

Integrated reverse osmosis/vacuum membrane distillation for enhanced arsenic removal and water recovery of brackish water desalination

Duong Thanh Dao^a, Hung Cong Duong^b, Stéphanie Laborie^{c,*}, Corinne Cabassud^c

^aUniversity of Science and Technology of Hanoi (USTH), 18 Hoang Quoc Viet Street, Cau Giay District, Hanoi, Vietnam, email: dao-thanh.duong@usth.edu.vn

^bSchool of Environmental Engineering, Le Quy Don Technical University, Hanoi, Vietnam, email: hungduongcong@gmail.com

^cTBI, Université de Toulouse, CNRS, INRAE, INSA, Toulouse, France, email: stephanie.laborie@insa-toulouse.fr (S. Laborie), cabassud@insa-toulouse.fr (C. Cabassud)

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ABSTRACT

Brackish water has attracted increasing attention as a promising source to augment fresh water supply in many areas around the world. However, the ubiquitously high content of arsenic in brackish water presents a vexing technical challenge to reverse osmosis (RO) desalination plants. In this study, an integrated RO/vacuum membrane distillation (VMD) process was investigated for enhanced As(III) removal and water recoveries of brackish water desalination without requirement of pre-oxidation step as in other conventional treatment processes. The experimental results demonstrate that As(III) removal and water flux of the single RO process were profoundly affected by the conditions of the brackish water feed and the process water recovery. At pH 10, the As(III) removal maximized at 90%, and sharply dropped to below 80% as the process water recovery exceeded 70%. Exceeding the process water recovery of 70% also significantly reduced the RO process water flux. On the other hand, the VMD process was able to further treat concentrated RO brines with a 100% As(III) removal and stable water flux. Thanks to advantage of VMD, the integrated RO/VMD process at the global water recovery of 95.5% achieved adequate global As(III) removal, bringing the As(III) concentration in the product water down to below the 10-ppb allowable maximum limit.

Keywords: Brackish water desalination; Reverse osmosis; Membrane distillation; Vacuum membrane distillation; Arsenic removal; Water recovery

1. Introduction

In recent decades, desalination of seawater and brackish water has been applied to augment fresh water supply in many water-stressed areas around the world [1–3]. According to the International Water Association, seawater and brackish water desalination plants worldwide have been able to meet daily fresh water demand of more than 300 million people, equivalent to >1% of the global population [4]. Given rapid technological advances, the cost of fresh water obtained via desalination of seawater and brackish water has been significantly reduced, coinciding with the steadfast growth of

the global desalination market [5]. Compared to seawater, brackish water has more diverse locations and lower salinity, hence offering a more affordable fresh water supply. Therefore, brackish water desalination has been deemed a practical solution to addressing fresh water scarcity in many areas, particularly in remoted inland locations [2,6].

In brackish water desalination, adequate removal of contaminants is vital to meet stringent standards for fresh water supply [7–9]. Amongst various contaminants, arsenic poses a considerable challenge to the practice of brackish water desalination and its removal is a key sanitary and environmental issue. Indeed arsenic contamination of

* Corresponding author.

brackish water can be induced by natural or anthropological activities, leading to detrimentally high arsenic concentration (i.e., several thousand ppb) in various brackish water sources [10,11]. In general, arsenic exists in both organic and inorganic forms. The organic species (monomethylarsenic and dimethylarsenic) are abundant in seafood, less harmful to the human health and readily eliminated by the body while the latter one is more prevalent in water and is considered more toxic [12]. Therefore, most of previous studies normally focus on inorganic arsenic form. Long-term of inorganic arsenic exposure can cause severe health problems to human including skin lesions, such as: hyperkeratosis and pigmentation changes, diabetes, circulatory disorders and cancer of bladder, lung, kidney and skin [12]; thus, a maximum allowable arsenic level of 10 ppb has been imposed by the World Health Organisation (WHO) for drinking water [10,13]. In this context, regulations on brackish water desalination with respect to arsenic removal have become increasingly stringent.

Reverse osmosis (RO) is the leading technology for desalination of brackish water for fresh water supply [14,15]. The RO process relies on a semi-permeable membrane and a high hydraulic pressure to produce fresh water from the brackish water feed. The excellent rejection of the RO membrane against dissolved salts and charged contaminants allows for the production of fresh water with significantly low salinity and contaminants concentration. However, most RO membranes exhibit limited rejection against neutrally charged contaminants, and RO membrane rejection against these toxic contaminants is also highly susceptible to the feed water characteristics (e.g., pH, salinity, and the presence of organic matters) and the process operating conditions (e.g., applied pressure and water recovery) [12,16–20]. Therefore, neutrally charged contaminants such as arsenic pose a serious challenge to the RO desalination of brackish water, given their high concentration in brackish water. In addition to arsenic, organic matters and sparingly soluble salts in brackish water present a risk of membrane fouling/scaling to the RO process [6,21]. As a result, most brackish water RO desalination processes are operated at water recovery higher than that of seawater RO but no more than 80% to prevent membrane fouling/scaling [22,23].

Practical approaches to increasing the arsenic removal and water recovery are vital to RO desalination of brackish water for fresh water-supply, particularly in remoted inland locations. Several studies have been conducted to investigate the effects of feed water characteristics and process operating conditions on the arsenic removal and permeate quality during RO treatment of brackish water. As a notable example, Teychene et al. [16] examined the rejection of metalloids (e.g., arsenic and boron) for different RO membranes operated on brackish water and seawater at different feed water pH and applied transmembrane pressure (TMP). A profound dependence of membrane arsenic rejection on feed water pH and membrane types was reported, and for brackish water RO could achieve a 99% arsenic rejection at feed water pH of 9.6 and TMP of 40 bar [16]. The authors reported that the RO process, given its 99% arsenic rejection rate, could obtain the permeate with arsenic level below the WHO guidelines under whatever process operating conditions [16]. It is, however, noteworthy that the brackish water feed used in the

study by Teychene et al. [16] contained only 50 ppb arsenic, which is by far lower than the arsenic levels reported in various brackish water sources [10,11]. Higher arsenic concentration in brackish water feeds might compromise the arsenic level in RO permeate, thus failing to meet the WHO guidelines. Víctor-Ortega and Ratnaweera [24] reported that a single RO process could only remove <80% arsenic (i.e., in form of arsenite, As(III)) from a feed water with initial arsenic concentration of 200 ppb (i.e., 100 ppb As(III) + 100 ppb As(V)). For this heavily arsenic laden brackish water feed, a doubled filtration RO process was required to fulfill the maximum allowable arsenic level of 10 ppb [24]. The double filtration treatment of brackish water feed inevitably leads to reduction in the RO process water recovery as the permeate from the 1st filtration is fed to the 2nd filtration for enhanced global arsenic removal efficiency. Therefore, there exists a trade-off between enhanced arsenic removal and improved water recovery in RO desalination of brackish water for fresh water supply.

Membrane distillation (MD) has recently been explored for treatment of brackish water with a particular focus on maximising water recovery [12,25–27]. Unlike the pressure-driven RO process, MD relies on a trans-membrane vapor pressure difference as the driving force for water transfer through its micro-porous membrane. Given this notable attribute, the MD process is significantly less subject to the salinity and osmotic pressure of the feed water, and hence workable with hyper-saline waters such as retentates from seawater or brackish water RO desalination. More importantly, since it can theoretically achieve 100% rejection of involatile contaminants (i.e., including toxic arsenic), the MD process allows for the production of fresh water with arsenic concentration by far below the 10-ppb legislated limit [12,28–29]. In one of our previous study [12], vacuum membrane distillation (VMD), as an advanced solution for arsenic removal without pre-oxidation step, was applied for a synthetic brackish solution containing arsenic (10 g/L NaCl and 300 ppb As(III)). As a result, VMD was capable to satisfy both As(III) rejection and desalination requirements to meet the required standard (MCL = 10 ppb), with over 99% and 99.5% of rejection efficiencies, respectively. Between them, the As(III) rejection rate was always stable at such high level, irrespective of high feed As(III) concentrations (up to 2,000 ppb). In addition, one more advantage of this process is to directly treat As(III) effectively even at neutral pH (i.e., pH 7), without requirement to increase pH (i.e., pH 10) as for the conventional technologies.

Nevertheless, this advanced technology still has some drawbacks. Although providing high As(III) and salt rejection efficiencies, the permeate flux achievement mainly depends on type of membrane employed and is still a big challenge. In our study [12], at the given operating conditions (fluoropore membrane, $T_f = 55^\circ\text{C}$, $P_p = 4,500\text{ Pa}$, $Re = 3,400$) for a brackish solution containing As(III), highest permeate flux at 14 kg/m²·h was only obtained. Besides that, another main drawback of this VMD process is the high level of total energy requirement. By applying the same pilot plant for seawater desalination, Mericq et al. [30] classifies three types of energy requirement in VMD operation, including: (i) the vacuum energy; (ii) the circulation energy and (iii) the heat energy. Among them, the heat energy requirement represents more

than 98% of the total energy requirements, which clearly shows that coupling VMD with solar heating or with waste heat recovery is promising. Our group, at TBI – Toulouse Biotechnology Institute, yet published many papers relative to the energy costs in membrane distillation for desalination, and notably on systems integrating solar energy [31–34]. In order to facilitate the feasibility of the VMD technology in the industry through lowering cost for energy, another possibility is to focus VMD on feed previously concentrated by a low energy consuming process, for example reverse osmosis. Owing to this integration, a lower quantity of feed flow to be treated by VMD is required, and therefore decreases the energy cost as well as membrane area. This concept was proposed by Mericq et al. [30] for over-concentrate retentate of a RO plant with a 40% recovery factor and a 38.9 g/L feed salt concentration. As a result, the feed volume can be reduced by a 1.6 factor and the water recovery increases from 40% to 89.1%. As the feed volume to be treated by VMD decreases, heat energy requirement is also reduced, leading to a lower energy cost.

Following the above-mentioned concept, this paper mainly aimed exploring and demonstrating the potential interest of the process for reaching the required quality level in case of brackish waters containing arsenic. Thanks to a lab-scale experimental approach that consists of an integrated RO/VMD process, whereby the retentate from RO was further treated by VMD, the influence of the properties of the brackish feed (pH, salinity, As(III) concentration and organic compounds) on the produced water flux and quality were explored. The experimental results from the individual RO and VMD process were subsequently employed to evaluate the global As(III) removal and water recovery of the integrated RO/VMD treatment of brackish water. The ultimate purpose of this study is to elucidate the optimal water recovery of the single RO and VMD process that allows for maximum obtainable global water recovery while fulfilling the legislated arsenic level in the product fresh water during the integrated RO/VMD treatment of arsenic affected brackish water.

2. Materials and methods

2.1. Materials

2.1.1. The lab-scale RO and VMD units

Lab-scale RO and VMD units were used in this study. The lab-scale RO unit had a stainless-steel membrane cell with a total feed volume of 500 mL. The flat-sheet membrane cell had an area of 63.6 cm² filter, and was equipped with a stirrer to provide agitation of the feed water to mitigate the effect of concentration polarization. Nitrogen gas from a cylinder was fed to the cell to regulate the transmembrane pressure between 24–32 bar to be applied for the experiments. Permeate from the RO cell was collected in a tank and continuously weighted using an electronic balance (Sartorius 1500S) connected to a computer. A thin-film composite polyamide RO membrane (i.e., osm-ESPA) with active area of 38.5 cm² provided by Hydranautics was used in the filter cell. Key characteristics of this RO membrane are shown in Table 1.

With its set-up was fully described in our previous study [27], the lab-scale VMD unit consisted of a hot feed cycle and a low pressure permeate cycle separated by a membrane. In the hot feed cycle, feed water in a 4-L thermostatic tank was pumped to the feed channel of the VMD membrane cell by a displacement pump (A/B Pumps) with capacity in range of 0–250 L/h. The temperature of the feed water was regulated in range of 25°C–60°C using a heating group. The feed water pressure at the inlet and outlet of the membrane cell was equal to the atmospheric pressure. On the other hand, vacuum or low pressure was applied in the permeate side of the membrane. During the VMD process, water vapor permeated through the membrane from the feed side was condensed in a trap using liquid nitrogen. Permeate water vapour flux passing through the membrane was measured by a BRONKHORST water thermal mass flow meter with capacity of 0–60 g/h. A data acquisition system was equipped to the lab-scale VMD unit for recording the feed water temperature at the inlet and outlet of the membrane cell and the permeate pressure.

The VMD membrane cell employed a hydrophobic flat-sheet polytetrafluoroethylene (PTFE) membrane (fluoropore), provided by Millipore Corporation, France. Key characteristics of this membrane are shown in Table 2. The cell had an effective membrane area of 57.75 cm² (i.e., length and width of 16.5 cm and 3.5 cm, respectively). The membrane coupon was sandwiched between two acrylic engraved semi-cells to form feed and permeate channels of 1 mm depth. Rubber gaskets and plastic spacers were used for sealing and maintaining the depth of the feed and permeate channels.

Table 1
Characteristics of the thin-film ESPA membrane used in the reverse osmosis unit

Specification	Value
Manufacturer	Hydranautics
Material	Polyamide
Molecular weight cut-off (g/mol)	<200
Salt rejection	>98.7% CaCl ₂
Water permeability at 20°C (L/m ² ·h·bar)	3.6
Contact angle (°)	69
Zeta potential at pH 7 (mV)	–7.7

Table 2
Characteristics of the polytetrafluoroethylene membrane used in the vacuum membrane distillation unit

Membrane characteristics	Value
Manufacturer	Millipore
Material	PTFE
Nominal pore size (µm)	0.22
Thickness (µm)	175
Porosity (%)	70
Contact angle (°)	124
Liquid entry pressure (bar)	4.2

2.1.2. Synthetic brackish water and RO retentate

Synthetic brackish water solutions were prepared using deionised (DI) water and analytical grade chemicals (e.g., sodium chloride, NaCl 98% (VWR-Belgium) and, sodium meta arsenite, NaAsO₂ ≥ 90% (Subra – France). The synthetic brackish water solutions had 10 g/L NaCl and 104 ppb As(III) which are representative salinity and arsenic concentration of arsenic affected brackish water in Vietnam. In the RO experiments, to test the effect of organic matter on membrane rejection and water flux, humic acid sodium salt (HASS) – C₉H₈Na₂O₄ 50% (Carl Roth – Germany) was added into the synthetic brackish water at concentration of 20 mg/L.

2.2. Analytical methods

As(III) and NaCl concentrations of water samples were analysed to assess the membrane rejection during the RO and VMD desalination tests. As(III) concentration was measured using an Optical Emission Spectrophotometer (ICP/OES Optima 2100DV, Perkin Elmer). On the other hand, NaCl concentration was measured using an electrical conductivity meter (CDM 210 Lab, WTW Germany). The electrical conductivity meter was workable in the range from 0.01 to 1,400 mS/cm. Given the measured electrical conductivity, the NaCl concentration of water samples was calculated using the following pre-determined empirical equations:

$$y = 0.5329x - 0.1344 \quad (1)$$

$$y = 0.7401x - 2.5668 \quad (2)$$

where y was the NaCl concentration (g/L) and x was the electrical conductivity (mS/cm). Eq. (1) was for the NaCl concentration of 0–10 g/L, whereas Eq. (2) was applied for the 10–300 g/L NaCl concentration.

Membrane rejections against As(III) and NaCl during the RO and VMD tests were calculated as follows:

$$\text{Reject} = \left(\frac{C_f - C_p}{C_f} \right) \times 100\% \quad (3)$$

where Reject was the membrane rejection (%), C_f and C_p , respectively the As(III) or NaCl concentration of the feed and permeate collected during the RO and VMD tests. It is worth noting that, in this case, the permeate concentration is the mean concentration of 250 mL cumulated volume of permeate samples (i.e., equivalent to 64.9 L/m²), which corresponds to a recovery of 50%.

Water recovery of the single RO, VMD, and the integrated RO/VMD process was calculated as the ratio of the accumulative obtained permeate with the initial feed water volume as below:

$$\text{Recovery} = \frac{V_{\text{permeate,accu}}}{V_{\text{feed,ini}}} \times 100\% \quad (4)$$

where $V_{\text{permeate,accu}}$ and $V_{\text{feed,ini}}$ were the accumulative volume of the permeate and the initial volume of the feed water (L), respectively.

In the experiments to test membrane fouling/scaling of the RO or VMD process, the membrane was removed from the test units at the completion of the experiments. The surface morphology of the fouled membranes was evaluated using a scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) (JEOL 5410 LV Instrumentation). Prior to membrane surface analyses, the fouled membranes were dried at room temperature for 24 h in a dust-free atmosphere and subsequently coated with a thin carbon layer.

2.3. Evaluation of global As(III) removal and water recovery of the integrated RO/VMD process

An integrated RO/VMD treatment of arsenic affected brackish water was explored for improved global As(III) removal and water recovery (Fig. 1), by operating separately the RO and VMD processes, in which the VMD feed was as the synthetic solution that represents the retentate from RO process at a very high concentration (i.e., [As(III)] = 7,000 ppb; [NaCl] = 300 g/L). Given its high rejection of involatile contaminants, the VMD unit could achieve high quality permeate from the RO retentate. Therefore, VMD permeate was blended with RO permeate to improve the global As(III) removal of the brackish water treatment. To run the simulation, several assumptions were proposed as: (i) brackish water feed to RO had constant compositions: 10 g/L NaCl, 104 ppb As(III), and 20 mg/L HASS; (ii) the VMD process was able to reject 100% NaCl and workable with NaCl concentration up to 300 g/L, equivalent to a global recovery rate of 95.5%, which is fixed as an initial parameter [30]; and (iii) effects of membrane fouling/scaling on water flux and membrane rejections of the RO and VMD process were not included.

The constrain of the simulation was to achieve a global water recovery of 95.5% (i.e., equivalent to the global feed water concentration factor >22) for the integrated RO/VMD treatment of brackish water. Membrane rejections of the RO and VMD process against As(III) and NaCl obtained from the tests were used as inputs to the simulation. The outputs of the simulation were the global As(III) concentration in the permeate and the RO as well as VMD water recoveries to achieve the global water recovery of 95.5%. Water recovery rates for both RO and VMD processes and global permeate As(III) concentration were calculated as below:

$$\text{Recovery}_{\text{RO}} = \frac{Q_{\text{P,RO}}}{Q_{\text{F}}} \times 100 \quad (5)$$

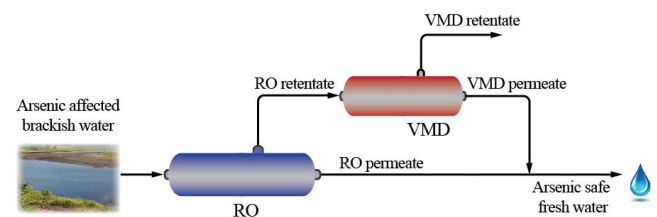


Fig. 1. Schematic diagram of the integrated reverse osmosis/vacuum membrane distillation process for the treatment of arsenic affected brackish water.

$$\text{Recovery}_{\text{VMD}} = \left(\frac{\text{Recovery}_{\text{Global}} - \text{Recovery}_{\text{RO}}}{100 - \text{Recovery}_{\text{RO}}} \right) \times 100\% \quad (6)$$

$$C_{p,\text{Global}} = \left(\frac{C_{p,\text{RO}} \text{Recovery}_{\text{RO}} + C_{p,\text{VMD}} \times (100 - \text{Recovery}_{\text{RO}}) \times \text{Recovery}_{\text{VMD}}}{\text{Recovery}_{\text{Global}}} \right) \times 100\% \quad (7)$$

where $\text{Recovery}_{\text{Global}}$ was the global water recovery of the integrated RO/VMD process and was set at 95.5%, $C_{p,\text{Global}}$, $C_{p,\text{RO}}$ and $C_{p,\text{VMD}}$ were the As(III) concentration in the permeate of the integrated RO/VMD, single RO, and single VMD process, respectively. Q_f is the inlet feed flow of the process.

3. Results and discussions

3.1. Treatment efficiency of the RO process of arsenic contaminated brackish water

3.1.1. Membrane rejection and water flux of the RO process of arsenic contaminated brackish water

In RO desalination, membrane rejection against contaminants is dependent on various factors including feed water quality and process operating pressure. As demonstrated in Fig. 2, membrane rejection against As(III) was significantly lower and more subject to the feed water pH and TMP than that against NaCl in the RO process of the brackish water feed. At the brackish water feed pH of 7, the RO membrane rejected only 52% and 60% of As(III) when operating at TMP of 24 and 32 bar, respectively. Elevating the feed water pH from 7 to 10 resulted in significant increases in the As(III) rejection at both TMP values (Fig. 2A). On the other hand, the NaCl rejection of the RO membrane was negligibly affected by the feed water pH and TMP, remaining high at >92% regardless of the feed water pH and the applied TMP (Fig. 2B).

The varied membrane rejection against As(III) during the RO process of brackish water feed at different pH was attributed to the interaction between the membrane and arsenic in the feed water. Indeed, the membrane As(III) rejection was induced mainly by the electrostatic repulsion force between the RO membrane and arsenic. At the feed water pH of 7, arsenic existed as neutral arsenite (H_3AsO_3) given its pKa of 9.2. When the feed water pH was raised to 10, arsenite dissociated to form negatively charged monovalent anions (H_2AsO_3^-). Because of the negative charge of the RO membrane (i.e., osm-ESPA), the electrostatic repulsion force of the membrane against the negatively charged anions was stronger than that against the neutral arsenite. Therefore, the membrane As(III) rejection was greatly higher at pH of 10 as compared to that at pH of 7. The trend observed in this study is consistent with the results reported in previous studies [16,20].

RO membrane rejections against arsenic and dissolved salts were also affected by water recovery and the resultant feed water salinity. As the water recovery of the RO process increased, As(III) and NaCl rejections gradually decreased at water recovery beyond 70%, and a drastic decline was observed at higher water recoveries (Fig. 3). Correspondingly to the decreased membrane rejections, As(III) and NaCl concentrations in the permeate exponentially increased when the process water recovery exceeded 70% (Fig. 3). It has been proved that RO membrane rejections are subject to the feed water salinity, which is an exponential function of water recovery. When the process water recovery exceeded 70%, dissolved salts in the feed water were concentrated more than 3 folds, leading to the sharp decline in membrane rejections against As(III) and NaCl.

The permeate flux of the RO brackish water treatment was also dependent on the feed water pH, applied TMP, and process water recovery. At water recovery <50%, the RO permeate flux linearly decreased with the increase in the process water recovery (Fig. 4). Moreover, higher permeate flux was achieved when operating the RO process at TMP of 32 bar compared to 24 bar (Fig. 4). The well-established relationship between permeate flux and process water recovery

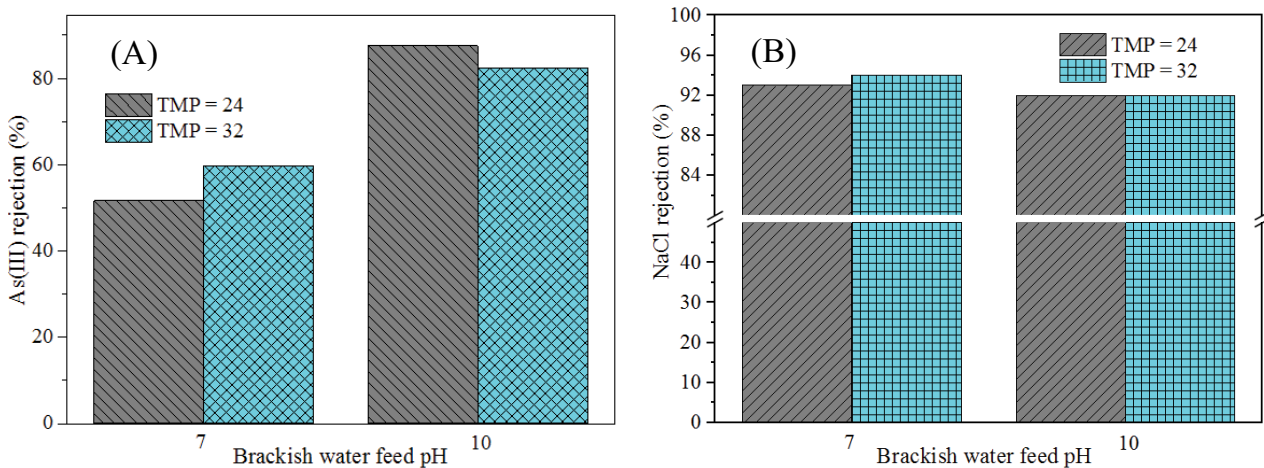


Fig. 2. Membrane rejection against (A) As(III) and (B) NaCl of the reverse osmosis process with the arsenic contaminated brackish water feed at different pH ($[\text{As(III)}] = 104 \text{ ppb}$ and $[\text{NaCl}] = 10 \text{ g/L}$).

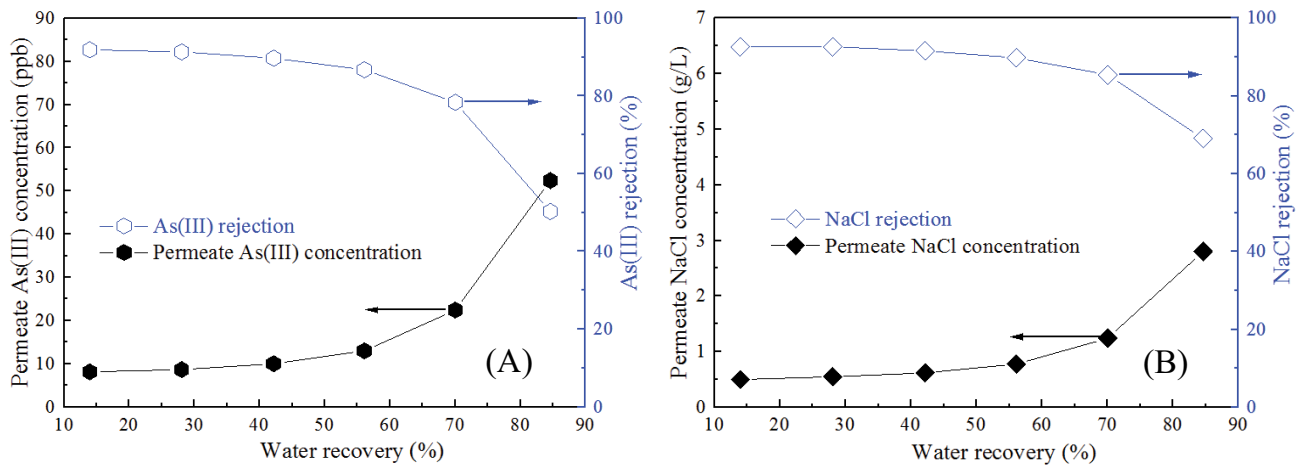


Fig. 3. Membrane rejection and permeate concentration vs. water recovery during the reverse osmosis process of brackish water feed regarding: (A) As(III) and (B) NaCl (pH10, TMP = 24 bar, $[\text{NaCl}]_{\text{initial}} = 10 \text{ g/L}$, $[\text{As(III)}] = 104 \text{ ppb}$).

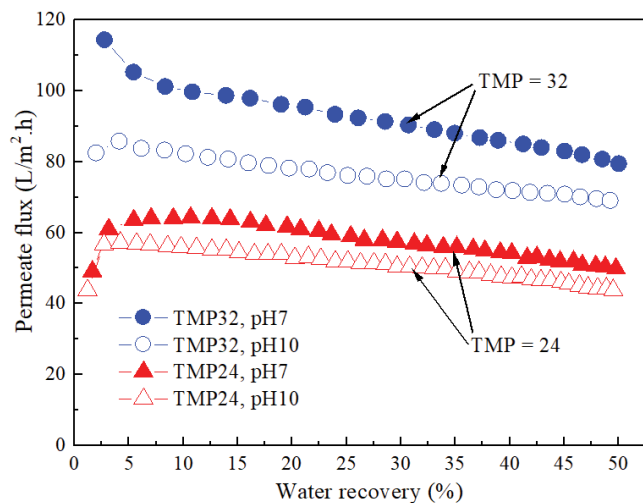


Fig. 4. Reverse osmosis permeate flux as a function of water recovery at different feed water pH and applied transmembrane pressure during the treatment of brackish water feed ($[\text{NaCl}]_{\text{initial}} = 10 \text{ g/L}$; $[\text{As(III)}] = 104 \text{ ppb}$).

(i.e., corresponding with feed water salinity) and the applied TMP is attributed to the driving force of the RO process. Of a particular note, discernibly higher permeate flux was achieved at the feed water pH of 7 than at pH 10. Like arsenic, the permeation of water through the RO membrane is regulated by the Donnan effect, which is closely dependent on feed water pH. It is also noteworthy that there existed a trade-off between permeate flux and arsenic rejection when feed water pH was adjusted from 7 to 10 (Figs. 2A and 4).

3.1.2. Co-effects of organic foulants on the membrane rejections and permeate flux of the RO process

The presence of organic matter at low concentration in the feed water was beneficial to the RO treatment of the brackish water with respects to contaminants removal. In the RO experiments to test the effect of organic matter on

membrane rejection and water flux, HASS – $\text{C}_9\text{H}_8\text{Na}_2\text{O}_4$ 50% (Carl Roth – Germany) was added into the synthetic brackish water at concentration of 20 mg/L. As shown in Fig. 5A and B, at pH 10 and TMP = 24 bar, the membrane rejections against As(III) and NaCl during the RO process of the brackish water with the initial HASS concentration of 20 mg/L were always slightly but noticeably higher than those during the process without HASS. Correspondingly, lower As(III) and NaCl concentrations were obtained in the permeate of the RO process of the feed water with HASS compared to those without HASS added. The results (Fig. 5A) also indicate that given the maximum allowable arsenic level in drinking water of 10 ppb, the single RO process of the brackish water with the initial As(III) concentration of 104 ppb is recommended to be operated at the water recovery below 60% and 45% for the feed water with and without HASS, respectively.

The co-effect of the organic matter on the improved membrane As(III) and NaCl rejections is attributed to the complexation of these contaminants in the feed water. It has been reported that organic matters associate with arsenic to form hypothetical colloidal arsenic or organic matter/arsenic complexes with larger sizes, which are more likely to be rejected by the RO membrane. For example, Brandhuber and Amy [35] reported that about half of arsenic in waters was associated with organic matters to form complexes with sizes of 500–10,000 Daltons. The complexation of organic matters with other contaminants has been also reported as the mechanism behind the enhanced RO membrane rejections in several previous studies [16,21,36].

The presence of the organic matter, however, exerted a slight impact on the permeate flux of the RO process with the brackish water feed (Fig. 5C). It is clearly that HASS at concentration of 20 mg/L had little influence on the osmotic pressure of the brackish water feed and hence the driving force for water transfer across the membrane. Thus, the light reduction in permeate flux of the RO process with the added organic matter might be attributed to the changes in feed water dynamic properties that leads to the alteration of the fouling layers on the membrane surface. These changes were more discernible at the process water recovery <20%

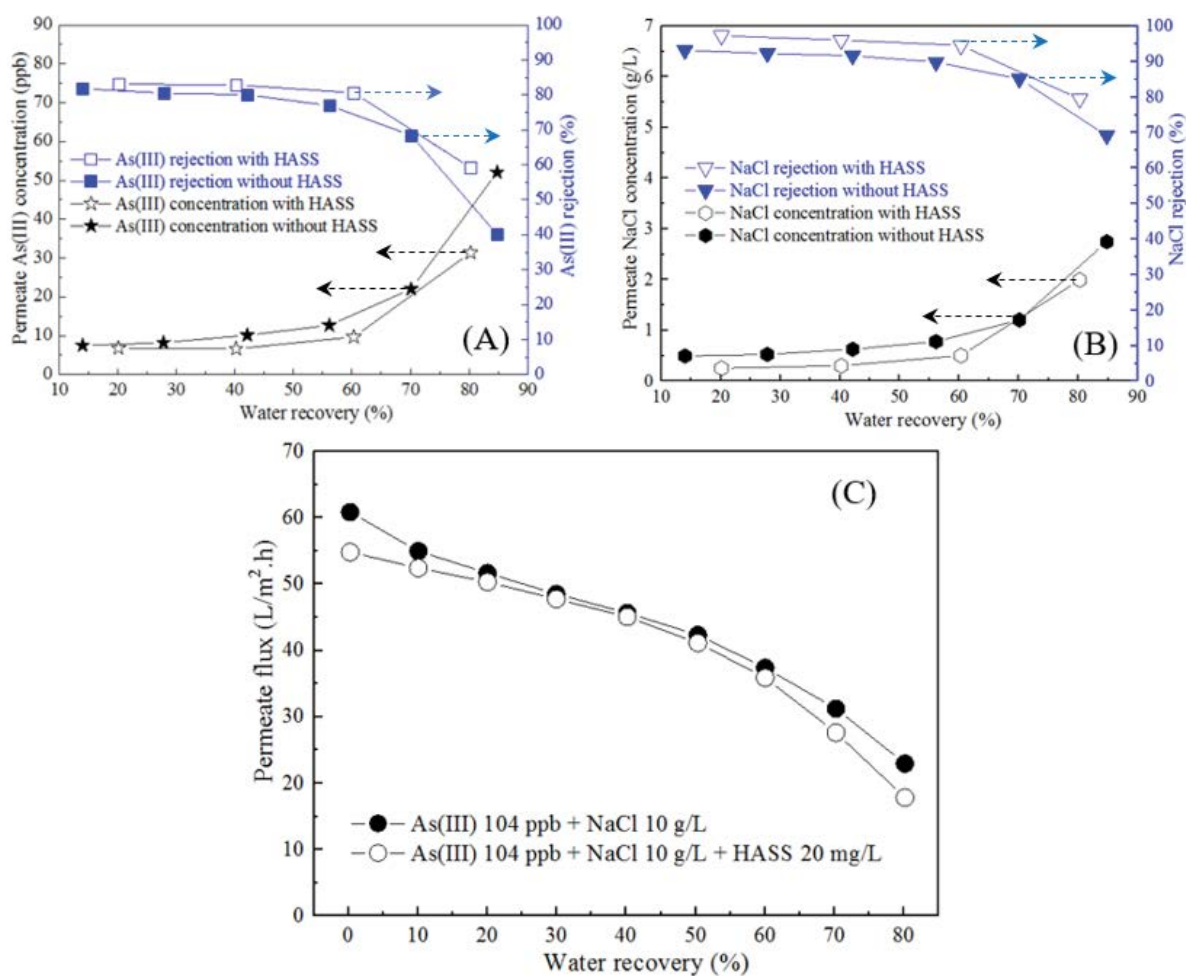


Fig. 5. (A) permeate As(III) concentration and membrane rejection against As(III), (B) permeate NaCl concentration and membrane rejection against NaCl, and (C) permeate flux of the reverse osmosis process of brackish water feed with and without HASS at different water recovery [$[\text{As(III)}]_{\text{initial}} = 104 \text{ ppb}$, $[\text{NaCl}]_{\text{initial}} = 10 \text{ g/L}$, $\text{pH} = 10$, $\text{TMP} = 24 \text{ bar}$].

(due to the high permeate flux that could aggravate the concentration polarisation effect) and >70% (because of the exponentially increased HASS concentration at high water recovery). Therefore, the permeate flux of the RO process with the HASS addition into the feed water at water recovery <20% and >70% diverged more from that of the process without HASS (Fig. 5C). Furthermore, the permeate flux of the RO process with and without HASS decreased rapidly at water recovery >70%.

It is noteworthy that the changes in feed water dynamic properties also led to the alteration of the fouling layers that deposit on the RO membrane surface at high process water recovery (i.e., 80%). This can be confirmed by the SEM-EDS analyses of the RO membrane surface at the completion of the experiments (Fig. 6). Indeed, more fouling with larger deposits was observed on the RO membrane surface that was experimented with the brackish water feed with HASS than the case without HASS (Fig. 6). Moreover, the EDS analysis confirms the presence of more arsenic in the deposits with the experiment with HASS compared to that without HASS. As discussed above, arsenic in the feed water had combined with HASS to form large complex,

hence facilitating the formation of larger deposits on the RO membrane surface.

3.2. VMD treatment of highly concentrated retentate from the RO process of arsenic contaminated brackish water

For these experiments, in order to improve water recovery and retentate minimization, synthetic solution that simulating the retentate from RO process at a very high concentration (i.e., $[\text{As(III)}] = 7,000 \text{ ppb}$; $[\text{NaCl}] = 300 \text{ g/L}$) was prepared for further treated by the VMD process. It was worth noting that choice of NaCl concentration of 300 g/L was the maximum mixed salt concentration (close to salt saturation at the operating temperature), which used to be tested for VMD by Mericq et al. [30]; while As(III) concentration of 7,000 ppb was chosen corresponding to initial feed As(III) concentration in resource of 1,750 ppb (estimated by a concentration factor of 4), which was still in range of 1–3,050 ppb of arsenic contamination in some places in the North of Vietnam.

As demonstrated in Fig. 7, the permeate flux and permeate quality of the VMD process were negligibly affected

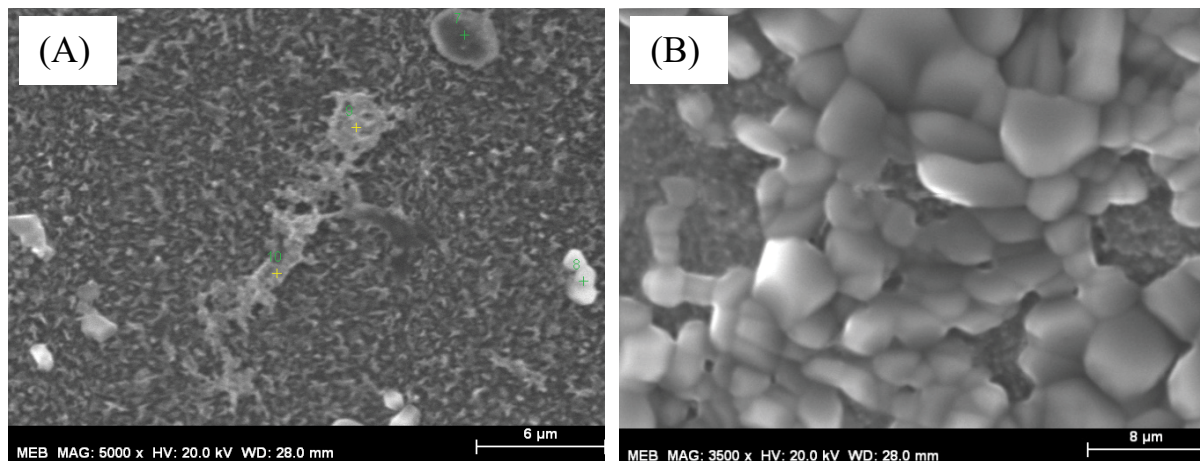


Fig. 6. Scanning electron microscopy images of the membrane surface after the reverse osmosis process of brackish water feed (A) without and (B) with the presence of HASS.

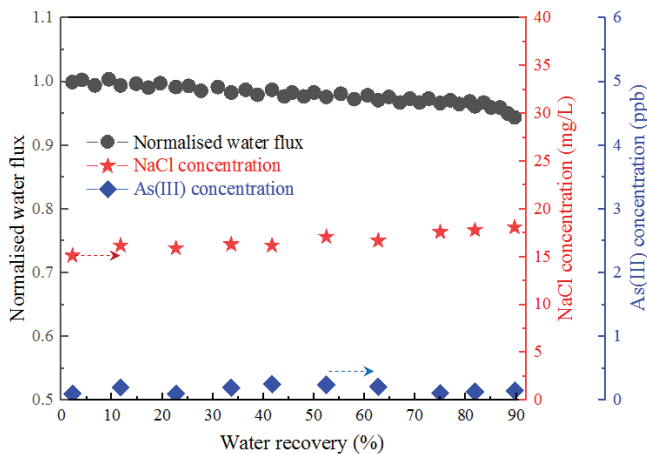


Fig. 7. Normalised water flux and the NaCl and As(III) concentration in the permeate vs. water recovery during the continuous vacuum membrane distillation treatment of the reverse osmosis retentate from arsenic contaminated brackish water [fluoropore membrane; [As(III)] = 7,000 ppb; [NaCl] = 300 g/L; $T_f = 40^\circ\text{C}$; $P_p = 4,500$ Pa; $Re = 3,400$].

by the VMD water recovery and thus by the salinity and the arsenic/HASS concentrations of the brackish water RO retentate. The normalized permeate flux of the VMD process was stable even when operating at water recovery of 80%. When pushing the VMD process water recovery beyond 80%, the normalized VMD permeate flux slightly reduced (Fig. 7). Throughout the VMD process, the NaCl concentration in the permeate of VMD remained below 20 mg/L while As(III) was only detected at trace level in the VMD permeate (Fig. 7). This observation indicates that membrane pore wetting did not occur, and the VMD process mostly achieved a complete rejection of salts and arsenic during the treatment of the concentrated brackish water RO retentate. This result is also adequate with those obtained in previous paper published by the same author [12].

SEM-EDS analysis of the membrane surface at the completion of the VMD process with the RO concentrated

retentate at water recovery of >80% confirms the formation of scale on the membrane surface (Fig. 8). This scale layer was composed predominantly of NaCl crystals with some extent of arsenic like that observed with the scale formed in the RO process of brackish water at 80%. Nevertheless, the effect of scale formation on the VMD performance (e.g., permeate flux and permeate quality) was marginal. The negligible effect of membrane scaling on the MD process performance could be attributed to the loose scale layer on the membrane surface resulted from the mild operating conditions (i.e., low water flux and low hydraulic pressure). This is consistent with the results previously reported in MD process of brackish water or seawater at high water recovery [30,37].

The experimental results reported here indicate that VMD can be viably combined with RO to facilitate the treatment of brackish water for fresh water production. Given the initial brackish water feed with 10 g/L NaCl and 104 ppb arsenic, the RO and VMD process can be operated at water recovery of 80% and 80%, respectively, resulting in the integrated RO/VMD global water recovery of 96% with acceptable permeate flux and membrane fouling/scaling. Operating at higher water recovery, arsenic rejection of the RO process can be compromised (Fig. 5A); however, RO permeate might be diluted by the high-quality VMD permeate to meet the allowable maximum arsenic level in the product water. This will be elucidated in the following section.

3.3. Integrated RO/VMD treatment of arsenic contaminated brackish water for enhanced arsenic removal and water recovery

The permeate As(III) concentrations obtained by the simulation of the integrated RO/VMD process reveal that combining RO with VMD for treatment of brackish water is beneficial with respects to global water recovery (Fig. 9). The single RO process of the brackish water feed (i.e., with 10 g/L NaCl, 104 ppb As(III), and 20 mg/L HASS) can meet the 10 ppb limit for permeate As(III) concentration when operating at water recovery of 42%. On the other hand, in the integrated RO/VMD treatment of the brackish water feed, the RO process can be operated at 70% water recovery together with 85% water recovery of the VMD process

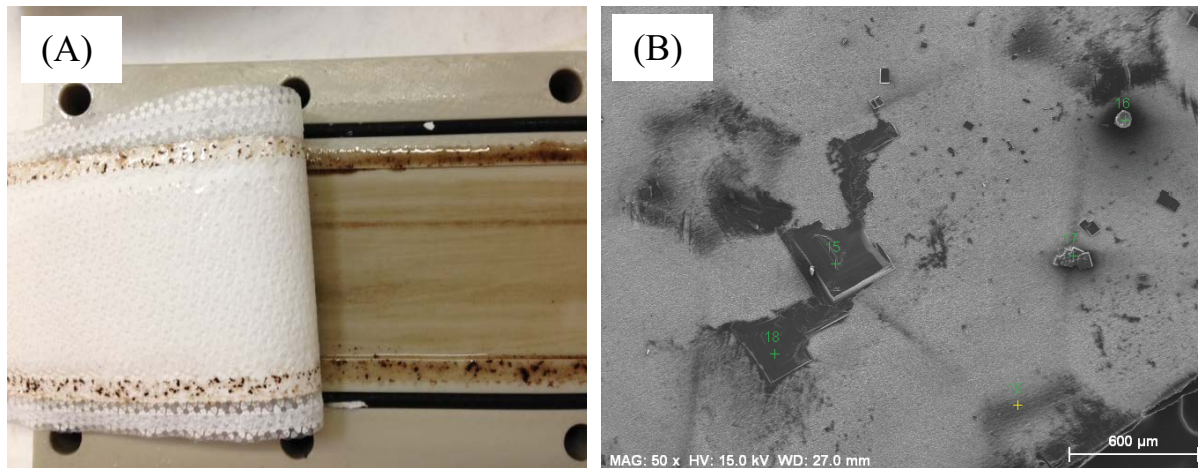


Fig. 8. (A) Real image and (B) scanning electron microscopy image of the scaled membrane surface after the vacuum membrane distillation process of the highly concentrated reverse osmosis retentate.

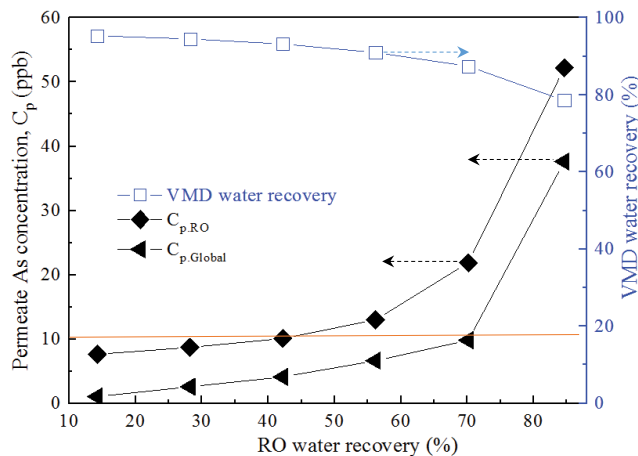


Fig. 9. Simulated permeate arsenic concentration and vacuum membrane distillation water recovery as functions of the reverse osmosis process water recovery during the integrated reverse osmosis/vacuum membrane distillation treatment of arsenic contaminated brackish water (Reverse osmosis input: $[As(III)] = 104$ ppb; $[NaCl] = 10$ mg/L; pH 10 and TMP 24 bar).

to fulfil the 10 ppb allowable maximum arsenic level in the product water (Fig. 9). Consequently, the integrated RO/MD process can obtain a global water recovery of 95.5% under the condition of the product water's arsenic concentration 10 ppb.

It is necessary to note that this significantly high simulated global water recovery is achieved with the assumption that membrane fouling/scaling exerts negligible effects on the arsenic rejection of the VMD membrane. In practical VMD treatment of real brackish water RO retentate, the precipitation of sparingly soluble salts (i.e., particularly silicate) at high water recovery might lead to membrane pore wetting [6], hence resulting in increased arsenic concentration in the product water obtained by the integrated RO/VMD desalination of brackish water. Therefore, further long-term studies on the VMD process of real brackish water RO retentate at high water recoveries are needed.

4. Conclusions

This study explored the integration of reverse osmosis with vacuum membrane distillation (VMD) to improve the As(III) removal and water recovery of brackish water desalination without requirement of pre-oxidation step to convert As(III) into As(V) as it is the case for other conventional treatment processes. The experimental results demonstrate profound influences of the brackish water characteristics (e.g., pH, salinity, arsenic concentration, and organic matters) and the process operating conditions (i.e., particularly water recovery) on the arsenic removal and permeate flux of the RO process. Elevating the feed water pH from 7 to 10 led to increased membrane arsenic rejection but decreased permeate flux. At the feed water pH of 10, the RO process at water recovery below 45% rejected 90% As(III), meeting the permeate arsenic allowable maximum level of 10 ppb. At higher water recoveries, the membrane As(III) rejection decreased, leading to excessive As(III) level in the RO permeate. The presence of organic matters at low content in the brackish water feed favoured the membrane arsenic rejection, enabling the RO process at 60% water recovery with the permeate arsenic level 10 ppb. Operating the RO process at high water recoveries also significantly reduced the RO permeate flux. On the other hand, the VMD process could treat the retentate from the brackish water RO operation at water recovery as high as 80% with negligible impact on VMD water flux and permeate quality. Given its nearly 100% arsenic removal, when applied to desalination of brackish waters the hybrid process based on a combination of VMD process with RO for the treatment of the RO retentate can achieve a global water recovery of 95.5% while fulfilling the condition of arsenic concentration in the product water 10 ppb.

Even though cost aspect in terms of energy consumption was not considered in this stage of the study. The study results clearly show that this coupling process was able obtaining water at the required quality level without using oxidation. This is a first brick in the knowledge on this process and it opens the door for further explorations and optimization, notably on the energy aspects but also with demonstration at larger scale and on longer term before being able to develop this process.

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