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DESALINATION BY CAPACITIVE DEIONIZATION IN MICROCHANNEL

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อรววรรยา ประกอบสุข : การแยกเกลือออกจากน้ำด้วยการแยกไอออนแบบการเก็บประจุในช่องการไหลขนาดไมโคร (DESALINATION BY CAPACITIVE DEIONIZATION IN MICROCHANNEL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. วรงค์ ปวราจารย์, 76 หน้า.

น้ำเป็นปัจจัยสำคัญสำหรับทุกชีวิต แม้ว่าพื้นที่บนโลกส่วนใหญ่จะมีน้ำปกคลุมเป็นปริมาณมาก แต่น้ำเหล่านั้นมีเพียงส่วนน้อยเท่านั้นที่เป็นน้ำจืด การขาดแคลนน้ำจืดเป็นปัญหาที่สำคัญที่ทุกประเทศสนใจแก้ไขมาโดยตลอด การกำจัดเกลือออกจากน้ำนับเป็นหนึ่งในวิธีการแก้ไขปัญหา การใช้ระบบการกลั่นหรือระบบรีเวอร์สออสโมซิส จะต้องใช้พลังงานอย่างมากในการแยกน้ำออกมา โดยแตกต่างจากการใช้หลักการแยกไอออนแบบการเก็บประจุ ซึ่งเป็นการดึงไอออนออกจากน้ำโดยการใช้ความแตกต่างของศักย์ไฟฟ้าทั้งสอง จึงมีศักยภาพที่จะพัฒนาได้ในผลลัพธ์ของเรื่องค่าใช้จ่าย ในงานวิจัยนี้ได้ศึกษาโดยประยุกต์ใช้หลักการแยกไอออนแบบการเก็บประจุในช่องการไหลขนาดไมโคร การทดลองต่างๆดำเนินการโดยใช้สารละลายโซเดียมคลอไรด์ ช่องการไหลขนาด 500 ไมโครเมตร, 750 ไมโครเมตร และ 1000 ไมโครเมตร ถูกสร้างให้อยู่ระหว่างแผ่นกราไฟต์สองแผ่น โดยแผ่นกราไฟต์ด้านหนึ่งถูกใช้เป็นขั้วไฟฟ้าด้านบวก และแผ่นกราไฟต์อีกด้านถูกใช้เป็นขั้วไฟฟ้าด้านลบ สภาวะของแรงทางไฟฟ้าที่ใช้แปรผันอยู่ในช่วง 0 โวลต์ ถึง 5 โวลต์ นอกจากนี้ แผ่นกราไฟต์ถูกปรับปรุงเพื่อเพิ่มความสามารถในการดูดซับ โดยการกระตุ้นด้วยไอน้ำที่อุณหภูมิ 1100 องศาเซลเซียส เป็นเวลา 30 นาที มีการเปลี่ยนขั้วไฟฟ้าต่างๆเพื่อใช้ทดสอบ ได้แก่ กราไฟต์ที่ถูกกระตุ้น, กราไฟต์ที่ฉาบด้วยทอง และเหล็กกล้าไร้สนิม ทั้งนี้พบว่า การใช้ช่องการไหลขนาดไมโครสามารถเพิ่มประสิทธิภาพในการกำจัดเกลือได้ โดยเป็นการลดความต้านทานการถ่ายโอนมวล การกำจัดเกลือออกจะได้ผลไม่ดีเท่าที่ควร เมื่อดำเนินการจ่ายไฟให้ระบบมากกว่า 2.06 โวลต์ เนื่องจากเกิดปฏิกิริยาอิเล็กทรอลิซิสร่วมด้วย วัตถุประสงค์ของงานวิจัยนี้ เพื่อศึกษาพฤติกรรมของการดูดซับทางไฟฟ้าของโซเดียมไอออนและคลอไรด์ไอออนผ่านช่องการไหลขนาดไมโคร และศึกษาผลของความเป็นรูพรุนของขั้วไฟฟ้าที่ส่งผลต่อประสิทธิภาพการกำจัดเกลือ

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Water is a crucial factor for all living organisms. Although majority of the earth is covered by water, only small fraction the earth’s water is fresh water. The lacking of freshwater is an issue that every countries would like to solve. Desalination is one of the solutions. Unlike distillation and reverse osmosis, which require a lot of energy, capacitive deionization relies on removal of ions from water by applied potential. Hence it has potential to be cost effective. In this study, the capacitive deionization is applied in a microchannel. The experiments were conducted using NaCl solution. The 500-μm, 750-μm, and 1000-μm microchannel were formed between a graphite sheet and another graphite sheet which were used as anode and cathode. The condition of the applied voltage was varied in the range of 0 - 5.0 V. Moreover, the graphite sheet was modified by steam activation at 1100°C and 30 minutes of dwell time to increase its adsorption capacity. Activated graphites, gold sputtering on graphites and stainless steels were varied as electrodes. It was found that the use of the microchannel could significantly enhance the desalination efficiency by reducing mass transfer resistance. The salt removal would not increase as expected when operated over 2.06 volts, concerning electrolysis reaction. This objective of the study was to investigate behavior of the electrosorption of sodium ions and chloride ions within microchannel and study effect of electrode porosity in terms of desalinated efficiency.

Department:	Chemical Engineering	Student's Signature	....
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CHAPTER I
INTRODUCTION

1.1 Introduction

Water is an important factor for all living organisms and it is crucial for survival of everybody. In the past, the shortage of water is not much a problem. Nowadays, many countries are facing a big problem of deficient water. Affordable clean water is a key challenge. Around 1,370 million cubic meters of water in the Earth's surface or approximately 97.2% is seawater. Major part of this is liquid water. The other part is other components that dissolves in water. Liquid water is equal to 96.5% of seawater and the remaining 3.5% is other components (salinity). Most of substances are abundant ions of sodium ions (Na^+) and chloride ions (Cl^-). Therefore, this study use sodium chloride solution representative of the seawater.

Removing salt from saline or seawater is well-known as desalination. There have been several methods of desalination using distillation, electrodialysis, or using membrane-based treatment technologies such as reverse osmosis, nanofiltration. The most widely used for desalination is reverse osmosis. In spite of this, reverse osmosis is expensive as mechanical energy recovery but capacitive deionization is cheap as electronic energy recovery. The weak point of those methods are hard maintenance, complex pretreatment, and high energy consumption. While capacitive deionization is the attention method that it is efficient for energy consumption for low ion concentrations.

The same point between capacitive deionization and electrodialysis are under the influence of the electric field allow only cations or only anions. The advantage of both methods are eco-friendly and economically profitable method of water desalination. Electrodialysis permeate their mass and simultaneously retain co-ions so that dilute and concentrate compartments are created and deionization occurs. By the way, electrodialysis consists membrane stack. The main limiting factor of electrodialysis is membrane fouling that can cause a dramatic increase of membrane electrical resistance and mass transfer resistance of the system.[1] Moreover, the needed permselective ion exchange membranes are costly and troublesome. Due to capacitive deionization removes ions from saline water but other technologies remove water from salt. There have been a number of valuable studies of a capacitive deionization which presenting evidence on using electrosorption cell. However, few studies focused on investigate the performance of desalination by capacitive deionization in microchannel.

In accordance with the advantages of capacitive deionization are plentiful. To bring about no costs for housing, pipes, and pumps because the capacitive deionization is not required high pressures. The operation of capacitive deionization is required low voltages, then it is a safe procedure. To be easier than reverse osmosis for energy recovery, the capacitive deionization uses electrical energy for regeneration but reverse osmosis is required energy recovery devices that have an effect on expensive cost and complication.

Capacitive deionization is an appropriate technology for treat saline/brackish water. When apply electrical voltages, ions in spatial channel between two oppositely charged electrodes are removed from aqueous solutions and adsorbed in electrical double layers. The strong point of capacitive deionization method is much simple process, safe for operation, and save cost for energy recovery devices. The electrode is required when has good electrical conductivity, high surface area, and large sorption capacity. Use of capacitive deionization with graphite as active electrodes material are interesting due to properties of porous structure, good electrical conductor and easy scalability. In addition, an activated graphite by steam activation is prepared in order to increase specific surface area/ porosity and enhance desalination efficiency.

Moreover, a microchannel is focused because it is much advantageous in terms of mass transfer, portability and energy efficient. This research presents the device that proposes how to apply the capacitive deionization in microchannel that are perceived as desalination. However, it would be of interest to try adsorbing ions from saline or seawater using method of capacitive deionization in microchannel.

1.2 Objectives

1.2.1 To investigate behavior of the electrosorption of sodium ions and chloride ions within microchannel

1.2.2 To investigate effect of porosity of graphite on desalination efficiency

1.3 Scopes of work

For operation ;

- The different electrodes, activated graphite, raw graphite, gold sputtering on graphite, and stainless steel were tested.
- The microchannel was varied from 500 to 1000 µm
- The feed was varied from 20 ppm to 5000 ppm of NaCl solution
- The applied potential was fixed in the range of 0 V to 5 V
- The residence time was set up in the range of 31 seconds to 500 seconds

For activation of graphite ;

- The activation temperature was set up in the range of 800 to 1100 degrees Celsius.
- The time for activation was held in the range of 30 minutes to 2 hours.

CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Capacitive deionization

The method of capacitive deionization, called CDI, is used for water desalination. The general principle of the capacitive deionization is removing salt from aqueous solution. When two electrodes are charged from external power supply, ions adsorb in electrical double layers. The electrode stored charge is form of electric field. Potential was applied to the electrode for attract ions. By the way, the electric field is driving force for ion adsorption and capacitance of capacitive deionization device [2]. When no applied potential to electrodes or no electric field, ions release to bulk solution. Electrosorption occurs in electrical double layers that excess ions adsorb at interface between an electrode and the solution.

As seen in Figure 2.1, Anions or ions with a negative charge are removed from solution and stored in positively charged electrode, named anode. While cations are removed and stored in negatively charged electrode, named cathode. The strong point of capacitive deionization is economical energy consumption while has satisfactory efficiency. Moreover, capacitive deionization is simple process, safe and inexpensive technology, energy efficient, no chemical additives, environmental friendliness and safe for operation. But capacitive deionization is mainly used as the method which desalinate the brackish water that is water with a low or moderate salt concentration

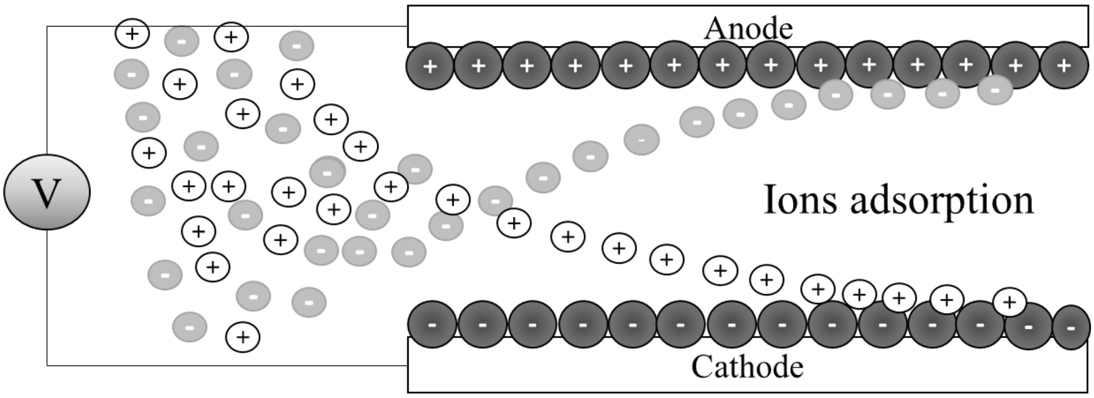


Figure 2.1 Schematic diagram of the capacitive deionization

In detail of related researches for desalination by capacitive deionization, almost researchers emphasize on salt removal ability. The electrode materials and the spacer between electrodes are various used.

Mostly Researchers had studied capacitive deionization experimental by used NaCl representative as salt solution. For example,

Researcher(s)	**solution**	**Initial concentration**
C.-L. Yeh et al., 2015	NaCl	0.5 mM (or 29.22 ppm) to 10 mM (or 584.4 ppm)
Wang et al., 2015	NaCl	100 ppm
Z.Chen et al.,2015	NaCl	5 mM (or 292.2 ppm)

By the way, some researcher used mixture of salt solution such as Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO^{3-}, and PO_4^{3-}. Ions can be effectively removed by using the method of capacitive deionization.

Figure 2.2 showed the specific energy consumption for capacitive deionization is less energy consumption than reverse osmosis desalination in the range of 100 ppm to 2000 ppm NaCl solution. [3]

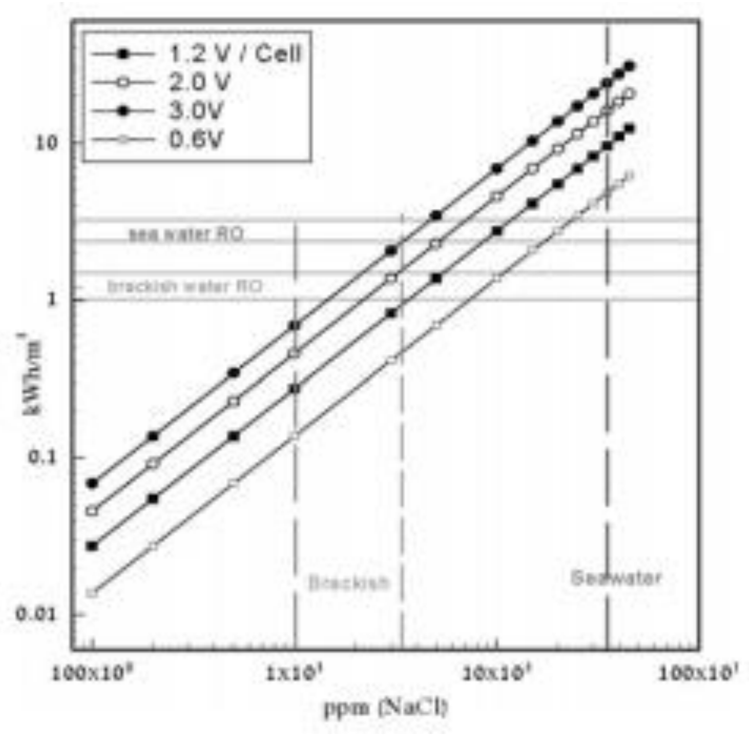


Figure 2.2 Specific energy consumption for CDI as a function of NaCl concentration and for different voltages, as compared with brackish and seawater RO desalination [3]

The electrosorption by capacitive deionization is indicated in Figure 2.3. The effluent is rapidly decreased in the earliest stage and quietly increase until equal concentration of raw solution. Energy consumption for capacitive deionization is demanded 32000 J/mole [2].

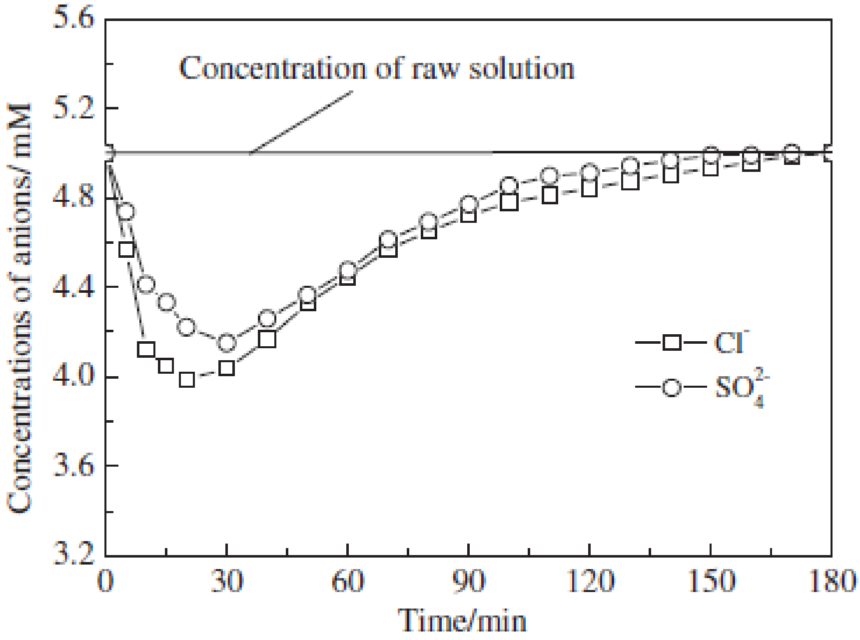


Figure 2.3 Electrosorption effluent curves of Cl^- and SO_4^{2-} in mixed solutions at 1.2V [4]

2.2 Electrical double layer (EDL)

Electrical double layer has occurred when surface become charged in solution and ions distribution neutralize co-ions and counter-ions nearby surface charge by adsorb counter ions at solid-liquid interface. Electrical potential from surface charge to bulk solution depends on potential decadence from surface as shown in Figure 2.4.

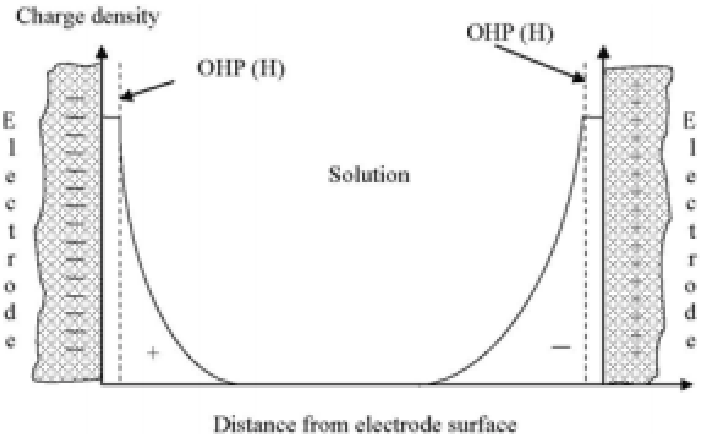


Figure 2.4 Schematic representative of charge distribution in an electrolyte solution in a two-electrode system (not to scale). [3]

2.3 Micro-scaled fluid channel (microchannel)

2.3.1 The comprehension and advantage of microchannel

Microchannel is used in a variety of devices integrating single-phase liquid flow. The agreement of channel thickness of micro-scaled fluid channel is not over 1 millimeters. Mostly, a microchannel is operated in continuous flow type. Generally, low Reynolds number laminar flows are obtained in the micro-scaled system [5]. A proper understanding of fluid flow in microscale system is essential for their design and operation. The advantage of microchannel are reduced mass transfer limitations, enhanced mixing, portability, and high surface area to volume ratios

2.3.2 Feature of microchannel

In this research, the microchannel devices were used in Center of Excellent in Particle technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

The assembly of the microchannel used in this work comprise acrylic, silicone gasket, electrodes, teflon sheet, rubber gasket, stainless steel and screw. It was shown in Figure 2.5.

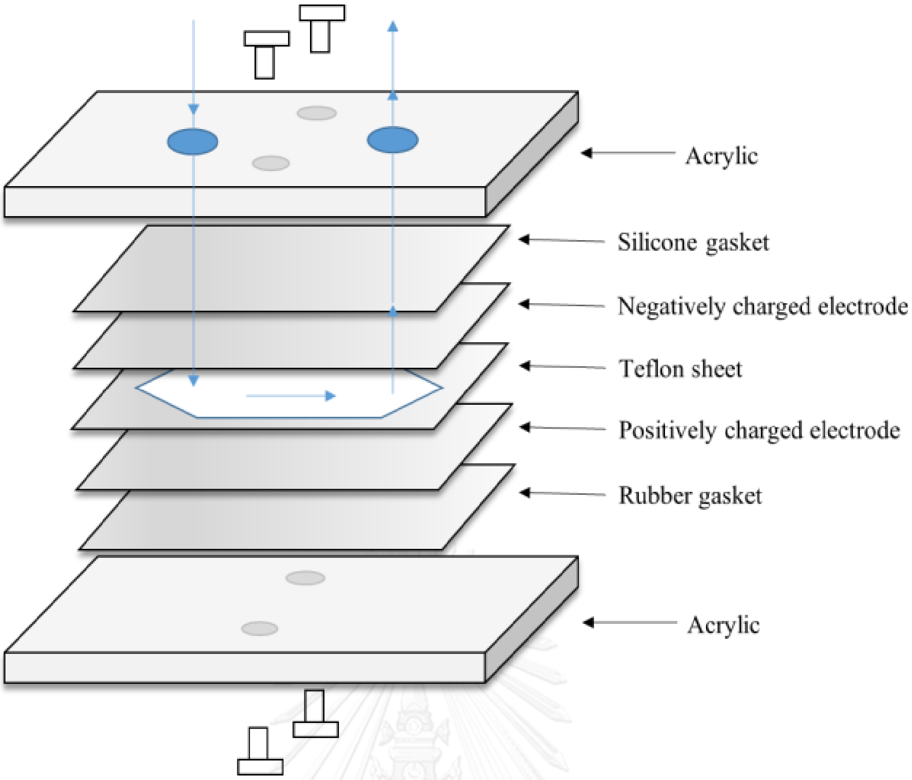


Figure 2.5 Schematic of microchannel and flow pathway

Description of figure 2.5

Acrylic

To perform a body of the channel, an acrylic dovetails one more acrylic by screws. On one side of an acrylic makes two holes for inlet and outlet pipe fitting and twist in screws on both side. Owning to screws perform a conductor. An acrylic dimension is 8.2 cm. × 8.6 cm. and its thickness is 1.5 cm.

Silicone sheet

The usefulness of a silicone sheet was in order to adjacently togetherness of stainless steel and an acrylic. Moreover, it would like to prevent the leakage of sodium chloride solution to leave from the device.

Stainless steel

Stainless steel was used as conductor together with screws. The dimensions of a stainless steel is equal to 5.4 cm. × 5.8 cm. The properties of stainless steel are conductible, durability, economical price, easily maintenance, and strength. Electrical conductivity is equal to 1.45×10^6 S/m.

Graphite sheet

Pure graphite was purchased from Masterpac-asia Co. Ltd. Graphite sheet was used as electrodes. The dimension of a graphite sheet was equal to 4.6 cm. × 5.0 cm. and the thickness was 1 mm. Electrical conductivity is approximately 2 to 3×10^5 S/m.

Graphite has found a wide range of applications. The selection electrode materials as graphite sheet, is due to efficiency in wastewater treatment, good electrical conductivity, porous structure, low residual current, easy scalability, chemical inertness, can be easily fabricated in different configuration sizes, its wide potential ranges and relatively low cost compared with other materials

The properties of graphite sheet were used as follows.

- Density = 1.12 g/cm^3
- Tensile Strength = 3.4 N/mm^2
- Stability under stress = 90 N/mm^2
- It can be used in range -200°C to 455°C (under oxidizing atmosphere).
- Maximum pressure is not over 80 bar.

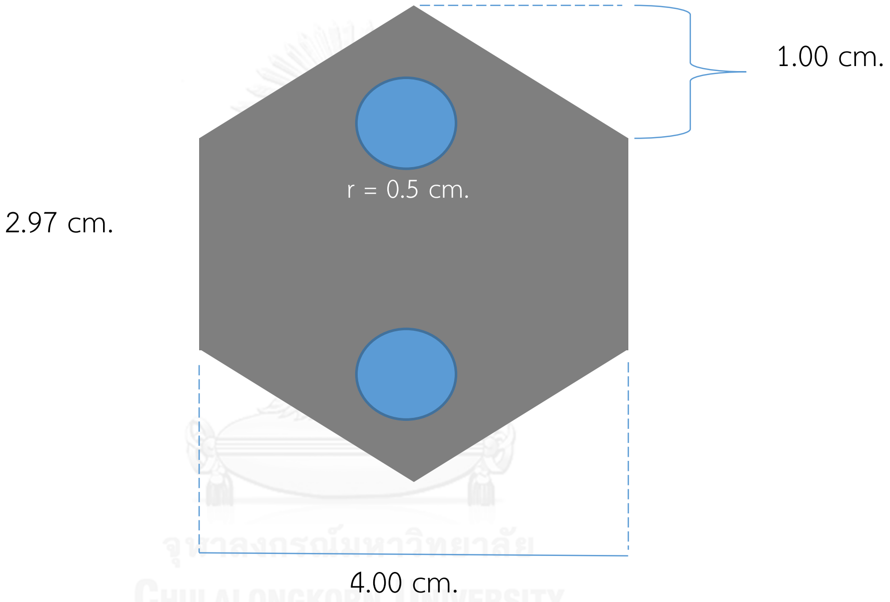


Figure 2.6 The Electrosorption area

Figure 2.6 presented the electrosorption area occurs between the electrodes. As follow, the calculation for electrosorption area was equal to

$$\text{Electrosorption area} = (2.97 \times 4.00) + (2 \times (1/2 \times 4.00 \times 1.00)) - (2 \times (\text{pi} \times 0.5^2))$$

$$= 11.88 + 4.00 - 1.5708$$

$$= 14.3 \text{ cm}^2$$

Then, the total area for electrosorption was equal to 14.3 cm^2.

Teflon sheet

A Teflon is the most important element for the microchannel. Because salt solution flows through the hexagonal channel as seen in Figure 2.7 and the electrosorption occurs in this region.

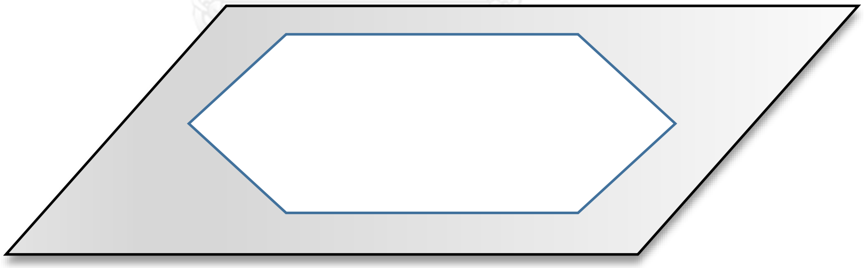


Figure 2.7 Flow pathway (hexagonal channel) of a teflon sheet

The pre-cut teflon sheet with thickness of 250 μm was used to determine the gap of the channel. When gap between electrodes is 500 microns, two sheets of Teflon were used. Meanwhile, three sheets of Teflon were determined for 750 microns. And four sheets of Teflon were determined for 1000 microns of gap.

Rubber gasket

In another side of device, a rubber gasket is inserted between stainless steel and acrylic in order to be tight and not slide.

Screw conductor

Screws represent electrical device as conductor. To be enter conduct to the microchannel device. Screws have to sufficient length as well.

2.4 Steam activation

An activation process is the method for improved specific surface area and porosity of carbon for obtaining activated carbon materials. As known that enhanced adsorption of material. The activation process can divide into two types: physical activation and chemical activation.

A chemical activation process is to enhance ability of specific surface area and pore structures by KOH or $ZnCl_2$. The temperature ranges is 150 to 900 degree Celsius. When finished chemical activation, it is necessary to wash off with water until no chemical residual. And the chemical, such as ZnCl2, using for chemical activation process can corrosion to the furnace.

Physical activation encouraged by using either gas (carbon dioxide) or steam. This operation is rather high temperatures approximately 800 to 1000 degrees Celsius. A physical activation has influenced to more porosity and larger pore sizes which expanded adsorption capacities. The activation with steam is used widely spread when compared with CO_2 because molecules are smaller than CO_2. The activated carbon by steam are maintain the original form. Moreover, this method is ecofriendly and economical. Physical activation develop pore structure as 3 stage [6]. For instance,

1. Opening inaccessible pores
2. Creating the new pores
3. Widening the exist pores into the mesoporous range

The comparison of chemical activation and physical activation are emphasized on cost and environment-friendly. The chemical activation has to use extremely amount of agents during chemical activation process cause abundantly wastewater and environmental contamination. Moreover, the chemical activation is complexity methods and high expenses due to treat and repair corrosive device. While Physical activation such as with steam is a good choice to get a wider pore-size distribution which compare to physical activation with CO_2 and not expensive process.

When finished physical activation, activated carbons can be used immediately while by chemical activation is required to wash chemical residuals. Then, this study focused on steam activation.

The reaction of steam activation; $C+H_2O \rightarrow H_2 + CO$ ---- 31 kcal

Mechanisms $C + H_2O \rightarrow C(H_2O)$

$C(H_2O) \rightarrow H_2 + C(O)$

$C(O) \rightarrow CO$

H_2 and CO will come off and causing pore.

Physical activation is widely used to improve surface area and porosity. The sample of materials were activated by physical activation such as serpentine [7], corn cobs [8], Sliced activated carbon from date palm tree fronds [9], Carbon residue from biomass gasification [6]. For serpentine as mentioned, when activated with steam the BET specific surface area increased from 8 m^2/g to be 15.8 m^2/g [7]. For activated carbons from corn cobs as mentioned, when finishing activated the BET specific surface area increased from 352 m^2/g to be 566 m^2/g [7].

Steam activation influences porosity and pore sizes of activated carbon. It enhanced degradation efficiency and adsorption capacities [10, 11]. The carbons from different preparation sources such as seeds of Mucuna mutisiana [12], pistachio shell [13], date stones [10], cellulose fibers [14] were activated by physical activaton with steam for increasing specific surface area, porosity, and adsorption capacities and studying the result of modulating the time and temperature of activation. Various physical activation temperature and hold time were varied such as 500 to 800’C for 0.5 to 6 h (under a nitrogen flow 100 cm^3 min^{-1}) [20], or 800 to 950°C for 1h [13], or 873 to 1173 K for 1 to 10 h hold time under nitrogen flow rate 100 cm^3 min^{-1} [12].

The strong points of activation to be activated carbon are using in large scale application, large specific surface area, excellent electrical conductivity [4]. Although there are excellent electrosorption performance more than activated carbon such as carbon aerogel, carbon nanofibers, carbon nanotubes but these material are not usual used in capacitive deionization because expensive and complicated production. It hardly used in industrial application.

2.5 Physical adsorption and chemical adsorption

Adsorption is the adhesion of sticking together of atoms, ions, or molecules of a gas, liquid, or dissolved solids, to the surface of a solid, or sometimes a liquid. An adsorption can be divided into two categories, depend on attractive forces at the surface, there are physical adsorption and chemical adsorption.

Mostly, attractive force for physical adsorption is caused by intermolecular Vander Waals's force which are weakly force. Physical adsorption can be readily reversed by simply heating and is transitory. On the other hand, chemisorption is the formation of chemical bond between solute and solid material. Chemical bond forces is stronger than force of physical adsorption but chemisorption is limited only monolayer adsorption and irreversible. While Physical adsorption forms multimolecular layer on adsorbent surface. Both physisorption and chemisorption also increases with increasing the surface area of adsorbent.

The difference between physical adsorption and chemical adsorption were shown in Table 2-1

Table 2-1 The comparison of physical adsorption and chemical adsorption

Parameter	Physical adsorption	Chemical adsorption
Force	Weak, long-range bonding	Short, short-range bonding
Temperature	$T < T_{\text{boiling point of the molecule}}$	All temperature
Heat of adsorption	Small (about 20-40 kJ/mol)	Large (about 40-400 kJ/mol)
Specificity	Not surface specific	Highly surface specific
Adsorption	Multimolecular layer	Unimolecular layer
Reversibility	Rapid, reversible	Slow, irreversible

CHAPTER III

EXPERIMENTAL

3.1 Experimental apparatus

The experimental apparatus is highlighted as follows.

- Stainless steel
- Teflon sheet
- Graphite sheet
- Syringe pump
- Syringe
- Electric wires
- DC generator
- Ammeter
- Voltmeter

3.2 Chemical substances

The chemicals in this research were dissolved Sodium Chloride (solid) in the deionization water.

For example, The meaning 20 ppm NaCl solution is dissolve NaCl(solid) 0.02 milligrams in 1 mL solution.

3.3 Apparatus set up

The apparatus was set up as shown in the following figure 3.1

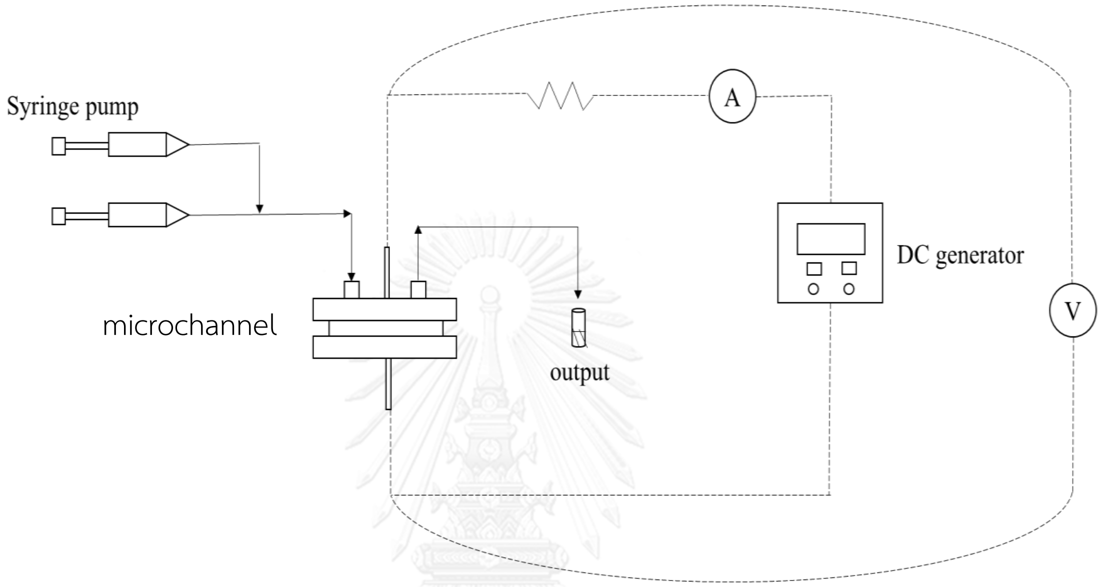


Figure 3.1 Schematic diagram of experimental desalination

3.4 Experimental procedures

(a) First of all, the microchannel was assembled. After this, the experiment was installed as shown in Figure 3.1.

(b) The salts solution was prepared as specified NaCl concentration prior to the NaCl solution was contained into syringes. Immediately after syringes were matched with the syringe pumps.

(c) The volumetric flow rate, based on microchannel volume and the various of residence time, was set up in order to continuous feed the solution into microchannel.

(d) The solution that had passed through the microchannel was collected for analysis. Chloride ions were analyzed by ion chromatography and analyzed sodium by atomic absorption spectrophotometer.

3.5 Activation of graphite

To enhance surface porosity of the graphite, steam activation was used.

(a) The graphite sheet was placed into the heating zone of a tube furnace

(b) Nitrogen gas was supplied to the furnace at the flow rate of 135 ml/min.

(c) Then, the activation temperature and holding time were varied. The system was heated up to setting temperature at the heating rate of 5 degree Celsius per minutes.

(d) For generating steam, the DI water being approximately 300 ml in volumetric flask was boiled on the heater.

(e) Once the system had reached the activation temperature, steam generated from deionization water was carried by the nitrogen gas into the system to activate the graphite. The activation was carried for setting time.

(f) The activated graphite was analyzed the surface area by nitrogen adsorption (BELSORP-mini).

3.6 Characterizations

3.6.1 N_2 physisorption or Brunaur, Emmett and Teller analysis (BET)

The specific surface area and porosity of activated graphite were determined by using Brunauer, Emmett and Teller (BET). The BET surface area were carried out using the BEL model BELSORP-mini-Japan apparatus. It was used in Center of Excellent in Particle technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University as shown in Figure 3.2. The graphite and activated graphite were analyzed for surface area by nitrogen adsorption (BELSORP-mini) at a temperature of 77 K.

Figure 3.2 N_2 physisorption

3.6.2 Ion Chromatography analysis (IC)

Ion Chromatography is a chromatography process which separates ions based on their attraction to the ion exchanger. Ion chromatography can divide into two groups, that are anion-exchange chromatography and cation-exchange chromatography. Using for analyze positively charged cations and negatively charged anions. It is often use for water analysis and quality control. It was used in Scientific and Technological Research Equipment Centre, Chulalongkorn University.

Figure 3.3 Ion chromatography

(http://www.st2-service.com/IC.htm)

After experimental desalination, the collected solution was analyzed ions concentration by ion chromatography.

The calculations of percent change from initial concentrations, % desalination, is given by

$$\% \text{ desalination} = \frac{C_0\text{-}C_t}{C_0} \times 100\%$$

whereas C_0 = initial concentration

C_t = output concentration

3.6.3 Atomic absorption spectrophotometer (AAS)

Atomic absorption spectrophotometer (AAS) is an analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. The method as Air-C_2H_2 Flame Atomic Absorption Spectrometry was used. In this research, an atomic absorption spectrophotometer, Varian Model AA280FS is used for determining the quantities of Sodium. It was used in Scientific and Technological Research Equipment Centre, Chulalongkorn University.

Figure 3.4 Atomic absorption spectrometry

(http://worldinfovr.co.in/all-technology/aas-atomic-absorption-spectrophometer/)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Electrosorption of chloride ions and sodium ions

In this manner, 20ppm salt concentration was used as initial feed solution. Residence time was specified at 300 second then feed flow rate was fixed at 8.58 ml/h. The area for electrosorption in 500 microns of channel was equal to 14.3 cm^2. The voltage was applied at 1.9 volts. This condition was used for determining the output concentration as shown in figure 4.1.

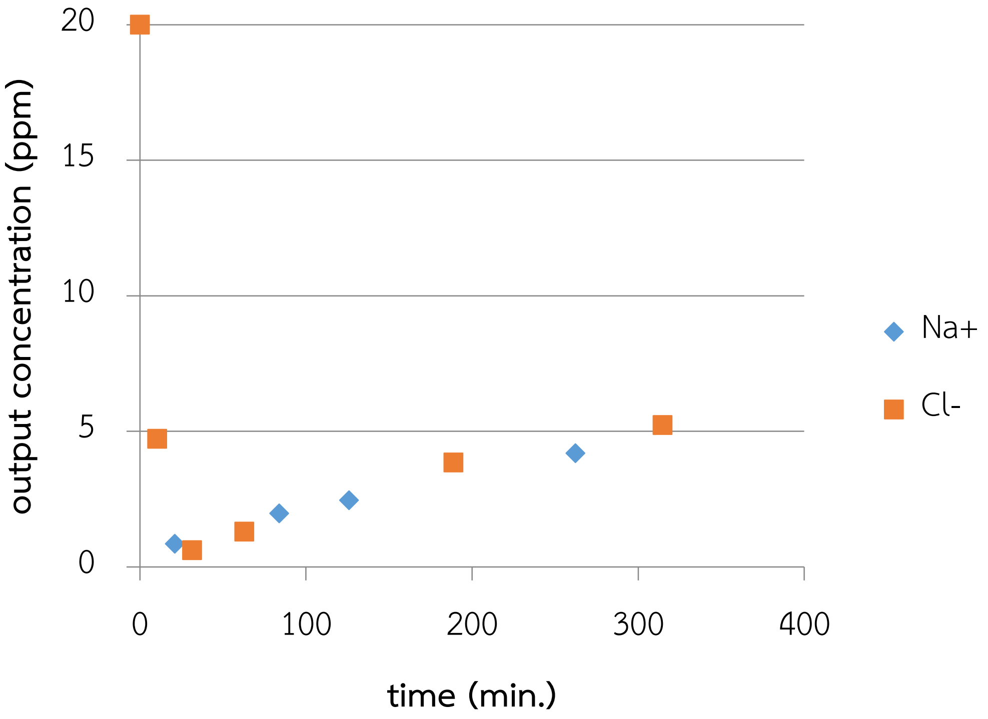


Figure 4.1 The output concentration from the experiment

It can observe that the graph of output concentration from the experiment in Figure 4.1 was desalinated from 20 ppm NaCl or initial concentration to be 0.62 ppm or 97% decreasing at time t = 31 minutes and gradually increased when time t elapsed. It can predict concentration of the solution will increase till equilibrium occur [4].

Basically, salt as sodium chloride which dissolved in deionization water were dissociated charged species turning to sodium ions (Na^+) and chloride ions (Cl^-). The ions were removed from the solution using their charge via an electric field.

In the part of results and discussion, various influences were determined in this research and the major results were investigated by amount of chloride ions. However, sodium ions were analyzed by Atomic absorption spectrophotometer. It was a same trend line in accordance with chloride as output concentration which shown in figure 4.1. To be conclude both of sodium and chloride were removed from the system in a similar way.

Accordingly, the results that can be also represented of sodium ions by determining chloride ions by ion chromatography.

In the matter of convert experimental data to percentaged desalination by equation, % desalination $= \frac{C_0-C_t}{C_0} \times 100\%$.

4.2 Influence of applied potential

As shown in Figure 4.2, The experiments were fixed as following conditions,

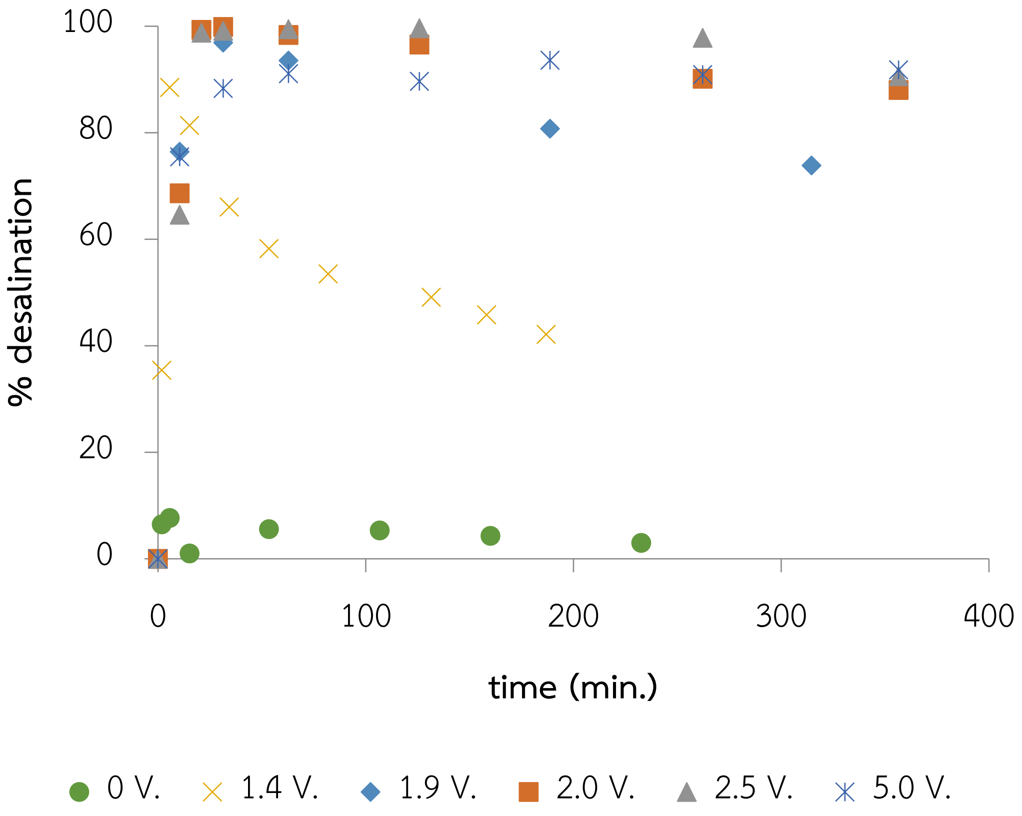


Figure 4.2 The percentage of desalination at different applied voltage with respect to the time of the experiment

1. Graphite were used as cathode and anode (or called charged electrodes).

2. Initial solution were equal to 20 ppm NaCl.

3. Residence time were fixed at 300 seconds.
4. Gap between electrodes were specified at 500 microns.

While the potential were applied to the system and varied as 0 volts (no potential), 1.4 volts, 1.9 volts, 2.0 volts, 2.5 volts, and 5.0 volts.

Figure 4.2 shows the tendency of the desalination at 0 V., 1.4 V., 1.9 V., 2.0 V., 2.5 V., and 5.0 V. of applied potential. The distinguishability between applied voltage and no voltage is obviously seen. It indicated electrical potential strongly affected for the system. However, it should be noted that the conventional adsorption is not the major cause for the desalination observed in this work since the amount of salt adsorbed on electrodes is negligibly small when no potentials is applied on the electrodes [15]. It is found that the increasing potential can improve the electrosorption efficiency. As X.Gao et al., 2015 said increasing volt cause salt removal increased. The surface potential related to the charge at surface and the thickness of double layer. This is a reasoning between ions and distance of electric field from surface. This can be explain by figure 2.4, which indicates the strength of electrostatic forces depend on surface potential.

To observe at 2.0 V, 2.5 V, and 5.0 V, the desalinated efficiency resembled while there were much differ in electric energy. This can be supposed the occurrence of other reaction besides electrosorption. The primary cause was expected to start up water splitting that obstructed electrosorption area on electrodes when operate over than 2.06 V, or called electrolysis reaction. For the purpose that can be satisfy with Wang et al., 2015 and Laxman et al., 2015 claimed applied DC voltage less than 2 volts will not occur electrolysis reaction [2, 16]. The argument for electrolysis reaction was indicated below.

Electrolysis reaction

- Reduction in the cathode

$Na^+ (aq) + e^- \rightarrow Na(s)$ $E_0 = -2.714$ V (1)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E_0 = -0.83$ V (2)

- Oxidation in the anode

$2Cl^- \rightarrow Cl_2 + 2e^-$ $E_0 = -1.360$ V (3)

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E_0 = -1.23$ V (4)

Then, Overall electrolysis reaction is

$$\boxed{6H_2O \rightarrow 2H_2 + O_2 + 4H^+ + 4OH^-}$$

where $E_{0,cell} = (-0.83) - (1.23) = -2.06$ V

The explanation of results at 2.0 V, 2.5 V, and 5 V in Figure 4.2 related with electrolysis reaction. Because sodium chloride solution is an electrolyte in water as Na^+ and Cl^-. When applied potential more than 2.06 V. to the system, the bubble on cathode which is hydrogen gas were occurred. It caused worse desalinated water. This is regarded as the limitation of capacitive deionization method.

4.3 Influence of residence time

As shown in Figure 4.3, the residence time were varied as 31 seconds, 200 seconds, 300 seconds, and 500 seconds. While the fixed condition in the experiments as following statement.

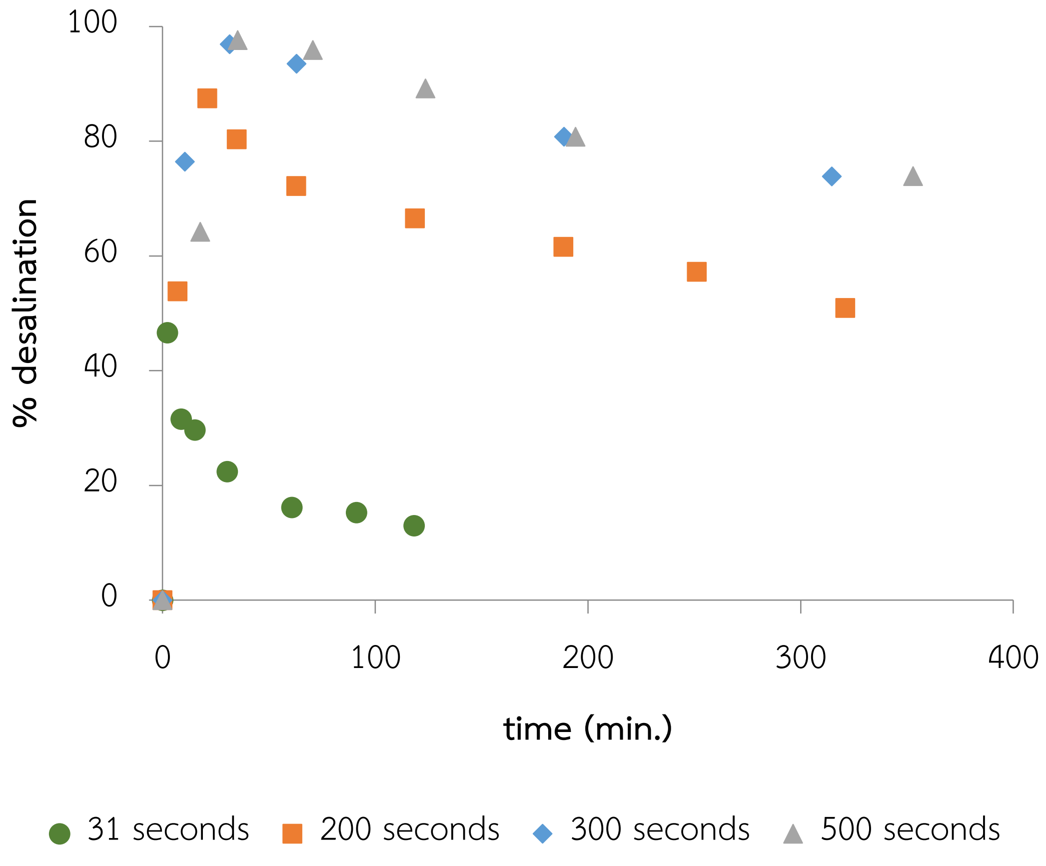


Figure 4.3 The percentage of desalination at different residence time with respect to the time of the experiment.

1. Graphite were used as cathode and anode (or called charged electrodes).
2. Initial NaCl concentration were equal to 20 ppm.
3. Applied voltage were equal to 1.9 V.
4. Gap between electrodes were 500 microns.

The meaning of residence time is the dwell time in the channel. The residence time depends on volume of channel and volumetric flow rate. As equation,

$$\text{residence time} = \frac{\text{volume of solution}}{\text{flow rate of solution}}$$

In this tested, the volume of channel were fixed at 0.72 milliliters due to 500 microns of gap and 14.3 cm^2 of electrosorption area. The residence time were differ as 31 seconds, 200 seconds, 300 seconds, and 500 seconds. Then, the volumetric flow rate were equal to 83.0 ml/h, 12.9 ml/h, 8.6 ml/h, and 5.1 ml/h, respectively.

Increased residence time brought more dwell time in microchannel due to fixed in volume and lower flow rate of solution.

To calculate the diffusion time from bulk solution (NaCl solution) to wall (surface of electrode) depend on the gap

Characteristic time (or time scale) for molecular transport is calculated from this equation

$$(t_{ch})_{mol} = \frac{L^2}{D_{AB}}$$

when L = characteristic length

D_{AB} = diffusivity for mass transport

= diffusion coefficient (m^2/s)

Considering,

$D_{Cl^-\ \text{in aqueous}}$ (at 25° C) = $2.03 \times 10^{-9}\ m^2/s$,

Gap = L = $500 \times 10^{-6}\ m^2$

Then, the diffusion time for ions transport is approximately 62 seconds.

It can be seen from Figure 4.3 that residence time affects desalinated efficiency. The longer residence time is greater in salt removal.

When 31 seconds of residence time was tested, it was not sufficient time for bulk solution diffuse to electrode then the percentage of desalination was just 46% and continuously decreased when time elapsed. Accordingly, this flow rate was too fast for this system and the bulk solution go away before diffusion occurred. When residence time were specified at higher than calculated diffusion time and varied as 200 seconds, 300 seconds, and 500 seconds, the result of 200 seconds of residence time was 87% of desalination at maximum. While the results at maximum points were 97% of desalination for both 300 seconds of residence time and 500 seconds of residence time.

It obviously seen the percentage desalination of 200 seconds of residence time was greater than 31 seconds of residence time but it was worse than 300 seconds and 500 seconds of residence time.

It denoted ions not transport to inner pores as it should be. Nevertheless, the ability of 300 seconds and 500 seconds of residence time were similar for desalination. Accordingly, 300 seconds of residence time was sufficient for transport time scale in the system. Referred to ions transport from solution to most of the pores and electrical double layer formation. By the way for 500 seconds of residence time, it has wasted a lot of time when residence time was too long due to flow rate was slow.

4.4 Influence of gap between electrodes

To determine the influence of gap between electrodes, there were fixed variables as following statement,

1. Graphite were used as cathode and anode (or called charged electrodes).
2. Initial NaCl concentrations is equal to 20 ppm
3. Residence time = 300 seconds
4. Applied voltages at 1.9 volts

The different conditions of gap between two electrodes were tested as 500 microns, 750 microns, and 1000 microns. Consequently,

The volumetric flow rate for 500 microns, 750 microns and 1000 microns of channel were equal to 8.58 ml/h, 12.9 ml/h, and 17.16 ml/h, respectively.

As obviously seen in Figure 4.4, the potential that applied to the system were fixed in the experiments.

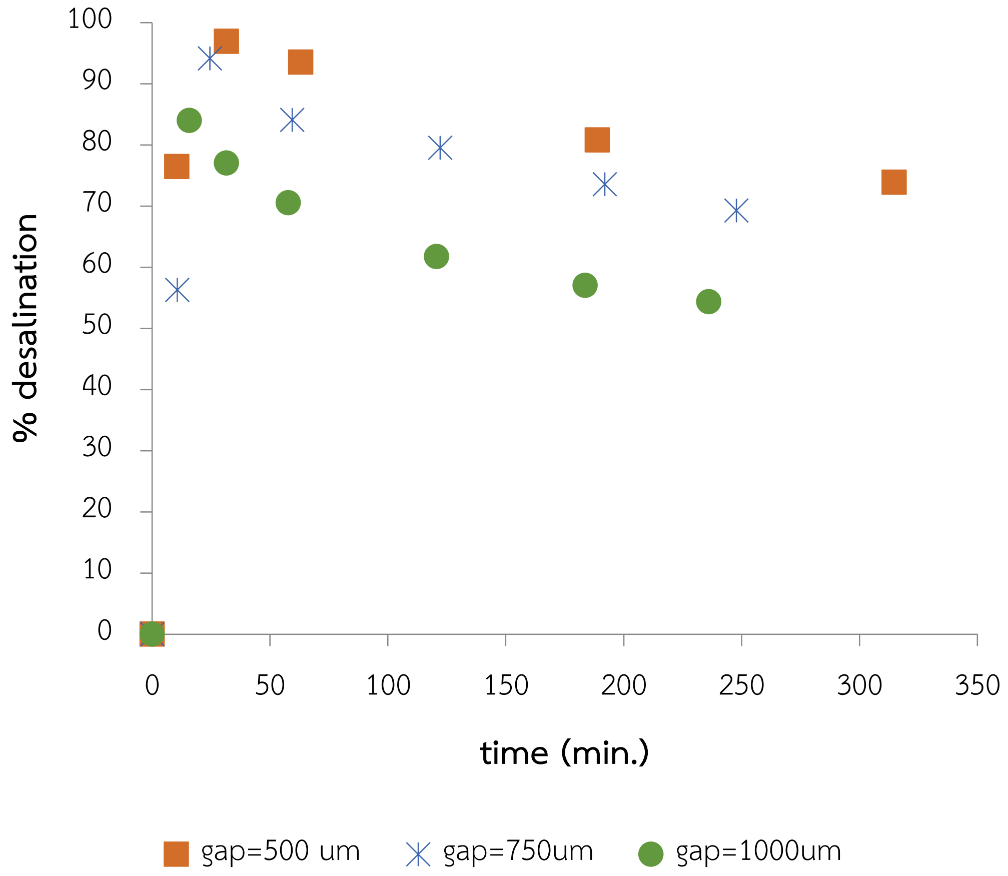


Figure 4.4 The percentage of desalination when gap between electrodes were varied at 500 μm, 750 μm, and 1000 μm

The result confirms that the gap size affects the salt removal efficiency. Because of continuous process, thus ions diffuse into the electrodes and also blow to output by convection. The salt removal efficiency were enhanced when the height of the microchannel was small because of the decreased diffusion distance to the electrodes. By fixing applied potential, the distance of electrical double layer in y-direction were the same. Then, the opportunities of ions were more pressed in electrical double layer region. It was easier for ions transport.

As mentioned in above topic in regard to influence of residence time that the diffusion time can calculate by equation $(t_{ch})_{mol} = \frac{L^2}{D_{AB}}$

Table 4-1 showed the diffusion time for 500 microns, 750 microns, 1000 microns are equal to 61.6 seconds, 138.5 seconds, and 246.3 seconds, respectively. It was confirmed the diffusion time is related with the gap. Narrower gap is easier for diffusion.

Table 4-1 Diffusion time depend on the gap between two electrodes

Gap	L (m)	$D_{chloride\ in\ aqueous}$ (m^2/s) [Bouazizi et al, 2011]	$(t_{ch})_{mol}$ (s)
500 µm	500×10^{-6}	2.03×10^{-9}	61.6
750 µm	750×10^{-6}	2.03×10^{-9}	138.5
1000 µm	1000×10^{-6}	2.03×10^{-9}	246.3

gap = 500 µm, vol. flow rate = 8.58 ml/h, characteristic velocity = 1.19×10-4 m/s

gap = 750 µm, vol. flow rate = 12.90 ml/h, characteristic velocity = 1.19×10-4 m/s

gap = 1000 µm, vol. flow rate = 17.16 ml/h, characteristic velocity = 1.19×10-4 m/

Although the volumetric flow rate were not equal but the characteristic velocity were the same. Then, the result in figure 4.4 can explain the gap between electrodes that affected to the system. When the height of the microchannel was small, the salt removal efficiency were enhanced. There were only effect of diffusion because the system were in the region of boundary layer.

In this case was accordant with Wang et al., 2015 [16] tested 2 mm. of optimized spacer between electrodes and claimed smaller plate distance could shorten distance for the formation of electrical double layer then the migration are faster. However, too narrow gap might be short circuit on electrode.

4.5 Influence of electrodes

4.5.1 Effect of activation temperature

In this research, graphite were used as electrodes in capacitive deionization. It can be improve graphite by activated with steam. As observed in Table 4-2, the specific surface area and pore volume were increased by increasing activated temperature.

Table 4-2 Results from N_2 physisorption when vary temperature for activation

BET Analysis			
Parameter	Graphite	Activated graphite at 800°C	Activated graphite at 1100°C
Activation Temp. [°C]	No	800	1100
Activation time [h]	No	1.05	1.05
$a_{s,BET}$ [m^2 g^{-1}]	13.5	23.12	27.31
Total pore volume [cm^3 g^{-1}]	4.52×10^{-2}	5.87×10^{-2}	6.79×10^{-2}
Mean pore diameter [nm]	13.366	10.162	9.9474

Specific surface area of graphite was 13.5 m^2g^{-1}. Activated temperature with 800 degree Celsius and 1100 degree Celsius for activated graphite were 23.12 m^2g^{-1} and 27.31 m^2g^{-1} in specific surface area, respectively. Total pore volume were expanded from 4.52×10^{-2} cm^3 g^{-1} to be 5.87×10^{-2} cm^3 g^{-1} for 800 degree Celsius of activation and be 6.79×10^{-2} cm^3 g^{-1} for 1100 degree Celsius of activation. It can reveal that activation made smaller in pore size and generated new pores. Increasing in activating temperature enhance carbon burn off and devolatilization.

However, if it was too high in activated temperature, it might be decreasing in surface area and pore volume. Because the accumulation of carbon was in the pores. The accumulation made gradually large pore size of carbon and generated pore fusions [9]. It was also increasing cost of activation [6].

4.5.2 Effect of holding time for activation

Table 4-3 compared activating variable as dwell time for activation. Temperature were fixed at 1100 degree Celsius. Holding time were varied as 30 minutes, 1 hour, and 2 hours.

Table 4-3 Results from N_2 physisorption when vary holding time for activation

BET analysis				
Parameter	Graphite	Activated graphite 1	Activated graphite 2	Activated graphite 3
Activation Temp. [°C]	No	1100	1100	1100
Activation time [h]	No	0.5	1	2
$a_{s,BET}$ [m^2 g^{-1}]	13.5	28.99	27.31	26.68
Total pore volume [cm^3 g^{-1}]	4.52E-02	6.97E-02	6.79E-02	6.42E-02
Mean pore diameter [nm]	13.366	9.6142	9.9474	9.6326

It can be observe well result in surface area and pore volume at 30 minutes of dwell time. In this operation, increasing holding time to be 1 hour and 2 hours appeared unchanged in surface porosity. In order that pore were widen and some pore walls were broken. Due to over contact time of carbon-steam reaction, then specific surface area were decreased.

4.5.3 Comparison of different charged electrodes in capacitive deionization

To determine the influence of electrode that affect the desalinated efficiency. The various electrodes as graphite, activated graphite, gold sputtering on graphite, and stainless steel were tested.

In the experiment as following in Figure 4.5 and shown in Table 4-4, the total area and the volume for electrosorption was specified at 52.44 cm^2 and 2.622 cm^3.

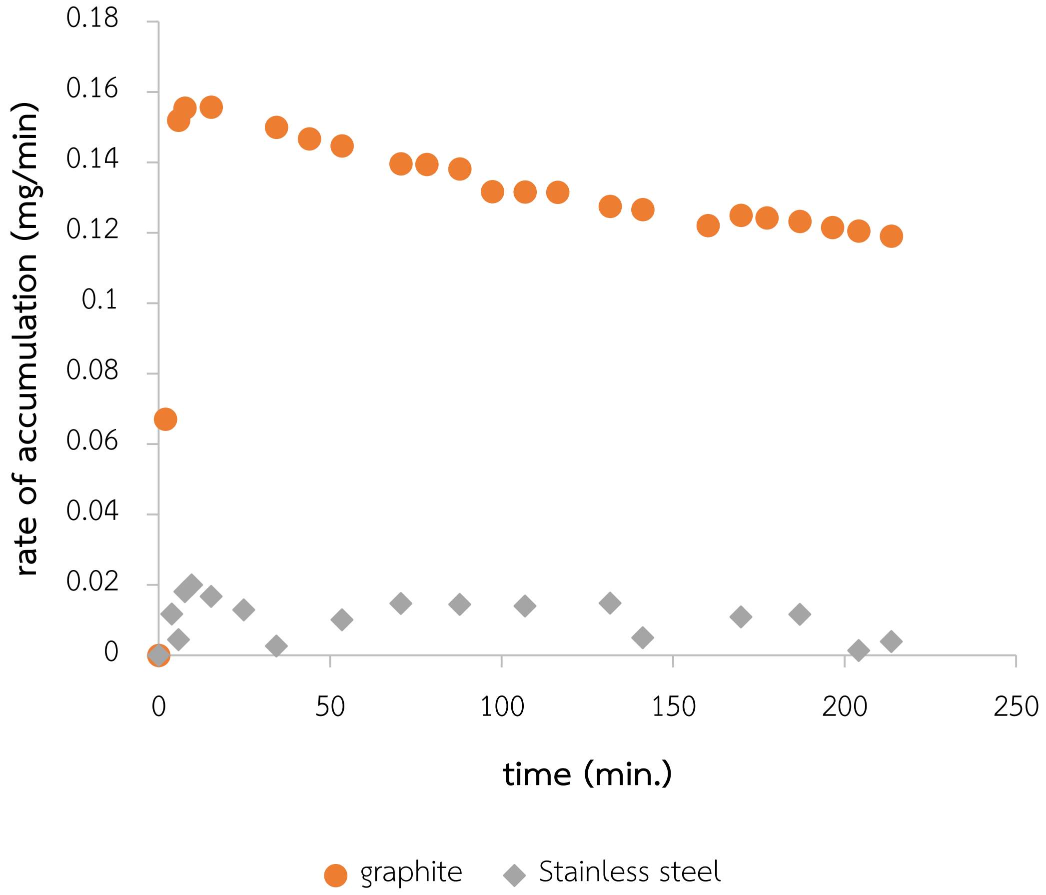


Figure 4.5 The amount of chloride ions accumulate against time on comparison of electrode like graphite and stainless steel

Table 4-4 The percentage of desalination for output concentrations compare with initial salt concentrations at time t.

Time (min.)	**Percentage of desalination**	
	Graphite	Stainless steel
2	42.68	3.49
6	96.57	2.87
15	97.99	9.64
34	95.33	8.25
71	88.77	9.38
141	80.47	3.18
187	78.32	7.40
214	75.69	2.54

Electrodes as graphite and stainless steel were compared. The concentration of NaCl solution was 20 ppm. The solution was supplied to the microchannel at the flow rate of 47.2 ml/h, which corresponds to the residence time of 200 seconds in the microchannel, by means of a syringe pump.

When the desalination by capacitive deionization in microchannel were operated, it obviously seen the performance of graphite electrode was much better than stainless steel while 1.9 volts of applied potential were fixed. The porosity of graphite was 0.045 cm^3/g and no porosity was observed for stainless steel.

From Table 4-4, it can observe the percentage desalination of stainless steel that used as electrodes was much worse than graphite. For stainless steel, the salt removal was approximately less than 10 percent. While the desalination for using graphite was approximately 98% at 15 minutes of operating time from beginning and lessen till equilibrium occurred. It denoted the importance of electrode porosity.

The desalination occurred when salt accumulated in the system. The total quantity of salt accumulated on graphite was 101 milligrams or 17.41 milligrams per grams of electrode. For used stainless steel as electrodes, the total amount of salt accumulated was 6.3 milligrams or 0.04 milligrams per grams of electrode. However, there are some adsorb occurred on stainless steel that implied there are some electrosorption in electrical double layer near surface.

The fact that graphite has surface porosity but stainless steel has no porosity. It seems the electrosorption on stainless steel was hardly. In comparison, the electrical double layer near surface that affected to the system was less than electrosorption in porosity of electrode approximately 15 times. Accordingly, it necessary to develop the porosity of electrode to enhance desalinated efficiency. Thereby, graphite were developed their specific surface area and porosity by steam activation method.

As mentioned in Table 4-5 that the BET specific surface area of graphite was increased from 13.5 m^2/g to 29.0 m^2/g when activated it.

Table 4-5. The comparison between graphite and activated graphite at 1100 degree Celsius and 30 minutes of dwell time

	Graphite	Activated graphite
BET specific surface area [$m^2 g^{-1}$]	13.52	28.99
Total pore volume [$cm^3 g^{-1}$]	4.52E-02	6.97E-02
Mesopore volume [$cm^3 g^{-1}$]	4.26E-02	6.20E-02
Mean pore diameter [nm]	13.366	9.6142

Figure 4.6 compared BET adsorption/desorption isotherm of graphite and activated graphite. The pore structure was expanded from 4.5×10^{-2} cm^3g^{-1} to be 7.0×10^{-2} cm^3g^{-1}. And the porosity as mesopores were increased from 4.3×10^{-2} cm^3g^{-1} to be 6.2×10^{-2} cm^3g^{-1}.

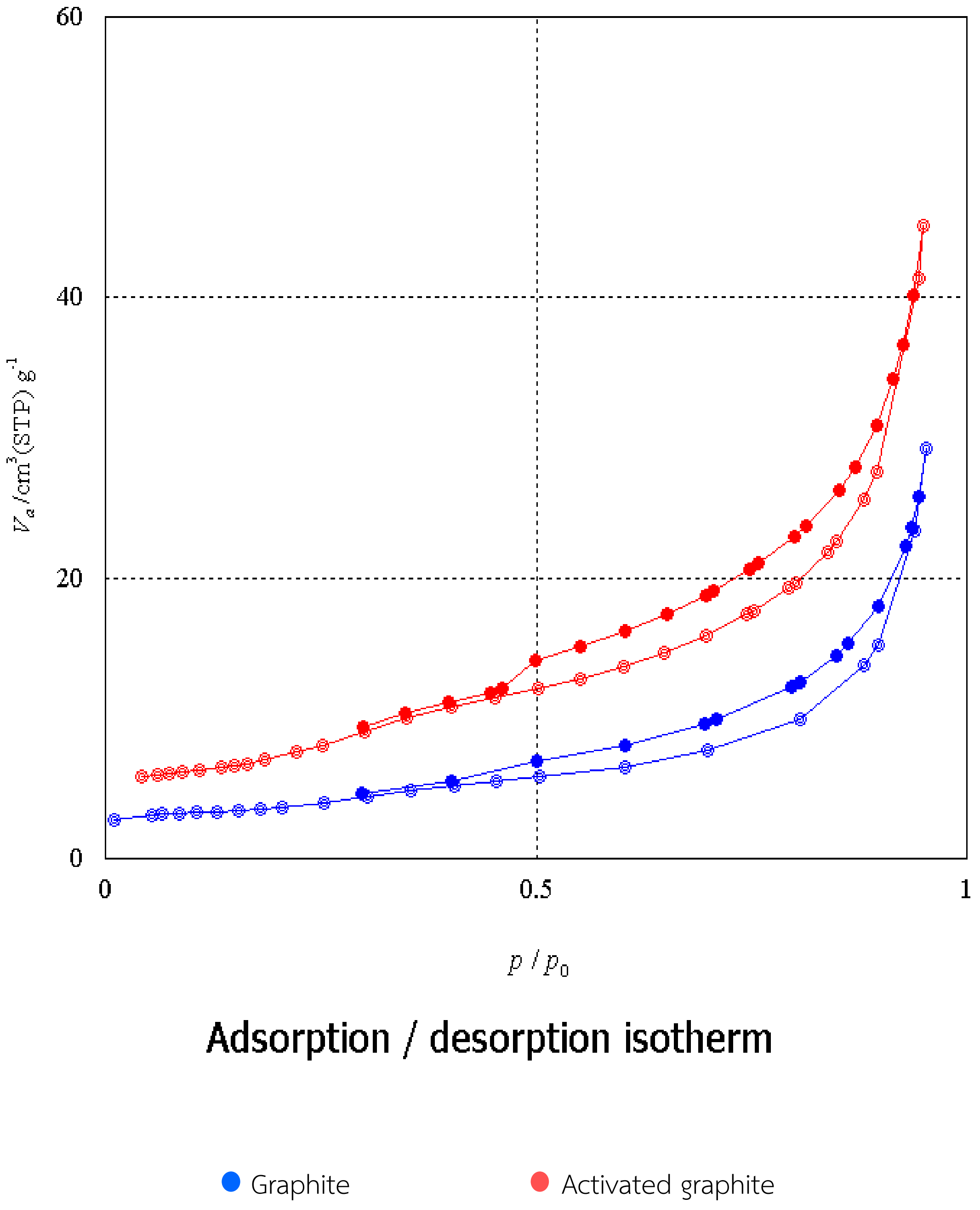


Figure 4.6 The adsorption/desorption isotherm of graphite and activated graphite by steam at 1100 degree Celsius and 30 minutes of dwell time

From Figure 4.7, regarding capacitive deionization in microchannel, the influence of electrode as graphite, activated graphite, gold sputtering on graphite were compared.

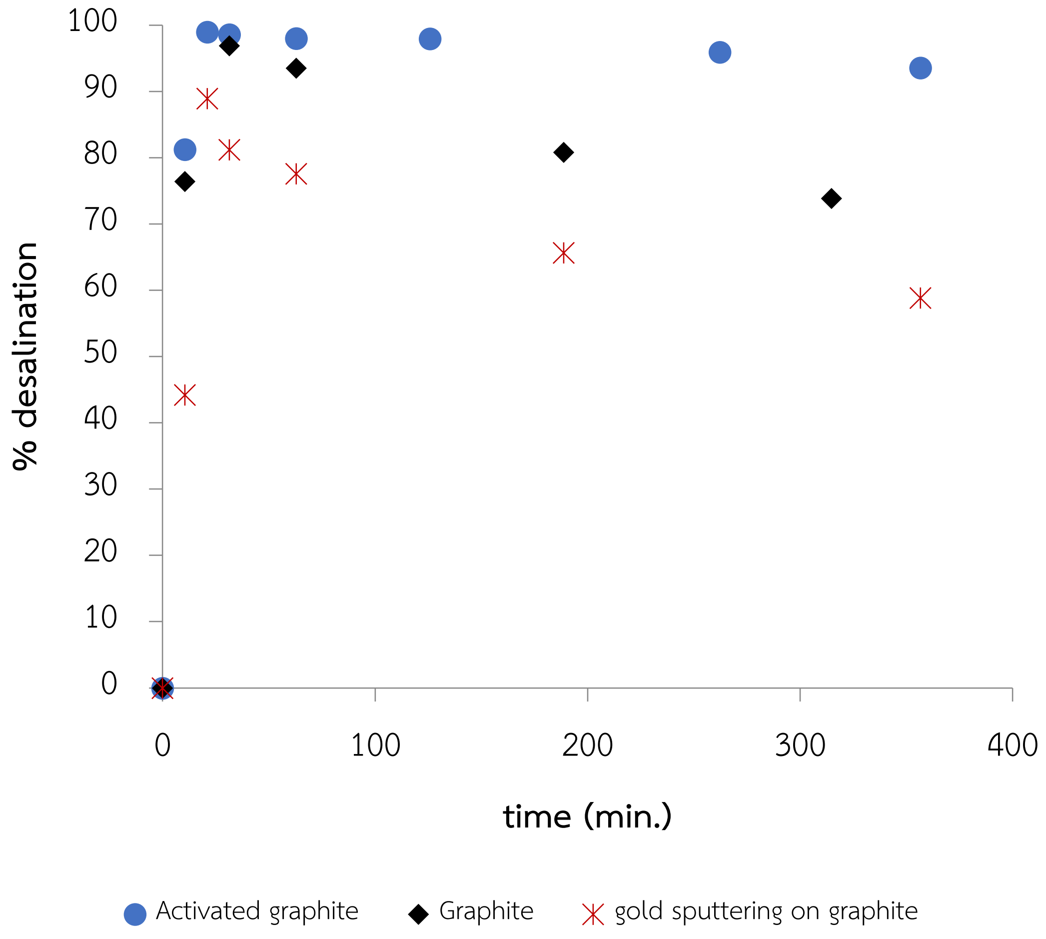


Figure 4.7 The percentage of desalination at different charged electrode with respect to the time of the experiment

The potential as 1.9 volts were supplied across the electrodes in the microchannel assembly. The conditions were fixed the residence time as equal to 300 seconds, gap between electrodes as 500 microns. Initial concentrations were equal to 20 ppm NaCl solution.

In terms of the desalination by capacitive deionization in microchannel, the desalinated efficiency as shown in Figure 4.7 were differed. At time t, activated graphite has ability of accumulation more than non-activated graphite due to ions capacities. Then, it was well done in desalination efficiency. For examples, to be achieved 95-99 percent salt decreasing, the activated graphite can be used for a long time as around 263 minutes but non-activated graphite were effectively used just for 62 minutes. Then, it should be regeneration. To sum up, activated graphite by steam activation were advantageous because it can use as charged electrode for longer time.

The activated graphite was good performance as capacitive deionization electrode rather than non-activated graphite. When salt solution contact with charged electrodes, ions transfer into electrical double layer near surface and porous network of electrode. Ions transportation was limited by surface porosity of electrodes. The pore structure of activated graphite has changed. Because activated graphite has more specific surface area for binding ions, the ability of adsorption was supplementary. Activated graphite caused increasing ion storage capacities. The activation developed pore structure of graphite to get well-balanced pore volume distribution by pore size. Also, the activation build up new pores, pore expanding, and opening inaccessible pores in the mesoporous range [6]. It was advantageous for used as electrode in capacitive deionization. Then, ions can almost all access through the pore [15].

When researchers mentioned about activation, almost all focused on the specific surface area and porosity of the carbon. While Y.-C. Tsai, R.-Doong, 2015 [17] claimed the activation caused changeable in surface area and functional group of carbon that is more hydrophilic functional group such as C-O, C-OH. When NaCl solution, comprising Na^+, Cl^-, and H_2O, oxygenated functional group promoted attraction of water due to water polarity. It caused electrolyte accessibility in porous structures. Nevertheless in this study, the percentaged desalination, as shown in Figure 4.7, likely increase by major increasing surface area of activated graphite.

Interesting when sputtered gold on graphite, the electrical conductivity was increased though the adsorption/desorption isotherm was the same. (As shown in Figure 4.8)

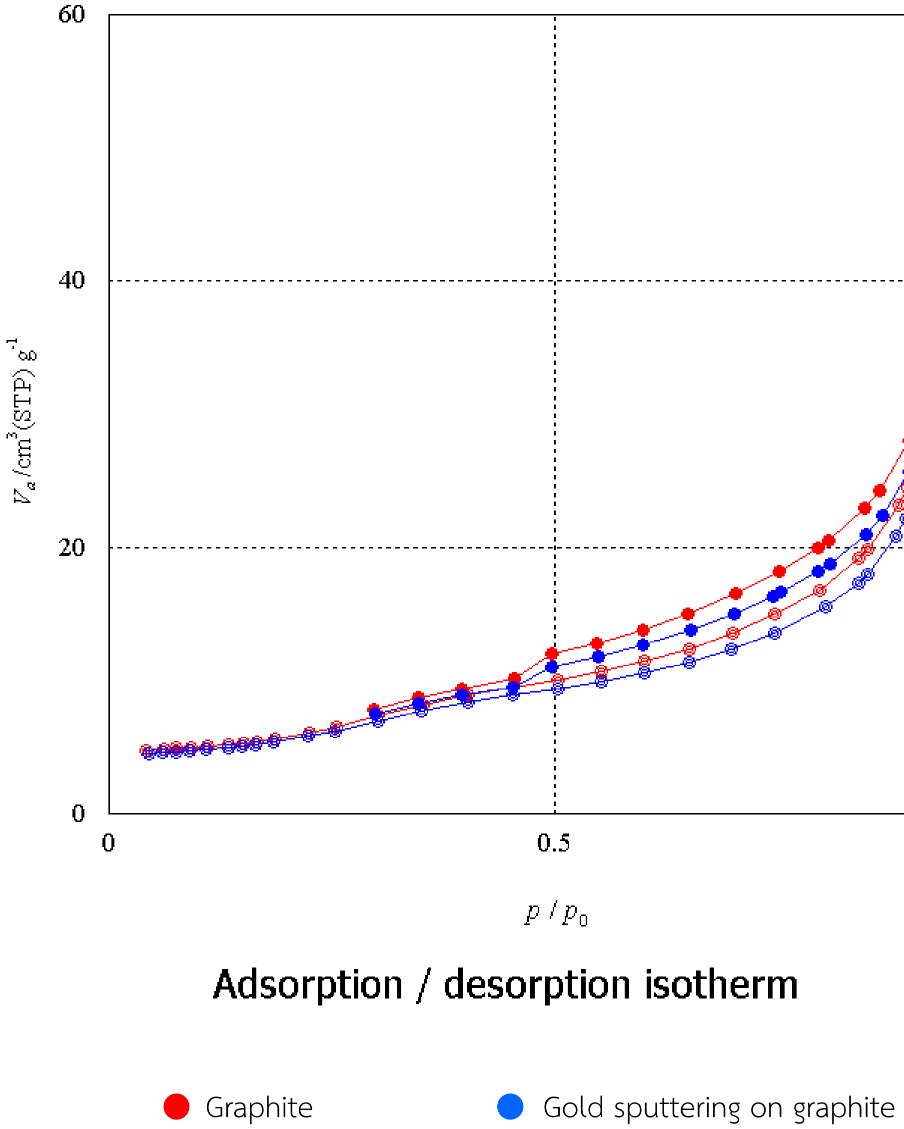


Figure 4.8 The adsorption/desorption isotherm of graphite and gold sputtering on graphite

Although, the surface porosity was changeless. But apparently seen in Figure 4.7, the desalination of gold sputtering on graphite was lower which compared to graphite electrode. It can predict functional group has changed. Partly carbon was missed. It may be mainly affect to differentiation of desalinated efficiency.

4.6 Comparison of electrode size

The condition, as fixed 500 microns of channel, 200 seconds of residence time, 1.9 volts applied to the system, were tested to compare effect of electrode size. The electrosorption area for small electrode like graphite was 14.3 cm^2. When electrode size is large, the electrosorption area was increased to 52.44 cm^2. The difference between large and small graphite size were 3.7 times. Initial feed flow rate for small and large size of electrode were 12.9 ml/h and 47.2 ml/h, respectively.

As seen in Figure 4.9 , the amount of ions per time were much accumulated on large electrode more than on small electrodes due to there were competitive advantage in electrosorption area.

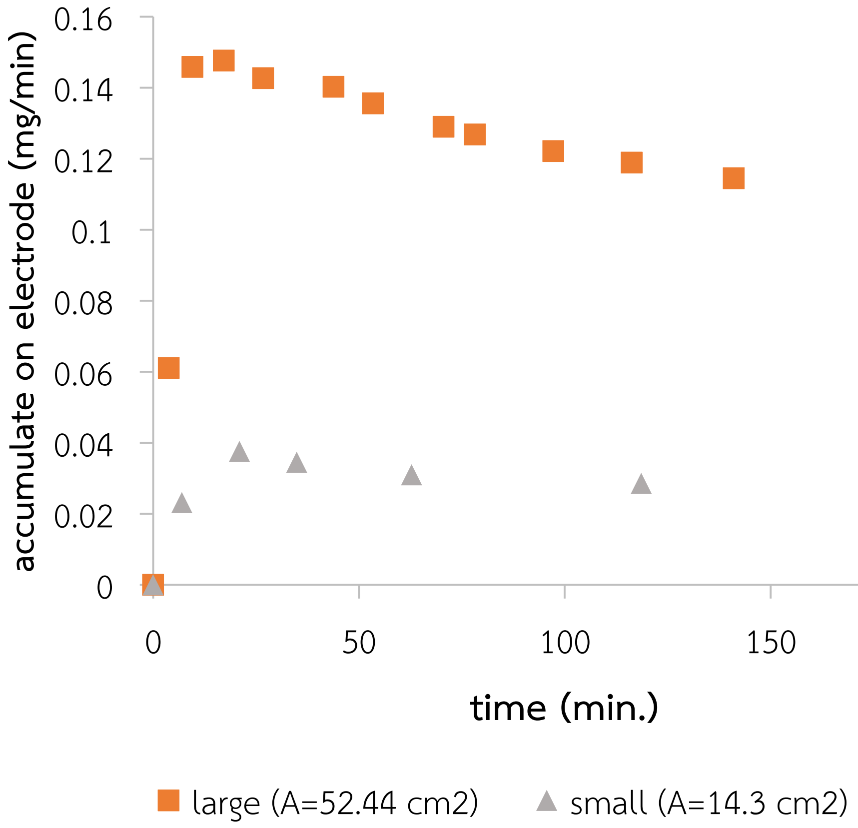


Figure 4.9 The amount of chloride ions accumulate on graphite against time in different size of electrode

However, when fixed residence time, the amount of ions per electrosorption area between large and small electrode that shown in Figure 4.10 were nearby at time t.

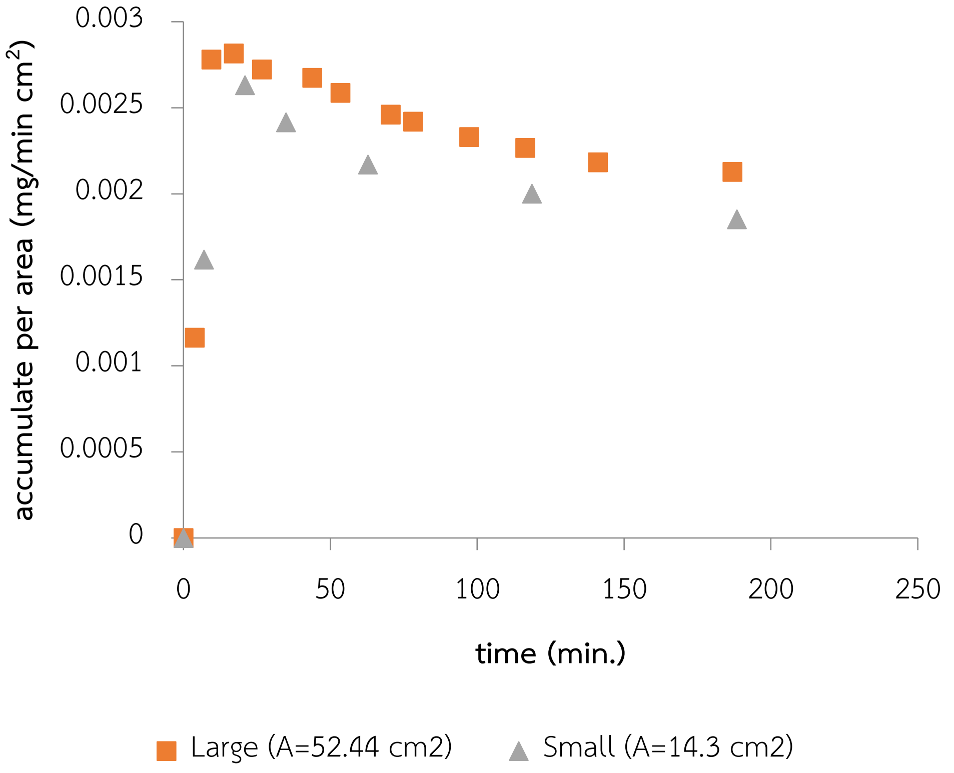


Figure 4.10 The accumulation rate of chloride ions on graphite per area in different size of electrode

Thus, the desalinated efficiency were little different although the electrosorption area of large electrode was 3.7 times of small electrode. It signify slightly influence of electrode size to desalinated efficiency as seen in Figure 4.11.

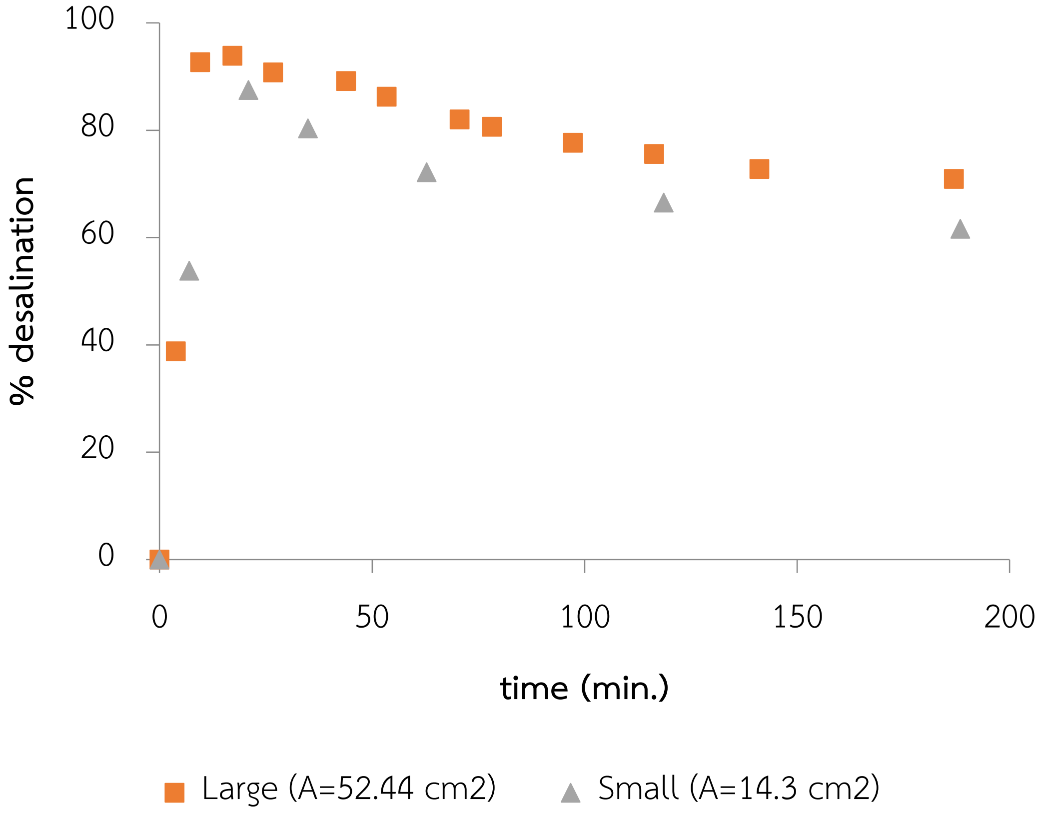


Figure 4.11 The percentage of desalination at time t which compared different size of electrode

In this case, there were as same specific surface area of graphite and equal electric field. As mentioned in influence of electrode, it was necessary for improve surface porosity of graphite rather than sized dimension.

To sum up, the larger electrode size was advantageous for faster flow rate. There were less waste of time and get more quantities of desalinated water at time t. For instance in the range of 60 minute, large electrode can produce 47.2 milliliters of desalinated water while small electrode produced 12.9 milliliters.

4.7 Influence of concentration

The conditions were fixed as specifying,

1. Graphite were used as cathode and anode (or called charged electrodes).
2. Residence time was fixed at 300 seconds
3. Applied voltage was 1.9 volts.
4. There were 500-μm microchannel.

NaCl solution were varied the concentration as 20 ppm, 100 ppm, 500 ppm, and 5000 ppm.

Figure 4.12 showed the desalinated efficiency. The desalination were decreased when initial salt concentration increased.

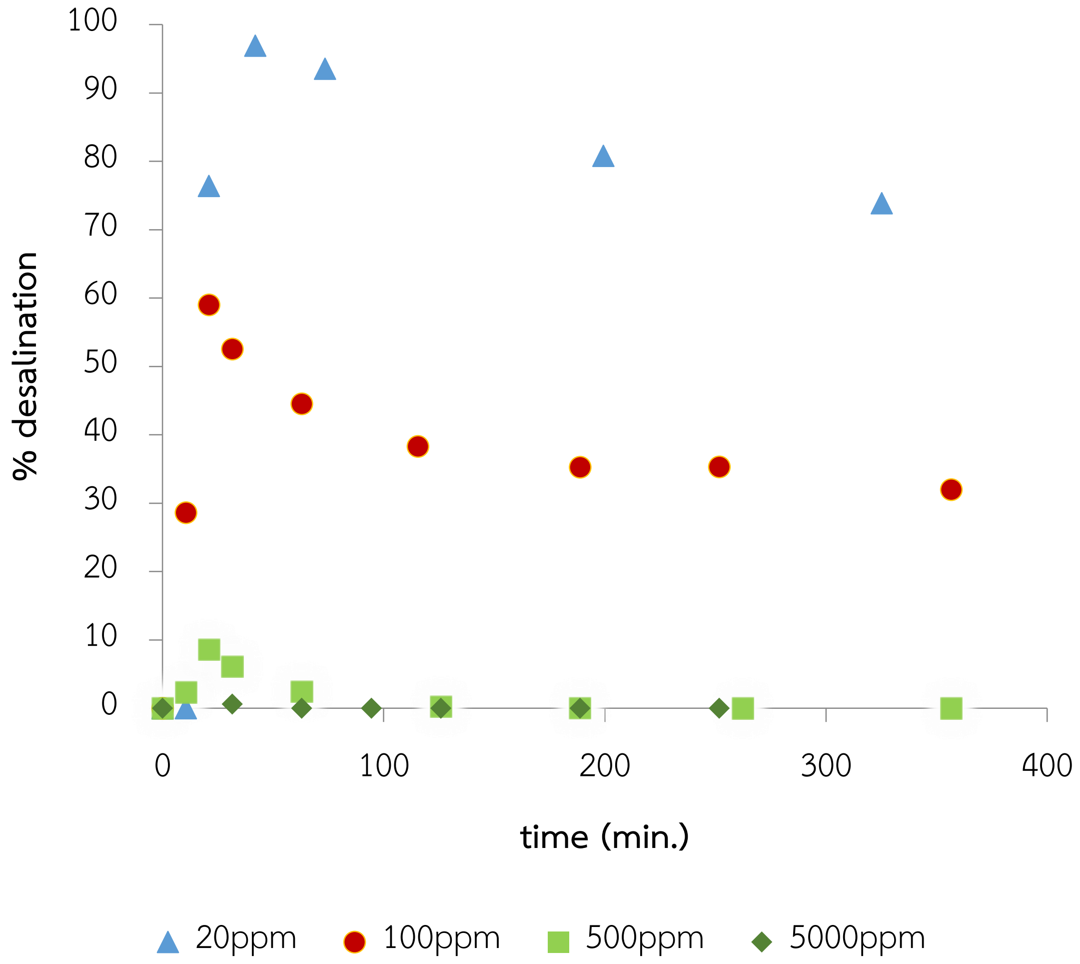


Figure 4.12 The percentage of desalination at different salt concentration with respect to the time of the experiment

When initial feed was 20 ppm NaCl solution, the salt removal was approximately 97% to 72% within 6 hours of operation. For 100 ppm NaCl solution of initial feed, the desalination was 59% to 32% decreased. While 500 ppm NaCl solution, the salt removal was 9% to 2.5% within 63 minutes of operation and nevermore desalinated beyond 63 minute. While 5000 ppm NaCl, it was hardly desalinated in this system.

When initial concentration were increased, representative the increasing of electrolyte concentration. While fixed gap and volume of channel, then the length for diffusion were as same. Figure 4.13 presented difference in initial salt concentration it was also difference in slope of graph.

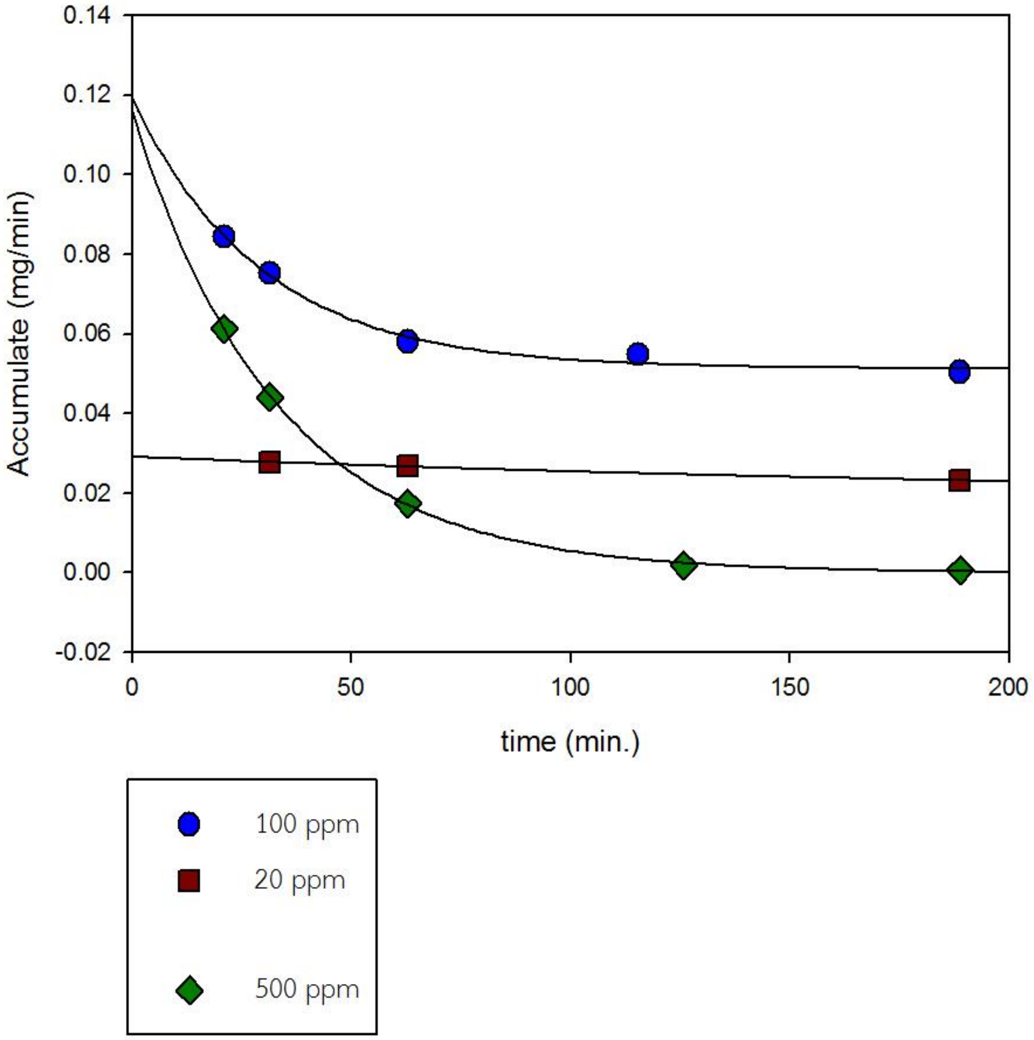


Figure 4.13 The amount of chloride ions accumulate on graphite against time in different initial NaCl concentration

The increasing of initial concentration caused even more accumulation on graphite electrode and more steep of accumulation rate respect to time.

From Table 4-6, there were the form of exponential decay. The slope for 20 ppm, 100 ppm, and 500 ppm were equal to 0.0112, 0.0680, 0.1159, respectively.

Table 4-6 The equation calculated from experimental data when varied concentration

Concentration (ppm)	**Accumulation equation (t= time, unit minutes)**	**Total electrosorption on electrode (mg)**
20	0.0179 + 0.0112exp(-0.0040t)	27.4284
100	0.0512 + 0.0680exp(-0.0339t)	40.9065
500	(-6.8069×10^{-5}) + 0.1159exp(-0.0304t)	1.9633

These evidence high concentration, it also high slope. Corresponding with Fick’s first law of diffusion as follow,

$$J^{*}_{Ay} = -D_{AB}\frac{dC_A}{dy}$$

Where J^{*}_{Ay} = rate of diffusion (or flux) of chloride ions in y-direction

D_{AB} = coefficient of diffusion

dC_A = concentration gradient

dy = position gradient

The accessibility of ions through graphite were faster due to higher concentration gradient. The diffusion were accumulated. Rate of diffusion was decreased until nearby saturated electrode.

When electrode were saturated, the desalinated efficiency turn to be zero. Because bulk concentration and concentration at electrode were equal. The diffusion were not appeared due to no driving force. Then, there were nevermore desalination.

In this part, graphite were used as electrodes. It obviously seen from Table 4-6, total ions attract on electrode were not equal when changed initial feed concentration to channel. To conclude, there were not only adsorption in the system. The electrosorption capacity were unequal because it happened compression in electrical double layer thickness. [15]

4.8 Surface chemistry

To calculate surface coverage of chloride ions on graphite electrode for improve the performance of capacitive deionization in microchannel.

The assumption was based on spherical sodium ions and also chloride ions. The area of spherical ion can calculated by

$$A_{ion} = \pi \times r^2$$

Hydrated radius [Z. Chen et al., 2015] → $Cl^{-}_{\text{hydrated radius}} = 3.31\ \dot{A}$,

Calculating, $A_{Cl^-} = 1.5205 \times 10^{-19}\ m^2$

Then,

The area for one chloride ion was approximately $1.5205 \times 10^{-19}\ m^2$.

Determining the electrosorption area,

The BET specific surface area of graphite considering by N_2 physisorption was equal to 13.519 m^2/g

Weight of graphite = 1.1366 g.

Then, the area for electrosorption $= 1.1366 \times \frac{13.519}{2}$

$= 7.6828\ m^2$

Assign monolayer adsorption,

If adsorb like monolayer on electrode, the total amount of chloride ions on graphite is equal to

$$\frac{7.6828}{1.5205E-19} = 5.053*10^{19} \text{ molecule}$$

Convert molecule to mole by divided 6.02×10^{23}

Then, the total amount of Cl^- on graphite = 0.0000839 mole

Experimental data,

Graphite were used as charged electrode and applied potential at 1.9 volts. The operating condition is 300 second of residence time, 500 micron of gap between electrodes. As seen in Figure 4.14,

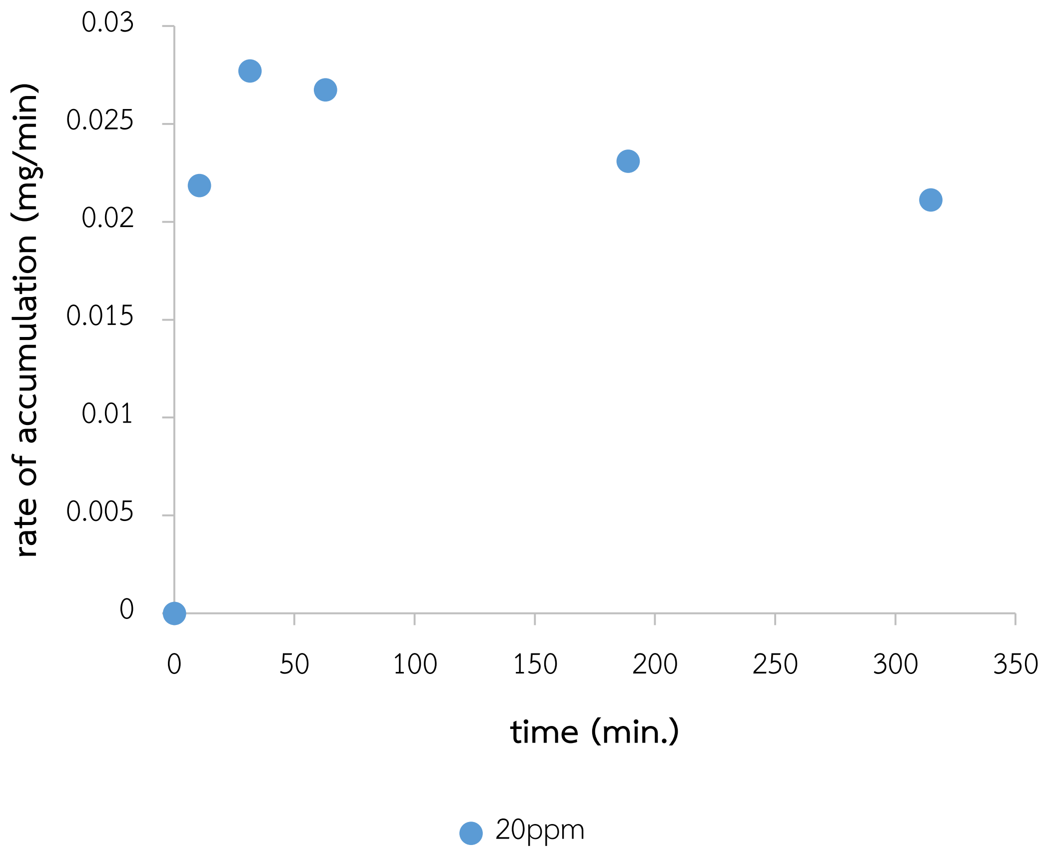


Figure 4.14 The amount of chloride ions accumulate on graphite against time by 20 ppm initial NaCl concentration

The accumulation equation related with time for 20 ppm NaCl concentration was exponential decay equation as following. (Note: R^2 = 0.9994)

$$E = 0.0179 + 0.0112\exp(-0.0040t)$$

Where E = rate of accumulation, mg/min

t = time, min

Integrate above equation from t_0 = 31.47 min. to t_f = 1410 min to get total electrosorption on electrode

$$\int_{31.47}^{1410} 0.0179 + 0.0112\exp(-0.0040t) \quad = \quad 27.4284$$

The total electrosorption on electrode = 27.4284 milligrams

Converted from mass to mole,

The molecular weight of chloride ion that is 35.45 g/mol

Then,

the total electrosorption on electrode was equal to 7.7371×10^{-4} mole

As above-mentioned, the calculation of surface coverage by chloride ions on electrode was 8.3932×10^{-5} mole.

Therefore, the result from experiment was compared with amount of ions by surface coverage. It has been argued that there were significant difference, this can cause several layers possible. Because chloride ions from experimental result was greater than chloride ions on surface coverage.

It has been found the performance of electrosorption that are physical adsorption.

4.9 Cycle

As shown in Figure 4.15, the experiment of each cycle applied voltages for 2 hours and discharged by short-circuit for 2 hours

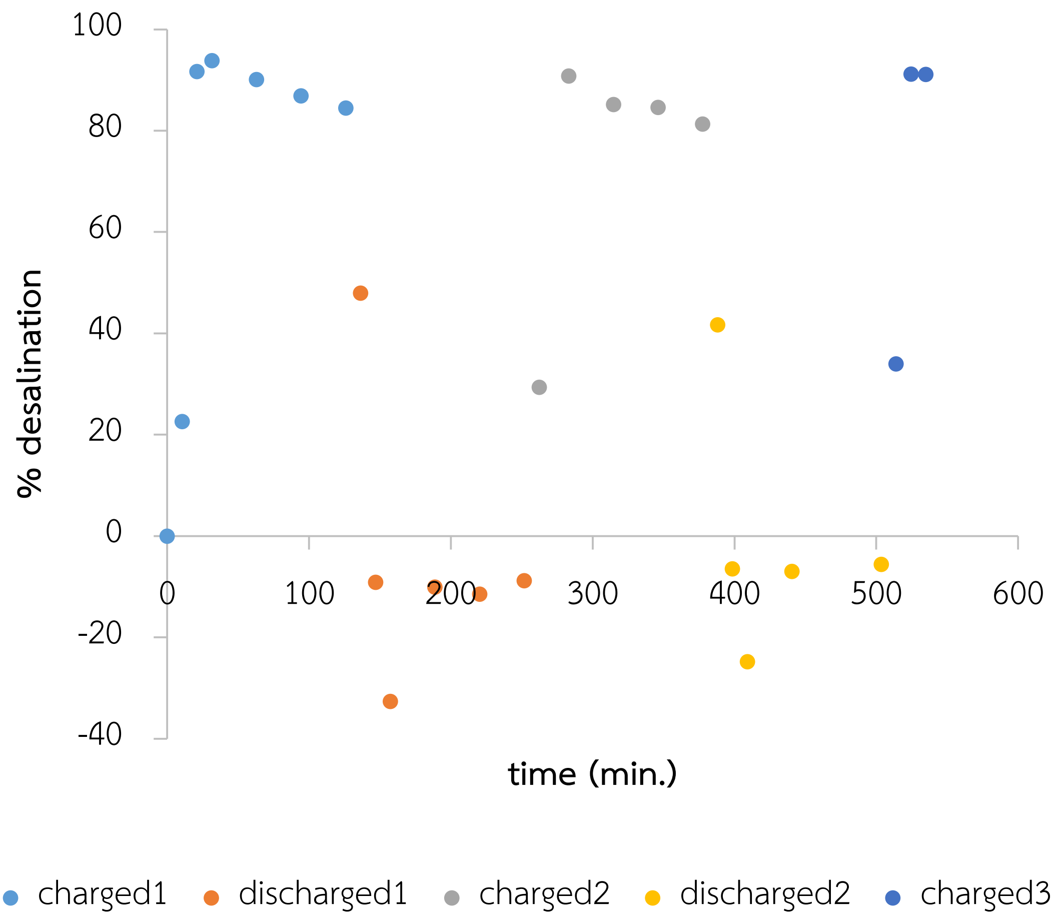


Figure 4.15 Charged-discharged cycle

Each cycle has same trend in desalination. When no external electric field, there were suddenly turn to be negative percentaged desalination. Ions were removed by flushing and it obviously seen the output solution turn into closely initial feed concentration when time elapsed. For discussion, ions were immediately released from electrode to bulk solution. It can reveal that no permanent bonding in performance of capacitive deionization. It was temporarily immobilized when formed electrical double layer inside the charged pores.

It has been confirmed that electrosorption of capacitive deionization in microchannel include physical adsorption and electric force.

Furthermore, it implied that graphite were good reproductively because there were nearby pure form when ion desorption and get same pattern in each cycle of desalination.

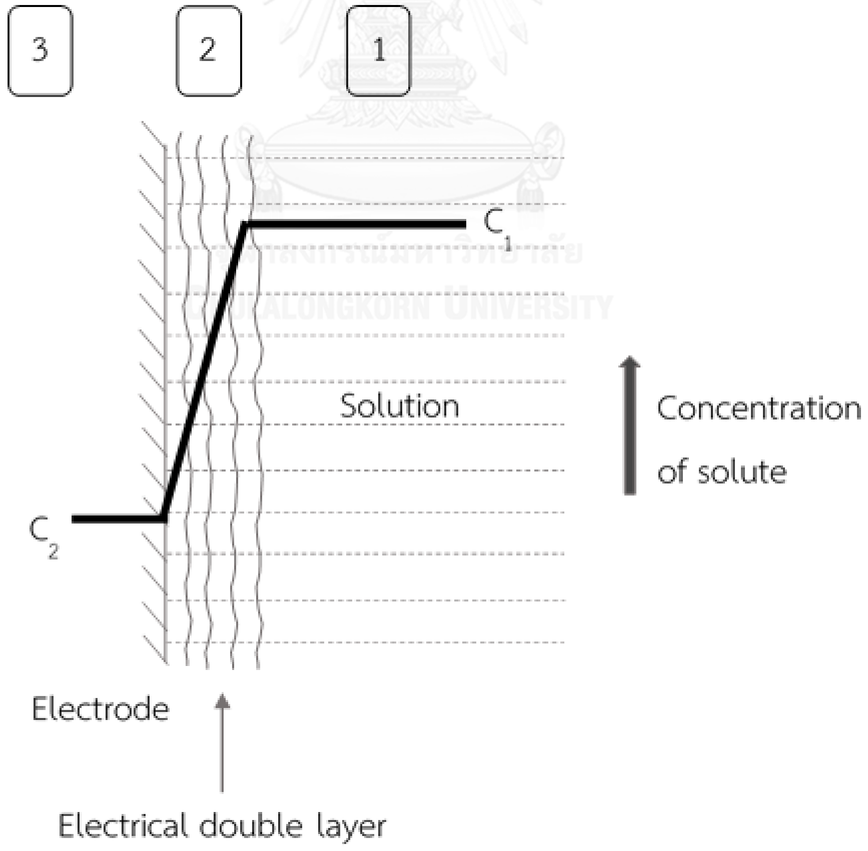
CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Summary of the results

5.1.1 Pattern of desalination by capacitive deionization in microchannel

The behavior of desalination by capacitive deionization can divided into 3 parts,



1) At bulk solution, electric force attracted counter ions from bulk solution to the electrodes.
2) At electrical double layer, the driving force is concentration gradient (dC_A/dy) and attracting counter ions by electric force.
3) At electrode, the ions were stored at electrode by electric force.

The operation was unsteady state due to accumulation at time t in the system that was continuous process. All results as data and graph were analyzed from the experiment. In concern with adsorption, the performance depends on fluid-solid equilibria and on mass-transfer rates. The several figure as shown in results, it indicated ions occupied in the unoccupied site that was called electrical double layer. It extract ions from the bulk solution. Electrical double layer depends on potential of the system. When there were equilibrium at electrode or nomore unoccupied site, the salt removal were not capable. Then, regeneration was necessary.

5.1.2 Ions adsorption and desorption

When applied potential, the ions was adsorbed in the electrical double layer both in electrode and near surface.

The desalinated efficiency significantly increased when

- Increasing applied voltage
- Increasing residence time
- Decreasing gap between anode and cathode (charged electrode)
- Increasing adsorption capacities

Because electrical double layer occurred when applied potential, then electrical double layer disappeared when stop electric and ions that previous adsorbed were released into the bulk solution. This system can simple regenerate and not complex.

5.1.3 Inference of electrode

In this study, the activated graphite enhanced the desalinated efficiency when compared with non-activated graphite because there were more specific surface area and pore volume. The specific surface area of activated graphite was 2.1 times of non-activated graphite. Activated graphite as electrode can use for 4 hour to produce 95 – 99 % of salt removal while non-activated graphite can produce the same quality just for 1 hour. It progress longer of operation before afresh electrode.

Furthermore, if functional group of carbon has changed, it would affect to salt removal efficiency.

Increasing size of electrode area caused higher in amount of ions related with time. When large electrodes were used, the flow rate of the solution were faster and quantities were higher.

5.1.4 Limiting of the system

1. Water splitting or electrolysis reaction was prevented by operate not over 2.06 volts.

2. This study minimize the gap to 500-μm microchannel. If gap is shorter than 500--μm, the operation would occur short circuit of the system.

3. It was not suitable for high salinity sources.

5.2 Conclusion

Desalination of NaCl solution by capacitive deionization in microchannel were investigated in the study. It has been clearly evidenced that capacitive deionization in microchannel improves desalination efficiency. The impact of the input electrical potential implied that the electrical double layer was occurred to improve desalinated efficiency. The salt adsorption capacity were enhanced when increasing surface area and mesoporosity of graphite. Additionally, the functional group of carbon has affected on desalination. The carbon porosity and chemical surface charge was related to salt removal in capacitive deionization cell. Capacitive deionization method used the combination of physical adsorption and electrostatic force.

5.3 Problem of the study and Recommendations

In the study, the microchannel device have to regularly assemble with circumspect. Be cautious short circuit if it too tight. And if it loose, it could be leak.

For used with higher salt concentrations and better performance, the electrode would develop to be maximize in surface porosity. Considering, the electrode have to flat and smooth surface to prevent leakage. Alternatively, the desalination could enhance when connect multiple devices with series in electricity.

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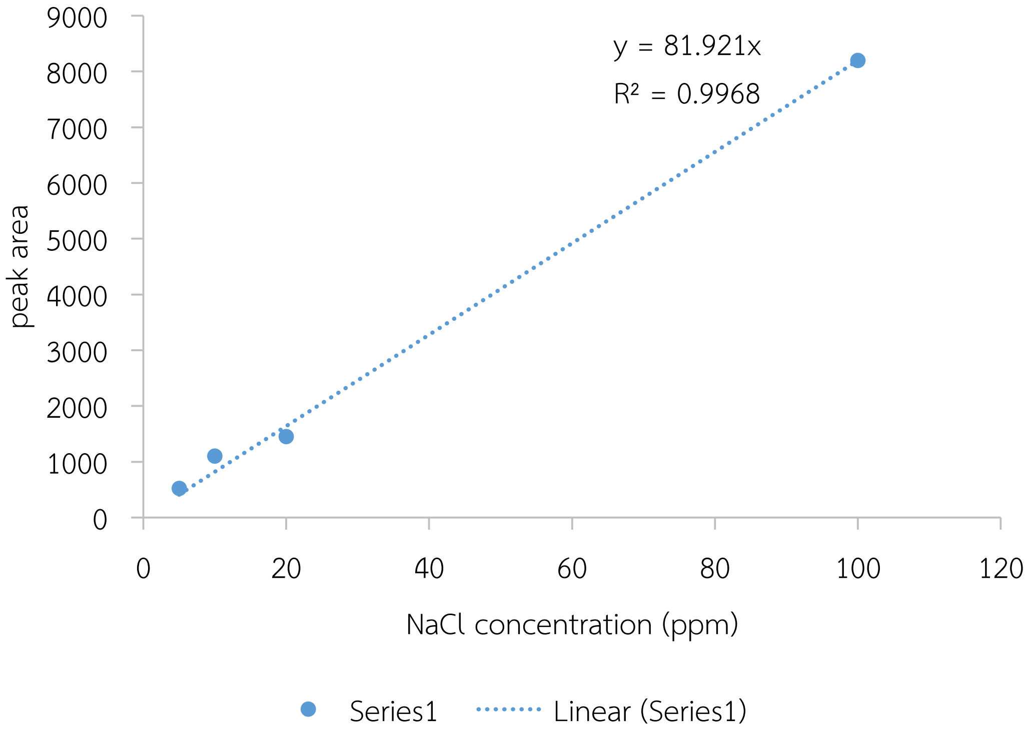
APPENDIX

APPENDIX A

Calibration curve of chloride ions (analyzed by ion chromatography)



APPENDIX B

Table of standard electrode potentials in Aqueous Solution at 25°C

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04
$K^+(aq) + e^- \rightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	-2.76
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	-0.04
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.16
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_3^-(aq) + 2OH^-(aq)$	0.17
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.22
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$ClO_3^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_2^-(aq) + 2OH^-(aq)$	0.35

$IO^-(aq) + H_2O(l) + 2e^- \rightarrow I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightarrow Cu(s)$	0.52
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightarrow ClO^-(aq) + 2OH^-(aq)$	0.59
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.44
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.82
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	2.01
$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87

Reference : http://hyperphysics.phy-astr.gsu.edu/hbase/tables/electpot.html

APPENDIX C

Reynolds number, Prandtl number, and Peclet number in the study

- **Reynolds number**

$$Re = \frac{\rho l_0 v_0}{\mu}$$

Where as

ρ = density of the fluid

l_0 = characteristic length = hydraulic diameter

v_0 = characteristic velocity

μ = dynamic viscosity

If 500-μm microchannel and volumetric flow rate was 8.6 ml/h, then characteristic velocity = 1.19×10^{-4} m/s

$$\text{Reynolds number} = \frac{2.17 \frac{kg}{m^3} \times \left(9.876\times10^{-4}\ m.\right) \times \left(1.19 \times 10^{-4}\ \frac{m}{s}\right)}{0.00193 \frac{kg}{m\ s}}$$

$$= 1.33 \times 10^{-4}$$

- **Prandtl number**

$$Pr = \frac{\hat{C}_p \mu}{k}$$

Where as

C_p = specific heat capacity

μ = dynamic viscosity

k = thermal conductivity

Then, $$\mathrm{Pr} = \frac{(0.871 \times 10^{3}\ \frac{\mathrm{J}}{\mathrm{kg\ C}})\ (0.00193\ \frac{\mathrm{kg}}{\mathrm{m\ s}})}{6.15\ \frac{\mathrm{W}}{\mathrm{m\ C}}}$$

$$\mathrm{Pr} = 0.27$$

- **Peclet number**

Peclet number = (Reynolds number) (Prandtl number)

= (Re) (Pr)

= $(1.33 \times 10^{-4})\ (0.27)$

= 3.58×10^{-5}

Pe << 1,

Total flux = Molecular flux

(No convective flux)

LIST OF PUBLICATION

1. Onwanya Prakobsuk and Varong Pavarajarn. “DESALINATION BY CAPACITIVE DEIONIZATION IN MICROCHANNEL”. Proceedings of the Pure and Applied Chemistry International Conference 2016, Bangkok, Thailand, February 9-11, 2016.

VITA

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