



## EVALUATION OF NITRATE REMOVAL BY MEMBRANE CAPACITIVE DEIONIZATION

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**Abstract**—Water is the symbol of existence of life. In the modern industrial era, we have used water so care less. To complicate matters, increasing groundwater extraction around the globe results in progressive salt water ingress in wells and aquifers. Potable water as well as water for agriculture and industry has become critical. 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 making Groundwater a centralized source of drinking water for millions of rural and urban families in Rajasthan. Unfortunately, Groundwater is deeper and contains high minerals and concentrated chemicals, making the water unfit to drink. Water quality standards are not meeting the prescribed Indian standards. Contamination of groundwater with nitrates is a major concern, especially for areas relying on this as a drinking water source. In this work, a capacitive deionization (CDI) system equipped with carbon electrodes coated with different metal oxides was studied to determine its ability to reduce nitrate concentrations. Results performed in a three-electrode cell were used as a proof of concept and demonstrated that coated electrodes had higher nitrate removal than that of uncoated electrodes, likely because of a reduction in hydrophobicity and an increase in surface area provided by the metal oxides. The study was carried out to evaluate efficiency of membrane capacitive deionization for removal of nitrate from underground water with elevated electric conductivity in the western Rajasthan. Accordingly, certain areas of Jodhpur and Jaisalmer districts were selected as the study area. The pilot plant (CapDI) manufactured by Voltea (Netherlands) was provided by In Now India Pvt. Ltd for carrying out this study. It is found that MCDI technology is very effective in nitrate removal if total dissolved solids concentration is less than 5000 mg/lt and percentage reduction of nitrate by MCDI technology is almost same as of by reverse osmosis technology. It was found that MCDI technology requires less power & gives more water recovery with low maintenance cost. Therefore it can be said MCDI technology is better than reverse osmosis technology.

**Keywords**- Nitrate, Membrane Capacitive Deionization (MCDI), Reverse Osmosis.

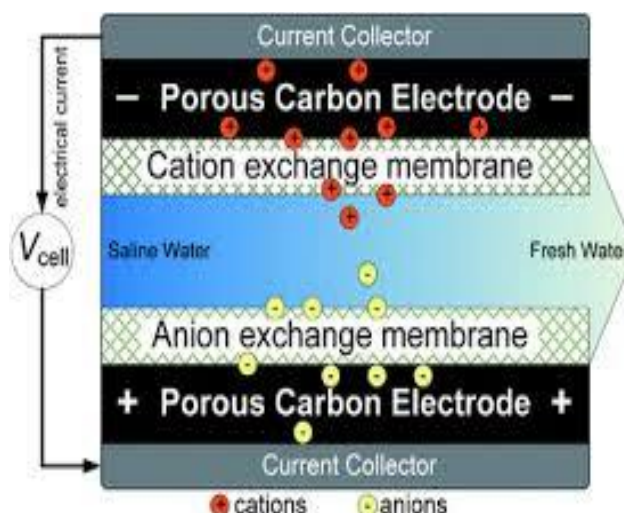
### I. INTRODUCTION

Groundwater, considered the most extracted resource on Earth, provides between 25% to 40% of the world's drinking water. Contamination by certain ions such as fluoride, perchlorate or nitrate is a threat to the availability of affordable potable water. In particular, nitrate represents one of the most serious problems due to its intensive application as a fertilizer and its high water solubility. Considering its low adsorption affinity in different kinds of soils, nitrate also appears highly likely to leach into groundwater wells and reservoirs. Its adverse health effects include its reduction into nitrite, which subsequently reduces hemoglobin to methemoglobin and alters the oxygen transport capacity within blood cells ('blue baby' syndrome), as well as its potential link with several kinds of cancer due to its ability to form nitrosamines when ingested in high concentrations. Moreover, from an environmental standpoint, the presence of nitrate in water bodies such as rivers or lakes may lead to eutrophication. Such increase in the algae population depletes dissolved oxygen in water, increasing the risk of death in certain aquatic organisms.

Membrane capacitive deionization is a new technology, which consumes less power and also the water recovery is much higher. The energy efficiency of Membrane Capacitive Deionization M(CDI) is due to the fact that the salt ions, which are the minority compound in the water, are removed from the mixture. Instead, other methods extract the majority phase, the water, from the salt solution. Furthermore, energy release during electrode regeneration (ion release, or electrode discharge) can be utilized to charge a neighboring cell operating in the ion electrosorption step and in this way energy recovery is possible<sup>5</sup>. CDI is a two stage process. In the purification step, A saltwater process stream flows between two electrodes held at a potential difference of around 1.2-1.5 V. Ions in the solution are attracted to the oppositely charged electrodes. The ions are electrosorbed onto the electrodes, removing them from the process stream, and the deionization cycle continues until the electrodes are saturated with ions. Then, during the regeneration cycle, the two electrodes are discharged or the polarity of the electrodes is reversed. This releases the ions into a waste stream, which has a much higher salt concentration than the process stream. One of the most promising recent developments in CDI is to include ion-exchange membranes (IEMs) in front of the electrodes, called Membrane Capacitive Deionization (MCDI).

## II. MEMBRANE CAPACITIVE DEIONIZATION

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



**Figure 1 Membrane Capacitive Deionization**

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 counter ion 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. The study was carried out keeping the current constant 240 ampere and voltage as a variable.

## III. STUDY AREA

In India, Rajasthan is considered as a major nitrate affected state in the country (Gopal and Bhargava, 1982). Nitrate levels in ground waters of Rajasthan have caused a great concern particularly in arid and semiarid climates. Nearly the whole Rajasthan is suffering from the problem of high nitrates with concentration ranging from 40 to 1000 mg/L (Sudhir Kumar et al., 2002). Mathur and Ranganathan (1985) found nitrate concentration ranging from 45 - 613 mg/L at Jodhpur city. Nitrate concentration in ground water varied from 8 mg/l at Phalodi to 199 mg/l at Tinwari, Osian. Exceptionally high concentration of 536 mg/l was observed at Mandore. Nitrate in excess of maximum permissible limit of 45 mg/l has been reported from parts of Osian, Phalodi, Mandore and Luni blocks. In Jaisalmer, Nitrate concentration in ground water has been found to vary from 10 mg/l at Lawa to 229 mg/l at Khudi. In about 64% of the samples analyzed, nitrate in excess of the maximum permissible limit of 45 mg/l has been reported. The study was conducted for water samples from Mathaniya, Ummednagar, Rampura, PWD colony of Jodhpur district and Tanot, Longewala, Ranao (border areas) of Jaisalmer district.

## IV. METHODOLOGY AND RESULTS

Membrane Capacitive Deionization Pilot Plant was established at PWD colony of Jodhpur where the source of water was tube well in the colony and other samples were collected from different areas of Jodhpur and army areas of Jaisalmer district which were transported in tankers. These water samples were treated and the reduction of nitrate ion was observed, where the Current capacity(240A) was fixed. the power consumption of the MCDI plant also varies with the variation in the electric conductivity of water, hence it was also taken as the secondary parameter. Plant observations are mentioned in the table below:

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

In the entire treatment process, the current was kept constant. The plant allowed the user to set desired percentage salt removal. By setting the desired percentage removal, the actual salt removal in the treated water was observed.

**Table 1 Observed percentage removal for each set percentage removal for Nitrate for different source stations**

| Source station | Feedwater conductivity ( $\mu\text{S/cm}$ ) | Feedwater Nitrate (mg/l) | Set Percentage removal |       |       |       |
|----------------|---------------------------------------------|--------------------------|------------------------|-------|-------|-------|
|                |                                             |                          | 60%                    | 70%   | 90%   | 99%   |
| Ummednagar     | 8880                                        | 245                      | 24.06                  | 48.70 | -     | -     |
| Rampura        | 2462                                        | 222.12                   | 36.97                  | 68.75 | 78.84 | 86.04 |
| Tanot          | 1850                                        | 220                      | 30.87                  | 69.58 | 83.41 | 85.79 |
| Mathaniya      | 5032                                        | 151                      | 22.81                  | 50.33 | 63.74 | -     |
| Ranao          | 2422                                        | 108                      | 28.24                  | 70.75 | 72.75 | 73.64 |
| PWD Colony     | 1833                                        | 100.61                   | 52.59                  | 64.20 | 83.10 | 87.07 |
| Longewala      | 2742                                        | 91                       | 29.37                  | 37.37 | 84.61 | 93.06 |

Water sample from different border areas of Jaisalmer district and some areas of Jodhpur was brought to the plant for testing. The machine was operated at different salt removal percentages, namely, 60%, 70%, 90% and 99%. It was observed that the plant was able to remove as much as 93% of the nitrate for Longewala water sample, while for other samples, with almost the same conductivity, the plant was found effective to remove about 85% of nitrate on an average. For sample Mathaniya, the plant could remove only upto 63.74% nitrate against the set removal of 90%. It was observed that for the water sample brought from Tanot, the conductivity was 1850  $\mu\text{S/cm}$  and Nitrate concentration was 220 mg/l, similarly the water sample brought from Ummednagar had conductivity of 8880  $\mu\text{S/cm}$ , and the nitrate concentration was about 245 mg/l. While the machine was able to remove upto 84.79% of nitrate in the sample from Tanot, the machine could only remove about 48% of nitrate from the Ummednagar sample, even when the nitrate concentration was almost same for both the samples. This indicates that when the conductivity of the water goes higher than 5000  $\mu\text{S/cm}$ , the plant does not work that effectively, as it reaches its maximum current.

**Table 2 Power consumption by CapDI plant during water treatment for varying nitrate concentration with set percentage removal is described in table below**

| Source     | Feed water Nitrate (mg/l) | Power consumption for set percentage reduction (KWH) |      |      |      |
|------------|---------------------------|------------------------------------------------------|------|------|------|
|            |                           | 60%                                                  | 70%  | 90%  | 99%  |
| PWD Colony | 100.61                    | 0.17                                                 | 0.35 | 0.54 | 0.78 |
| Rampura    | 224.12                    | 0.19                                                 | 0.36 | 0.62 | 0.81 |
| Longewala  | 93                        | 0.19                                                 | 0.36 | 0.62 | 0.84 |
| Ranao      | 109                       | 0.19                                                 | 0.42 | 0.81 | 0.86 |
| Tanot      | 233                       | 0.26                                                 | 0.76 | 0.89 | 0.98 |
| Mathaniya  | 150                       | 0.26                                                 | 0.89 | 0.98 | -    |
| Ummednagar | 235                       | 0.86                                                 | 1.06 | -    | -    |

**Table 3 Observations of various RO plants for almost similar nitrate concentrations in water as were in CapDI plant**

| S.No. | Source     | Plant Capacity (LPH) | Feed Water Nitrate(mg/l) | Nitrate in outlet (mg/l) | Observed Percentage Reduction | Power consumption (KWH) |
|-------|------------|----------------------|--------------------------|--------------------------|-------------------------------|-------------------------|
| 1     | Shergarh   | 1000                 | 120                      | 10                       | 93.43                         | 4                       |
| 2     | Kirmsariya | 1000                 | 144                      | 13                       | 91.80                         | 4                       |
| 3     | Bap        | 1000                 | 92                       | 7                        | 93.44                         | 4                       |
| 4     | Salawas    | 500                  | 258                      | 9                        | 96.97                         | 3                       |
| 5     | Shetrawa   | 1000                 | 293                      | 14                       | 94.56                         | 4                       |
| 6     | Gotan      | 500                  | 210                      | 13                       | 94.59                         | 3                       |

From the above two tables, it is clear that the power consumed by the Reverse osmosis (RO) plant is much higher than the power consumed by Capacitive deionization plant, for the same nitrate ion concentration in the feed water. Although at some places it was observed that RO plant was able to remove nitrate ion slightly more than the capacitive deionization plant, but since the capacitive deionization plant was able to bring the nitrate concentration below the permissible limit, it was ignored because the power consumption was almost one third for the capacitive deionization than that of RO plant.

## V. CONCLUSIONS

Nitrate removal capacity of the Membrane Capacitive deionization was analyzed for groundwater collected from different areas of Jodhpur district and border areas of Jaisalmer district of Rajasthan. The aim was to study the nitrate removal capacity of the membrane capacitive deionization technology. The power consumption capacity of the machine was also observed. Electric conductivity was taken as secondary parameter, as the power consumption and nitrate ion removal was highly affected by the electric conductivity of the feed water. During the process, it was observed that the machine attained salt reduction up to 90% when the electric conductivity was less than 5000  $\mu\text{S}/\text{cm}$ , and for conductivity more than 5000  $\mu\text{S}/\text{cm}$ , the machine could only attain 48% salt reduction before the machine reached its maximum current capacity. Water samples from Ummednagar and Rampura had almost similar nitrate ion concentrations, namely 235 mg/l and 224.12 mg/l respectively but the electric conductivity of Ummednagar was 8880  $\mu\text{S}/\text{cm}$  and that of Rampura was 2462  $\mu\text{S}/\text{cm}$ . For these two samples it was observed that while the Cap DI plant was able to remove the nitrate ion from Rampura water sample by 86%, it could only remove approximately 48% of the nitrate ion concentration from Ummednagar water sample, before reaching its maximum current capacity (240A).

The water recovery was observed to be 67% constant throughout the whole process. When compared with RO plant, it was observed that the membrane capacitive deionization consumed only about 30% of the total power consumed by the RO plant, against the same nitrate ion concentration in the feed water.

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