Journal of Membrane Science 493 (2015) 19–27

Contents lists available at ScienceDirect

Journal of Membrane Science

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

A PVC–silica mixed-matrix membrane (MMM) as novel type of membrane bioreactor (MBR) membrane

M.R. Bilad [a], L. Marbelia [a], C. Laine [b], Ivo F.J. Vankelecom [a,*]

[a] Centre for Surface Chemistry and Catalysis, Faculty of Bioscience Engineering, KU Leuven, Kasteelpark Arenberg 23, Box 2461, 3001 Leuven, Belgium
[b] Amer-Sil S.A., Zone Industrielle, L-8287 Kehlen, Luxembourg

ARTICLE INFO

Article history:
Received 21 October 2014
Received in revised form
8 May 2015
Accepted 9 May 2015
Available online 18 June 2015

Keywords:
Membrane fouling
Mixed matrix membrane
Wastewater treatment
PVC membrane

ABSTRACT

A highly porous mixed matrix membrane (MMM), made from polyvinyl chloride (PVC) and silica, commonly used as separator in lead acid batteries, is screened here in a first feasibility study as a potential novel type of MBR membrane to treat synthetic wastewater encouraged by: (i) its high chemical and thermal stability and (ii) its high porosity. Its performance was compared with two commercial flat-sheet MBR membranes, a chlorinated PE and a PVDF membrane, in terms of hydraulic performance and membrane fouling. The COD removals of the three membranes were similar. The critical flux measurement also showed the potential of the MMM, being 18 LMH compared to 21 LMH for the commercial membranes. However, both short and long-term filtration tests showed that the MMM suffers from a severe irreversible fouling attributed to the blocking of the large pore mouths, which could not be removed via the applied chemical cleaning with NaOCl. Nevertheless, in a long-term test, despite the occurrence of pore blocking, other types of fouling exist to a much lesser extent in the MMM which maintains its performance comparable with the two commercial membranes.

1. Introduction

Membrane bioreactors (MBRs) have become more popular for treatment of both municipal and industrial wastewaters, and are expected to lead to the next generation of biological wastewater treatment technologies [1,2]. Despite the classic membrane fouling problem, the need to apply highly permeable membranes has constantly been emphasized in recent reviews [3–5]. In MBRs, membranes principally act as a selective barrier retaining particles larger than their effective pore size, and allowing the treated water to pass through them [6].

Full-scale MBR plants mostly apply phase inverted polymeric membranes [1]. These polymers include polyvinylidene fluoride (PVDF), polyethylsulphone (PES), polyethylene (PE), polypropylene (PP), polysulfone (PS), and polyacrylonitrile (PAN) [1,6,7]. Many alternative filters have proven to also give a good effluent quality and are thus sometimes found to be suitable to substitute the traditional MBRs membranes, such as non-wovens [8,9], meshes [10–12], filter cloths [13] or nanofiber-based membranes.

However, one major problem limiting the application of these filters is the fouling due to their rough surface, a rather large pore size (especially at the pore entrance) and wide pore size distributions [8,14]. Therefore, the sludge flocs can penetrate or enter the filter matrix and then be entrapped in the voids inside and block the membranes. Such blockage is very difficult to be removed by shear stresses from the feed side as applied currently in MBRs, especially since only limited backwashing is allowed for the flat-sheet filters/membranes [1].

Based on the reasons above, research still continues, especially in terms of new membrane materials development or filtration and cleaning procedure modification in order to reduce membrane fouling [15]. In terms of membrane materials, membrane properties, such as pore size and distribution, porosity, hydrophilicity, and surface roughness and or charge are known to influence the fouling mechanism and propensity [3,16–20].

In this study, a highly porous and hydrophilic mixed-matrix membrane (MMM) is applied as a novel membrane type in a lab-scale MBR for wastewater treatment. This filter has been developed, produced and also commercialized by Amer-Sil for lead–acid battery separator for more than 40 years [21]. It is produced by a patented low temperature extrusion process of polyvinyl chloride (PVC) and silica, resulting in a filter with a very high chemical and thermal stability, in addition to a narrow bimodal pore size distribution focused around 0.04–0.055 μm and 2–3 μm. The membrane pores thus range in between aforementioned alternative filters (i.e. cloth, woven and non-woven) and the traditional polymeric membranes (mostly micro- and ultrafiltration), and thus should be suitable for MBR purposes. The high stability of this material opens clear perspectives with respect to

* Corresponding author. Tel.: +32 16 321594; fax: +32 16 321998.
E-mail address: ivo.vankelecom@biw.kuleuven.be (I.F.J. Vankelecom).

http://dx.doi.org/10.1016/j.memsci.2015.05.074
0376-7388/

the cleaning possibilities for fouled membranes and a potentiality extended lifetime.

The study was performed in a lab-scale high-throughput MBR (HT-MBR) [22] to compare MMM with two commercial MBR membranes. The short-term filterability and long-term filtration were performed. At the end of the filtration, a series of fouling autopsy was carried out to understand further the observed fouling phenomena.

2. Materials and methods

2.1. Membrane bioreactor set-up

The activated sludge was taken from an Aquafin wastewater treatment plant (Leuven) and maintained in a lab-scale high-throughput MBR (HT-MBR) [22]. The MBR was operated immediately after inoculation, and can thus be considered as not in full steady-state operation yet. The HT-MBR set-up (HTML, Belgium, www.html-membrane.be/) has a working volume of 18.6 L and is equipped with a coarse and fine air bubble aeration mechanism for membrane and biological aeration, respectively. The system was operated at a hydraulic retention time (HRT) of 24 h and sludge retention time (SRT) of 40 days, by daily withdrawing ± 0.5 L sludge.

The feed solution was prepared by diluting an aqueous 0.45 mL/L molasses stock solution to mimic the characteristics of domestic wastewater. The diluted molasses solution was chosen as feed wastewater because of the following reasons: it does not require pre-fine screening, it has a good COD/N ratio and contains sufficient trace elements [23]. The composition of the feed solution is provided in Table S1 of the Supplementary information.

2.2. Membranes and module preparation

Three sets of membranes were used in this study: the MMM, commercial polyvinylidene fluoride (PVDF) and commercial hydrophilised chlorinated polyethylene (PE) membranes (Table 1). The MMM filter was supplied by Amer-Sil and the two commercial membranes (PE from Kubota and PVDF from Toray) were obtained from commercially available A4 modules of the corresponding membranes.

All membranes were potted to form membrane modules with an effective membrane area of each 0.016 m^2. Each membrane was potted in duplicate into two different modules, resulting in six modules in total. A flat-sheet membrane was fixed to a PVC frame by glueing the edges together using two-component epoxy glue (UHU-Plus end-fest 300, Germany). To pot them, the membrane sheets were folded to form a small envelope. Both membrane sides were separated by two sheets of spacer in the interior of the module. Each spacer has a thickness of ± 2 mm. More detailed information about the module potting is available elsewhere [22]. MMM has ribs in the interior side of the module allowing preparation of a spacer-free module.

2.3. Filtration experiments

Prior to the filtration test, the dry membrane modules were wetted by soaking them into 40% ethanol/water solution for 1 h, followed by conditioning via filtration with clean water at a flux of 56 LMH for 3 h. Inside the reactor, each membrane module was connected to an individual permeate line, an individual vacuum gauge and passed to a separate channel in the multi-channel peristaltic pump (Watson-Marlow 205U 16 Channel Pump, UK) using isoprene manifold tubes (Watson-Marlow, UK). The filtration flux was adjusted by changing the rotation speed of the pump.

2.3.1. Flux-stepping filtration

The flux-stepping step was performed using the pristine membranes and was according to the common flux-step method [24]. A flux of 3 LMH was set respectively as the initial flux and the step height, with 10 min of step duration. All filtrations were performed in a total permeate recycle mode. The fouling rates (in this case proportional to the rate of pressure drop) of each flux were calculated and a threshold value of $dP/dt \geq 0.1$ kPa/min was used to distinguish between low- and high-fouling regimes. The performance of membranes was directly compared by the flux-value where they cross from low- to high-fouling regimes. This value is also known as critical flux (CF). However, to avoid confusion of many CF terminologies, the term of threshold flux is adopted in this study.

2.3.2. Long-term filtration

During the long-term filtration test which carried out for 53 days, a net fixed flux of 16 LMH was applied as commonly used for the full-scale installation of the two commercial membranes tested, and the filtration was performed in an 8/2 cycle (8 min filtration followed by 2 min relaxation), resulting in the applied (gross) flux of 20 LMH. No backwashing was applied, as recommended by the commercial membrane suppliers. The same procedure was also applied for the MMM, since no prior information exist regarding the operation of this filter. The filtration was run continuously until few membranes reached the critical TMP of ± 15–20 kPa, which is the maximum pressure allowed by the pump to maintain a constant flux. Continuing the filtration beyond that situation would lower the flow rate of the membranes with high TMP (beyond critical TMP), thus lowering its flux and also reducing the HRT of the reactor.

2.3.3. Membrane cleaning

Seven membrane chemical cleanings were performed during the test. Just after the flux-stepping filtration, all membranes were cleaned before starting the long-term filtration. The cleaning was also performed every time after a long-term filtration finished (when reaching the critical TMP), before the next run was started. The cleaning was performed by taking the membrane out from the reactor and flushing the membrane surface with tap water for

Table 1
Main characteristics of the membranes used in this study.

Parameter	MMM	PVDF	PE
Nominal pore size (using ImageJ, μm)	[a]	0.4	0.08
Nominal pore size (supplier data, μm)	[b]	0.22	0.03
Surface porosity (%)	70.2[c]	11.0	0.2
Overall thickness (μm)	660	165	320
Cross-section morphology	Symmetric	Asymmetric	Asymmetric

[a] Image J was not applicable to measure pore size and surface porosity of the MMM.
[b] The MMM pores are bimodal, with two distinct pore sizes of 0.04–0.05 and 1–2 μm.
[c] The value is as volume porosity because of symmetric nature of the membrane.