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Porous membranes for ballast water treatment from microalgae-rich seawater

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ABSTRACT

The ballast waters from ships pose a major threat to oceans, notably because of the spread of microorganisms. The present study evaluates the techno-economic feasibility of implementing the membrane process to remove microalgae from seawater to be ballasted in a single step during planktonic bloom. The optimal conditions for the microfiltration of complex and reproducible synthetic seawater are a permeate flux and specific filtered volume of 100 $L.h^{-1}.m^{-2}$ and 75 $L.m^{-2}.cycle^{-1}$, respectively. Recovery of the membrane process represents about 76.6% and 62.7% of the annual cost for a cruise ship (5400 passengers) and liquefied natural gas (LNG) carrier (75,000 m^3 of liquid natural gas), followed by the membrane replacement cost (13.4% and 21.9%, respectively). The treatment costs are competitive with conventional treatments, even when the membrane process is more feasible for cruise ships due to its smaller capital cost and footprint.

1. Introduction

Representing about 90% of global trade, shipping is the main means of transporting raw materials, consumer goods, essential foodstuff, and forms of energy (IMO). The number and capacity of vessels increased by 3.4% and 6.9%, respectively, from 2006 to 2010, which will continue to increase in the coming years (Institute of Shipping Economics and Logistics, 2010).

Ballast water is essential for safe shipping operations, but its disposal causes ecological, economic and health problems with the transfer of harmful organisms and pathogens (bacteria, virus, microbes, plankton, cysts, eggs, etc.) to the host environment. The introduced species can become invasive, thus outcompeting native species (Gollasch, 2002). Therefore, an International Convention for the Control and Management of Ships' Ballast Water and Sediments was adopted in 2004. Ships are required to maintain the Ballast Water Exchange Standard (regulation D-1) and the Ballast Water Performance Standard (Regulation D-2), which stipulate a ballast discharge with a maximum concentration of 10 viable organisms per cubic meter or milliliter for those >50 μm or 10–50 μm in size. The concentration of *Vibrio cholerae*, *Enterococcus*, and *Escherichia coli* must be below 1, 100, and 250 CFU.100 mL^{-1}, respectively. Certain states impose more stringent standards. For example, the discharge of viable organisms, irrespective of their size, will be prohibited after 2020 in California Waters (Dobroski et al., 2007; State Land Commission, 2009). As underlined by Quilez-Badia et al. (2008) (Quilez-Badia et al., 2008), regulating the discharge is problematic in the case of larger organisms, despite a similar invasion risk. For instance, ballast water containing 78,000 cysts of *Prorocentrum lima* per cubic meter (diameters ranging from 70 to 75 μm) would require approximately 4-log reduction in cyst concentration to meet the performance standard, whereas no treatment would be needed for *Fibrocapsa japonica* with similar concentration (diameters ranging from 15 to 20 μm) (Doblin and Dobbs, 2006). These standards do not apply to some harmful microalgae capable of forming blooms, such as *Phaeocystis* spp., *Pfiesteria* sp., and *Chrysochromulina* sp., as they are <10 μm in size (Gollasch et al., 2007). However, these microalgae are highly capable of settling and ultimately dominating the host environment due to their small sizes, abundance in seawater, and capacity to survive under hostile conditions by forming cysts or spores (Gregg and Hallegraeff, 2007). Indeed, Bolch and de Salas (2007) demonstrated the introduction, probably via ballast waters, of *Gymnodinium catenatum* and *Alexandrium tamarensis* from Southeast Asia to Australia (Bolch and de Salas, 2007).

Several treatment processes or methodologies of ballast water are currently being implemented, such as water exchange (coastal water discharge into open seas and the reverse), physical and mechanical treatments (hydrocyclone, sieve, filter, ultraviolet (UV) radiation, microwaves, heat treatment, and ultrasound), and primarily chemical treatments (chlorine, peroxyacetic acid, and bromine). Some of these treatments are not always efficient in removing small microorganisms, others generate by-products that accumulate in the marine environment, and some others need highly concentrated and efficient solutions depending on the type and physiological state of microorganisms (size,

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morphology, cell wall structure, etc.) or water characteristics. Moreover, some of these processes could be very expensive (further described in the supplementary material section).

Among all treatment processes, membrane filtration is of great interest. Porous membranes (ultra- or microfiltration) are used in large-scale desalination plants to feed reverse osmosis units without (i) microorganisms and (ii) large amounts of organic matter (detailed in the supplementary material section). Membrane filtration requires some posttreatments such as the addition of chemicals and discharge of concentrates, the part retained by the membrane, into the ocean. Moreover, the quality of treated water is constant throughout the filtration process, irrespective of the input seawater characteristics (Zhang et al., 2006; Xu et al., 2008). The microalgae contained in seawater can be completely retained. Indeed, Castaing et al. removed *Heterocapsa triquetra*, *Alexandrium minutum*, and *P. lima* from seawater by membrane filtration (Castaing, 2011; Castaing et al., 2009). We have already demonstrated that *Nannochloropsis oculata*, one of the smallest microalgae in seawater, and *Skeletonema costatum* can be completely removed by micro- and ultrafiltration (50 kDa of polyacrylonitrile, 100 kDa of polyethersulfone (PES), and 0.1 μm of polyvinylidene fluoride) of seawater (Guilbaud et al., 2013).

Nevertheless, the optimal conditions for process control must be determined to ensure complete removal of the smallest microalgae in a cost-effective manner. In the present work, a membrane process (microfiltration on a 0.1-μm polyvinylidene difluoride (PVDF) membrane) is implemented to remove, in a single step, all microalgae contained within seawater to be ballasted, even in the case of planktonic blooms. The removal of microalgae from raw seawater will facilitate the subsequent treatment of ballast water during deballasting. In our previous work, we demonstrated the efficiency of this membrane pilot plant in complete removing microalgae (Guilbaud et al., 2013). Indeed, some revival tests were conducted on the produced water: 500 mL of water was filtered on sterile membrane discs (0.2 μm) and then held in a petri box with f/2 medium with 9 g.L^{-1} of agar. The boxes were placed in an illuminated incubator at 16 °C. Even after 4 weeks of culture, microalgae did not grow. Moreover, the chlorophyll a concentration and the dissolved organic carbon of permeates produced by the membrane pilot plant were always below 0.1 μg.L^{-1} and 0.4 mg.L^{-1}, respectively. Therefore, in addition to purification, the hydraulic performance of this system must be enhanced for an economical estimation. Thus, a specific methodology, adaptable to other processes, is adopted for the present work in order to mitigate membrane fouling and allow sustainable filtration. Then, economic evaluation is realized for the ballasting of cruise ships with a capacity of 5400 passengers and tankers transporting 75,000 m^3 of liquefied natural gas (LNG).

2. Material and methods

2.1. Seawater preparation

The effect of filtration conditions on the performance of a given membrane can only be evaluated if exactly the same resource is filtered. Nevertheless, the properties and composition of natural seawater vary depending on the time of day, weather, tide, season, and locality (Aminot et al., 2004). Therefore, based on a bibliographic review, a seawater model suspension has been prepared. It represents real seawater sampled in the main global maritime exchange zones (see the supplementary material section). Seawater sampled in three of the four main geographic zones of ballasting (North America, Europe (Mediterranean and North), and Southeast Asia) contains a maximum phytoplankton concentration, referred to as microalgae bloom, of about 1.2 × 10^8 cells.L^{-1} (details in the supplementary material section). For seawater not necessarily within the current ballasting zones, the algal concentrations can reach several hundred thousands of microalgae per milliliter (Castaing, 2011; Castaing et al., 2009; Pitcher et al., 2007; Lindholm and Nummelin, 1999). The seawater of ballasting zones are mainly composed of diatoms and dinoflagellates with higher rates of diatoms, notably *S. costatum* (renamed *Skeletonema marinoï*). *Azadinium spinosum* is one of the smallest dinoflagellates present in natural blooms (5–12 μm) (Krock et al., 2009). Thus, a complete removal of the latter microalga by the membrane process will cause others to be removed as well. *N. oculata*, a nontoxic microalga (hence easier to handle in the laboratory), ranges from 2 to 6 μm in size, close to that of *A. spinosum*. Thus, for the present work, seawater is prepared with 75% of *S. costatum* and 25% of *N. oculata* (ratio often encountered in natural seawaters), with a total cell concentration of 1.2 × 10^8 cells.L^{-1} representative of the important algal bloom (Guilbaud et al., 2013). *S. costatum* and *N. oculata* are grown, respectively, in a raceway fed by natural drilling seawater and in an airlift with controlled conditions (fed-batch, pH = 8, in f/2 media (Guillard, 1975; Guillard and Ryther, 1962)). Sodium chloride is added to the preparation to adjust the conductivity of reconstituted seawater to 44 mS.cm^{-1}. Thus, the concentrations of organic matter (2.2 ± 0.3 mg$_{TOC}$.L^{-1}), suspended solids (3.2 ± 0.6 mg.L^{-1}), and chlorophyll (Chl a) (79.4 ± 3.5 mg.L^{-1}) of the prepared seawater fall within the concentration ranges of natural seawater (Table 1).

2.2. Description of membrane pilot plant and operating conditions

Membrane filtration is performed in the dead-end mode from the inside to the outside of the hollow fiber. For the present work, PVDF membranes are chosen. These membranes are used in the world's largest seawater desalination plants (Magtaa, Algeria; Tianjin, China, etc.). PVDF offers good mechanical resistance as well as chlorine and chemical tolerance (Vial and Doussau, 2003; Pearce, 2007a, 2007b; Casana, 2012). The mean pore diameter of the PVDF membrane is 0.1 μm. The surface area of the membrane is 0.12 m^2 and the permeability 1463 L.h^{-1}.m^{-2}.bar^{-1} at 20 °C. The conditions of filtration and backwash correspond to those usually adopted on an industrial scale for seawater desalination: specific filtered volume (permeate flux multiplied by time of filtration) ranging from 50 to 100 L.m^{-2} at 100–200 L.h^{-1}.m^{-2} followed by backwash at 2.08 L.m^{-2} (Table 2) (Teuler et al., 1999; Brehant et al., 2002; Heijman et al., 2005; Xu et al., 2007; Jezowska et al., 2009).

Four sequences of filtration–backwash are performed for each permeate flux and specific filtered volume. The same specific filtered volume is obtained, whereas the permeate flux is changed by adjusting the duration of the filtration cycle. Thus, the fouling intensity can be evaluated for the same (i) specific filtered volume, that is, the similar amount of matter brought to the membrane, or (ii) permeate flux. The filtrations are performed at constant permeate flux, hence constant flow rate, to allow continuous filling of the ballast tanks. Irrespective of the filtration conditions, the specific volume of backwash is kept constant at 2.08 L.m^{-2} (backwash flux multiplied by backwash time) in the same range of magnitude as that classically encountered on an industrial scale (further described in the supplementary material section). According to conventional operating conditions, the flow rate of backwash is always 2.5 times higher than the filtration rate (details within the supplementary material section).

The average fouling resistances (R_c), which correspond to the resistance offered by fouling during fluid flow, are determined according to Darcy's law:

$$J_p = \frac{TMP}{\mu \times (R_m + R_c)}$$

where J_p is the permeate flux (m^3.s^{-1}.m^{-2}), TMP the transmembrane pressure (i.e., difference in pressure on each side of the membrane (Pa)), μ the permeate dynamic viscosity (Pa.s), R_m the membrane resistance (m^{-1}), and R_c the fouling resistance (m^{-1}).

The residual resistance is also calculated. It is induced by the matter that is not removed from the membrane after backwash (Fig. 1).

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