Membrane filtration coupled with wet air oxidation for intensified treatment of biorefractory effluents

C. Pinchai, M. Monnot, S. Lefèvre, O. Boutin and P. Moulin

ABSTRACT

This work aims to analyse the performances of a new hybrid process: membrane filtration to concentrate biorefractory wastewater before treatment by a hydrothermal process such as wet air oxidation. The aim is to obtain a complete discharge of the effluent in the environment. The three different synthetic wastewaters under study were pharmaceutical wastewater, grey wastewater and bilge wastewater. The results of the membrane filtration showed high retention rates as it could reach between 75% and 100% of total organic carbon retention, more than 99% of turbidity removal and more than 70% of hydrocarbon retention. Moreover, it was possible to achieve high concentration factors comprised between 17 and 40 times. Membrane fouling was chemically reversible regardless of the type of pollution. Then, the treatment of the membrane retentates by wet air oxidation process (300 °C, 15 MPa) could eliminate more than 83% of organic pollution for all the tested effluents. In summary, the hybrid intensified process could finally decrease the volume and the waste load of wastewater before possibly discharging it into the environment.

Key words | hybrid process, membrane separation, process intensification, wet air oxidation

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INTRODUCTION

Wastewater from factories or municipal sources may contain non or poorly biodegradable pollutants called refractory compounds. Treatment is thus needed before discharging into the environment. However, using the classical biological treatment is inefficient in removing these compounds, which can cause harmful effects in the environment. Among the potential wastewaters, pharmaceutical wastewater, bilge wastewater and grey wastewater in the case of separated networks are of particular interest. A first treatment step consists of using membrane processes. Reverse osmosis (RO) can effectively treat wastewater containing pharmaceuticals by removing more than 98% of the chemical oxygen demand (COD) (Beier *et al.* 2010; Ravikumar *et al.* 2014). Ultrafiltration (UF) can treat grey wastewater by removing 20–50% of total organic carbon (TOC) and more than 92% of turbidity (Ramona *et al.* 2004; Nghiem *et al.* 2006) and UF (300 kDa) can also treat real bilge wastewater by removing 97.7% of hydrocarbons and 98.4% of turbidity (Ghidossi *et al.* 2009). The membrane permeates are of good quality but these membrane processes generate highly concentrated retentates in small volumes. The next objective is to treat these concentrated retentates, which contain refractory compounds. One of the possible options to treat these retentates is wet air oxidation (WAO). This process brings organic pollutants into contact with air or oxygen as an oxidizing agent under water subcritical conditions (temperature between 150 and 325 °C; total pressure between 2 and 30 MPa) (Kolaczkowski *et al.* 1999). WAO is suitable for the effluents concentred between 20 and 200 $g{\cdot}L^{-1}$ of low biodegradable COD (Lefèvre *et al.* 2011).

Above 200 $g{\cdot}L^{-1}$, the large quantity of oxidant necessary for a complete mineralization can lead to high compression costs (Lefevre *et al.* 2012). Finally, below 20 $g{\cdot}L^{-1}$ (and rather below 5 $g{\cdot}L^{-1}$), classical advanced oxidation processes are generally more adapted (Andreozzi 1999). Nevertheless, WAO could remain competitive in this range of COD concentrations because (i) the oxidant is often air, which can be free in comparison to ozone, for instance, (ii) the WAO is suitable for turbid effluents containing suspended solids (Amaral-Silva *et al.* 2016; Minière *et al.* 2019).

In addition, WAO consumes high energy for pumping, pressurizing, mixing and heating even with auto-thermal operation (Slavik *et al.* 2015). However, thanks to the small

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Table 1 | Main characteristics of the studied effluents (± standard deviation)

	TOC ($mgC{\cdot}L^{-1}$)	Turbidity (NTU)	Conductivity ($\mu S{\cdot}cm^{-1}$)	pH
Synthetic pharmaceutical wastewater	115 ± 8	18 ± 7	36 ± 12	6.40 ± 0.02
Synthetic bilge wastewater containing hydrocarbons	53 ± 10	46 ± 9	14 ± 7	6.9 ± 0.2
Synthetic grey wastewater containing surfactants	63.7 ± 0.4	34 ± 7	$(4 \pm 3) \times 10^2$	7 ± 1

volumes (retentates) obtained after the first membrane step, the feasibility of coupling membrane processes and WAO is studied. The observation was focused on (i) membrane fouling, quality of permeate, volumetric concentration factor, regeneration and sustainable flux, (ii) quality of the WAO treatment, residual pollution and (iii) proportion of inlet effluent flow that can be released into the environment.

MATERIAL AND METHODS

Effluents

The preparation of synthesized effluents was based on the literature (Hourlier *et al.* 2010; Colón *et al.* 2015; Rozman *et al.* 2017) and the feedback of the industrial partner (A3I). The characteristics of effluents are presented in Table 1. For the synthetic pharmaceutical wastewater, the TOC was from four different dissolved drugs (ibuprofen, paracetamol, amoxicillin and clavulanic acid). As these molecules were very small, RO filtration was relevant. For the synthetic bilge wastewater, the TOC should be high (around 1,057 ± 306 $mgC{\cdot}L^{-1}$ due to it containing mineral oils). Considering the lower solubility of mineral oils in water, the TOC measured was very much underestimated. For the synthetic grey wastewater, the surfactants were the main cause of TOC values. UF was suitable for these two last effluents because of the sizes of the molecules.

Membrane processes and wet air oxidation of membrane concentrates

The RO module used (RE2540-SHN) was from Toray (Japan) with 2.2 m^2 of filtration area. The filtration pilot-plant worked in a close-loop crossflow mode having constant TMP (10 bar) and recirculation flowrate (500 $L{\cdot}h^{-1}$). The initial feed volume was 50 L. For the cleaning after each test, sodium hydroxide (NaOH) at room temperature and pH 13 during at least 60 min was applied if distilled water rinsing was inefficient.

The UF membranes used (300 kDa Kleansep ceramic TiO_2 – Al_2O_3) were from Orelis Environnement (France) with 1.178 m length, 25 mm diameter and different membrane surface resulting from the different number of channels. The filtration pilot plant worked in a close-loop crossflow mode having constant TMP (1.0–1.5 bar) and recirculation velocity (4 $m{\cdot}s^{-1}$). The initial feed volume was higher than 50 L. For the cleaning after each test, sodium hydroxide (30 $g{\cdot}L^{-1}$) and sodium hypochlorite at 60 °C for at least 30 min or nitric acid (5 $g{\cdot}L^{-1}$) at 50 °C for at least 30 min were applied before rinsing with distilled water until the pH was back to a neutral value.

A part of the membrane concentrates were treated then by WAO in a 200 mL batch reactor. The isolation of the system was done by the injection of pure nitrogen at a total pressure of 0.7 MPa. Then, pure air containing dioxygen was introduced to induce the oxidation. For the operating conditions, the temperature was up to 300 °C and the total pressure was 15 MPa for an hour.

Analyses

The TOC meter (TOC-L, Shimadzu, Japan), using a non-purgeable organic carbon method with a sensitivity of 0.5%, the pH meter (Sension + pH31, Hach, USA), the conductimeter (Sension + EC7, Hach, USA) and the turbidimeter (Turb 550 IR, WTW, Germany) were the equipment used to evaluate the total organic carbon (TOC), the pH, the conductivity and the turbidity respectively. The hydrocarbon concentration was measured by an external laboratory using the NF T 90-114 method.

Process performance analysis

For the performance of the membrane processes, the volumetric concentration factor (VCF) shown in Equation (1) involves the reduction of wastewater volume before being treated by the WAO. The V_{feed} is the initial volume

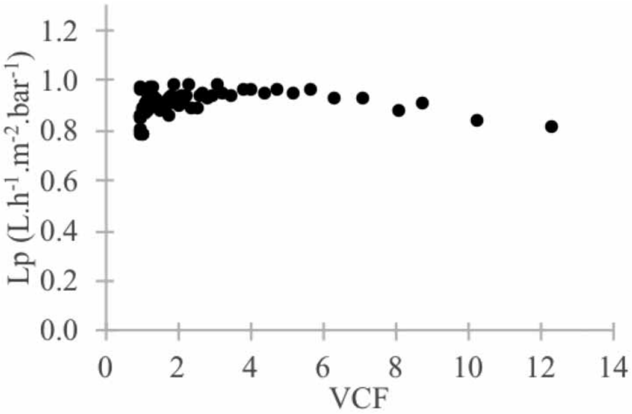

Figure 1 | Permeability at 20 °C of the RO membrane of pharmaceutical wastewater as a function of the VCF.

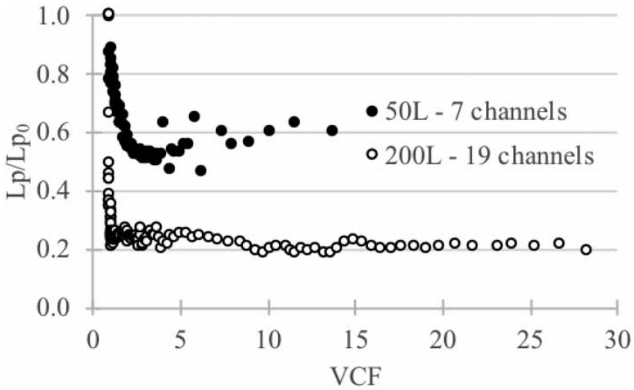

Figure 3 | Normalized permeability at 20 °C of the UF membranes during grey wastewater filtration (TMP = 1 bar).

of the solution and $V_{retentate}$ is the remaining volume of retentate.

$$VCF = \frac{V_{feed}}{V_{retentate}} \quad (1)$$

According to the quality of the membrane permeates, the rejection rates (RR) were evaluated with Equation (2) where C_p is the pollutant concentration in the permeate and C_r is the pollutant concentration in the retentate.

$$RR = 1 - \frac{C_p}{C_r} \quad (2)$$

For the WAO process, the quality of the treated effluent was associated with the mineralization rates presented in Equation (3) where $[TOC]_{outlet}$ and $[TOC]_{retentate}$ are the TOC concentration in the WAO treated effluent and feed solution respectively.

$$Mineralization\ Rate = 1 - \frac{[TOC]_{outlet}}{[TOC]_{retentate}} \quad (3)$$

RESULTS AND DISCUSSION

Coupling RO and WAO to treat pharmaceutical wastewater

For the RO treatment of 50 L of pharmaceutical wastewater, Figure 1 shows the permeability at 20 °C as a function of the VCF. Comparing with pure water permeability at the same temperature before the test ($1.0\ L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$), the deviation was less than 20%. The reduction of turbidity and the TOC were higher than 99.8% and 99.7% respectively. Finally, the TOC of the overall permeate and the retentate

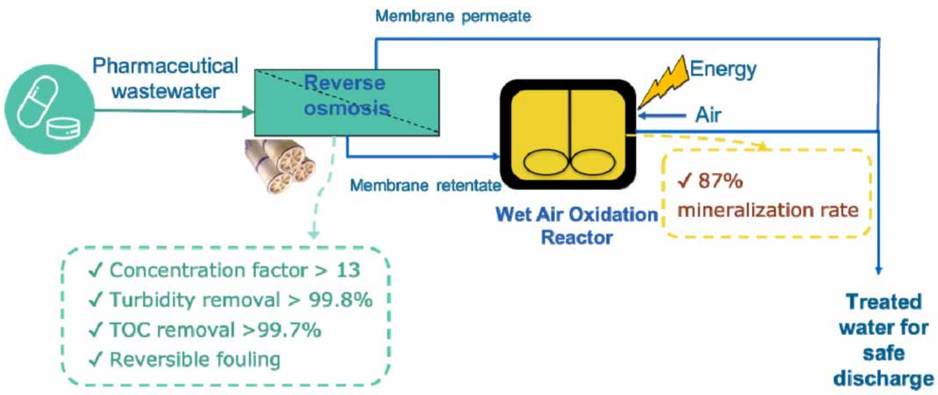

Figure 2 | Results obtained for the coupling of RO and WAO to treat pharmaceutical wastewater.

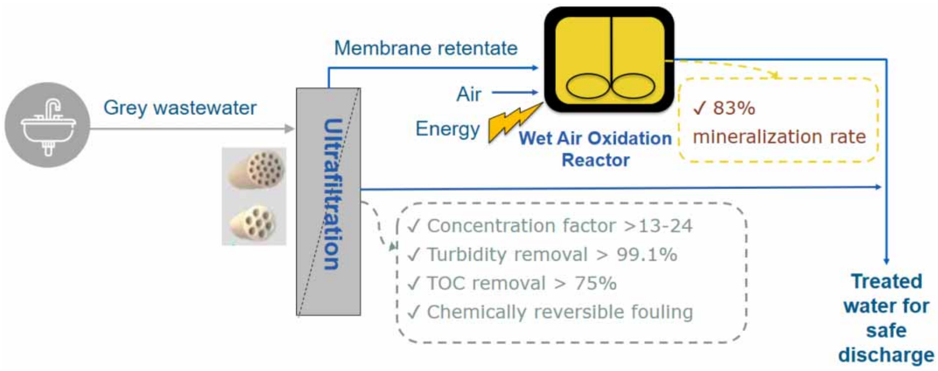

Figure 4 | Results obtained for the coupling of UF and WAO to treat grey wastewater.

were 14 $mgC{\cdot}L^{-1}$ and 1,507 $mgC{\cdot}L^{-1}$ respectively, with a final VCF of more than 13. The fouling was low and mainly reversible by rinsing with distilled water. For the WAO treatment of the RO retentate, the TOC removal was 87% corresponding to a concentration of 196 $mgC{\cdot}L^{-1}$. Figure 2 shows a graphical summary of the main results obtained.

Coupling UF and WAO to treat grey wastewater

For the UF treatment of different filtered volume of grey wastewater (300 and 800 $L{\cdot}m^{-2}$), Figure 3 shows the normalized permeability as a function of the VCF. Both curves of UF treatment decreased sharply to a VCF of 1 to 4 before stabilizing around 20% to 60% of the initial permeability despite the slight differences at the beginning. The removal rate of turbidity was higher than 99.1%, which represented a turbidity in the permeate under 0.2 NTU, and the TOC removal rate was around 75%. This means that the membrane with a molecular weight cut-off of 300 kDa could remove the surfactants with smaller molecular weight (<500 Da) and representing the major

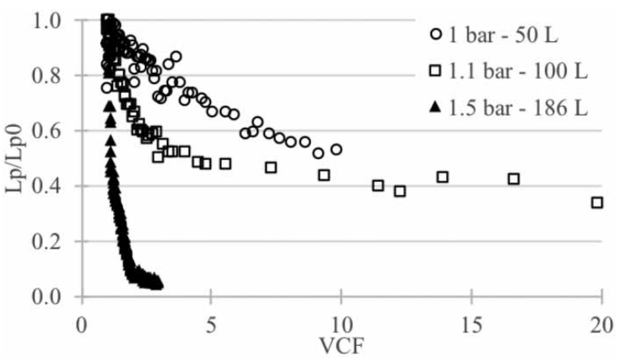

Figure 5 | Normalized permeability at 20 °C of the UF membranes during bilge wastewater as a function of the VCF.

type of compounds in the grey wastewater. The explanation could be the formation of micelles by the surfactants giving a bigger size of compound molecules (Oschmann *et al.* 2005). Finally, the TOC concentrations of the retentate were 292 $mgC{\cdot}L^{-1}$ and 344 $mgC{\cdot}L^{-1}$, corresponding to more than 13 times or 24 times volume reduction, for the 50 L and 200 L of initial volume respectively. The fouling was chemically reversible by basic (NaOH) and acidic (nitric acid) solutions. For the WAO treatment of the UF retentate, the TOC removal was 83%, corresponding to a concentration of 53 $mgC{\cdot}L^{-1}$. Figure 4 shows a graphical summary of the main results obtained.

Coupling UF and WAO to treat bilge wastewater

For the UF treatment of different filtered volumes of bilge wastewater (50 L, 100 L and 186 L), Figure 5 shows the normalized permeability decrease with the increase of VCF. As the first part of the curves increased in the order of the applied TMPs, it could be concluded that the TMP had the biggest influence on the permeability drop. Applying the highest TMP (1.5 bar) for the 186 L initial volume gives a permeability close to zero at the end of the test. There was fouling caused by oil or hydrocarbon behaviour, which coalesced and formed a layer on the surface (Dickhout *et al.* 2017). Thus, the TMP should be less than 1.1 bar to prevent this problem. The reduction of turbidity was more than 99.5% and the retention of hydrocarbon was higher than 90% to almost 100%. However, the HC concentrations in the permeates were still less than 15 $mg{\cdot}L^{-1}$, which is the limit of HC discharge into the environment (ocean) due to the Marpol regulation 73/78. The retentate volume was finally reduced up to 20 times. The fouling was chemically reversible by chemical cleaning. Considering the 186 L test, the fouling was oil

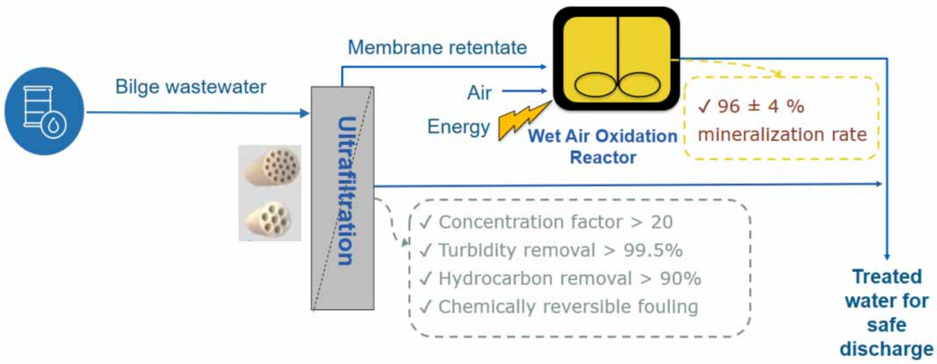

Figure 6 | Results obtained for the coupling of UF and WAO to treat bilge wastewater.

lining inside the pores under the compression forces and could be removed effectively by backwashing with distilled water. For the WAO treatment of the UF retentate, the TOC removal was 96 ± 4%, corresponding to a concentration of 286 ± 69 mgC·L^{-1}. Figure 6 shows a graphical summary of the main results obtained.

CONCLUSIONS

To treat wastewaters from factories or municipal sources that contain refractory compounds, the feasibility of coupling membrane processes and WAO was studied. The different types of synthesized wastewater for the tests were pharmaceutical wastewater, grey wastewater and bilge wastewater. For the coupling of RO and WAO to treat pharmaceutical wastewater, RO removed more than 99.7% of pharmaceutical molecules in water. Membrane fouling was reversible by rinsing with distilled water. The RO process reduced by 13 times the initial volume to treat. Pharmaceutical molecules of the remaining volume of concentrated retentate were removed by 87% after WAO treatment. For the coupling of UF and WAO to treat grey wastewater mainly containing surfactants, UF removed more than 99% of turbidity and 75% of the TOC. The fouling was chemically reversible. However, for a real effluent, a pre-treatment (50 or 100 microns) should be applied to remove the larger particles such as textile residues and hair that are generally found in grey wastewater. The UF reduced by up to 24 times the initial volume to treat. Organic pollutants of the remaining concentrated retentate were removed by 83% after WAO treatment. For the coupling of UF and WAO to treat bilge wastewater, UF removed more than 99% of turbidity and more than 90% of hydrocarbons. The fouling was chemically reversible. Moreover, it is recommended to use a TMP under 1.1 bar to prevent fouling on the surface and inside the pores of the membrane. The UF reduced by up to 20 times the initial volume to treat. Hydrocarbons of the retentate were removed by more than 96% after WAO treatment.

Using the hybrid process membrane concentrations followed by WAO oxidation of the retentate could drastically reduce the energy consumption for the treatment of different types of wastewater. Lastly, the mix between the membranes' permeate and the treated effluents after WAO treatment could be discharged into the environment respecting most of the international standards in terms of COD and TOC concentrations: a total discharge in the nature of the effluents could be expected.

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