ZINC ION REMOVAL FROM WASTEWATER BY ELECTRODIALYSIS

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ABSTRACT

This paper describes a robust design method for separation of zinc ions from a solution using a laboratory electrodialysis (ED) setup. An experimental investigation is presented to determine the optimum configuration of factors for the best performance. In order to optimize the performance, the factors which have the greatest influence have to be identified and their optimum values chosen. In this research, Taguchi method was used initially to plan a minimum number of experiments. An orthogonal array of experiments was used to allow simultaneous variation of several factors and investigation of interactions between them. An L_9 orthogonal array (four factors in three levels) was employed to evaluate the effects of factors on response. Ionics membranes with moderate ion exchange capacities were used. The optimal levels determined for the four influential factors are: concentration 1000 ppm, temperature 60 °C, flow rate 0.07 mL/s and voltage 30 V. Comparing results obtained by Asahi glass membranes with those obtained by Ionics membranes, it was found that using a membrane pair with higher Ion Exchange Capacity (IEC) improves the performance. The highest removal percentage was found to be 97.67% and 98.73% for the two types of membranes. Statistical analysis, ANOVA, was then employed to determine the relationship between the experimental conditions and the yield levels.

Key Words: Electrodialysis, Wastewater treatment, Taguchi method, Experimental design, ANOVA, Zinc removal

INTRODUCTION

Zinc is a PBT chemical. PBT chemicals are chemicals that do not easily breakdown or decrease in potency after they are released into the environment, tend to accumulate in the environment, be absorbed or ingested by plants and animals, accumulate in animal and plant tissues and pass through the food chain and cause long-term human health or ecological problems [1].

Zinc is one of the most common elements in the earth's crust. It is found in air, soil and water and is present in all foods. Pure zinc is a bluish-white shiny metal. Zinc is an essential element in people's life, but too much zinc is harmful and can also damage human health. Eating large amounts of zinc, even for a short time, can cause stomach cramps, nausea and vomiting [2]. For longer periods, it can cause anemia, pancreas damage and lower levels of high density lipoprotein cholesterol (a good form of cholesterol).

Pollution prevention has become a central part of the thinking for regulators, chemists, chemical engineers, process engineers and others in chemical manufacturing. Efforts have been undertaken to identify new processes that inherently produce less pollution to be used in tomorrow's processing plants. New technologies to recover and reuse current waste process streams also are enjoying interest. ED is an electro membrane process with current widespread use in production of salt from seawater and potable water. Recent advances and improvements have opened the way for ED to become useful for resource recovery and in-plant chemical processing. These new applications will offer increased options for pollution prevention opportunities.

ED began in the early 1900's as a modification to dialysis by addition of electrodes and applying a direct current to increase the rate of dialysis in many ways. However, since the 1940's, ED has developed into a membrane separation process that differs from dialysis in many ways. Today, ED refers to an electrolytic process for separating an aqueous electrolyte feed solution into a concentrate or brine and a dilute or desalted water by means of an electric field and ion selective membranes [3].

To optimize the design of an existing process, it is necessary to identify which factors have the greatest influence and which values produce the most consistent performance. Experimenting with the design variables one at a time or by trial and error until a first feasible design is found, is a common approach to design optimization. However, this approach can lead to a very long and expensive time span for completing the design process. Using factorial design of experiments, a technique for laying out experiments when multiple factors are involved, helps researchers to determine the possible combinations of factors and to identify the best combination. However, in industrial settings, it is extremely costly to run a number of experiments to test all combinations.

Taguchi approach has developed rules to carry out experiments, which further simplify and standardize the experiment design, along with minimize the number of factor combinations that are required to test for the factor effects. In Taguchi method, the results of experiments are analyzed to achieve the following objectives: (1) to establish the best or optimal condition for the product or process, (2) to establish the contribution of individual factors and (3) to estimate the response under optimal conditions. A commonly applied statistical treatment, Analysis of Variance (ANOVA), is used to analyze the results of experiments on response and to determine how much variation each factor contributes. By studying the main effects of each factor, the general trends of the influencing factors, towards the performance, can be characterized. The characteristics can be controlled, such that a lower or a higher value in a particular factor produces the preferred result. Thus, the levels of influencing factors, to produce the best results, can be predicted.

EXPERIMENTAL

The ED plant consisted of a feed tank where wastewater was stored, two pumps (RESUN submersible pump, P = 4 W, total head = 0.5 m) and a self designed ED cell. The cell was packed with a pair of ion exchange membranes (cation and anion) and a pair of platinum electrodes (anode and cathode) [4].

Membranes used in these experiments were (AR204SXR412) and (CR67,MK111) anion and cation exchange membranes made by Ionics incorporated, Watertown, Massachusetts, USA, supplied by Arak petrochemical complex, Iran.

Effective area of each membrane was $60\times65\ mm^2$ while thickness of dilution cell (center) was 4 mm and thickness of each concentrate cell (left and right) was 3 mm. Both electrodes were made of pure platinum [5]. Area of each electrode was $4.2\times4.2\ mm^2$. A rectifier (RST SPASTELL TRFO) supplied required DC power at different voltages.

An analytical grade salt (zinc sulfate, Merck) was used in all experiments to make solutions with wastewater qualities. The purpose of these experiments was to study the effect of voltage, flow rate, temperature and concentration on ED cell performance. Atomic absorption was used for Zn determination in dilute solution.

Taguchi experimental design was used for conducting the experiments. This method steps are as follows [6]:

1- Determining the quality characteristic to be optimized (i.e. separation percent).
2- Identifying the noise factors which are either uncontrollable or are too expensive to control (i.e. room temperature, pH variation in cell, occurring electrolysis on electrodes, concentration polarization, precipitation on membranes and voltage variation) [7].
3- Identifying the control factors and their alternative levels; According to previous results in related works, four factors (temperature, concentration, flow rate and voltage) each with three levels (low, medium and high) were chosen [8, 9].
4- Designing the matrix experiment by selecting the appropriate orthogonal array for control factors. For this study an L_9 orthogonal array was chosen based on the number of factors and their levels (four factors each in three levels).
5- Conducting the matrix experiment.
6- Analyzing the data and determining optimum levels for the control factors. Taguchi method uses a statistical measure of performance called signal-to-noise (SN) ratio for data analyzing. For the larger the better responses, as in this study, the following relation is used to calculate SN ratio:

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

where, n is the number of experiments and y_i is the response at each experiment. In this study y is separation percent and is defined as follows:

$$y : separation\ percent = \frac{C_0 - C}{C} \times 100 \qquad (2)$$

where, C_0 and C are feed and dilute concentrations, respectively.

7- Predicting the performance at these levels

8- Conducting a confirmation experiment using the predicted optimum levels for the control factors [6, 7, 11, 12, and 13].

After performing the statistical SN analysis, ANOVA needs to be employed for estimating error variance and determining the relative importance of various factors. ANOVA is a particularly powerful way to analyze experimental data. ANOVA is usually presented as a table showing the sums of squares, degrees of freedom, the mean squares and the associated F-tests of significance [14, 15].

RESULTS AND DISCUSSION

This section is based on the eight steps mentioned in experimental section. Table 1 contains $\overline{y}$ and SN for each run. Table 2 contains $\overline{y}$ and SN of membranes for all factor levels.

In Figure 1, the effects of controllable factors on the mean response and SN are displayed. According to the results, increasing temperature, concentration and voltage increases SN and the mean response due to reduction of electrical resistance of feed solution. Notice that there is almost no difference between SN and mean values for $C_{500\ ppm}$ and $C_{1000\ ppm}$. The mean response at 500 ppm is even greater than the mean response at 1000 ppm because a concentration polarization phenomenon is more important at higher concentrations. With the aid of Duncan's multiple range test, which is a statistical manner of comparison of the means, it was observed that higher concentration than 500 ppm has almost no effect on separation performance.

Table 1 $\bar{y}$ and SN values for each run

run	Controllable factors				$\bar{y}$	SN
	T(°C)	C(ppm)	F(mL/s)	V(V)		
1	25	100	0.07	10	26.48	28.45
2	25	500	0.7	20	8.05	18.11
3	25	1000	1.2	30	11.05	20.84
4	40	100	0.7	30	19.16	25.56
5	40	500	1.2	10	7.56	17.55
6	40	1000	0.07	20	83.67	38.45
7	60	100	1.2	20	10.80	20.64
8	60	500	0.07	30	97.67	39.80
9	60	1000	0.7	10	15.85	23.97

At higher flow rates, SN and mean values fall and separation performance decreases, because more flow rate means less residence time and thus ions that are between the membranes do not have enough time to transfer through the membranes.

Table 2 $\bar{y}$ and SN values for all factor levels

Factor	Level	$\bar{y}$	SN
Temperature (°C)	25	15.19	22.47
	40	36.80	27.19
	60	41.44	28.13
Concentration (ppm)	100	18.82	24.88
	500	37.76	25.15
	1000	36.86	27.76
Flow rate (mL/s)	0.07	69.28	35.57
	0.7	14.35	22.55
	1.2	9.80	19.68
Voltage (V)	10	16.63	23.33
	20	34.18	25.73
	30	42.63	28.73

In terms of maximizing SN, T_{high} (60 °C), C_{high} (1000 ppm), F_{low} (0.07 mL/s) and V_{high} (30 V) were selected. In terms of maximizing the mean response, T_{high} (60 °C), C_{medium} (500 ppm), F_{low} (0.07 mL/s) and V_{high} (30 V) were chosen.

Comparing results obtained by Ionics membranes as in this study with those obtained by Asahi glass membranes (AMV and CMV anion and cation exchange membranes made by Asahi Glass Co., Tokyo, Japan), it was found that performance of Asahi glass membranes was better than that of Ionics membranes. Better performance of Asahi glass membranes can be attributed to their higher IEC (4.4, 5.2, 2.8 and 2.4 meq/gr dry for AMV, CMV, AR204SXR412 and CR67, MK111, respectively, as reported in product catalogues of Ionics and Asahi glass) [16].

As IEC increases both ion conductivity and swelling increase, while ion-permselectivity decreases. The reason for reduction of ion-permselectivity is facilitation of coion diffusion into the swollen polymer membrane network since the Donnan exclusion does no longer work efficiently. Reduction of ion-permselectivity and mechanical stability with increasing IEC can be avoided by crosslinking the membranes. This reduces the membrane swelling [16,17]. Thus, the results show that desalination and ion removal rates enhance with increasing IEC of membranes.

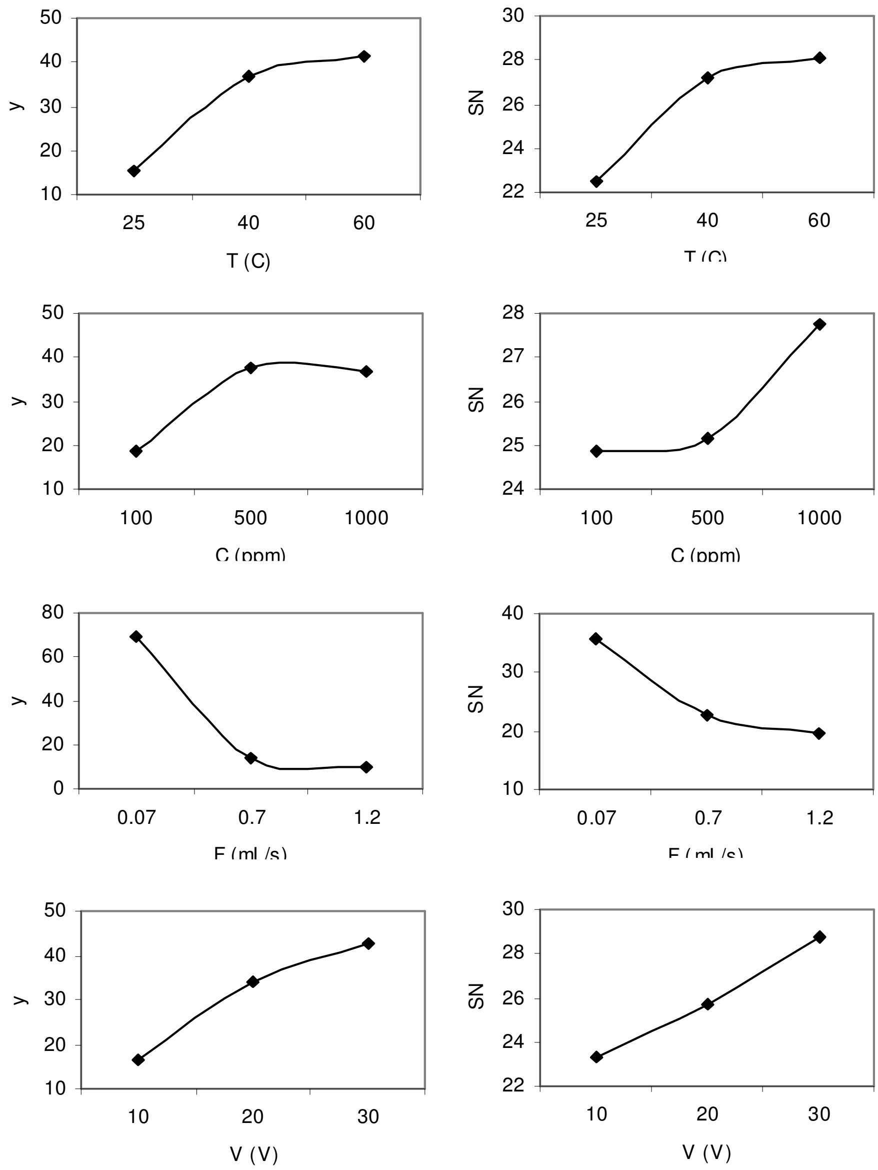

Figure 1 Effect of (a) Temperature on $\bar{y}$, (b) Concentration on $\bar{y}$, (c) Flow rate on $\bar{y}$, (d) Voltage on $\bar{y}$, (e) Temperature on SN, (f) Concentration on SN, (g) Flow rate on SN, and (h) voltage on SN

Based on seventh and eighth steps of Taguchi method, performance of the ED cell at optimum and other levels were predicted and then some of these results confirmed by confirmation experiments. So with spending less time and cost, acceptable results can be derived. Some of these results are presented in Figure 2.

Analysis of variance was used to determine the factors that influence the mean response. Sum of square, variance, ratio of factor variance to error variance (F) and contribution percent of each factor on response (P), evaluated based on mean response, is presented in Table 3. According to these results, flow rate has the greatest effect on mean response.

F value of all factors is greater than extracted F value of the table for α (risk) = 0.05 (F = 4.26) and α = 0.01 (F = 8.02). It means that variance of all factors is significant compared with variance of error and all of them have significant effect on the response. P values of temperature, concentration and voltage are almost the same and are smaller than that of flow rate (69.22%) which means that flow rate is the most influential factor.

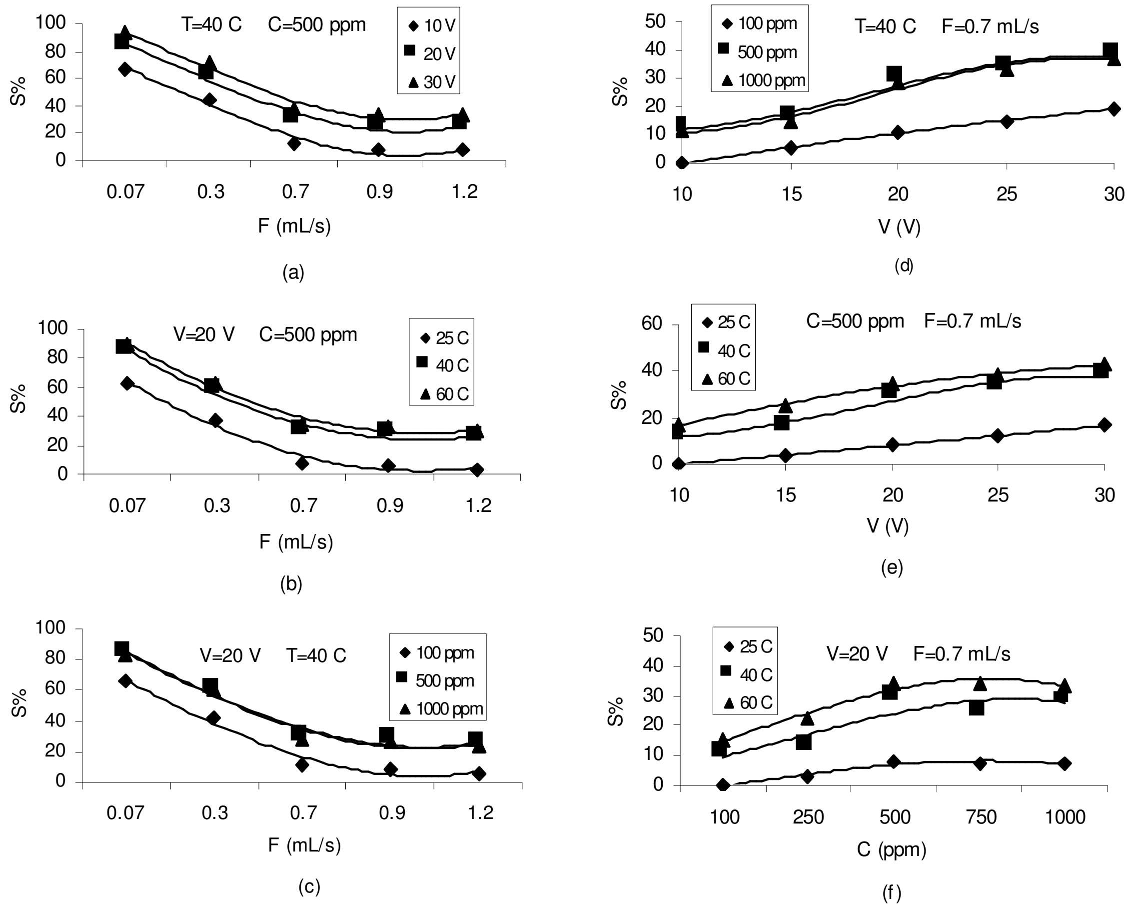

Figure 2 Separation percent at different (a) Flow rates and voltages, (b) Flow rates and temperatures, (c) Flow rates and concentrations, (d) Voltages and concentrations, (e) Voltages and temperatures and (f) Concentrations and temperatures

Table 3 Statistical results based on $\bar{y}$

Factor	d.o.f	SS	Variance	F	P
Flow rate	2	13148.54	6574.27	7324.5	69.22
Voltage	2	2354.05	1177.02	1311.3	11.10
Temperature	2	2110.44	1055.22	1175.6	12.38
Concentration	2	1370.39	685.19	763.4	7.28
Error	9	8.08	0.90	-	-

CONCLUSION

In this paper Taguchi data analysis method was utilized to determine optimal operating condition of experiment. An application of Taguchi method was illustrated in separation of zinc ions to plan a minimum number of experiments. For this purpose, a SN ratio which measures quality and an orthogonal array which is used to study design parameters simultaneously were employed. ANOVA was then applied to evaluate the relative importance of the effect of various factors. Trials on the response using a L_9 orthogonal array indicates that high level of factor T (60 °C), medium level of factor C (500 ppm), low level of factor F (0.07 mL/s) and high level of factor V (30 V) give the highest levels of separation. It was also observed that factor F (flow rate) has the largest contribution to the total sum of squares and correspondingly has a major effect on the total variation of separation. However, all factors have significant effect on the response. In order to conduct a verification experiment, an additive model was used to predict value of recovery under optimum and some other conditions. The results point out that the proposed SN ratio and ANOVA analysis can be effectively used to determine the optimum level, to evaluate the effect of relative magnitude of each factor on separation percent and to estimate the error variance. Electrodialysis was also found very effective for zinc removal from wastewater.

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