

Arsenic removal from drinking water by direct contact membrane distillation

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Abstract. In this study, the treatability of arsenic (As) contaminated water by direct contact membrane distillation (DCMD) at different delta temperatures (ΔT) 30, 40 and 50°C has been investigated. Two different pore sizes (0.22 μm and 0.45 μm) of hydrophobic membranes made of polyvinylidene fluoride (PVDF) were used. The membrane pore sizes, the operating temperatures, the feed solution As concentration and conductivity have been varied during the experimental tests to follow the removal efficiency and flux behavior. Both membranes tested had high removal efficiency of arsenite (As (III)) and arsenate (As (V)) and all permeates presented As concentration far lower than recommended 10 $\mu\text{g/L}$ of world health organization (WHO). As concentration was below detection limit in many permeates. Conductivity reduction efficiency was over 99% and the transmembrane flux (TMF) reached 19 $\text{L/m}^2\cdot\text{h}$ at delta temperature (ΔT) of 50°C with PVDF 0.45 μm membrane. The experimental results also indicated that 0.45 μm pore sizes PVDF membranes presented higher flux than 0.22 μm pore sizes membranes. Regardless of all operating conditions, highest fluxes were observed at highest ΔT (50°C).

Keywords: arsenic removal; contaminated water; hydrophobic membrane; membrane distillation

1. Introduction

Arsenic (As) is a chemical element naturally released into the environment by volcanoes and erosion from mineral deposits. It is also released into the environment from human activities, some agricultural and industrial sources (Singh *et al.* 2015). As contamination of water, especially groundwater has become a serious issue that focused many countries attention worldwide, (Qu *et al.* 2009, Criscuoli *et al.* 2012). Millions of people from South-East America to Argentina, Taiwan, China, Nepal, Bangladesh and India are now affected by groundwater contamination of As (Manna *et al.* 2010, Pal and Manna 2010, Singh *et al.* 2015). Among those countries, Bangladesh and West Bengal (India) are most affected; where arsenic is found in high level concentrations in groundwater, up to 1 mg/L (Petrusevski *et al.* 2007, Criscuoli *et al.* 2012, Jiang *et al.* 2013).

In the environment, As is found in both organic and inorganic forms. They are mostly odorless and tasteless and they do not show any change in the water visible appearance, and thus often remain undetected unless complex analytical techniques are used (Petrusevski *et al.* 2007, Wilson *et al.* 2008). As exists mainly in four oxidation states; arsenate (As (V)), arsenite (As (III)), arsenic

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(As (0)) and arsine (As (-III)) and its solubility depends on the pH and ionic environment. As (III) and As (V) are generally considered to be the dominant species of inorganic As in natural waters (Qu *et al.* 2009). As are well known highly toxic to all forms of life. They are carcinogen, and considered as one of the world's most hazardous chemicals found in water (Jiang *et al.* 2013, Mondal *et al.* 2013). Inorganic arsenicals are generally known more toxic than organic ones. They contamination of groundwater has become one of the most serious problem in water environment. Exposure to As contaminated water can lead to a number of health problems. It can cause increased risks of cancer in the skin, lungs, liver, kidneys, and bladder (Jiang *et al.* 2013). But also non-cancer effects including cardio-vascular, pulmonary, immunological, neurological and endocrine (e.g., diabetes) disorders can occur. These disturbances can eventually lead to death, (Qu *et al.* 2009, Pal and Manna 2010). Drinking water is now recognized as the major source of human intake of As in their most toxic (inorganic) forms. Regarding their toxicity to human, the maximum contaminant level (MCL) for As has been lowered in drinking water from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ by World Health Organization (WHO) in February, 2002 (Petrusevski *et al.* 2007, Qu *et al.* 2009, Pal and Manna 2010, Mondal *et al.* 2013, Caniyilmaz 2013). However, in some countries like India, Bangladesh, Taiwan, China and Vietnam, the MCL for As is still 50 $\mu\text{g/L}$ (Jiang *et al.* 2013, Mondal *et al.* 2013). Considering the ubiquitous state of As, when applying the WHO provisional guideline for drinking water, a population more than 100 million people worldwide including more than 45 million people in developing Asiatic countries (being exposed to more than 50 $\mu\text{g/L}$) are at risk (Singh *et al.* 2015).

Many strategies have been developed to remove As from contaminated groundwater. The removal of As highly depends on the chemistry and composition of the As contaminated water. The major mode of removing As from water is by physical-chemical treatment such as adsorption, coagulation, ion-exchange, membrane technologies (microfiltration, ultrafiltration, nanofiltration, reverse osmosis, hybrid membrane technologies...) and phytoremediation (phytostabilisation, phytoextraction...), (Çakmakci *et al.* 2009, Jiang *et al.* 2013, Elcik *et al.* 2013, 2015, Singh *et al.* 2015). Most of the methods do not remove As (III) as efficient as As (V) (Petrusevski *et al.* 2005, Qu *et al.* 2009, Criscuoli *et al.* 2012, Jiang *et al.* 2013). In addition, the requirement of multiple chemical treatments, pre- or post-treatment of the effluent, high running and capital cost as well as handling of As contaminated sludge are among some major disadvantages of physico-chemical processes (Pal and Manna 2010). Another major problem associated with chemical methods is the requirement of oxidation of As (III) to As (V) before the achievement of a possible satisfactory removal of As. Membrane technologies are capable of removing all kinds of dissolved solids including arsenic from water, however, while high-pressure membranes (nanofiltration and reverse osmosis) have the high potential of removing As (Pal 2015a) by solution diffusion mechanism, low-pressure membranes fail to reject As in polluted waters, unless coupled with physical-chemical methods. Elcik *et al.* (2013) investigated the removal of As from drinking water using low pressure membranes. They reported that As (III) or As (V) was not rejected by the membranes, however membrane filtration after ozone oxidation and iron coagulation removed up to 85% and 96% of 100 and 1000 $\mu\text{g/L}$ As (III), but still, effluent target concentration (10 $\mu\text{g As/L}$) was not reached.

Recently, membrane distillation (MD) has been investigated as a possible alternative technique for the treatment of water contaminated by As. MD is a thermally driven process, in which water vapor transport occurs through a non-wetted porous hydrophobic membrane (Meng *et al.* 2015, Boubakri *et al.* 2015). The driving force of MD is the vapor pressure difference created by temperature difference across the membrane; hot feed side and cold cooling side (Pal 2015b). In its

principle, only water vapor and volatile compounds can pass through the membrane, all non-vaporizable particles such as As are rejected. During the process, the membrane must not be wetted; its original material is water repellent (hydrophobic) keeping water to pass through it unless the applied hydrostatic pressure is higher than the membrane liquid entrance pressure (LEP) (Pal 2015). Membrane distillation technique was mostly used in desalination, but now it is extended to water recycling, food and pharmaceutical sectors. It has several advantages compared to conventional techniques; it operates at lower temperature compared to conventional distillation processes, at lower pressure in comparison with pressure-driven membrane systems, it also provides high treatment efficiency with very high rejection of ions, macromolecules, colloids, cells and other non-volatiles compounds, it is more efficient and economical in terms of energy use specially when renewable energies are used (Boubakri *et al.* 2015, Kezia *et al.* 2015, Wang and Chung 2015). Membrane fouling is the main problem encountered in all membrane separation processes, however, due to large membrane pore sizes in MD and the direct contact of the membrane with the vapor (instead of liquid) at the vapor–liquid interface (at the feed side) largely reduce membrane fouling and clogging in MD process compared to other membrane technologies (Pal 2015b). Membrane wetting encountered during long-term MD can be reduced when using higher hydrophobic and uniformly distributed smaller pores membranes as reported by Wang and Chung (2015). There are four main MD configurations depending on the cooling side arrangement and the way effluent is collected from the MD module (Wang and Chung 2015). These configurations are direct contact membrane distillation (DCMD), sweeping-gas membrane distillation (SGMD), vacuum membrane distillation (VMD) and air gap membrane distillation (AGMD). DCMD, in which condensed vapor (usually water) on the permeate side of the membrane is in direct contact with the membrane is the simplest, cheapest and popular configuration among these configurations (Meng *et al.* 2015). For AGMD and DCMD water vapor condensation takes place inside the membrane module, external condenser is not required contrarily to SGMD and VMD (Abu-Zeid *et al.* 2015). The module complexity is reduced in the first two configurations and an additional expense for external condenser is not necessary. Most of researches carried in the field of heavy metals removal such as As with MD system showed almost 100% rejection efficiency from the contaminated groundwater (Criscuoli *et al.* 2012, Manna *et al.* 2010, Pal and Manna 2010). These results are interesting and may be an opening door for As free groundwater in the future.

Dao *et al.* (2016) used VMD to remove As (III) in synthetic arsenic contaminated water in Vietnam. They reported up to 98.5% rejection and they yielded permeate with As (III) concentration meeting the required standard for drinking water. Manna and Pal (2016) used a cross-flow flash vaporization membrane distillation (FVMD) with a composite flat-sheet polytetrafluoroethylene (PTFE) membrane to remove arsenic up to 99% from contaminated groundwater. They reported that, no arsenic was detected in all permeate samples. Similarly, Bhattacharya *et al.* (2014) investigated the removal of toxic chromium (VI) from simulated water with a DCMD and reported a successful rejection. The system was efficient to remove all kind of heavy metals. Tomaszewska *et al.* (2001) used MD system to investigate the concentration of solutions containing hydrochloric acid (HCl) and salts used to clean metal surfaces before electroplating. They reported the effectiveness of the MD system to recover HCl from industrial effluent and permeate was purified enough to be reused during electroplating processes. Similarly, Chen *et al.* (2013) conducted successfully a study with DCMD to reduce industrial wastewater and recover gold. They recovered by electrolysis up to 90% gold solution initially concentrated by DCMD. Karakulski *et al.* (2009) investigated the treatability of acidic saline wastewater generated

during steel wire manufacturing. They stated that the obtained permeates were clean water free of metals with electrical conductivity at a level of 3-5 $\mu\text{S}/\text{cm}$ and this permeate water was presented suitable to be reused in the industry.

As mentioned above, intake of As through water causes serious health threats, however proposed mostly physico-chemical treatment methods failed to meet the regulations addressed by WHO, or expensive and multiple step processes are required to reduce As concentration to an acceptable level in water. The effective rejection of non-volatile components during a single step treatment of the MD process can be used efficiently to treat heavy metals such as As due to their known non-vaporable nature. The aim of this study is to access an effective treatment of arsenic contaminated drinking water by MD. A polyvinylidene fluoride (PVDF) hydrophobic membrane is used with pore sizes of 0.22 μm and 0.45 μm , in a modified direct contact membrane distillation (DCMD) to investigate the treatability of synthetic arsenic contaminated drinking water. The effect of membrane pore size, feed and distillate temperature, salinity, As concentration in the feed, and the operating time on the As removal efficiency and flux are investigated.

2. Materials and methods

2.1 Membrane distillation unit

A laboratory scale modified DCMD apparatus made of Teflon with a flat-sheet membrane cell (Membrane-Solution) was used. Generally encountered problem in DCMD configuration is transmembrane heat loss. Loussif and Orfi (2016) investigated a comparative study of DCMD, AGMD and SGMD configurations and reported that DCMD configuration provided the highest permeate quality while SGMD showed the highest thermal efficiency. The modification in the present DCMD configuration intended to minimize heat loss in the system consequently to enhance the treated water flux by separating the cooling part of the system by a stainless steel plate. A gap similar to the one in AGMD, is created in the membrane module at the permeate side, but still cool water is used to condense permeate vapor. A schematic diagram of the modified DCMD set-up is shown in Fig. 1.

The effective membrane area was 150 cm^2 . The feed tank, the heater and the cooler were built locally to achieve the required feed and distillate temperature. The volume of the feed tank was 5 L and the tank was wrapped and heated by 1 kW electrical heating elements. The heating and cooling systems ensured the heating of the feed tank solution and the cooling of the vapor formed in the permeate side of the membrane, respectively. CAT Pump 2SF35SEEL-Stainless Steel Direct-Drive Plunger Pump and Watson Marlow Peristaltic pump 323 Du/D were used to circulate feed hot solution and cooling water in the DCMD module, respectively. The flow-rate, temperatures and operating pressures were monitored by a flow-meter, digital temperature probes and manometers, respectively. A digital balance connected to a personal computer was used to measure the permeate water mass and to calculate the flux.

2.2 Experimental conditions

Experiments were conducted for initial As (III) and As (V) concentration of 100 $\mu\text{g}/\text{L}$ and 1000 $\mu\text{g}/\text{L}$. The pressure, feed solution flow rate and temperature of cooling water were almost kept constant at 0.5 bars, 4.5 liter per minute (LPM) and 10°C, respectively. Heat-exchanger was used to keep constant cooling water. The study was carried out at three different feed temperatures (40, 50 and 60°C) giving different ΔT of 30, 40 and 50°C.

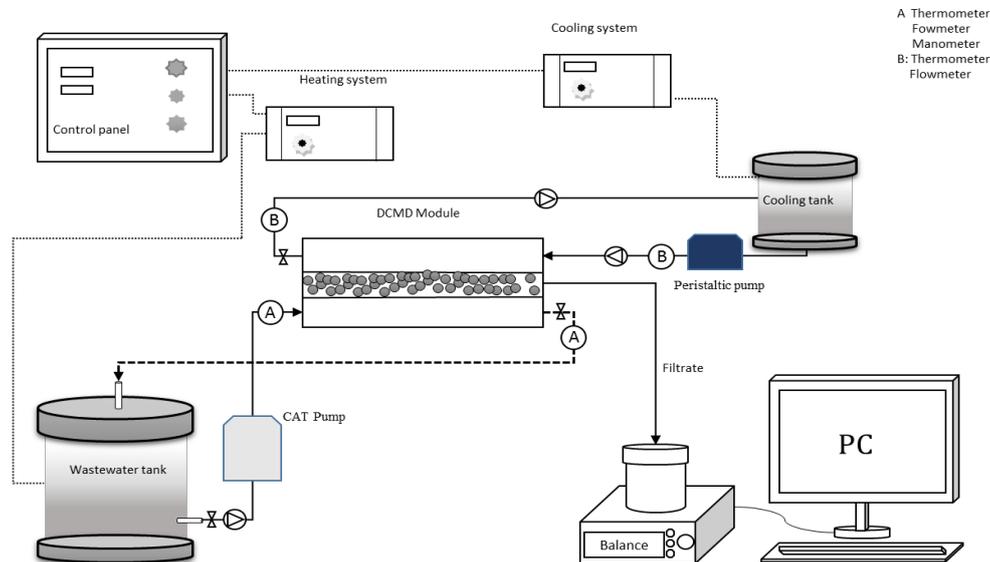


Fig. 1 Schematic flow diagram of the lab scale modified DCMD

Table 1 Characteristics of the membranes

Membrane structure	Pore size (μm)	Thickness (μm)	Flow rate (ml/min/cm ² @10psi)	Bubble point (psi)	Wettability
PVDF 0.22	0.22	140-180	4.5-6.3	16-20	Hydrophobic
PVDF 0.45	0.45	120-180	10.5-16.5	14.5-17.5	Hydrophobic

Table 2 Tap water characteristics

Parameters	Values	Parameters	Values
SO ₄ ⁻² , (mg/L)	120	Br ⁻ , (mg/L)	0.15
PO ₄ ⁻³ , (mg/L)	0.16	F ⁻ , (mg/L)	0.14
NO ₃ ⁻ , (mg/L)	1.5	pH	7.5
Cl ⁻ , (mg/L)	97	Temperature, (°C)	21.7

2.3 Membranes

Two different pore sizes (0.22 μm and 0.45 μm) hydrophobic membranes made of Polyvinylidene fluoride (PVDF) manufactured by Membrane-Solution-LLC were used. Their main characteristics are summarized in Table 1.

2.4 Reagents and stock solutions

The synthetic arsenic, As (III) and As (V), contaminated waters used as feed solutions were prepared by diluting 0.1 N sodium arsenite and arsenate stock solution (3.75 g/L as As) (Merck, Germany; 99% purity) in tap water to obtain As (III) and As (V) concentration of 100 or 1000

Table 3 Characteristics of arsenic contaminated water

Contaminants	As concentration ($\mu\text{g/L}$)	pH	Conductivity ($\mu\text{S/cm}$)
Arsenite	100 & 1000	7	633-804
Arsenate	100 & 1000	7	689-695

$\mu\text{g/L}$. The pH of the tap water used was approximately close to neutral value (typical of real groundwater) so that the oxidation state of As of these feeds does not change. The characteristics of the tap water are shown in Table 2 while the characteristics of the synthetic feed As solution used during this study are presented in Table 3.

2.5 Analytical methods

Total As was measured using Perkin-Elmer Analyst 400 graphite furnace atomic absorption spectrometer equipped with a graphite tube atomizer and programmable auto sampler. High purity argon gas was used to purge the volatilized matrix materials and to protect the heated graphite tube from air oxidation. As electrodeless discharge lamps (EDL) were used at a wavelength of 193.7 nm with a slit width of 2.7 nm. Operating currents of electrodeless discharge lamps were 400 mA. Conductivity being the ability of a water solution to conduct electricity, determines the amount of dissolved salt in a solution. It is a general indicator of water quality; it can be used to monitor processes in the water/wastewater (Levlin S-100 44). Conductivity was measured at room temperature ($24\pm 1^\circ\text{C}$) using Thermo Scientific Orion 5-Star Plus pH/ ORP/ ISE /Conductivity /DO Meter.

3. Results and discussion

3.1 Conductivity reduction

In water, conductivity is affected by the presence of inorganic dissolved solids. Initial conductivities of feed water (tap water) used for this study were approximately between 600 and 800 $\mu\text{S/cm}$. Permeate from the MD unit showed very low conductivity. The conductivity rejection efficiency was generally over 90% for both As (III) and As (V) as shown in Fig. 2. Conductivity of all permeates was low with smaller pore size membranes (0,22 μm) having the lowest conductivity. Low permeate conductivity is the result of dissolved ions, including As, being retained by the hydrophobic membrane. In fact, all non-evaporable components in feed solution cannot pass through the hydrophobic membranes pores; they are kept at the feed side. Because of the low initial conductivity, less than 1000 $\mu\text{S/cm}$, rejection efficiency may look not very high (about 90%) but effluent conductivity is very low, approximately 10 $\mu\text{S/cm}$ in some cases.. At an increasing feed temperature, it is shown an exponential raise of the permeate conductivity. Chen *et al.* (2013) pointed out the existence of a strong negative correlation between feed conductivity and permeate flux, flux itself correlated with feed temperature. As shown in Fig. 2, permeate conductivity increased almost 2 fold when feed temperature increased from 40 to 60 $^\circ\text{C}$ (ΔT from 30 to 50 $^\circ\text{C}$). This may due to the slight evaporable nature of some components at high temperature, which may participate to conductivity. In addition, high temperatures increase dissolved ions mobility. It also affects membrane hydrophobicity and pore sizes because it flexibilizes the membrane structure. Consequently, some dissolved ions can force the more vulnerable membrane pores and pass

through it, raising slightly the effluent conductivity at high temperature. However, almost permeate was distilled water low in mineral contents.

A second part of the study consisted of increasing the conductivity of the feed solution to approximately 2500 $\mu\text{S}/\text{cm}$, 5000 $\mu\text{S}/\text{cm}$ and 10000 $\mu\text{S}/\text{cm}$ by dissolving some salt in the solution. The intension was to follow As rejection behavior and the flux trend at high salinity. Even though raising conductivity slightly decreased the rejection efficiency of the As, the influence was negligible. In previous work with boron contaminated water, Boubakri *et al.* (2015) investigated the effect of operating parameters on boron removal from seawater using membrane distillation process and stated that feed salt concentration had no significant influence on permeate flux and boron rejection rate. Similar behavior has been recorded in our work; As have been removed from all feed solutions up to 99% and their concentrations in the permeate remained very low. Permeate

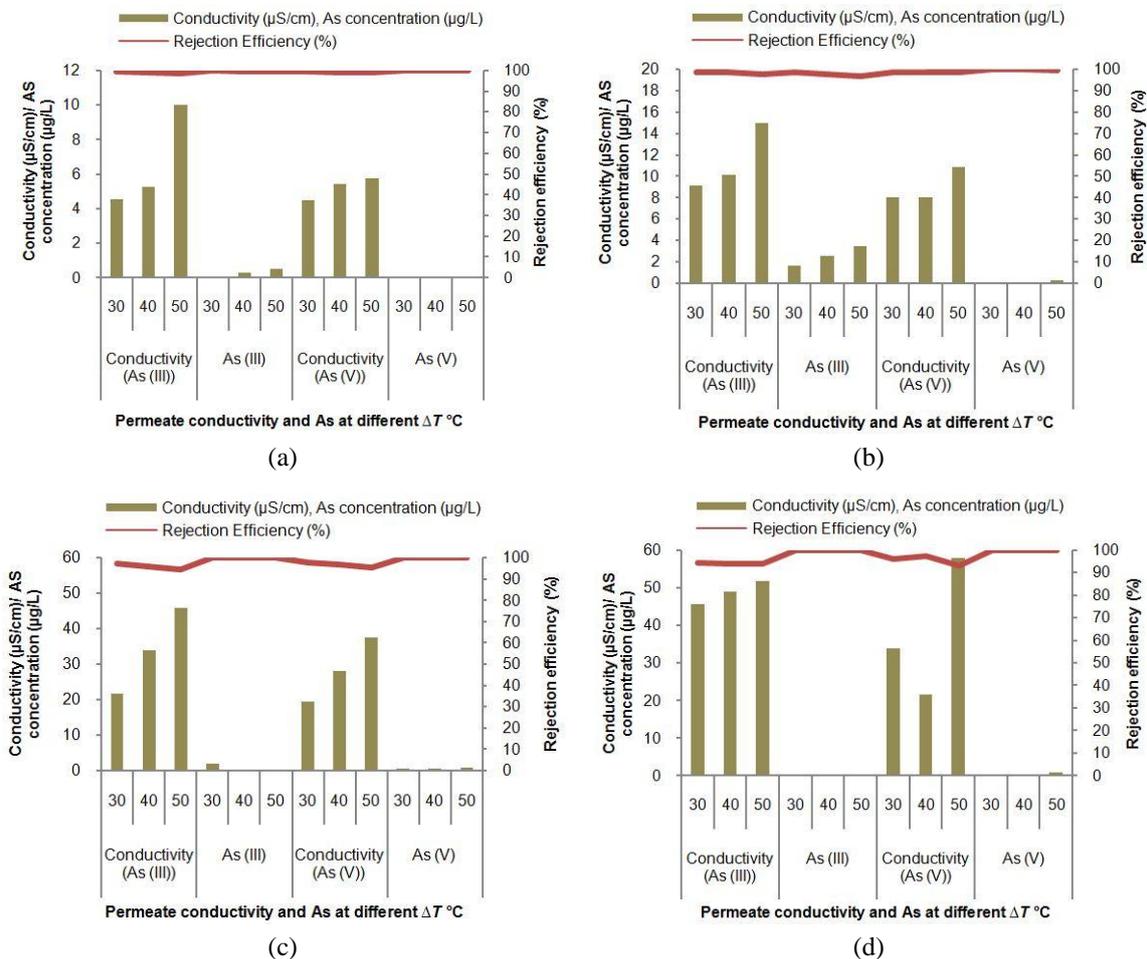


Fig. 2 Rejection efficiencies of conductivity and As: (a) PVDF 0.22, feed solution conductivity 633 $\mu\text{S}/\text{cm}$, feed solution As concentration 100 $\mu\text{g}/\text{L}$; (b) PVDF 0.45, feed solution conductivity 633 $\mu\text{S}/\text{cm}$, feed solution As concentration 100 $\mu\text{g}/\text{L}$; (c) PVDF 0.22, feed solution conductivity 804 $\mu\text{S}/\text{cm}$, feed solution As concentration 1000 $\mu\text{g}/\text{L}$; (d) PVDF 0.45, feed solution conductivity 804 $\mu\text{S}/\text{cm}$, feed solution As concentration 1000 $\mu\text{g}/\text{L}$

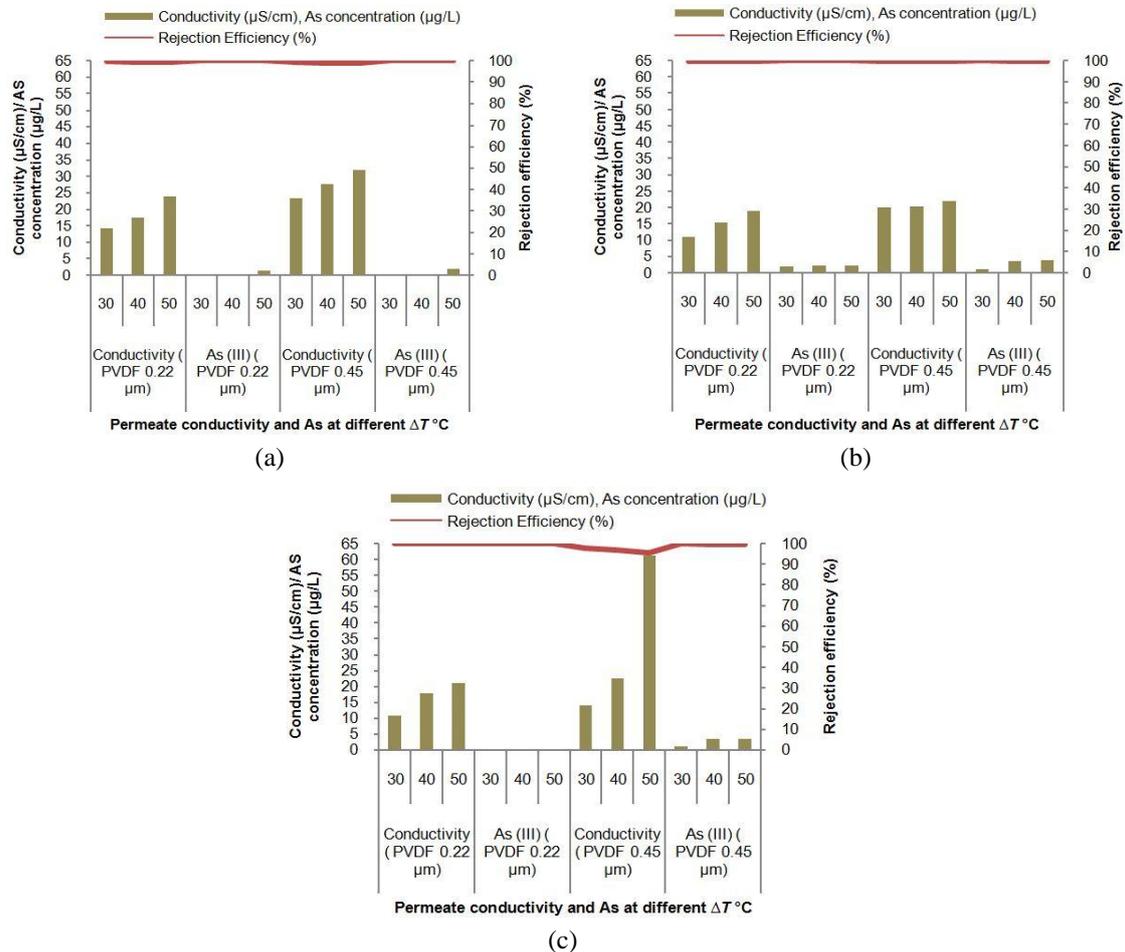


Fig. 3 Influence of salinity on conductivity and As (III) rejection: (a) PVDF 0.22 μm and PVDF 0.45 μm , feed solution conductivity 2665 $\mu\text{S/cm}$, feed solution As (III) concentration 1000 $\mu\text{g/L}$; (b) PVDF 0.22 μm and PVDF 0.45 μm , feed solution conductivity 5140 $\mu\text{S/cm}$, feed solution As (III) concentration 1000 $\mu\text{g/L}$; (c) PVDF 0.22 μm and PVDF 0.45 μm , feed solution conductivity 10030 $\mu\text{S/cm}$, feed solution As (III) concentration 1000 $\mu\text{g/L}$

conductivity were slightly influenced by initial salt concentration. It is assumed that some salt settled on the membrane surface at feed side and may cause slight diffusion mechanism of salty solution into the permeate and deteriorate its quality. Nevertheless the membranes presented good rejection of the salt, and permeate conductivity was very low as shown in Fig. 3.

3.2 Arsenic removal

During this study with DCMD, As (III) and As (V) as well as all non-evaporable substances in the feed solution were importantly kept in the concentrate flow. All As tested, regardless of their oxidation state were reduced to a very minimum concentration in the permeate. Because of the hydrophobic nature of the membranes used, water and non-evaporable compounds do not pass

through it. Theoretically, it is expected that only mineral free water vapor passes through the membrane and condense once in contact with the cooling area of the module. The removal of As with membrane distillation takes profit of this characteristic. Due to their tiny size, As particles can force the membrane barriers when pressure is applied in some membrane filtration and conventional filters and pollute the permeate water. In the present study, no pressure is required and the hydrophobic membranes prevent all water to pass through their pores and carry some particles with it. Only vaporized molecules can pass through the membrane in a vapor state. No vaporizing compounds such as As (III) and As (V) are kept away from the membrane pores and are retained at the feed side as concentrate. Criscuoli *et al.* (2012) investigated As removal with vacuum membrane distillation and reported same results. As was removed to under detectable concentration in all effluent and they stated that this result is due to the fact that in VMD only volatile species, like water vapor, are transferred through membrane micropores, while the nonvolatile species, like As, are retained.

As (III) and As (V) concentration in the effluent and the removal efficiency are shown below in Fig. 4. Almost 100% As (III) and As (V) removal have been achieved in this study. As stated by Criscuoli *et al.* 2012, the rejection efficiency does not depend on the oxidation state of the As (As (III) or As (V)). The rejection was satisfactory and permeate As concentration was below the recommended 10 $\mu\text{g/L}$ by WHO. Many other researchers (Criscuoli *et al.* 2012, Qu *et al.* 2009, Manna *et al.* 2010, Pal and Manna 2010, Manna and Pal 2016 and so on) reported the same efficiency of MD for As rejection and most of them claimed over 99% rejection and As concentration below recommended WHO 10 $\mu\text{g/L}$ concentration. Very small amount, negligible, passed through the membrane by size exclusion mainly due to the non-uniform nature of the pores and their possible denaturation when high temperature is applied to their structure. As a result, As is treated in a one step process without any requirement of converting arsenite into arsenate before being treated. In fact, many technics in the literature can remove As (V), with some limits, however As (III) removal remained difficult and an important pathway of As (III) removal is required, its oxidation into arsenate followed by its removal (Caniyilmaz 2003, Elcik *et al.* 2013). But this causes further pollution and higher the treatment cost. For instance Elcik *et al.* (2013) achieved up to 96% As (III) removal during oxidation technics followed by different ultrafiltration membranes treatment. They stated that an entrapment of As (V) with the iron coagulates significantly improved the arsenic rejection by ultrafiltration membranes. In addition it was observed that (Fig. 2) As concentration in the feed solution did not affect the rejection efficiency of both As (III) and As (V). Both initial feed concentration of 100 $\mu\text{g/L}$ and 1000 $\mu\text{g/L}$ yielded As free permeate or very low concentration. Same result was reported by Manna and Pal (2016) where they varied feed As concentration from 500 to 2000 $\mu\text{g/L}$ in a flash vaporization membrane distillation module. During the 6 hours operating time for each membrane set, no significant variation is observed in As rejection efficiency. It was obvious that the membrane was not wetted and was capable to be used for many hours without it losing its integrity as reported by Manna and Pal (2016).

Fig. 5 shows the behavior of As removal at high salinity water. When raising the feed solution conductivity approximately up to 2500, 5000 and 10000 $\mu\text{S/cm}$ by adding some salt, arsenic removal efficiency was not very much influenced. As (V) has been removed to over 99% and arsenite concentration in the permeate remained very low in all treatment conditions. Boubakri *et al.* (2015) observed the same result during boron removal with DCMD. In fact, hydrophobic membranes had no selective rejection of non-volatile solute. As a consequence, the feed salt concentration had no important influence on As rejection performance. However, at high

temperature (60°C heating temperature), the tortuosity of the membrane pores and the negative effect of temperature may cause some small particles to escape and contaminate the effluent solution, this may explain the presence of As (III), approximately 3.5 µg/L in some permeates.

3.3 Transmembrane flux

The parameters to assess the MD separation performance can be expressed in several ways but one of the most important parameter is the flux as it has direct impact on system implantation cost and its feasibility. The experimental flux (J) can be expressed as follows

$$J = \frac{m_p}{A_m * t} \quad (1)$$

where m_p , A_m and t are permeate mass, membrane area and operation time, respectively (Pal and Manna 2010, Yarlagađda *et al.* 2011). Many parameters such as temperature, feed pH, feed concentration and flow rate, membrane properties, operating time and fouling are known among many others to deeply influence the flux (Manna *et al.* 2010, Pal and Manna 2010, Yarlagađda *et al.* 2011, Abu-Zeid *et al.* 2015, Dao *et al.* 2016). Flux of the different type of membranes and feed solution used during this study are depicted by the graphs in Figs. 4, 5 and 6. The highest fluxes are observed at the highest ΔT (50°C) with PVDF 0.45 membranes as shown in Fig. 4.

In this study, as seen in Fig. 4, the flux increased with raising ΔT . The highest flux observed was approximately 19 Kg/m².h at ΔT equal 50°C with PVDF 0.45 µm with 1000 µg/L As. Criscuoli *et al.* (2012) reported the increase of the flux from 3 to 12.5 kg/hm² during VMD treatment of As at 20°C and 40°C, respectively. Well known as temperature dependent in MD process, the flux was strongly influenced by not only feed temperature but also membrane structure and pore size. In fact, higher temperature foster vapor formation and consequently the driving force (Yarlagađda *et al.* 2011). Feed solution heated at 60°C ($\Delta T = 50^\circ\text{C}$), regardless of membrane structure and pore size presented better flux compared to those heated at 40°C ($\Delta T = 30^\circ\text{C}$) and 50°C ($\Delta T = 40^\circ\text{C}$). This exponential increase of flux with high feed temperature is

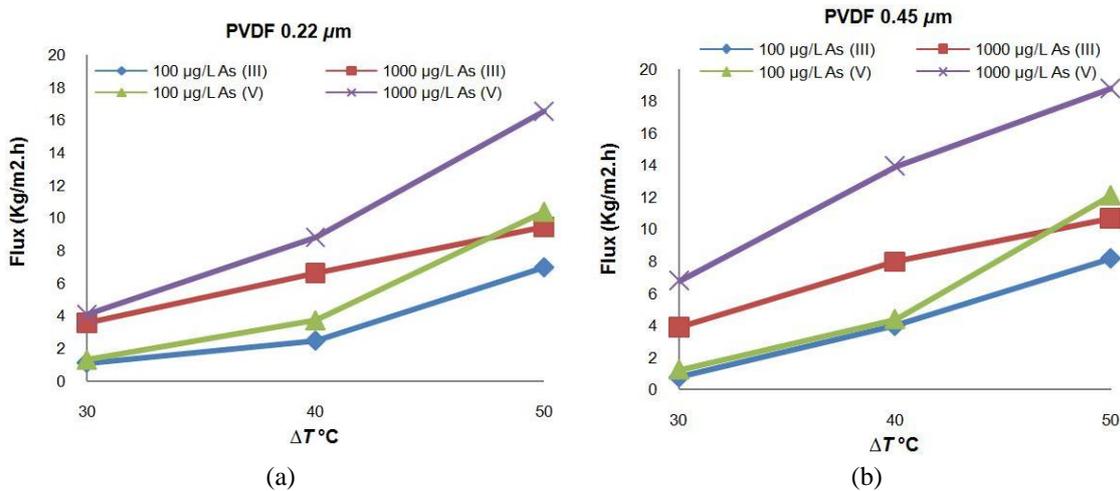


Fig. 4 The influence of ΔT : a strong positive correlation between ΔT and transmembrane flux

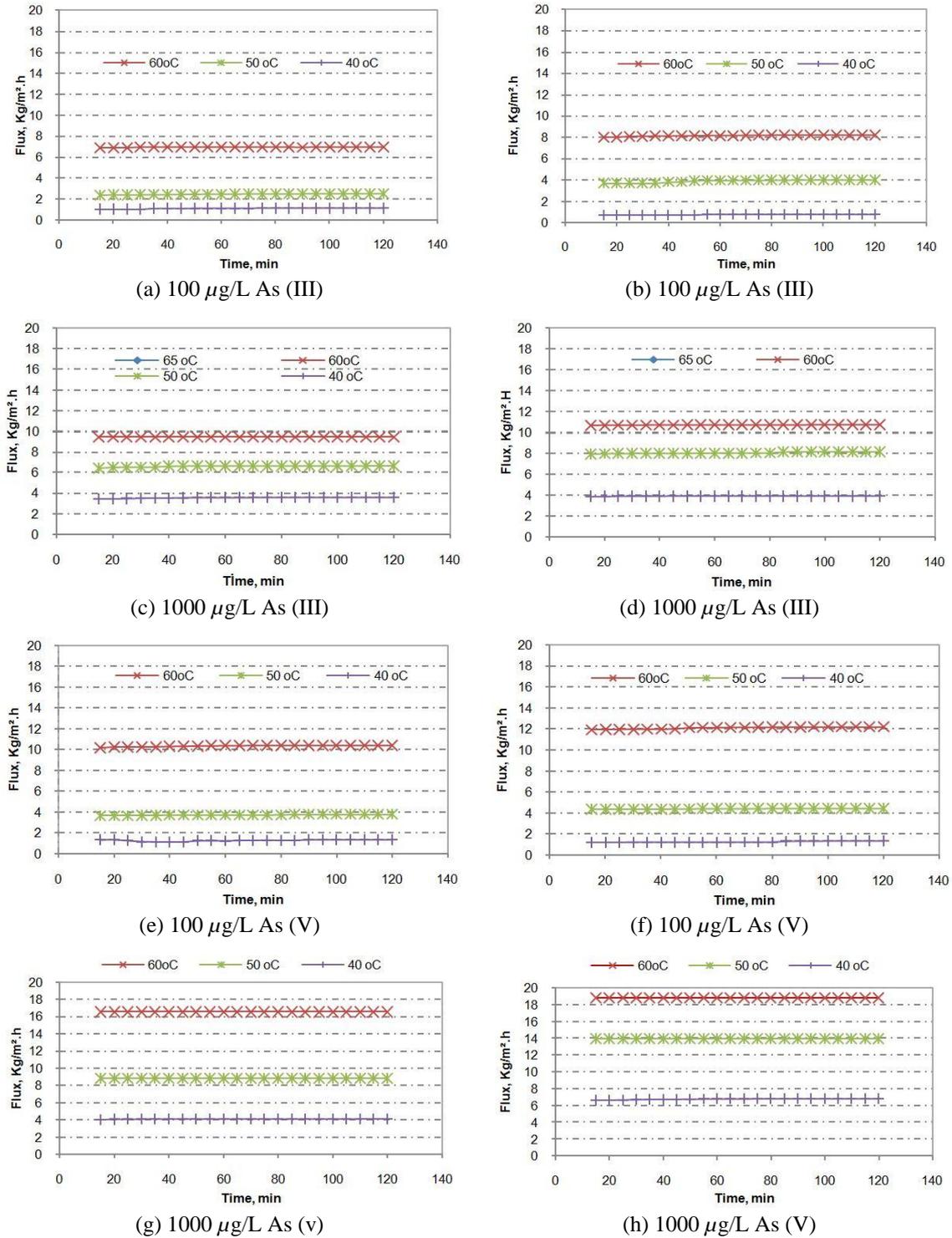


Fig. 5 Transmembrane flux over increasing temperature of Arsenite As (III) and Arsenate As (V) 100 and 1000 $\mu\text{g/L}$ contaminated drinking water: (a) PVDF 0.22 μm ; (b) PVDF 0.45 μm

unanimously approved by researchers. However, high feed temperature can cause some undesirable chemicals in the feed solution to vaporize and alter the permeate quality. In addition, the integrity of the membrane structure is threatened when temperature is high, only membranes withstanding high temperature can be used in this purpose. Treatment at low feed temperature may not be successful in term of flux but the effluent quality remained higher.

As depicted by Fig. 5, larger pore size membranes yielded higher permeate flux compared to smaller pore size membranes. Permeate flux is proportional to the pore size of the membrane as reported by Abu-Zeid *et al.* 2015. Large pores facilitated mass transfer; high amount of water vapor crossed the membrane per unit of time and as a consequence more vapor was condensed and collected at the permeate side. However, it is worth to underline that smaller particles such as

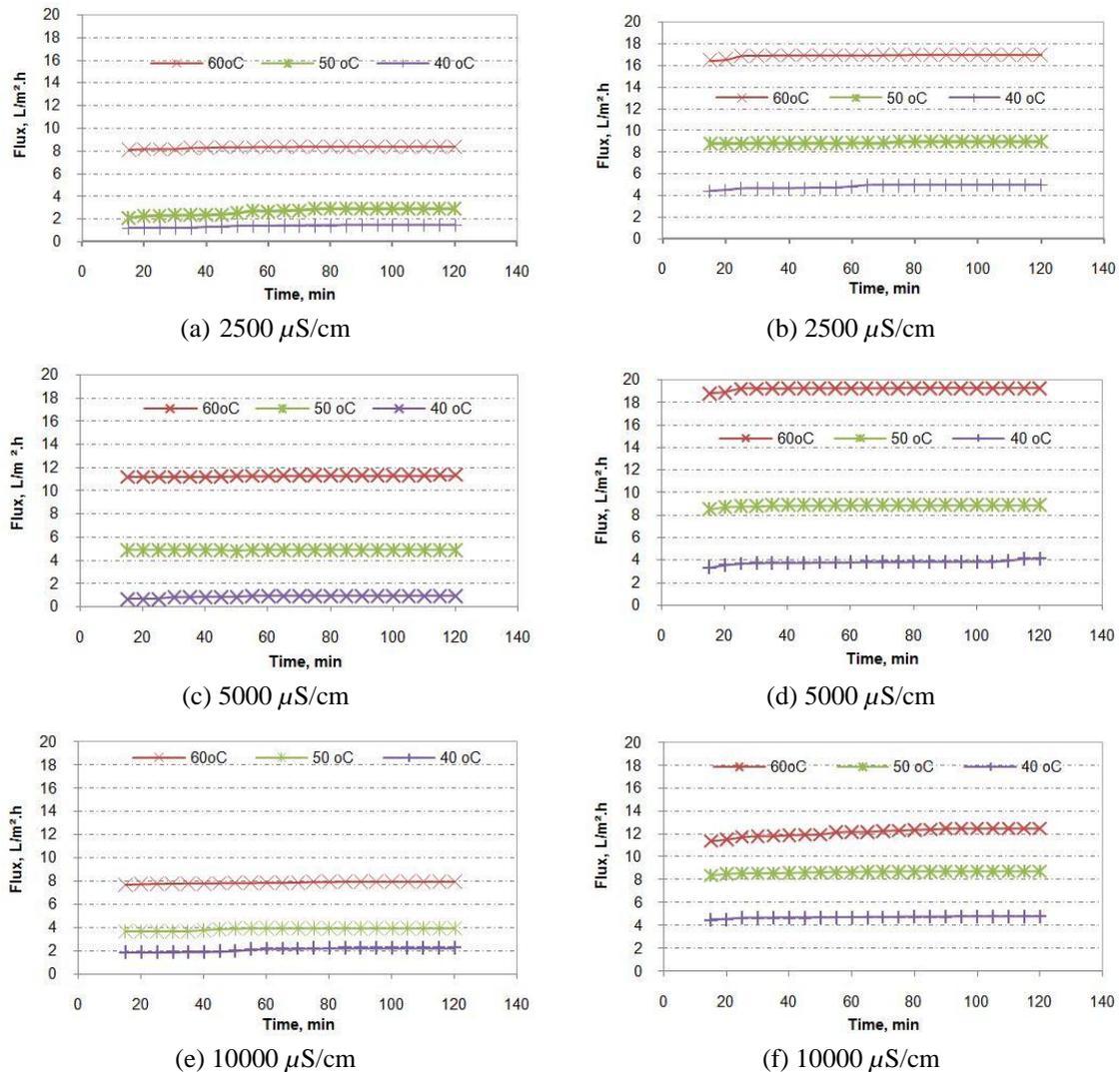


Fig. 6 Transmembrane flux over increasing temperature and salinity of As (III) 1000 $\mu\text{g}/\text{L}$ contaminated drinking water: (a) PVDF 0.22 μm ; (b) PVDF 0.45 μm

inorganic dissolved ions at high concentration may force larger pores and pass through them, worsening the permeate quality. The smaller the pore size was the lower the flux was but the higher the achieved permeate quality was. In this study it was also noticed that the flux remained stable during the 6 hours experimental study for each membrane set. Neither membrane fouling nor wetting was observed. Criscuoli *et al.* (2012) reported similar results; they stated during synthetic arsenic polluted water treatment with MD that there was no fouling issue. Bhattacharya *et al.* (2014) and Manna and Pal (2016) observed similar membrane behavior using PTFE membrane for the removal of chromium (VI) and As, respectively. During As (III) removal from brackish groundwater by VMD, Dao *et al.* (2016) reported similar flux behavior for a short-term operation (2 h). They stated that long-term operation can lead to accumulation of inorganic and organic matter upon membrane surface and cause membrane fouling that eventually will reduce the flux. Manna and Pal (2016) worked for 40 hours and stated there was no flux drop during this period. In fact, it is believed that in a typical MD process, the permeate flux remains relatively stable for several hours, before declining (Levlin 2012). No considerable decline of the flux occurs over time because liquid-vapor interface of the MD process sustains the system and reduces any rapid decline of the flux due to feed concentration.

The second part of the study revealed that the flux increased with slight increase of salinity. Fig. 6 presents the flux behavior when feed solution conductivity is increased from 2500 to 10000 $\mu\text{S}/\text{cm}$. The salt in the feed solution may coprecipitated with As (III) ions and settled in the feed tank. The feed solution circulating in the module being less concentrated in pollutants (settled in the tank), the transmembrane flux gets high and no fouling or scaling takes place. When salt concentration is very high, salt may deposited on the membrane surface and caused membrane scaling. Abu-Zeid *et al.* 2015 reported that the flux decrease is due to high concentration of non-volatile solute which reduces the driving force. Transmembrane flux reduced at 10.000 $\mu\text{S}/\text{cm}$ where salt concentration was very high. An increase of salt concentration of the feed solution caused some physical and chemical properties such as viscosity and concentration to take place. This phenomenon has an impact on the interface membrane-solution and concentration polarizations as well as temperature polarization take place and caused the flux drop. Feed solution characteristics and concentration strongly affected both effluent quality and transmembrane flux.

4. Conclusions

Arsenic removal being one of the environmental engineers challenge to meet WHO suggested maximum concentration have been investigated in this study using a modified direct contact membrane distillation unit. Both arsenic and arsenate have been removed successfully with PVDF membranes and effluent As concentration was such low below detection in some cases. The results of this study may be drawn as follows:

- Conductivity was removed up to 99% and the highest effluent conductivity was observed at the highest heating feed solution with larger pore size membrane. Membrane properties, feed temperature and feed solution initial salt concentration had high influences on conductivity removal.
- As (III) and As (V) concentrations were decreased below target concentration of 10 $\mu\text{g}/\text{L}$ as recommended by WHO. The efficiency of the removal did not depend on the oxidation state of As. Effluent concentration was below detection for both As species in many of the tests conducted. Membrane characteristics and feed solution temperature played a role in removal

efficiency. As concentration (100 and 1000 $\mu\text{g/L}$) and salt concentration did not influence importantly the removal inefficiency.

- Temperature was the most important parameter that affected the flux. An increase in ΔT showed an exponential increase of the flux in almost conditions. In addition to temperature, membrane characteristics such as pore size, also affected flux. 0.45 μm pore size membrane achieved better flux in comparison with 0.22 μm pore size membrane. The increase of salt concentration of the feed solution slightly increased the flux but flux drop occurred at very high salt concentration. However, further studies are necessary to understand the chemical effect of this phenomenon.
- A long-term pilot scale study using varied salts may be required for a better understanding of the flux behavior over time, membrane wetting and the influence of the salts on As rejection by MD system.

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