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Membrane Capacitive Deionization Technology and Reverse Osmosis for Fluoride Removal from Water – A Comparative Study

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Abstract *—Ion-exchange membranes (IEMs) are unique in combining the electrochemical properties of ion exchange resins and the permeability of a membrane. They are being used widely to treat industrial effluents, and in seawater and brackish water desalination. Membrane Capacitive Deionization (MCDI) is an emerging, energy efficient technology for brackish water desalination in which these ion-exchange membranes act as selective gates allowing the transport of counter-ions toward carbon electrodes. Rajasthan is the only state where all most all the districts are affected by high fluoride (beyond the permissible limit). In 23 districts the fluorosis problem can be visualized at various intensity level i.e. Dental fluorosis, skeletal fluorosis, nonskeletal manifestation etc. Various Technologies have been developed so far for deflouridation. Many Reverse osmosis plants have been installed in Rajasthan for removal of fluoride from ground water. But, it is associated with high power consumption, scaling and fouling of membranes and reduced water recovery. This sets up a need for more energy efficient device with less maintenance and operational cost with overcoming shortcomings of reverse osmosis. Membrane capacitive deionization is the emerging technology which utilizes constant current method with varying voltage to remove salts from underground water. The pilot plant (CapDI) manufactured by Voltea (Netherland) was provided by In Now India Pvt. Ltd for carrying out this study. It was found that Capacitive deionization technique is very efficient in removal of low salinity feed water sources. Energy consumption is quite low approximately only 20 to 30% of energy utilized by reverse osmosis. And flow recovery rate of CapDI plant is also high than reverse osmosis plant.*

Keywords-*Fluoride, Membrane capacitive deionization, Reverse Osmosis.*

I. INTRODUCTION

Capacitive Deionization (CDI) is an electrochemical desalination technology which employs porous carbon electrodes to adsorb ions from water (Jung et al., 2007; Tsouris et al., 2011; Huang et al., 2012; Rica et al., 2012; Kim and Yoon, 2013; Mossad and Zou, 2013; Zhao et al., 2013a; Omosebi et al., 2014; Lei et al., 2015; Tang et al., 2015). Upon applying a voltage difference between two electrodes, cations are adsorbed from the water into the negatively polarized electrode (cathode), while anions are adsorbed into the positively polarized electrode (anode). During this adsorption step, or charging step, feed water flows through the cell and is desalinated, resulting in a deionized water effluent. After the electrodes are saturated, the electrodes are short-circuited and ions are released, which is called the desorption or discharging step.

An ion-exchange membrane consists of a polymer matrix in which ionic groups are fixed to the polymeric backbone. Depending upon the charge of the ionic group, IEMs are categorized as either anion-exchange membranes (AEMs) or cation-exchange membranes (CEMs). The most common positively charged groups fixed in the former are –NH3 + , –NRH2 + , –NR2H+ , and NR3 + , which allow the transport of anions and reject cations. On the other hand, CEMs contain –SO3 −, –COO−, PO3 2−, and PO3H−, which allow the transport of cations and reject anions. The combination of a cation and anion exchange membrane produces a third type of membrane known as a bipolar ion exchange membrane.

Fluorosis is an important public health problem in 24 countries, including India, which lies in the geographical fluoride belt that extends from Turkey to China and Japan through Iraq, Iran and Afghanistan. Of the 85 million tons of fluoride deposits on the earth's crust, 12 million are found in India. Hence it is natural that fluoride contamination is widespread, intensive and alarming in India. The available data suggest that 15 States in India are suffering from fluorosis (fluoride level in drinking water >1.5 mg/l), and about bout 62 million people in India suffer from dental, skeletal and non-skeletal fluorosis. Out of these; 6 million are children below the age of 14 years. The main source of fluoride in groundwater is the rocks which are rich in fluoride. Rajasthan is the largest state, which covers 10% of the country area but receives only 1/100 of the total rains. It shares only 1/10 of the average share of water than rest of the country. The geographical and geological setup leads to deterioration of water quality. Therefore, state faces acute water crisis. The great Indian Thar Desert covers where extremely arid and dry climate conditions prevail, receiving 5 mm to 20 mm annual rainfall. Groundwater is deeper and contains high mineral concentrated chemicals which makes the water unfit to drink. The eastern part of the state is semi desert and hilly, therefore the water availability in this region is also limited. Due to arid and semi arid climate and insufficient surface water resources, Rajasthan is indebt heavily on ground water for drinking and for agriculture purpose. Unfortunately, the groundwater quality in a large number of districts is not according prescribed standards. Rajasthan is the only state where all most all the districts are affected by high fluoride(beyond the permissible limit). In 23 districts the fluorosis problem can be visualized at various intensity level i.e. Dental fluorosis, skeletal fluorosis, nonskeletal manifestation etc. the study made by Rajasthan Voluntary Health Association in 1994 have showed that the total number of villages having fluoride problem in rajasthan is 2433 covering nearly 2.6 million population. Moreover, nearly 30,000 people are drinking water with concentration of 10.0 mg/l.

II. MEMBRANE CAPACITIVE DEIONIZATION

Desalination by MCDI is done by applying constant current with varying voltage , so method is known as constant current(CC).

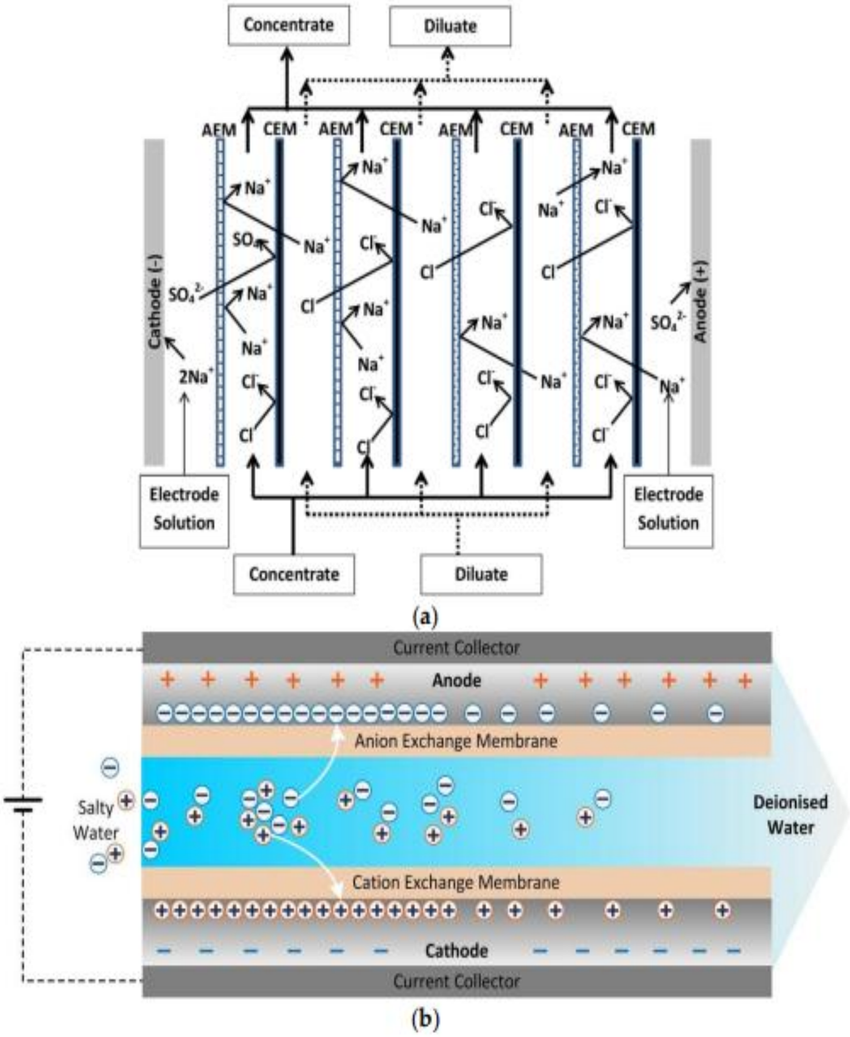

Figure 1 (a) Electro dialysis; and (b) Membrane Capacitive Deionization (MCDI) during adsorption.

In CC-operation the effluent salt concentration level remains at a fairly constant value, namely at a constant low value during adsorption, and at a constant high value during desorption. Another advantage of CC operation is that one can precisely tune the effluent salt concentration level by adjusting the electrical current, or water flow rate, as control parameters. CC operation works only in MCDI and not in CDI. Instead, in CDI-CC the effluent salinity changes throughout the adsorption step, indicating that the salt adsorption rate is not constant, even though in CC-mode operation. This is due to the fact that in CDI the electrical current is partially compensated by counterion adsorption and for the other part by co-ion desorption. The co-ion desorption effect decreases at high voltages and then the current is directly proportional to water desalination rate, but this is not yet the case at low cell voltages. Thus the salt adsorption rate by the full cell pair changes as function of time and this is why in CDI-CC the effluent salinity does not quickly level off to the desired constant. For CC operation in combination with membranes (MCDI-CC), Constant levels of the effluent salt concentration are quickly reached after start of a new adsorption step, because the co-ions are kept within the electrode structure and only counter ions carry the ionic current[3]. The study is carried out keeping the current constant 240 ampere and voltage as a variable.

III. STUDY AREA

Some places of Rajasthan (Mathaniya, Ummednagar, Rampura, PWD colony Jodhpur and Tanot, Longewala, Ranao) of Jodhpur and Jaisalmer districts were taken as study places as in these districts underground water have higher Fluoride concentrations. Where, PWD Colony situated in Jodhpur, have maximum fluoride concentration.

IV. METHODOLOGY AND RESULTS

The Pilot Plant (CapDI) was established at PWD colony of Jodhpur where tube well was the source of water. Other water samples were collected and transported in tankers from different selected underground sources. By keeping Water recovery, Current capacity (240 A), Number of cycles (3) as constants, all these samples were treated and reduction in TDS was assessed. Electric conductivity was taken as secondary parameter, as power consumption of the plant varies with variation in electric conductivity. The plant specifications were as given below.

Plant Specifications:

- Model: System IS 6 (Have 6 units of M(CDI) module)
- Instant Flow Rate: 0.5 – 6.1 m3/h
- Net Produced Flow: 2.4 – 3.5 m3/h
- Salt Removal: 25-98% (Adjustable)
- Water Recovery: 40-90% (Adjustable)
- System Power Requirement Single - Phase (4 kW)
- Water Feed Pressure: ≥ 6.0 m3/h , 3 bar
- Water Temperature 5 - 60 °C (40 - 140 °F)
- Number of cycles: 3 (Kept Constant)

In whole process current remains constant for a certain set percentage removal in both pure and waste cycle. When cycle changes from pure to waste, the current drops to zero and starts increasing to certain value. After reaching certain value it becomes constant for that cycle and voltage varies with increasing or decreasing percentage removal. By adjusting the desired set percentage removal in the plant will be reflected in the percentage change in electric conductivity. The removal of salts from MCDI with respect to reduction in salt concentration from RO was studied.

Table 1 Comparative data of fluoride removal by CapDI and RO of similar feed concentration from Longewala and Aao.

Treatment process	Source	Plant Capacity (LPH)	Fluoride in feed water (mg/l)	Fluoride in treated water (mg/l)	Fluoride removal efficiency	Power Consumed
CapDI	Longewala	1000	1.40	0.087	92.68	0.85
RO	Aao	1000	1.3	0.12	90.5	4

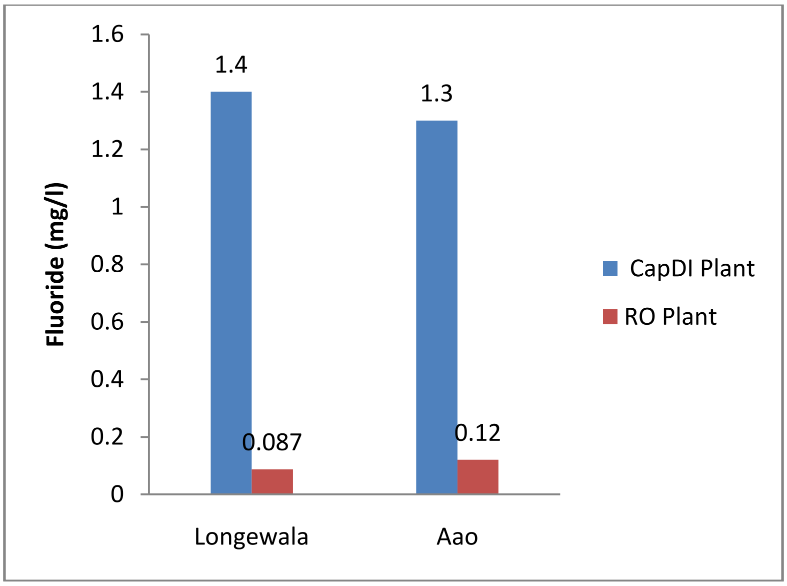

Figure 2 Reduction in fluoride by CapDI and RO of similar feed concentration from Longewala and Aao

Table 2 Comparative data of fluoride removal by CapDI and RO of similar feed concentration from Ummednagar and Jur.

Treatment process	Source	Plant Capacity (LPH)	Fluoride in feed water (mg/l)	Fluoride in treated water (mg/l)	Fluoride removal efficiency	Power Consumed
CapDI	Ummednagar	1000	3.23	1.4	61.87	1.09
RO	Jur	1000	3.3	0.16	95.77	4

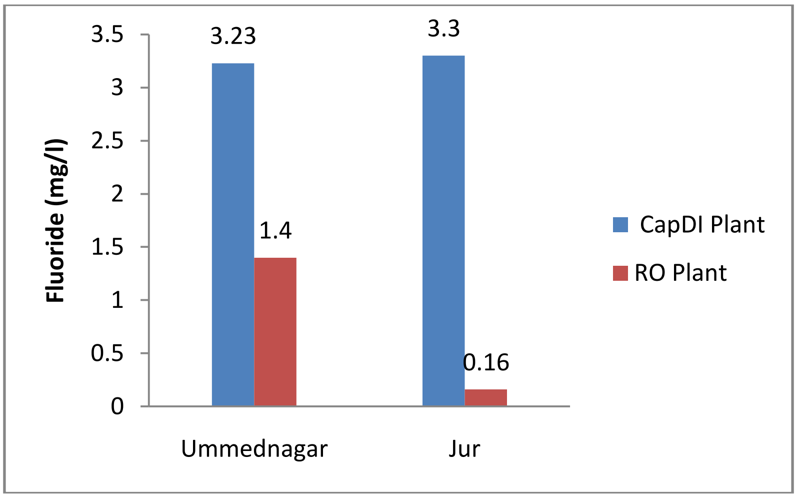

Figure 3 Reduction in fluoride by CapDI and RO of similar feed concentration from Ummednagar and Jur

Sample from Ummednagar was with maximum Electric Conductivity 8991 µS/cm, machine reached its maximum current capacity 240A on 75% set percentage removal. Whereas, data collected from Jur where Reverse osmosis technology is used, 96% fluoride removal took place with 13, 164 µS/cm Electric Conductivity

Table 3 Comparative data of fluoride removal by CapDI and RO of similar feed concentration from Rampura and Bhawad.

Treatment process	Source	Plant Capacity (LPH)	Fluoride in feed water (mg/l)	Fluoride in treated water (mg/l)	Fluoride removal efficiency	Power Consumed
Rampura	1000	CapDI	4.1	0.79	84.53	0.92
Bhawad	1000	RO	3.6	0.21	98.96	4

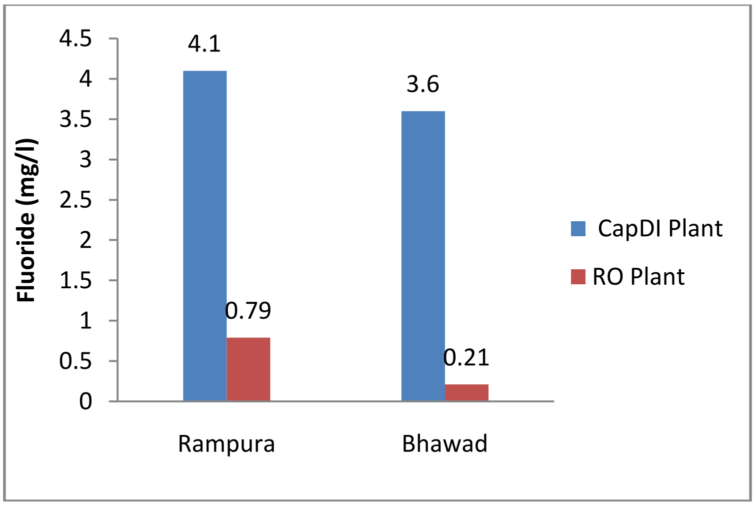

Figure 4 Reduction in fluoride by CapDI and RO of similar feed concentration from Rampura and Bhawad

Table 4 Comparative data of fluoride removal by CapDI and RO of similar feed concentration from Mathaniya and Bhikamkor

Treatment process	Source	Plant Capacity (LPH)	Fluoride in feed water (mg/l)	Fluoride in treated water (mg/l)	Fluoride removal efficiency	Power Consumed
Mathaniya	CapDI	1000	4.48	2.6	50.27	1.05
Bhikamkor	RO	1000	4.5	0.4	96.65	4

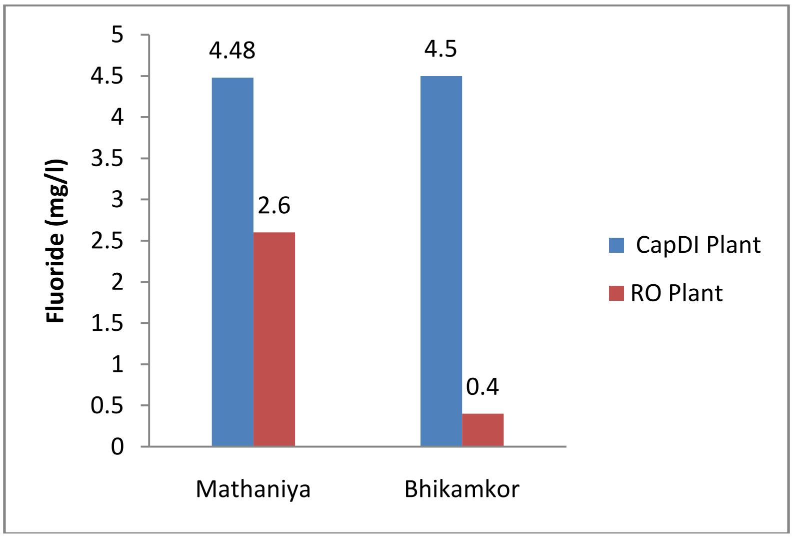

Figure 5 Reduction in fluoride by CapDI and RO of similar feed concentration from Mathaniya and Bhikamkor.

V. CONCLUSIONS

Study was carried out on the raw water sample collected from the various location situated in Jodhpur and Jaisalmer district out of which three locations Tanot, Longewala, and Ranao are situated at border area of Jaisalmer. And other locations of Jodhpur district are Mathaniya, Ummednagar, Rampura, PWD colony. The water was directly feed to the capacitive deionization plant and treated for various preset percentage removal efficiency of salt and analyzed for Fluoride removal, power consumption and percentage flow recovery.

For a comparative study with RO plant, data of various location having similar Fluoride Concentration in raw water collected from web site of Public health engineering department, Rajasthan. It was found that Capacitive deionization technique is very efficient in removal of low salinity feed water sources (EC< 3,000 mg/L). Energy consumption is quite low, approximately only 20 to 30%of energy utilized by RO Plant. CapDI plant have small footprint almost half the size of RO plant. There is no issue of fouling in CapDI plant which is usually seen in RO plant, fouling of hydrophobic membrane when the membrane is wetted. However, (M) CDI facilitates 68 to 70% recovery without scaling issues. Though, higher conductivity hinders the removal of fluoride, but increase in current capacity can lead to increased fluoride removal. And increased recovery, lower scaling issues, less power consumption proves Membrane assisted capacitive deionization, to be more energy efficient than reverse osmosis.

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