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THE EFFECTS OF FERRIC IRON AND ORGANIC MATTER ON ARSENITE REMOVAL FROM WATER BY DIRECT CONTACT MEMBRANE

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ABSTRACT

The present study investigated the influence of ferric iron (Fe (III)) and organic matter (OM) on arsenite (As (III)) rejection from a synthetic contaminated water by direct contact membrane distillation (DCMD). Two different pore sizes (0.22 µm and 0.45 µm) of hydrophobic membranes made of Polytetrafluoroethylene (PTFE) were used at different feed temperature (40, 50 and 60 oC). The operating temperatures, the feed solution Fe (III) and OM concentration have been varied during the study to follow pollutants rejection efficiency and flux behavior. Fe (III) and OM concentration in the solution did not affect negstively As(III) rejection; both membranes used had high rejection efficiency and permeate arsenic (As) concentration was lower than recommended 10 µg/L. As (III) concentration was below detection limit in many permeates. Fe(III) and OM contributed to higher rejection of As(III) and better transmembrane flux. Conductivity and As(III) was rejected up to 99%. In presence of Fe(III) and at feed temperature of 40 and 50 oC, As(III) was non-detectable in the permeate.

Keywords: Arsenite removal, contaminated water, hydrophobic membrane, membrane distillation.

DOĞRUDAN TEMASLI MEMBRAN DİSTİLASYONU İLE SUDAN ARSENİT GİDERİMİNDE FERRİK DEMİR VE ORGANİK MADDENİN ETKİSİ

ÖZ

Bu çalışmada doğrudan temaslı membran distilasyonu (DCMD) ile sentetik kontamine sudan arsenit (As (III)) giderimine ferrik demir (Fe (III)) ve organik maddelerin (OM) etkisi incelenmiştir. Hidrofobik karakterdeki 0,22 ve 0,45 µm por çaplarına sahip politetrafloroetilen (PTFE) hidrofobik membranları kullanılmış ve farklı besleme sıcaklıklarında (40, 50 ve 60 oC) çalışılmıştır. Giderim verimi ve akıdaki değişimleri gözlemlemek için farklı çalışma sıcaklıklarında ve farklı Fe (III) ve organik madde konsantrasyonlarına sahip besleme suları ile çalışılmıştır. Besleme suyundaki Fe (III) ve OM konsantrasyonu As (III) giderimini olumsuz etkilememiştir ve kullanılan membranlarda yüksek giderim verimi elde edilmiş ve süzüntüde arsenik (As) konsantrasyonu 10 µg/L olan limit değerin altında olmuştur. Farklı çalışmalarda elde edilen süzüntülerin pek çoğunda As (III) konsantrasyonunun tespit sınırının altında olduğu belirlenmiştir. Fe (III) ve OM membran akısının yükselmesine ve daha yüksek As (III) giderimine katkıda bulunmuştur. İletkenlik ve As (III) giderim verimi 99%'a ulaşmıştır. Fe (III) bulunan besleme suyu ile 40 ve 50 oC'de yapılan çalışmalarda süzüntüdeki As (III) konsantrasyonunun tespit sınırının altında olduğu belirlenmiştir.

Anahtar Sözcükler: Arsenit giderimi, kontamine su, hidrofobik membran, membran distilasyonu.

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1. INTRODUCTION

Arsenic (As) mainly present in organic and inorganic form is a pollutant released naturally or and anthropologically into the environment. It is highly toxic (especially inorganic one) and is known to be a serious groundwater pollutant in many countries [1], [2], [3]. Millions of people from South-East America to Argentina, Taiwan, China, Nepal, Bangladesh and India are now affected by groundwater contamination of As [3],[4],[5]. As exists mainly in four oxidation states; arsenate (As (V)), arsenite (As (III)), arsenic (As (0)) and arsine (As (-III)). Its solubility depends on the pH and ionic environment. However, As (III) and As (V) are the dominant species of inorganic As in natural waters [1]. The exposure to arsenic contaminated water can lead to a number of health problems. As can cause increased risks of cancer in the skin, lungs, liver, kidneys, and bladder [6] and so many other diseases that can eventually lead to death. Drinking water being the major source of human intake of As in its most toxic forms, the maximum contaminant level (MCL) for As has been lowered in drinking water from 50 mg/L to 10 mg/L by World Health Organization (WHO) [1], [5], [7], [8], [9]. This MCL cannot be respected by countries including more than 45 million people in developing Asiatic countries (being exposed to more than 50 μg/L) and are at risk [3].

The major physical-chemical treatment method such as adsorption, coagulation, ion-exchange, pressure driving membrane technologies [3][6][10][11] used to remove As from contaminated waters are expensive and more importantly fail to efficiently remove As (III) [1], [2], [6], [8] and are source of sludge rich in chemicals. Moreover, chemical methods need to oxidize As(III) to As(V) before any achievement of a possible satisfactory removal. Membrane distillation (MD) can be used to overcome the limits observed in the physico-chemical methods for As removal. Some researches carried in the field of heavy metals removal such with MD showed almost 100% rejection efficiency, [2][4][5]. MD is a thermally driven process in which vapor pressure difference being the driving force, is created due to temperature difference across the membrane, [12] and water vapor transport occurs through a non-wetted porous hydrophobic membrane [13], [14]. Four main configurations, direct contact membrane distillation (DCMD), sweeping-gas membrane distillation (SGMD), vacuum membrane distillation (VMD) and air gap membrane distillation (AGMD), are widely used in MD. Each configuration defers from the other by the arrangement of the cooling side. The DCMD, in which condensed vapor on the filtrate side of the membrane is in direct contact with the membrane is the most simple, cheapest and popular configuration of these configurations [14].

The present study aimed to investigate the rejection of As(III) and the influence of OM and Fe(III) on the rejection efficiency and transmembrane flux. As(III) contaminated tap water will be treated with PTFE 0.22 μm and 0.45 μm in a DCMD configuration. The effect of membrane pore size, feed temperature, Fe (III) and OM concentration in the feed on the rejection efficiency of As(III) and trans-membrane flux (TMF) were investigated.

2. MATERIALS AND METHODS

2.1. Membrane Distillation Unit

During the experimental study, a laboratory scale modified DCMD apparatus was used. A gap is created in the MD membrane module at the permeate side, but still cool water is used to condense permeate vapor. The modification intended to minimize heat loss by conduction in order to enhance the treated water flux by separating the cooling part of the system by a stainless steel plate. A schematic diagram of the DCMD set-up is shown in Figure 1. The effective membrane area was 0.015 m^2. The volume of the feed tank was 5 L and the solution was heated by 1 kW electrical heating elements. CAT Pump 2SF35SEEL-Stainless Steel Direct-Drive Plunger Pump and Watson Marlow Peristaltic pump 323 Du/D were used to circulate feed hot wastewater 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

The experiments were conducted with an initial As(III) concentration of 100 µg/L. The pressure, the feed solution flow rate and the temperature of the cooling water were almost kept constant at 0.5 bars, 4.5 liter per minute (LPM) and 10 °C, respectively. A heat-exchanger was used to keep constant the temperature of the cooling water. The study was carried out at three different heating temperatures (40, 50 and 60 ^{0}C) giving different ΔT of 30, 40 and 50 ^{0}C.

2.3. Membranes

Two different pore sizes, 0.22 µm and 0.45 µm, hydrophobic membranes made of polytetrafluoroethylene (PTFE) manufactured in China by Membrane-Solution-LLC were used. Their liquid entrance pressure (LEP) were 5,5 and 4,5, respectively

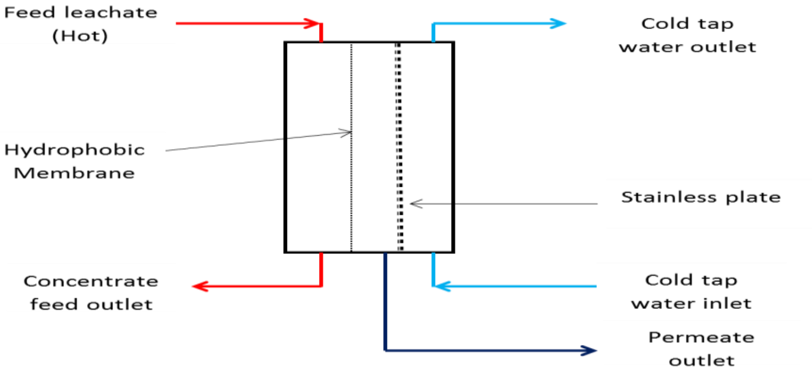

Figure 1. Schematic flow diagram of the lab scale modified DCMD module

2.4. Reagents and Stock Solutions

Synthetic arsenic As (III) contaminated solution were prepared by diluting 0.1 N sodium arsenite stock solution (3.75 g/L as As) (Merck, Germany; 99% purity) in tap water to obtain As (III) concentration 100 µg/L used as feed solution. Ferric Chloride ($FeCl_3$) and potassium hydrogen phthalate ($C_8H_5KO_4$) were used to prepare Fe(III) and OM solution, respectively. The pH of the tap water used was approximately close to the neutral value (typical of the one of real groundwater) so that the oxidation state of As does not change. The characteristics of the tap water are shown in Table 1 while the characteristics of the synthetic feed As solution used during this study is presented in the Table 2.

Table 1. 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

Table 2. Characteristics of the synthetics As(III) contaminated solution

Characteristics	As(III) , mg/L	Conductivity, µS/cm	Fe (III), mg/L	OM, mg/L	pH
Content	100	690	2.5-5	5-10-20	7

2.5. Analytical Methods

Total As(III) and Fe (III) were measured with 3111 B standard methods 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. Total organic carbon (TOC) was determined with SM 5310 B standard methods. Conductivity was measured at room temperature using Thermo Scientific Orion 5-Star Plus pH/ ORP/ ISE /Conductivity /DO Meter.

3. RESULT AND DISCUSSION

3.1. Conductivity Rejection

The conductivity of the synthetic feed solution in this study was approximately 690 µS/cm. The permeate conductivity after being treated with DCMD is presented in Figure 2. The conductivity was reduced nearly to 40 µS/cm when As (III) is directly treated and the rejection efficiency was over 90%. We also observed that the conductivity rejection was higher when organic matter or ferric iron is added to the feed solution. In these cases, the permeate conductivity fell to approximately 5 µS/cm when feed temperature vary from 40 to 50 °C. The rejection was over 99% is most cases. In addition, the conductivity in the permeate increased with increasing feed temperature and with larger pore size membranes.

Low permeate conductivity observed in the permeate is the result of dissolved ions, including As, being retained by the hydrophobic membrane. All non-evaporable components in feed solution cannot pass through the hydrophobic membranes pores; they are kept at the feed side. However, permeate conductivity increased with increasing feed temperature regardsless of the membranes used and the feed solutions characteristics. This phenomenon is due to high motility of dissolved ions at high temperature and the negative effect of temperature on membrane structure. At high temperature, the membrane hydrophobicity is affected, membranes are flexibilized, tortuosity increases and membrane pores can be deformed. Some dissolved ions take advantage of this vulnerable state of the membrane and may possibly escape through the membrane pores and as a consequence a slight increase of permeate conductivity. When Fe (III) or OM is added in the feed solution, they participate to increasing co-precipitation with As(III) and many other ions responsible for conductivity. Precipitated compounds settle in the feed tank and are kept away from the membrane active surface. That may reduce the amount of ions passing through the membrane pore and consequently reduced the permeate conductivity.

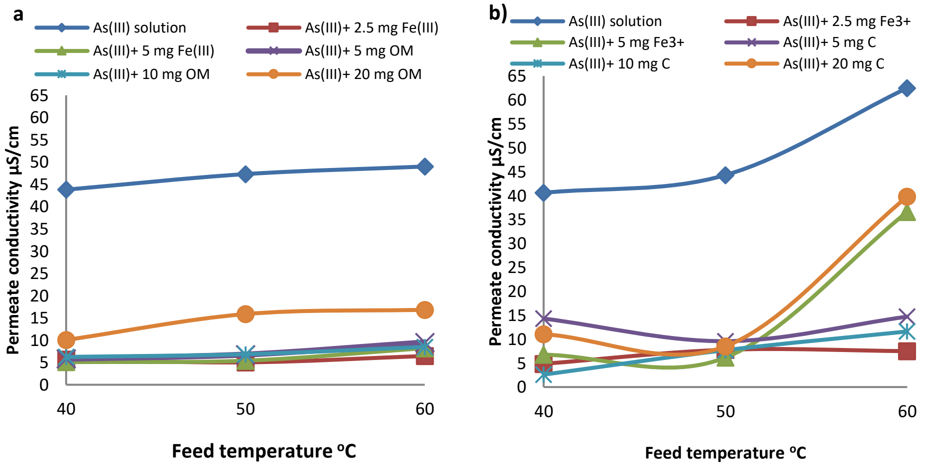

Figure 2. Rejection of conductivity for different feed solution over increasing feed temperature; a) PTFE 0.22 µm, b) PTFE 0.45µm

3.2. Fe(III) and Organic Mater (OM) Rejection

Fe(III) and OM have been efficiently rejected by both membranes used. Fe(III) was not detectable in the permeate. Metals cannot evaporate; they can only pass through the membrane by size exclusion when they are pressurized on the membrane surface. Due to the coprecipitation with As(III) ions, Fe(III) are mainly retained in the feed tank and rejected as concentrate. The OM in the feed however can evaporate at high temperature. As presented in Figure 3, the permeate solution was affected by the OM, and the concentration of OM in the permeate increased with larger pore size membrane and higher feed temperature. At low feed temperature, OM in the permeate was low but evaporation took place. At high temperature, some OM in feed solution being volatile organic compounds may evaporate and passed through the membrane as supported by Koczka and Mizsey [15], and possibly participated to an increase of the OM concentration in the permeate.

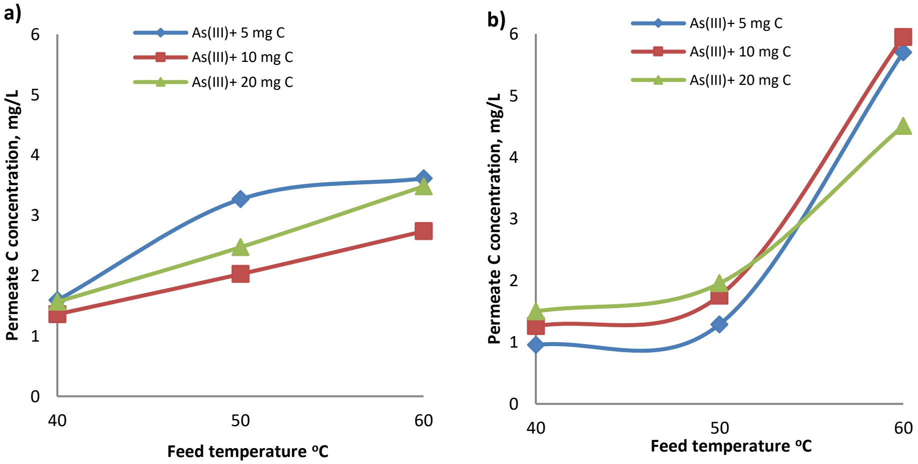

Figure 3. Fe(III) and OM rejection at different feed temperature and initial concentration in the feed solution; a) PTFE 0.22µm, b) PTFE 0.45µm

3.3. Arsenic Rejection

As (III) rejection from a synthetic feed and the rejection behavior when Fe(III) or OM is added in the feed was followed and results are depicted in Figure 4. Regardless of the treatment conditions, As(III) was rejected with both membranes and permeate As(III) concentration was far lower than 10 µg/L recommended by World Health Organization (WHO) and Turkish Standard of TS266 for safe drinking water. Figure 4 shows As(III) concentration in the permeate of both membrane with different feed solutions. The rejection efficiency was over 90% in most of the results presented. However, the rejection was higher when Fe(III) or OM are added in the feed solution at moderate concentration. Fe(III) addition resulted to the best rejection; As(III) was non-detectable in the permeate at low feed temperature.

Due to 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. No vaporizing compounds such as As (III) are retained at the feed side in the concentrate. Criscuoli et al. [2] investigated arsenic removal with vacuum membrane distillation (VMD) and reported similar 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. Many other researchers [1], [2], [4], [5], [16] reported similar efficiency of MD for As rejection and most of them claimed over 99% rejection and As concentration below recommended by WHO and TS266 10 µg/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.

On the other hand, OM or Fe(III) when added in the feed solution may cause the formation of some aggregates with As(III) particles and settle in the feed tank by co-precipitation as reported by Caniyilmaz [7] and Han et al. [17]. Larger aggregates formed are readily kept in the feed tank and less As(III) circulate in the MD module. Concentration polarization, membrane clogging and any transport of As(III) through the membrane by size exclusion is highly reduced. However, feed temperature need to be controlled; high temperature may destabilize the aggregates formed and some particles can escape and pollute the permeate solution. During the 6 hours operating time for each membrane set, no significant variation is observed in As(III) rejection efficiency. It was obvious that the membrane was not wetted and can be used during hours without it losing its efficiency as reported by Manna et al. [16].

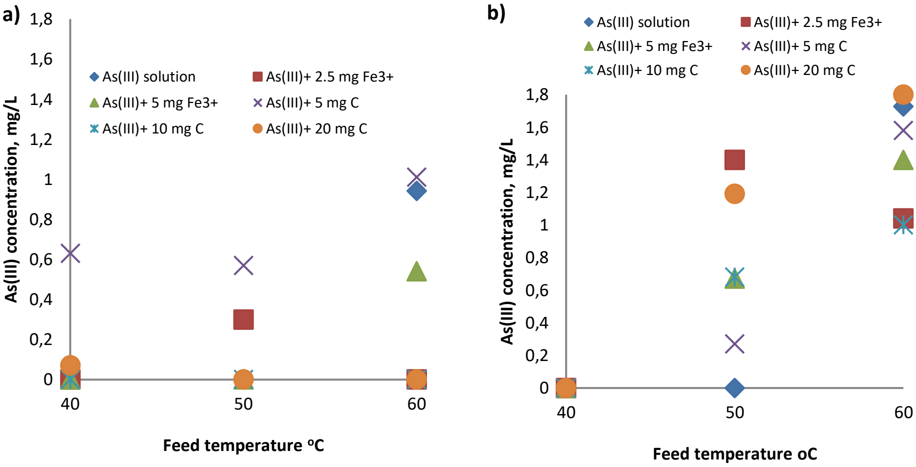

Figure 4. As(III) rejection at different feed temperature and different feed solution; a) PTFE 0.22µm, b) PTFE 0.45µm

3.4. Transmembrane flux

The membrane flux is considered to access the economic feasibility of any treatment. 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 TMF [4], [5], [18]. Flux of both membranes and feed solution used during this study are depicted in Figure 5. The highest flux was observed at the highest feed temperature (60 ºC) with PTFE 0.45µm membrane using a feed solution containing Fe(III). Regardless of any other parameter, the flux increased with raising feed temperature. MD is well known as temperature dependent. In fact, higher temperature foster vapor formation and consequently an increase of the driving force [18]. Gradually increase of temperature from 40 to 60 ºC caused the flux to increase gradually. At high temperature, temperature gradient between the feed and the permeate surface of the membrane increased the driving force, large amounts of vapor was produced from the feed side which created higher vapor pressure inside the channel, and caused an increase of the flux through the membrane pore. Criscuoli et al. [2] reported a flux increase from 3 to 12.5 kg/hm2 during VMD treatment of As at 20 °C and 40 °C, respectively. Membrane pore size as well controlled the flux; higher flux was observed with larger pore size membrane which facilitated the passage of vapor through the membrane pore.

In addition, when comparing the flux out of As(III) feed solution and those where Fe(III) or OM were added, the flux remained very high in the presence of Fe(III) and OM. The highest fluxes of PTFE 0.22 µm at 60 ºC of As(III) only, As(III)+10mg/L OM and As(III)+5mg/L Fe(III) were 7.85, 11.62 and 16.76 L/m^2.h, respectively. The increase of flux when Fe(III) or OM is present in the solution is probably due to the sedimentation power of these chemicals. Fe(III) presented the highest flux because it has better coagulation and co-precipitation power with As(III). During the treatment, OM and Fe(III), when present in the feed solution, formed some aggregates with particles and many other ions in the solution. These aggregates can easily precipitate and concentrate in the feed tank. The feed solution circulating in the module being less concentrated in pollutants (settled in the tank), the transmembrane flux is high and no fouling or scaling take place.

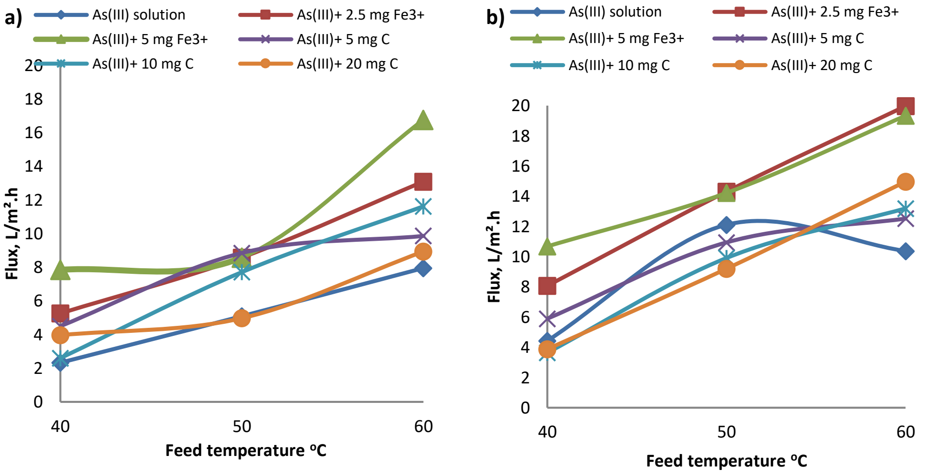

Figure 5. Transmembrane flux over increasing temperature of Arsenite As (III); a) PTFE 0.22 µm, b) PTFE 0.45 µm

4. CONCLUSION

The present study investigated with success the rejection of As(III) with a direct contact membrane distillation unit. Conductivity and As(III) was removed up to 99%. In the presence of Fe(III) in feed solution, As(III) rejection improved and no arsenic was detected in the permeate. Membrane pore size, feed temperature and feed solution had high influence on conductivity removal, As(III) removal and transmembrane flux. The highest flux of 19.97 L/m^2.h were observed with PTFE 0.45 at 60 °C with As(III)+2.5 g/L Fe(III) as feed solution. Advanced investigation with a pilot scale experimental setup may be required for a better understanding of the flux behavior over time, membrane resistance and the system efficiency for As rejection.

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REFERENCES / KAYNAKLAR

[1] Qu, D., Wang, J., Hou, D., Luan, Z., Fan, B., Zhao, C. (2009), "Experimental study of arsenic removal by direct contact membrane distillation", Journal of Hazardous Materials, 163, 874–879.
[2] Criscuoli, A., Bafaro, P., Drioli, E. (2012), "Vacuum membrane distillation for purifying waters containing arsenic", Desalination xxx xxx–xxx.
[3] Singh R., Singh S., Parihar P., Singh V.P., Prasad S.M. (2015). "Arsenic contamination, consequences and remediation techniques: A review", Ecotoxicology and Environmental Safety112(2015)247–270. doi.org/10.1016/j.ecoenv.2014.10.009.

[4] Manna, A.K., Sen, M., Martin, A.R., Pal, P. (2010), "Removal of arsenic from contaminated groundwater by solar-driven membrane distillation", Environ. Pollut., 158, 805-811.

[5] Pal, P., Manna, K.A. (2010), "Removal of arsenic from contaminated groundwater by solar-driven membrane distillation using three different commercial membranes", Water Res., 44, 5750-5760.

[6] Jiang, J-Q., Ashekuzzaman, S. M., Jiang, A., Sharifuzzaman, S. M., Chowdhury, S.R. (2013) , "Arsenic contaminated groundwater and its treatment options in Bangladesh", Int. J. Environ. Res. Public Health, 10, 18-46.

[7] Caniyilmaz, S. (2003), "Arsenic Removal from Groundwater By Fe-Mn Oxidation And Microfiltration", B.S., Middle East Technical University.

[8] Petrusevski, B., Sharma, S., Schippers, J.C. (UNESCO-IHE), Shordt, K. (IRC) (2007), "Arsenic in Drinking Water", March 2007 IRC International Water and Sanitation Centre.

[9] Mondal, P., Bhowmick, S., Chatterjee, D., Figoli, A, Van der Bruggen, B. (2013), "Remediation of inorganic arsenic ingroundwater for safe water supply: A critical assessment of technological solutions", Chemosphere, 92, 157–170.

[10] Cakmakci, M., Baspinar, A. B., Balaban, U., Uyak, V., Koyuncu, I. , Kinaci, C. (2009), "Comparison of nanofiltration and adsorption techniques to remove arsenic from drinking water", Desalination and Water Treatment, 9, 149–154.

[11] Elcik, H., Cakmakci, M., Sahinkaya, E., Ozkaya, B. (2013), "Arsenic removal from drinking water using low pressure membranes", Ind. Eng. Chem. Res., 52, 9958−9964.

[12] Pal P. (2015). "Arsenic Removal by Membrane Distillation", 2015 Elsevier Inc. doi.org/10.1016/B978-0-12-801281-9.00005-9.

[13] Boubakri, S., Bouguecha, A-T., Dhaouadi, I., Hafiane, A. (2015), "Effect of operating parameters on boron removal from seawater using membrane distillation process", Desalination, 373, 86–93.

[14] Meng, S., Yea, Y., Mansouri, J., Chen, V. (2015), "Crystallization behavior of salts during membrane distillation with hydrophobic and superhydrophobic capillary membranes", Journal of Membrane Science 473, 165–176.

[15] Koczka, K., Mizsey, P. (2010). New area for distillation: wastewater treatment. Chemical Engineering 54/1 41–45.

[16] Manna A.K., Pal P., (2016). "Solar-driven flash vaporization membrane distillation for arsenic removal from groundwater: Experimental investigation and analysis of performance parameters", Chemical Engineering and Processing 99 (2016) 51–57. doi.org/10.1016/j.cep.2015.10.016.

[17] Han, B. and Wickramasinghe, R., "Arsenic Removal From Drinking Water By Flocculation And Microfiltration", Department of Chemical Engineering, Colorado State University, CO 80523-1370, USA.

[18] Yarlagadda, S., Gude, V.G., Camacho, L.M., Pinappu, M. , Deng, S. (2011), "Potable water recovery from As, U, and F contaminated ground waters by direct contact membrane distillation process", J. Hazard. Mater., 192, 1388-1394.

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