Galvanostatic Removal of Lead from Simulated Chloride Wastewaters using a Flow-by Fixed Bed Electrochemical Cell: Taguchi approach

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Abstract— The Taguchi parameter design approach was used to find the optimal conditions for electrolytic Pb(II) removal using a flow-by fixed bed electrochemical cell composed of a vertical stack of stainless steel screens. The investigated process parameters were initial metal ion concentration, current, flow rate, and mesh number of screen. Removal, current efficiencies, and energy consumption were considered as responses for the optimization of metal removal. An orthogonal array L_9, the signal-to-noise(S/N) ratio, and the analysis of variance were used to analyze the effect of selected process parameters and their levels on the performance of Pb(II) removal.The results indicated that concentration and current have the major effect on performance of lead removal. Flow rate and screen mesh number have lower contribution on the performance of Pb(II) removal and their contributions are close in all responses. The optimum values of control factors were Pb(II) initial concentration 200ppm, current 0.58A, flow rate 7l/min ,and mesh number 40 wire/in. The highest current and removal efficiencies were 48.5% and 89.7% respectively with energy consumption (2.43kwhkg^{-1}). The results of confirmatory runs under the optimum conditions indicated that this methodology is more efficient in optimizing the process parameters.

Index Terms— Heavy metals, Electrochemical reactor, Lead, Flow-by electrode, Taguchi method.

1 INTRODUCTION

THe increase in legal pressures and restrictions are forcing industries to accept responsibility for the treatment of wastewaters in an attempt to minimize pollution. Wastewater generated during the processing of lead-acid batteries contains Pb (II), which is very toxic to the environment and to living beings. Thus, before discharging this wastewater into sewers, effluent treatment must be carried out in order to decrease the concentration of the metallic ion [1].A number of techniques have been used to remove lead or other heavy metals from wastewater effluents; including chemical precipitation [2], electrodialysis [3],ion exchange process[4,5], adsorption onto activated carbon [6, 7],low cost adsorbents such as kaolin, bentonite, blast furnace slag and fly ash [8],ion imprinted polymer [9,10], organic-based ligand precipitation [11],membrane and reverse osmosis processes [12]. The industrial utilization of these methods has been found to be limited, because of the high capital and operating costs and/or the ineffectiveness in meeting stringent effluent standards [13].

Electrochemical treatment methods are attractive since they can combine metal removal with metal recovery in its pure form, without sludge generation. The inherent advantage of this technology is its environmental compatibility due to the fact that the main reagent, the electron, is a 'clean reagent' [14, 15]. The increasing use of electrochemical technologies in the environmental treatment is due to the utilization of porous materials as three dimensional electrodes in the design of electrochemical cells [16]. One of the main advantages of this kind of electrode derives from the fact that it can provide high specific surface area as well as high mass transfer rate.Two principal configurations for the three dimensional electrodes have been developed: the flow-through configuration, where fluid flow and current are parallel; and the flow-by configuration, where the fluid flows perpendicularly to the current [17].Unfortunately the flow- through porous electrode has met with a limited success on the commercial scale in view of the non-uniformity of current and potential distribution, poor selectivity and low conversion per pass [18]. To avoid these shortcomings, attention has been directed to the flow-by electrode which has other advantages such as the possibility of using it in the form of a divided or undivided filter press type cell [18-23]. Several types of flow-by electrode have been proposed, for example, carbon or metal particles [24, 25], metallic or metal plated foams and felts [26, 27], and reticulated vitreous carbon [28]. The main drawback of these electrodes, however, is the fact that continuous metal deposition leads to clogging of the pores by the deposited metal. In addition, they suffer from the high pressure drop .Besides, flow-by fixed bed electrodes made of small particles, metal felt and metal foam may entrap gas bubbles(H_2) which are likely to evolve simultaneously with the main reactions from dilute solutions with a consequent increase in the cell resistance and electrical energy consumption [29].The use of screens and expanded metals in building three dimensional electrodes offers many advantages, such as high specific area, high turbulence-promoting ability, high porosity and relatively low pressure drop, ease of coating with a catalyst, and ready availability at modest cost [30]. In addition, they present a rigid structure and are relatively easy to construct.

Specifically for Pb (II) ions, several works on their removal from aqueous solutions using three dimensional electrode were reported [31-38] .In all these studies, experiments were carried out by changing one of the variables and fixing the others. However, the variables may interact strongly. These interactions can be determined using Taguchi design of experiment, which also allows determination of the optimal

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conditions, due to its capacity for extracting relevant information from the system under study [39]. Another advantage of the Taguchi design is the possibility to find the smallest number of experiments that must be carried out to obtain the desired information with statistically acceptable results.

In this work the removal of Pb (II) from a simulated wastewater was investigated under galvanostatic conditions using flow-by fixed bed electrochemical cell composed of a vertical stack of stainless steel screens. Moreover, independent variables such as initial concentration of Pb (II), current, flow rate, and mesh number were simultaneously studied through Taguchi design in order to obtain the best experimental conditions for removing Pb (II).The choice of stainless steel as cathode material is based on the observation of previous works that stainless steel has been proved to be very effective as a cathode for metal removal from wastewaters [40-43]. This material showed a good stability as cathode and could also be anodically polarized during its regeneration process without damage. Furthermore, stainless steel is an inexpensive material when compared to graphite felt or reticulated vitreous carbon (RVC) which have been extensively used in wastewaters treatment. The choice of a vertical orientation of stack is based on the observations of Storck et al.[19] and Mobarak et al.[44] that this geometry is better for scale-up as the current and potential distribution are uniform.

2 EXPERIMENTAL WORK

2.1 Materials and system

The dual continuous-flow cell design is shown schematically in Fig. 1. The system consists of an electrochemical cell, two (5liters) capacity Perspex reservoirs for the catholyte and the anolyte, two magnetic recirculation pumps(EHEIM kerisel), and two sets of flowmeters with a flow range from 60 to 480 l/h, for controlling the catholyte and anolyte flow rates. This arrangement enables the recirculation of anolyte and catholyte in two separated loop through the reactor in a batch recycle mode. The experiments were conducted at ambient temperature and under galvanostatic conditions. The current control was achieved by using a constant current source (Power Supply—model UNI-T: UTP3315TF-L).Cell current and potential were measured using multimeters type Pro'skit MT-1210 and MT-1280 respectively.

The design of flow-by cell in this study was established on the criteria recognized by Risch and Newman [45]. According to their criteria, a flow-by reactor with an aspect ratio of the electrode length to thickness, $L/t > 5$, will produce a maximum processing rate than a flow-through configuration. The aspect ratio of present cell is 33.33.The electrochemical cell shown in Fig.2 was basically a rectangular flow channel constructed from two machined blocks of poly tetrafluoroethylene(PTFE).The first is the cathodic chamber having external dimensions(30x14x2.5cm) while the second is the anodic chamber with dimensions(30x14x3.5cm).The anodic chamber has two cavities; internal (10x10x2.2cm)in which graphite block (10x10x2cm) working as anode was fixed and external (24x10x0.5cm) in which the anolyte is flowing over the anode upward. The anode was grooved lengthwise to increase its surface area. The cathode chamber has also two cavities; internal (10x10x0.6cm) in which copper plate (10x10x0.5cm) working as current feeder was fixed, and external (24x10x0.3cm) in which the catholyte passes through two stacks of screens: the first composed of seven polypropylene meshes with mesh number (30 wire/inch) working as calming zone. The second composed of five stainless steel screens (10x10 cm) working as flow-by cathode. The current feed to the electrodes was provided by screw connectors through the walls of the cell. A saturated calomel reference electrode within a Teflon Luggin capillary passes the cathode chamber through a 3mm-hole drilled at the back near the copper plate. The anodic and cathodic chambers were separated from each other by a cationic membrane (IONIC-64LMR) which was supported on both sides with 2mm thickness PTFE perforated plates. The cell was held vertically and the electrolytes were circulated upwards.

Chemicals used were $PbCl_2$, NaCl, and boric acid. All were reagent grade. The electrolytic solutions were freshly prepared with doubly distilled water, the testing containing metallic ions solutions were prepared in such a way that the metallic concentration was between 50-200 mg/l in supporting electrolyte consisting of 0.5M NaCl and 0.1 M H_3BO_3 with final pH of 5 adjusted by using NaOH or HCl. It is important to point out that such solutions were prepared trying to resemble the amount of metallic ions and pH of a typical composition contained in an effluent generated by a lead-acid batteries industry [46]. The catholyte reservoir was furnished by 4.0 liters of electrolytic solution containing the heavy metal ion while the anolyte reservoir was furnished with supporting electrolyte only at the same volume. The catholyte was purged with high purity nitrogen (99.999%) for 30 min, while a nitrogen atmosphere was maintained over the solution during the experiment to prevent contamination with oxygen. At predetermined times, the lead concentration was determined by sampling the catholyte and analyzing it by atomic absorption spectrometry (Varian SpectrAA 200 spectrometer) using an air/acetylene flame. The performance of electrochemical system for removing lead was studied by data analysis via Taguchi method based on same electrolysis time (40min).

Three stainless steel screens (316-AISL) were used with mesh numbers 30, 40, and 60 wire/inch respectively. Table1 shows the properties of the screens. The porosity of screen was calculated by measuring weight /area density of the screen and using Eq.(1), then the specific surface area was calculated according to Eq.(2)[47]:

$$\varepsilon = 1 - \frac{m_s}{\rho_s l a_s} \quad (1)$$

$$s = (1-\varepsilon) r \quad (2)$$

Where ε is the porosity, r the ratio of surface to volume of the wire forming the screen (cm^{-1}), $r=4/d$, m_s/a_s the weight /area density(g/cm^2), l the thickness of screen(cm),$l=2d$,ρ_s density of stainless steel316-AISL ($8.027 g/cm^3$)[48] and s the specific surface area (cm^{-1}).The woven type of screen was determined by using Olympus BX51M with DP70 digital camera system and the diameter of wire was measured by digital caliper.

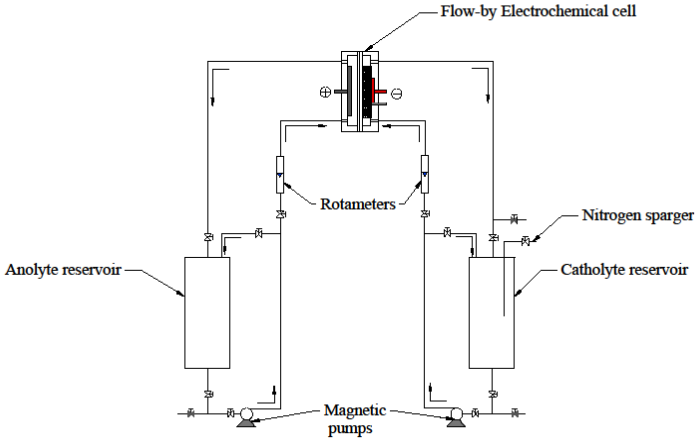

Fig.1. Schematic view of the batch recirculation electrochemical system

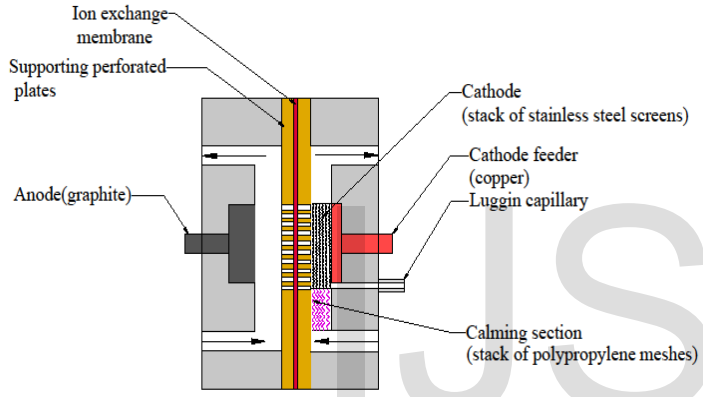

Fig. 2. The flow-by electrochemical cell

Table 1. Screen parameters

Mesh number wire/inch	**30**	**40**	**60**
Woven type	Plain square	Plain square	Full twill
Wire diameter(cm)	0.03	0.025	0.02
Weight/area density(g/cm^2)	0.1237	0.1224	0.1291
Screen porosity	0.7146	0.6889	0.6345
Specific area (cm^{-1})	38.055	49.810	73.099

The most important parameter in treatment of heavy metals is the applied current to the cell. Most of previous works did not explain the bases on which they selected the range of current used in the experimental design[49,50] .In the present study, the current was selected to be equal to the limiting current under which the reaction rate is maximum. Therefor linear voltagramms curves were proceeded under two conditions: case-1{[Pb] =50ppm, flow rate=3l/min, mesh no. 30wire/inch}, and case-2 {[Pb] =200 ppm, flow rate=7l/min, mesh no. 60wire/inch} as shown in Fig.3.These voltagramms were obtained by increasing the current stepwise and measuring the steady state cathode potential against a saturated calomel reference electrode. The limiting current is found at the middle point of a straight line that follows the plateau region and is limited by E_{max} and E_{min} [51].The limiting currents for reduction of lead at cases (1 and 2) were -0.58 and -1.2A respectively. The cathode potential related to these currents was -810 mV vs. SCE.

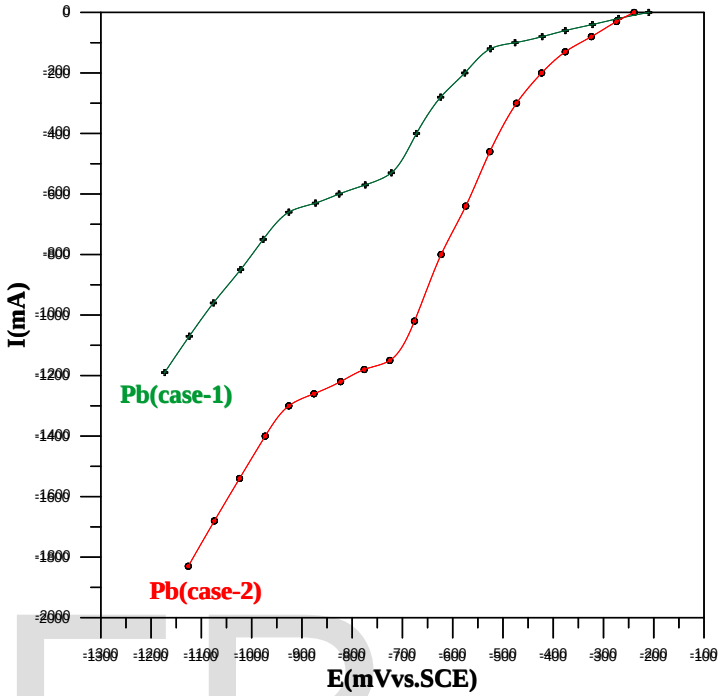

Fig. 3. Linear voltammetric curves for reduction of lead on the stack of stainless steel screens electrode Supporting electrolyte (0.5 M NaCl+0.1M H_3BO_3), pH=5, screens No. =5.

2.2 Taguchi Method

The traditional methods for experimental design are complex in nature and difficult to use. In addition, these methods require a large number of experiments when the process parameters increase. In order to minimize the number of experiments, a powerful tool has been designed for high quality systems by Taguchi. Taguchi approach has got high adoptability and can be applied with confined knowledge of statistics, hence gained wide popularity in engineering application [39]. The major steps required for the experimental design in this method are (1) determination the objective function, (2) identification the control factors and their levels, (3) selection the appropriate orthogonal array (OA), (4) experimentation, (5) analysis of the data and determination of the optimal levels, and (6) experimentation confirmation [52]. Four factors {initial concentration (C (0)), current (I), flow rate (Q), and mesh number of screen (N)} with three levels were selected as shown in Table 2. L_9 (3^4) standard orthogonal array presents in Tables 3 was employed. This array is most suitable to provide the minimum degrees of freedom as 9 {= 1 + 4 x (3–1)} required for the experimental exploration. With the selection of L_9 (3^4) orthogonal array, the number of experiments required is reduced to nine, which in classical combination method using full factorial experimentation would require3^4=81 number of experiments to find the influencing parameters [53].

Table 2. Control factors and their levels in the experimental design

Factors / level	C(0) (ppm)	I (A)	Q (l/min)	N (wire/inch)
1	50	0.58	3	30
2	125	0.89	5	40
3	200	1.2	7	60

Table 3. Taguchi L_9 (3^4) orthogonal array for lead removal

Factors / Exp. No.	Coded value				Real value			
	A	B	C	D	C(0)	I(A)	Q	N
1	1	1	1	1	50	0.58	3	30
2	1	2	2	2	50	0.89	5	40
3	1	3	3	3	50	1.2	7	60
4	2	1	2	3	125	0.58	5	60
5	2	2	3	1	125	0.89	7	30
6	2	3	1	2	125	1.2	3	40
7	3	1	3	2	200	0.58	7	40
8	3	2	1	3	200	0.89	3	60
9	3	3	2	1	200	1.2	5	30

To analyze the results, Taguchi method uses a statistical measurement of performance called signal-to-noise (S/N) ratio, where signal represents the desirable value (i.e. the mean for the output characteristic) and noise represents the undesirable value (i.e. the square deviation for the output characteristic). Therefore, the S/N ratio is the ratio of mean square deviation. Its unit is dB. The S/N ratio equation depends on the criterion for the quality characteristic to be optimized. There are many different possible S/N ratios, however, three of them are considered standard and are generally applicable in the most situations: larger is better (LTB), small is better (STB), nominal is better (NTB). In this study, the larger is better (Eq. 3) are removal efficiency and current efficiency while the small is better (Eq. 4) is energy consumption, the following relations are used for S/N calculations [39]:

$$\left(\frac{S}{N}\right)_{LTB} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right] \quad (3)$$

$$\left(\frac{S}{N}\right)_{STB} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}y_i^2\right] \quad (4)$$

Where n is the repetition number of each experiment under the same conditions for design parameters and y_i is the response of each experiment. A larger S/N noise ratio corresponds to better quality characteristics. Therefore, the optimal level of process parameters is the level of highest S/N ratio. The nine Taguchi experiments were conducted twice to ensure the reliability of experimental data for a signal-to noise analysis. Removal efficiency (RE), current efficiency (CE) and energy consumption (EC) were evaluated as follows [54]:

$$\mathrm{RE} = \frac{c_i - c_o}{c_o}\times 100 \quad (5)$$

Where C_i is the initial metal concentration (ppm), C_o the outlet metal concentration (ppm) after certain interval of time Δt(s).

$$CE = \frac{100 z_i . F \Delta m}{M_i I \Delta t} \quad (6)$$

Where z_i is the number of electrons; F the Faraday constant (96487Asmol^{-1}); Δm (g) the mass deposited at the interval of time Δt(s); M_i the molar mass (g/mol), I the applied current (A).

$$EC = \frac{2.788\times 10^{-4} VI\Delta t}{\Delta m} \quad (7)$$

Where V is the cell potential (V).

3 RESULTS AND DISCUSSION

Table 4 represents the L_9 orthogonal array results considering two replicates per run. The analysis of these results is made with the help of software package MINITAB-17and using general linear model. The base time for comparison was selected to be (40min) while the time of electrolysis of each run was 120 min.

Table 4. Results of experimental design for lead removal

Exp. No.	Final-Conc. (ppm)		Response					
			RE (%)		CE (%)		EC kwh/kg	
	Replica		Replica		Replica		Replica	
	1	2	1	2	1	2	1	2
1	9.6	7.4	79.66	84.43	10.06	10.65	11.3	10.7
2	5.8	6.8	88.07	86.0	7.46	7.29	19.4	19.9
3	2.2	4.0	95.43	91.68	5.94	5.71	29.2	30.4
4	12.5	16	89.80	87.18	29.44	28.58	3.96	4.07
5	6.0	10	95.0	91.67	19.88	19.19	7.42	7.69
6	2.9	8.5	97.62	93.02	15.37	14.64	11.3	11.8
7	16.4	22	91.55	88.66	47.53	46.03	2.29	2.36
8	8	16	95.83	91.67	32.09	30.7	4.59	4.80
9	5.3	13	97.29	93.36	24.63	23.63	6.93	7.34

The results indicate that current efficiency for lead removal is not higher than 50%. This may be attributed to the effect of side reaction (H_2 evolution) on the reduction of metal ion during the electrolysis process. Also since the operation is at constant current, the cathode potential will increase during the electrolysis leading to higher contribution of side reaction. Removal efficiency approaching 97% could be obtained at 40 min while a complete removal of lead was achieved at the end of electrolysis of each run

3.1 Analysis of signal-to-noise ratio

Table 5 shows the S/N ratios calculated based on Eqs. (3, 4) for all the responses of experiments presented in Table 4. The influence of each control factor on the responses is obtained from the response table (Table 6) which represented graphically in Fig. 4 respectively. The response table shows

the average of the selected characteristic for each level of the factors. It includes ranks based on delta statistics, which compare the relative magnitude of effects. The delta statistic is the highest average for each factor minus the lowest average for the same. Ranks are assigned based on delta values; rank 1 is assigned to the highest delta value, rank 2 to the second highest delta value, and so on [52]. With respect to main effect plot of S/N ratio, the x-axis indicates the value of each process parameter at three level, and the y-axis the response S/N values. The main effect plots are used to determine the optimal design conditions to obtain the optimal value of the responses.

Table 5. The S/N ratios for all responses

Exp. No.	RE (%)	CE (%)	EC(kwhkg^{-1})
	SN ratio	SN ratio	SN ratio
1	38.2701	20.2928	-20.8314
2	38.7920	17.3558	-25.8643
3	39.4161	15.2972	-29.4837
4	38.9350	29.2479	-12.0725
5	39.3966	25.8110	-17.5626
6	39.5757	23.5168	-21.2609
7	39.0914	33.3981	-7.3232
8	39.4330	29.9305	-13.4432
9	39.5785	27.6461	-17.0701

Table 6. Response Tables for Signal to Noise Ratios

RE (LTB)	Level	Conc. (ppm)	I (A)	Q (l/min)	N (wire/inch)
	1	38.83	38.77	39.09	39.08
	2	39.30	39.21	39.10	39.15
	3	39.37	39.52	39.30	39.26
	Delta	0.54	0.76	0.21	0.18
	Rank	2	1	3	4
CE (LTB)	1	17.65	27.65	24.58	24.58
	2	26.19	24.37	24.75	24.76
	3	30.32	22.15	24.84	24.83
	Delta	12.68	5.49	0.26	0.24
	Rank	1	2	3	4
EC (STB)	1	-25.39	-13.41	-18.51	-18.49
	2	-16.97	-18.96	-18.34	-18.15
	3	-12.61	-22.60	-18.12	-18.33
	Delta	12.78	9.20	0.39	0.34
	Rank	1	2	3	4

According to Table 6, current has the greatest influence on the removal efficiency followed by concentration, flow rate and mesh number, while concentration has the major effect rather than other variables with respect to current efficiency and energy consumption. It is clear that flow rate and mesh number have the lower and the same degree of effect on all responses. According to Fig.(4), the optimum levels of the controlling factors can be determined depending on the highest value of S/N ratio as shown in Table 7.

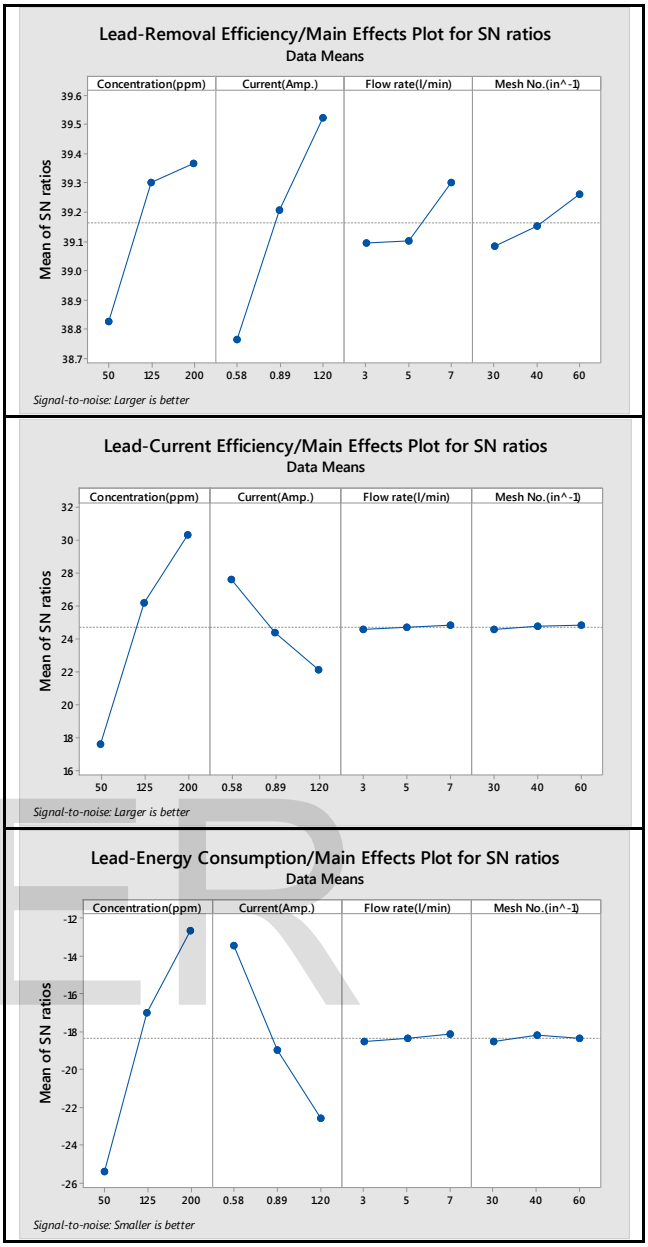

Fig. 4 Main effect plots **of SN ratios in lead removal**

Table 7. Optimum levels of the control factors

Response	Factors / level	C(0)	I	Q	N
RE (%)	1	200	1.2	7	60
CE (%)	2	200	0.58	7	60
EC(kwhkg^{-1})	3	200	0.58	7	40

3.2 *Analysis of Variance (ANOVA)*

ANOVA is a statistical technique, which can infer some important conclusions based on analysis of the experimental data. The method is very useful for revealing the level of significance of influence of factor(s) on a particular response. It separates the total variability of the response into contributions of each of the factors and the error [52, 55].The

analysis of ANOVA was performed by statistical package, Minitab-17 using general linear model. ANOVA table shows the sum of the square (SS), the degree of freedom (DF), adjusted sum of squares (Adj SS), adjusted mean of square (Adj MS), the percentage contribution of each parameter (Contrib.), F-value, and P-value. Percent contribution indicates the relative power of a factor to reduce variation. For a factor with a high percent contribution, a small variation will have a great influence on the performance [39]. Statistically, F-test provides a decision at some confidence level as to whether these estimates are significantly different. Larger F-value indicates that the variation of the process parameter makes a big change on the performance [56]. P-value determines the significant of each factor on response where value of less than 0.05 (for a confidence level of 95%) indicates that the factor is significant. The results of analysis of variance (ANOVA) are summarized in Table 8. The results show that the contribution of the four factors i.e. concentration of lead ion, current, flow rate, and mesh number in terms of removal efficiency were 28.52, 48.96, 4.23, and 2.35% respectively, while in terms of current efficiency were 73.01, 20.79, 3.03, and 3.04% respectively, and in terms of energy consumption were 64.85, 26.15, 4.4, and 4.5% respectively. It is clear that current has the greatest contribution on removal efficiency while concentration is the dominant variable in case of current efficiency and energy consumption. These observations are in consistence with the response table results.

Table 8. Analysis of Variance for lead removal

	Source	DF	SS	Contrib.	Adj SS	Adj MS	F-Value	P-Value
RE	C(0)(ppm)	2	108.464	28.52%	108.464	54.232	8.05	0.010
	I(A)	2	186.241	48.96%	186.241	93.120	13.82	0.002
	Q(l/min)	2	16.083	4.23%	16.083	8.042	1.19	0.347
	N(wire/inch)	2	8.924	2.35%	8.924	4.462	0.66	0.539
	Error	9	60.661	15.95%	60.661	6.740		
	Total	17	380.373	100 %				
	Model	S 2.596	R^2 84.05%	R^2(adj.)69.88%	Press 242.645	R^2(pred.) 36.21%		
CE	**Source**	**DF**	**SS**	**Contrib.**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
	C(0)(ppm)	2	2067.43	73.01%	2067.43	1033.72	2530.10	0.000
	I(A)	2	588.82	20.79%	588.82	294.41	720.60	0.000
	Q(l/min)	2	85.72	3.03%	85.72	42.86	104.91	0.000
	N(wire/inch)	2h	85.98	3.04%	85.98	42.99	105.23	0.000
	Error	9	3.68	0.13%	3.68	0.41		
	Total	17	2831.64	100%				
	Model	S 0.639	R^2 99.87%	R^2(adj.) 99.75%	Press 14.708	R^2(pred.) 99.48%		
EC	**Source**	**DF**	**SS**	**Contrib.**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
	C(0) (ppm)	2	803.10	64.85%	803.104	401.552	2740.89	0.000
	I(A)	2	323.85	26.15%	323.853	161.927	1105.27	0.000
	Q (l/min)	2	54.50	4.40%	54.501	27.251	186.01	0.000
	N (wire/inch)	2	55.69	4.50%	55.687	27.843	190.05	0.000
	Error	9	1.32	0.11%	1.319	0.147		
	Total	17	1238.46	100 %				
	Model	S 0.383	R^2 99.89%	R^2(adj.) 99.80%	Press 5.274	R^2(pred.) 99.57%		

The P-values indicate that all factors are significant with respect to current efficiency and energy consumption. While concentration, mesh number and flow rate appear to be insignificant with respect to removal efficiency.This behavior may be attributed to the fact the removal efficiency depends entirely on the driving force used to extract the metal from solution (applied current). The R^2 static, which is the measure of the proportion of the total variability explained by the model is close to (1) in two responses (current efficiency and energy consumption). The same behavior was obtained with respect to the adjusted R^2 which utilized to consider the model significance since it is useful when comparing the model with different number of terms. The results show that adj.R^2 is not significantly different from the ordinary R^2.The adequacy of the model can be predicted from the residual plots Fig. (5) [56]. The interpretations of each residual plot for the present experiments are given below:

- Normal probability plot indicates that the data are normally distributed and the variables are influencing the response. Outliers don't exist in the data.
- Residuals versus fitted values indicate that the variance is constant and a non-linear relationship exists.
- Histogram proves that the data are not skewed and no outliers exist.
- Residuals versus order of the data indicate that there are systematic effects in the data due to time or data collection order.

It can be concluded that all the values are within the control range, indicating that there is no obvious pattern and unusual structure and also the residual analysis does not indicate any model inadequacy.

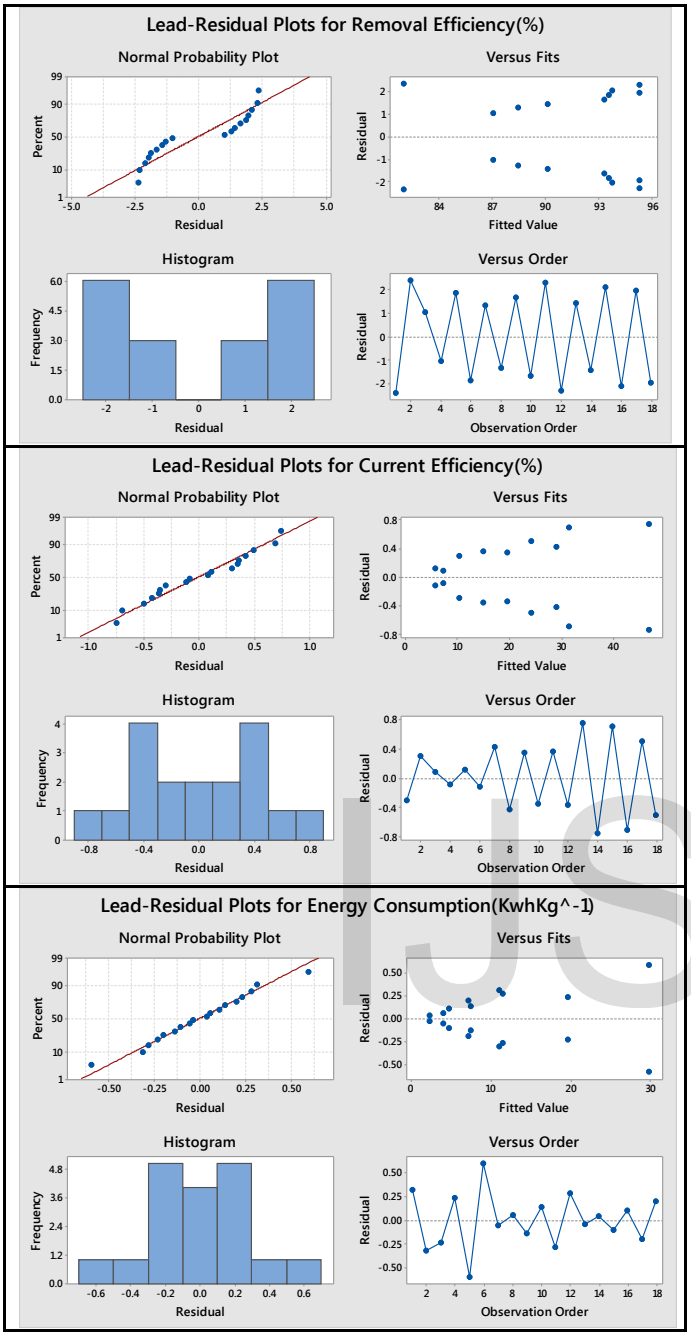

Fig. (5) Residual plots for lead removal

3.3 Confirmation Test

The confirmation experiment is the final step in the first iteration of the design of the experiment process. The purpose of the confirmation experiment is to validate the conclusions drawn during the analysis phase. The confirmation experiment is performed by conducting a test with a specific combination of the factors and levels previously evaluated. The confirmation experiment is a crucial step and is highly recommended by Taguchi to verify the experiment results. If the results of the confirmation runs are not consistent with the expected conclusions, a new Taguchi method design is required [39]. Table 7 shows three sets of optimum control factors levels could be adopted, the first is based on removal efficiency, the second on current efficiency while the third on energy consumption. Therefor a comparison between these optimum levels must be done to determine the suitable one to be adopted in confirmation test. From the electrochemical engineering point of view, the performance of electrochemical reactors is evaluated based on the fact that current efficiency and energy consumption of the process must be higher as possible as with respect to former and lower as low as possible with respect to later[56]. Since energy consumption is a linear function of current and voltage drop, it is recommended to adopt the comparison between the predicted values of current and removal efficiencies based on general linear model as shown in Tables (9, 10).The results of predicted values of removal efficiency (Table 9) show that level one gives higher removal efficiency (99%), while adopting the second or third levels lead to 90% removal efficiency. With respect to current efficiency, Table 10 indicates that current efficiency drops drastically when the first optimum level is adopted to about two third of its value in the second or third optimum levels. So the third optimum level of control factors should be adopted from economical point of view since it gives higher current efficiency. The third level is the condition of run 7 in the experimental design, however a new experiment based on these conditions was achieved to confirm the results of run 7 as shown in Table 11. A comparison between experimental value and predicted value of current efficiency showing an error of less than 5%, thus design of experiments by Taguchi method was successfully used to predict the performance of lead removal using a flow-by electrochemical cell.

Table 9. The predicted values of removal efficiency for optimum levels of control factors

Optimum level	Control factor				Predicted removal efficiency (%)		
	C(0)	I	Q	N	Fit	95% CI	95% PI
1	200	1.2	7	60	99.069	94.916; 103.221	91.876; 106.261
2	200	0.58	7	60	91.217	87.064; 95.37	84.024; 98.41
3	200	0.58	7	40	90.103	85.950; 94.256	82.910; 97.296

Table 10. The predicted values of current efficiency for the optimum levels of control factors

Optimum level	Control factor				Predicted current efficiency (%)		
	C(0)	I	Q	N	Fit	95% CI	95% PI
1	200	1.2	7	60	32.073	31.051; 33.095	30.302; 33.844
2	200	0.58	7	60	45.802	44.78; 46.825	44.031; 47.573
3	200	0.58	7	40	46.781	45.759; 47.803	45.010; 48.552

Table11. Result of confirmation test based on current efficiency

Optimum Control factors				Exp. RE%	Exp. CE%	Pred. CE%	%Error
C(0)	I	Q	N				
200	0.58	7	40	89.7	48.5	46.78	3.544

Comparing results of the present work (Table12) with those previously obtained by Almeida et al.[57,58] using response surface methodology under galvanostatic mode and Gasparotto et al. [59] under potentiostatic mode, it is evident that the Taguchi method helped to obtain an improved electrochemical system performance. Two changes in the electrochemical cell design (using flow-by configuration and screens cathode) improved the turbulence promotion of the present system and leading to increase mass-transfer rate. The present electrochemical cell design has the ability to reduce the concentration of lead from 200ppm to less than 20ppm at 40min with energy consumption (2.43 kwhkg^{-1}) which is more economic in comparison with previous studies. On the other hand, complete removal of Pb (II) starting from 200ppm could be obtained at 120 min with current efficiency (25%) which is more economic in comparison with that obtained by Gasparotto et al. [59]using flow-through cell design in potentiostatic mode. Therefore the present design gives higher performance than those previously used in lead removal.

Table 12. Comparison of Pb (II) removal from diluted solution using flow-by cell (present work) with flow-through cell operating in galvanostatic and potentiostatic mode (previous work).

Method	C(0) (ppm)	$t_{90\%}$ (min)	CE (%)	RE (%)	EC (kwhkg^{-1})
Galvanostatic [this work]	200	40	48.5	89.7	2.34
Galvanostatic [57][a]	50	30	35	98	1.5
Galvanostatic [58][b]	50	25	22	93	4.1
Potentiostatic [59][c]	50	42	17	81	5.3

[a] At 70 mA and 200 L h^{-1}, [b] at –0.25 A and 250 L h^{-1} by using a factorial design, [c] at –0.90 V vs. SCE and 250 L h^{-1}

4 Conclusion

The present study provides a practical, efficient, rapid and inexpensive way of treating wastewater containing lead ions. The use of Taguchi design was useful for the optimization of the electrolytic removal process in a relatively small number of experiments; the conditions predicted by the developed models are in good agreement with the experimental results, as confirmed by variance analysis. According to the experimental and statistical analyses, concentration and current have the major effect on the electrochemical cell performance while the flow rate and mesh number did not substantially affect it.Three sets of optimum control factors levels were obtained via application Taguchi design, the first is based on optimization of removal efficiency, the second based on current efficiency while the third based on energy consumption. It may be concluded that removal efficiency higher than 99% could be achieved if the first optimum level is adopted but with a large drop in current efficiency (32 %) while 90% removal efficiency could be achieved at 40 min with current efficiency approaching 50% if the third optimum level is adopted. Current efficiency higher than 50% could not be achieved whatever the conditions to be used because of the effect of side reaction (H2 evolution).The used electrochemical reactor presented economic advantages when comparing the energetic cost of recovering Pb ions to other commercial processes. Therefore the cell design used in this study showed a good performance in the removal of lead from simulated effluents.

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