Effects of operational conditions on the electrosorption efficiencies of Capacitive deionization

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ABSTRACT

Capacitive deionization (CDI) represents a novel electrosorption process for the desalination of brackish water. The CDI working principle depends on the use of porous carbon materials as electrodes. CDI electrodes possess a charged surface that results in adsorption of salt ions by being charged in low voltage and it desorbing the salt ions by applying a reverse potential to the electrodes. CDI has many advantages due to its low energy consumption, low environmental pollution, and low fouling potential. The objective of this study is to investigate the effect of different operational conditions (TDS concentration, temperature, flow rate) on the CDI electrosorption efficiency and energy consumption and to investigate the effect of silica on the treatment efficiency. Laboratory scale experiments were conducted by using a commercial CDI with activated carbon electrodes developed by Aque EWP. CDI achieves TDS removal efficiency of 95.26% and 54.37% at TDS influent concentration of 500 and 3500 mg/l respectively. TDS removal efficiency decreased from 90.43% to 65.79% by increasing the flow rate from 1 to 4.5 l/min. By raising the influent temperature from 20 to 50 °Celsius, the TDS removal efficiency decreases from 90.43% to 79.25%. The electrosorption removal efficiency is inversely proportional to the flow rate, TDS concentration and the temperature. Silica does not have any effect on the CDI electrosorption efficiency and does not lead to scaling of electrodes. CDI energy consumption is inversely proportional to the flow rate and directly proportional to the TDS concentration.

INTRODUCTION

Nowadays many countries are suffering fresh water shortages, as a result of population growth and increases in the standard of living. In addition to the huge exploitation and contamination of natural fresh water resources by industry, agriculture and municipalities (Zou et al., 2008; Barman et al., 2009; Bouhadana et al., 2010). Various researchers (Hall & Day, 2009; Anderson et al., 2010) have indicated that water will be the oil of the 21st century and also that scarcity of fresh water may lead to warfare as oil did in the past. Water desalination stands out as a key tool to resolve the water crises, as it can produce fresh water suitable for human consumption as well as life activities. There are several different technologies used for saline water desalination based on thermal methods, membrane methods, electrochemical methods and other methods (Isabel & Schafer, 2010). However, these technologies still have many disadvantages that need to be overcome, such as high energy consumption, membrane fouling, secondary pollution and high expense for operation and maintenance (Matsuura, 2001; Li et al., 2010). Hence, it is urgent to develop a cost-effective and environmentally-friendly desalination technology.

Capacitive deionization (CDI) is a desalination process that has the potential to solve most of the critical problems that face the other desalination technologies, namely energy consumption and membrane problems (Barman et al., 2009). CDI operates at a relatively low electrical voltage (typically 0.8-2 V) for the removal of ions and it doesn't produce any secondary regeneration wastes (Oren, 2008; Anderson et al., 2010). In addition, CDI doesn't require pressure driven membranes or high pressure pumps so that it avoids the scaling problems that always occur with conventional membrane based technologies for desalination (Xu et al., 2008; Seo et al., 2010). During the purification cycle of CDI, the feed solution flows through high capacitive electrodes formed from conductive porous carbon materials, where the adsorption of ions takes place in the double layer formed at the surface of the electrodes. Cations and anions from the feed solution are drawn towards the cathode and anode respectively. After a time of operation the electrodes are saturated with ions and the effluent salinity rises over the allowable limits. Regeneration of electrodes is then required by applying a reverse potential to the electrodes to get rid of the adsorbed ions into the waste stream (Ryoo & Seo, 2003; Gao et al., 2007, Broséus et al., 2009).

Many achievements have been done on the study of CDI, but CDI still needs much attention from researchers before it can be used as a commercial technology. Most research efforts have focused on developing novel electrode materials and enhancing its properties (Zou et al., 2008). Few papers paid attention on the effect of operational conditions to CDI, the ion selectivity for CDI especially in complex multi-ionic solutions and the using of asymmetric electrodes for CDI. It is essential to gain a better understanding of CDI's potential as a practical desalination technology. Furthermore, silica is one of the elements that always found in seawater and brackish water. Silica fouling has been indicated as one of the major unresolved problems in most desalination technologies (Sahachaiyunta et al., 2002). Such a study is necessary because silica may have a great effect on the electrosorption performance.

In this work, several electrosorption experiments were conducted by using a commercial CDI technology (CDI technology from AQUA EWP) at different flow rates, feed solution TDS concentrations and solution temperatures. The treatment efficiency and energy consumption were analysed. Also the effect of silica on the treatment efficiency of CDI was determined.

MATERIALS AND METHODS

The commercial CDI pilot plant

The commercial CDI unit used in this research was developed by AQUA EWP, USA. Fig. 1 shows a schematic diagram of the used CDI unit. As shown in figure 1, the influent water is pumped from a storage tank through a pre-filter and afterwards passes over a flow weir to measure the influent flow to two carbon electrode cells connected in series. The electrodes within the cell are chargeable by applied DC potential in the range of 1 to 1.5 VDC. The whole operational cycle of the CDI takes 2.5 minutes. The cycle consists of two main steps, the regeneration mode step and the purification mode step. The regeneration step commences with 30 seconds when the effluent solenoid valve (SV1) and the influent solenoid valve (SV0) are closed and the supplied power is off, followed by another 30 seconds when the effluent waste solenoid valve (SV2) and the influent solenoid valve (SV0) are opened and the power is turned on with opposite

polarity of 1.5 VDC. After 60 seconds the regeneration step finished. The purification step is started immediately following this and it takes 90 seconds to purify the feed solution. Here the influent solenoid valve (SV0) and the effluent solenoid valve (SV1) are opened. The CDI contains a critical acid cleaning tank for the cleaning of the electrodes when the purification doesn't meet the standards. A heater was supplied to maintain the required temperature for the feed solution.
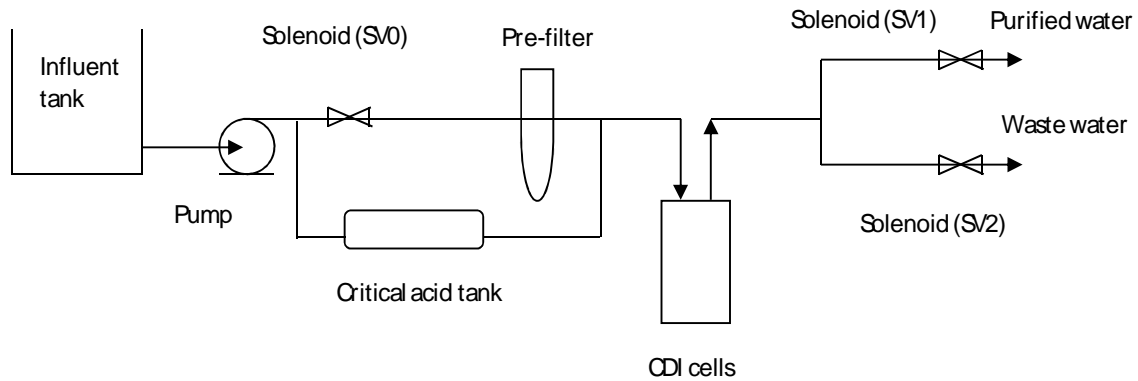

Fig. 1: CDI schematic diagram

Electrodes materials and composition

Fig. 2 shows a schematic diagram of the CDI cells construction. The electrodes are mainly composed of activated carbon with an organic binder. Each cell contains a mass of 1354 grams of activated carbon. As shown in figure 2, the electrodes within the cell consist of a conductive surface sandwiched between layers of activated carbon. A non-conductive spacer material separates the plates from each other. These electrodes are connected to the two sides of DC power supply by using connecting leads.
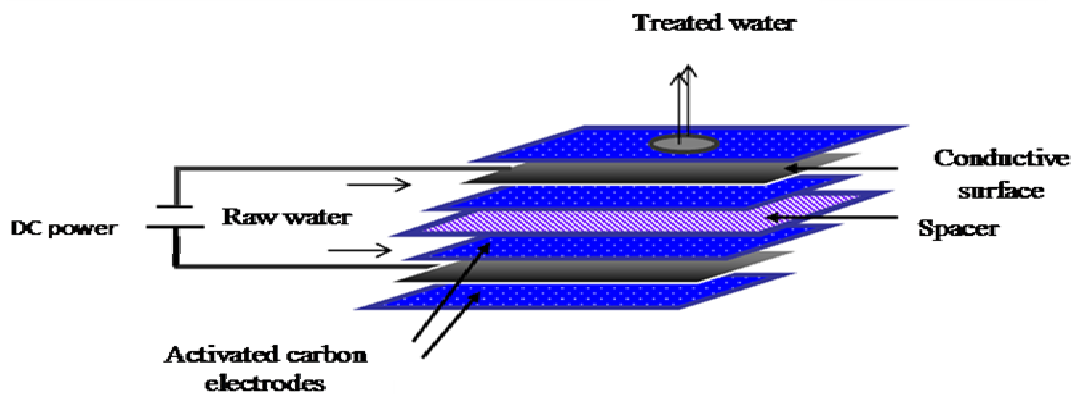

Fig. 2: CDI construction schematic diagram

Synthetic feed solutions

Synthetic solutions were prepared to feed the CDI unit. The synthetic solutions were prepared by dissolving NaCl and $Na_2SiO_3.9H_2O$ in deionised water with different concentrations according to the experiment conditions. Suitable stock solutions were prepared to facilitate the process.

Experimental methods

A series of laboratory experiments were conducted to investigate the effect of operational conditions (TDS concentration, flow rate, temperature) on the CDI electrosorption efficiency and energy consumption. These experiments were conducted as follows: First the TDS concentration of the feed solution was gradually increased from 500 to 3500 mg/l at a temperature of 24 °Celsius and a flow rate of 2 l/min. Second the flow rate was gradually increased from 1 to 4.5 l/min at a TDS concentration of 1000 mg/l and a temperature of 24 °Celsius. Finally the temperature of the feed flow was gradually increased from 20 to 50 °Celsius by means of a heater at a flow rate of 2 l/min and a TDS concentration of 1000 mg/l. The TDS concentration of the purified stream for each run was measured 10 times every 2.5 min by means of a conductivity meter. In these experiments, NaCl was used to prepare the feed solution with the required concentrations. The energy consumption of the CDI unit was measured by using a Todae power meter.

To investigate the effect of silica on the CDI electrosorption efficiency, a series of 2 experiments was conducted. In both experiments, the feed solution TDS concentration was 1000 mg/l and the silica concentration was maintained to be 60 mg/l by using $Na_2SiO_3.9H_2O$. The first and second experiments were operated at a flow rate of 2 l/min and 4 l/min respectively. The purified and waste stream TDS and silica concentration of the CDI was measured every cycle. Silica concentration was measured by using the HACH molybdosilicate colorimetric method. Cary 100 Bio UV spectrophotometer was used to analysis the peak absorption of silica at a wave length of 452 nm.

RESULTS AND DISCUSSION

Electrosorptive performance of CDI at different solution temperatures

Fig. 3a shows the purified stream TDS concentration of the CDI unit at different temperatures, and the inset shows the mean values of TDS concentration and its standard deviation (Δ).It is clearly shown that the purified stream TDS concentration increases gradually by increasing the solution temperature. These results are consistent with the results reported by Xu et al. (2008) in treating brackish produced water from a natural gas operation site.

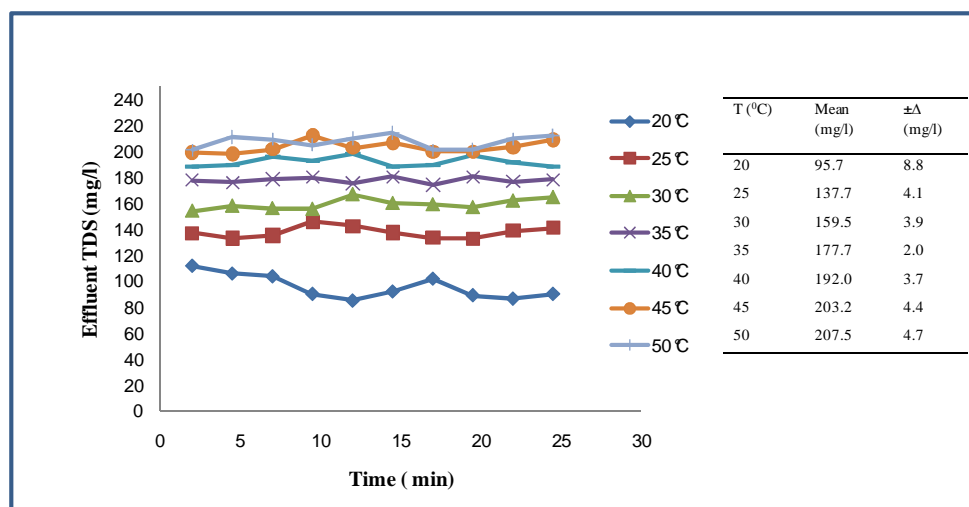| T (^{0}C)	Mean (mg/l)	±Δ (mg/l)
20	95.7	8.8
25	137.7	4.1
30	159.5	3.9
35	177.7	2.0
40	192.0	3.7
45	203.2	4.4
50	207.5	4.7

Fig. 3a: TDS at different feed solution temperatures. The inset shows the specific values

Fig. 3b shows the relationship of electrosorption removal efficiency and solution temperature. It can be noticed that the electrosorption efficiency follows a decreasing trend from 90.43% to 79.25% when the solution temperature increased from 20 to 50 °Celsius. So that it can be noticed that the electrosorption removal efficiency is inversely proportional to solution temperature. The difference in electrosorption removal efficiency decreases for a solution temperature between 40 and 50 °Celsius. It was explained that by decreasing the temperature of the solution, a hydrophobic-hydrophilic transition appears on the structure of interfacial water and the affinity between activated carbon and interfacial hydrated ions became stronger (Wang et al., 2008). As a result, higher electrosorption removal efficiency at low temperature may be caused by the transition from hydrophobic to hydrophilic transitions on the surface of the activated carbon.
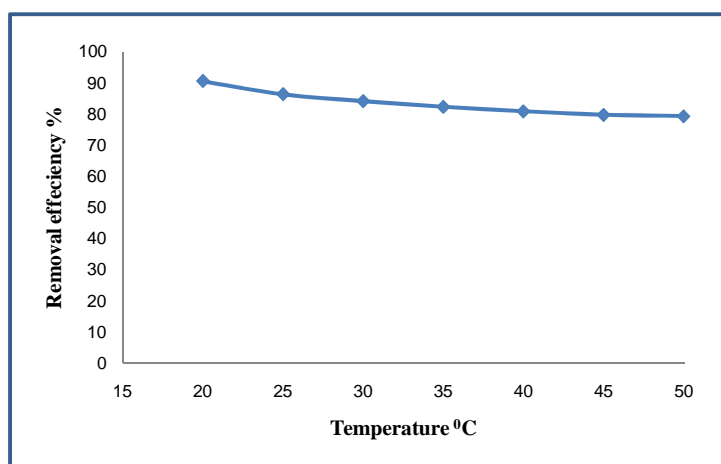

Fig. 3b: Removal efficiency as a function of solution temperature

Effect of flow rate on electrosorption efficiency and energy consumption

Fig. 4a depicts the variation of the purified stream TDS concentration with different flow rates, and the inset shows the mean values of TDS concentration and its standard deviation (Δ). It is clearly shown that the TDS concentration increases gradually by increasing the flow rate. The electrosorption removal efficiency follows a decreasing trend from 94.18% to 65.79% when the flow rate increased from 1 to 4.5 l/min.

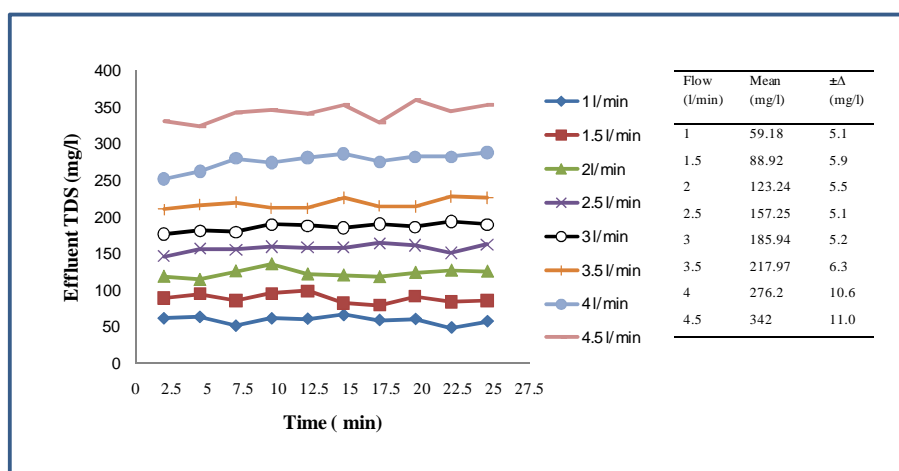| Flow (l/min)	Mean (mg/l)	±Δ (mg/l)
1	59.18	5.1
1.5	88.92	5.9
2	123.24	5.5
2.5	157.25	5.1
3	185.94	5.2
3.5	217.97	6.3
4	276.2	10.6
4.5	342	11.0

Fig. 4a: Purified stream TDS at different flow rates. The inset shows the specific values

Fig. 4b shows the dependence of electrosorptive capacity and flow rate. From the figure, it was noticed that the electrosorptive capacity decreased gradually from 13.91 to 9.71 mg TDS per gram of activated carbon by increasing the flow rate from 1 to 4.5 l/min. As a result, salt removal efficiency and electrosorption capacity is inversely proportional to flow rate. This is caused as a result of higher flow rate which introduces a higher force applied on the flow that is higher than the electrosorptive force and therefore decreases the electrosorptive capacity and salt removal efficiency. These results are consistent with the results reported by Li et al. (2010).
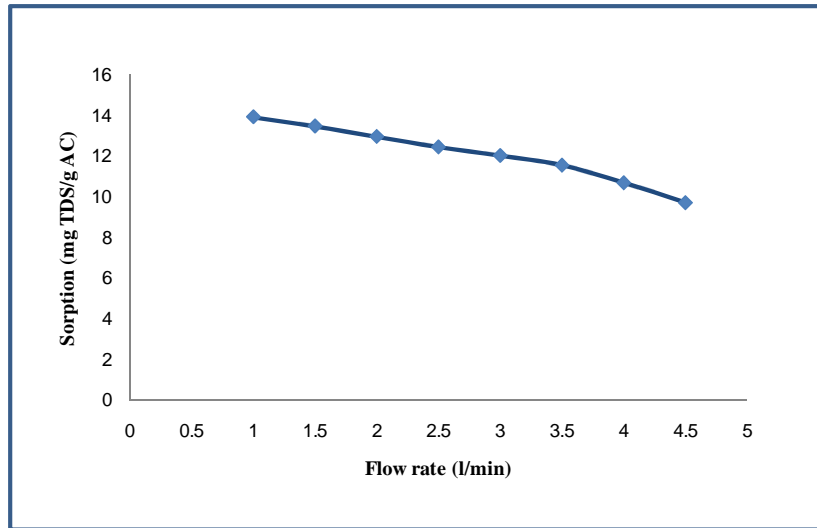

Fig. 4b: Effect of flow rate on sorption capacity of the activated carbon

Fig. 5 shows the effect of different operational flow rates on the energy consumption. From the figure, it is seen that as the flow rate increases the energy consumption decreases. It was noticed that the energy consumption deceased from 6.67 to 1.85 kWh per m^3 of purified water by increasing the flow rate from 1 to 4.5 l/min. As a result, the optimum operational flow rate is not only depending on the electrosorption removal efficiency but also on the energy consumption.
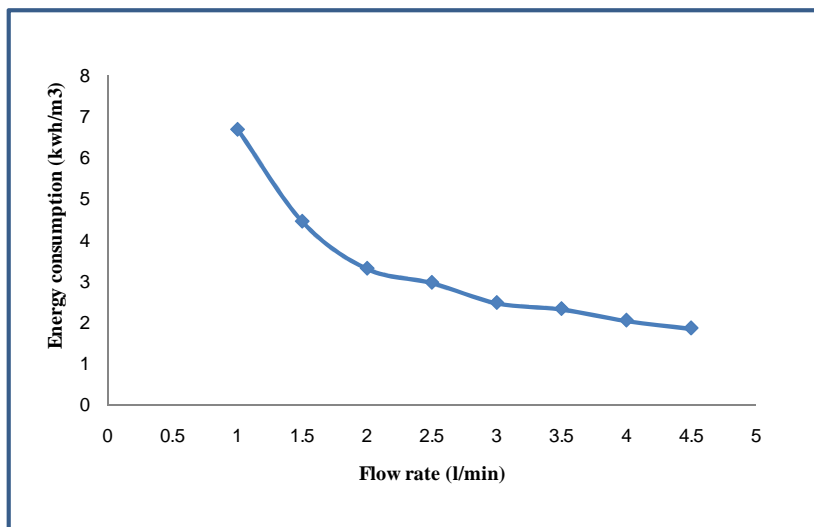

Fig. 5: Effect of operational flow rate on energy consumption

Effect of feed TDS concentration on electrosorption efficiency and energy consumption

Fig. 6a shows the dependence of salt removal efficiency on initial feed TDS concentrations (500, 1000, 1500, 2000, 2500, 3000, 3500 mg/l) at constant flow rate of 2 l/min and temperature of 24 °Celsius, and the inset shows the mean values of TDS concentration and its standard deviation (Δ). It is clearly shown that the TDS removal efficiency decreases gradually by increasing the initial feed TDS. The TDS removal efficiency was 95.27% and 54.37% by using initial feed TDS of 500 and 3500 mg/l respectively. Fig. 5b shows that the increase of the initial feed TDS results in an initially linear increase of electrosorption capacity. After the initial feed TDS was greater than 3000 mg/l, the electrosorption capacity remains constant, reaching 25.5 mg TDS per gram of activated carbon. For porous electrodes, the electrical double layer is created inside the pores rather than only on the electrode surface, so that pores should increase the electrical capacity of the electrodes. However, the size of the pores has a great effect on the capacity due to the overlap of electrical double layer inside the pores that may occur especially in microporous (<2 nm) and partly in mesoporous (2–50 nm) regions. This overlapping prevents ions from adsorbing inside the pores resulting in a lowering of the electrosorption capacity (Lin et al., 1999; Yang et al., 2001). Farmer et al. (1996) reported that the electrical double layer thicknesses increased from 1 to 20 nm by decreasing the electrolyte solution concentration from 0.1 to 10^{-4} M. This study shows that increasing the feed TDS concentration improves the electrosorptive capacity of activated carbon by reducing the electrical double layer thicknesses. However, the overlapping of micropores still limits the performance of electrosorptive capacity.
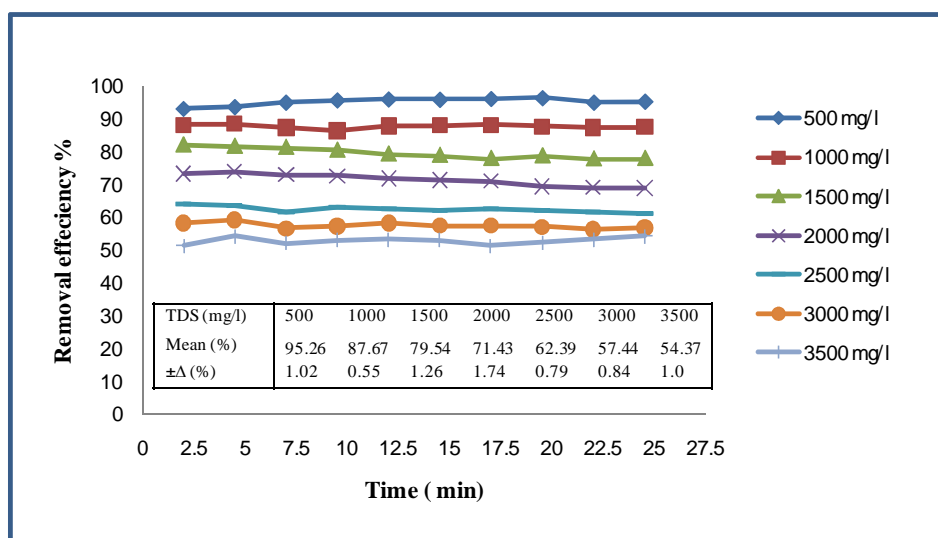

TDS (mg/l)	500	1000	1500	2000	2500	3000	3500
Mean (%)	95.26	87.67	79.54	71.43	62.39	57.44	54.37
±Δ (%)	1.02	0.55	1.26	1.74	0.79	0.84	1.0

Fig. 6a: Removal efficiency at various initial TDS. The inset shows the specific values

Fig.7 shows the effect of initial feed TDS concentrations on the CDI unit energy consumption. From the figure, the CDI energy consumption increased gradually from 2.64 to 5.56 kWh per m^3 of purified water when the initial feed TDS increased from 500 to 3500 mg/l at a flow rate of 2 l/min. This may be related to the improvement of the electrosorptive capacity that affects the CDI energy consumption. This implies that high TDS concentration related to energy consumption should be employed for industrial CDI process design and operation.
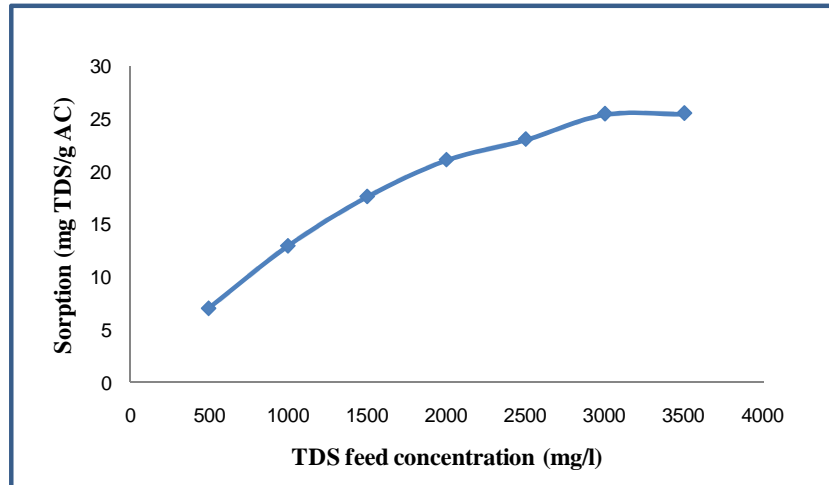
Fig. 6b: Effect of TDS feed concentration on sorption capacity of the activated carbon
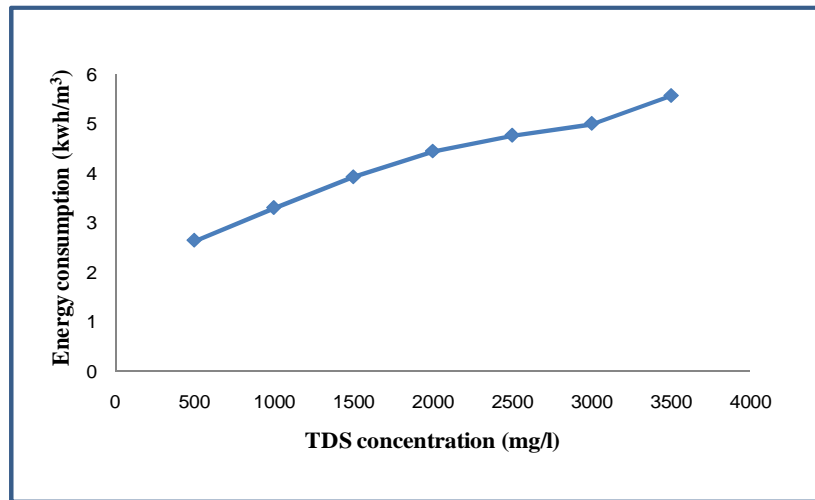

Fig. 7: Effect of TDS feed concentration on energy consumption

Effect of reactive silica element on the electrosorptive performance

Fig. 8 shows the CDI unit purified stream TDS and silica concentration at flow rates of 2 and 4 l/min respectively, initial feed concentration of 1000 mg/l and silica concentration of 60 mg/l. The TDS removal efficiency was about 87.85% and 72.73% at flow rates of 2 l/min and 4 l/min respectively. It was noticed that there is not any effect of silica on the treatment efficiency of the CDI unit as a result of comparing these results with that done in the absence of silica. Silica removal efficiency was very little in the range of 9% at flow rate of 2 l/min and decreased to 3% at flow rate of 4 l/min. The removed silica may be a result of using low flow rate and synthetic feed solution that helps in the dissociation of silica salt. Also it was noticed that silica concentration in the CDI waste stream was in the range of 64 mg/l and 63 mg/l at flow rates of 2 l/min and 4 l/min respectively, which is higher than that of the feed solution. These show that the removed silica does not accumulate on the electrodes. As a result, silica does not result in fouling problems for CDI unit and it will remain in the treated water. Silica in drinking water does not have any harmful effects on human health and it may be able to reduce the risk of developing Alzheimer disease in elderly women (Gillette-Guyonnet et al., 2005).
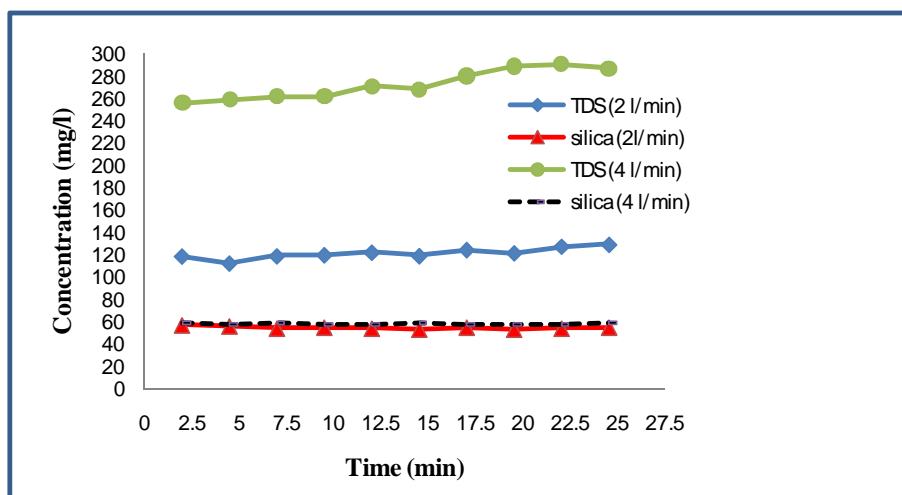
Fig. 8: purified stream TDS and silica concentration at flow rates of 2 and 4 l/min

SUMMARY AND CONCLUSIONS

The capacitive deionisation is effective at removing salt from water stream without exposing the environment to any harmful impacts. The operational conditions of the CDI can be adjusted according to the required treated water quality. For the tested CDI unit, the power consumption ranged between 6.67 to 1.85 kWh/m^3 by using a flow rate between 1 and 4.5 l/min. power consumption ranged between 2.64 to 5.56 kWh/m^3 by using a raw water TDS concentration between 500 and 3500 mg/l TDS. As the solution temperature decreases, the salt removal increases. As the flow rate and the raw water TDS concentration increase, the salt removal efficiency decreases. Silica was not removed from the treated water using the CDI but the presence of silica in drinking water doesn't have any harmful effects on the human health. Deterioration of carbon electrodes or electrode fouling was not observed throughout the using of silica in the raw solution. CDI could be a unique alternative for brackish water desalination. Further improvement especially in the electrosorptive capacity of electrodes and operational performance would be welcome for the practical application of this technology.

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Mohamed Ahmed Abd El Hakim Mossad works as a teaching and research assistant in the Public Works Engineering Dept., Faculty of Engineering, Mansoura University. He received his B.Sc. in Civil Engineering from Mansoura University in 2005. In 2008, he received his mater degree in environmental engineering from Dundee University. He has contributed in the environmental and structural design of many water and wastewater treatment projects. Now, he is a PhD student at the University of South Australia.