



An experimental study on some parameters for defluoridation using Capacitive Deionization with carbon electrodes

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Manuscript received online 15 December 2019, revised and accepted 26 December 2019

Capacitive Deionization has the potential to be a promising desalination method that can compete with the conventional techniques like reverse osmosis, multistage distillation etc. This research is focused on the fabrication of carbon electrodes for Capacitive Deionization. Initially experiments were performed with the varying proportions of PVDF (Polyvinylidene fluoride) to obtain its optimum composition for electrodes. Once the optimum composition for PVDF was obtained, having sufficient mechanical strength and favourable capacitive characteristics for the electrosorption of ions, further experiments were carried out for the electrode composition of AC:GP:PVDF::70:17:13 wt%. The experiments were conducted by varying voltage and pH on a sample of distilled water, which was further extended to tap water. It was observed that a maximum removal efficiency for F⁻ ions of 98% for distilled water and 95% for tap water was obtained at a voltage of 1.5 V and a pH of 8.0. The regeneration of the electrodes was achieved by depolarizing them at 0.0 V.

Keywords: Activated Carbon (AC), Capacitive Deionization, PVDF, Graphite Powder (GP), electrosorption.

Introduction

Water covers almost 75% of the earth's surface and is one of the most important resource needed for the sustenance of life forms on earth. But only around 3% of the total water is available as potable water. However, with the increase in population, the severity for the shortage of clean drinking water has also increased. Around 1.2 billion people around the world lack access to clean drinking water¹, 2.6 billion with little to no sanitation, millions of people dying every day (3900 children per day) with diseases transmitted through unsafe water and human excreta². In India alone, around 600 million people face high to extreme water stress, 75% do not have drinking water on the premise and around 84% rural households do not have piped water supply. 70% of the water in India is contaminated and India currently ranks 120 among 122 countries in water quality index³. As per Worldwatch Institute, by the year 2025 approximately two-thirds of the world may face water scarcity⁴. As there is more brackish water than clean water, water desalination can be an alternative for the remedy of brackish water. Apart from the conventional desalination techniques like reverse osmosis, multistage distillation etc., Capacitive Deionization (CDI)

has proved to be an emerging and fast growing electrochemical desalination technique. Capacitive Deionization is an electrical process which extracts ions from the water through the application of potential difference across the electrodes. This paper deals with the study conducted on the removal of F⁻ ions from feed water using CDI. Over the past few years there has been a drastic increase in the research and development of CDI technology⁵. The idea of CDI conceptualized in the 1960s with the discovery of demineralization process using electrochemical cell reactor⁶. Idea of graphite like materials for electrode came in 1961⁷. The term CDI was coined in 1996⁸. The recent advancements include the development of membrane CDI⁹, flow-through electrodes¹⁰, flow electrodes¹¹, hybrid CDI¹², the modified Donnan mathematical model for CDI¹³, and the discovery of key correlations between pore size and electrosorption performance. In CDI process, electrode material plays a very crucial role in improving the performance of the process. An ideal electrode material should have a high specific surface area, high conductivity, good wettability, and low cost material¹⁴. Carbon material satisfies most of the requirements and hence more focus has been given on the development of carbon mate-

rials like carbon aerogels, activated carbon, ordered mesoporous carbon, carbon nanotubes, activated carbon fibre and their composites¹⁵, Graphene-like nanoflakes (GNFs)¹⁶.

Fluoride in groundwater can be caused by both natural and anthropogenic sources. The high levels of fluoride in groundwater is causing increased concerns worldwide. Increased consumption of fluoride (>1.5 mg/L) can cause permanent deformations of bones and skeletal and dental fluorosis. On the other hand fluoride level of 0.5–1.5 mg/L has beneficial effects on human health. Around 27 countries and 200 million inhabitants across the world consume drinking water with excess fluoride¹⁷. While in India, as per the report of Ministry of Environment and Forests, Government of India (State of Environment Report, 2009), it is estimated that 19 states of India are affected with fluorosis impacting an approximate population of around 65 million, of which around 6 million are children¹⁷. Hence it is the need of the hour to tackle the problem of fluoride with some new cost-effective and energy efficient method and Capacitive Deionization has the potential to be a prominent contender for the task. Moreover, it can also be extended for the use of wastewater treatment¹⁸.

Materials and methods:

Fabrication of activated carbon electrodes:

For the fabrication of the electrodes, activated carbon powder (specific surface area = 1124 m²/g, Qualikems fine Chemicals Pvt. Ltd.), graphite powder and poly(vinylidene fluoride) (PVDF, average Mw ~ 180,000, Sigma-Aldrich) polymer binder and N,N-dimethylacetamide (DMAc, 99%, Loba Chemie, Mumbai, India) as a solvent were used to make the electrodes. The chemicals were stirred on a hot plate magnetic stirrer for about 6 h to obtain a homogenous mixture. The carbon slurry was coated onto an aluminium sheet and dried at 120°C for 2 h to form a carbon sheet. The sheet was further dried at 80°C in vacuum oven for 2 h to remove any residual organic solvents. Each AC electrode had an effective surface area of 16 cm×9 cm. Varying proportions of activated carbon, graphite powder and PVDF was tried before the optimum composition was reached. The PVDF content was 13 wt% of the carbon electrode. Fig. 1 shows the steps involved in the fabrication of the carbon electrode.

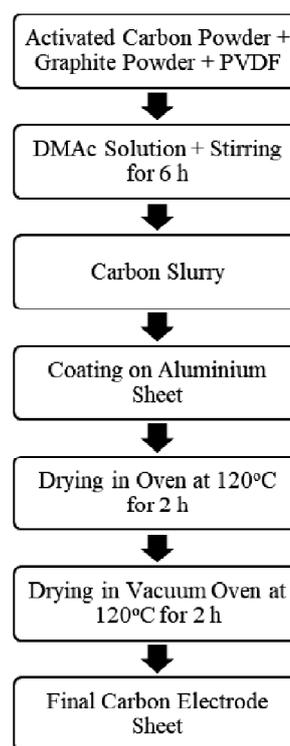


Fig. 1. Flowchart for steps involved in the carbon electrode sheet fabrication.

Electrosorption experiments:

The electrosorption experiments were performed in a batch model to test the performance of the fabricated electrodes and the CDI system.

The system consisted of electrosorption cell, conductivity meter (TCM 15+, TOSCHON Industries Pvt. Ltd., Ajmer), and a potentiostat (BK-1502DD, BAKU). The dimension of each plate is 110 mm×90 mm. The two opposite electrodes were separated by 4 mm spacer. The configuration of one half of the cell is poly(methyl methacrylate) (PMMA) sheet cover, aluminium plate, carbon electrode for electrodes coated on only one side. For both sides coated electrode: carbon electrode, aluminium sheet, and carbon electrode. A total solution volume was about 2.3 L in each experiment. The variation of the solution conductivity was monitored throughout the experiment. The final concentration of the fluoride was measured using ion meter (HI 4222, HANNA).

Each experiment was performed until there was no apparent conductivity variation. Several experiments were repeated under same conditions to confirm the results. In the

experiments, the electrosorption efficiency (%) is defined in eq. (1) as follows:

$$\text{Electrosorption efficiency} = \frac{(C_0 - C_e)}{C_0} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations respectively¹⁹.

Selection of optimum proportion of materials:

Among the components in the CDI system, the electrode is the most important component because an optimum composition is required to manufacture the electrode with the desired properties, particularly when using activated charcoal powder. To choose the optimum proportion of PVDF, varying proportions of Graphite Powder and PVDF were tried at varying proportions by making electrodes on a small scale by changing the proportions while keeping the rest of the parameters like surface area, current, influent concentration, as constant.

A potential difference of 1.5 V was applied across the electrodes and the experiments were carried out for a duration of 15 min each. Table 1 lists the various electrode compositions used for the determination of optimum composition of electrode along with the % removal of F^- ions from the feed water.

Table 1. Different electrode composition and % F^- ions removal

Electrode	Type 1	Type 2	Type 3
Materials	ACP:CCB: PVDF	ACP:CCB: PVDF	ACP:CCB: PVDF
Composition	70:15:15	70:17:13	70:19:11
Average removal efficiency (%)	10.32	13.63	8.35

A varying PVDF compositions of 11 wt%, 13 wt%, and 15 wt% were selected and an optimum dose of PVDF was obtained at 13 wt% giving the maximum removal efficiency for F^- ions for a duration of 15 min while keeping rest of the other parameters as constant.

Characterization:

The hydrophilicity of the electrode depends on the topography of the surface of the coating for CDI electrodes. Adequate porosity and ordered pore patterns are required

for adequate hydrophilic surface to generate a well-developed diffusion layer. The electrode was analyzed with Scanning Electron Microscopy (SEM) with a sample of 1 cm² size for electrodes of composition 70:17:13, both before and after its use. The Scanning Electron Microscopy (SEM) instrument used was of model EVO-Scanning Electron Microscope MA15/18 produced by the company Carl Zeiss Microscopy Ltd. The Energy Dispersive Detector (EDS) is produced by Oxford Instruments Nanoanalysis with model number 51N1000 – EDS System. Fig. 2 shows the SEM image of electrode before its use for the fluoride removal. It can be seen that materials have very well been attached to the surface with no excess binder and a lot of small pores have been developed resulting in the increase in the number of adsorption sites. Fig. 3 shows the SEM image of the electrode after its use for fluoride removal. It is clear from the image that F^- ions are completely adsorbed on the surface and the pores have been filled.

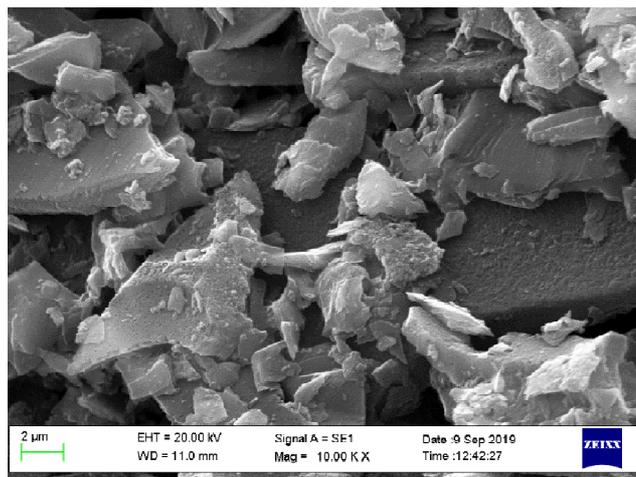


Fig. 2. SEM image of electrode before use.

Results and discussion

The experiments conducted for the determination of optimum composition shows that adsorption efficiency increases with increase in PVDF content to a certain extent and then decreases. Increasing the content of PVDF binder in carbon electrode decreases the specific surface area.

Variation of voltage:

The experiments were carried out with batch mode self-made lab scale CDI set up. The voltage was first set at 1.4 V

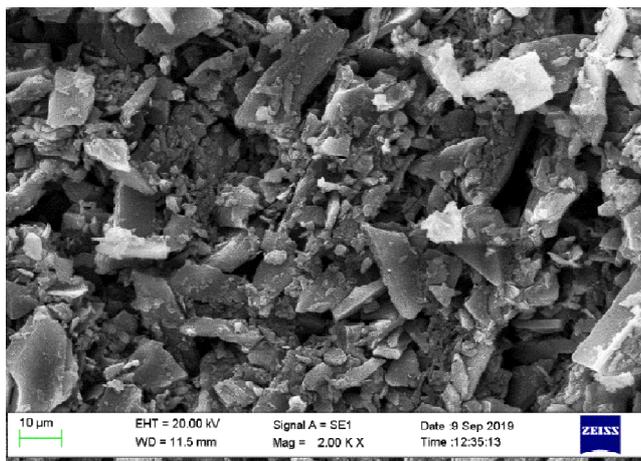


Fig. 3. SEM image of electrode after desalination process.

and then further increased to 1.5 V and 1.6 V in subsequent experiments. It was observed that removal of F^- ions first increased when the voltage was increased from 1.4 V to 1.5 V but on further increasing the voltage to 1.6 V resulted in the decrease of the removal efficiency. The F^- ions removal efficiency observed was 89.37% for 1.4 V, 92.26% for 1.5 V and 89.51% for 1.6 V. Fig. 4 shows the variation of % removal of F^- ions with time for the various sets of experiments performed. The % removal of F^- ions first increases

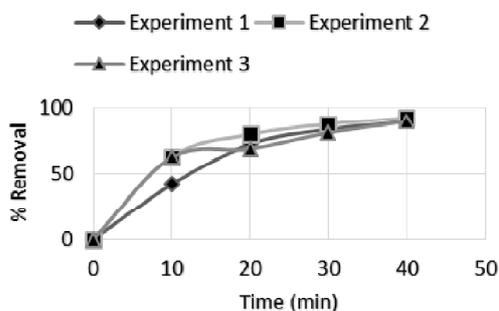


Fig. 4. Fluoride removal (%) vs time for voltage variation.

with time as the number of adsorption sites present are large but with time as the adsorption sites are nearing exhaustion, the removal efficiency becomes constant. The same trend is shown for graphs in Fig. 5 and Fig. 6 respectively. The % removal of F^- ions obtained was highest at 1.5 V. For further experiments, the potential difference across the electrodes was fixed at 1.5 V.

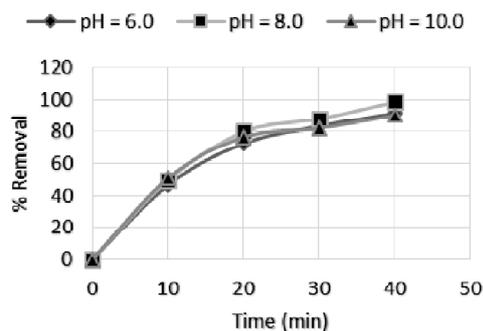


Fig. 5. Fluoride removal (%) vs time for pH variation.

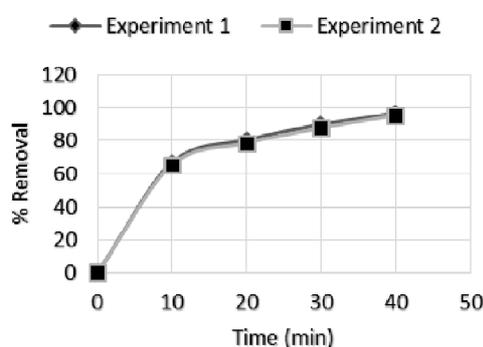


Fig. 6. Fluoride removal (%) vs time for tap water.

Variation of pH:

The pH value is one of the important characteristics affecting the quality of water and the treatment system to be adopted. Various studies have reported the effect of pH on defluoridation. Ku and Chiou (2002) reported that alumina, in the pH range of 5 to 7, as an adsorbent is effective for fluoride removal²⁰. Another study by Singano *et al.* (1995) revealed that magnesite calcined into magnesia shows optimal fluoride removal in the pH range of 10 to 11²¹. In this experiment, the effect of pH is studied on the fluoride removal using Capacitive Deionization. The pH is varied from 2.5 to 10 while keeping all other parameters like voltage and temperature constant. Fig. 5 shows the variation of % removal of F^- ions with time for the various sets of experiments performed at varying pH.

In very acidic medium i.e. $pH < 4$, no significant removal of fluoride was obtained. This could be due to the shielding of the zeta potential due to H^+ ions thus resulting in the decrease in the electronegativity of the surface²². The removal

efficiency tends to increase with the increase in pH. The % removal at pH 6.0 was 91.34%. The highest % removal was at pH 8 which was 98.49%.

However, there was a slight decrease in the % removal at pH 10 and this efficiency will further reduce in highly alkaline solutions i.e. pH > 10. This could be due to the fact that at high pH, the hydroxyls (OH⁻) starts competing with the fluoride ions for the remaining sites on the surface.

Experiments on tap water:

The optimum conditions obtained from the above set of experiments i.e. voltage = 1.5 V, pH = 8.0 were used for the purification of tap water. Two sets of experiments were performed using the tap water with artificially augmented fluoride levels. The average % removal of F⁻ ions was found to be 96.12% at the aforementioned conditions. Fig. 6 shows the variation of % removal of F⁻ ions with time for the various sets of experiments performed.

Conclusions

A desalination system consisting of batch mode flat stack type CDI device was successfully fabricated. The experiments were performed both on synthetic samples of distilled water and tap water. At the optimum pH of 8.0 and a potential difference of 1.5 V the maximum % removal of F⁻ ions from the feed water was obtained to be 98.49% and 96.12% from the distilled water and tap water samples respectively. It showed that most of the F⁻ ions were adsorbed on the electrode surface. Based on these results the PVDF13, comprising 70 wt% Activated Carbon, 17 wt% Graphite Powder, 13 wt% PVDF, has presented good performance in terms of electrosorption capacity. The electrodes can be regenerated by depolarizing the electrodes.

Acknowledgement

The authors are thankful to the Indian Institute of Technology (Banaras Hindu University), Varanasi for supporting this research work.

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