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Low-cost ceramic membrane bioreactor: Effect of backwashing, relaxation and aeration on fouling. Protozoa and bacteria removal

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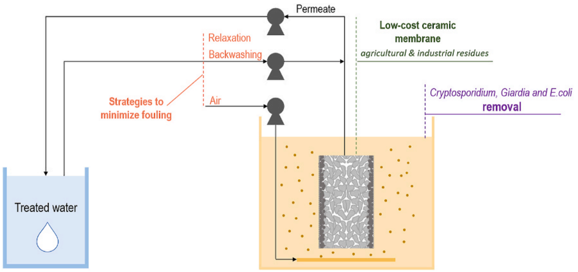
HIGHLIGHTS

- Low-cost ceramic membranes in a laboratory scale membrane bio-reactor.
- A combination of backwashing and relaxation gave the lowest fouling.
- Membranes with and without thin layer were compared.
- A composite membrane with thin TiO_2 layer provided the best performance.
- High effectiveness in the removal of *E. coli*, *Cryptosporidium* oocysts and *Giardia* cysts.

GRAPHICAL ABSTRACT



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ABSTRACT

Membrane biological reactors (MBR) constitute an alternative to conventional wastewater treatments for improved recovery, reuse, and recycling of water. MBRs have a smaller footprint, provide better biotreatment and achieve a high-quality effluent. This work analyses the use of MBRs innovative low-cost ceramic membranes for wastewater treatment. We propose low-cost ceramic membranes as an alternative to the more expensive commercial ceramic membranes. Low-cost membranes were made of clay, calcium carbonate, potato starch, almond shell and chamotte. We synthesized two different selective layers, from clay and/or TiO_2. We characterized the membranes (pore diameter and water permeance) and their performance in a laboratory scale MBR. To mitigate membrane fouling and preserve the continued operation along time, the effect of different operating cycles was measured, considering two physical cleaning strategies: relaxation and backwashing. Cycles of 9 min of operation, 30 s of relaxation and 1 min of backwashing provided the lowest fouling rate. We investigated the effect of air scouring on fouling by operating with different air flow rates. Once experimental conditions were optimized, the overall performance of the different ceramic membranes was tested. The membrane with a TiO_2 thin layer provided the best resistance to fouling, as well as a good retention capacity of *E. coli*, *Cryptosporidium* oocysts and *Giardia* cysts.

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1. Introduction

Membrane Bioreactors (MBRs) have been widely improved since Dorr-Olivier launched the first proposals in the early 70s of the past century (Bemberis et al., 1971). At the beginning, external membrane modules were added in series to conventional activated sludge (CAS) treatments. Around 1989, Yamamoto proposed the submerged modules, in which the membranes were inside the water treatment tank (Yamamoto et al., 1989). This helped to reduce the energy consumption due to the pumping of water to the external module. Many developments, as can be seen in the monography by Judd (2006) dedicated to this topic, have contributed to make MBRs a valuable tool in the wastewater treatment. The advantages can be summarized as follows:

- The decanter employed in CAS is not needed, thus saving space.
- Higher concentration of biomass (mixed liquor suspended solids -MLSS-) can be achieved, which results in better removal of organic pollutants or higher processing capacity.
- Higher solid retention time, which results in lower sludge yield.
- Better removal of protozoa, bacteria and viruses.

This last advantage could be a key factor for the implementation of MBRs in the treatment of wastewater in rural areas. For example, the existence of *Giardia* cysts and/or *Cryptosporidium* oocysts in the effluent from conventional wastewater treatments has been reported in such cases (Ramo et al., 2017). *Cryptosporidium* is considered a reference pathogen for drinking water (WHO, 2006), and it is included in the Directive 2003/99/EC of the European Parliament and the Council of the European Union on the monitoring of zoonosis and zoonotic agents. It seems that CAS is not suitable to provide a large reduction of this microbial contamination. Thus, a tertiary treatment is needed if the final effluent must fulfil some quality requirements. On the contrary, MBR using membranes with an appropriate pore size can provide a highly efficient removal of microbial pollutants, and thus could be the most suitable wastewater treatment to satisfy these more demanding new requirements.

On the other hand, membrane fouling and the high cost of the membrane are the major drawbacks of MBR technology. Fouling occurs when the membrane surface and pores are covered and clogged by microbial substances (Teng et al., 2018). This fouling can be perceived by the increment in transmembrane pressure (TMP) with permeation flux and therefore it rises the energy consumption, leading to higher operation costs. This phenomenon depends on several factors, such as operating conditions, membrane materials and properties, flux, wastewater influent and biomass (Bagheri and Mirbagheri, 2018).

Reducing membrane fouling is crucial in MBR technology in order to ensure a cost-effective process. Several strategies have been employed to control fouling: physical cleaning operations (periodic permeate backwashing or relaxation) (Habib et al., 2017; De Souza and Basu, 2013; Ye et al., 2011), membrane scour aeration (Braak et al., 2011; Sun et al., 2016), chemical cleaning of membranes (Han et al., 2016; Li and Elimelech, 2004; Wang et al., 2014), rotating membranes (Ruigómez et al., 2016), ultrasounds (Chen et al., 2006; Xu et al., 2013), quorum sensing and quenching (Feng et al., 2020; Liu et al., 2019; Yeon et al., 2009) and membrane surface modification and functionalization (Lakshmi Prasanna and Vijayaraghavan, 2015; Moghadam et al., 2015; Yang et al., 2018; Zhang et al., 2021). Fouling phenomena have been extensively investigated for polymeric membranes, but much less for ceramic membranes.

Most of the MBRs are based on polymeric membranes, while ceramic membranes represent a small part of the market (Judd, 2006). The latter are more resistant to chemical attack and provide a longer life than their polymeric counterparts, but they have a higher cost which has stopped a wider use. Most commercially available ceramic membranes are based on expensive and difficult to process materials (alumina, titania, zirconia, etc). Thus, the cost is in the order of thousands of €/m^2, while polymeric membranes have prices comprised between 10 and 100 €/m^2.

In the last two decades, many researchers have tried to develop ceramic membranes based on low-cost materials (clay, coal ash, local minerals) (Yang et al., 2018; Lakshmi Prasanna and Vijayaraghavan, 2015; Moghadam et al., 2015; Zhang et al., 2021; Lorente-Ayza et al., 2016a,b; Hubadillah et al., 2018; Lorente-Ayza et al., 2015; Mestre et al., 2019; Jeong et al., 2017; Henriques et al., 2019; Manni et al., 2020; Lorente-Ayza et al., 2016a,b; Kumar et al., 2016; Mouratib et al., 2020). The preparation of these low-cost membranes usually includes, among the raw materials, an organic compound (e.g., starch) that is removed during sintering and acts as pore generator. It may be expected that, if the technology currently employed for ceramic tile production was adapted to the manufacture of ceramic membranes, the achievable cost would be similar to those of ceramic tiles. The cost of these membranes manufactured on an industrial scale would be around 25 €/m^2, according to an estimation based in updating the results obtained by the UITC in the H2020 European REMEB project (REMEB), which focused on membranes very similar to those used in this article. With these prices, they would be cost competitive against polymeric ones. A good discussion about the factors affecting the economy of MBRs was provided by Judd (2017). Previous studies testing low cost ceramic membranes in MBR, have shown a promising performance (Mahmudul Hasan et al., 2011; Tewari et al., 2010).

Since the beginning of the century, ceramic membrane bioreactors have gained attention due to the advantages brought by the ceramic membranes and the full-scale market has grown with installations in USA, Japan, Netherlands, Singapore, etc. Nevertheless, the full commercial application of this technology requires more research on both reducing the cost of ceramic membranes, and fouling mitigation to achieve a stable long term operation (Asif and Zhang, 2021; Helmi and Gallucci, 2020).

This work aims to test the performance of a newly developed low-cost flat ceramic membrane in a laboratory plant simulating the operation of an MBR. For this purpose, several low-cost ceramic membranes made with waste materials were tested, and the operating conditions needed to achieve a suitable performance (i.e., low fouling rate) have been studied. The removal efficiency of *Escherichia coli* and two different protozoa (*Cryptosporidium* oocysts and *Giardia* cysts) with the above-mentioned low-cost ceramic membranes was also studied, in order to assess if these membranes can achieve the high removal efficiency of polymeric membranes (Bodzek et al., 2019; Hai et al., 2014).

2. Materials and methods

2.1. MBR system description

The bioreactor (MBR) consisted of a cylindrical PVC tank with a volume of 30 L equipped with two air diffusers. The first one, was placed under the membrane to limit fouling by dragging in the plane membrane (flow rates ranging 500–900 cm^3 min^{-1}). The second one, was a ring aerator placed at the bottom of the reactor (2000 cm^3 min^{-1}), and was used to stir the mixture and to provide dissolved oxygen to the liquor. The submerged flat vertical sheet ceramic membrane had an effective filtration area of 0.032 m^2 and was placed between two baffles that simulated parallel membranes. The inoculum was activated sludge from a nearby urban wastewater treatment plant (WWTP). The dissolved oxygen concentration was in the interval of 4–6 mg L^{-1} (measured with a dissolved oxygen meter, *Thermo Scientific Orion Star A113)*. The temperature ranged from 21 to 28 °C. The bioreactor operated with synthetic wastewater, prepared according to DIN 38412 L26 (250 mg L^{-1} glucose, 200 mg L^{-1} meat peptone, 160 mg L^{-1} meat extract, 40 mg L^{-1} urea, 46 mg L^{-1} KH_2PO_4, 2 mg L^{-1} $MgSO_4$ and 7 mg L^{-1} NaCl). It was fed with a peristaltic pump (*DINKO Instruments D*-25VT*)*, maintaining a constant level in the bioreactor with a controller connected to an ultrasonic distance sensor. The permeate was withdrawn with a peristaltic pump at a constant flux of 15 L h^{-1} m^{-2}. The flux was measured volumetrically by collecting the permeate over a known period. A pressure gauge (*WIKA A-10*) monitored (data were recorded every 15 s) the transmembrane pressure (TMP). Only TMP readings higher than the preceding ones were retained, so backwashing and relaxation data are not shown in plots. To carry out the membrane backwashing, another peristaltic pump (*DINKO Instruments D*-25VT) was used to pump back the permeate to the membrane at a constant flow of 50 mL/min. All the peristaltic pumps were controlled by an *ad-hoc* LABVIEW® program interface. Each filtration phase finished when a preestablished time was achieved. It was followed immediately by a fixed time for relaxation and finally backwashing. This cycle, consisting in filtration-relaxation-backwashing, was repeated over and over again until the end of the experiment.

Mixed liquor suspended solids (MLSS) were measured by filtering 50 mL of the sample through a glass microfiber filter (1.6 μm) and dried at 105 °C for 24 h. Afterwards, a gravimetric analysis was carried out. The MLSS concentration was maintained at 5.5 ± 1.3 g/L. The soluble chemical oxygen demand (COD) was measured using a spectrometric method with a reagent kit (Lovibond). COD removal efficiencies (RE) of the MBR were calculated following Eq. (1), where subscripts *inf* and *eff* stand for incoming flow and effluent, respectively.

$$RE = \frac{COD_{inf} - COD_{eff}}{COD_{inf}} \times 100\ \% \tag{1}$$

2.2. Membrane composition and characterization (pore size and permeance)

Two kinds of clay-based porous supports were prepared: M_Starch and M_Almond. M_Starch was composed of clay, chamotte, calcium carbonate and potato starch in a weight ratio of 40:20:20:20. The low cost recycled ceramic membrane (M_Almond), was constituted by residues obtained from agricultural and industrial processes, with a composition 40:20:20:20 wt% (clay, almond shell, marble dust waste and fired tile scrap).

Ceramic flat sheet supports were manufactured at UICT (University Institute of Ceramic Technology) by extrusion and sintered at 1150 °C. The supports were 20 cm long, 10 cm wide and 1 cm thick. Longitudinal channels inside the ceramic piece collected the permeated water. The membrane characterization was completed by determining the water permeance and pore size. For the last one, the bubble point method was used (Lorente-Ayza et al., 2017). Water permeance was assessed by measuring water flow while the applied pressure was gradually increased. Characterization properties of these supports and of the finished membranes (with selective layer) will be described later.

Membranes were prepared by depositing a selective layer on the porous support by dip coating. The supports were submerged in an aqueous suspension containing the ceramic raw materials and several rheological additives and, after a short time of contact, removed from the suspension (immersion and extraction were carried out at constant speed). Afterwards, they were sintered at 1120 °C. Five different layers were tested, as shown in Table 1. Three of them were made with materials like those of the support (SL55, SL60 and SL70). The fourth one was a commercial TiO_2 powder. The last one included two layers, the first one made with low-cost materials and the second one with TiO_2.

Table 1
Composition of the different selective layers.

Selective layer	Clay (wt %)	Chamotte (wt %)	Marble dust (wt %)	TiO_2 (wt %)
SL55	55	40	5	–
SL60	60	35	5	–
SL70	70	26.3	3.7	–
TiO_2	–	–	–	100
SL55_TiO_2[a]	55	40	5	100

[a] Double selective layer.

2.3. Plant operation

Six different types of cycles (i.e., C0 to C5) of relaxation and backwashing in continuous mode were applied to the MBR, each of them accounting for 30 h (Table 2). The relaxation and backwashing times have been established according to the literature. Data from pilot plants indicate that between 4% and 20% of the operating time is used in physical cleaning (Judd, 2006). The same membrane was used in all the runs. The membrane was subjected to chemical cleaning after each test using 2100 ppm citric acid and 1000 ppm sodium hypochlorite for 1 h. After that, we checked that the permeance had not decreased.

The impact of aeration on fouling was assessed by varying the air flow rate below the membrane zone. These experiments were carried out in three stages in which aeration flow was increased (500–700 – 900 $cm^3\ min^{-1}$). It should be noted that the first day of operation is not considered for fouling calculation, since we found that the first hours did not have the same behaviour as the subsequent ones. The fouling rate for each stage was obtained as the average slope of the line that represents TMP vs time. The experiments were conducted for three membranes (M_Almond_SL55, M_Almond_SL60, M_Almond_SL70).

The behaviour of the different ceramic membranes was tested in a series of experiments carried out in the MBR, all under the same conditions (Critical flux $<50\ L\ m^{-2}\ h^{-1}$; operation cycle schedule: 9′ Permeate – 30″ Relaxation – 30″ Backwashing; Aeration flow: 700 $cm^3\ min^{-1}$; permeate flux: 15 $L\ m^{-2}\cdot h^{-1}$; F/M: 0.027 kg (COD)·kg^{-1} (TSS)·day^{-1} and temperature >19 °C. The feed (synthetic wastewater) had a chemical oxygen demand (COD) of 503 ± 52 mg L^{-1}.

2.4. Detection of bacteria and protozoa

Two bacterial indicators of faecal contamination: (total coliform and *Escherichia coli)* were studied according to the Spanish norm *UNE-EN-ISO-9308-1:2014* (AENOR, 2014). *Colinstant Chromogenic Microinstant® Agar* was used as culture medium for the detection of presence or absence of these bacteria in the activated sludge and in the effluent.

Cryptosporidium oocysts and *Giardia* cysts were detected according to the *U.S. Environmental Protection Agency Method* 1623 (U.S EPA, 2005). This method has four steps: filtration, centrifugation, immunomagnetic separation and direct immunofluorescence staining (Ramo et al., 2017). These protozoa were analyzed both in the activated sludge and the MBR treated water. The number of oocysts/cysts inoculated in the bioreactor for these experiments was enough so that they could be detected in the permeate if their retention was not very high. The detection limit was 1 oocyst (or cyst) per litre. The filtered water was continuously collected up to a total of 50 L. The experiments were performed for several membranes. The removal efficiency of oocysts/cysts was calculated as follows (Eq. (2)):

$$\mathrm{Log(removal)} = \mathrm{Log(influent\ concentration)} - \mathrm{Log(effluent\ concentration)} \tag{2}$$

3. Results and discussion

3.1. Membrane characterization

As mentioned before, the characterization performed on each

Table 2
Length of periods for Permeation – Relaxation – Backwashing cycle types.

Cycle	Permeation	Relaxation	Backwashing
C0	t	–	–
C1	9′	0′	1′
C2	9′	1′	1′
C3	4′30″	0′	1′
C4	9′	30″	30″
C5	9′	30″	1′

membrane included the measurement of the pure water permeance, the bubble point and the average pore diameter. Values for the three parameters are shown in Table 3. The highest permeance and mean pore diameter (dp_{50}) were obtained for M_starch support. However, when a selective layer was deposited on it (e.g., M_Starch_SL60), a sharp drop in both parameters was noticed with respect to the membrane support, suggesting defects in the coating process that translate into a high bubble point. For the low-cost membranes based on residues, the support M_Almond had a significant lower permeance than the bare support M_Starch. Nevertheless, when a selective layer was deposited on it, the permeance did not significantly decrease with respect to its counterpart and the average pore diameter remained almost equal (M_Almond_SL60 vs M_Starch_SL60).

As the clay content in the three membranes with selective clay-based layers (M_Almond_SL55, M_Almond_SL60, M_Almond_SL70) increased, the permeance decreased. This change may be due to a higher densification of the layer. On the other hand, the double-layer membrane (M_Almond_SL55_TiO_2), showed a decrease in the permeance and pore size. The same effect was observed in the membrane with a single TiO_2 layer.

3.2. *Effect of backwashing and relaxation*

As can be seen in Fig. 1 A), significant differences in TMP were observed among all the operation cycles for the membrane M_starch. Backwashing and relaxation data have not been plotted in the following figures in order to ease the understanding (i.e., avoid noise) of the behaviours for the different cycle types described in Table 3. Thus, the data plotted correspond to real time but only in filtration slots. The continuous mode, without physical cleanings (C0), showed a sharp increase of TMP in a few minutes. This increase demonstrated the importance of establishing operating cycles to mitigate membrane fouling but without losing sight of the MBR efficiency. This efficiency depends on the average amount of filtered water per hour. Since relaxation and backwashing reduce the average flow rate of filtered water, the length of these steps should be carefully chosen. For C1 cycle, in which there was no relaxation but had 1 min of backwashing and filtration steps of 9 min, high TMP values were obtained (ca. 600 mbar in 30 h). Attending to these results, a relaxation (1 min) was incorporated in C2 cycle, while maintaining the same lengths for filtration periods and backwashing. The increase in transmembrane pressure was not as pronounced as it was in the previous one, but also reached very high values. This result showed that backwashing alone is less effective than relaxation in the reduction of fouling (Wu et al., 2008). In the C3 cycle the conditions of C1 were maintained, changing to half the permeation period, achieving less TMP due to the higher frequency of backwashing. The cycle was less efficient, since the fraction of time employed to obtain filtered water was reduced from 90% to 82%. To achieve a compromise between the average flow rate of filtered water and membrane fouling, the C4 cycle was tested, obtaining low TMP values. C5 cycle featured the lowest TMP because more backwashing time (1 min) was added. Nevertheless, the difference in TMP for C4 and C5 was almost negligible and C4 was slightly more efficient than C5 (decreasing from 90% to 86% in the average flow). Thus, C4 was the optimum cycle to mitigate fouling.

Table 3
Water permeance, bubble point ($d_{bubble\ point}$) and average pore size (dp_{50}) for membranes.

Membrane	Water permeance ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$)	$d_{bubble\ point}$ (μm)	dp_{50} (μm)
M_Starch	4425	14.2	8.3
M_Starch_SL60	326	43.4	2.4
M_Almond	2372	22.0	4.4
M_Almond_SL55	1321	13.9	3.0
M_Almond_SL60	1122	14.6	2.5
M_Almond_SL70	977	14.9	3.0
M_Almond_SL55_TiO_2	683	0.96	0.7
M_Almond _TiO_2	731	2.89	0.5

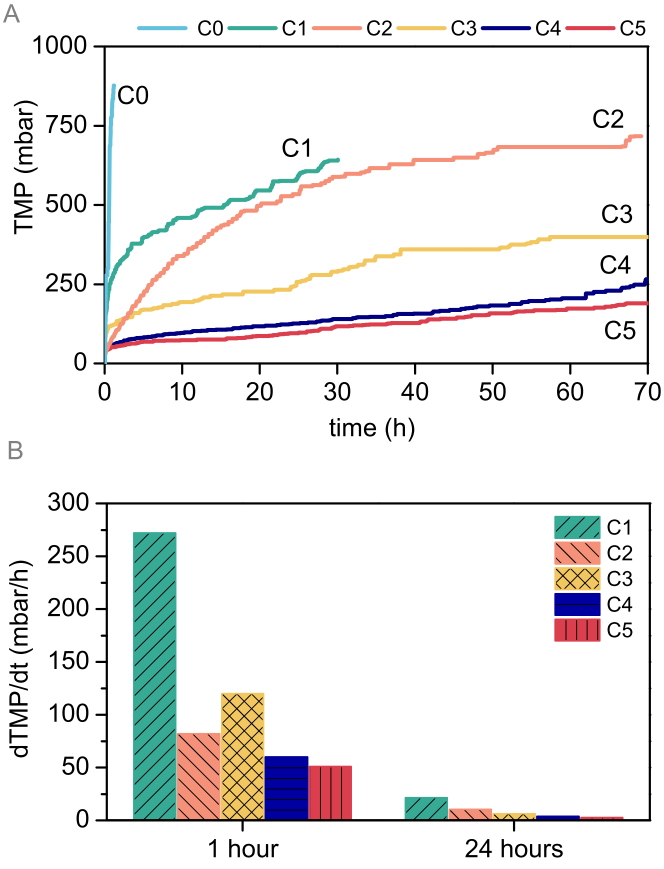

Fig. 1. A) TMP vs time for the different operating cycles and B) Changes in fouling rate over time (membrane M_starch). (backwashing and relaxation slots not plotted for the sake of clarity).

Fouling rate ($d(TMP)/dt$) was calculated at different intervals of the experiments (at 1 and 24 h). At the beginning of the filtration (first hour), a high fouling rate was observed for all cycles, as can be seen in Fig. 1 B). It is noteworthy that C1 featured the upmost fouling rate. Also, those cycles without relaxation time (C1 and C3), showed a higher fouling rate, although it was not noticeable over time because the C3 cycle exhibited a low fouling rate at 24 h.

In summary, relaxation and backwashing mitigated fouling. The absence of relaxation increased membrane fouling, especially along the first hours of the experiment, although it can be mitigated with more frequent backwashing periods (C1 vs C3). However, the combination of both physical cleanings (C4 and C5), offered the optimum conditions with the lowest fouling rate of 4 mbar/h in 24 h of experiment.

3.3. *Bubble aeration in membrane area*

Aeration in the membrane area is one of the key strategies to reduce fouling. In the MBR, the air bubbles and activated sludge rose parallel to the membrane creating a turbulence that dragged the surface, delaying membrane fouling. Three air flow rates were tested (500, 700 and 900 $cm^3\ min^{-1}$). These experiments were carried out with three different membranes, all of them under the same operating conditions and with a filtration flux of 15 $L\ m^{-2} \cdot h^{-1}$. As expected, fouling rate decreased as airflow increased. As shown in Fig. 2, the same trend was maintained for all the membranes, diminishing the fouling rate when air scouring increases. Additionally, M_Almond_SL70, the membrane with the lowest permeance, had the highest fouling rate. For this membrane, an increase from 500 to 700 $cm^3\ min^{-1}$ exhibited a reduction of 47% on fouling rate,

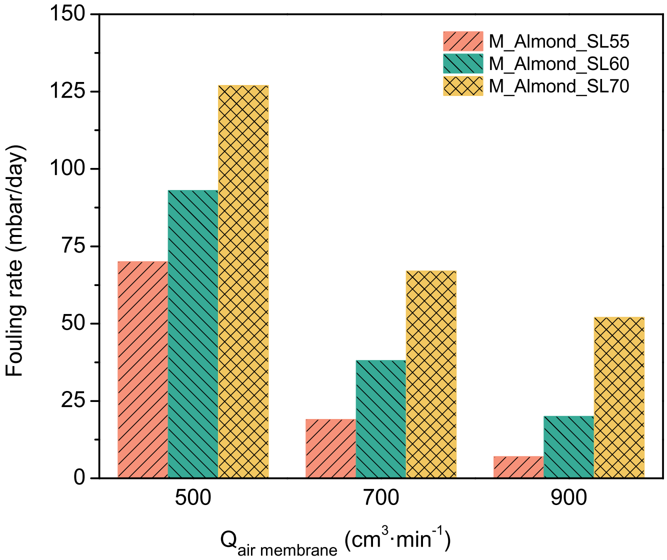

Fig. 2. Fouling rate vs air flow in the membrane zone for several membranes.

while an increment from 700 to 900 cm^3 min^{-1}, showed an additional fouling rate reduction of 25%. Further, the fouling rate diminution was more significant from 500 to 700 cm^3 min^{-1} than from 700 to 900 cm^3 min^{-1}. This effect was observed for all the membranes, although the reduction from 500 to 700 cm^3 min^{-1} was greater as the permeance increased (59% M_Almond_SL60 and 72% for M_Almond_SL55).

Since one of the disadvantages of MBRs is the high energy cost associated with air compression, it is interesting to find a trade-off between energy consumption and fouling. To do that, and since the differences in fouling rates for 700 and 900 cm^3 min^{-1} were not pronounced, the airflow of 700 cm^3 min^{-1} may be considered as the best of those measured. The intermediate flow (700 cm^3 min^{-1}) corresponds to a specific oxygen demand in the membrane area (SAD_m) of 1.15 m^3 h^{-1} m^{-2}. This value is within the range of reference values of MBR plants, from 0.18 to 1.28 m^3 h^{-1} m^{-2} (Drews, 2010). In addition, MBRs of flat membranes usually have a higher SAD_m value, because they usually work at a higher flux.

3.4. Overall performance of the MBR with different membranes

A long-term filtration of the MBR reacting media was performed with several low-cost ceramic membranes. They were tested under the same conditions, with a flux of 15 L m^{-2} h^{-1}. The comparison for all the membranes in the MBR in terms of TMP is shown in Fig. 3. The supports (M_Starch and M_Almond) have not been considered, since they achieved high values of TMP too early (M_Starch achieved 500 mbar in 60 h and M_Almond, 600 mbar in 30 h). For most membranes, the increase of the TMP can be differentiated in two stages: the first 3–5 days, with a sharp increment that indicates the cake formation, and the following days, with a slight increase. Attending to the three membranes with different percentage of clay in the selective layer, M_Almond_SL55 performed better than M_Almond_SL60 and M_Almond_SL70 due to its higher permeance. Therefore, increasing the clay content (apart from 55%) in the selective layer (see Table 1) was not beneficial. However, M_Starch_SL60, with the lowest permeance, had the same evolution of TMP over time that M_Almond_SL60, although M_Starch_SL60 had less permeance (see Table 3). The increase in TMP for all these membranes was associated with a diminution in the membrane permeance, due to the formation of a thick biofilm of cake upon the membrane. However, all these membranes (M_Starch_SL60, M_Almond_SL55, M_Almond_SL60 and M_Almond_SL70) offered elevated TMP values (about 250 mbar in 150 h).

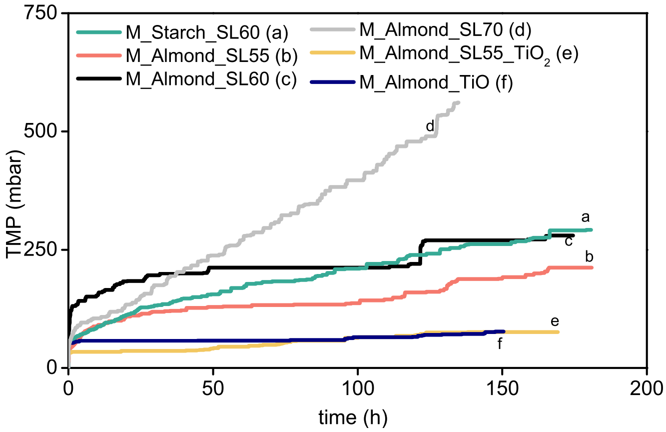

Fig. 3. TMP vs time for all the different low-cost ceramic membranes mentioned in Table 3.

When the pressure reached more than 400 mbar, the membranes were taken out from the tank and chemically cleaned with sodium hypochlorite and citric acid, following the above described procedure. After that, water permeance was measured again and the results showed that membranes had lost between 30 and 50% of the initial permeance. Trying to improve the performance of the membranes, selective layers of TiO_2 were tested. These membranes (M_Almond_TiO_2 and M_Almond_SL55_TiO_2) exhibited constant and lower TMP than those without TiO_2 layer, being their permeance after testing and chemical cleaning, equivalent to the one observed at the beginning of the test. Membranes with a selective layer of TiO_2 had smaller pore size that those with selective layer based on clay (Table 3). Also, the TiO_2 based membranes showed similar values of TMP along time (Fig. 3), showing high resistance to fouling. The double-layer membrane, M_Almond_SL55_TiO_2, had a more homogeneous pore size distribution. This suggests that when pore size diminish, the effect of fouling decreased dramatically. As an example, M_Almond_SL55_TiO_2 reached a TMP of only 70 mbar after 25 days of continuous operation. The results clearly revealed that membranes with smaller pores (membranes with selective TiO_2 layer) had lower fouling tendency. These observations suggest that membrane fouling mechanisms for larger and smaller pore-sized membranes might be different. Fouling of large pore membranes might be probably attributed to pore blocking by organic or inorganic compounds, being these more irreversible (Le-Clech et al., 2006).

For all the low cost membranes fabricated with recycled material, the COD removal fluctuated from 95% to 99%, and the COD of the effluent ranged from 30 to 6 mg·L-1. This accomplished the water quality standard for wastewater discharge in Spain (RD 509/1996 (Ministerio de Obras Públicas, 1996), which is a national transposition of the European Directive 91/271/EEC on Urban Waste Water Treatment (Council of the European Communities, 1991). Therefore, the removal of organic compounds has been proved to be high enough with low-cost membrane bioreactor technology.

3.5. Removal of protozoa and bacteria by the MBR

All the experiments showed the presence of *Escherichia coli* in the activated sludge, although it was not detected in the effluent. The faecal coliforms, which are generally used as indicators to determine the degree of disinfection, were also analyzed during the experiment. Their presence was observed in all the effluents except for those treated with the membranes with TiO_2 layer. For these membranes neither *E. coli* nor coliforms were noticed in the effluent after being analyzed. This may be explained by the smaller pore size that provides more retention. These results demonstrated the best quality of MBR treated water in comparison to conventional systems (Hai et al., 2014; Valderrama et al., 2012).

Table 4 shows the results of the experiments performed to measure the removal efficiency of both protozoa. As it can be seen, the amount of

Table 4
Cryptosporidium oocysts and *Giardia* cysts analysis in activated sludge, filtered water and the removal log. Analysis as norm (U.S EPA, 2005).

Membrane	Activated sludge		Inoculum (in 30 L)		Filtered (48 h-96 h–144 h)		Removal log	
	Cryptos.	Giardia	Cryptos.	Giardia	Cryptos.	Giardia	Cryptos.	Giardia
M_Starch	4	180	100000	100000	<1	<1	3.54	3.94
M_Starch_SL60	4	180	100000	100000	<1	<1	3.54	3.94
M_Almond_SL55	2	56	180000	125000	<1	<1	3.78	3.77
M_Almond_SL60	3	128	150000	125000	<1	<1	3.71	3.90

Cryptosporidium oocysts and *Giardia* cysts of the activated sludge was very similar in all cases. The inoculums were slightly higher in the last two experiments (M_Almond_SL55 and M_Almond_SL60), to check the removal efficiency with higher concentrations.

Each experiment was performed with a different membrane. The first one (M_Starch) is the only that did not have a selective layer. In all cases, the retention efficiency was 99.99% for both protozoa. Considering that *Cryptosporidium* oocysts have a size between 4.5 and 8 μm and *Giardia* cysts of 20 μm, the conclusion is that retention has been produced by the layer of microorganisms formed in the membrane, since the membrane with the lowest bubble point pore was 13.9 μm, much larger than the *Cryptosporidium* oocysts.

Ramo et al. (2017) analyzed the concentration and removal efficiency of *Cryptosporidium* oocysts and *Giardia* cysts in 23 wastewater treatment plants located at the 20 most populated towns in Aragón (north-eastern Spain). The highest removal efficiency values found in these conventional systems were 2.34-log for *Giardia* and 1.8-log for *Cryptosporidium*. In contrast, the MBR with low-cost ceramic membranes tested in this work provided values close to 4-log for *Giardia* and 3.5-log for *Cryptosporidium*, revealing that these membrane bioreactors are a very competitive alternative to conventional sewage treatment plants for removal of both protozoa.

4. Conclusions

Low-cost ceramic membranes were characterized (permeance and pore size), and reported to be suitable for MBRs. Those membranes with selective layer showed lower permeance and pore size. The permeance decrease was sharper for those membrane that used potato starch as porosity promoter agent. The permeance of M_Starch_SL60 decreased by 93% respecting to M_Starch. Membranes with selective layer based on TiO_2 (M_Almond_SL55_TiO_2 and M_Almond_TiO_2) offered the smallest pore sizes (0.7 and 0.5 μm). Most membranes prepared with waste materials (M_Almond) operated in MBR achieving TMP below 250 mbar after 150 h.

Considering the MBR process, the operating cycle 4 (C4) showed the lowest fouling rate (9 min of permeation, 30 s of relaxation and 30 s of backwashing). Increasing the air flow rate in the membrane area resulted in lower fouling rates but at higher cost. To reach a compromise between fouling and costs, an air flow rate of 700 $cm^3\ min^{-1}$ was selected as optimum, since effect on fouling rate of an increase from 700 to 900 $cm^3\ min^{-1}$ was not as significant as the increase from 500 to 700 $cm^3\ min^{-1}$.

The membranes with a selective TiO_2 layer, M_Almond_SL55_TiO_2 and M_Almond_TiO_2, were able to operate without exceeding a TMP of 0.1 bar in 25 days. In addition, they exhibited the highest quality of the effluent both from the physical-chemical and from the microbiological point of view.

MBRs with the low-cost ceramic membranes tested in this study provided a removal efficiency of 99.99% for *Giardia* cysts and *Cryptosporidium* oocysts. In addition, no *E. coli* was detected in the permeate. Those results confirm that these bioreactors are a competitive alternative to conventional wastewater treatment plants for removal of these bacteria and protozoa.

Author contribution statement

Patricia Ugarte: Data curation; Formal analysis; Investigation; Visualization; Roles/Writing – original draft; **Ana Ramo**: Investigation; Writing – review & editing; **Joaquín Quílez**: Methodology; Resources; Supervision; Validation; Writing – review & editing; **María del Carmen Bordes**: Investigation; Writing – review & editing; **Sergio Mestre**: Methodology; Resources; Supervision; Validation; Visualization; Writing – review & editing; **Enrique Sánchez**: Methodology; Resources; Supervision; Validation; Visualization; Writing – review & editing; **José Ángel Peña**: Conceptualization; Formal analysis; Funding acquisition; Methodology; Project administration; Resources; Supervision; Validation; Visualization; Writing – review & editing; **Miguel Menéndez**: Conceptualization; Formal analysis; Funding acquisition; Methodology; Project administration; Resources; Supervision; Validation; Visualization; Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

AENOR, 2014. UNE-EN ISO 9308-1:2014 “Detección y recuento de Escherichia coli y de bacterias coliformes”.

Asif, M.B., Zhang, Z., 2021. Ceramic membrane technology for water and wastewater treatment: a critical review of performance, full-scale applications, membrane fouling and prospects. Chem. Eng. J. 418, 129481 https://doi.org/10.1016/j.cej.2021.129481.

Bagheri, M., Mirbagheri, S.A., 2018. Critical review of fouling mitigation strategies in membrane bioreactors treating water and wastewater. Bioresour. Technol. 258, 318–334. https://doi.org/10.1016/j.biortech.2018.03.026.

Bemberis, I., Hubbard, P., Leonard, F., 1971. Membrane sewage treatment system-potential for complete wastewater treatment. Am. Soc. Agric. Eng. 71–878, 1–28.

Bodzek, M., Konieczny, K., Rajca, M., 2019. Membranes in water and wastewater disinfection – review. Arch. Environ. Protect. 45, 3–18. https://doi.org/10.24425/aep.2019.126419.

Braak, E., Alliet, M., Schetrite, S., Albasi, C., 2011. Aeration and hydrodynamics in submerged membrane bioreactors. J. Membr. Sci. 379, 1–18. https://doi.org/10.1016/j.memsci.2011.06.004.

CEC (Council of the European Communities), 1991. Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. Off. J. Eur. Union 135, 40–52.

Chen, D., Weavers, L.K., Walker, H.W., 2006. Ultrasonic control of ceramic membrane fouling: effect of particle characteristics. Water Res. 40, 840–850. https://doi.org/10.1016/j.watres.2005.12.031.

De Souza, N.P., Basu, O.D., 2013. Comparative analysis of physical cleaning operations for fouling control of hollow fiber membranes in drinking water treatment. J. Membr. Sci. 436, 28–35. https://doi.org/10.1016/j.memsci.2013.02.014.

Drews, A., 2010. Membrane fouling in membrane bioreactors-Characterisation, contradictions, cause and cures. J. Membr. Sci. 363, 1–28. https://doi.org/10.1016/j.memsci.2010.06.046.

Feng, X., Guo, W., Zheng, H., Yang, S., Du, J., Wu, Q., Luo, H., Zhou, X., Jin, W., Ren, N., 2020. Inhibition of biofouling in membrane bioreactor by metabolic uncoupler based on controlling microorganisms accumulation and quorum sensing signals secretion. Chemosphere 245, 125363. https://doi.org/10.1016/j.chemosphere.2019.125363.

Habib, R., Asif, M.B., Iftekhar, S., Khan, Z., Gurung, K., Srivastava, V., Sillanpää, M., 2017. Influence of relaxation modes on membrane fouling in submerged membrane bioreactor for domestic wastewater treatment. Chemosphere 181, 19–25. https://doi.org/10.1016/j.chemosphere.2017.04.048.

Hai, F.I., Riley, T., Shawkat, S., Magram, S.F., Yamamoto, K., 2014. Removal of pathogens by membrane bioreactors: a review of the mechanisms, influencing factors and reduction in chemical disinfectant dosing. Water (Switzerland) 6, 3603–3630. https://doi.org/10.3390/w6123603.

Han, X., Wang, Z., Wang, X., Zheng, X., Ma, J., Wu, Z., 2016. Microbial responses to membrane cleaning using sodium hypochlorite in membrane bioreactors: cell integrity, key enzymes and intracellular reactive oxygen species. Water Res. 88, 293–300. https://doi.org/10.1016/j.watres.2015.10.033.

Helmi, A., Gallucci, F., 2020. Latest developments in membrane (Bio)reactors. Processes 8, 1–39. https://doi.org/10.3390/pr8101239.

Henriques, J.D. de O., Pedrassani, M.W., Klitzke, W., Oliveira, T.V. de, Vieira, P.A., Mariano, A.B., Vieira, R.B., 2019. Fabrication and Characterization of Low Cost Ceramic Membranes for Microfiltration of Acutodesmus Obliquus Using Modified Clays, vol. 24. Matéria, Rio Janeiro.

Hubadillah, S.K., Othman, M.H.D., Matsuura, T., Ismail, A.F., Rahman, M.A., Harun, Z., Jaafar, J., Nomura, M., 2018. Fabrications and applications of low cost ceramic membrane from kaolin: a comprehensive review. Ceram. Int. 44, 4538–4560. https://doi.org/10.1016/j.ceramint.2017.12.215.

Jeong, Y., Lee, S., Hong, S., Park, C., 2017. Preparation, characterization and application of low-cost pyrophyllite-alumina composite ceramic membranes for treating low-strength domestic wastewater. J. Membr. Sci. 536, 108–115. https://doi.org/10.1016/j.memsci.2017.04.068.

Judd, S., 2006. The MBR BOOK - Principes and Applications of Membrane Bioreactors for Waste and Wastewater Treatment. PERGAMON.

Judd, S.J., 2017. Membrane technology costs and me. Water Res. 122, 1–9. https://doi.org/10.1016/j.watres.2017.05.027.

Kumar, R.V., Goswami, L., Pakshirajan, K., Pugazhenthi, G., 2016. Dairy wastewater treatment using a novel low cost tubular ceramic membrane and membrane fouling mechanism using pore blocking models. J. Water Proc. Eng. 13, 168–175. https://doi.org/10.1016/j.jwpe.2016.08.012.

Lakshmi Prasanna, V., Vijayaraghavan, R., 2015. Insight into the mechanism of antibacterial activity of ZnO: surface defects mediated reactive oxygen species even in the dark. Langmuir 31, 9155–9162. https://doi.org/10.1021/acs.langmuir.5b02266.

Le-Clech, P., Chen, V., Fane, T.A.G., 2006. Fouling in membrane bioreactors used in wastewater treatment. J. Membr. Sci. 284, 17–53. https://doi.org/10.1016/j.memsci.2006.08.019.

Li, Q., Elimelech, M., 2004. Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms. Environ. Sci. Technol. 38, 4683–4693. https://doi.org/10.1021/es0354162.

Liu, J., Eng, C.Y., Ho, J.S., Chong, T.H., Wang, L., Zhang, P., Zhou, Y., 2019. Quorum quenching in anaerobic membrane bioreactor for fouling control. Water Res. 156, 159–167. https://doi.org/10.1016/j.watres.2019.03.029.

Lorente-Ayza, M.-M., Mestre, S., Sanz, V., Sanchez, E., 2016a. On the underestimated effect of the starch ash on the characteristics of low cost ceramic membranes. Ceram. Int. 42, 18944–18954. https://doi.org/10.1016/j.ceramint.2016.09.046.

Lorente-Ayza, M.-M., Orts, M.-J., Gozalbo, A., Mestre, S., 2016b. Preparation of chamottes as a raw material for low-cost ceramic membranes. Int. J. Appl. Ceram. Technol. 13, 1149–1158. https://doi.org/10.1111/ijac.12579.

Lorente-Ayza, M.-M., Pérez-Fernández, O., Alcalá, R., Sánchez, E., Mestre, S., Coronas, J., Menéndez, M., 2017. Comparison of porosity assessment techniques for low-cost ceramic membranes. Boletín la Soc. Española Cerámica y Vidr. 56, 29–38. https://doi.org/10.1016/J.BSECV.2016.09.002.

Lorente-Ayza, M.-M., Orts, M.J., Pérez-Herranz, V., Mestre, S., 2015. Role of starch characteristics in the properties of low-cost ceramic membranes. J. Eur. Ceram. Soc. 35, 2333–2341. https://doi.org/10.1016/j.jeurceramsoc.2015.02.026.

Mahmudul Hasan, M., Shafiquzzaman, M., Shafiul Azam, M., Nakajima, J., 2011. Application of a simple ceramic filter to membrane bioreactor. DES 276, 272–277. https://doi.org/10.1016/j.desal.2011.03.062.

Manni, A., Achiou, B., Karim, A., Harrati, A., Sadik, C., Ouammou, M., Younssi, S.A., El Bouari, A., 2020. New low-cost ceramic microfiltration membrane made from natural magnesite for industrial wastewater treatment. J. Environ. Chem. Eng. 8 https://doi.org/10.1016/j.jece.2020.103906.

Mestre, S., Gozalbo, A., Lorente-Ayza, M.M., Sánchez, E., 2019. Low-cost ceramic membranes: a research opportunity for industrial application. J. Eur. Ceram. Soc. 39, 3392–3407. https://doi.org/10.1016/j.jeurceramsoc.2019.03.054.

Ministerio de Obras Públicas, T. y M.A., 1996. Real Decreto 509/1996, de 15 de marzo, de desarrollo del Real Decreto-ley 11/1995, de 28 de diciembre, por el que se establecen las normas aplicables al tratamiento de las aguas residuales urbanas. Boletín Of, del Estado, España.

Moghadam, M.T., Lesage, G., Mohammadi, T., Mericq, J.P., Mendret, J., Heran, M., Faur, C., Brosillon, S., Hemmati, M., Naeimpoor, F., 2015. Improved antifouling properties of TiO2/PVDF nanocomposite membranes in UV-coupled ultrafiltration. J. Appl. Polym. Sci. 132, 13–15. https://doi.org/10.1002/app.41731.

Mouratib, R., Achiou, B., El Krati, M., Younssi, S.A., Tahiri, S., 2020. Low-cost ceramic membrane made from alumina- and silica-rich water treatment sludge and its application to wastewater filtration. J. Eur. Ceram. Soc. 40, 5942–5950. https://doi.org/10.1016/j.jeurceramsoc.2020.07.050.

Ramo, A., Del Cacho, E., Sánchez-Acedo, C., Quílez, J., 2017. Occurrence and genetic diversity of Cryptosporidium and Giardia in urban wastewater treatment plants in north-eastern Spain. Sci. Total Environ. 598, 628–638. https://doi.org/10.1016/j.scitotenv.2017.04.097.

REMEB. Eco-Friendly ceramic membrane bioreactor (MBR) based on recylced agricultural and industrail wastes for waste water reuse. https://cordis.europa.eu/project/id/641998. Last accessed 2022/03/08.

Ruigómez, I., Vera, L., González, E., González, G., Rodríguez-Sevilla, J., 2016. A novel rotating HF membrane to control fouling on anaerobic membrane bioreactors treating wastewater. J. Membr. Sci. 501, 45–52. https://doi.org/10.1016/j.memsci.2015.12.011.

Sun, J., Liang, P., Yan, X., Zuo, K., Xiao, K., Xia, J., Qiu, Y., Wu, Q., Wu, S., Huang, X., Qi, M., Wen, X., 2016. Reducing aeration energy consumption in a large-scale membrane bioreactor: process simulation and engineering application. Water Res. 93, 205–213. https://doi.org/10.1016/j.watres.2016.02.026.

Teng, J., Shen, L., He, Y., Liao, B.Q., Wu, G., Lin, H., 2018. Novel insights into membrane fouling in a membrane bioreactor: elucidating interfacial interactions with real membrane surface. Chemosphere 210, 769–778. https://doi.org/10.1016/j.chemosphere.2018.07.086.

Tewari, P.K., Singh, R.K., Batra, V.S., Balakrishnan, M., 2010. Membrane bioreactor (MBR) for wastewater treatment: filtration performance evaluation of low cost polymeric and ceramic membranes. Separ. Purif. Technol. 468, 276–307. https://doi.org/10.1016/j.seppur.2009.11.022.

U.S EPA, 2005. Method 1623: Cryptosporidium and Giardia in Water by Filtration. IMS/FA.

Valderrama, C., Ribera, G., Bahí, N., Rovira, M., Giménez, T., Nomen, R., Lluch, S., Yuste, M., Martinez-Lladó, X., 2012. Winery wastewater treatment for water reuse purpose: conventional activated sludge versus membrane bioreactor (MBR). A comparative case study. Desalination 306, 1–7. https://doi.org/10.1016/j.desal.2012.08.016.

Wang, Z., J., Ma, C.Y., Tang, K., Kimura, Q., Wang, X., Han, 2014. Membrane cleaning in membrane bioreactors : a review. J. Membr. Sci. 468, 276–307. https://doi.org/10.1016/j.memsci.2014.05.060.

WHO (World Health Organization, 2006 [WWW Document]. http://www.who.int/water_sanitation_health/gdwqrevision/cryptodraft2.pdf.

Wu, J., Le-Clech, P., Stuetz, R.M., Fane, A.G., Chen, V., 2008. Effects of relaxation and backwashing conditions on fouling in membrane bioreactor. J. Membr. Sci. 324, 26–32. https://doi.org/10.1016/j.memsci.2008.06.057.

Xu, M., Wen, X., Huang, X., Yu, Z., Zhu, M., 2013. Mechanisms of membrane fouling controlled by online ultrasound in an anaerobic membrane bioreactor for digestion of waste activated sludge. J. Membr. Sci. 445, 119–126. https://doi.org/10.1016/j.memsci.2013.06.006.

Yamamoto, K., Hiasa, M., Mahmood, T., Matsuo, T., 1989. Direct solid-liquid separation using hollow fiber membrane in an activated sludge aeration tank. Water Sci. Technol. 21, 43–54. https://doi.org/10.2166/wst.1989.0209.

Yang, Y., Qiao, S., Jin, R., Zhou, J., Quan, X., 2018. Fouling control mechanisms in filtrating natural organic matters by electro-enhanced carbon nanotubes hollow fiber membranes. J. Membr. Sci. 553, 54–62. https://doi.org/10.1016/j.memsci.2018.02.012.

Ye, Y., Chen, V., Le-Clech, P., 2011. Evolution of fouling deposition and removal on hollow fibre membrane during filtration with periodical backwash. Desalination 283, 198–205. https://doi.org/10.1016/j.desal.2011.03.087.

Yeon, K.M., Cheong, W.S., Oh, H.S., Lee, W.N., Hwang, B.K., Lee, C.H., Beyenal, H., Lewandowski, Z., 2009. Quorum sensing: a new biofouling control paradigm in a membrane bioreactor for advanced wastewater treatment. Environ. Sci. Technol. 43, 380–385. https://doi.org/10.1021/es8019275.

Zhang, K., Yang, Y., Qiao, S., Zhou, J., Quan, X., 2021. Alternating current-enhanced carbon nanotubes hollow fiber membranes for membrane fouling control in novel membrane bioreactors. Chemosphere 277, 130240. https://doi.org/10.1016/j.chemosphere.2021.130240.