organic contaminants.

Compound	CAS number	Formula	MW (g/mol)	Halogen content (by weight)	Log D (at pH 8)	Chemical structure
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	215.7	0.16	2.63	
Linuron	330-55-2	$C_9H_{10}Cl_2N_2O_2$	249.1	0.28	3.20	
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	0.24	0.57	
Clozapine	5786-21-0	$C_{18}H_{19}ClN_4$	326.8	0.11	3.42	
Risperidone	106266-06-2	$C_{23}H_{27}FN_4O_2$	410.5	0.05	2.63	
Hydroxyzine	68-88-2	$C_{21}H_{27}ClN_2O_2$	374.9	0.09	2.02	
Triclosan	3380-34-5	$C_{12}H_7Cl_3O_2$	289.5	0.37	4.76	
Triclocarban	101-20-2	$C_{13}H_9Cl_3N_2O$	315.6	0.34	5.74	

Source: SciFinder Scholar, data calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (1994-2007 ACD/Labs).

Table 2: Basic biological performance of the MBR system.

TOC removal (%)	MLSS (g/L)	MLVSS/MLSS	pH of the MLSS	Effluent conductivity (µS/cm)
98.8 ± 0.2	8.6 – 10.0	0.9	7.5 ± 0.1	559 ± 19



(**Compounds**: 1. atrazine, 2. linuron, 3. diclofenac, 4. clozapine, 5. risperidone, 6. hydroxyzine, 7. triclosan, 8. triclocarban)

Figure 1: Insufficiency of BIOWIN index to describe halogenated trace organics removal by MBR. Primary biodegradability model from the Biodegradation Probability Program for Windows (BIOWIN) software package developed by US-EPA (EPIWEB 4.0) was utilized. Error bars represent the standard deviation of 16 measurements.