

## URANIUM SEPARATION FROM WASTEWATER BY ELECTRODIALYSIS

\*<sup>1</sup>A. Zaheri, <sup>2</sup>A. Moheb, <sup>3</sup>A. R. Keshtkar, <sup>1</sup>A. S. Shirani

<sup>1</sup>Department of Nuclear Engineering, Shahid Beheshti University, Tehran, Iran

<sup>2</sup>Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran

<sup>3</sup>Nuclear Fuel Cycle School, Nuclear Science and Technology Research Institute, Tehran, Iran

Received 4 March 2010; revised 24 July 2010; accepted 13 October 2010

### ABSTRACT

Uranium is a toxic and radioactive heavy metal found in nuclear effluents and should be treated by considering economic and environmental aspects. In this study, uranium separation from synthetic effluents by electrodialysis was investigated. Taguchi method was used to plan a minimum number of experiments. An orthogonal L<sub>27</sub> array (three factors in three levels) was employed to evaluate the effects of flow rate (5, 15 and 30 mL/min), voltage (10, 20 and 30 V) and feed concentration (200, 500 and 1000 mg/L) on performance of uranium separation. ANOVA method was applied to evaluate the relative effect of each factor. Results showed that increasing voltage and decreasing flow rate improves performance, and initial concentration does not affect it considerably. The effect of flow rate was more significant. Electrodeionization was applied for final treatment of dilute solutions. The effect of magnesium ions in the feed solution caused a decrease in uranium removal. The relation between current and voltage was linear. A comparison between actual and theory energy consumption showed a considerable difference due to concentration polarization. Based on the results, electrodialysis was found to be very effective for uranium removal from wastewaters.

**Key words:** Uranium; ANOVA; Electrodialysis; Electrodeionization; Membrane; Taguchi

### INTRODUCTION

The nuclear industry generates a broad spectrum of low and intermediate level liquid radioactive wastes (International Atomic Energy Agency, 2004). The main sources of such waste are as follows: uranium and thorium mining and milling, nuclear fuel cycle operations (uranium conversion and enrichment, fuel fabrication and spent fuel reprocessing), operation of nuclear power plants, decontamination and decommissioning of nuclear facilities, institutional uses of radioisotopes (medicine, industry, agriculture, research reactors and test facilities) (Zakrzewska, 2006). The toxic nature of uranium (VI) ions, even at trace levels, has been a public health problem for many years. For this reason, removal of uranium from

wastewater is of great importance (Yusan, 2008). To ensure the safe discharge into the environment liquid radioactive waste has to fulfill very strict requirements connected with the limits of radioactive substances and other chemical, biological and suspended impurities. To reach the standards described in national regulations, the waste has to be treated, including volume reduction and reduction of radioactive compounds and other solutes in the effluent. Many methods may be used for liquid radioactive waste treatment including: chemical precipitation, sedimentation, ion exchange, thermal evaporation, biological methods and membrane permeation. Membrane methods have been already applied in some nuclear centers around the world (Zakrzewska, 2001).

\*Corresponding author: Email: adib.mis@gmail.com  
Tel:021 82 06 44 92

Membrane processes can be considered as the most energy-saving separation techniques. Separation abilities of membranes allow the elimination of many non-effective and energy consuming methods and their replacement by new, modern, and environment friendly technologies (Zakrzewska, 2001). The suitability of processes such as reverse osmosis, nanofiltration, electrodialysis (ED), Donnan dialysis and liquid membranes has been supported by a number of researches (Korus, 1999; Zhang, 2002).

Electrodialysis with ion-exchange membranes represents one of the most important membrane methods (Sadrzadeh, 2007). Continuous processes such as electrodialysis, electrodialysis reversal (EDR), and filled cell electrodialysis or otherwise called continuous electrodeionization (CEDI) comprise alternating permselective cation exchange membranes and anion exchange membranes, which under the influence of the electric field allow only cations or only anions respectively, to permeate their mass and simultaneously retain co-ions, so that dilute and concentrate compartments are created and deionization occurs. ED has been successfully performed over the last decades mainly in the production of potable water from brackish or seawater, regeneration of ion exchange resins and production of pure or ultrapure water, demineralization and deacidification in food or pharmaceutical processing, purification of radioactive wastewater in nuclear power plants and recovery of water and valuable metals from industrial effluents (Konstantinos, 2008).

Continuous electrodeionization is a hybrid separation process of electrodialysis and conventional ion exchange (IX). Compared to water deionization by IX, the CEDI has the advantage of a continuous process and no regeneration of the ion exchange resin is required which is generally labor intensive and costly. Compared to ED, the CEDI has the advantage that the conductivity in the resin filled dilute cell is increased by more than two orders of magnitude (Woo Lee, 2007).

The performance of ED depends on a set of parameters such as cell design, feed and product concentrations, flow rates, current density and permselectivity of membrane (Mohammadi *et al.*, 2004).

There are some literatures on heavy metal removal from aqueous solutions by electromembrane processes. Mohammadi explained the effect of voltage, flow rate, temperature and concentration on lead separation from wastewater using electrodialysis (Mohammadi *et al.*, 2004). Sadrzadeh studied the effect of influential factors on separation of Na, Cu, Zn, Pb and Cr from wastewater using electrodialysis (Sadrzadeh, 2007). Bazrafshan studied the evaluation of cadmium and pesticide removal from industrial wastewater by electrocoagulation process. In their study, each wastewater was containing ions in concentrations of 5, 50 and 500 mg/L. The percent of ion removal was measured at pH of 3, 7 and 10 and in electric potential range of 20, 30 and 40 volts. The results obtained at different electrical potential showed that initial concentration can affect the efficiency removal and for higher concentration of cadmium or pesticide, higher electrical potential or more reaction time is needed. The highest electrical potential (40V) produced the quickest treatment with >99% cadmium and pesticide reduction occurring after only 20 min (Bazrafshan, 2006 and Bazrafshan, 2007).

Malakootian and Yousefi investigated the efficiency of electrocoagulation process in removal of water hardness under different conditions. Drinking water of Kerman (southeast of Iran) was used in the experiments. Results showed the efficiency of 95.6% for electrocoagulation technique in hardness removal. pH and electrical potential had direct influence on hardness removal in a way that the highest efficiency rate was obtained at pH=10.1, potential difference of 20 V and detention time of 60 minutes (Malakootian, 2009).

The only experience on uranium separation from aqueous solution using electrodialysis was done by Zaki (Zaki, 2002). He studied the transport of uranium ions through cation exchange membranes. Different parameters affecting the transport of U(VI) were studied. These parameters include: nitric acid concentration in the feed solution, stripping solution concentration and applied electric field. The optimum flux of U(VI) was  $6.5 \times 10^{-8}$  geq/cm<sup>2</sup> at the conditions of  $10^{-3}$  M HNO<sub>3</sub> in the feed solution, 0.5 M Na<sub>2</sub>CO<sub>3</sub> in the

stripping solution, current density = 25 mA/cm<sup>2</sup> and voltage = 30 V. The obtained model in the study correlates the mass transfer as a function of current density and voltage as variables and takes into account the electro-osmotic effect (Zaki, 2002).

The main objective of this work was to investigate the ability of electrodialysis for continuous removal of uranium from aqueous solutions in a bench scale unit. The effects of three operating parameters of voltage, flow rate and feed concentration were studied. CEDI was then used for final treatment of the dilute solutions in which ED is limited. This work could be considered as the first research in which aqueous solutions containing uranium is treated by continuous electrodialysis.

### MATERIALS AND METHODS

The laboratory size ED unit consisted of a feed tank where the wastewater was stored, a tank for rinsing solution, a peristaltic pump, and an ED stack (Fig. 1). The stack was composed of three compartments and was packed with a pair of ion-exchange membranes (cation and anion) and a pair of platinum-coated electrodes (anode and cathode).

The effective area of each membrane was 50×50 mm<sup>2</sup>, while the thickness of the dilution cell (middle cell) and each electrode cell (left and right) was 10 mm. Hence, the volume of dilute cell was 25 cm<sup>3</sup> and the area of each electrode was 45×45 mm<sup>2</sup>. A multilayer polymeric mesh spacer was used in the middle part of the membrane stack to control concentration polarization phenomenon. A DC power supply was used to apply an external

voltage in the range of 0 – 30 V. The outlet flow rate of the dilute solution was evaluated manually by measuring the time required to fill a graduated cylinder.

Uranyl nitrate hexahydrate and deionized water were used in all experiments to produce feed solutions. Each sampling was done 15 minutes after regulating parameters to ensure that the system is steady state. The concentrations of all samples were measured by Inductively Coupled Plasma (ICP). The rinsing solution in all experiments was 0.05 M solution of NaNO<sub>3</sub>. All of the experiments were carried out at room temperature.

Three factors in three levels were chosen based on the results in the related works (Mohammadi *et al.*, 2004a, b) as follows:

Feed concentration: 200, 500 and 1000 mg/L

Flow rate: 5, 15 and 30 mL/min

Voltage: 10, 20 and 30 V

The matrix experiment was designed by selecting the appropriate orthogonal array (L<sub>9</sub>) for controlling parameters. Taguchi recommends analyzing the mean response (y) for each run and also suggests analyzing variation using an appropriately chosen signal to noise ratio (SN). For the larger and better responses, the following relation is used for SN calculation:

$$SN = -10 \log \left( \frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (1)$$

Where n is the number of experiments. In these experiments the system is optimized when the response is as large as possible, so it deals with factor levels that maximize the SN ratio (Sadrzadeh, 2007).

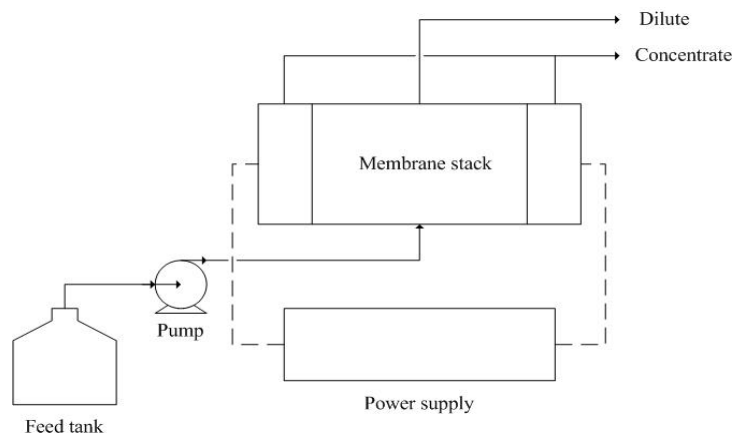


Fig. 1: Simplified flow diagram of the ED unit

Analysis of variance (ANOVA) was used to determine the factors that influence the separation percentage. Taguchi-oriented practitioners often use ANOVA to determine the factors that influence the average response and the factors that influence the signal to noise ratio (Mohammadi et al., 2004a).

In this research, electrodeionization was also applied to achieve low concentration solutions as a final treatment of ED outlet solutions. To make EDI system, only the dilute compartment of ED cell was filled with 20 cm<sup>3</sup> cation exchange resin that enhances the transport of uranium ions under the driving force of direct current. A solution containing 25 mg/L uranium was used as the feed solution. This solution was fed to the electrodialysis and electrodeionization systems, separately.

To investigate the effect of presence of magnesium ions in the feed solution on uranium removal, a solution containing uranium and magnesium was prepared using Mg(NO<sub>3</sub>)<sub>2</sub> · 10H<sub>2</sub>O and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (Merck Co.). Since mass transfer in ion exchange process is based on the amount of ions in unit mole, so the same molar concentration of 0.42 mM was considered for each ion. This molar concentration is equal to the molar concentration of a 200 mg/L single element (i.e. uranium) solution.

The theoretical power consumption  $E_{\text{theory}}$  to achieve a certain separation is given by the expression:

$$E_{\text{theory}} = Vz\Delta CQF \tag{2}$$

Where V is the theoretical voltage drop across the stack, z is the valence of the salt, ΔC is the difference in molar concentration between the feed and the dilute solutions, Q is the feed flow rate and F is the Faraday constant (Baker, 2004). The flux of uranium diffusion through cation exchange membrane could be evaluated by the expression:

$$J = \frac{\Delta CQMz}{A} \tag{3}$$

Where ΔC is the difference in molar concentration between the feed and the dilute solutions, Q is the feed flow rate, M is molar weight of uranium, z is the valence of the salt and A is the area of membrane.

### RESULTS

Controllable factors, their levels and responses are presented in Table 1. The experiments with the mesh spacer and without the mesh spacer were performed, separately to see the effect of spacer in the results. The data obtained from the experiments were analyzed by Taguchi method. Results of mean responses and SN values are presented in Table 2. The Taguchi method employs graphs of the marginal means of each factor in which the effect of controllable factors on SN and mean response are displayed, respectively (Fig. 2). Sum of squares (SS), mean square (MS), and ratio of factor variance to error variance (F) and contribution percentage of each factor on response (P) are presented in Table 3. Using ANOVA analysis, the contribution percentage of each factor on response was gained and is presented in Fig. 3.

Table 1: Taguchi L<sub>9</sub> orthogonal array and responses

Run	Factors			Current (A)	Separation without spacer (%)	Separation with spacer (%)
	Concentration (mg/L)	Flow rate (mL/min)	Voltage (V)			
1	200	5	10	0.1	67.7 ± 0.65	85.8 ± 3.5
2	200	15	20	0.2	59.7 ± 0.15	73.6 ± 5.1
3	200	30	30	0.3	59.9 ± 0.15	59.6 ± 0.2
4	500	5	20	0.2	93.2 ± 1.10	98.1 ± 2.5
5	500	15	30	0.3	84.3 ± 3.55	91.4 ± 3.2
6	500	30	10	0.1	12.9 ± 2.1	17.1 ± 0.55
7	1000	5	30	0.3	96.5 ± 0.75	98.3 ± 0.15
8	1000	15	10	0.1	29.4 ± 0.7	28 ± 0.8
9	1000	30	20	0.2	33.1 ± 0.9	31.3 ± 0.7

Table 2: Mean response (y) and SN values for all levels of factors

Factor	Value	Mean response (y)	Signal to noise ratio (SN)
Concentration	200	62.4	35.9
	500	63.4	33.3
	1000	53.0	33.2
Flow rate	5	85.8	38.6
	15	57.8	34.5
	30	35.2	29.3
Voltage	10	36.6	29.3
	20	62.0	35.1
	30	80.2	37.9

In the experiments, the amount of voltage was regulated on 10, 20 and 30 V. The current was dependent upon the voltage and the load in the cell. According to the Table 1, an exact linear relation between current and voltage can be seen (Fig. 4).

A comparison of the theoretical energy consumption and the actual energy consumption of the electro dialysis system was carried for three runs; the runs 3, 5 and 8 which were known as the most energy saving runs in each concentration (Fig. 5).

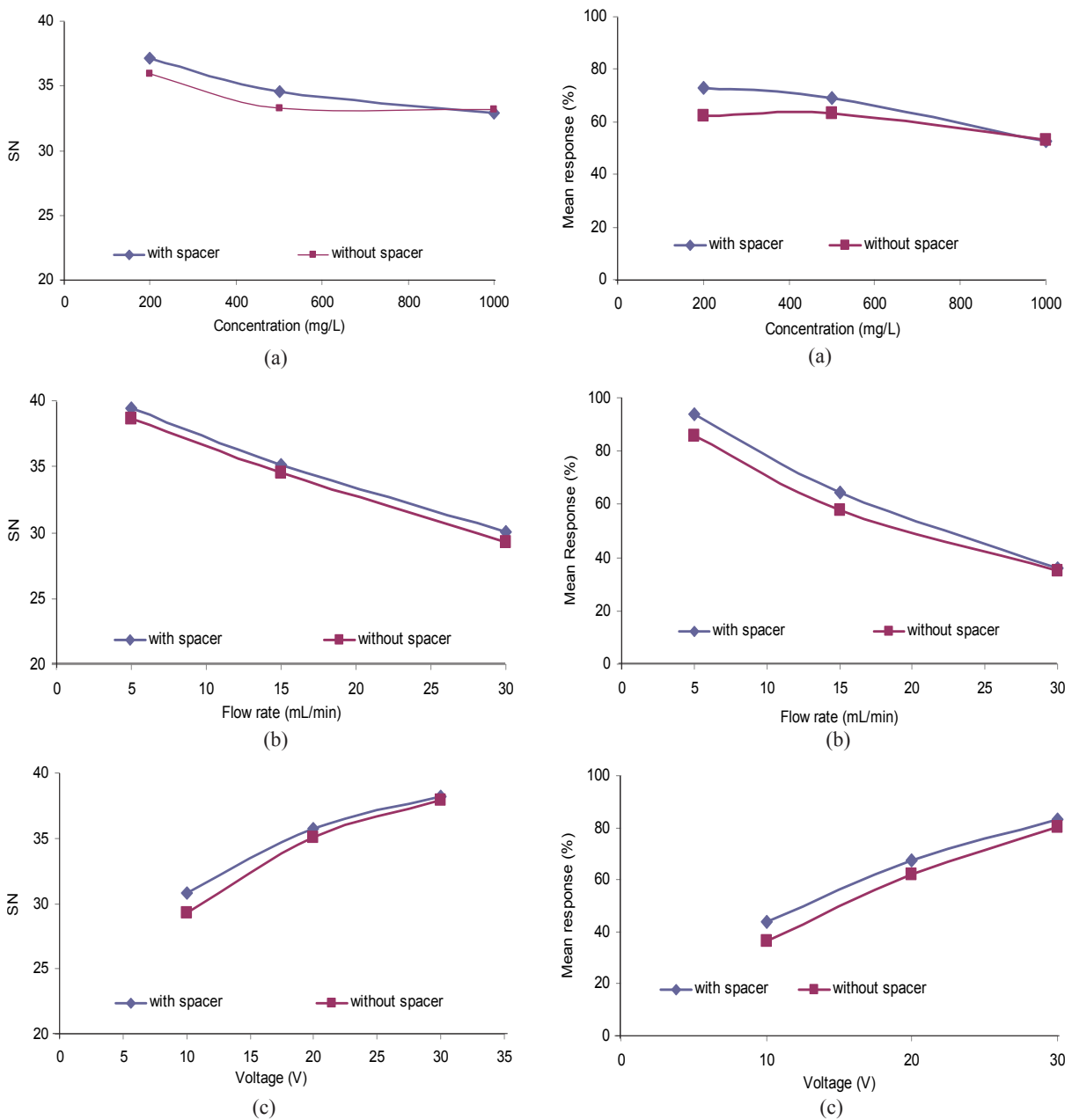


Fig. 2: Effect of (a) concentration, (b) flow rate and (c) voltage on signal to noise ratio (SN) and mean response

Considering that the ED method is limited in low concentrations, its outlet cannot discharge to the environment directly. Therefore using a method for final purification is necessary. As was said before, CEDI is an appropriate process for

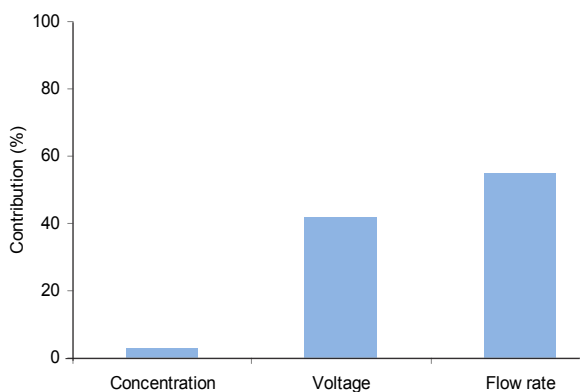


Fig. 3: Contribution of each factor on the response

Table 3: Statistical results based on separation percentage

Factor	SS	MS	F	P
Concentration	197.33	98.66	0.13	3
Flow rate	3855.12	1927.56	31.03	55
Voltage	2937.21	1443.04	23.23	42

refining the final diluted solutions. Hence, four tests were carried on a dilute (25 mg/L) uranium solution. The experiments also compare the ED and CEDI for purification of dilute solutions. The results are presented in Table 4.

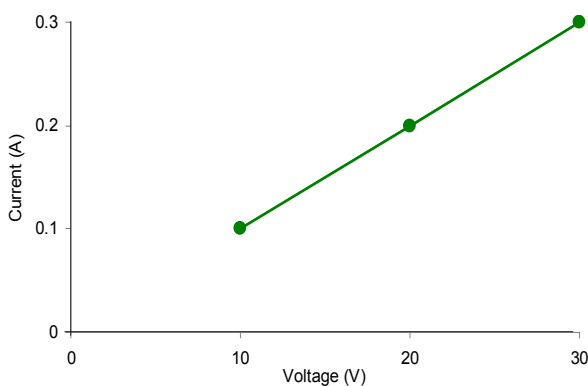


Fig. 4: Current vs. voltage in ED; gradient of the plot (apparent conductance) = 0.01 1/ohm

Three runs were also carried out to investigate the effect of presence of magnesium in the feed solution. These three tests were not repeated due to adequate qualitative responses. The results are shown in the Table 5.

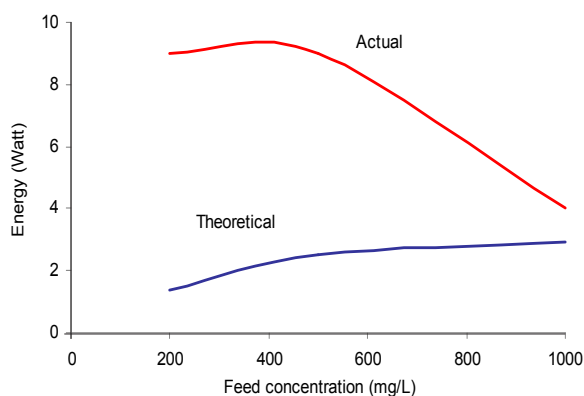


Fig. 5: Comparison of the theoretical and actual energy consumptions of the electro dialysis system

## DISCUSSION

According to the Fig. 2, increasing voltage increased SN and mean response, as it was expected. However, increasing concentration caused lower resistance of solution but the concentration polarization phenomenon was more effective at higher concentrations. It was observed that a concentration higher than 500 mg/L had almost no effect on separation percent, even a negative effect could be seen (Fig. 2). Increasing flow rate had two effects; 1) negative

Table 4: Experimental conditions and results of comparison of ED and electrodeionization (for a solution containing 25 mg/L uranium)

Run	Q (mL/min)	E (V)	I (A)	S <sub>CEDI</sub>	S <sub>ED</sub>
1	5	2.5	0.05	More than 98	10
2	5	5	0.1	More than 98	24
3	10	2.5	0.05	More than 98	4
4	10	5	0.1	More than 98	16

effect because of less residence time 2) positive effect because of making turbulence in dilute chamber. The net effect of increasing flow rate was negative (Fig. 2). The maximum separation percent (98.3%) was obtained at operating conditions, concentration = 1000 mg/L; flow

Table 5: experimental conditions and results of treatment of the solution containing U and Mg

Run	Q (mL/min)	I (A)	E (V)	S for mixed solution		S for single(U) solution
				S <sub>Mg</sub>	S <sub>U</sub>	
1	5	0.1	10	59.1	64.3	85.8
2	15	0.2	20	53.2	59.4	73.6
3	30	0.3	30	50.8	60.8	59.6

rate = 5 mL/min and voltage = 30 V and using spacer.

Using equation (3), the maximum flux value of uranium in the ED was calculated equal to  $4.1 \times 10^{-6}$  geq/cm<sup>2</sup> s.

At the same work (Zaki, 2002) the maximum flux at the same conditions (same uranium concentration and voltage) was gained ( $6.5 \times 10^{-8}$  geq/cm<sup>2</sup>). The reason of differences may refer to the differences in the ED stacks. In our work, the ED system was continuous and therefore solution moved at a cross flow mood. But the ED system in that research was a batch cell through in which no moving occurred, so concentration polarization appears intensively and the flux of uranium was limited.

Another point that can be seen in Table 1 and Fig. 2 is that the spacer increased uranium separation but its effect is considerable only in low concentration. Increasing uranium separation due to using spacer is evident because the spacer controls concentration polarization. But low effect of spacer, especially at high concentrations, may result from low speed of solution in the membrane stack in bench scale units. It is recommended that the recycle flow and lower thickness of dilute chamber is used to make a turbulence flow in the cell and therefore to eliminate concentration polarization as far as possible. It is also clear in Table 1 that the effect of spacer in the system is higher for lower concentrations and flow rates. This may be due to higher electrical resistance of solution in low concentrations and low flow rates (and consequently low turbulence). In these conditions, more concentration polarization appears. Therefore, using spacer to control the polarization phenomena can be more effective than in higher flow rates and concentrations.

Using ANOVA, it was shown that contribution percentage of concentration and voltage was lower than flow rate (Fig. 3). This means that flow rate has been the most influential factor (55%) on the process performance.

Separation percentages in Table 1 mean that the outlet product of ED cell needs a final treatment. The ED process can be considered as the main step of a purification plant to pretreat the wastewater at high concentrations. At low concentrations, the performance of ED process is limited, because of low conductivity of dilute solutions. Therefore, if the wastewater contains the radioactive or dangerous metals, a final treatment such as ion exchange or continuous electrodeionization is necessary to achieve a very dilute product and to ensure safe discharging of dilute products into the environment. ED can also be used to increase volume reduction of a wastewater by concentration of the retentate flow of a purification method such as reverse osmosis.

As it is clear in Table 4, electro dialysis is limited for low concentrations because of high electrical resistance of the solution, while continuous electrodeionization has an approximately complete uranium removal. Due to presence of negatively charged groups of cation exchange resins, the electrical conductivity of dilute chamber is high enough for uranium ions to immigrate easily through the solution. Of course, it must be considered that by adding ion exchanger material to the dilute chambers, capital investment (resin consumption) and a part of operating costs (more pumping costs due to more head loss through chamber) are increased; however, another part of operating costs (including electric power) is reduced. Therefore, electrodeionization may be applied for final treatment of dilute solutions of uranium after pretreatment by electro dialysis.

In a given electric field, the electric current is a measure of ion migration. Because the magnitude of the electrical current directly relates to the rate of ion transport in the electrolyte solution and ion exchange membrane, the measurement of current vs. voltage characteristics will help to determine the rates of ion transport in different regions. Usually, the current vs. voltage characteristics show a linear relationship. The ratio of current vs. voltage is known as the electrical conductance and plays an important role in the ionic separation process. The electrical conductance not only depends on the ion concentration, but also on the rate of ion transport. Generally, it is difficult to measure individual conductance for ion transport in the electrolytic solution and in the

ion exchange membrane separately. Therefore, an apparent conductance is given by the gradient of the plot of current vs. voltage curve. In the constant electric field, the change of electric current, and then apparent conductance, will represent the change of the rate of ion transport (Yu, 2003). As it is shown in Fig. 4, the apparent conductance in the electro dialysis was 0.01/Ohm. Table 4 shows that the apparent conductance in the electrodeionization was 0.02 /Ohm. So the apparent conductance has increased by more than two orders of magnitude, due to adding ion exchange resins in the dilute cell.

The actual energy consumed was higher than the theoretical value (Fig. 5). Most of the difference results from concentration polarization effects. The concentrations of ions in the solutions adjacent to the membrane surfaces are significantly lower than the bulk solution values. That is, the actual voltage drop used in Equation (2) is several times larger than the voltage drop in the absence of polarization. The result is to increase the actual energy consumption several times above the theoretical minimum value.

Based on the results shown in table 5 and composition of these results with runs 1, 2 and 3 in Table 1, it is clear that the presence of magnesium ions in the solution decreased uranium separation. This could be due to heaviness of uranium and hence more slow moving in the solution than magnesium. Hence, if a certain separation of uranium is desired, more voltage difference and hence more energy is necessary.

Finally, electro dialysis was found to be very effective for pretreatment of wastewaters containing uranium and also to concentrate a retentate of a treatment plant.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Atomic Energy Organization of Iran for the financial support to carry out this work and also thank M. Ghasemi for his help concerning the experiments.

## REFERENCES

- Baker, R. W., (2004). Membrane technology and applications. 2<sup>nd</sup> Ed. John Wiley & Sons, Ltd. 410.
- Bazrafshan ,E., Mahvi, A. H., Nasseri, S., Mesdaghinia, A. R., Vaezi, F., Nazmara, Sh., (2006). Removal of Cadmium from Industrial Effluents by Electrocoagulation Process Using Iron Electrodes. Iran. J. Environ. Health. Sci. Eng. **3**(4): 261-266.
- Bazrafshan, E., Mahvi ,A. H., Nasseri, S., Shaieghi, M.

- ,(2007). Performance Evaluation of Electrocoagulation Process for Diazinon Removal from Aqueous Environments by Using Iron Electrodes. Iran. J. Environ. Health. Sci. Eng. **4**(2): 127-132.
- International Atomic Energy Agency, (2004). Application of Membrane Technologies for Liquid Radioactive Waste Processing. Technical reports series No. 431, Vienna, Austria.
- Konstantinos, D., (2008). Continuous electrodeionization through electrostatic shielding. Electrochim Acta. **53**: 2953–2962.
- Korus, I., Bodzek, M., Loska, K., (1999). Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation–ultrafiltration process. Sep. Purif. Technol., **17**: 111–116.
- Malakootian, M., Yousefi, N., (2009). The Electrocoagulation Process Using Aluminum Electrodes in Removal of Hardness from Water. Iran. J. Environ. Health. Sci. Eng. **6** (2):131-136.
- Mohammadi, T., Moheb, A., Sadrzadeh, M., Razmi, A., (2004). Separation of copper ions by electro dialysis using Taguchi experimental design. Desalination., **69**: 21-31.
- Mohammadi, T., Razmi, A., Sadrzadeh, M., (2004). Effect of operating parameters on Pb<sup>2+</sup> separation from wastewater using electro dialysis. Desalination, **167**: 379-385.
- Sadrzadeh, M., Razmi ,A., Mohammadi ,T., (2007). Separation of monovalent, divalent and trivalent ions from wastewater at various operating conditions using electro dialysis. Desalination, **205**: 53-61.
- Woo, Lee J., Ho Yeon, K., Hoon Song, J., Hyeon Moon, S., (2007). Characterization of electroregeneration and determination of optimal current density in continuous electrodeionization. Desalination, **207**:276-285.
- Yu, Z., and Admassu, W., (2003). Critical Change in Apparent Conductance and Ion Exchange Limit in Membrane Electro dialysis. Separ. Sci. Technol. **38** (7) :1561–1583.
- Yusan, S., Doyurum Akyil, S., (2008). Sorption of uranium (VI) from aqueous solutions by akaganeite. J. Hazard. Mater., **160**: 388–395.
- Zaki ,E. E., (2002). electro dialysis of uranium through cation exchange membranes and modeling of electro dialysis processes. J. Radioan. Nucl. Ch. Ar., **252**(1): 21-30.
- Zakrzewska-Trznadel, G., (2006). Membrane processes for environmental protection: applications in nuclear technology. Nukleonika, (51), (Supplement 1), S101–S111.
- Zakrzewska-Trznadel, G., Harasimowicz, M., Chmielewski, A. G., (2001). Membrane processes in nuclear technology-application for liquid radioactive waste treatment. Sep. Purif. Technol., **22-23**: 617–625.
- Zhang, L.M., and Chen, D. Q., (2002). An investigation of adsorption of lead (II) and copper(II) ions by water-insoluble starch graft copolymers, Colloids Surf. A. Physicochem. Eng. Aspects, **205**: 231–236.