Bioresource Technology 204 (2016) 17–25

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Inorganic fouling of an anaerobic membrane bioreactor treating leachate from the organic fraction of municipal solid waste (OFMSW) and a polishing aerobic membrane bioreactor

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HIGHLIGHTS

- Landfill leachate was treated in a Submerged Anaerobic Membrane BioReactor.
- More than 90% COD removal was obtained at an HRT of 0.4–0.6 days.
- Monohydrocalcite precipitated on the membrane causing flux drop.
- Hydroxyapatite precipitated in the aerobic polishing step.

ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form 23 December 2015
Accepted 25 December 2015
Available online 31 December 2015

Keywords:
Anaerobic digestion
Submerged Anaerobic Membrane BioReactor (SAMBR)
Aerobic membrane bioreactor
Landfill leachate
Inorganic fouling

ABSTRACT

The treatment of leachate (Average TCOD = 11.97 g/L, 14.4% soluble) from the organic fraction of municipal solid waste was investigated using a Submerged Anaerobic Membrane BioReactor (SAMBR), followed by an aerobic membrane bioreactor (AMBR) to polish this effluent. This paper investigated the exact nature and composition of the inorganic precipitate in each of the reactors in the process. The flux decreased due to precipitation of calcium as monohydrocalcite ($CaCO_3{\cdot}H_2O$) containing traces of metals onto the SAMBR membrane because of high CO_2 partial pressures. Precipitation of calcium in the AMBR was also observed due to a higher pH. In this case, phosphorus also precipitated with calcium in two different phases: the background layer contained calcium, oxygen, carbon and small amounts of phosphorus (2–6.7%), while flakes containing calcium, oxygen and higher amounts of phosphorus (10–17%) were probably hydroxyapatite ($Ca_5(PO_4)_3OH$).

1. Introduction

The main advantages of membrane bioreactors (MBR) include rapid start-up and a higher loading rate than classical technologies (Stephenson et al., 2000), which combines in one unit the removal of COD, solids and nutrients, thus giving rise to a small footprint and a very high quality permeate with no suspended solids. Anaerobic MBRs have the added advantage of producing energy in the form of biogas, and produce very little excess sludge reducing the burden of sludge disposal. In a Submerged Anaerobic Membrane BioReactor (SAMBR) the membrane is submerged within the reactor, and membrane cleaning is accomplished by recirculating the biogas as large bubbles underneath the membrane to scour it and alleviate biofouling. Several researchers have also achieved fouling reduction by gas sparging (Hong et al., 2002; Li et al., 2005), and other turbulence promoting techniques such as gas/liquid slug flow (Mercier-Bonin et al., 2001) or polymeric particles (Imasaka et al., 1989). However, fouling remains the main drawback of MBRs since it reduces flux through the membrane, and increases trans-membrane pressure (TMPs) drops. Nevertheless, fouling can enhance COD removal since the fouling layer acts as a secondary membrane and enhances the rejection of low molecular weight (MW) solutes.

Fouling can occur by: adsorption or deposition of macromolecules onto the membrane surface; by adsorption onto the pore surface; or, by complete pore-blocking. The phenomenon is exacerbated by concentration polarisation as it increases the concentration of macromolecules and particles in the vicinity of the membrane. Fouling can also be related to biological growth due to cell attachment and extracellular polymeric substances (EPS) filling the void spaces between the particles in the cake (Chu et al., 2005). Other fouling can be attributed to components in the feed such as proteins, colloids and particulate materials.

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http://dx.doi.org/10.1016/j.biortech.2015.12.074

Colloids cover a wide size range, from a few nanometers to a few micrometers, and can comprise clay minerals, colloidal silica, iron, aluminium, and manganese oxides, organic colloids and suspended matter, and calcium carbonate precipitates (Boussu et al., 2006; Mahvi and Razavi, 2005). Dissolved ions may also precipitate in the form of struvite which is an inorganic precipitate with the chemical formula: $MgNH_4PO_4{\cdot}6H_2O$, and has been reported by several investigators as playing a key role in flux decline (Choo and Lee, 1996; Kang et al., 2002). Kang et al. (2002) reported that struvite was found to have accumulated inside the pores of a zirconia skinned inorganic membrane, but not in an organic polypropylene membrane. Choo and Lee (1996) also found that struvite plays a significant role in the consolidation of biomass cakes on the membrane surface. Struvite is expected to be a problem in MBRs treating municipal solid waste (MSW) or the leachate because it contains all the elements required to form struvite. Struvite precipitation is also facilitated when the pH increases, and as a result acidic solutions are required to dissolve the inorganic foulant (Kang et al., 2002). Other inorganic foulants in anaerobic environments can also include $CaCO_3$ polymorphs such as calcite, aragonite, vaterite, monohydrocalcite, ikaite and amorphous calcium carbonate (in order of decreasing stability) (Meiron et al., 2011; Salek et al., 2016). However, the precipitation of inorganic salts can also be affected by module geometry and membrane materials (Shih et al., 2005), and there is limited information on the effect of these factors on fouling mechanisms. Consequently, there is very little information available describing inorganic fouling on membrane surfaces (Shirazi et al., 2010).

In the SAMBR, biogas is recirculated to scour the membrane surface which results in high CO_2 partial pressures. Information about inorganic fouling under these conditions in a SAMBR treating leachate from the organic fraction of municipal solid waste (OFMSW) is poorly documented. This paper presents a detailed investigation into the fate of inorganics and dissolved ions in a novel process treating OFMSW leachate, and identifies the inorganic foulants on the membranes.

2. Methods

2.1. Leachate from the organic fraction of municipal solid waste (OFMSW)

The synthetic leachate used in this study was producing in a bench scale anaerobic reactor (20 L) from real components of Municipal Solid Waste: 41.3% kitchen wastes, 10.8% garden wastes and 47.9% paper wastes on a wet basis as documented in a previous study (Trzcinski and Stuckey, 2009a). The leachate had the following properties: pH: 6–7.5, SCOD: 1070–2925 mg/L (average: 1730 mg/L), TCOD: 5.72–26.78 g/L (average: 11.97 g/L), Volatile fatty acids: 155–1290 mg/L as COD (average: 570 mg/L), ammonia–nitrogen: 7–140 mg N/L (average: 44 mg N/L), Phosphorus: 3.9–24 mg P/L as orthophosphates (average: 11 mg/L).

2.2. Membrane bioreactors (MBRs)

The Submerged Anaerobic Membrane BioReactor (SAMBR) was a three litre reactor fitted with a Kubota polyethylene flat sheet membrane of 0.1 m^2 of total surface and a pore size of 0.4 microns. The SAMBR was maintained at 35 ± 1 °C, and details of the reactor and inoculation can be found elsewhere (Trzcinski and Stuckey, 2009b). The SAMBR was fed continuously at organic loading rates in the range of 1–19.8 g COD L^{-1} day^{-1} (average: 8.1 g COD L^{-1} day^{-1}).

One pump was used to set a constant flux through the membrane, while some of the permeate was recycled back to the SAMBR in order to set the hydraulic retention time (HRT). The biogas sparging rate was set at 5 L/min (LPM) to minimize cake formation on the membrane. The permeate from the SAMBR was fed to an aerobic membrane bioreactor (AMBR) for polishing. The AMBR was identical to the SAMBR except that it was maintained at ambient temperature (21–22 °C), and was inoculated with aerobic biomass from a wastewater plant at an initial MLTSS and MLVSS of 3 and 2.3 g/L, respectively, and air was used to mix the reactor contents at 2 LPM.

2.3. Analytical methods

The measurement of pH (Jenway 3020 pH Meter) was accurate to within ± 0.02 units. The measurement of Mixed Liquor Total Suspended Solids (TSS), Volatile Suspended Solids (VSS) and Fixed Suspended Solids (FSS) was carried out weekly according to Standard Methods (APHA, 2012). The coefficient of variation (COV) for ten identical samples was 4%, 3.1% and 7.1% for TSS, VSS and FSS, respectively. The Soluble Chemical Oxygen Demand (SCOD) analysis was carried out biweekly as in Standard Methods (APHA, 2012) after filtration through a 0.45 μm filter (Sartorius, Minisart), and the COV for ten identical samples was 2.6%. Volatile fatty acids (VFAs) were measured biweekly using a Shimadzu Gas Chromatograph with a flame-ionized detector and a SGE capillary column (12 m × 0.53 mm ID-BP21 0.5 μm); the COV was 3% for ten identical samples. Ammonia–nitrogen was measured biweekly using the Nesslerization method by reading absorbance at 425 nm on a Shimadzu spectrophotometer; the COV was 6.6% for 10 identical samples. The measurement of orthophosphates was carried out biweekly according to the vanadomolybdophosphoric acid colorimetric method described in Standard Methods (APHA, 2012). The absorbance was read on a spectrophotometer at 470 nm, and the coefficient of variance for ten identical samples was ±0.6%.

The method for alkalinity followed the procedure described in Standard Methods (APHA, 2012). Weekly samples were titrated potentiometrically to an end-point of pH 4.5 with 0.1 N H_2SO_4. The COV for 10 identical samples was within 2.7%. The calculation of alkalinity is shown below:

$$\text{Alkalinity as mg CaCO}_3/\text{L} = \text{A} \times \text{N} \times 50,000/\text{mL sample}$$

where A = ml standard acid used, N = normality of standard acid. The ions Na^+, K^+, Mg^{++}, Ca^{2+}, Cl^-, PO_4^{3-}, were analyzed weekly using an Ion Chromatograph (Dionex) as described by the American Public Health Association (APHA, 2012). The COV for the ions listed above were 2%, 0.2%, 0.5%, 0.6%, 1.1% and 3.4% for 5 identical samples, respectively. The detection limit was between 50 and 100 ppb.

Fouled membranes were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. SEM samples were fixed overnight at 4 °C in 3% glutaraldehyde and kept at pH 7.2 by a 0.1 M phosphate buffer. Samples were then dehydrated in a graded ethanol/water series (10–30–50–70–90–100%) for 20 min at each concentration, and then dried for a day at 30 °C. Samples were sputtered-coated with gold or carbon (30 mA for 2.5 min, vacuum 0.2 Torr) prior to SEM-EDX analyses. Specimens were examined and photographed under a scanning electron microscopy (JEOL JSM-5610LV). Energy Dispersive X-ray analysis was conducted with an EDX-60 (Oxford instrument-incax-sight), and the EDX analyzer was connected to a scanning electron microscope (model JSM-840A). More than one point on the sample was analyzed by EDX. Powdered inorganic precipitates from the membranes were also analyzed using a Bruker AXS using X-ray Fluorescence technology (XRF). The exact number of replicates is given along with the results.