ON THE CHALLENGE OF DEVELOPING CAPACITIVE DEIONIZATION SYSTEMS FOR WASTEWATER TREATMENT: IS IT REAL?

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Abstract

Due to the increasing worldwide water scarcity associated to the climate change there is the need to increase the reinjection of wastewater into the overall water cycle. As consequence wastewater treatment is within the largest energy use sector in many developed countries. In recent years, Capacitive Deionization (CDI), which is based on the principle of electrosorption of ions on charged high surface-area electrodes, the same as charging and discharging an electrochemical double layer capacitor [1] (see Figure 1), has been reported to be a promising technology which is an alternative to other classical water treatment methods such as reverse osmosis (RO) and evaporation processes. We see that this technology is gaining increased scientific interest since 2006 [2]. However, not too many publications indicate the feasibility of the kWh/m^3 consumption in CDI systems for brackish water treatment (500 – 30 000 ppm). The common assumption proposes that the main problem may be the ions adsorption capability of the electrode material during discharging. In fact the desorption processes may be even more problematic, in energy efficiency terms, since experiences diffusional difficulties when submitted to relatively high current [3].

This presentation will provide an overview of current strategies for operating these systems aiming to improve energy recovery and lead this process to the point of making these systems an option for use in water treatment plants.

Keywords

Capacitive Deionization (CDI), Wastewater Treatment, Electrosorption, Salt removal efficiency.

Introduction

According to the IPCC Technical paper "Climate Change and water" water and its availability and quality will be the main pressures on, and issues for, societies and the environment under climate change [4]. Due to the always increasing worldwide water scarcity associated to the climate change there is the need to increase the reinjection of wastewater into the overall water cycle. The reuse of treated waste water has been identified as a potential way for addressing long term imbalances between water demand and water supply, therefore reducing the vulnerability of water and environmental resources to climate change and man-made pressures.

On the other hand, successful adaptation to the impacts of climate change on water depends also on the extent to which water management can be integrated into other sectorial policies such as agriculture, energy, cohesion and health. In this project energy aspects are specifically addressed. The energy efficiency of the technologies applied to water reuse must be taken into account since advanced wastewater treatment technologies usually consume a significant amount of energy, thus contributing to the climate change through the CO_2 emissions associated to the generation of the electric power consumed in the water treatment.

Capacitive deionization (CDI) represents a promising technology that can be benchmarked with some of the Best Available Technologies for waste water reclamation and reuse such as Reverse Osmosis (RO) and Electrodialysis Reversal (EDR). The substitution of those technologies for Capacitive Deionization aims at providing similar or better performance than existing technologies particularly in terms of the flow rate of effluents per cubic meter of treated water, together with a significant reduction of energy consumption per cubic meter of wastewater treated. Capacitive Deionization is an electrochemical water treatment process that allows one to purify saline water by removing ionic species while storing energy simultaneously, using a straightforward, non-energy intensive and low environmental impact fashion. The key to CDI is the adsorption of charged particles (ions) in the electrical double layer (EDL) of an electrode upon polarization by a direct current (DC) power source. It is essentially the same as charging a double layer capacitor [5, 6].

During deionization (or charging), a brackish water stream is circulated through polarized electrodes, usually based on porous activated carbon materials, resulting in a less concentrated output (permeate). In the regeneration step (or discharge), a wash solution is circulated while the electrodes are depolarized, so that ions are desorbed from the electrodes and pass into the bulk of the solution, resulting in a stream of higher concentration (brine). A schematic view of the CDI system is shown in Figure 1.

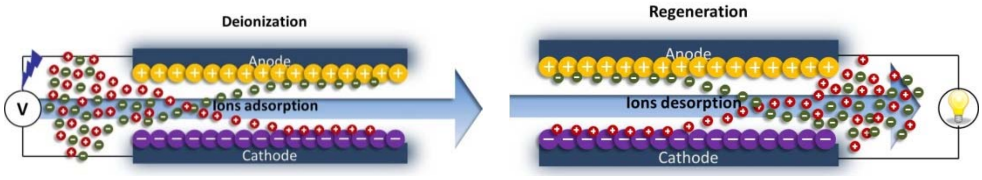

Figure 1. Schematic diagram of capacitive deionization showing deionization and regeneration steps.

Environmental Problem

One of the main environmental problem to human habitation on this planet is fresh water scarcity. The remediation to this problem proposed in this work is waste water reuse. Curiously, the current best available technologies that are being applied to make waste water reusable are generating two additional environmental problems:

- They are energy intensive technologies that may have a remarkable contribution to increase CO_2 emissions.
- They generate important amounts of effluents consisting on rejected streams with high concentrations of dissolved salts.

This landscape is depicted in the Figure 2.

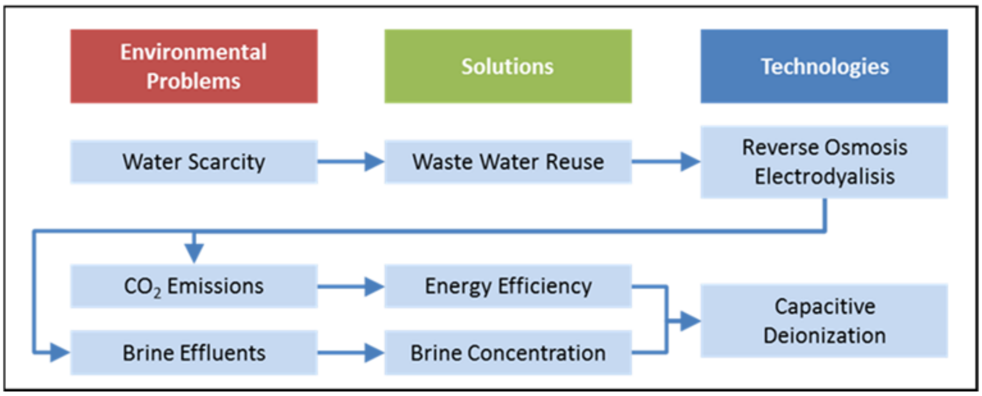

Figure 2. Schematic diagram of the relationships between the environmental problem, the solutions proposed and the technologies available or to be developed.

In the next sections the three environmental problems addressed by the project will be analysed in detail.

A. Water scarcity

Water scarcity occurs where there are insufficient water resources to satisfy long-term average requirements. It refers to long-term water imbalances, combining low water availability with a level of water demand exceeding the supply capacity of the natural system. Water availability problems frequently appear in areas with low rainfall but also in areas with high population density, intensive irrigation and/or industrial activity.

Currently the main way of assessing Water Scarcity is by means of the Water Exploitation Index (WEI) applied on different scales such as national, regional, river basins, etc. The WEI is the average demand for freshwater divided by the long-term average freshwater resources. It illustrates to which extent the total water demand puts pressure on the available water resource in a given territory and points out the territories that have high water demand compared to their resources. Figure 2 shows the WEI for several European countries in 2009.

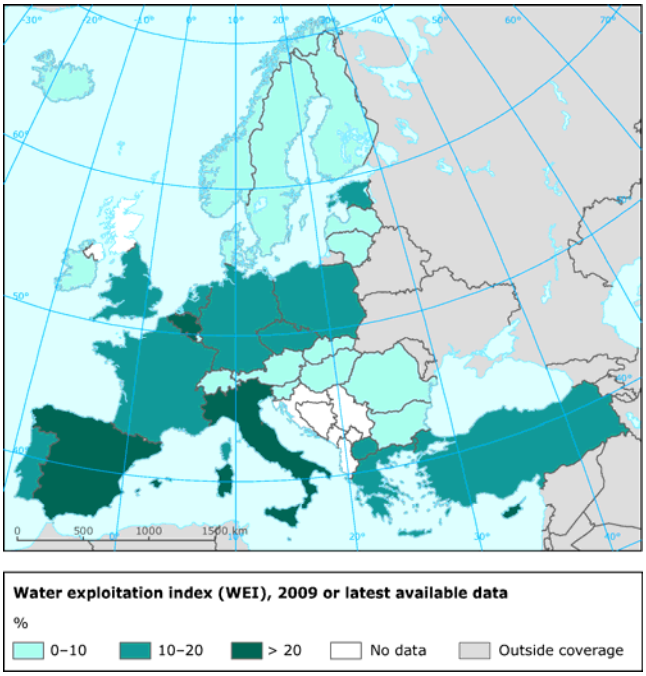

Figure 2. Water Exploitation Index (WEI) [7].

In 2007 the Commission issued a Communication on Water Scarcity and Droughts [8] in which the vulnerability of water and environmental resources to climate change was evaluated. The Communication included a suggestion to consider additional water supply infrastructures as one of the policy instruments to revert the trends of water scarcity and the vulnerability to droughts in the EU.

In 2012, in the stakeholder consultations leading to the Blueprint to Safeguard European Waters [9], water re-use for irrigation or industrial purposes emerged as an issue requiring EU attention. Re-use of water from waste water treatment or industrial installations is considered to have a lower environmental impact than other alternative water supplies such as water transfers or desalination, but it is only used to a limited extent in the EU. The reason for that was attributed to the lack of common EU environmental and health standards for re-used water and the potential obstacles to the free movement of agricultural products irrigated with reused water. For the next years the Commission will look into the most suitable EU-level instrument to encourage water re-use, including a regulation establishing common standards, which is expected for 2015 [9].

A successful result of the CDI technology will make available a new technology that will become waste water re-use easier and less costly. We consider that this could become a way to reduce the existing obstacles to the extension of the water re-use in some regions of the EU. It is also expected that this new technology could become an additional element within the instruments to be used by the Commission and Member Estates to encourage water re-use in the next future.

B. CO_2 emissions

Current trends in energy supply and use are economically, environmentally and socially unsustainable. In its Energy Technology Perspectives studies, the International Energy Agency (IEA) demonstrated that an energy technology revolution would be required to achieve a 50% reduction in CO_2 emissions by 2050, compared with 2005 levels (BLUE Map scenario). Such a revolution will involve rapid development and deployment of a portfolio of energy efficiency, renewable energy, carbon capture and storage, nuclear power and new transport technologies, as can be seen in Figure 3 [10].

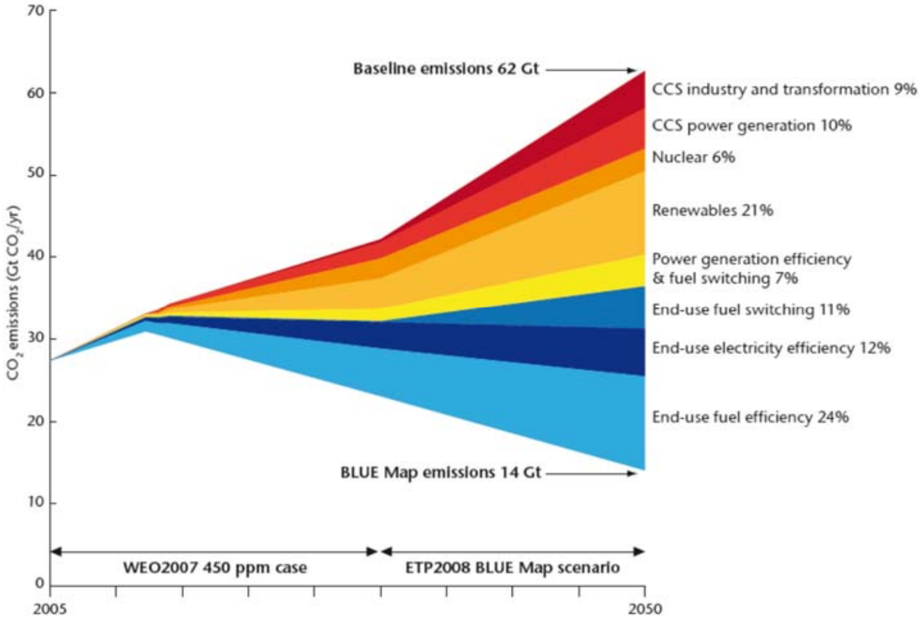

Figure 3. Portfolio of low-carbon energy technologies and their impact in CO2 emissions in the horizon of 2050 [10].

Note from Figure 3 that the impact of increasing the efficiency in the end-use of electricity is the 3rd major source of CO_2 reductions, just after the efficiency in the end-use of fuel and the renewable generation.

On the other hand it is well known the close relationship between energy and water. Energy cannot be produced without water consumption, and fresh water needs an important amount of energy to make it available to the population. Moreover, taking into account the full water use cycle (Figure 4) there is a big amount of energy consumed per unit of water.

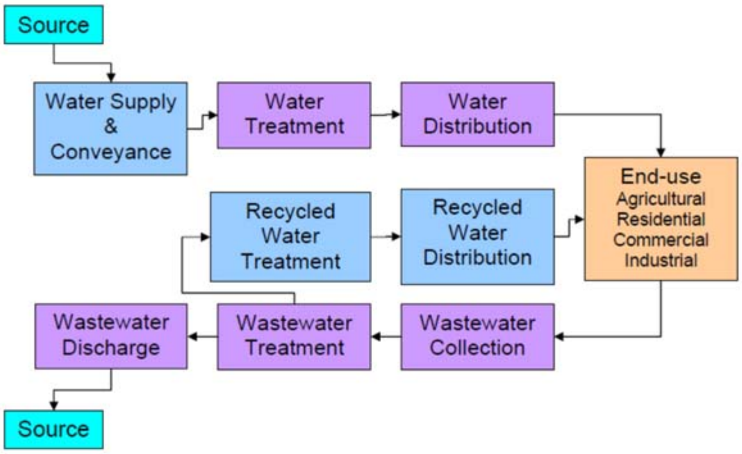

Figure 4. Block diagram of the Water Use Cycle [11].

Energy is consumed in each one of the blocks drawn in Figure 4. Specifically in the block of wastewater treatment, it is clear that all wastewater treatment systems require energy, though some require more than others depending on the quality of the waste stream, the level of treatment required, and the treatment technologies used. Energy use for wastewater treatment is steadily increasing with adoption of more stringent water quality rules. However, by increasing the quality of wastewater effluent, more recycled water can be added to the water supply portfolio.

From the above, the only way to limit the increase in energy consumption in a framework of higher quality requirements and higher level of treatment of the waste stream is to use low energy intensity technologies, One of the targets of Capacitive Deionization is demonstrate that it can be a less energy intensive technology than other such as RO and EDR in the treatment of high salinity wastewater to make it reusable. This energy saving will not be just restricted to the own treatment plant. CDI will also result in energy savings on effluents processing, since lower flows are obtained, reducing the area or the energy required for their evaporation. Accordingly, the carbon footprint will be lowered.

C. Water recovery / Concentrated effluents

The major environmental problem associated with a desalination plant is how to get rid of the surplus of concentrated brines. In most cases, these brines cannot remain on land because of the danger they pose to the underlying groundwater and because of other potential and severe environmental impacts [12].

The severity of these effects differs in different areas according to: (a) the hydrogeological nature of the point of disposal; (b) the biological sensitivity of the affected habitat; (c) the type of desalination plant, its size, the required secondary structures and infrastructure. Environmental awareness and preliminary planning can minimize the adverse effects of the desalination process on the environment [12].

At present, approximately 48% of desalination facilities in the US and most others including many of the Middle East states dispose their concentrates to surface waters. Other concentrate disposal options include deep well injection, land application, evaporation ponds, brine concentrators, and zero liquid discharge (ZLD) technologies. In all these cases, disposal of brines have an environmental impact, whose effects are not sufficiently evaluated yet [13].

The application of Capacitive Deionization will have the main consequence of producing a minor flow rate of concentrate per unit of treated water, which means that the water recovery is very high. The usual concentration of salts in the concentrate stream from RO or EDR is about 2 to 4 times that of the feed water, with a maximum around 75 – 80 g/L TDS, while in the case of Capacitive Deionization this maximum is expected to be around 200 g/L TDS, which means about 2.5 times more concentration, and so the flow rate will be proportionally smaller. Such concentrated brine will be less costly to evaporate or concentrate further to make a solid residue or a saline by-product out of the brine effluent. As above stated, this will contribute to reduce the carbon footprint of treated wastewater.

Capacitive Deionization innovative aspects

A. Current technologies for Waste Water Treatment (WWT) and reuse

Reverse Osmosis

It is the most common membrane process in use for water deionization or for desalination. A semi-permeable membrane separates two solutions of different concentrations. A high pressure must be applied to force the salts to cross the membrane from the less concentrated to the more concentrated solution overcoming the osmotic pressure and the pressure loss of diffusion through the membrane [12].

At present, Reverse Osmosis (RO) systems deliver high performance water purification at the lowest life-cycle costs. However, pressure-based membranes have several inherent technical and economical limitations, particularly where high feed recoveries are essential. The most severe impediment to high recovery is the osmotic pressure of the feed solution that has to be overcome by applying a very high hydrostatic pressure in the feed water with high pressure pumping. For feeds with total dissolved solids (TDS) levels typical of seawater, recoveries approaching 50% and beyond are seldom feasible; for brackish water levels of TDS, recoveries beyond 80% are rarely economical.

Electrodialysis

It is a membrane process in which a bundle of membranes is placed between two electrodes and an electric field is induced. It is mostly suitable for brackish water and for the remediation of polluted wells [12].

It is beyond the scope of this proposal to describe in details how the Electrodialysis and Electrodialysis Reversal work, but it is important to mention that EDR systems are ideal to desalinate challenging brackish waters such as surface water and wastewater. Applications for EDR technology include municipal drinking water and wastewater treatment and reuse projects.

Electrodialysis has inherent limitations. It works best at removing low molecular weight ionic components from a feed stream. Non-charged, higher molecular weight and less mobile ionic species will not be significantly removed. Furthermore, the concentration that can be achieved in the electrodialysis brine stream is limited by the membrane selectivity loss due to the Donnan exclusion mechanism and water transport from the treated water (or diluate) to the brine (or concentrate) caused by osmosis. Despite this disadvantage, in general, significantly higher brine concentration can be achieved by a properly configured electrodialysis than by reverse osmosis, and the problem of scaling is less severe in electrodialysis than in reverse osmosis.

In contrast to reverse osmosis, electrodialysis becomes less economical when extremely low salt concentrations in the product are required, as the current density becomes limited and current utilization efficiency decreases as the feed salt concentration becomes lower. The cause is that with fewer ions in the solution to carry current, both ion transport and energy efficiency greatly declines. This is not a problem when the treated water is aimed to be reused, because in that case TDS should not be less than 300 - 500 mg/L, which is an acceptable limit for electrodialysis.

B. Examples of application of RO and EDR for WWT and reuse

In this section some representative examples have been selected to show that the choice between EDR and RO depend on the specific characteristics of the feed water, the level of water recovery and the requirements for reuse of the treated water.

The water recovery EDR plant operated by the City of Suffolk in Virginia (USA) has three stages and achieves 94% water recovery. This water recovery is so high because the relatively low TDS of the feed water results in relatively low normality difference between the dilute and concentrate streams. In these conditions, EDR has a lower operating cost than RO and a much higher water recovery; therefore it is the preferred technical solution [14].

In the City of Edmonton City authorities approached Petro-Canada with a proposal to provide membrane-treated wastewater effluent from its Gold Bar Waste Water Treatment Plant (WWTP) that could be further recycled to Petro-Canada’s refinery. A combination of ultrafiltration (UF) membranes and reverse osmosis units was selected to remove ionic impurities. The treated wastewater is then used in the production of hydrogen and steam at the Edmonton refinery. In this case a low content of salts in the recycled water is crucial to avoid damages to the process units of the refinery; therefore RO was the preferred technical option [15].

An EDR plant located on Grand Canary Island (Spain) operates on a 5,000 to 7,000 mg/L feed water at 85% water recovery. The higher TDS increases water transfer and the additional stages increase cross leakage, therefore it is not possible to reach water recoveries as high as in the Suffolk case. Actually, RO would have a lower operating cost on this higher TDS water, but there is another critical aspect to select EDR instead of RO. In the volcanic Canary Islands, with approximately 55 mg/l of silica in the feed water, EDR was selected as the best technology because it could achieve a much higher water recovery than RO as it does not reject or concentrate silica. The RO cost advantage would be lost with the much larger volume of waste required to prevent silica scaling [16].

C. Innovative aspects of Capacitive Deionization

Capacitive Deionization appears as an alternative technology to RO and EDR in wastewater recovery plants. It will be applied essentially to the same streams of the WWTP as RO and EDR do. An example can be seen in Figure 5.

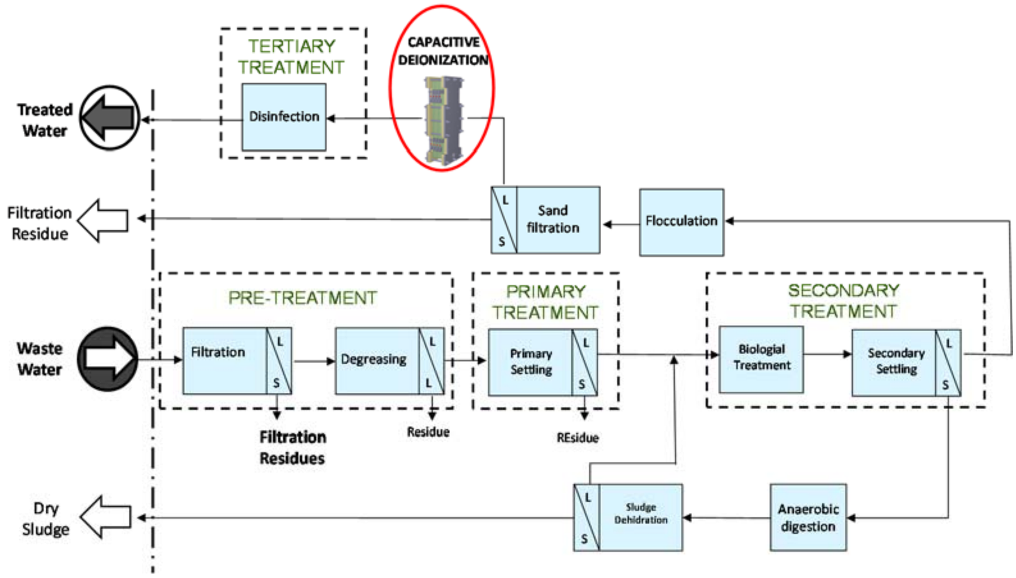

Figure 5. Schematic drawing of a WWTP with a Capactitive Deionization unit.

The most innovative aspects of CDI with respect to the other two technologies are:

- CDI does not use membranes.

In consequence membrane problems such as fouling do not occur. It is not necessary to use de-fouling reagents. Additionally, water recovery is no longer limited to the water and ion transport characteristics of the membranes. The main consequence of this fact is that the content of salts in the concentrate brine is just limited by the solubility of salts in the operating aqueous medium. Successful tests have been already made with excellent regeneration results in brines with up to 200 g/L of NaCl. As a result of this, the water recovery will be higher than in EDR and much higher than in RO. According to the laboratory and bench tests carried out with CDI prototypes, water recovery will be over 90% for TDS lower than 20 kg/m^3 and would be over 80% for sea water (35 kg/m^3 TDS). Because of the above, energy efficiency, and thus energy intensity, will not depend on the percentage of water recovery.

The Table 1 below makes a summary of figures of merit of CDI compared to RO and EDR in terms of water recovery.

Table 1. Water recovery comparison between CDI, RO and EDR

TDS Concentration at inlet (kg/m^3)	CDI Water Recovery (%)	RO Water Recovery (%)	EDR Water Recovery (%)
1	99%	80%	95%
3	98%	80%	90%
9	95%	60%	80%

- During the regeneration cycle, CDI recovers a major part of the energy applied during the previous deionization cycle.

This is a huge difference with EDR, provided that in this last no energy recovery is possible, therefore the minimum consumption is determined by the thermodynamics of the ion removal process taking into account the equivalent weight of the ions removed and the Faraday's constant.

In the case of RO it is possible to recover a great part of the pumping energy consumed to pressurize the feed water by means of rather complex systems such as Pelton turbines, isobaric chambers or pressure exchangers. This is particularly important in the case of high-pressure membranes used for high salinity water. Low pressure membranes do not allow such a remarkable recovery.

In CDI energy recovery is quite simple because it applies a simple concept of charge and discharge of an electrochemical capacitor. The charge of the capacitor corresponds to the deionization cycle, while the discharge corresponds to the regeneration cycle. The net energy consumption in electrochemical capacitors comes from the inefficiencies in the charge-discharge cycles, also known as round-trip efficiency. A conventional electrochemical capacitor can reach efficiencies over 95%. The experiments at laboratory and bench scale have shown that round-trip efficiencies between 70 to 85% can be achieved. In Figure B6 the calculated energy consumption for three CDI cases (efficiencies of 70 – 80 and 85%) is compared to the energy consumption in EDR and RO [17].

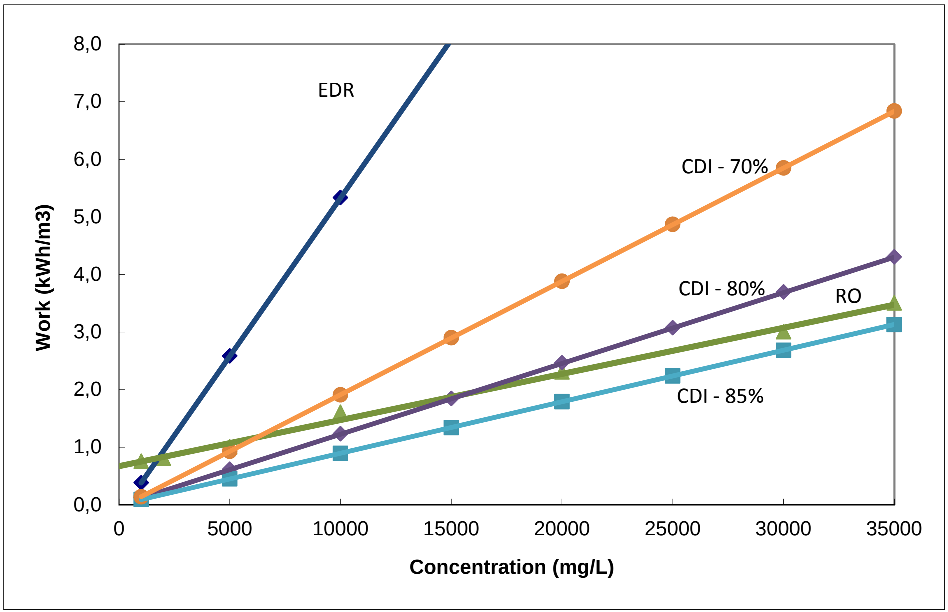

Figure 6. Energy intensity of CDI compared to EDR and RO. [RO data from [17].

From the Figure 6, it is clear that EDR is energetically better than RO only if TDS of the waste water is below 2000 mg/L, while CDI is expected to be less energy intensive than EDR in all cases.

Compared to RO, CDI is less energy intensive. Even for low efficiency, CDI performs better than RO. For 70%

efficiency it consumes less energy than RO at TDS below 5000 mg/L. If the efficiency is increased up to 80%, CDI is the best alternative up to TDS as high as 15000 mg/L, which is higher than most of the WWTP with saline wastewaters.

The Table 2 below makes a summary of figures of merit of CDI compared to RO and EDR in terms of energy consumption.

Table 2. Energy consumption comparison between CDI, RO and EDR

TDS Concentration at inlet (kg/m^3)	CDI$^{(2)}$ Energy Consumption (kWh/m^3)	RO$^{(1)}$ Energy Consumption (kWh/m^3)	EDR Energy Consumption (kWh/m^3)
1	0.1	0.7	0.4
3	0.3	0.8	1.5
9	1.0	1.4	4.8

(1) If low pressure membranes are used.
(2) 80% efficiency is assumed.

Conclusions

This work aims to demonstrate the environmental and socio-economic benefits of Capacitive Deionization as an innovative technology for removal charged soluble species dissolved in waste water. Compared to the existing technologies (RO, EDR) this concept will require lower energy consumption per equivalent of charged species and it will generate a smaller flow rate of effluent stream, because it allows generating concentrated brines. Furthermore, this technology does not require membranes and does not need high pressure in the feed stream to offset osmotic pressure. However, as we noted in this work, these CDI systems are performing as supercapacitors and therefore, while they are cleaning water they are also storing energy. Therefore, to achieve this, there are several factors to be resolved related to the cost of materials, regeneration rates, fouling and long-term stability that have not been adequately addressed until this time.

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