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Effect of operating conditions on speciation and bioavailability of trace metals in submerged anaerobic membrane bioreactors

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HIGHLIGHTS

- Trace Metal (TM) retention of SAMBRs reduced when pH, HRT and SRT were decreased.
- Metal speciation generally became more bioavailable with decreases in HRT, SRT, pH.
- Sensitivity to changes and retention in anaerobic digester varied between TMs.
- Fe had the most and Mn had the least significant changes in speciation.

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ABSTRACT

This study investigated the effect of changes in pH (7, 6.5 and 6), hydraulic retention time (HRT) (6 h, 4 h, and 2 h), solids retention time (SRT) (100 d and 25 d) on the speciation of trace metals (TMs) in submerged anaerobic membrane bioreactors (SAMBRs). The results showed that the metal retention capacity of SAMBRs reduced when the pH, HRT and SRT were reduced i.e. up to 21.9%, 39.1%, and 17.1%, respectively, but it was also found that the speciation of these TMs generally shifted towards highly bioavailable fractions i.e. Soluble and Exchangeable. The degree of shifting in speciation depended on the affinity of the TMs for anaerobic sludge and their sensitivity to the changes. TMs with the most and the least significant changes in speciation were Fe and Mn, respectively.

1. Introduction

The importance of trace metals (TMs) in anaerobic digestion has been studied extensively in the literature, however, understanding the factors controlling the bioavailability of TMs is still limited. Although the total metals supplied should be sufficient, in the anaerobic environment these metals may not be present in a bioavailable form that can be utilized by the microorganisms (Zitomer et al., 2008). Even full bioavailability does not mean that the required TMs are all utilized by the bacterial population (Oleszkiewicz and Sharma, 1990). The bioavailability of TMs for microbial uptake and growth in anaerobic bioreactors is dependent on affinity of the TMs towards anaerobic sludge sites (Artola et al., 2000; Leighton and Forster, 1997) which will further control the retention capacity of TMs in anaerobic reactors. On the other hand, the TM bioavailability strongly depends on the metal speciation, and this in turn can be affected by some of the reactor operating parameters such as pH, hydraulic retention time (HRT), and possibly solids retention time (SRT) (Thanh et al., 2016). Most of the studies on these operating parameters in the literature were carried out for only several TMs such as Fe, Co, or Ni. However, anaerobic bioreactors require supplementation of a range of TMs which have different degree of affinity towards anaerobic sludge and their speciation could change in different ways under different operating conditions. Therefore, there is a lack of study that can evaluate the bioavailability of all the required TMs at the same time.

Changes in pH can not only affect the performance of the anaerobic microorganisms, it can also dramatically influence the fate of TMs in anaerobic digestion, and these effects can be interrelated. A number of studies have been carried out in up-flow anaerobic sludge bed (UASB) reactors to determine the correlation between TM speciation and the changes in pH (Dong et al., 2013;

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Gonzalez-Gil et al., 2012; Lopes et al., 2008; van Hullebusch et al., 2005b). Generally, these studies showed that an increase in pH led to the transformation of TMs from available mobile fractions like their "exchangeable" component, to stable organic or residue forms which reduced their bioavailability. In contrast, a reduction in pH resulted in the dissolution of TMs into solution, shifting them from non-bioavailable fractions (residual and organic/sulfide) towards more bioavailable fractions (exchangeable and carbonates).

Understanding of the relationship between HRT and TM speciation in anaerobic processes is very limited. Cestonaro do Amaral et al. (2014) studied the distribution of Cu and Zn in swine wastewater in an up-flow bio-digester; they found that when the HRT was reduced from 17.86 d to 7.57 d, the metal retention capacity of the bioreactors decreased. While other metal fractions remained the same or decreased, the less bioavailable oxidizable fraction comprised of the metals associated with organic matter/sulfide increased, indicating that the metals became less bioavailable to anaerobic microorganisms.

Finally, SRT is another important operating parameter for anaerobic bioreactors, as the SRT needs to be maintained at a certain level so that there is sufficient active population present in the reactors to enable anaerobic digestion to proceed efficiently. At long SRTs, it is expected that TMs accumulate and are present in high levels in the bioreactor, and also that the majority of the metals are associated with the biomass, either on the surface or inside of the biomass. Therefore, at short SRTs it is possible that the high daily biomass removal rate will alter the total content of TMs and change their speciation. There has been no study in the literature carried out to determine how the SRT could influence TM speciation in anaerobic bioreactors.

The reactor configuration plays an important role in the dynamics of TMs as it affects the metal retention capacity of anaerobic bioreactors (Thanh et al., 2016). Most of the studies in metal speciation and bioavailability have been carried out in UASB or conventional CSTR reactors. The anaerobic membrane bioreactor (AnMBR) is one of the most advanced anaerobic reactor designs available as it offers independent control of the SRT and HRT, which then allows larger volumes of wastewater to be treated on a smaller footprint, prevents any loss of biomass into the effluent (Kunacheva et al., 2017), and hence there will be no TMs associated with the biomass escaping into the effluent.

Considering these facts, this study was aimed at exploring how the changes in operating parameters in a SAMBR, i.e. pH, HRT, and SRT, can influence the bioavailability of TMs, i.e. Fe, Co, Ni, Zn, Mn, and Mo, by monitoring their speciation over time under a variety of reactor operating conditions.

2. Material and methodologies

2.1. Experimental plan

2.1.1. Anaerobic sludge cultivation

Seed sludge was obtained from anaerobic digesters at a municipal wastewater treatment plant (Ulu Pandan Water Reclamation Plant, Singapore) and grown in a 5 L laboratory mixed batch reactor for more than 5 months to achieve a sufficient population of anaerobic microorganisms. The seed reactor was fed once every week in fill-and-draw mode (7 days HRT), and the feed was based on that used by Ketheesan et al. (2016).

2.1.2. SAMBRs

The set-up of SAMBRs used for this study was described in detail by Zhou et al. (2016). The reactor had a working volume of 3.2 L and was separated into two zones by a baffle. A Kubota flat sheet polyethylene membrane module (0.4 μm pore size) with a total surface area of 0.116 m^2 was immersed into the reactor. The flux of the membrane was set at 20 L per square meter per hour (LMH) for all starting conditions (pH 7, 6 h HRT, and 100 d SRT) using a membrane flux pump. Biogas was re-circulated with a vacuum pump (B100 SEC, Charles Austin) through a stainless steel tube diffuser which generated coarse bubbles in order to mix the biomass in the reactor, and clean the surface of the membrane (minimise membrane fouling), and the sparging rate was controlled by a gas flowmeter (101 Flo-Sen, Cole Palmer) at 3–4 L per minute (LPM).

A carbohydrate-protein substrate was supplemented with metal nutrients to serve as the synthetic wastewater. The SAMBR wastewater was maintained at approximately 500 ± 20 mg COD/L based on that used by Akram and Stuckey (2008), and was comprised of glucose (360 mg COD/L), peptone (110 mg COD/L), meat extract (30 mg COD/L), sodium bicarbonate (2000 mg/L), and essential minerals: K_2HPO_4 (80 mg/L), $CoCl_2{\cdot}6H_2O$ (2.38 mg/L), $FeCl_2{\cdot}4H_2O$ (15.8 mg/L), $MnCl_2{\cdot}4H_2O$ (0.75 mg/L), $NiCl_2{\cdot}6H_2O$ (0.45 mg/L), $Na_2MoO_4{\cdot}2H_2O$ (0.375 mg/L) and $ZnCl_2$ (0.31 mg/L). The reactors were operated in a water bath at mesophilic temperature i.e. 35 ± 2 °C, which is optimal for most methanogens.

Three independent experiments with changes in pH, HRT, and SRT were carried out in three SAMBRs with the same configuration, i.e. SAMBR1, SAMBR2, and SAMBR3, respectively. The steady state (control) conditions for these SAMBRs were defined as 500 mg/L COD, pH 7, 6 h HRT and 100 d SRT.

2.1.3. Changes in pH

SAMBR1 was operated at steady state conditions at neutral pH 7 for 36 d. The pH was subsequently reduced to 6.5 and then 6 by adding diluted HCl to adjust the pH. The reactor was operated at each pH for about 8 d, which constitutes 32 HRTs, and previous work in this lab has showed that steady state occurs in this time (Kunacheva et al., 2017). At the end of the pH 6 run, no further pH adjustment was carried out on the feed, and the SAMBR was allowed to recover until the pH was back to neutral.

2.1.4. Changes in HRT

SAMBR2 was operated under steady state conditions at 6 h HRT for 53 d. The HRT was subsequently reduced from 6 h to 4 h, and then to 2 h by increasing the membrane flux. In order to maintain a constant liquid level in the SAMBR, the speed of the influent pumps was increased, i.e. double and triple, respectively. The SAMBR was operated at each HRT for 5 d, SRT was maintained at 100 d, whereas, VSS was 10.2 g/L at the start of 6 h HRT. At the end of the 2 h HRT run, the membrane was removed and the cake layer on the membrane surface was carefully collected by rinsing with de-ionized water, and the physical parameters and TM composition in the cake layer were analysed.

2.1.5. Changes in SRT

SAMBR3 was operated under steady state conditions at an SRT of 100 d with the daily removal of 32 mL of sludge for almost 3 months; during this time samples were collected several times to establish baseline conditions. Before the SRT was reduced to 25 d, it was temporarily reduced to 75 d and 50 d for 1 week each to ensure a smooth transition. To maintain 25 d SRT, 128 mL of sludge was removed every day from the reactor for 27 d. This SRT is considered as the optimal operating SRT to achieve minimum normalized production of soluble microbial products (SMPs) in an anaerobic CSTR (Kuo et al., 1996).