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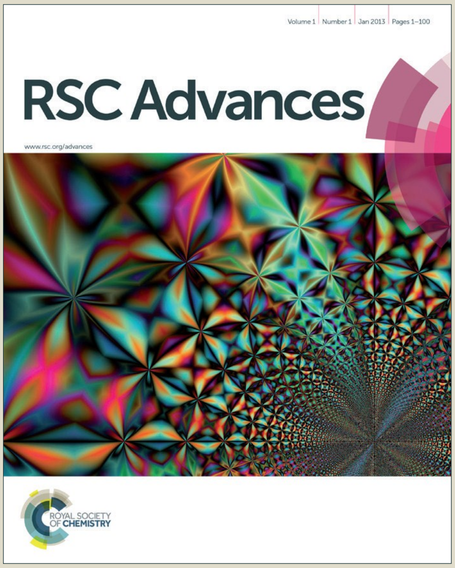

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ARTICLE

Efficacy of polyethylene interpolymer membranes for the fluoride and arsenic ions removal during desalination of water via electrodialysis

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Herein, we report the comparative fluoride and arsenic ions removal efficacies of three different pairs of ion exchange membranes viz. indigenously developed polyethylene interpolymer based ion-exchange membranes, commercial ionsep and fujifilm type I membranes during desalination via the electrodialysis process. Different experiments were conducted in a domestic electrodialysis unit (effective membrane area 20 cm X 10 cm) using 30 pairs of each type of membrane pairs. Both the interpolymer and commercial fujifilm type I membranes could effectively reduce fluoride concentration (14.4 ppm) present in ground water of Rajasthan, India to a drinking water permissible limit (<1.5 ppm). The commercial ionsep membrane could not reduce such high concentration of fluoride ion to permissible limit of drinking water. This is attributed to the moderate water uptake and high fluoride ion transport number of interpolymer and commercial fujifilm type I membranes than that of ionsep membrane. All three different types of ion-exchange membranes could effectively reduce arsenate ion of concentration of 800 ppb (maximum concentration present in Indian water) to permissible limit of drinking water (~ 10 ppb). The ions removal efficacy of membranes depends on concentration of both fluoride and arsenate ions present in salt water.

Introduction

The demand for fresh ground water is increasing day by day worldwide. Unfortunately, the ground water is contaminated with different ions such as fluoride, arsenic, nitrate etc. Fluoride, in addition to arsenic and nitrate ion is one of the contaminants of water for human consumption stated by the World Health Organization (WHO), which cause large-scale health problems. The amount of fluoride ion in drinking water should be <1.5 ppm as per guidelines provided by WHO, above which can cause various health problems such as birth, reproduction, immunological defects, dental and skeletal fluorosis.[1,2] In India, more particularly ground water of Rajasthan and Gujarat, is contaminated with fluoride ion. The concentration of fluoride ion present in ground water varies from 3 ppm to 15 ppm. Arsenic ion is also a toxic and carcinogenic element for human health.[3] WHO had recommended safe arsenic permeable limit through drinking water is 10 ppb. In India, West Bengal and Assam, are two most arsenic affected states. The arsenic contamination varies from 200 ppb to 800 ppb whereas the total dissolved solid content (TDS) of water is only 200-500 ppm. Therefore, removal of fluoride and arsenic ions from drinking water is desirable to maintain healthy life in the above mentioned states.

Membrane technologies such as ultrafiltration, nanofiltration (NF) and thin film composite reverse osmosis (TFC RO) technologies are used for successful removal of fluoride (F^-) ion from water.[4] Removal of F^- (17.9 ppm) ion from ground water of Morocco using different NF and RO membranes has been reported.[5] F^- removal with low energy RO membranes as well as with creamic membranes was also reported.[6,7] The separation process using RO or NF membranes is robust but the main drawback of these two technologies is that both NF and TFC RO membranes undergo fouling.

Electrodialysis (ED) process using cation exchange membrane (CEM) and anion exchange membrane (AEM) has been used for water desalination.[8-10] The advantages of ED over RO and NF membrane based separation techniques include low energy cost, minimum water loss through reject water and higher membrane life due to less fouling.[11] As regards water desalination ED is advantageous than RO process when the TDS of water is upto 3000 ppm. For example, ED process requires 75%, 50% and 30% less energy than RO process at feed water TDS 1000, 2000 and 3000 ppm respectively.[11] ED process has been used for the removal of F^- ion from Moroccan ground water (TDS 1100-3000 ppm and F^- ion concentrations 1.8-4.5 ppm).[12-14] Combination of adsorption and ED process has also been reported for the removal of F^- ion.[15] Removal of F^- from geothermal water of Turkey[16], groung water of Pine Hill Farm, Australia[17] (TDS 5000 ppm, F^- ion concentration 2.8 ppm) and artesian well-water in Brazil[18] (F^- concentration 5-20 ppm) by ED process has also been reported.[16-18] In all the above mentioned ED processes[16-18] commercial neosepta[16,17] and asahi Glass Co membranes[18] were used. Removal of F^- ion from brackish water of India (TDS 2100-4800 ppm with additional F^- ion concentration 5-

20 ppm) by ED process using polyethylene-polystyrene interpolymer based CEM and AEM were also reported.[19] The above mentioned membranes reduced the F^- concentration to <1.5 ppm. The main drawback of interpolymer based AEM is its preparation by chloromethylation of styrene moiety using hazardous chloromethyl methyl ether (CME).[19] Since CME, is a banned chemical in India, the preparation of AEM using CME is restricted.[20]

On the other hand, arsenate ion removal (As^{5+}) from ground water of China using commercial nanofiltration membrane (toray) has been reported.[21,22] The removal efficiency of As^{5+} ion depends on the operating conditions.[23,24] TFC RO membranes have also been used for removal of As^{5+} from ground water.[25,26] There is only one report of removal of As^{3+} by ED process from ground water using commercial SKS membranes.[27]

The above literature reports reveal that there is no report of removal of high concentration of F^- ion (around 15 ppm) at low water TDS (500-680 ppm). The removal of As^{5+} from water by ED process is not reported in literature. Therefore, the main objective in this work is the desalination of brackish water of TDS 500-2000 ppm containing additional amount hazardous F^- (12-14.4 ppm) by ED process. Our another objective is the removal of arsenate ion (As^{5+}) of concentration 200-800 ppb ions from water (TDS 200-500 ppm) by ED process. The indigenously developed polyethylene polystyrene interpolymer based CEM and polyethylene poly4-methyl styrene interpolymer based AEM were used in both the experiments. The performance of polyethylene interpolymer based membranes towards the removal of F^- and As^{5+} ions during water desalination was compared with two different types of commercial ionexchange membranes by ED process under similar experimental conditions.[28] Ployethylene interpolymer based membranes are mechanically strong, stable towards exposure with acid and alkali. We reported the use of these interpolymer membranes for brackish water desalination via ED[28] and ultrapure water production via electrodeionization.[29] Herein, desalination along with defluoridation efficiencies of the indigenous polyethylene based membranes, commercial ionsep and fujifilm type I membranes were compared by performing the desalination of ground water as well as synthetic water samples (containing 12-14.4 ppm F^-) by ED process at 1.5 volt/cell pair applied potential. It was observed that both the indigenously developed interpolymer based membrane and commercial fujifilm membranes could effectively reduce F^- ion concentration to 1.5 ppm whereas commercial ionsep membrane could reduce F^- ion concentration ca. 2.34 ppm. The effect of hydration of the membrane on the F^- ion removal efficiency has been established. Similarly the dearsenification efficiency of the above mentioned three different membranes was evaluated by ED process during As^{5+} (concentration 200-800 ppb) ion removal from water (TDS 200-500 ppm) at 1.5 volt/cell pair applied potential. All the three different types of membranes could effectively remove As^{5+} ion (concentration upto 800 ppb) which is the maximum concentration of As^{5+} present in Indian ground water. The power consumption and current efficiency during F^- and As^{5+} ions removal has been compared and correlated with ion transport number and/or degree of hydration of the above membranes.

Experimental

Materials

4-methylstyrene (4-MS) (96%) and divinyl benzene (DVB) (80%) were purchased from Sigma-Aldrich Chemicals was used as received. Styrene (St), N-bromosuccinimide (NBS) and benzoyl peroxide (BPO) were purchased from TCI, Japan. Film grade high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) were purchased from Reliance Industries, India. Sodium fluoride, ethylene dichloride, xylene, toluene, chlorosulfonic acid were purchased from S D Fine Chemicals India. Sodium arsenate dibasic heptahydrate, 98% ($Na_2HAsO_4.7H_2O$) were purchased from Sigma Aldrich. Zinc powder and sulfamic acid were purchased from Finar Chemicals, India. The polyethylene-polystyrene inter-polymer based cation exchange membrane (CEM) and polyethylene-poly4-methylstyrene interpolymer based anion exchange membrane (AEM) have been designated as CEM_{inter} and AEM_{inter} respectively. CEMs purchased from ionsep and fujifilm are designated as CEM_{ionsep} and $CEM_{fujifilm}$. AEMs purchased from ionsep and fujifilm are designated as AEM_{ionsep} and $AEM_{fujifilm}$. Ground water of Ganeshpura, Jhunjhunu, Rajasthan, India of TDS 680 ppm contains fluoride (F^- = 14.4 ppm), chloride (Cl^- = 300 ppm), sulfate (20 ppm), carbonate (8 ppm), bicarbonate (4 ppm), calcium (10 ppm), magnesium (10 ppm), sodium (280 ppm) and potassium ions (40 ppm) respectively.

Preparation of interpolymer based CEM_{inter} and AEM_{inter}

CEM_{inter} was prepared by three step processes starting from the free radical polymerization of St and DVB in presence of 80:20 w/w ratio of HDPE and LLDPE. BPO (1wt%) was used as initiator and mixture of xylene and toluene was used as solvents. The PE/PSt interpolymer pellets were converted to PE/PSt interpolymer film by blow extrusion process. CEM_{inter} was prepared by treatment of PE/PSt interpolymer film with 80:20 (v/v) mixture of ethylene dichloride (EDC) and chlorosulfonic acid at room temperature for 3.5h. AEM_{inter} was prepared by four step processes starting from polymerization of 4-MS, DVB in presence of 90:10 w/w mixtures of HDPE and LLDPE. Mixture of xylene and toluene was used as solvent and 1 wt% BPO was used as initiator.The PE/P4-MS interpolymer pellets were converted to PE/P4-MS interpolymer film by blow extrusion process. AEM_{inter} was prepared by treatment of PE/P4-MS interpolymer film with NBS and BPO in presence of EDC at 70 ^{0}C for 48h. The quaternary ammonium moiety in the brominated film was incorporated after reaction with trimethyl amine for 6h at room temperature. The detailed procedure of the preparation of both type of interpolymer pellets and interpolymer films has been mentioned in supporting information (†ESI). Both the CEM_{inter} and AEM_{inter} were washed consecutively with 1 M HCl and 1 M NaOH followed by washing with large excess of distilled water. The membranes were stored in 0.1 M NaCl solution before use in ED unit.

Characterization

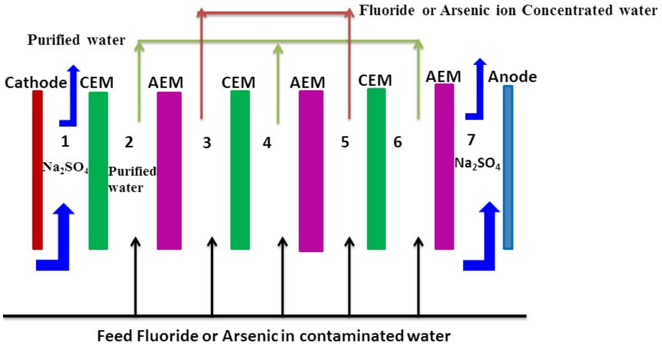
Physical and electrochemical characterization of CEMs and AEM

The physical characterization such as water uptake (%) of all the the membranes used in this work was determined by measuring the gain of weight of the membranes by using the procedure reported by us earlier.[28,29] The ion-exchange capacity (IEC) of CEMs and AEMs was determined by titration method.[28,29] The membrane conductivity (K^m) and transport number (t^+/t^-) of all the CEMs and AEMs used in this work were measured by measuring the membrane resistance and membrane potential respectively.[28,29] All the detailed characterizations methods have been provided in supporting information (†ESI).

ED experiment

The water desalination using AEM_{inter} and CEM_{inter} was determined by ED process using an in-house prepared ED cell. Scheme 1 shows the design of ED unit and the membrane arrangements in the cell.

The electrode housing, cathode and anode were made of rigid PVC sheet, stainless steel and titanium tantalum respectively. A parallel-cum series flow arrangement of water through membranes was used in the ED unit. Peristaltic pumps were used to recirculate the inlet and outlet streams. Three different compartments such as diluate, concentrate and electrode wash compartments exist in the ED unit. Both the electrode wash compartments were circulated with dilute Na_2SO_4 solution (0.01 % w/V) to avoid oxidation reduction reaction on the electrode surface. Desalination experiments were carried out in ED unit of effective membrane area 200 cm^2 using 30 pieces of each type of membranes (total membrane area 12000 cm^2) using salt solution with varying TDS and varying F^- (12.2-14.4 ppm) and arsenate (As^{5+}) (200-800 ppb) ions concentrations under recirculation mode of operation. Equal volume (1 L) of salt solution circulated in both the diluate and concentrate compartment. A fixed 45 volt potential (1.5 volt/cell pair) was applied between the electrode in all the experiments by means of AC-DC rectifier. The change of current value with desalination time was recorded in all the experiments. Similarly separate defluoridation /dearsenification experiments were carried out in the same ED unit with commercial ionsep and fujifilm type I membranes under similar experimental conditions.



Scheme 1. Schematic arrangement of membranes in ED unit

Determination of F^- and As^{5+} concentration in water after ED process

The F^- ion concentration in both the diluate and concentrate compartment was analyzed by a fluoride selective electrode (Orion BNWP 9609) attached to a pH meter (Orion Versa Star of Thermo Scientific). The As^{5+} ion concentration in both the diluate and concentrate compartment was measured in a PerkinElmer atomic absorption spectrophotometer (AAS-100) at 193.7 nm wavelength using flame-fias technique.[30]

Determination of power consumption and current efficiency

Power consumption and current efficiency are two important parameters that judge the suitability of any power driven separation process. Power consumption (W in $KWhKg^{-1}$) during ED process is defined as the amount of energy needed to transport one Kg of NaCl from diluted compartment to concentrated compartment. W has been calculated using the following equation:[9-11,28,29]

$$W=\int_0^t VIdt/w \qquad (1)$$

where V is the applied voltage; I is the current (amp); dt is the time (h) allowed for the desalination process; and w is the weight of salt (Kg) removed.

The current efficiency (CE) is defined as the fraction of the current transported by the specific ion and has been calculated using the following equation:[9-11,28,29]

$$\text{CE (\%)}=\frac{wxF}{MxNxQ}\text{x100} \qquad (2)$$

where F is the Faraday constant (26.8 Amp.h $mole^{-1}$); M is the molecular weight of NaCl (58.5), N is the number of membrane pairs used in the ED unit (30 pairs), Q is the amount of electricity passed throughout the system (Amp.h) during the defluoridation and dearsenification experiments. It is noted that both the W and CE(%) values were calculated considering NaCl removal, but the ED experiments were continued until the F^- and As^{5+} concentrations in diluate compartment reaches <1.5 ppm and 10 ppb respectively during all the defluoridation and dearsenification study.

Results and Discussions

Physical and Electrochemical Characterizations of different ion-exchange membranes

Three different pairs of membranes viz. (i) inter polymer-based CEM_{inter}/AEM_{inter}, (ii) $CEM_{ionsep}/AEM_{ionsep}$ and (iii) $CEM_{fujifilm}/AEM_{fujifilm}$ were employed in ED unit for purification of water (containing NaCl and As^{5+} or F^-). CEM_{inter} consist of $–SO_3H$ containing crosslinked network of polyethylene and polySt and polyDVB.[28] AEM_{inter} consists of polyethylene based cross-linked network of poly(4-MS) and polyDVB in which the $–CH_3$ moieties were converted to quaternized amine groups by the process reported earlier by us.[28] The detailed FT-IR characterization of CEM_{inter} and AEM_{inter} has been mentioned in supporting information (Fig.S1, †ESI). Table 1 summarizes the water uptake, IEC, K^m, t values (Na^+, Cl^-, and F^-) of different ion-exchange membranes used here for ED experiments.

Table 1. Physical and electrochemical properties of CEMs and AEMs used for this work.

Samples	Thickness (mm)	Water uptake (%)	IEC (meq g^{-1})	K^m (mS cm^{-1})	t^+ or t^- (Na^+ and Cl^-or F^-)	
					Na^+/Cl^-	Na^+/F^-
CEM_{inter}	0.20	29	2.45	2.86	0.94	0.93
AEM_{inter}	0.20	20	1.30	1.12	0.92	0.91
CEM_{ionsep}	0.40	40	2.00	3.70	0.86	0.85
AEM_{ionsep}	0.40	40	2.20	3.20	0.85	0.82
$CEM_{fujifilm}$	0.14	30	2.07	2.17	0.93	0.91
$AEM_{fujifilm}$	0.13	25	2.12	2.69	0.91	0.89

The average water uptake values (hydration) of CEM_{inter}/AEM_{inter} pair (24.5%) is close to average hydration value of $CEM_{fujifilm}/AEM_{fujifilm}$ pair (27.5%) and lower than $CEM_{ionsep}/AEM_{ionsep}$ pair (40%). On the other hand, the average IEC values for these membranes are 1.875 $meqg^{-1}$, 2.095 $meqg^{-1}$ and 2.1 $meqg^{-1}$ respectively whereas average t $[(t^++t^-)/2]$ values are 0.93, 0.92 and 0.855 when NaCl was used as an electrolyte. The lower water uptake of inter-polymer and fujifilm membranes lowers the back diffusion of ions with water molecule and maintained good transportation of ions.[9-11] High degree of hydration (water uptake) of ionsep membranes lowers the t values of all ions. The t value of F^- was lowest with ionsep. For removal of F^- ion, it is essential to compare the t values of these membranes using NaF as an electrolyte. The average t values during F^- ion transportation were 0.92, 0.90 and 0.835 for interpolymer, fujifilm and ionsep membranes which are slightly lower than the average t values obtained during Cl^- transport. This small variation in average t values affects the F^- transportation behaviour by the above membranes a lot. This transportation behaviour may be due to higher hydration energy of F^- ion than that of Cl^- ion.[31]

F^- removal by ED process

Water desalination experiments with TDS 540-2186 ppm and an additional F^- ion content 12.1-12.6 ppm have been carried out by ED using indigenous interpolymer based and two commercial membranes (ionsep and fujifilm type I) at applied potential 1.5 volts/cell pair under recirculation mode of operation. Separate desalination experiments were also carried out using these membrane pairs with water sample (F^- content 14.4 ppm and TDS 680 ppm) collected from Ganeshpura, Jhunjhunu, Rajasthan, India. Fig. 1 A, 1 B and 1 C shows the remaining F^- concentration with ED time plots in diluate compartment using three different types of ion exchange membranes.

It is seen from Fig. 1 that the concentration of F^- was brought down from 14.4 ppm to <1.5 ppm in diluate compartment at both high and low water TDS with interpolymer membranes and commercial fujifilm membranes. The commercial ionsep membrane could not reduce F^- concentration to <1.5 ppm by ED. It may take long time to reduce F^- concentration to <1.5 ppm with commercial ionsep membranes. It has been observed that 90, 84 and 91% of F^- ions have been removed from ground water sample of Rajasthan by interpolymer, ionsep and fujifilm type I membranes respectively. Figs. 2 A, 2B and 2C show the decrease of TDS of water in diluate compartment with defluoridation time for interpolymer, commercial ionsep and fujifilm-type I membranes during desalination of water containing 500-2000 ppm NaCl and 12 ppm F^- ion. Figs. 2A, 2B and 2C also includes the desalination of ground water sample of Rajasthan carried out with the above three membranes.

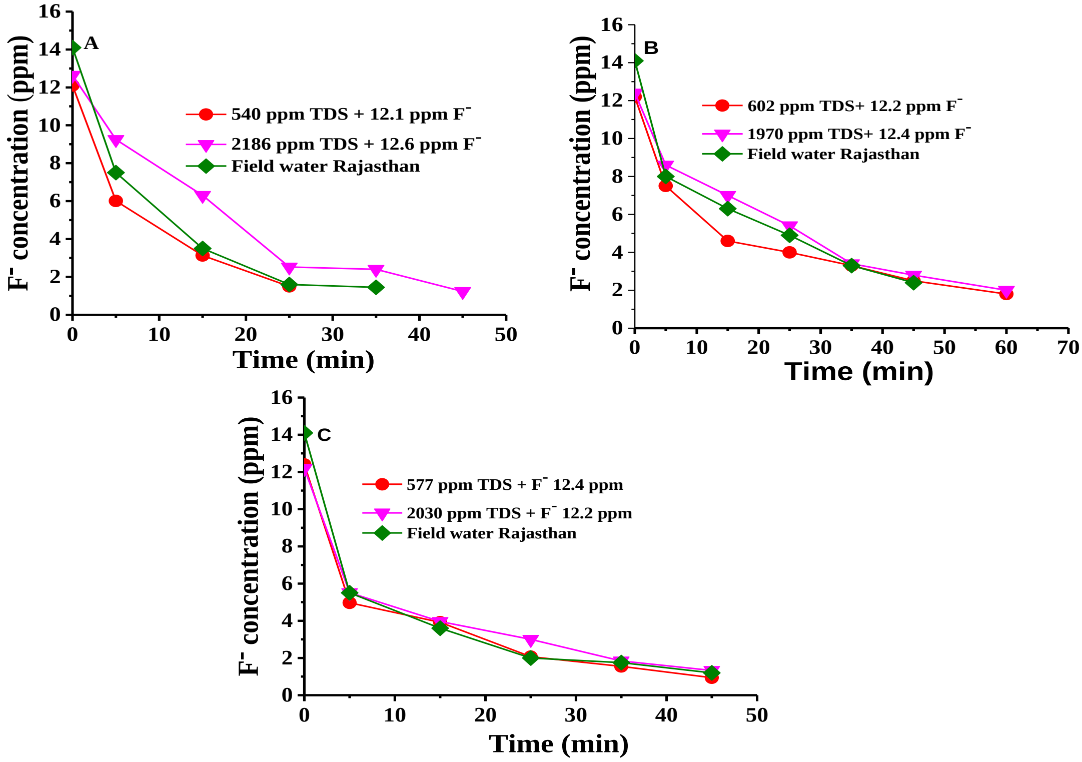


Fig. 1 F^- concentration in diluate compartment with time during ED with (A) interpolymer (B) ionsep and (C) fujifilm-type I membranes.

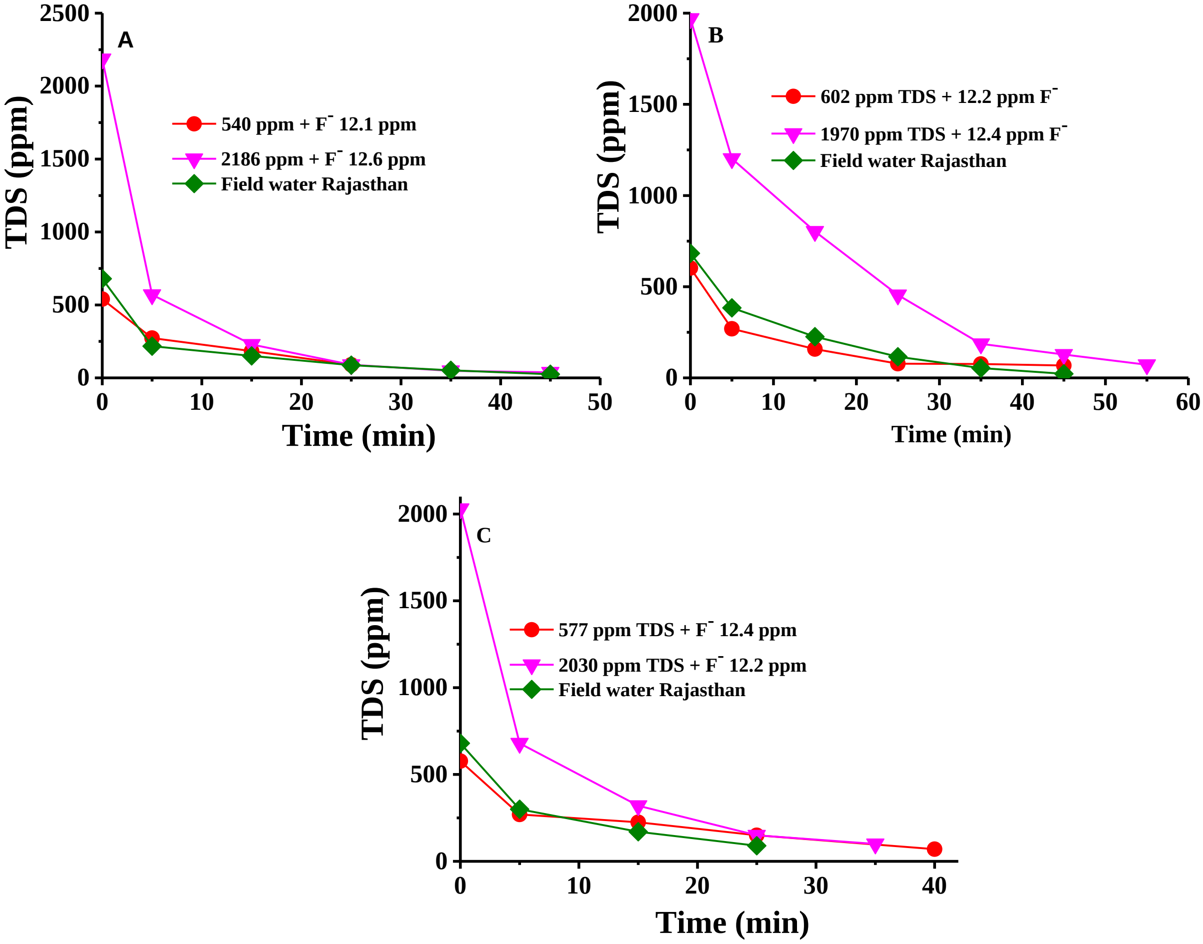


Fig. 2 TDS of diluate compartment with time during ED experiment with (A) interpolymer (B) ionsep and (C) fujifilm-type I membranes.

Fig. 2 thus indicates that the TDS of water also gets lowered to drinking level limit during defluoridation. Hence, interpolymer and Fujifilm type I membranes are best suited for desalination of water containing harmful F$^-$ ion to WHO permissible limit.

Table 2 shows the comparative F$^-$ ion removal efficacies of different types of ion-exchange membranes from water of different TDS, additionally contaminated with different concentrations of F$^-$. The unit running time for our experiments (Table 2, entries 6-11) was 45-60 minutes.

Table 2. Comparative F^- removal efficacies of different types of ion-exchange membranes during desalination via the ED process.

Type of membrane used	Source of water	Water uptake (%)	Feed water TDS (ppm)	Feed water F^- (ppm)	Final TDS (ppm) of water in diluate compartment	Final F^- (ppm) in diluate compartment	Reference
ACS,neosepta	Morocco	20-30	1127	1.80	656	0.50	24
ACS,neosepta	Morocco	20-30	1127	4.50	594	1.00	24
ACS, neosepta	Pine Hill Farm, Australia	20-30	4255	2.80	500	1.50	28
ACS, neosepta	Morocco	20-30	3000	3.00	400	0.63	27
AMX/CMX neosepta	Balcova geothermal, Turkey	25-30	1026	7.72	33	0.06	26
interpolymer	Rajasthan, India	24.5	680	14.40	25	1.45	This work
fujifilm-type I	Rajasthan, India	27.5	680	14.40	90	1.33	This work
ionsep	Rajasthan, India	40.0	680	14.40	22	2.34	This work
interpolymer	NaCl solution	24.5	2186	12.60	38	1.23	This work
fujifilm-type I	NaCl solution	27.5	2080	12.20	43	1.23	This work
ionsep	NaCl solution	40.0	1970	12.40	72	1.60	This work

It has been observed from Table 2, (entries 6-11) that both the interpolymer as well as commercial fujifilm type I membranes can reduce high F^- ion concentration (12.2-14.4 ppm) to <1.5 ppm at both high and low water TDS (680-2186 ppm) under the similar experimental conditions (such as ions concentration of source water and ED unit operating time are same). On the other hand, commercial ionsep membranes failed to reduce F^- concentration to <1.5 ppm when the concentration of F^- ion in salt water was 12.4 ppm or above. Other commercial membranes (ACS and AMX neosepta, Table 2, entries 1-5) can effectively reduce the F^- ion concentration to permissible limit of drinking level when water contains relatively low concentration of F^- (1.8-7.72 ppm). Data of F^- ion removal from salt water with ACS and AMX neosepta membranes are not available when F^- ion concentration is ca. 12.2 ppm or above.

The inferior F^- ion removal efficacy of ionsep membrane compared to interpolymer and fujifilm type I membranes at F^- concentration ca. 12 ppm in salt water is due to comparatively high water uptake of the former membrane than the later membranes. Therefore, the back diffusion of ions along with water enhanced which lowers the transport number of the ionsep membrane and hence, the efficacy towards F^- ion removal reduces (Table 1) by this membrane.[9-11]

Maximum F^- ion removal efficiency of ionsep membranes by ED pocess

Since, the commercial ionsep membranes cannot reduce high concentration of F^- (ca. 12 ppm or above) to permissible limit of drinking water (<1.5 ppm), it is necessary to find out the maximum amount of dissoved F^- ion that can be removed by this membrane from water by ED process. Therefore, additional ED experiments were conducted with water of TDS 500 ppm and containing varying amount of F^- (0.5 to 6 ppm) under recirculation mode of operation. The applied potential used was 1.5 volt/cell pair. The results have been presented in Table 3.

Table 3. Defluoridation results by ED at low F^- concentration using commercial ionsep membrane.

Serial no	Time (min)	Initial TDS (ppm)	Required power consumption (Watt.min)	Final TDS (ppm)	Initial F^- (ppm)	Final F^- (ppm)
1	35	500	1.25	109	0.5	0.051
2	35	500	1.25	98	1.0	0.199
3	35	500	1.25	89	6.0	0.672

It is observed from Table 3 that commercial ionsep membrane at fixed power consumption (1.25 Watt.min) can remove almost 89.8 % and 88.8% F^- ion from the water when 0.5 and 6 ppm F^- ion is present in water. The final F^- concentration in diluate compartment was <1.5 ppm. Therefore, if the contaminated F^- ion concentration increases from 6 ppm, long time (higher power consumption) may be required to bring F^- ion concentration to drinking water permissible limit (< 1.5 ppm).

Tranport behavior of F^- ion through different membranes

We have earlier discussed that (Table 1) the average t of F^- ion is marginally and consistently lower than that of Cl^- or Na^+ ion for all the membranes. Hence, it is essential to find out the transport behaviour of Cl^- and F^- (when present in small quantity in water) through these three different types of membranes. Hence, two separate ED experiments were conducted using feed water containing (i) 500 ppm KCl and 10 ppm NaF and (ii) 500 ppm KCl and 10 ppm NaCl. The concentrations of F^- ion in case of experiment (i) and concentration of Na^+ ion (which is equivalent to concentration of Cl^- ion) in case of experiment (ii) in the diluate compartments were measured at different time intervals. Figs. 3 A and B show the F^- concentration vs time and concentration of Na^+ (equivalent to Cl^-) vs time plots respectively for all three different membranes. These experiments indicates that removal of small amount of Na^+ (equivalent to Cl^-) is faster by all three membranes than the removal of similar amount of F^- from water. Thus small change in transport property of ions (marginally lower t of F^- compared to that of Cl^-) causes greater effect on F^- ion removal efficacy of the membranes. Such small differences in t between F^- compared to that of Cl^- may be attributed to the higher degree of hydration (hydration energy) of F^- ion compare to that of Cl^- ion.[31] On the other hand, the t value of Na^+ is thus influenced by the type of counter ion (Table 1). For example t value of Na^+ was somewhat lower when the counter ion was F^- (NaF was electrolyte) than that of Cl^- (NaCl was electrolyte) for all experiments. This may be the reason for faster transport of Na^+ than that of F^-.

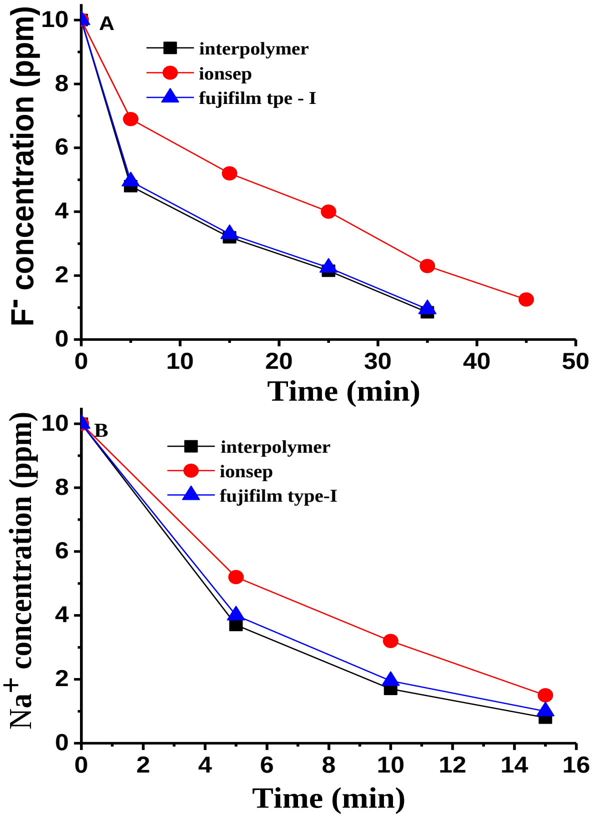
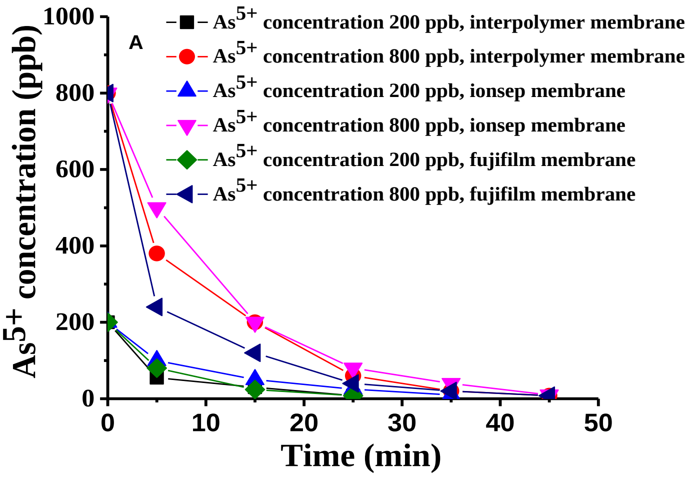


Fig. 3 Concentrations of (A) F^- and (B) Na^+ in diluate compartments with time using three different types of membranes.

As^{5+} removal by ED process

The As^{5+} removal efficacy of three different membranes was also carried by ED process under recirculation mode of operation. The experiments were conducted with water TDS 200 and 500 ppm. Since the ground water of India mostly contains the As^{5+} concentration (200 ppb-800 ppb), the concentration of As^{5+} salt was kept 200 ppb and 800 ppb in the synthetic salt mixture of TDS 200 ppm and 500 ppm. Fig. 4A and 4B shows the As^{5+} concentration in diluate compartment with dearsenification time carried out with water of TDS 200 ppm (Fig. 4A) and with water TDS 500 ppm (Fig. 4B) for interpolymer, fujifilm and ionsep membranes respectively.



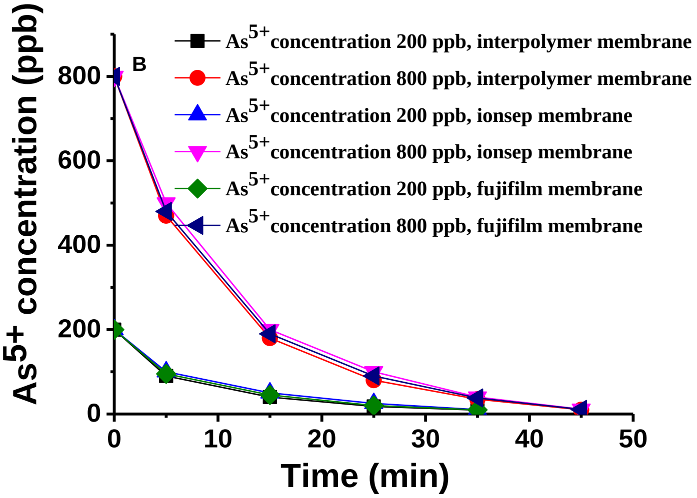


Fig. 4 As^{5+} concentration in diluate compartment with time during ED experiment with all three different types of membranes at different TDS (A) 200 ppm and (B) 500 ppm.

It is clearly observed from Figs. 4A and 4B that all the three different types of membranes reduce As^{5+} concentration from 800 to 10 ppb. The good As^{5+} ion removal efficacy of the membranes is attributed to the low concentration of As^{5+} in salt water which was not influenced by the water uptake of the membranes. However, at high concentration of As^{5+} in the salt water the water uptake values of the membranes may affect the comparative As^{5+} ion removal efficacy.

Determination of W and CE values during F$^-$ and As^{5+} ions removal by ED

The feasibility of any separation process via ED is determined by measuring the W and CE (%) values during the process. The W and CE (%) values during F$^-$ and As^{5+} ions removal using three different types of membranes has been measured from the current values obtained at different time interval during the whole defluoridation and dearsenification process using equations 1 and 2 and presented in Tables 4 and 5. The experimental time was dependent on F$^-$ and As^{5+} ions removal rate. The experiment was stopped when the concentration of F$^-$ in the diluate compartments was minimum viz. <1.5 ppm for membranes except ionsep. For ionsep the final F$^-$ ion concentration was achieved in the diluate compartments were 2.40, and 2.34 ppm respectively for entries 5 and 6 in Table 4. Similarly, during As^{5+} removal the final concentration of As^{5+} in the diluate compartments were 8.5, 9.2 and 9.8 for interpolymer, fujifilm and ionsep membranes.

Table 4. Determination of W and CE values during F$^-$ ion removal by ED process. The experimental time was set to the point when the F$^-$ ion concentration in diluate compartment was minimum (<1.5 for a and for b F$^-$ concentration = 2.34 and 2.40 ppm).

Types of membranes	**Feed water TDS (ppm)**	**F$^-$ concentration (ppm)**	**W (KWh Kg^{-1})**	**CE (%)**
[a]interpolymer	2186	12.6	0.943	75.0
[a]interpolymer	680	14.4	1.346	50.0
[b]ionsep	1970	12.4	1.898	60.0
[b]ionsep	680	14.4	2.400	30.0
[a]fujifilm-type I	2080	12.2	1.200	72.0
[a]fujifilm-type I	680	12.4	1.430	45.0

The W value was decreased and CE (%) value was increased at comparatively high water TDS for all the three different types of membranes. This is usually due to high ionic concentration of the feed solution which enhanced the current and favours the faster F$^-$ ion removal.[9-11] The obtained W and CE (%) values are comparable during F$^-$ removal from water at both high and low water TDS for interpolymer and fujifilm membranes (Table 4, entries 1,2, 5 and 6). The obtained W value is higher and CE (%) value is lower with ionsep membranes (Table 4, entries 3 and 4). This once again supports the slower F$^-$ ion transportation with the ionsep membranes than the other two membranes.

Table 5. Determination of W and CE values during As^{5+} removal by ED process. The experiment was stopped when As^{5+} concentration was reached 10 ppb in diluate compartment.

Types of membranes	**Feed water TDS (ppm)**	**As^{5+} concentration (ppb)**	**W (KWhKg^{-1})**	**CE (%)**
interpolymer	200	800.4	1.24	74.5
ionsep	212	800.2	1.32	70.0
fujifilm-type I	216	800.8	1.26	73.5

It has been observed from Table 5 that the W and CE (%) values of all the three different types of membranes are not much different for all the membranes during As^{5+} removal. Strictly, the ionsep membranes showed somewhat low performance than the other two membranes. The low W and high CE achieved with any types of membranes during As^{5+} removal may be due to low concentration of As^{5+} (800 ppb) in feed salt water.

Conclusion

We have demonstrated the removal of fluoride ion (14.4 ppm) and arsenate ions (800 ppb) from salt water by ED process under recirculation mode using three different types of ion-exchange membranes. Indigenously developed interpolymer and commercial fujifilm type I membranes effectively reduced fluoride ion concentration to <1.5 ppm at both low and high water TDS, whereas the commercial ionsep membrane could not lower the fluoride concentration to permissible limit of drinking water at high F$^-$ concentration (14.4 ppm). Approximately 90%, 91% and 84% of fluoride ions from ground water of Rajasthan were removed by indigenously developed interpolymer based and commercial fujifilm type I, ionsep membranes by ED process. The power consumption values were 1.346 KWhKg^{-1}, 1.43 KWhKg^{-1}, 2.40 KWhKg^{-1} and current efficiency values were 50%, 45%, 30% respectively during fluoride removal from ground water of Rajasthan (TDS 680 ppm and F$^-$ concentration 14.4 ppm) with interpolymer, fujifilm type I and ionsep membranes respectively. The value of power consumption and current efficiency obtained during fluoride ion removal by ED process using indigenously developed interpolymer based membranes and commercial fujifilm type I membranes are comparable, whereas for commercial ionsep membranes, the of power consumption value was higher and current efficiency value was lower during fluoride removal from water sample of Rajasthan. This may be due to high water uptake and low fluoride ion transport number of ionsep membranes than the other two membranes, which allows the back diffusion of fluoride ions with water in the diluate compartment. Comercial ionsep membrane can reduce fluoride concentration to < 1.5 ppm when the concentration of present fluoride ion in salt water is upto 6 ppm. On the other hand, all the three different types of ion exchange membrane combinations can effectively reduce arsenate (As^{5+}) concentration from 800 ppb to < 10 ppb by ED. Almost 98.75-99% arsenate salts are removed by all three types of membranes by ED process. The power consumption during arsenate removals for both interpolymer and fujifilm type I membranes were similar and lower than ionsep membranes.

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Notes and References

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Electronic Supplementary Information (†ESI) available: Preparation of the PE-PSt and PE/P4-MS inter-polymer Film, FT-IR spectra of CEM$_{inter}$ and AEM$_{inter}$, Physical and electrochemical characterizations of different membranes

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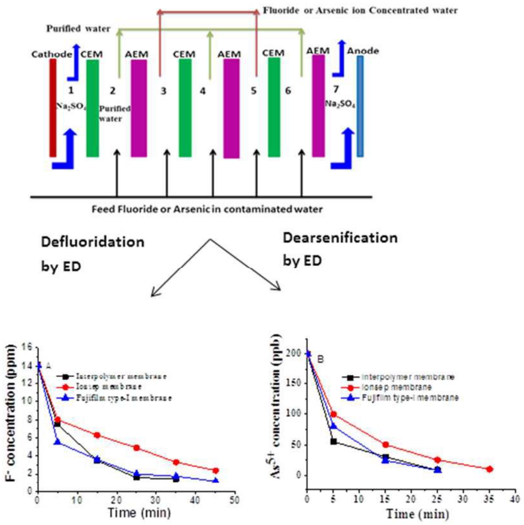

Decrease of Fluoride and Arsenic ions concentration with all the three different types of membranes by electrodialysis

254x190mm (96 x 96 DPI)