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Effects of operating parameters on the removal performance of electrodialysis for treating wastewater containing cadmium

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ABSTRACT

To evaluate the feasibility of electrodialysis for cadmium removal from wastewater containing cadmium in high concentration, the effects of initial concentrations of dilute and concentrate, flow rate and applied voltage on the removal of cadmium were experimentally investigated with batch operation mode. The limiting current density (LCD) linearly increased with the cadmium concentration and the flow rate. The elapsed time to reach 0.1 mg Cd/l was directly proportional to initial concentration of dilute, and the concentration of concentrate insignificantly affected the removal rate. Increase of the flow rate gave a positive effect on the removal rate, but the effect became unimportant at flow rate greater than 2.4 l/min. Volume of dilute was continuously decreased by electro-osmotic water transfer, whereas the volume of concentrate was increased. Removal rate was increased with the applied voltage. The increment of the removal rate, however, was decreased as the applied voltage increases. From the operation of the electrodialysis module used in this study, the flow rate of 2.4 l/min and the applied voltage corresponding to the 80~90% of LCD are recommended as a proper operating condition for cadmium removal from highly concentrated cadmium solutions.

Keywords: Electrodialysis; Cadmium; Ion-exchange membrane; Wastewater treatment; Heavy metal; Limiting current density

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1. Introduction

The amount of pollutants and their characteristic are increasing due to various causes such as industrial development, increase of population, urbanization process, etc. Especially, the contamination of water by heavy metals is one of major environmental problems in the world. Heavy metals are not only toxic to aquatic flora and fauna even in low concentrations, but also capable of being assimilated, accumulated and concentrated by organisms. The discharge of industrial wastewaters contaminated by heavy metals to river or sewage system, therefore, should be strictly regulated to reduce environmental impact, and the treatment of the wastewaters has been the center of attention. The various treatment methods to purify the wastewaters contaminated by heavy metals include precipitation, solvent extraction, oxidation, reduction, adsorption, reverse osmosis, evaporation, filtration, air stripping, cementation, ion exchange, electrodialysis, biosorption, etc [1–4].

Cadmium is one of toxic heavy metals and its major sources released into environment are the wastewater or the sludge from electroplating, nickel-cadmium battery production, smelting, photoelectric cells, alloy manufacturing, phosphate fertilizers, mining and refining processes [5]. Compared to other heavy metals, cadmium and cadmium compounds are relatively water-soluble, therefore more mobile in soil and generally more bio-available. This characteristic of cadmium results in

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bio-accumulation of an element which is toxic to plant and animal life. Cadmium accumulated in the human body can cause erythrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity. Cadmium ions have little tendency to hydrolyze at $pH \leq 8$, but all cadmium ions exist as the hydroxo-complex at $pH > 11$. The drinking water guideline recommended by World Health Organization (WHO) and American Water Works Association (AWWA) is 0.005 mg Cd/l [2,5,6].

Various techniques, such as chemical precipitation, adsorption, ion exchange, electrodialysis, cementation, electrodeionization, biosorption, membrane filtration, etc., have been used to remove cadmium ions from wastewaters [1–11].

Electrodialysis is one of membrane separation techniques consisted in the selective separation of ionic species in a solution by the transport through ion-exchange membranes using mainly an electric field. Compared with other techniques, electrodialysis has many advantages such as relatively small area and space for installation, easy installation and operation, stable operation even at the unexpected change of pollutant composition, very small sludge production, no need of additional chemicals, no phase change during operation, lower energy consumption than that of reverse osmosis, etc [12]. As one of drawbacks, it is reported that electrodialysis is not economical for especially treating dilute solution because of its high electrical resistance and the development of concentration polarization phenomena [13]. Conventional electrodialysis is used today in a large variety of applications such as water desalination, elimination of toxic compounds from industrial effluents, removal of certain electrolytes from food and chemical products, production of ultra pure water, recovery of metal or acid from steel industries, etc [14,15].

In spite of the technical advantages of electrodialysis, the researches to apply electrodialysis for treating the wastewaters contaminated by cadmium in a high concentration are very limited. The aim of this study is to experimentally investigate the feasibility of electrodialysis system for treating the synthetic wastewater containing cadmium in high concentration. The feasibility is evaluated by measuring of limiting current density (LCD) and the effects of the operating parameters such as cadmium concentration, operating voltage and flow rate on removal efficiency.

2. Experimental

2.1. Electrodialysis system

As depicted in Fig. 1, an electrodialysis is the process for the transport of ionic species in a cell arrangement, so-called membrane stack, consisted of cation- and anion-exchange membranes in alternating series forming an array of individual cells between two electrodes. A cell means the room between one cation-membrane and one anion-exchange membrane. An electrical potential difference formed between electrodes makes the cations migrate towards the negatively charged cathode, whereas the anions migrate to the positively charged anode. The cations can easily permeate the cation-exchange membrane, but cannot penetrate the anion-exchange membrane. On the contrary, the anions can permeate only the anion-exchange membrane. The cations and the anions are consequently concentrated in alternating compartments formed between cation- and anion-exchange membranes, and the ions in the other compartments are almost removed [14,15].

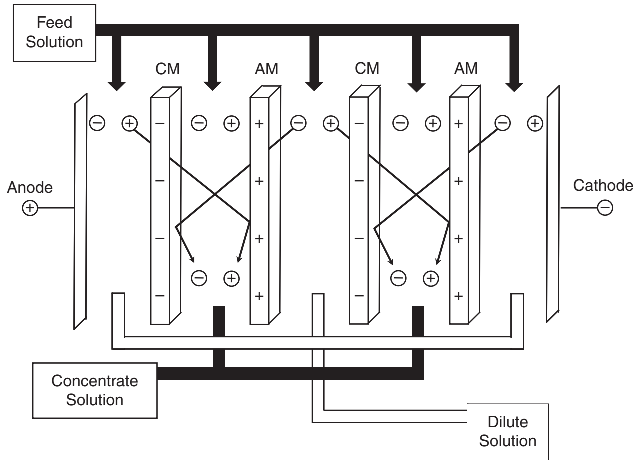

Fig. 1. Principle of electrodialysis.

Two types of operation mode, batch and continuous operations, are possible. Batch operation is generally used to achieve a high degree dilution or concentration from a feed solution. In continuous operation, multiple passes through a series of membrane stacks are needed for high purification of a feed solution. Ionic permeability through ion-exchange membranes in electrodialysis process depends on the solution characteristics and the operating parameters such as characteristic of ionic species, ionic concentration in a feed, solution pH, flow rate, current density, ionic selectivity of ion-exchange membrane for ionic species in a solution, etc. The suitable properties of ion-exchange membrane used to electrodialysis include high perm-selectivity, low electrical resistance, enough mechanical strength, high chemical stability, etc.

The solution to be concentrated during operation is referred to as ‘concentrate’, and the solution to be diluted is referred to as ‘dilute’ in this study. Fig. 2 shows the schematic diagram of electrodialysis apparatus used in

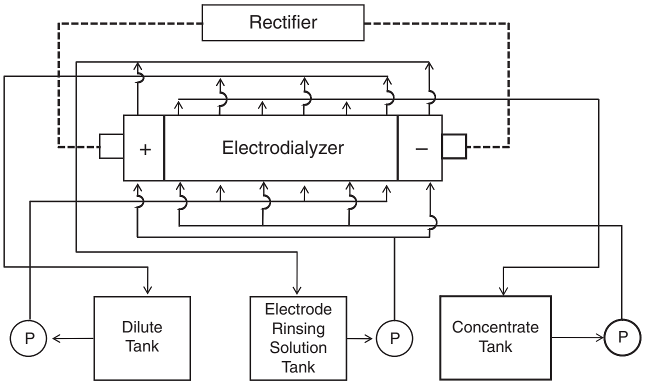

Fig. 2. Schematic diagram of electrodialysis apparatus.

this study. The apparatus consists of a membrane stack, a dilute tank, a concentrate tank, an electrode rinsing solution tank, a rectifier for the supply of constant voltage or current, and three magnetic pumps for circulating each of three solutions. Each of three solution tanks is all 6 l capacity. CH–0 model of AGC Engineering Co. Ltd., Japan is used as the membrane stack. The stack consists of 10 cell pairs. One cell pair includes one sheet of cation-exchange membrane, one sheet of anion-exchange, and 2 spacers for supporting each membrane and well distributing feed solutions. Table 1 shows the specifications of ion-exchange membranes and membrane stack.

2.2. Experimental method

Solutions of various cadmium concentrations were prepared with high purity $Cd(NO_3)_2 \cdot 4H_2O$ of Junsei Chemical Co. and de-ionized water as synthetic wastewaters. The prepared concentrations were 100, 200 and 300 mg Cd/l, because industrial wastewater highly contaminated by heavy metals generally expresses the cadmium concentration of 30~300 mg Cd/l. 4 wt.% Na_2SO_4 aqueous solution was used as electrode rinsing solution.

Every experiment was carried out with batch operation mode in this study. Before the start of operation, the prepared wastewater was filled in the dilute tank as an initial dilute, and the solution with a specific cadmium concentration was also fed to concentrate tank as an initial concentrate. During the operation, the dilute, the concentrate and the electrode rinsing solution were continuously circulated through the path of tank-membrane stack-tank. All operations were conducted with constant voltage mode by the rectifier and at room temperature.

The effects of three operating variables on the cadmium removal efficiency in dilute were experimented. They were the concentration of wastewater, the flow rate of dilute and the applied voltage. Before starting these experiments, limiting current densities (LCDs) were measured at different operating conditions in order to determine allowable operation ranges for each of the operating variables. The experiments for the effects of flow rate and wastewater concentration were conducted with the constant applied voltage, which was 80% of the cell voltage corresponding to LCD. Except the experiments for the effect of the concentration of concentrate, the same concentrations of dilute and concentrate were used to every experiment. The operating ranges were 0.8~3.2 l/min for the flow rate, and 70~90% of the cell voltage corresponding to LCD for the applied voltage. Initial volumes of dilute, concentrate and electrode rinsing solution were 5, 5 and 4 l, respectively. During the operations, sampling time and volume were 10 min and 3 ml. Cadmium concentrations were measured by Model Spectraa-55B Atomic Absorption Spectrometer of Varian Inc.

3. Results and discussion

3.1. LCD

The concentration polarization refers to the depletion and accumulation of ions at membrane surfaces in electrodialysis. If the concentration polarization is

Table 1
Specifications of ion-exchange membranes and membrane stack

	Cation-exchange membrane	Anion-exchange membrane
Model name	Selemion CMV	Selemion AMV
Type of membrane	Strong acidic cation permeable membrane	Strong basic anion permeable membrane
Thickness (μm)	130	130
Counter-ion	Na^+	Cl^-
Effective area of membrane	$0.021\ m^2$/sheet	
Size of membrane	160 × 280 mm	
Space between membranes	0.75 mm	
No. of cell pairs	10	

occurred, ionic concentration at membrane surface is decreased in dilute cells, and is increased in concentrate cells. The concentration polarization, therefore, can cause several problems such as the precipitation of salts by the excess of their solubility limits in concentrate cells and the depletion of salts in dilute cells. The precipitation of salts results in the increase of electrical resistance and the damage of membranes by solid deposition. The depletion of salts gives rise to the drastic increase of electrical resistance and the occurrence of water dissociation. The water dissociation makes pH value at the surface of anion-exchange membrane higher and at surface of cation-exchange membrane lower. These phenomena make pH value at the surface of anion-exchange membranes increase, bring about the precipitation of multivalent ions on the membranes, and damage the membranes. The maximum current density is reached when the salt concentrations at the surface of membranes become zero in dilute cells. The maximum current density is referred to as LCD. Electrodialyzer, therefore, should not be operated above LCD. Namely, LCD means the permissible limit of operating condition [14–16].

LCD can be experimentally determined by measuring the cell voltage (V)-current (I) relation of electrodialyzer and the overall resistance (V/I)-reciprocal current density (1/I) relation [17,18]. The operating parameters, such as flow rate, ionic concentration in a solution, a gap between membranes etc., affect LCD [16,19]. In this study, I-V relation was used to determine LCD, and ionic concentration in a solution and flow rate were selected as the operating parameters for determination of LCD.

The experiments for the effect of ionic concentration in a solution on LCD were conducted in the constant flow rate of 2.4 l/min. Three different initial concentrations of 100, 200 and 300 mg Cd/l for dilute and concentrate were experimented, and the initial concentrations of dilute and concentrate were same. Fig. 3 shows the V-I relations for each concentration, which were made from the measurement of cell voltage change for the current increment of 0.02 A at a time. The LCDs were graphically determined by finding the point that the two straight lines to represent the data before and after inflection point intersect. The measured LCDs for each of three concentrations were 0.586, 1.16, and 1.76 mA/cm^2, respectively. LCDs linearly increased with the cadmium concentration (Fig. 4). This phenomenon is resulted from the increased concentration gradient, i.e., driving force for mass transfer, in the diffusion boundary layers formed between bulk solution and ion-exchange membrane in cells, as influent ionic concentration increases.

The effects of flow rate on LCD were experimented with the constant initial cadmium concentration of 200 mg/l for both dilute and concentrate. The flow rates of 0.8, 1.6, 2.4 and 3.2 l/min were used in the experiments, and Fig. 5 shows the V-I relation for each of flow rates. Using the same way as the experiments for the effect of concentration, the measured values of LCDs corresponding to each flow rate were 0.571, 0.738, 1.16 and 1.38 mA/cm^2, respectively. The LCDs were proportional to the increase of flow rate (Fig. 6). Thickness of diffusion boundary layer decreases with the increase of flow rate. It gives rise to reduce ionic mass transfer resistance on the membrane surface [19].

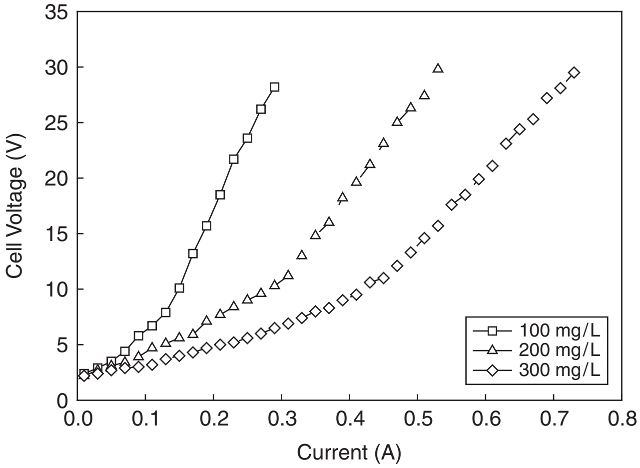

Fig. 3. V-I measurements at various cadmium concentrations.

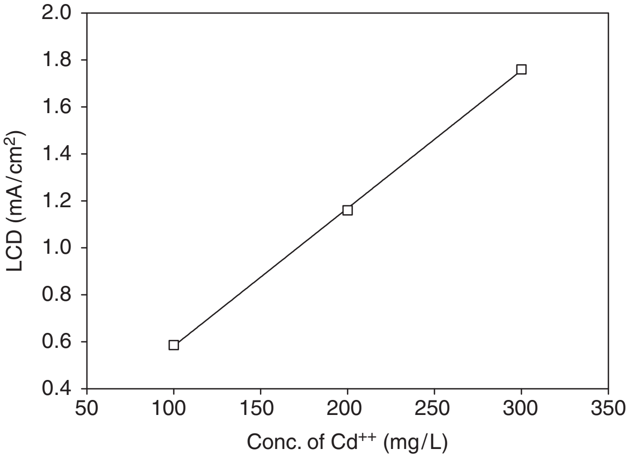

Fig. 4. Limiting current densities at various cadmium concentrations.

3.2. *Effect of cadmium concentration*

The experiments for the effect of cadmium concentration in dilute were conducted with the three different cadmium concentrations of dilute. Flow rate, applied voltage and initial concentration of concentrate were

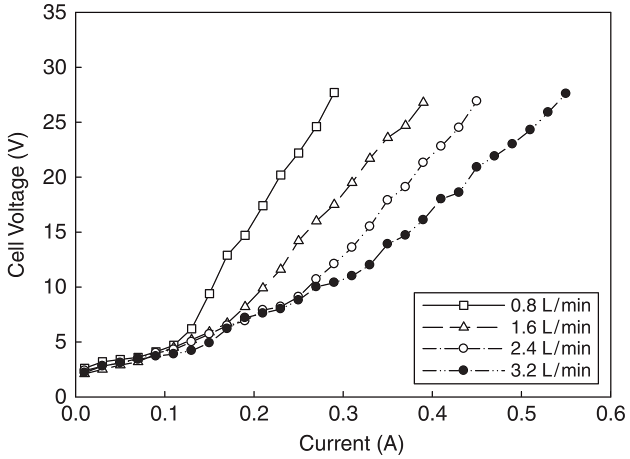

Fig. 5. V-I measurements at various flow rates.

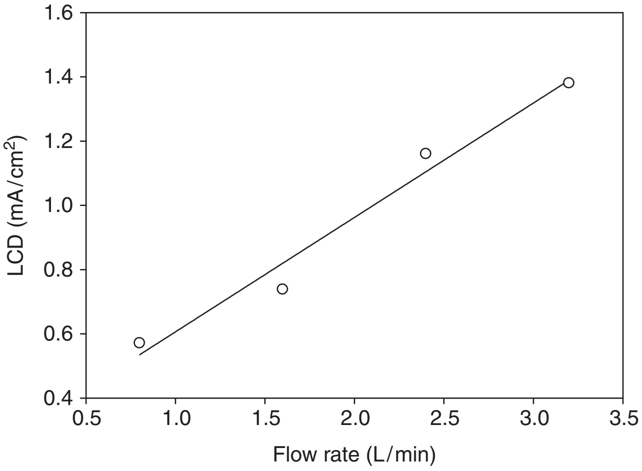

Fig. 6. Limiting current densities at various flow rates.

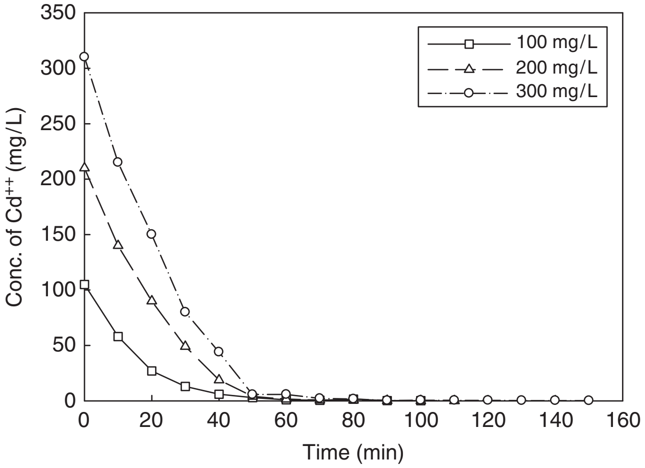

Fig. 7. Effect of dilute concentration on cadmium removal.

fixed with 2.4 l/min, 5.92 V, and 200 mg Cd/l, respectively. 5.92 V was equivalent to 80% of cell voltage corresponding to LCD at 2.4 l/min.

Fig. 7 shows the cadmium concentration change in dilute according to elapsed time of operation. Each operation was ended when the cadmium concentration of dilute reaches 0.1 mg Cd/l, which is referred to target concentration in this study. The target concentration is originated from water quality regulation for discharge of wastewater in Korea. Depending on the concentration of dilute, the elapsed times for achieving the target concentration were 90 min for 100 mg/l, 100 min for 200 mg/l and 150 min for 300 mg/l. The elapsed time was directly proportional to initial concentration of wastewater.

Effect of initial concentration of concentrate was experimented with the same operating condition as above except the dilute concentration of 200 mg/l. Initial concentrations of 100 and 300 mg/l were selected. Fig. 8 shows the cadmium concentration change in dilute according to elapsed time of operation. Slightly better removal efficiency in high initial concentration of concentrate was observed at the early stage of operation. This is resulted from the smoothness of electric current flow by high electrolyte concentration in both dilute and concentrate cells. Meanwhile, the concentration of concentrate became much higher than initial concentration in the latter part of operation, and the concentration of dilute became much lower than initial concentration. In this circumstance, the large concentration difference between dilute and concentrate can be acted as a resistance for the diffusive mass transfer of cadmium on the membrane surfaces in concentrate cells. The elapsed times to reach the target concentration were 120 min for 100 mg/l and 130 min for 300 mg/l. The small difference

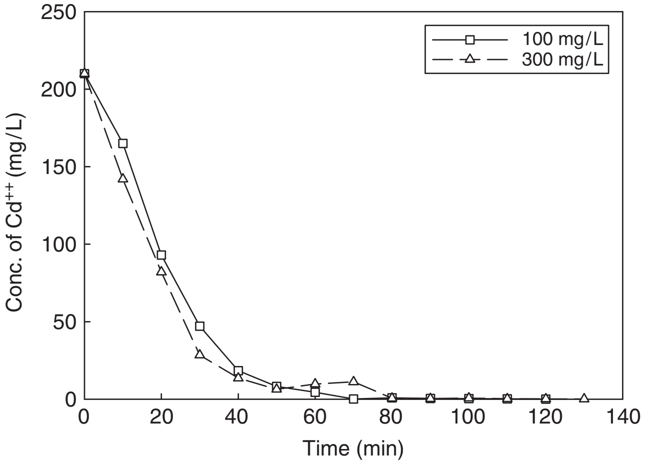

Fig. 8. Effect of concentrate concentration on cadmium removal from dilute.

of elapsed times, however, shows that the effect of the resistance for diffusive mass transfer by concentration difference is not serious in electrodialysis.

3.3. *Effect of flow rate*

Four different flow rates of 0.8, 1.6, 2.4 and 3.2 l/min were used to the experiments for the effect of flow rate. The operating condition except flow rate was fixed with 200 mg/l for initial concentrations of both dilute and concentrate and 5.92 V for applied voltage.

Fig. 9 shows the cadmium concentration change in dilute according to the change of flow rate. The elapsed times needed to reach the target concentration were 175 min for 0.8 l/min, 140 min for 1.6 l/min, 100 min for 2.4 l/min and 95 min for 3.2 l/min.

The thicknesses of diffusion boundary layers on the cation- and anion-exchange membrane surfaces in dilute and concentrate cells are inversely proportional to flow rate. The lessened layer decreases the resistance for mass transfer and improves mass transfer rate of cadmium ion through the layer. On this way, the elapsed time was consistently decreased according to increase of flow rate from 0.8 l/min to 2.4 l/min. The elapsed times for 2.4 and 3.2 l/min, however, did not show a noticeable difference. This phenomenon can be understood by the explanation that the decrease of mass transfer boundary layer thickness has a favorable effect on the removal rate of cadmium ion up to a limited flow rate but the decrease of residence time in cells offsets the effect of layer thickness shrinkage in higher flow rate.

Water transport through ion-exchange membranes is composed of two driving forces. The first is osmotic water transfer due to a chemical potential difference by an ionic concentration difference across the membrane, and the second is electro-osmotic water transfer due to hydrated ions transported through the membrane. Osmotic water transport is generally low in a membrane with a high fixed ion concentration. The electro-osmotic water transfer, therefore, acts as a main source of water transport in electrodialysis process [15].

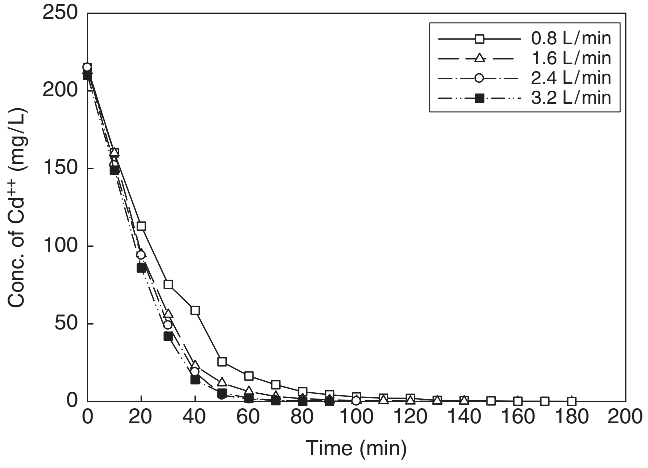

Fig. 9. Effect of flow rate on cadmium removal from dilute.

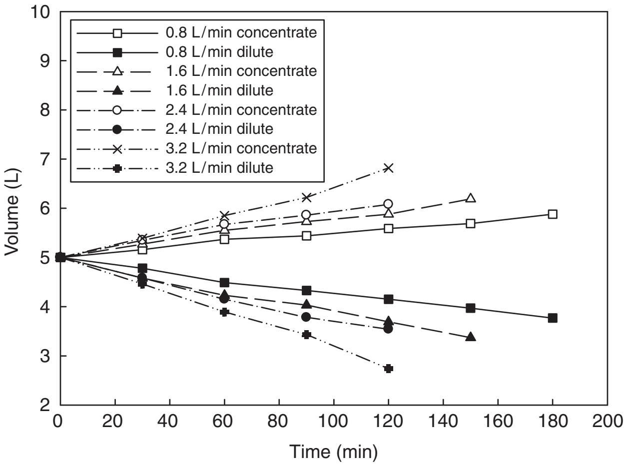

Fig. 10. Volume changes of dilute and concentrate in various flow rates during operation.

Fig. 10 expresses the volume changes of dilute and concentrate in various flow rates during operation. The volume of dilute was continuously decreased, whereas the volume of concentrate was increased. In addition, the rate of volume increase in concentrate tank was proportional to flow rate. This is equivalent to the increase of removal rate with flow rate. Considering the water transport, actual removal percentages of cadmium ion from dilute at 0.8, 1.6, 2.4 and 3.2 l/min after 120 min operation were 99.27, 99.94, 99.96 and 99.99%, respectively.

3.4. *Effect of applied voltage*

Experiments for the effect of applied voltage were carried out at the constant voltages of 70, 80 and 90% of the cell voltage corresponding to LCD at an operating condition. Initial concentrations of both dilute and concentrate and flow rate were 200 mg/l and 2.4 l/min.

Fig. 11 shows the cadmium concentration change in dilute according to the change of applied voltage. The elapsed times for reaching the target concentration were 175 min for 70%, 100 min for 80% and 90 min for 90%. Due to strength of electrical current as driving force for mass transfer, the higher applied voltage, the faster removal rate. The increment of removal rate, however, was blunted as the applied voltage increases. Considering removal rate, current efficiency and the problems possibly induced from the operation at near or over LCD such as a rapid decrease of current efficiency by

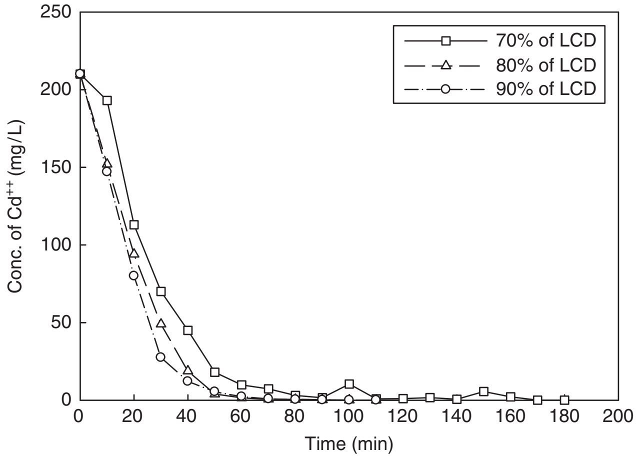

Fig. 11. Effect of applied voltage on cadmium removal from dilute.

water dissociation, precipitation of metal hydroxide, membrane fouling and voltage drop, the applied voltage equivalent to 80~90% of cell voltage corresponding to LCD is recommended for an efficient and safe operation of electrodialysis.

4. Conclusions

A laboratory study was conducted to investigate the feasibility of electrodialysis system for treating the synthetic wastewater containing cadmium in high concentration. The feasibility is evaluated by measuring of the effects of the operating parameters such as cadmium concentration, operating voltage and flow rate on removal efficiency. First of all, LCDs were measured in various operating conditions consisted of cadmium concentration and flow rate to determine a proper range for applied voltage.

The elapsed time to reach the target concentration was linearly proportional to initial concentration of wastewater in the initial concentration range of 100~300 mg Cd/l. The effect of the concentration of concentrate on removal rate was insignificant, because the effect of the resistance for diffusive mass transfer by concentration difference is not serious in electrodialysis.

Removal rate in dilute was increased with flow rate up to 2.4 l/min in the flow rate range of 0.8~3.2 l/min due to the favorable effect on removal rate of cadmium ion by the decrease of mass transfer boundary layer thickness. The insignificant increase of removal rate in higher than 2.4 l/min was resulted from the decrease of residence time in cells. By electro-osmotic water transfer as a main source of water transport through ion-exchange membranes, the volume of dilute was continuously decreased, whereas the volume of concentrate was increased. The rate of volume increase in concentrate tank was proportional to flow rate.

Removal rate was increased with the applied voltage due to strength of electrical current as driving force for mass transfer. The increment of removal rate, however, was blunted as the applied voltage increases.

From the operation of the electrodialysis module used in this study, the flow rate of 2.4 l/min and the applied voltage corresponding to the 80~90% of LCD are recommended as a proper operating condition for cadmium removal from highly concentrated cadmium solutions.

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