Effects of sulphur on the performance of an anaerobic membrane bioreactor: Biological stability, trace organic contaminant removal, and membrane fouling

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ABSTRACT

This study investigated the impact of sulphur content on the performance of an anaerobic membrane bioreactor (AnMBR) with an emphasis on the biological stability, contaminant removal, and membrane fouling. Removal of 38 trace organic contaminants (TrOCs) that are ubiquitously present in municipal wastewater by AnMBR was evaluated. Results show that basic biological performance of AnMBR regarding biomass growth and the removal of chemical oxygen demand (COD) was not affected by sulphur addition when the influent COD/SO_4^{2-} ratio was maintained higher than 10. Nevertheless, the content of hydrogen sulphate in the produced biogas increased significantly and membrane fouling was exacerbated with sulphur addition. Moreover, sulphur increase considerably affected the removal of some hydrophilic TrOCs and their residuals in the sludge phase during AnMBR operation. By contrast, no significant impact on the removal of hydrophobic TrOCs was noted with sulphur addition to AnMBR.

Key words: Anaerobic membrane bioreactor (AnMBR), sulphur increase, trace organic contaminants (TrOCs), biogas production, bioenergy.

1 Introduction

Wastewater treatment and reuse is essential to protect public health and secure a sustainable water supply (Shannon et al., 2008). Nevertheless, wastewater treatment and reuse is energy-intensive. It has been estimated that municipal wastewater treatment accounts for approximately 3% electricity consumption and 5% greenhouse gas emission on a global basis (Li et al., 2015b). In particular, most current wastewater treatment plants (WWTPs) are based on aerobic biological processes, which require intensive energy for aeration (Li et al., 2015b). It is noteworthy that aerobic treatment is not a suitable platform for resource recovery, because organic carbon (a source of energy) and nitrogen (a valuable nutrient) in wastewater are converted into carbon dioxide and nitrogen gas, respectively (Ansari et al., 2017).

Given global efforts to curve greenhouse gas emission, many water utilities have actively explored new treatment alternatives to reduce their energy footprint and even achieve energy self-sufficiency (Shen et al., 2015; Nghiem et al., 2017). Amongst these potential alternatives, anaerobic treatment is particularly promising. Compared to aerobic processes, anaerobic treatment does not only consume significantly less energy, but also produce methane, which is a renewable fuel. In particular, anaerobic membrane bioreactor (AnMBR) has emerged as a promising technology to achieve energy neutrality in future WWTPs. AnMBR integrates the membrane separation process with anaerobic treatment to simultaneously achieve the recovery of water and energy from waste streams. It has been well established that AnMBR has much less energy consumption and lower sludge production in comparison with its aerobic counterpart (Liao et al., 2006; Lew et al., 2009; Skouteris et al., 2012).

Currently, AnMBR has been applied mostly for the treatment of industrial waste streams. Municipal wastewater often has a low content of organic carbon, thus, is not ideal for anaerobic treatment (Visvanathan and Abeynayaka, 2012; Judd, 2016). To overcome this issue, several techniques to fortify municipal wastewater have been explored and developed. They include co-digesting municipal wastewater with other high strength waste streams, such as liquid food waste (Tuyet et al., 2016; Becker et al., 2017), and pre-concentrating municipal wastewater by membrane processes, such as forward osmosis (FO) (Zhang et al., 2014; Ansari et al., 2016). Nevertheless, the co-digestion of food waste and municipal wastewater can undesirably increase the sulphate load to AnMBR due to the high sulphate content of food waste (Drews et al., 2005; Meng et al., 2009; Zhang et al., 2014). On the other hand, the pre-concentration of municipal wastewater by FO can also result in the enrichment of sulphate in the concentrated stream (Ansari et al., 2017). In addition, industrial wastewater from pharmaceutical and chemical manufacturing industry, pulp and paper production, and food processing may also contain high sulphur content (Siles et al., 2010).

Effects of sulphate on anaerobic treatment have been demonstrated in previous studies. High sulphate concentration can strengthen the competition of sulphate reducing bacteria over methanogenic microbes for available organic substrates, thereby reducing biogas production during anaerobic treatment. Moreover, sulphate can induce the precipitation of non-alkaline metals in anaerobic reactors, limiting their availability as micro-nutrients for methane producing microbes (Oude Elferink et al., 1994; Siles et al., 2010). In addition, sulphate reduction produces hydrogen sulphate (H_2S), which is a corrosive, malodourous, and toxic gas (Muyzer and Stams, 2008; Sarti and Zaiat, 2011; Park et al., 2014). H_2S can readily penetrate bacterial cell membrane and denature native proteins inside the cytoplasm producing sulphide and disulphide cross-links between polypeptide chains (Siles et al., 2010). It is noteworthy that the negative impact of sulphate on anaerobic treatment may be alleviated by maintaining an adequate COD/SO_4^{2-} ratio (> 10) to provide sufficient organic substances for both methane producing and sulphate reducing microbes (Rinzema and Lettinga, 1988). In some cases, with adequate organic matter, sulphate addition is beneficial to methane production by promoting the degradation of propionic acid (Li et al., 2015a). Thus, in practice, the undesirable effects of sulphur shocks on anaerobic treatment can be potentially alleviated by adjusting the ratio between carbon- and sulphate-rich substrates.

An emerging issue in wastewater treatment and reuse is the ubiquitous occurrence of trace organic contaminants (TrOCs) (Luo et al., 2014). TrOCs are emerging chemicals of significant concern that typically include but are not limit to steroid hormones, pharmaceuticals, personal care products, surfactants, pesticides, and disinfection by products (Ternes et al., 2004; Kummerer, 2009). They present in wastewater and other water bodies at trace concentrations (i.e., up to several micrograms per litre) (Luo et al., 2014). Although there remains uncertainty, these TrOCs can adversely impact the health of living organisms by inducing estrogenic, mutagenic, endocrine disrupting and genotoxic effects (Schwarzenbach et al., 2006).

Recent studies have demonstrated the removal of TrOCs by AnMBR. Monsalvo et al. (2014) investigated the removal of 38 TrOCs by AnMBR and reported over 90% removal for nine compounds; while others were removed by less than 50%. They further postulated that the main mechanisms of TrOC removal in AnMBR included biodegradation, adsorption onto biosolids, and deposition onto the membrane surface. Wijekoon et al. (2015) subsequently related the removal of TrOCs by AnMBR their physiochemical properties, particularly hydrophobicity and molecular structure. Their results showed that all hydrophobic compounds out of 27 TrOCs were removed by more than 70%; while the removal of hydrophilic TrOCs varied significantly, relying on their intrinsic biodegradability, which was further governed by their molecular structures. However, until now, little is known about the impact of sulphate on the performance of AnMBR, particularly the removal of TrOCs.

This study aims to investigate the effects of sulphur on the performance of AnMBR with an emphasis on biological stability, TrOC removal, and membrane fouling. Sulphur content of AnMBR influent was gradually increased by adding sodium sulphate (Na_2SO_4). Biological stability was evaluated in terms of biomass concentration and biogas production. The removal of bulk organic matter and TrOCs by AnMBR was assessed. In addition, membrane fouling profile during AnMBR operation with sulphur increase was also elucidated. Results from this study provide unique insights to AnMBR applications for the treatment of sulphur-rich wastewater and the co-management of wastewater and sulphur-rich food waste.

2 Materials and methods

2.1 Synthetic wastewater and trace organic contaminants

A synthetic solution was used in this study to simulate high strength domestic wastewater (Wijekoon et al., 2015). The synthetic wastewater was consisted of 4000 mg/L glucose, 750 mg/L peptone, 175 mg/L potassium dihydrogen phosphate, 175 mg/L magnesium chloride, 2250 mg/L sodium acetate, 175 mg/L urea, 45 mg/L ferrous chloride, 10 nickel chloride, 6 mg/L cobalt chloride, and 4 mg/L ammonium molybdate. Key physicochemical properties of the synthetic wastewater were determined every four days. The synthetic wastewater contained 1176 ± 30 mg/L chemical oxygen demand (COD) and 6.3 ± 0.4 mg/L total nitrogen (TN). The electrical conductivity and pH of this synthetic wastewater were 5.9 ± 2.5 mS/cm and 6.9 ± 0.2, respectively.

A set of 38 TrOCs with diverse physiochemical properties was selected in this study. These compounds represent major TrOC groups, namely pharmaceuticals, personal care products, industrial chemicals, and pesticides, which are ubiquitous in municipal wastewater (Luo et al., 2014). A combined stock solution of all 38 TrOCs was prepared in pure methanol and stored at -18 °C in the dark. These TrOCs were introduced daily into the synthetic wastewater at a concentration of approximately 2 µg/L of each compound.

2.2 AnMBR system

A lab-scale AnMBR system was used in this study. Detailed description of the AnMBR system has been provided elsewhere (Song et al., 2016). Briefly, the AnMBR system was mainly consisted of a bioreactor, an external microfiltration (MF) membrane unit, and several peristaltic pumps. The bioreactor was made of stainless steel with an effective working volume of 20 L and a head space of 8 L in case of unexpected foaming in the reactor. A peristaltic pump (Masterflex L/s, USA) controlled by a water level sensor (Omron, Japan) was used to feed the bioreactor. An industrial grade hose pump (ProMinent, Australia) was used to circulate the mixed liquor from the bottom to the top of the bioreactor to maintain a well-mixed condition. A peristaltic pump (Masterflex L/s, USA) was used to circulate the mixed liquor through a ceramic MF membrane (NGK, Japan), which was housed in an external column module, and then back to the bioreactor. A ceramic membrane was used because of its resistance to corrosive chemicals, such as cleaning reagents and harsh environmental conditions, such as high temperature for chemical cleaning. The MF membrane had a pore size of 0.1 µm and an effective area of 0.09 m^2. Another peristaltic pump (Masterflex L/s, USA) was used to extract water from the membrane module in a suction and relaxation cycle of 14 min on and 1 min off, respectively. This operational cycle was specifically employed to alleviate membrane fouling.

The bioreactor was wrapped with a rubber hose, which was connected to a proportional-integral-derivative controlled heater (Neslab RTE7, Thermo Scientific, USA), to maintain the mixed liquor temperature at 35 °C. The bioreactor and all pipelines were insulated with polystyrene foam to minimize heat loss. A biogas counter was used to measure the rate of biogas production. A Tedlar sampling bag was also used to collect biogas for composition analysis. Trans-membrane pressure (TMP) was continuously monitored by a high resolution (± 0.1 kPa) pressure sensor (Extech Equipment, Australia) to indicate the profile of membrane fouling.

2.3 Experimental protocol

The AnMBR system was inoculated with anaerobic digesters from a local wastewater treatment plant (Wollongong, NSW, Australia) and fed with the synthetic wastewater under laboratory conditions as mentioned below. When AnMBR had achieved a stable removal of bulk organic matter (indicated by COD) for more than two months, sulphur content in the synthetic wastewater was increased gradually by adding Na_2SO_4. Stepwise increase of 100 mg/L sulphate every 10 days was adapted to avoid mortal effects of sulphur shock on anaerobic digesters. In this study, the influent sulphate concentration was increased up to 600 mg/L, corresponding to a decreased of the COD/SO_4^{2-} ratio to approximately 10, which is commonly considered as a threshold for effective anaerobic treatment of sulphur-containing wastewater (Hu et al., 2015; Yurtsever et al., 2016). The permeate flux was maintained at approximately 2 L/m^2h, resulting in a hydraulic retention time (HRT) of 5 days. This relatively long HRT was applied to allow for the adequate biodegradation of organic substances and mitigation of membrane fouling. Sludge samples (approximately 100 mL) were collected daily, leading to an operating sludge retention time (SRT) of 180 days. The mixed liquor pH was maintained at approximately 7 throughout AnMBR operation by periodically adding sodium bicarbonate into the bioreactor. Membrane backwashing was conducted ex-situ when the TMP reached approximately 0.9 bar.

2.4 Basic analytical methods

Mixed liquor pH and electrical conductivity were monitored using an Orion 4 Star Plus portable pH/conductivity meter (Thermo Scientific, USA). COD of the feed, mixed liquor supernatant, and effluent, was measured based on the standard dichromate method using high range plus digestion vials (Hatch, USA). Oxidation reduction potential (ORP) was monitored by a WP-80D dual pH-mV meter (TPS, Australia). Biogas composition was analysed using a biogas meter (Biogas 5000, Geotech, UK) (Nghiem et al., 2014). Alkalinity, mixed liquor suspended solids

(MLSS) and mixed liquor volatile suspended solids (MLVSS) concentrations were measured based on the Standard Methods for Examination of Water and Wastewater.

2.5 TrOC analysis

TrOC concentrations in the aqueous phase were determined by an analytical method previously reported by Wijekoon et al. (2015). Briefly, this method included solid phase extraction (SPE) and liquid chromatography followed by quantitative determination by tandem mass spectrometry with electrospray ionisation. Duplicate samples (250 mL for each) were analysed each time. Samples were spiked with a surrogate solution containing 50 ng of an isotopically labelled version of each target TrOC. Hydrophilic/lipophilic balance cartridges (Waters, Millford, MA, USA) were preconditioned with 5 mL methyl tert-butyl ether, 5 mL methanol and 10 mL reagent water, and then used for TrOC extraction. After SPE, cartridges used for TrOC extraction were rinsed twice with 5 mL reagent and dried completely using a stream of nitrogen for 50 min. All cartridges loaded with TrOCs were stored at 4 °C in sealed bags until elution and analysis. Analytes were eluted from the loaded cartridges with 5 mL methanol and then 5 mL methanol/methyl tertiary butyl ether (1/9, v/v) into centrifuge tubes. The resultant extract was concentrated under a stream of nitrogen to approximately 100 µL and then diluted to a final volume of 1 mL with methanol.

Analytes were separated using an Agilent1200 series high performance liquid chromatography (HPLC) system (Palo Alto, CA, USA) on a Luna C18 (2) column (Phenomenex, Torrence CA, USA). Peaks were identified and quantified by isotope dilution method using an API 4000 triple quadrupole mass spectrometer (MS) (Applied Biosystems, Foster City, CA, USA) that was equipped with a turbo-V ion source and employed in both positive and negative electro-spray modes. The detection limit of this analytical method was 5 ng/L for all analytes except for meprobamate and bisphenol A (10 ng/L) and aspartame, propylparaben (20 ng/L). Detailed description of the HPLC–MS/MS settings is available elsewhere (Wijekoon et al., 2015)

Feed and permeate samples were collected weekly for the analysis of TrOCs to determine their removal by AnMBR:

$$R = \frac{C_f - C_p}{C_f} \times 100\%$$

where C_f and C_p were TrOC concentrations in the feed and permeate, respectively.

TrOC concentrations in the sludge phase were determined based on a method reported previously by Yang et al. (2016). Briefly, the mixed liquor was first centrifuged at 3750g for 20 mins to obtain sludge pellet, which was then freeze-dried completely using an Alpha 1–2 LD plus Freeze Dryer (Christ GmbH, Germany). The dry sludge was grounded to powder before weighing 0.5 g into a glass tube and being thoroughly mixed with 5 mL methanol, followed by ultrasonication at 40 °C for 10 min. The mixture was then centrifuged at 3270 g for 10 min to obtain supernatant, which was collected into an amber bottle. The ultrasonication and centrifugation steps were repeated after mixing 5 mL blend of dichloromethane and methanol (1:1 v:v) with the remaining sludge in the test tube. Supernatants from these two centrifuge steps were mixed completely; while residual methanol and dichloromethane were purged using nitrogen gas. Milli-Q water was added to obtain a 250 mL aqueous sample for TrOC extraction and analysis according to the method described above.

3 Results and discussion

3.1 Biomass concentration

An increase in the influent sulphur content up to 600 mg/L (as sulphate), corresponding to a decrease in the COD/SO_4^{2-} ratio from 60 to 10, did not significantly affect the biomass concentration as indicated by both the MLSS and MLVSS concentrations during AnMBR operation (Fig. 1). In this study, the MLSS and MLVSS concentrations were stable at approximately 15.0 ± 1.4 and 10.0 ± 1.5 g/L, respectively, with a MLVSS/MLSS ratio of around 0.6. The stable MLVSS/MLSS ratio also confirms that sulphate addition to the influent did not cause any increase in the MLSS inorganic fraction. Results shown in Fig. 1 are consistent with reports from other anaerobic treatment systems, where no significant impacts on biomass concentration were observed with sulphur increase provided the influent COD/SO_4^{2-} ratio was at or above the threshold of 10 (Hu et al., 2015). Indeed, the COD/SO_4^{2-} ratio of the influent significantly affects the performance of anaerobic treatment systems by governing the competition between sulphate reducing bacteria and other bacteria, particularly predominant species belonged to *proteobacteria* (Sarti et al., 2010).

[Figure 1]

3.2 Removal of bulk organic matter

No significant impact on the removal of COD was observed with sulphur increase in the AnMBR influent. As can be seen in Fig. 2, COD removal by AnMBR was stable at approximately 98% when sulphate addition to the feed solution was increased to 600 mg/L. This result is consistent with the stable biomass concentration as discussed above, corroborating that sulphur increase does not significantly affect the basic performance of AnMBR regarding the biomass growth and biodegradation of bulk organic matter, as long as the the influent COD/SO_4^{2-} ratio is above 10. Similar results were also observed by Sarti et al. (2010) who reported that COD removal by an anaerobic sequencing batch biofilm reactor was not impacted by an increase in the influent sulphur content. Sarti et al. (2010) attributed their observation to the fact that organic carbon was the dominating energy source for microbial metabolism. It is noteworthy that sulphate reducing bacteria appeared to proliferate in AnMBR with sulphur addition, as indicated by a significant increase in the H_2S production (Fig. 3). Despite the competition between methane-producing and sulphate-reducing bacteria in the anaerobic bioreactor, they both utilize organic carbon for assimilation (Hu et al., 2015), thereby contributing a relatively stable COD removal by AnMBR.

[Figure 2]

3.3 Biogas production

Sulphur increase significantly affected biogas production during AnMBR operation (Fig. 3A). Without sulphate addition to the influent (i.e., the first 10 days), biogas production of AnMBR varied slightly between 0.4 and 0.6 L/g COD_{added}. When 100 mg/L SO_4^{2-} was added to the AnMBR influent between day 10 and 20, biogas production gradually decreased to 0.2 L/g COD_{added} (Fig. 3A). A significant reduction also occurred to the methane content in the produced biogas when 100 mg/L SO_4^{2-} was added to the influent. Such observed reductions in both biogas production and its methane content could be attributed to the adverse effects of sulphur loading on methanogens (Hu et al., 2015). Similar variations in biogas production were also noted in the following AnMBR operation with a step-wise increase of the influent SO_4^{2-} concentration up to 600 mg/L (i.e. increasing100 mg/L every 10 days). Although biogas production could be recovered to some extent when the influent

SO_4^{2-} concentration was maintained at a certain level for a few days, a downward trend to approximately 0.2 L/g COD$_{added}$ was observed when SO_4^{2-} addition was increased to 600 mg/L (Fig. 3A).

[Figure 3]

The reduced methane content in biogas with sulphur increase can be attributed to the competition of sulphate reducing bacteria over methane producing microbes (Silva et al., 2002; Hu et al., 2015). Hu et al. (2015) reported that sulphur increase could enhance the utilization of electrons by sulphate reducing bacteria. Indeed, sulphate addition increased considerably the H_2S production (Fig. 3B), suggesting the active metabolism of sulphate reducing bacteria. Moreover, the produced H_2S inside the anaerobic bioreactor could be toxic to methanogenic bacteria and archaea by diffusing through their cell membranes and denature their functional proteins (Siles et al., 2010). Nevertheless, despite a continuous increase in the influent SO_4^{2-} concentration up to 600 mg/L, the methane content in the produced biogas was recovered to its initial level (approximately 62%) from day 25 onward. This observation confirms that at a COD/SO_4^{2-} ratio at or above 10, there was adequate organic carbon for both methane producing and sulphate reducing bacteria, thereby maintaining the basic performance of anaerobic systems after microbial acclimatization. It is noted that biogas purification to remove H_2S, for example by adsorption using inert materials, is necessary for effective and safe methane utilization when sulphate-rich wastewater is treated by AnMBR in practice.

3.4 Membrane fouling

High sulphate addition to the influent exacerbated membrane fouling during AnMBR operation (Fig. 4). The TMP value was stable at approximately 0.5 bar when the influent SO_4^{2-} concentration was lower than 200 mg/L, indicating no notable membrane fouling at a low sulphur content. A sharp TMP increase was observed when the SO_4^{2-} concentration was increased to 300 mg/L, possibly due to an enhancement in the concentration of soluble microbial products (SMP) and extracellular polymeric substances (EPS) in the mixed liquor at a high SO_4^{2-} concentration. Indeed, Kobayashi et al. (2015) reported that the high sulphate concentration (> 200 mg/L) could considerably increase the release of carbohydrate and protein, which are major constitutes of SMP and EPS, from anaerobic digesters, during the operation of up-flow anaerobic sludge blanket reactors. Both SMP and EPS play an important role in the formation of cake layer on the membrane surface and pore blockage in either aerobic or anaerobic MBR systems (Lin et al., 2012). As a result, to maintain a sustainable water production, membrane backwash using the AnMBR effluent was conducted on day 35 when the TMP increased to 0.85 bar. Nevertheless, similar increase in the TMP profile was observed when the influent SO_4^{2-} concentration was further increased, thereby requiring another membrane backwash on day 65.

[Figure 4]

3.5 Removal of trace organic contaminants

3.5.1 General removal performance

TrOC removal by AnMBR is governed by their physiochemical properties, including hydrophobicity and molecular features. Based on the predictive framework developed by Wijekoon et al. (2015), TrOC removal in AnMBR could be categorized by their effective octanol – water partition coefficient (i.e. Log *D*) at a certain mixed liquor pH. Thus, in this study, the selected 38 TrOCs were classified as hydrophilic (Log $D < 3.2$) and hydrophobic (Log $D > 3.2$) as the mixed liquor pH was stable at 7.

All hydrophobic TrOCs with Log $D > 3.2$ were well removed by over 50% in AnMBR with bisphenol A as the only exception (Fig. 5A). No discernible effects on the removal of these hydrophobic compounds were observed with sulphur increase. The effective removal of these hydrophobic TrOCs by AnMBR has also been demonstrated by Wijekoon et al. (2015) under comparable experimental conditions and can be attributed to their adsorption onto sludge due to hydrophobic interactions. Bisphenol A is a precursor monomer for the production of many plastics and can leach out from plastic materials. Thus, the low removal of bisphenol A (less than 20%) could be an experimental artefact associated with its release from plastic components (e.g. tubing) of the experimental system. Indeed, low bisphenol A removal by anaerobic treatment has also been reported in several previous lab-cale studies (Monsalvo et al., 2014; Wijekoon et al., 2015).

[Figure 5]

The removal of hydrophilic TrOCs (Log D < 3.2) by AnMBR was highly variable (Fig. 5B). It has been established that the removal of hydrophilic TrOCs by either aerobic or anaerobic MBR was dependent primarily on their intrinsic biodegradability given their relatively weak adsorption onto sludge (Wijekoon et al., 2015). In this study, some hydrophilic compounds could be effectively removed by AnMBR regardless of the sulphur content in the influent. The removal of these compounds was over 60% and they included aspartame, caffeine, sulfamethoxazole, trimethoprim, PFOS, carazolol, verapamil, hydroxyzine, simazine, amitriptyline, omeprazole, and linuron. Indeed, the effective removal of these hydrophilic TrOCs by AnMBR has also been reported by Wijekoon et al. (2015) who attributed their high biodegradability to the presence of electron donating functional groups, such as hydroxyl and amine, in their structures. In addition, most of these hydrophilic compounds had nitrogen in the molecular structure, which probably made them amenable to anaerobic treatment (Wijekoon et al., 2015).

Several hydrophilic TrOCs were poorly removed by AnMBR (Fig. 5B). These compounds were ketoprofen, paracetamol, meprobamate, ibuprofen, dilanfin, TCEP, diclofenac, carbamazepine, germfibrozil, DEET, atrazine, diuron, and diazepam. The low removal of these hydrophilic compounds could be ascribed to their poor biodegradability due to the presence of electron withdrawing functional groups, such as chloro and amide, irrespective of the presence of any electron donating functional groups in their molecular structure (Monsalvo et al., 2014; Wijekoon et al., 2015).

Unlike hydrophobic TrOCs, sulphur addition to influent could significantly affect the removal of hydrophilic TrOCs in AnMBR (Fig. 5B). These hydrophilic TrOCs could be categorised into three groups based on their removal variations along with the influent SO_4^{2-} addition from 0 to 600 mg/L. In the first group, the removal of two hydrophilic compounds, namely caffeine and trimethoprim, continuously decreased as the influent SO_4^{2-} concentration increased. The reason for the decreased removal of these two compounds is not clear, but possibly due to the toxicity of H_2S to microorganisms that were responsible for the removal of these two compounds. By contrast, in the second group, SO_4^{2-} addition led to an increase in the remove of propylparaben and linuron, which have relatively high hydrophobicity. At the mixed liquor pH of 7, the Log *D* values of propylparaben and linuron were 2.8 and 3.12, respectively. Thus, the observed increase in their removal could be attributed to the enhanced hydrophobic interaction between these two compounds and sludge with SO_4^{2-} increase in the influent. Indeed, as discussed above, it has been reported that high SO_4^{2-} concentration could increase the release of EPS and thus enhance the hydrophobicity of anaerobic sludge (Kobayashi et al., 2015). Most hydrophilic TrOCs belong to the third group, which showed an initial decrease and then increase in the removal by AnMBR with continuous increase in the influent SO_4^{2-} concentration. These TrOCs included ketoprofen, paracetamol, ibuprofen, carazolol, TCEP, dilantin, simazine, diclofenac, carbamazepine, germfibrozil, DEET, atrazine, diuron, and diazepam. The results could be attributed to microbial adaption to the SO_4^{2-} addition, which therefore recovered the biodegradation of these hydrophilic compounds.

3.5.2 TrOC adsorption on sludge

A major factor governing TrOC adsorption onto biosolids during AnMBR operation is their hydrophobicity. Although hydrophobic TrOCs with Log *D* > 3.2 could readily absorb onto sludge particles, their residual in sludge phase was relatively low with a few exceptions (Fig. 6A). The observed low residual concentrations of these hydrophobic TrOCs in the sludge phase could be attributed to their high biodegradation, which also determines TrOC resides in the biosolids (Wijekoon et al., 2015). Of the 10 hydrophobic TrOCs, t-octylphenol exhibited the highest accumulation in the sludge phase, followed by triclosan, triclocarban, and nonylphenol, respectively. Triclosan and triclocarban are known to be persistent to biodegradation due to the chloro functional group (which is a strong electron withdrawing functional group) in their molecular structure. On the other hand, both t-octylphenol and nonylphenol are degradation by-products of alkylphenols, which are widely used in domestic detergents. It is noted that concentrations of all hydrophobic TrOCs in the sludge phase were relatively stable regardless of sulphur addition to the influent.

[Figure 6]

Of the 28 hydrophilic TrOCs, only four compounds accumulated considerably in sludge phase with concentrations higher than 200 ng/g total solid (Fig. 6B). They were carazolol, paracetamol, amitriptyline, and hydroxyzine. Of a particular note, when the SO_4^{2-}concentration increased from 0 to 600 mg/L, the concentration of paracetamol in sludge decreased significantly (Fig. 6B), probably due to the enhanced biodegradation with the proliferation of sulphate reducing bacteria, thereby improving its overall removal by AnMBR (Fig. 6B). On the other hand, the residual concentrations of carazolol, amitriptyline, and hydroxyzine in the sludge phase increased with SO_4^{2-} addition. This result could be attributed to the change of biomass characteristics, for example, surface charge and hydrophobicity, caused by an enhanced release of EPS with sulphur addition (Kobayashi et al., 2015).

4 Conclusion

There were no discernible effects on the biological activity and COD removal by AnMBR despite an increase in the influent SO_4^{2-} concentration provided that COD/SO_4^{2-} ratio was above 10. However, increasing sulphur content resulted in some variations in biogas production and a notable increase in the production of H_2S during AnMBR operation. Sulphur addition did not significantly affect the removal of hydrophobic TrOCs. By contrast, the removal of some hydrophilic TrOCs was considerably affected by sulphur increase. In addition, the residual concentrations of some hydrophilic TrOCs in biosolids were also impacted by sulphur addition.

Supplementary data

Supplementary data of this study can be found in the e-version of this paper online.

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LIST OF FIGURE

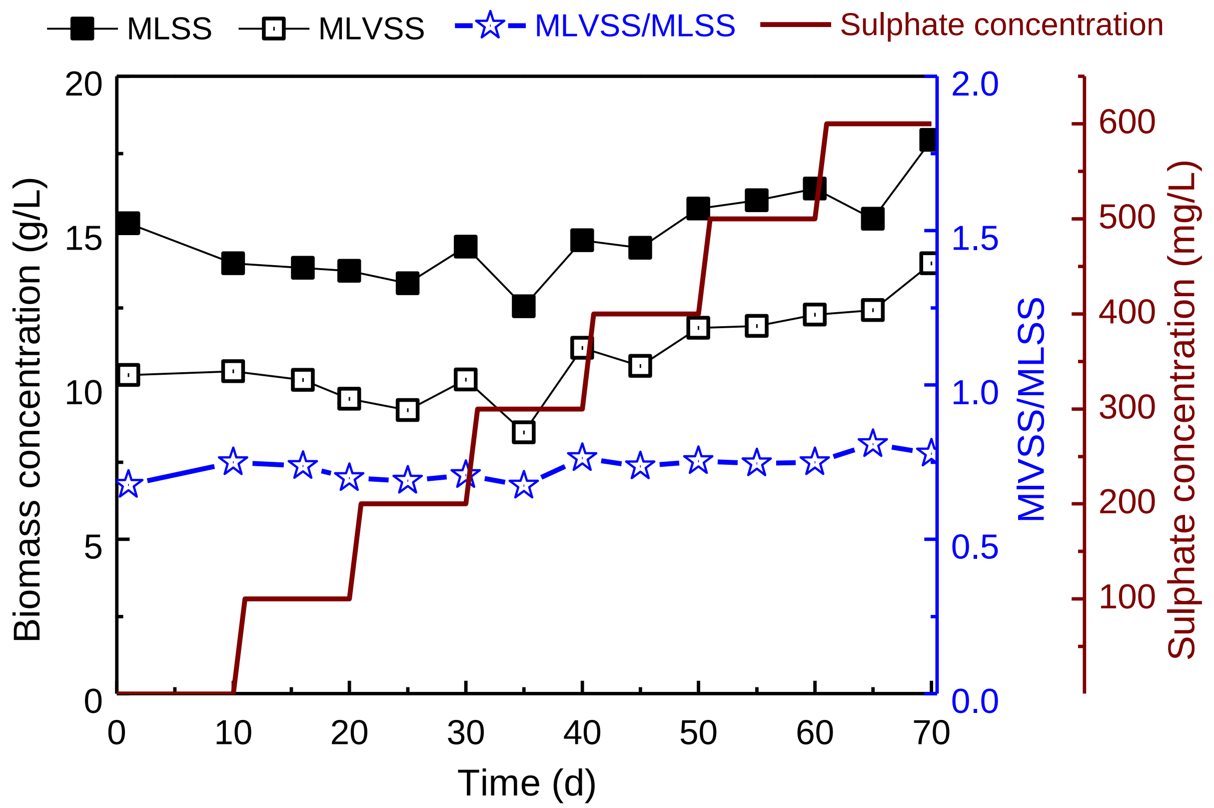

Fig. 1: Effect of sulphate addition on biomass concentration (i.e. MLSS and MLVSS contents) during AnMBR operation. Sulphate concentration in the synthetic wastewater was increased to 600 mg/L with an increment of 100 mg/L every 10 days. Experimental conditions: HRT = 5 d; mixed liquor pH = 7 ± 0.1; temperature = 35 ± 1 °C**.**

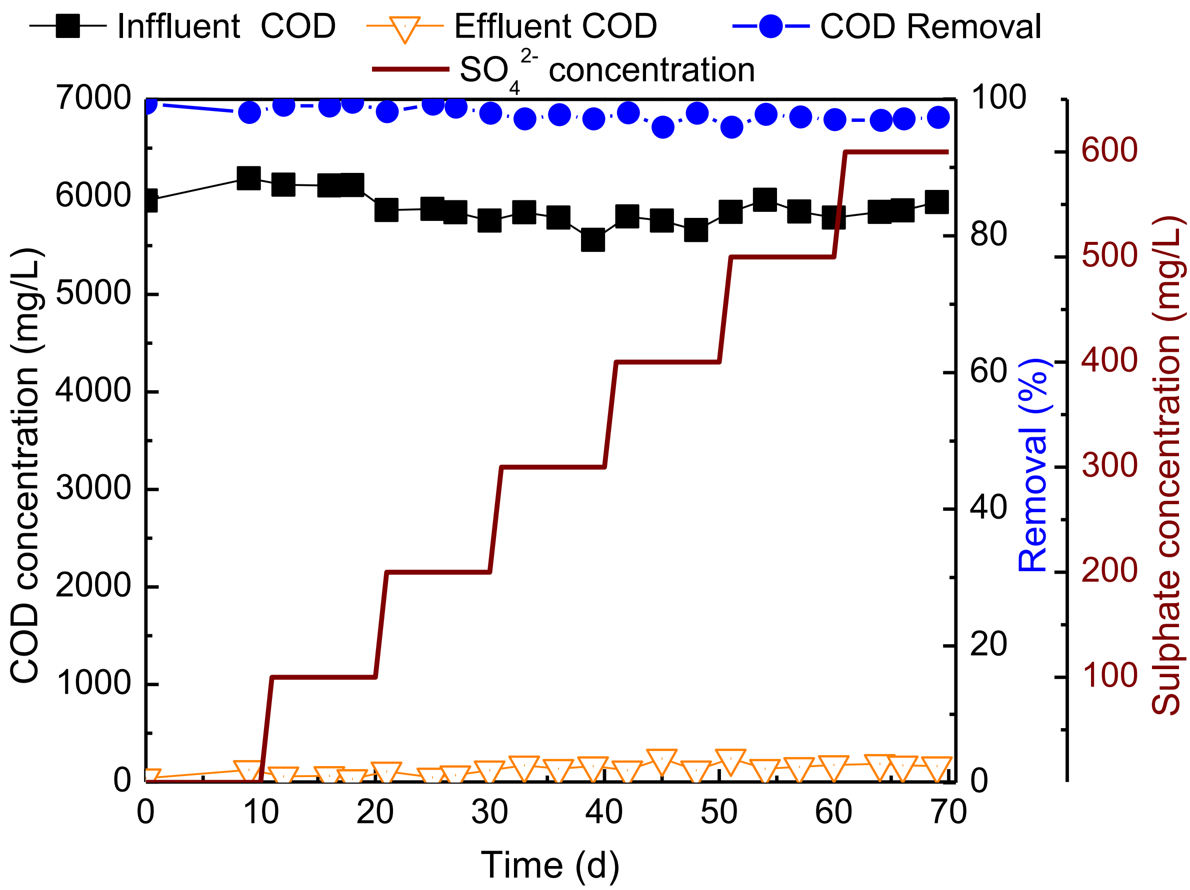

Fig. 2: Effect of sulphate concentration on COD removal by AnMBR. Sulphate concentration in the synthetic wastewater was increased to 600 mg/L with an increment of 100 mg/L every 10 days. Experimental conditions are shown in Fig. 1.

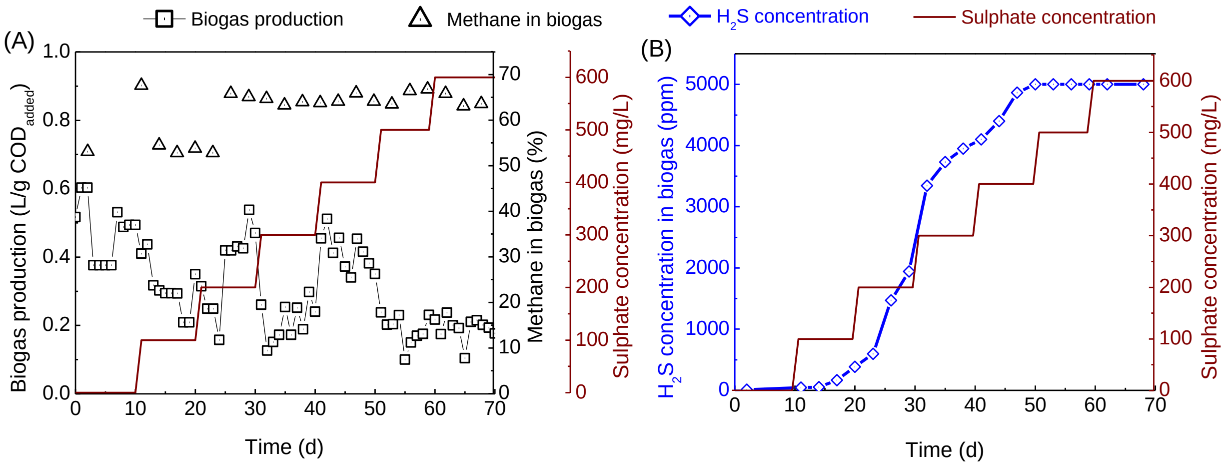

Fig. 3: Effect of sulphate concentration on (A) biogas production and methane content, (B) H_2S concentration in biogas during AnMBR operation. Sulphate concentration in the synthetic wastewater was increased from 0 to 600 mg/L with an increment of 100 mg/L every 10 days. Experimental conditions are as described in Fig. 1.

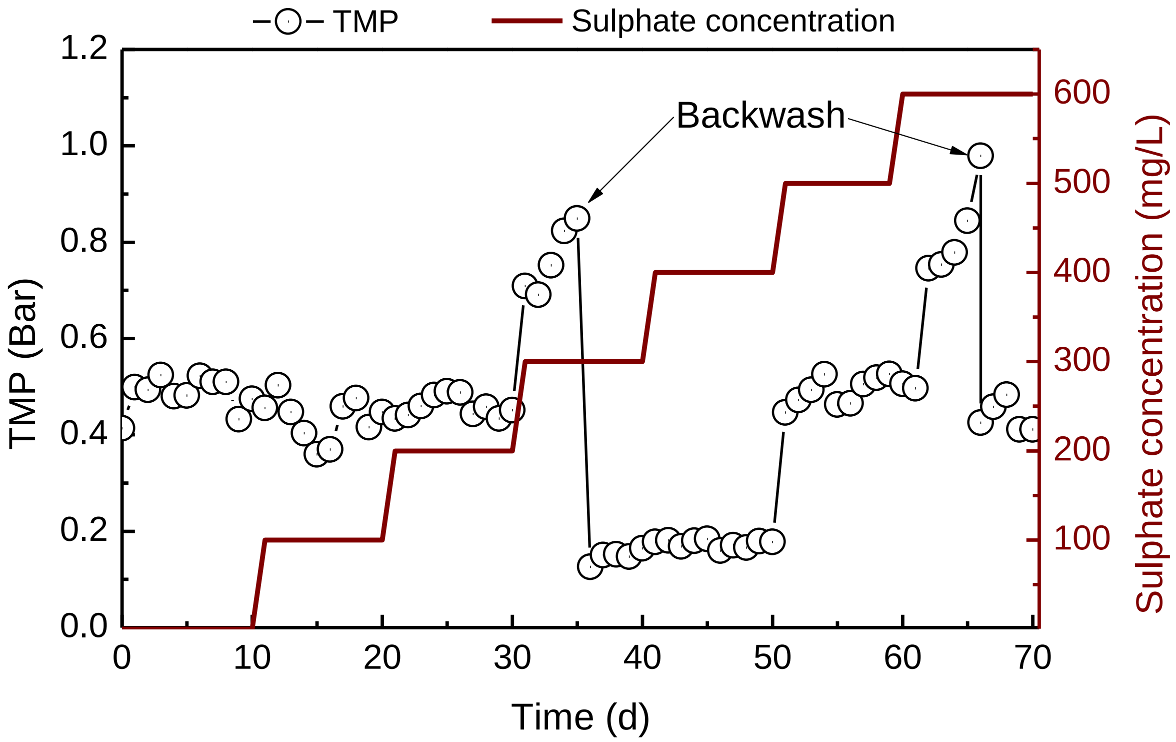

Fig. 4: Variation of the TMP profile during AnMBR operation. Membrane cleaning was conducted by backwashing using the AnMBR effluent. Experimental conditions are as described in Fig. 1.

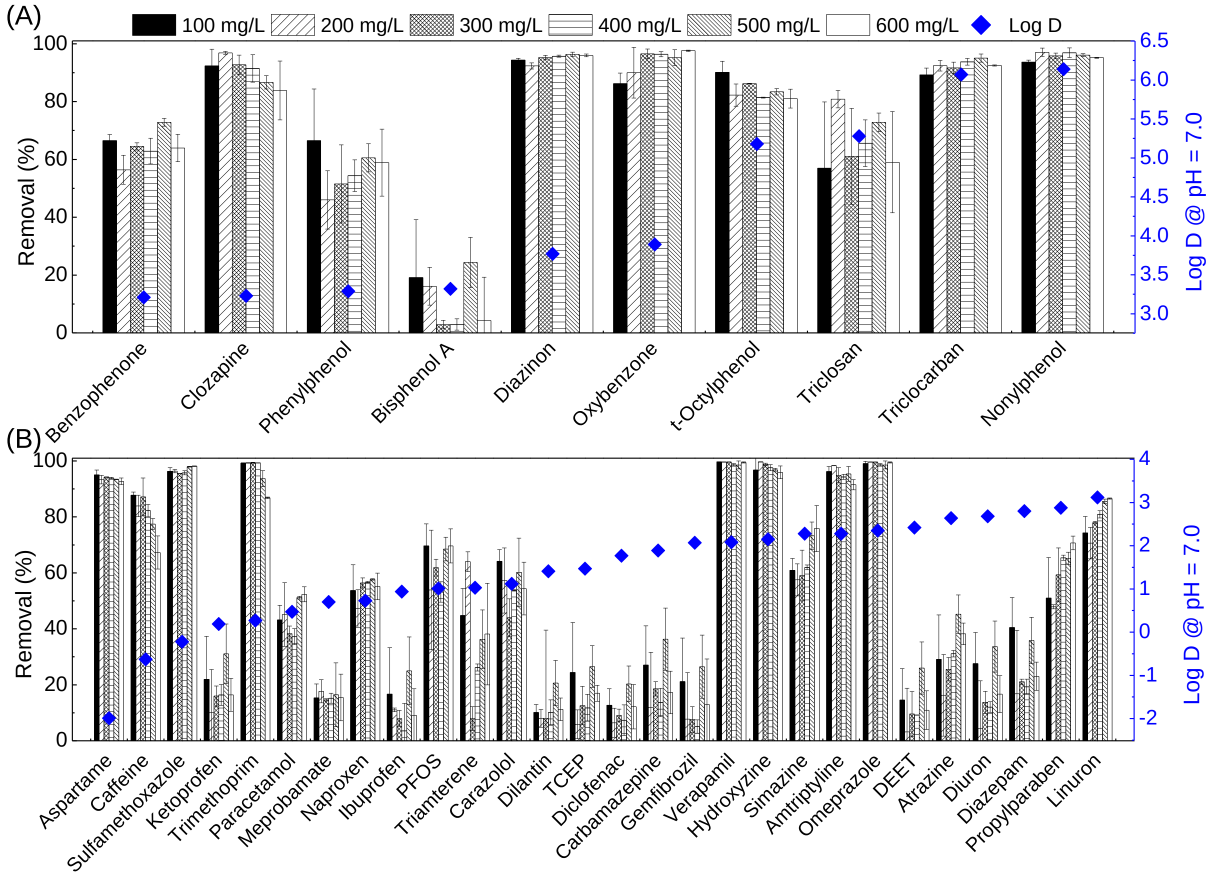

Fig. 5: Effects of sulphate concentration on the removal of (A) hydrophobic (i.e. compounds with Log $D > 3.2$ at pH 7) and (B) hydrophilic (i.e. compounds with Log $D < 3.2$ at pH 7) TrOCs by AnMBR from the aqueous phase. Error bars represent the standard deviation from two measurements at each sulphate concentration (once every five days). Experimental conditions are given in Fig. 1.

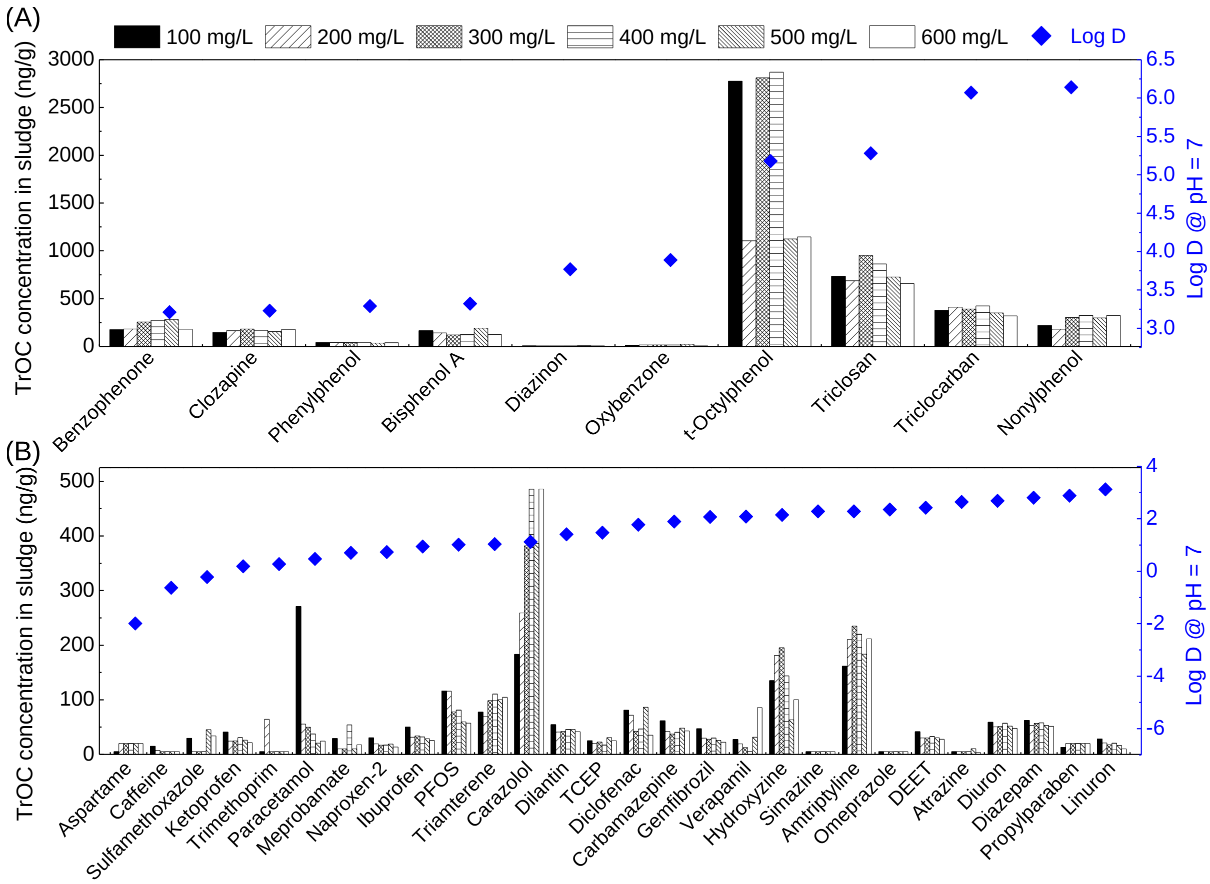

Fig. 6: Effect of sulphate concentration on the residual of (A) hydrophobic and (B) hydrophilic TrOCs in the sludge phase during AnMBR operation. Experimental conditions are given in Fig. 1.