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A study on modeling and simulation of capacitive deionization process for wastewater treatment

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ABSTRACT

Wastewater treatment is an important issue in the era when water resources are continuously decreasing world-wide in the face of increasing demand. The need for cheap and energy efficient wastewater utilization technologies is thus drawing continuous attention. Capacitive Deionization (CDI) was recently proposed as a novel alternative replacing for the conventional membrane methodologies. This paper is concerned with simulation of the separating saline from the wastewater effectively using CDI. After actual experiments of CDI to assess their basic behaviors, their behaviors are mathematically formulated and its associated parameters are identified accordingly. The corresponding model is implemented in Matlab simulink to show how it can be operated in preparation for the wider applications. The proposed simulation framework could be further expanded to evaluate the performance in terms of economical feasibility against other separation methods.

1. Introduction

Under the strengthened global water crisis, it is an imperative task to secure water supply. Considering the difficulty of securing water directly from nature, reusing less contaminated wastewater after treatment can be an alternative not to be neglected. A number of wastewater treatment methods have been thus proposed and widely implemented in practice such as ion-exchange, reverse osmosis, evaporation methods. For example, the ion-exchange transforms ions in waters using polymer resin (Bolto and Pawlowski, 1987). When it reaches the capacity limit, it should be regenerated. But this involves the secondary wastewater because of the regenerant it makes. Reverse osmosis is most widely used for seawater desalinization, water purifier, water treatment for boiler, etc (Rautenbach *et al.*, 1997). Since the brines in contaminated waters are separated from the difference between diffusion coefficients using high pressure, expensive equipment and power should be prepared. In the electro-dialysis process, ionic component of a solution are separated through the use of semipermeable ion-selective membrane (Tchobanoglous *et al.*, 2004). It is mainly applied for making salt or collecting organic materials. The evaporation method has been used for a long time due to the very simple operating principle and equipment and the resulting high purity fresh water (Tchobanoglous *et al.*, 2004). Nonetheless, very expensive energy cost in phase change between liquid–gas–liquid is a serious disadvantage. It is widely used as a tool to desalination of seawater and leachate. It is an issue to tackle high investment and operation cost to employ the above conventional wastewater retreatment facilities surpassing the current price.

Capacitive Deionization Technology (CDT)^{TM} is a low-pressure non-membrane desalination process, with the potential to be a powerful tool in the desalination toolbox of the future. Desalination by CDT^{TM} occurs when a saline solution flows through an unrestricted capacitor type module consisting of numerous pairs of high-surface area, such as carbon aerogel, electrodes (Welgemodoed and Shutte, 2005). CDI is regarded as one of the most efficient and economic technology and many studies have been made thereafter (Farmer *et al.*, 2010; Pekala *et al.*, 1998; Welgemoed and Schutte, 2005). It is mainly due to a number of reasons. First it focuses on only separating ions. Therefore it saves lots of energy while other methods such as evaporation and reverse osmosis force us to spend a large amount of water. Secondly it has fairly simple desorption and regeneration process and economically promising against other membrane methodologies.

The rest of this paper is as follows: After the concept of CDI is presented, actual experiments of simple scale are outlined with the illustration of the result. The mathematical representation of the CDI is then presented with the identification of parameters from the experiment. A simulation framework is described in Matlab simulink.

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2. Capacitive Deionization Technology (CDI)

The basic concept of Capacitive Deionization Technology (CDI) is as follows: Contaminated waters are flown between two electricity charged electrodes made of multipore carbons. The ions are absorbed into two opposite electrodes and deionized and the waters are purified. Since the carbonated electrodes are multipore electrode and relatively wide surface areas, a large number of ions can be removed.

CDI is mainly distinguished from other wastewater treatment like reverse osmosis and evaporation method in terms of energy consumption. It is energy efficient because it only needs to move the target ions and no specific part for separation which make the life of the facility long. The electrode is not damaged during the purification and easy for maintenance. Therefore CDI has been regarded as an efficient and economical technique and many works are in progress these days.

Lawrence Livermore National Laboratory (LLNL) named using carbonated Resorcinol-Formaldehyde (RF) aerogel electrolyte CDI (Farmer *et al.*, 1994). This paper uses this for experiment and simulation. Fig. 1(a) shows LLNL separating. CDI is developed by LLNL for purification system using carbonated RF aerogel electrode. More comprehensively it was since 1960s when methods on electrochemical ion separation were discussed. In the initial CDI, electrodes were made by way of accumulating powder type multipore carbonated materials in packed bed. It was made either in parallel or cross type. The packed bed type structure shows a good performance because it has wide contact area between the inlet contaminated water and electrode surface.

But there is a problem of the pressure drop because of separator and packed carbon powder. There is some damage in actually necessary amount and operational difficulties.

In order to overcome these, carbonated RF aerogel electrode was proposed as separating electrode structure which was named as CDI by LLNL. The separation system in this paper is also based upon this. Fig. 1(a) shows the separating electrode structure by LLNL. It was designed that a room with a certain depth are made between two electrodes to make the inlet water flown out without pressure drop except the packed bed structure. This design is possible because electrode is made of carbonated RF aerogel. That is to say, since it is made of monomers and has relatively big pores more than mesopore, it has good electric conductivity and easy for ions to approach. Therefore it was not necessary to design the structure like the packed bed CDI to induce contaminated waters to the surface of carbonated powders. Separating type electrode CDI can have efficient separating ability in the fast flow rate.

Fig. 1(b) illustrates a system consisting of multiple unit cells in combinatorial. At first, the contaminated water inserted from the top into the first cell. The contaminated water is affected perpendicular by electric field. Part of ions for being removed move and stick to the surface of the electrolyte. The contaminated water after passing the first unit cell is inserted into the second electrode using the hole and follows the same path over multiple times and the final purified water flows out of the system. The system by LLNL consists of multiple unit cells in parallel in order to gain two advantages. It helps to have the effect of an imaginary effect of sum of unit cells and it also increases the time the contaminated water stays in the system to have more chance of being purified.

By adjusting the number of unit cells, we can modify the purification capability in response to the request. Fig. 2 describes the result by using separating electrode-type CDI system which consists of 192 unit cells. The operation voltage is 1.2 V, flow rate is 15 mL/min and conductivity of inlet contaminated water is 100 μS/cm. The conductivity decreased below 1 μS/cm after 10 h of operation and it means that 99% of NaCl has been removed. We can see that the conductivity of outlet water increases after 10 h. It is because NaCl is saturated over carbonated RF aerogel electrolyte.

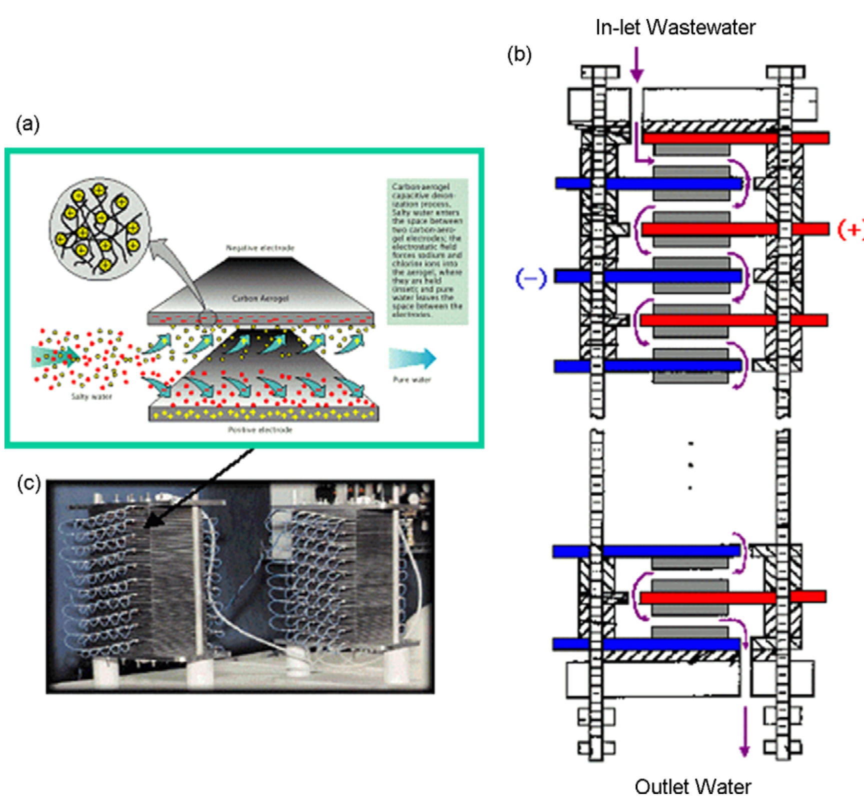

Fig. 1. Water treatment system using carbon aerogel by LLNL.

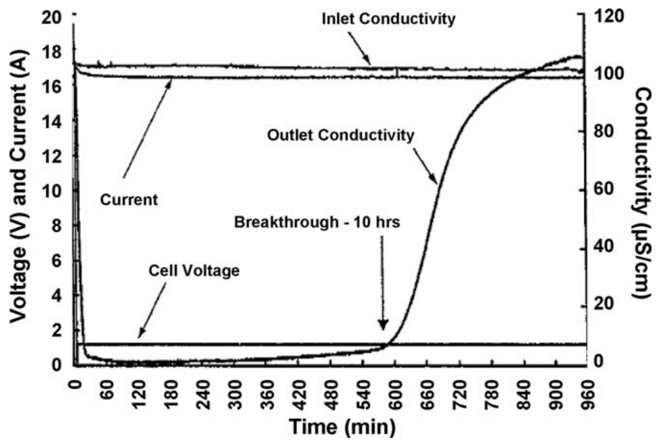

Fig. 2. Conductivity variation of the waste water over time using CDI system (Pekala *et al.*, 1998).

3. Experiment of CDI unit cell

In order to model CDI system, the first task is to obtain data from CDI unit cell experiments. The unit cell is outsourced by the external company which specializes it (Capacitive Deionization Technology Systems, Inc.). The experiments have been conducted using it. For the purpose of clear measurement of ions, NaCl is selected that is most widely used. Conductivity is measured to distinguish the difference before and after its generation mode. The experiment specifications are as follows: The concentration of the inlet brine water is divided into three 500, 1000, and 1500 mg/L. Voltage is 1.5 V in the purification mode and −0.1 V in the regeneration mode to remove ions adsorbed to electrodes. The experiment has been done in the following procedure:

1. Install power, pump, CDI unit cell, conductivity meter.
2. Input NaCl 1500 mg/L into unit cell with the constant velocity of 70 mL/min.
3. Measure conductivity of the outlet from the unit cell.
4. Set the voltage 1.5 V in generation mode and −0.1 V in regeneration mode respectively.
5. Continue the above processes for the case of generation, regeneration and continuous mode.
6. Modify the initial density of NaCl into 1000 mg/L, 500 mg/L and repeat the procedures 1 and 5.

The results from the above experiments are graphically depicted in Figs. 3(a)–(c) and 4(a) and (b).

4. Analysis using Levenberg–Marquardt method

In order to construct a mathematical model representing the CDI process, reaction equations to represent purification and regeneration processes are established and the corresponding parameters are identified.

The purification and regeneration processes are illustrated in Fig. 5 assuming that all input and output flow rates are the same. Thus each process is represented using the relationship of inlet, outlet and adsorption/desorption concentrations.

The purification and regeneration processes are expressed as the following differential equations:

Purification:

$$\frac{dC}{dt} = (C_{in} - C - \alpha_1 C_A) \times \alpha_3 \tag{1}$$

$$\frac{dC_A}{dt} = (-\alpha_2 C_A) \times \alpha_3 \tag{2}$$

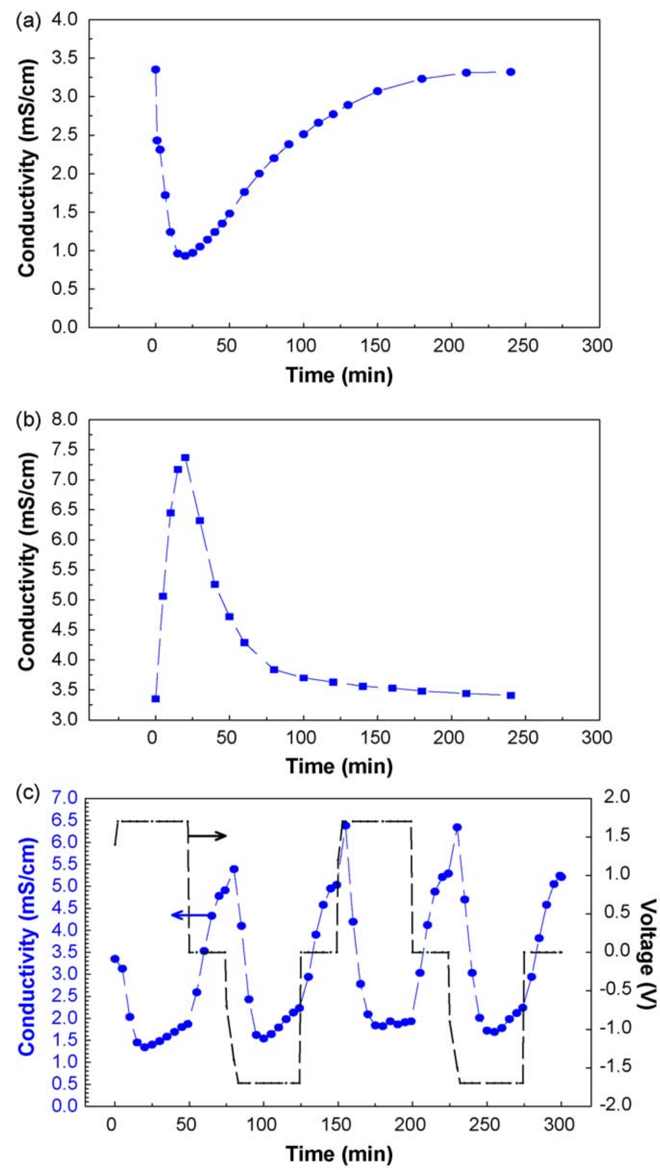

Fig. 3. Result for the initial density of 1500 mg/L. (a) Purification, (b) regeneration, and (c) continuous mode.

Regeneration:

$$\frac{dC}{dt} = (C_{in} - C + \alpha_4 \times (1 - C_A)) \times \alpha_6 \tag{3}$$

$$\frac{dC_A}{dt} = (-\alpha_5 \times (C_A - 1)) \times \alpha_6 \tag{4}$$

where C_{in} and C are inlet concentration and outlet concentration of NaCl respectively. C_A represents absorption concentration and desorption concentration for the purification and regeneration processes respectively. The parameters minimizing the difference between the existing data and the reaction equations are identified using Levenberg–Marquardt method which can be represented in (5):

$$P(i) = P(i-1) - \left[\frac{d^2V}{dP^2|_{P=P(i-1)}} + \alpha I\right]^{-1} \left[\frac{dV}{dP|_{P=P(i-1)}}\right] \tag{5}$$

This method computes P that minimizes the objective function V. Here i denotes iteration number and α is a very small parameter.

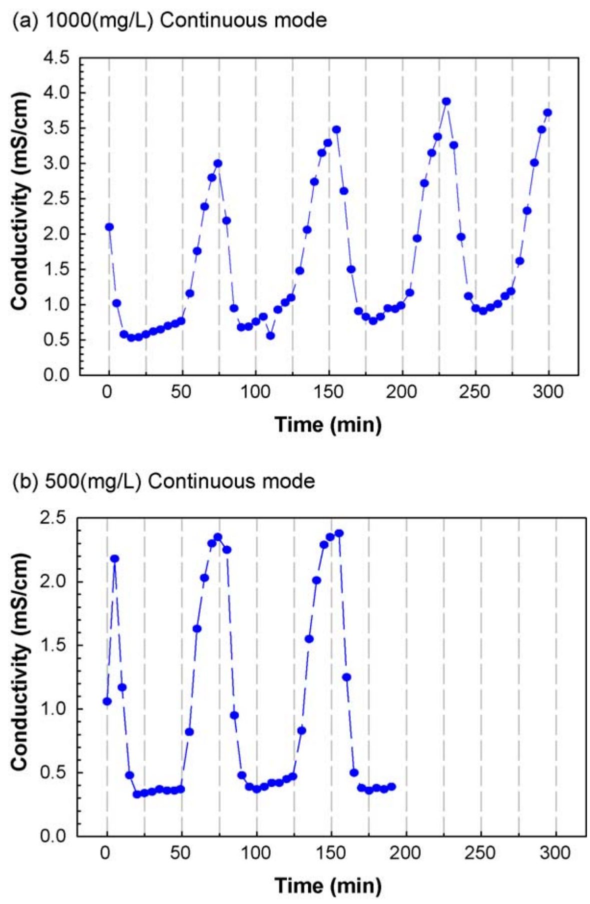

Fig. 4. Result of initial density of (a) 1000 mg/L and (b) 500 mg/L.

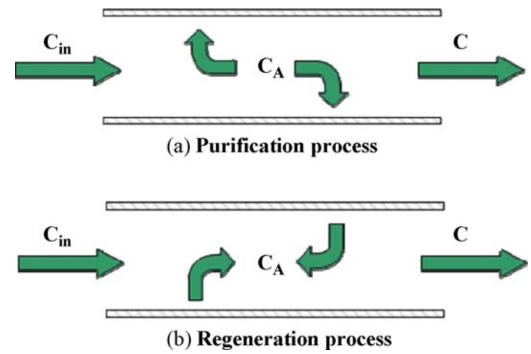

Fig. 5. Reaction scheme (a) purification and (b) regeneration process.

$\mathrm{d}V/\mathrm{d}P|_{P=P(i-1)}$ and $\mathrm{d}^2V/\mathrm{d}P^2|_{P=P(i-1)}$ is the first and second order partial differential over objective function V and parameter P. When α is reduced much smaller, the convergence will be accelerated but it could be diverged. Therefore its value should be adjusted appropriately to speed up the convergence rate without being diverged.

$$\frac{\partial V(P)}{\partial P} = \left[\frac{\partial V(P)}{\partial P_1} \quad \frac{\partial V(P)}{\partial P_2} \quad \cdots \quad \frac{\partial V(P)}{\partial P_n}\right]^T \tag{6}$$

$$\frac{\partial^2 V(P)}{\partial P^2} = \begin{bmatrix} \frac{\partial^2 V(P)}{\partial P_1^2} & \frac{\partial^2 V(P)}{\partial P_2 \partial P_1} & \cdots & \frac{\partial^2 V(P)}{\partial P_n \partial P_1} \\ \frac{\partial^2 V(P)}{\partial P_1 \partial P_2} & \frac{\partial^2 V(P)}{\partial P_2^2} & \cdots & \frac{\partial^2 V(P)}{\partial P_n \partial P_2} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 V(P)}{\partial P_1 \partial P_n} & \frac{\partial^2 V(P)}{\partial P_2 \partial P_n} & \cdots & \frac{\partial^2 V(P)}{\partial P_n^2} \end{bmatrix} \tag{7}$$

$$P = [P_1 \quad P_2 \quad \cdots \quad P_n]^T \tag{8}$$

Here the objective function V is defined as follows:

$$V = \frac{(C - C\_\mathrm{hat})^T (C - C\_\mathrm{hat})}{\mathrm{length}(C)} \tag{9}$$

where C denotes concentration of experimental data and C_hat denotes the concentration of the reaction rate. The above differential equations are solved using ODE45 in Matlab. Levenberg–Marquardt method is employed to obtain the parameters minimizing objective function V. The corresponding values are as follows:

Purification:

$$\alpha_1 = 15.9427, \alpha_2 = 1.8866, \alpha_3 = 0.0383 \tag{10}$$

Regeneration:

$$\alpha_4 = 9.8048, \alpha_5 = 1.4090, \alpha_6 = 0.0266 \tag{11}$$

The values of the above parameters do not apply to all concentration profiles of the input flow because the values are computed for one case with some input concentration. As input concentration changes, the degree of purification and regeneration also changes. The parameter α_1, α_4 representing the process of purification and regeneration should also reflect the change of the input concentration. We employed (12) from the equation representing electrophoretic deposition in order to express the relationship of α_1, α_4 with the input concentration because it is assumed that this mechanism and the deposition are similar.

$$\alpha_{1,2} = \beta_1 \times (1 - \exp(-\beta_2 \times C_{\mathrm{in}})) \tag{12}$$

Levenberg–Marquardt method is also used again to compute the corresponding parameters (β_1 and β_2) using the values α_1, α_4 and the inlet concentrations for all cases. The resulting values of the parameters and optimized in Matlab using are as follows: β_1, β_2 of α_1, α_4 are denoted in (13) and (14).

$$\alpha_1: \quad \beta_1 = 12.3596, \beta_2 = 8.5832 \tag{13}$$

$$\alpha_4: \quad \beta_1 = 7.6667, \beta_2 = 8.8889 \tag{14}$$

5. Result

The experiment conducted has been implemented into Matlab simulation as can be seen in Figs. 6–9. Figs. 6–8 illustrates the CDI unit cell and Fig. 9 graphically describes a stack consisting of eight cells. The four graphs show the result of voltage variations as the number of unit cells increase from 1, 3, 6 and 8. It can be confirmed that the more unit cells are, the higher the generation ability is. For example, for a single cell, conductivity is changed from 3.35 mS/cm to 2.20 mS/cm for 8 cell stack, it reduced into 0.20 mS/cm. Therefore an advanced purification system can be constructed by manipulating the number of CDI unit cells to obtain a desired level of desalinated water treatment.

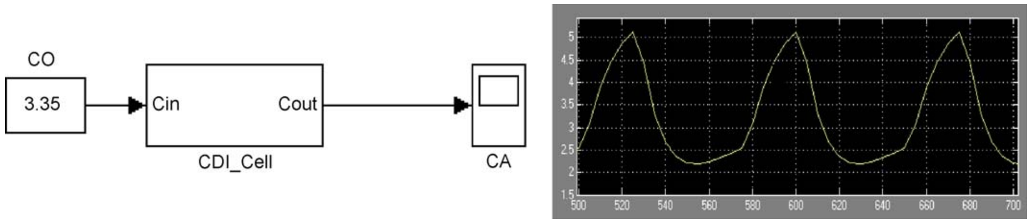

Fig. 6. (a) Matlab configuration and (b) corresponding simulation graph result.

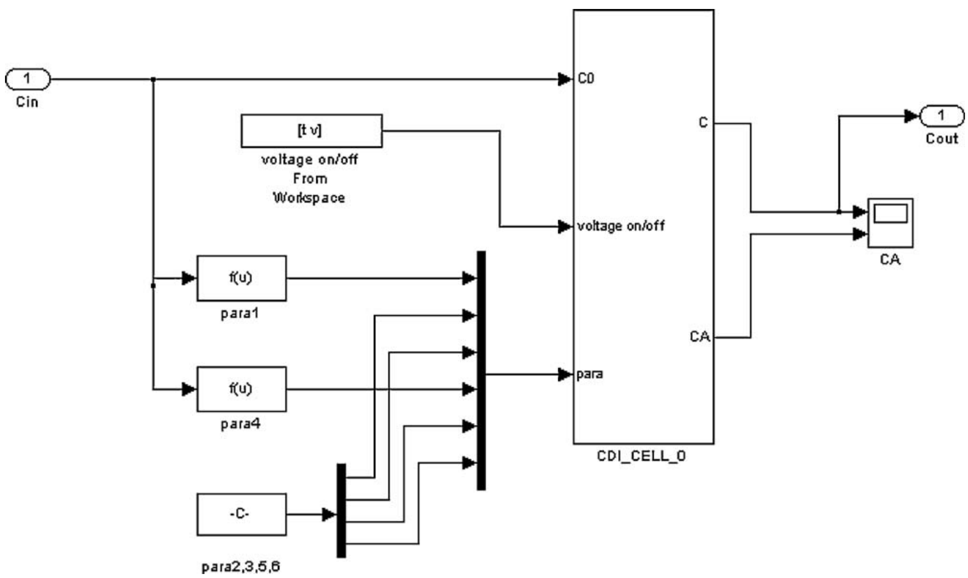

Fig. 7. Schematic diagram of CDI_Cell in Fig. 6.

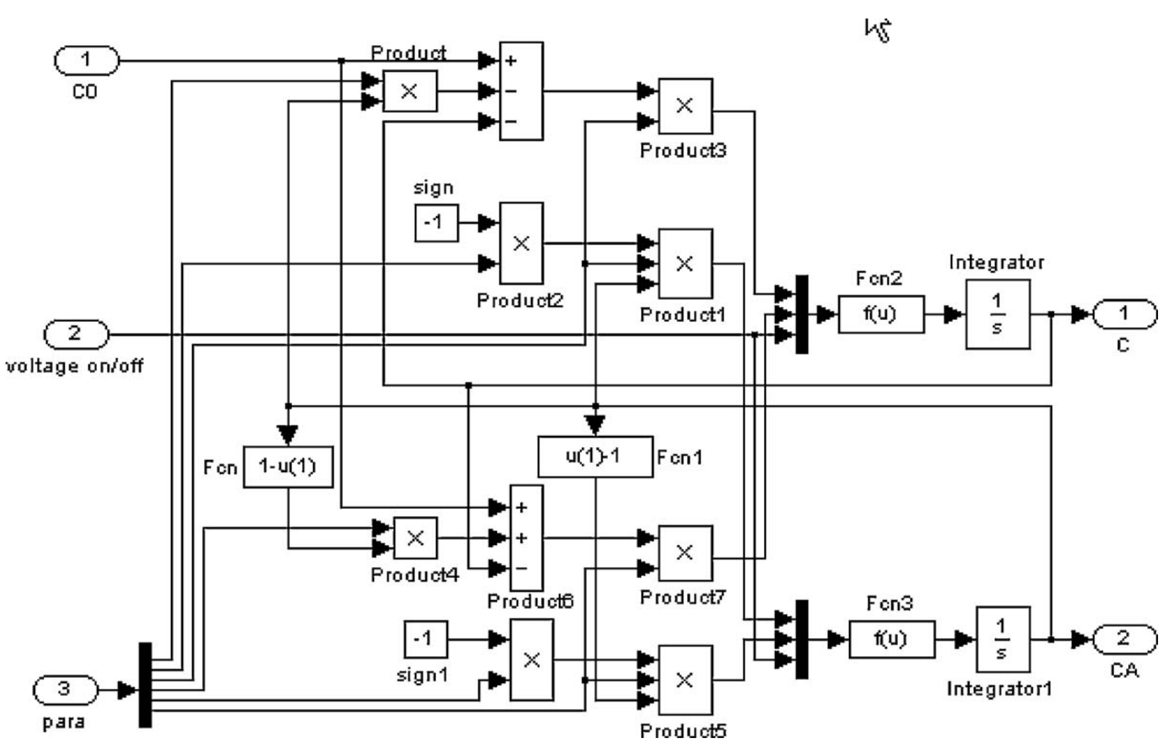

Fig. 8. Schematic diagram of CDI_Cell_0 in Fig. 7.

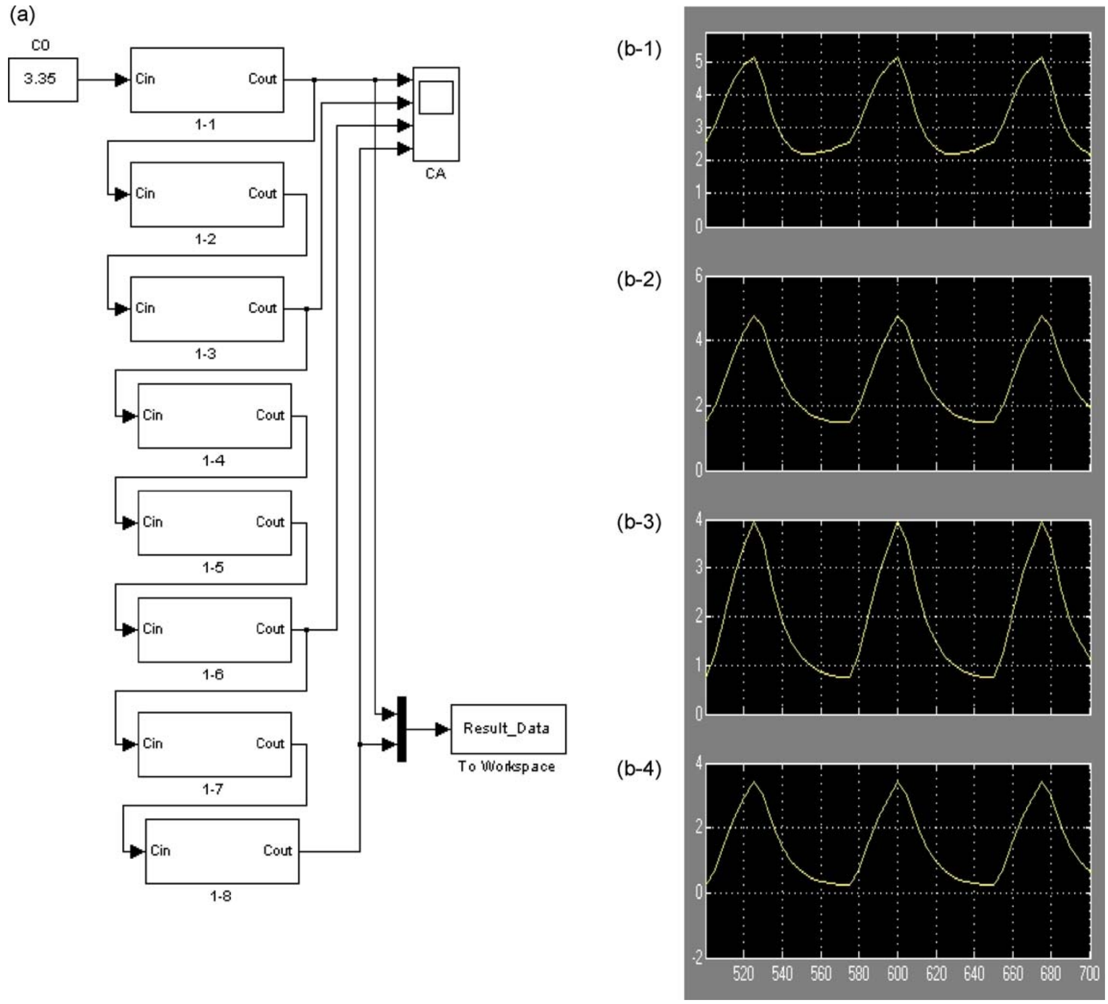

Fig. 9. (a) Matlab configuration of 1 stack with 8 CDI cells and (b) corresponding simulation result. (b-1) 1 unit cells, (b-2) 3 unit cells, (b-3) 6 unit cells, and (b-4) 8 unit cells.

6. Discussion and conclusion

Under the ever-increasing global water crisis, the need for improving desalination technology in terms of cost and performance has never been stronger than before. CDI has been drawing increasing attention due to its economic advantage against conventional separation methodologies such as evaporation, reverse osmosis. Many works are under progress to make the more efficient, effective methodology. In line with this, this paper provided a simulation work for a CDI system based upon experiment of CDI unit cells. It can be further expanded to simulate a system consisting of multiple stacks. From these simulation works, it will be able to control the flow rate of the contaminated water. That will allow us to evaluate the performance and economic feasibility of employing CDI in actual desalinization processes. In order to do this, we need to make the amount of the contaminated water to be constant because flows from multiple stacks should be constant to make the process continuous.

Acknowledgement

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