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Research Article

Review on Capacitive Deionization: A Novel Method of Water Purification

N. Deepa Priya*, K. Saravanan

Department of Chemical Engineering, Kongu Engineering College, Perundurai, Erode, Tamilnadu – 638 060. India.

*Corresponding author's e-mail: dppriya1984@gmail.com

Abstract

Shortage of potable water in remote communities and rapid depletion of ground water have led to development of pressure driven and electrochemical technologies like reverse osmosis, electro dialysis and capacitive deionization. Capacitive deionization is a promising process technology to purify brackish and saline water. Though the concept of capacitive deionization was initiated in 1960's, the last decade has seen rapid development of process and material technology. Commercially viable plants are now available for applications ranging from potable water production to treatment of cooling tower makeup. This article discusses the concept, process design principles, electrode materials and energy requirement for this novel process. Operating problems including fouling and scaling are dealt with. A brief note on environmental impact of this process is given.

Keywords: Membrane capacitive deionization; Desalination; Electrode materials; Energy requirement.

Introduction

Water is the basic requirement for sustenance of life. As the world population is increasing, the demand for water is growing at a rapid rate. The available fresh water resources are limited. Nearly 97% of the water in the earth is salty and hardly 0.3% of the water is potable [1]. Thus the mankind is forced to tap brackish and saline water sources to feed the water needs of the society. In many countries like India nearly 25% of the population lives in areas of water shortage. It is essential to develop economically viable technologies to desalinate water.

Principally, there are three major technologies available today for desalination: thermal evaporation, reverse osmosis and electro dialysis [2]. Thermal evaporation, even though practiced in Middle-East and African countries is a costly option requiring high levels of thermal energy input. Reverse osmosis, basically a pressure-driven filtration process, requires significant amounts of energy. Also, reverse osmosis systems cannot handle a wide variety of raw water supplies that have varying amounts of dissolved salts, trace minerals etc. Electro dialysis requires an application of electric field but has lower requirement of energy. However, elaborate controls are required to maintain optimum conditions and due care should be taken in the selection of membranes.

The conceptual study of capacitive deionization was initiated in the early 1960's and electrodes were developed in the early 70's [3]. The mechanism and theoretical models of capacitive deionization were enunciated in late 70's. The dawn of a new millennium saw a lot of research work in developing novel electrodes for the system: ordered mesoporous carbon, carbon nanotubes, carbon electro gels etc. Recently, membrane capacitive deionization incorporating ion exchange membranes have been introduced to improve performance. Current research work is focussed on reducing energy inputs and solving operational issues like scaling. Presently, capacitive deionization modules are commercially available to treat a wide variety of raw water supplies.

Process description

Nowadays, capacitive deionization is being thought of as a cheap, low-energy, high-yield process alternative to reverse osmosis and electrodialysis, with applications ranging from water softening to seawater desalination. The term capacitive deionization implies two functions. Deionization involves removal of cations and anions from water. The term "capacitive" is used to denote porous electrodes

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that attract charged ions from water and subsequently store them. Capacitive deionization (CDI) is thus an electrochemically controlled method for removing salt from brackish and saline streams. A stream of salt water flows between pairs of high surface area electrodes that are held at a potential difference of around 1.2-1.5 volts. The potential difference should not exceed the point at which the bonds in the water molecule between the hydrogen and the oxygen atom breaks up. This voltage is also called Nernst Voltage or Standard Electro Potential of water, $E^{0}_{cell} = -1.23\ volts$ [4].

Ions and other charged particles are attracted to and held on the electrode of opposite charge. The negative electrode attracts positively charged ions (cations) such as sodium, calcium etc. while the negative ions like chloride, sulphate etc. are attracted by the positively charged electrode (Figure 1). In due course, the electrodes become saturated with ions. Ionic concentration of outlet solution will increase until it reaches the same concentration as that of inlet indicating no electro-sorption takes place in the electrodes. It is thus necessary to clean the electrodes to restore their ability to adsorb ions. That is, the cell needs to be regenerated. The regeneration process (Figure 2) can be performed either by short circuiting the electrodes or by applying an opposite voltage to the electrodes. During this process, the ions on the electrodes are flushed out of the system, a concentrated brine solution results. The regeneration may also return a fraction of the energy input. This will help to lower the energy requirement of the process and enhance its commercial viability. In most of the commercial designs, nearly 75-80% of the feed comes out as deionized water.

Electro-sorption forms the basic principle of capacitive deionization describing the interaction of molecular species and ions with charged interfaces for chemical conversion and temporary storage and separation. With the variety of molecular species ranging from metal and salt ions up to protein and specialty molecules like pharmaceuticals, and the multitude of flat and porous electrode materials, that one can think of, the system configuration can be tailored to meet the specific demands of the user.

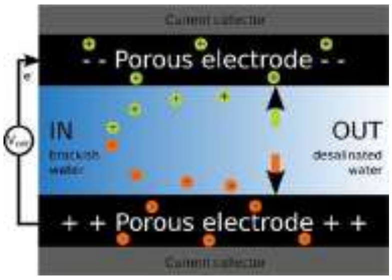

Figure 1. Capacitive deionization – purification mode

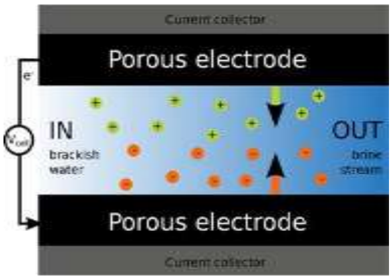

Figure 2. Capacitive deionization – regeneration mode

Electrode materials

Proper choice of electrode is very important to ensure that the separation process exhibits optimum performance. Electrode material should ideally have the following characteristics [5]:

- Fast response of the entire surface area to electro-sorption / electro-desorption
- Ability to tolerate frequent voltage changes
- Specific surface area required for electro-sorption should be as much as possible
- Electronic conductivity should be more
- Simply shaped according to design requirements
- Less tendency for scaling, bio and organic fouling
- Chemical and electrochemical stability for wide range of pH values

Initially, porous carbon electrodes were utilized for use as both anode and cathode. Subsequently many researchers have developed novel materials which have enhanced the performance of CDI systems. The following materials have been proposed for commercial applications.

Activated Carbon (AC)

Commercial activated carbon electrode with a high specific area of 1000-3500 m^2/g has found widespread use in commercial units. Resin derived activated carbon can be synthesized as beads, fibers, or monoliths. Most of the activated carbons are usually powders composed of micrometer sized particles. Resin helps in reducing hydrophobicity, an undesirable property for CDI electrode. The pore diameter of AC's is in the range of 1.10-2.40 nm, electrical resistance of 3.5-15 Ωcm^2 and capacitance of 100-120 F/g [6].

Ordered mesoporous carbon (OMC)

Ordered mesoporous carbon with high surface area, appropriate pore size and well cross-linked porous structure is likely electrode material for capacitive deionization [7]. OMCs show a highly periodic hexagonal or cubic arrangement of mesopores which may improve the transport of salt ions through the pore network. OMCs are synthesized with a pore size between 3.3 and 4.0 nm and specific surface area between 950 and 1594 m^2/g. Specific capacitance is about 100-180 F/g and electro-sorption capacity of 4.5 – 15 μmol/g.

Carbon Aerogel (CA)

CAs which have specific surface area between 400 and 1100 m^2/g with a high electrical conductivity of 25-100 S/cm and a low mass density less than 0.1 g/ml have been synthesized in the form of powders, beads, thin films and monoliths [8]. They are composed of a network of rather dense carbon nanoparticles. They have low electrical resistivity, less than 40mΩ.cm.

Carbide-Derived Carbons (CDC)

Carbide-derived carbons [9] can be synthesized to exhibit extremely, narrowly distributed microspores and no mesopores. However, pores in CDCs are not arranged in an orderly fashion. CDCs are synthesized by etching carbide powders in dry chlorine gas at high temperatures of 300-1100^{o}C. They can also be derived from monoliths, fibers, or thin films. Activated CDCs can have specific surface area up to 3200 m^2/g. Pore size is normally in the range of 15 to 50 nm and specific capacitance of 18 F/g.

Carbon Nanotubes (CNT) and Graphene

Carbon nanotubes [10] and graphene [11] have been developed as alternate materials for electrodes of CDI process. Multi-walled carbon nanotubes have surface area between 50-129 m^2/g. CNT's have better desalination capacity compared with activated carbons. Electrodes consisting of graphene flakes added to graphite powder and a polymeric binder has a surface area of 2220 m^2/g. Mesoporous carbon/graphene composite electrodes have higher salt adsorption capacity and faster ion immobilization rate compared to active carbons. Graphene's and CNT's have high theoretical conductivity in excess of 7000 S/m.

Miscellaneous

Some researchers have proposed carbon aerogel-silica composites as electrodes [12] for CDI cells. Addition of silica could improve the mechanical properties and wettability of electrodes. In addition, the preparation time of electrode material could be reduced significantly. Carbon blacks having dense carbon nanoparticles with a specific surface of 120 m^2/g and having a high electrical conductivity are additives to film electrodes composed of porous carbons.

In general, carbon derived carbons have high salt adsorption capacity and operate with cell voltage of 1.4 V. Even though multi-walled carbon nanotubes have low salt adsorption capacity, they can tolerate high initial salt concentration. Some researchers have concluded that mesoporous carbon based electrodes have superior salt adsorption capacity compared to carbon aerogel base electrodes.

Membrane capacitive deionization (MCDI)

Process description

Traditionally, CDI was as a membrane-free technology. In order to improve the performance, membranes have been used in CDI cells. The membranes are located in front of both porous electrodes [13]. The ion exchange membranes allow only positive ions to pass through negatively charged electrode and only negative ions to pass through positively charged electrodes (refer Figure 3(a).

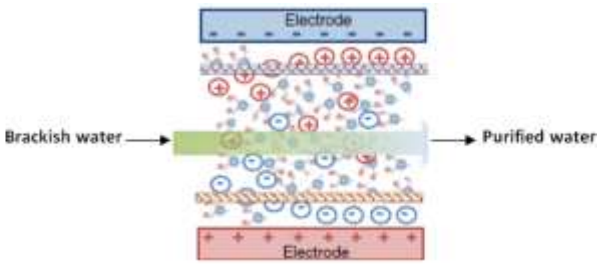

Figure 3(a). Membrane capacitive deionization – Purification Mode

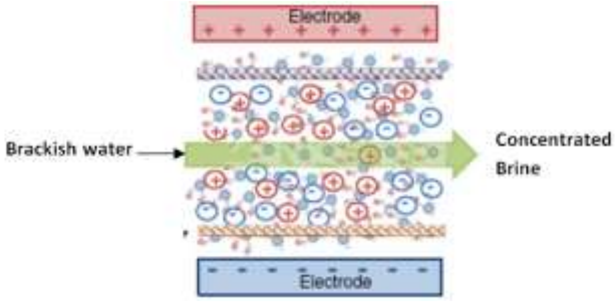

Figure 3(b). Membrane capacitive deionization – Regeneration Mode

Regeneration Process

Regeneration is to be performed when the surface of the electrodes gets saturated with the ions, and the salt concentration in the product water will be same as that of influent. The major drawback of CDI is in regeneration [13]. During the process of regeneration (refer Figure 3(b)), the polarity of electrode potential on the electrode is changed. This will not only help to desorb the adsorbed ions but also attract and adsorb oppositely charged ions from the bulk of the fluid. That is ion desorption and adsorption occur simultaneously during this time. This results in incomplete regeneration of electrodes, lowering of adsorption capacity of electrodes and higher regeneration cycle time. This also causes residual ion accumulation blocking the way of other ions during the subsequent purification step. In order to get around this problem, ion exchange membranes were introduced and were placed adjacent to each of the electrodes. These membranes assist in preventing adsorption during the regeneration step. The cations permeate through cation exchange towards the negative electrodes and anions through anion exchange membranes towards positive electrodes.

Merits of MCDI

During regeneration process, the presence of cation exchange membranes prevents anions from permeating through the membrane towards the now positive electrodes and is retained in the bulk of the fluid. In the same manner, cations cannot permeate through anion exchange membranes. Regeneration of electrodes is thus facilitated and the time required for regeneration is reduced. The introduction of ion exchange membranes has significant effect on ion transport kinetics. Several researchers have used MCDI to remove nitrate and sodium ions [14] from solutions using CDI units. Energy recovery in MCDI systems could be higher compared to that in CDI systems during the regeneration period (the current which is generated as a result of release of ions from the electrode could be withdrawn from the system for reuse). Energy savings could also be achieved through the selection of highly conductive electrodes and ion exchange membranes. Process parameters including flowrate and temperature of operation could be optimized to reduce energy consumption [15] in CDI cells.

Energy requirements

The approximate energy requirement for different purification processes is given in the following Table 1.

Table 1. Energy Requirements

Separation system	Energy Requirement (KWh/m^3)	Reference
Multi stage filtration	10 - 16	[16]
Multiple Effect Distillation	6 - 9	[16]
Reverse Osmosis	3 - 10	[17]
Electro Dialysis	3 - 6	[18]
Capacitive Deionization	0.1-2.03	[19,20]

Scaling and fouling

Scaling

Scaling of electrodes is one of the major problems associated with CDI. Brackish water may contain calcium and magnesium ions, which may appear to be harmless in concentrations normally encountered but can create precipitates at high levels of concentration. During operation, the negative electrode electrosorbs positive ions, including calcium and magnesium ions. The buildup of calcium and magnesium ions may lower the electro-sorption capacity of electrode and thus the performance of the unit.

Fouling

Fouling can be thought of as the settling of solids on a surface creating an extra layer of electrical, thermal and/or physical resistance. Scaling is rather a different phenomenon involving a physio-chemical change which causes crystallization, precipitation and/or solidification of components from the solution onto the surface. Fouling is normally caused by organic compounds and scaling by organic and inorganic compounds. In comparison with reverse osmosis and electro dialysis, fouling in CDI and MCDI will be less due to the existence of a regeneration stage, which cleans the membranes and electrodes and hence prevents the build-up of salts and precipitates.

Remedial Measures

Biofouling of electrodes such as carbon aerogels can impede electric charging with the electrodes followed by loss of electro-sorption efficiency. The energy consumption may thus go up. To prevent the bacterial growth by adsorbed organic material on CDI electrodes, influent solution could be pretreated to reduce the concentration of total organic carbon. Mild organic acids like citric acids have been proposed for descaling. However, the process is to be monitored continuously to determine the timing, frequency and duration of descaling.

Purification cost

Purification cost depends on many factors like type of technology, energy cost, feed water salinity, capacity of the unit and factory-specific conditions. In general, it can be said that CDI will be cost effective for low to medium salinity feed water. For brackish water, the cost of purification by CDI compares favorably with that of reverse osmosis. However, in the case of sea water desalination purification costs are 30-40% higher for CDI compared to reverse osmosis.

Advantages of capacitive deionization

Low water wastage compared to reverse osmosis systems that waste more than 25-40% of water. The maximum water wastage in CDI systems is only 20%. Low operating cost – CDI systems require no chemical and have low requirement of consumables for operation. Simple Operation - CDI systems have built in controller that automates the working of the system to suit the local conditions. Requires less space to operate including for pretreatment. Unlike membrane based treatment technologies like reverse osmosis, CDI does not require high pressure. Thus the cost for pipes and equipment could be lower. CDI requires low voltages. Hence, safety issues are almost non-existent. CDI is suitable for operation in remote areas, since it can be operated on solar energy. In this respect, the technology may be considered environmentally clean.

Applications of capacitive deionization

Potable water for remote areas –CDI can be used to provide potable water for communities where electricity and water scarcity exist by using alternate energy sources like solar or wind.

As a drinking water solution in schools, universities, community centers, offices, shopping complexes - CDI systems produce high quality treated drinking water and can provide better health benefits thus, making it an ideal drinking water solution for schools, offices, shopping complexes, offices, apartments and residential blocks etc.

Power plants and Process Industries – CDI systems will be cost effective for treating blow down water from cooling towers, boilers and diesel engines.

CDI systems have also been proposed for Removal of radio nuclides from low level radioactive waste, production of high purity water for semiconductor industry and removal of salt from ground water for agricultural use.

Environmental impacts

Both CDI and MCDI have one problem in common: disposal of concentrated brine solution. Several methods have been suggested and most simple method is through use of evaporation ponds. Both CDI and MCDI have to deal with environmental impacts within the manufacturing process of electrodes and ion-exchange membranes and their disposal strategy. The life expectancy of electrodes and ion exchange membranes are estimated to be 10 years and 10-15 years respectively. However, more intensive research is required to develop methods for their safe disposal.

Conclusions

Capacitive deionization is a novel method for treating brackish and salt waters. CDI has acquired importance in recent times, especially for providing potable water for remote villages which do not have grid connected electricity or water supply. Development of new electrodes and ion exchange membranes has progressively reduced the cost of purification. CDI is an attractive option for treating make up water for cooling towers, diesel engines and for producing drinking water residential blocks and shopping complexes. Intensive research efforts are required to reduce energy requirement and make the process cost effective for desalination of sea water.

Conflicts of interest

Authors declare no conflict of interest.

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