DEFLUORIDATION OF ETHIOPIAN RIFT VALLEY REGION WATER USING REVERSE OSMOSIS MEMBRANES

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ABSTRACT

Defluoridation of Ethiopian Rift Valley Region (ERVR) raw ground water using reverse osmosis (RO) membranes was studied. Four RO membranes, CA995PE, HR98PP, LFC and ESPA delivered by DSS and Hydranautics were investigated for the retention of fluoride in fluoride water. All four membranes were observed to effectively retain fluoride. The fluoride retention of the membranes were in the ranges from 94 to 99 % and larger than those of chloride. The LFC membrane was tested for Ethiopian Rift Valley Region raw ground water. For the same range of feed concentration, the retention and permeate fluoride concentration is comparable for raw ground water and artificially constituted fluoride water. However, the membrane fouling was serious. About 85 % of the flux loss was recovered by treating the membrane with HNO_3 solution with $pH = 2$ at $50^{O}C$. The true causes of the fouling and the best treatment for the fouled membranes requires further investigation.

INTRODUCTION

Background

Fluoride in drinking water could be beneficial or detrimental for health depending on its concentration and total amount ingested. The presence of fluoride is beneficial for calcification of dental enamel, in particular for children under eight years old. However, excess fluoride intake causes dental and skeletal fluorosis [1]. The recommendation of WHO is from 0.5 to 1.5 ppm [2]. For tropical region, the safe fluoride concentration should not exceed 0.8 ppm because of the relatively high drinking water consumption [1,3].

The Ethiopian Rift Valley Region is one of the regions in the world where the groundwater resources are contaminated by excess fluoride. A recent analysis of the water from this region shows that the fluoride concentration ranges on average from 5 to 25 mg/litre [4]. Dental and skeletal fluorosis is prevalent in the region. The problem also affects many other developing nations in Africa and Asia. To express the seriousness of the fluoride problem in these regions, WHO quoted the observation of one researcher visiting China as follow:

"The farmer with the black teeth seemed fine the first time I saw him - out all day working. I know that he carried on drinking the same fluoride-rich water he had drunk since he was born. Five years later when I returned to the village his legs had buckled under him. He was practically a cripple. I don't know what he did for a living any more" [5].

In order to solve the problem, an alternative water source should be used or the fluoride in the ground water should be reduced to an acceptable level. The common alternative is raw surface water from rivers, which requires elaborate treatment before it can be made potable. For some towns in the region such solutions have been used, but it has not become a sufficient drinking water source. For instance, Nazareth that is the largest town in the region with a population of about 200 000 has got only 10 % of its drinking water supply from treated surface water. The major population uses highly contaminated ground water. Besides, the treatment is prohibitively costly in capital cost and in maintenance, and in particular it is not suitable for sparsely populated small habitations. In such a case, treating ground water is a better viable option where sufficient amount is available, and even to supplement the existing water supply of some of the towns. The treatment of ground water does not require a complex treatment plant, except for a removal of fluoride and other dissolved potentially harmful minerals.

Treatment Methods

The conventional and commonly used defluoridation methods are chemical coagulation and filtration (C/F), lime softening (LS), adsorption using activated alumina and ion exchange synthetic resins (IE) [3,6]. C/F uses commercially procured coagulants such as aluminium sulphate. LS uses lime and its effectiveness depends on the presence of magnesium ions in water, which removes the fluoride ion. When the magnesium ion in the water is not sufficient for fluoride removal, magnesium oxide should be added to the water before the LS process is run. The performance of both C/F and LS system accomplish good fluoride removal when optimum operating conditions, e.g. pH, amount of the coagulant and temperature, are maintained. However, they are not appropriate for small-scale operation because of high initial cost and the need for well-trained operators. Adsorption using activated alumina is very effective in removing fluoride from water. The contaminant of fluoride is adsorbed in an activated alumina bed or column. It is suitable both for small and large systems. IE uses charged anion resins to catch fluoride ions in the water. Also this method can be used for both small and large system. However, both activated alumina and synthetic resins are rather expensive due to limited capacity for fluoride and the need for regeneration agents.

Recently, RO and nanofiltration (NF) membrane separation processes have become viable options for the removal of fluoride. RO and NF can remove about 93 – 95 % and 80-90 % of the fluoride, respectively [7]. They give a much more efficient removal of fluoride ion than any of the other methods. In addition, the processes dc chemicals. The recovery of water is about [illegible] RO and 15 to 20 % for NF. The processes are simple to operate and can be used for small-scale treatment. But, the low recovery, in particular for NF, makes the processes inappropriate in water scarcity regions. Generally, they are also known to be expensive processes to build and to operate. They need close monitoring and regularly cleaning of fouled membranes or changing of old ones. But recent literature shows that these processes may become cheaper than the others [7, 8] at higher capacities.

Thus, it is worth considering the applicability of the membrane processes for enterprises that need efficient water treatment units and for treating the drinking water of the towns in the region. In this paper, we studied the rejection of four RO membranes and corresponding fluxes for model water with different fluoride concentrations and for the actual water at different operating pressures on one selected membrane.

THEORY

Both *RO* and *NF* dense nonporous membranes are used to remove smaller molecular size solutes such as inorganic salts or small molecular weight organic molecules from a solvent. The denser membrane requires higher trans-membrane pressure (ΔP) to overcome the higher hydrodynamic resistance compared to the porous membranes: microfiltration and ultrafiltration membranes. Moreover, the osmotic pressure has to be overcome.

The effective water flux through the membranes can be represented by:

$$J_W = L_W(\Delta P - \sigma\Delta\pi) \qquad (1)$$

where L_W is water permeability coefficient, $\Delta\pi$ is osmotic pressure difference across the membrane, and σ is the reflection coefficient of the membrane towards that particular solute. The L_W depends on water diffusivity and solubility in a membrane, temperature and membrane thickness.
The solute flux can be described by:

$$J_S = L_S(C_f - C_s) \qquad (2)$$

where L_S is the solute permeability coefficient, C_f is feed side solute concentration and C_p is permeate solute concentration. The L_S depends on solute diffusivity and solubility and membrane thickness.

The retention of a membrane for a given solute is given by:

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f} \qquad (3)$$

For low flux RO membrane where concentration polarization (CP) is insignificant (ΔP is constant), J_w increases linearly with ΔP. Since large flux RO membranes are emerging in the market, the prospect of CP is high, and hence, the $\Delta\pi$ may also increase with ΔP causing deviation from linear relation.

EXPERIMENTAL

Laboratory Test Unit

Experiments were carried out on the laboratory test unit shown schematically in Figure 1 at Norwegian University of Science and Technology (NTNU). The module consists of a feed tank with total volume 35 dm^3, equipped with a heater (Watlow screw plug immersion heater, material Inconel 600, effect 2 kW) and a water heat exchanger, a pump (Hydra-Cell G10 XD, engine effect 3 kW), a pass line, and a flat-sheet membrane cell. The bypass line controlled with a needle valve (Whitey union bonnet valve) and the main line was controlled with a back pressure valve (Tescom). The pressure transmitter (Keller type PR21, 0-100 bar, current output 4-20 mA) and temperature transmitter (PR type 5333A1, Pt-100°C, current out-put 4-20 mA) were placed upstream of the membrane cell, while the flow meter (Flomid-MC, Tecfluid, electro magnetic flow meter, 0-20 dm^3/minute, current output 4-20 mA) was connected to the main line downstream the membrane cell. The accumulated permeate was weighed on a balance (Explorer, Ohaus, capacity 0.00-410.00 g). The membrane cell was a cross-flow flat sheet stainless steel (SS316) membrane cell made at NTNU. The total active membrane area was 60 cm^2 (60x100 mm). The pressure, temperature, flow rate and flux were automatically measured and the data stored in a computer. The Field Point data acquisition system from National Instruments was used together with the Labview program. The process variables were normally recorded every 20 seconds.

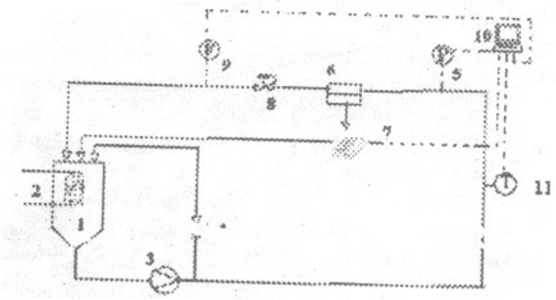

Figure 1 Ultrafiltration experimental unit.
(1) Feed tank, (2) heat exchanger, (3) pump, (4) by-pass control valve (needle valve), (5) pressure transmitter, (6) membrane module, (7) a weight balance, (8) back pressure valve, (9) flow meter, (10) computer and (11) temperature transmitter.

Flat-sheet membranes: CA995PE and HR98PP (from DSS), and ESPA and LFC (from Hydranautics) were used to study the retention of fluoride ion. All membranes are composite membranes: Cellulose Triacetate/Diacetate blend film on polyester, thin film composite on polypropylene and polyamide composite membrane, respectively. The manufacturers' performance specifications of the membranes are given in Table 1.

Table 1: Characteristics of the membranes

Membranes	pH	Pressure (bar)	Temperature (°C)
CA995PE	5-6.5	1-50	0-30
HR98PP	2-11	1-60	0-60
ESPA	3-10	1-40	0-45
LFC	3-10	1-42	0-45

Before start of the experiments the membranes were conditioned with pure water at 20 bar and low flow at room temperature for 2 hours.

Feed: Fluoride Rich water

Two types of feed were used. One was artificially constituted fluoride water (ACFW) at different concentration and naturally fluoride rich water collected from ERVR raw ground water. The former was used to study the retention of four membranes for three different concentrations. The latter was used to evaluate the performance of the selected membrane. The characteristics of the feed are given in Table 2.

Procedures

Complete recycling mode

0-45In the study of the retention of CA995PE, HR98PP, ESPA and LFC reverse osmosis membranes for fluoride; artificially constituted fluoride water was used. The process was run under complete recycling mode, i.e. the retentate and permeate were recycled to the feed tank, thus keeping the concentration in the feed tank constant. The experiments were run for one hour for each feed concentration at 25°C and selected pressures. Each membrane was run with three feed concentrations, about 6, 20 and 60 ppm. Feed and permeate samples were collected at the end of each run.

Concentrating mode

The water collected from the Ethiopian Rift Valley was filtered using the LFC reverse osmosis membrane. The permeate was continuously withdrawn until 80 % of the water was recovered or to the membrane had lost 50 % of its original flux.

RESULTS AND DISCUSSION

After pre-treatment of the membranes, the pure water fluxes were measured for series of trans-membrane pressure drops (ΔP) and NaCl retentions were determined at conditions prescribed by manufacturers. ESPA had the largest flux and CA995PE had the least while the retention of NaCl was the opposite. Figure 2 shows pure water flux vs. ΔP. Table 3 shows the retention of the four membranes. The retention of the ESPA membrane was determined to be 8 % lower than the values given by the manufacturers while the other three membranes showed about 2 % variation.

Table 2: Feed water characteristics

Feed type	pH	F^- (ppm)	Ca^{2+} (ppm)
Artificial	7.0	6-60	10 ppm
Rift valley	7.0	6	---

Table 3: Chloride retention of the membrane at conditions prescribed by manufacturers.

Membrane type	Operating condition			Retention (%)
	T (°C)	Pressure (bar)	Feed conc. (ppm)	
AC995PE	25	15.0	2000	93
HR98PP	25	10.0	2000	94
ESPA	25	10.5	1500	87
LFC	25	15.5	1500	97

Complete Recycle Mode run for Artificially Constituted Fluoride Water

To determine the fluoride retention the CA995PE and HR98PP membranes were run at 30 bars. The ESPA and LFC membranes were run at about 10 bars and 20 bars, respectively, which gave about equal flux to that of HR98PP membrane. Table 4 shows the average fluxes and retention for three different fluoride feed concentrations. There was no significant difference observed between pure water flux and artificially constituted fluoride water flux since the fluoride waters have very low fluoride concentration so the concentration polarization effect is negligible.

As seen in Table 4, the permeate fluoride concentration was determined for each membrane for all feed concentrations. For the CA995PE, HR98PP and LFC membranes, the permeate fluoride concentration obtained were well below 1 ppm for all three feed concentrations. For the ESPA membrane, the standard is met only for feed with fluoride concentration of about 4.6 ppm. For all membranes, the observed retention of the fluoride was larger than that of chloride (compare Table 3 and Table 4). Although the fluoride crystal radius (0.136 nm) is smaller than chloride crystal radius (0.181 nm), the hydrated radius of fluoride (0.352 nm) is larger than that of chloride's (0.332 nm). The hydrated size has an effect on the mobility and diffusivity, thus, affecting the permeation through the membrane.

The larger the hydrated size of the ions, the lower the mobility and diffusivity of the ions in the water. If the fluoride is to be concentrated to the extent 90 % water is recovered, all membranes except the ESPA membrane may be used.

Concentrating Mode run Result for ERVR Raw Ground Water

The LFC membrane was chosen for its good retention and better flux to run for ERVR raw ground water. The water was first filtered through 1 μm white filter paper. The filter paper got a yellowish colour, probably by small particles retained from the water. About 12 litres of water was added to feed tank. The permeate was continuously withdrawn for about 10 hours until

Table 4: The concentration of fluoride in permeate and retention for different membranes and feed concentrations of artificially constituted water

Membrane Type	ΔP (bar)	Flux ($g/m^2.s$)	Feed (ppm)	Permeate (ppm)	Retention (%)
CA995PE	30.6	22.79	06.4 ± 0.6	0.2 ± 0.14	96.8 ± 1.2
	30.6	22.51	22.4 ± 0.3	0.3 ± 0.00	98.7 ± 0.1
	30.0	21.91	62.9 ± 1.1	0.4 ± 0.08	99.4 ± 0.1
HR98PP	30.5	30.87	05.9 ± 0.1	0.3 ± 0.08	95.7 ± 0.7
	30.7	30.21	22.8 ± 0.5	0.5 ± 0.28	97.8 ± 0.6
	30.4	29.69	61.3 ± 1.3	0.5 ± 0.23	99.3 ± 0.2
ESPA	10.2	31.45	04.6 ± 0.4	0.5 ± 0.14	89.2 ± 1.0
	10.0	32.12	24.8 ± 0.3	3.2 ± 1.94	87.3 ± 3.8
	09.5	31.31	73.3 ± 0.7	5.5 ± 0.07	92.6 ± 0.1
LFC	20.2	32.32	05.0 ± 0.0	0.3 ± 0.00	94.0 ± 0.0
	19.9	31.45	26.8 ± 0.0	0.5 ± 0.08	98.3 ± 0.1
	21.1	29.00	82.0 ± 0.0	0.7 ± 0.23	99.2 ± 0.1

about 60 % of the water was removed. The flux and pressure vs. time is plotted on Figure 3. The figure shows that pressure reading showed fluctuation of 5 bar about the average. Such fluctuation may be attributed to poor damping effect of the damper fitted to the pump.

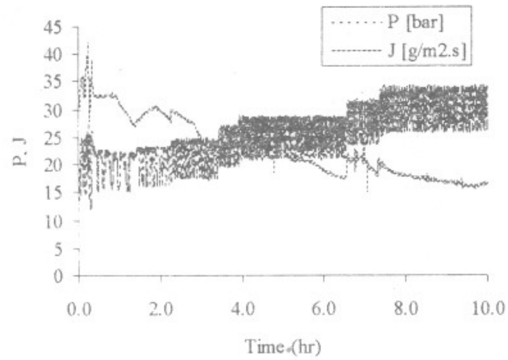

Figure 3.Pressure and flux vs. time during reverse osmosis of actual water from rift valley

There was serious fouling of the membrane. In order to maintain nearly constant permeate flux the pressure increased on average from 20 to 30 bar. Even then the flux decline continued. After 85 % of the initial feed volume was withdrawn, the operation was stopped and the membrane was flushed with pure water three times. The fouled membrane had about 18 $g/m^2.s$ flux at 20 bar. The membrane was also treated by Ultra12 alkaline cleaning agent at 50°C for 30 minute. However, there was no significant measurable improvement of pure water flux. Later, it was cleaned by HNO_3 solution at pH=2 and 50°C for 30 min and followed by flushing with pure water, which resulted in recovery of 70 % of the flux loss cloud be recovered (about 26.5 $g/m^2.s$ pure water flux could be obtained). Still significant flux remains to be recovered. The cause for the fouling may be dissolved minerals, such as $CaCO_3$, and humic material found in ground water. Thus, the cause of the fouling of the membrane and cleaning procedures need further study.

Permeate and concentrate samples were drawn at certain time intervals and analyzed for concentration of fluoride. The result is given in Table 5. Almost the same retention was obtained as for artificial fluoride water. The permeate fluoride concentration is well below WHO guidelines.

Table 5: The concentration of fluoride in permeate and concentrate, and retention at different time intervals for actual water from the Rift Valley.

Time (hour)	F - concentration (ppm)		Retention (%)
	Concentrate	Permeate	
0.0	3.1	--	--
1.0	4.9	0.3	94
3.5	5.4	0.3	94
6.0	6.7	0.5	93
10.0	8.3	0.6	93

CONCLUSION

Reverse osmosis membranes were observed to effectively retain fluoride from fluoride rich water. For artificially constituted fluoride water of concentration ranging from 6 to 60 ppm, three of the membranes (CA995PE, HR98PP and LFC) gave permeate fluoride concentrations well below 1 ppm, which is the WHO drinking water guideline. Even the ESPA membrane met with this demand for feed fluoride concentration of 6 ppm. The fluoride retention of the membranes ranged from 94 to 98 % and were larger than that of chloride.

The LFC membrane was chosen to be tested for ERVR raw groundwater because of its good flux and retention. The retention and permeate fluoride concentration obtained were comparable with those obtained with artificially constituted fluoride water for corresponding feed fluoride concentration range but the membrane was heavily fouled in a short time. About 85 % of the flux loss was recovered by treating the membrane with HNO_3 solution of pH=2 and 50°C. The cause of the fouling may be $CaCO_3$, which is the cause of natural hardness of water. The true causes of fouling and best treatment for cleaning the fouled membrane require further investigation.

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