# Evaluation of electrocoagulation process performance with anionic polyelectrolit in the removal of Mn (II) and Fe (II) from surface water - application of response surface methodology (RSM)

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## ABSTRACT

*Electrocoagulation is an electrochemical method for treatment of water and wastewater. The present study has been evaluated the performance of electrocoagulation method with anionic polyelectrolit in batch mode for removal of iron and manganese from surface water. Soleymanshah dam of sonqor located in the northeastern part of Kermanshah Province, Iran. The water of this dam contains high level manganese. The design of experiments was based on a central composite design (CCD), and the analyze of data carried out using response surface methodology (RSM). According to the analyze of the process, the effects of significant variables such as voltage (5-25), reaction time (20-60), temperature (10-30), anionic polyelectrolit (0.1-0.3 mg/L) on the removal efficiency of iron and manganese from surface water were investigated, using aluminium electrodes at natural pH. Iron and manganese concentrations and aluminum residual in the treated water were measured using inductively coupled plasma. The results of the ANOVA analysis showed that the model fitted well with manganese and iron reduction. At the optimum conditions (voltage of 5 volt, reaction time of 20 min, temperature of 10 °C and anionic polyelectrolit 0.3 mg/L). In this condition, manganese and iron removal were 77.5%, 75% respectively and aluminum residual in treated sample was 0.154 mg/L. The results showed that electrocoagulation process with anionic polyelectrolit is an effected method for manganese and iron removal from surface water.*

**Key words:** electrocoagulation, anionic polyelectrolit, surface water, manganese, iron, aluminum electrode, response surface method.

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## INTRODUCTION

The accessibility of safe drinking water is a high priority subject for human existence and quality of life. Surface water is one of the major drinking water sources in throughout the world. In effect of contact with the soil surface,

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water will contain some impurities. Therefore, the quality of surface waters will depend on the environment of the catchment [1].

Among the inorganic elements entered naturally and artificially into water resources, iron and manganese are very important [2]. Iron and manganese, which are the most abundant metals in the earth's crust, occur naturally in water resources. Water penetration through soil can dissolve minerals containing manganese and iron [3]. Iron and manganese compounds are in the water as sulfates, carbonates, chloride, phosphates and also in the form of humic compounds [4]. These elements are usually present in water as divalent ions ($Fe^{+2}$ and $Mn^{+2}$) [5]. According to the Safe Drinking Water Act (SDWA), drinking water standards for iron and manganese are 0.3 mg/L and 0.05 mg/L, respectively [6]. At values higher than standard levels of iron and manganese, water quality problems such as metallic taste, odor and brown color, stain and deposition of iron and manganese precipitates in the water distribution systems will be created [7, 8]. These compounds in wastewater cause colouration and also represent a serious risk to aquatic life. In addition, their presence in drinking water constitutes a potential human health hazard Physicochemical methods such as lime softening, ion exchange and oxidation followed by filtration with different agents have been successfully tested for the elimination of these metals from water [2, 9]. However, these methods often lead to secondary products that are not significantly eliminated by the same technique and can be more hazardous than the original compound. The oxidation of manganese by aeration is a slow process in natural pH [10]. Therefore, manganese oxidation is conventionally done by a strong oxidant such as chlorine, hypochlorite, potassium permanganate, chlorine dioxide or ozone [11]. Disadvantages of chemical treatments are high costs, neutralization of the effluent and problems of sludge disposal [12]. The need to disinfect and safe drinking water and also disadvantages of mentioned methods has encouraged both researchers and engineers to develop new and cost-effective methods for Mn and Fe removal [13].

Among the different techniques presented to eliminate heavy metals from water solutions, the coagulation procedure has proved to be very efficient. The coagulation usually follows a precipitation step occurring after an increase of pH obtained by addition of NaOH or lime. Coagulation is accomplished by adding coagulants like iron chloride $FeCl_3$ or aluminum sulfate $Al_2(SO_4)_3$ to the medium. Electrocoagulation pretreatment is an alternative to conventional chemical coagulation, where the ions responsible for the coagulation, mainly $Fe^{3+}$ or $Al^{3+}$, are in situ generated by the anodic dissolution of iron or aluminum electrodes. The advantages of electrocoagulation over conventional chemical coagulation include (1) no alkalinity consumption, (2) no change in bulk pH, (3) the direct handling of corrosive chemicals is nearly eliminated and (4) can be easily adapted for use in portable water treatment units especially during emergencies.

In the recent years, electrocoagulation process has been used for the removal of oil and grease [15] chemical oxygen demand (COD) [16], dyes [17], heavy metals [18], turbidity [19] and microorganisms from drinking water and wastewaters [20]. The removal mechanisms of contaminant in electrocoagulation process may involve coagulation, oxidation, reduction, decomposition, deposition, absorption, adsorption, sedimentation and flotation [21]. When a direct current is applied to the electrodes, the anode electrode is dissolved by electrolysis, and generates metallic ions which are good coagulants [22]. At the cathode electrode, the $OH^-$ ions are produced during water electrolysis and can react with the metallic ions and produce metal hydroxides [23, 24]. The metal hydroxides produced ($Al(OH)_3$ or $Fe(OH)_3$) can adsorb and settle both soluble and colloidal contaminants.This study evaluations electrocoagulation process and anionic polyelectrolit (with Aluminum electrode) in the removal of Mn (II) and Fe (II) from surface water by application of response surface methodology (RSM).

**EXPERIMENTAL SECTION**

**2.1. Experimental**
Water samples were taken from the Soleymanshah dam located in northeastern of Kermanshah province, Iran. Water sampling was carried out according to the instruction mentioned in the book for standard techniques of water and wastewater experiment [25]. Physicochemical properties of the water of the soleymanshah dam are presented in Table1. The pH of samples was constant. Before any experiment, the temperature was adjusted to the values stated in the experimental design. After the treatment process was added anionic polyelectrolit with low rapid mixing and samples were filtered with whatman filter paper of 0.45 μm in order to remove the flocs. Then the filtered samples were analyzed for iron, manganese and aluminum residual.

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**Table1. Properties of water sample**

| Rows | Parameter | Quantity range |
|------|-----------|----------------|
| I | Manganese (mg/L) | 0.1- 0.582 |
| II | Iron (mg/L) | 0.09- 0.2 |
| III | Total hardness(mg/L caco$_3$) | 180-240 |
| IV | Total alkalinity(mg/L caco$_3$) | 180-247 |
| V | Turbidity (NTU) | 0.5-0.8 |
| VI | EC (µs/cm) | 484-539 |
| VII | pH | 7.6- 8 |

**2.2 Electrocoagulation (EC) reactor configuration**
Electrical coagulation operation of water samples was carried out in a Plexiglas reactor (with dimension of 20×20×20cm and effective volum 3 lit) in a batch mode. The EC reactor was equipped to a stirrer. Four electordes with dimensions of 30×30×1mm made of aluminum plates were connected to a digital DC power supply (MICRO,PW-4053S,Iran) in Bipolar-Series connection mode. The distance between electrodes in electrocoagulation cell was 30 mm in all experiments. Before each run, organic impurities and the oxide layer on electrode surfaces were removed by sand paper and then were dipped in a HCL solution for 5 min.

**1.Digital D.C.power supply**
**2.Aluminum electrodes**
**3. water sample**
**4.stirring**
**5. electrocoagulation reactor**
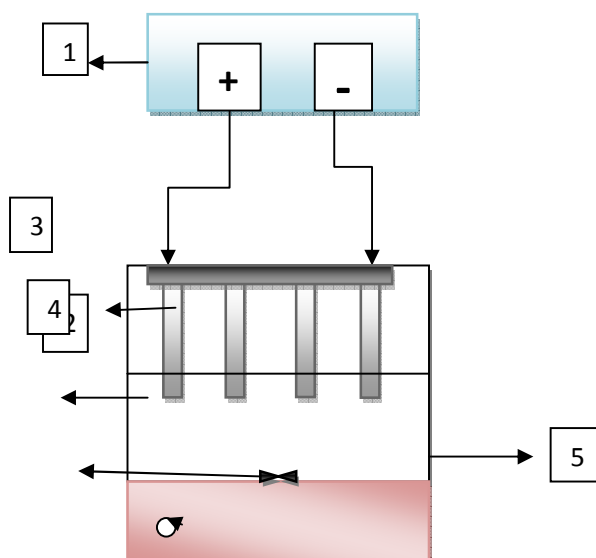


**Fig1. schematic diagram of the electrocoagulation reactor**

**2.3. Analytical methods**
The residual iron, manganese and aluminum in the water samples were determined using inductively coupled plasma (Perkin Elmer, Optima 7300 DV). pH was measured with Microprocessor pH 537.

**2.4. Experimental design**
In this study, the Design Expert Software (Stat-Ease Inc., version 6.0.6) was used for the data analysis and design of experiments. The RSM employed in the current study was a central composite design (CCD) involving four different factors, voltage (A), temperature (B) anionic polyelectrolit (C) and reaction time (D). The region of exploration for the process was taken as the area enclosed by voltage (5-25 V), reaction time (20-60 min), temperature (10-30˚C), anionic polyelectrolit (0.1-0.3 mg/L) boundaries (Table 2) . The Mn and Fe removal were evaluated based on the CCD experimental plan. The design consisted of 2k factorial points augmented by 2k axial points and a center point where k is the number of variables. The levels of four operating variables vary from a low to high value which are numerically expressed or coded as   -1.5 and 1.5. Intermediate level is coded as ''0''. These five levels were assessed based on the full facecentered CCD experimental plan. Accordingly, a total of 30 experiments were employed in this work, including 25 experiments designed in a factorial design (including 12 factorial points, 12 axial points and 1 center point), and 5 replications at the center point to get good estimate of

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experimental error. Repetition experiments were conducted after other experiments followed by order of runs designed by central composite design (CCD) as indicated in Table 2.

**Table 2. Range and levels of the variables**

| Variable | Range and levels | | | | |
|---|---|---|---|---|---|
| | -1.5 | -1 | 0 | 1 | +1.5 |
| A, Voltage | 5 | 10 | 15 | 20 | 25 |
| B, Temperature | 10 | 15 | 20 | 25 | 30 |
| C, Anionic polyelectrolit | 0.1 | 0.15 | 0.2 | 0.25 | 0.3 |
| D, Reaction time | 20 | 30 | 40 | 50 | 60 |

**Table3. Experimental conditions and response values of central composite design**

| Run | Variables | | | | Response | | |
|---|---|---|---|---|---|---|---|
| | Voltage (volt) | Temprature | Anionic polyelectrolit | time | Fe removal% | Mn removal% | Residual Al (mg/L) |
| 1 | 5 | 10 | 0.1 | 20 | 73.3% | 75% | 0.184 |
| 2 | 5 | 10 | 0.1 | 60 | 75% | 77.5% | 0.309 |
| 3 | 5 | 10 | 0.3 | 20 | 75% | 77.5% | 0.154 |
| 4 | 5 | 10 | 0.3 | 60 | 76.6% | 80% | 0.228 |
| 5 | 25 | 10 | 0.1 | 20 | 76.6% | 81.25% | 0.392 |
| 6 | 25 | 10 | 0.1 | 60 | 78.3% | 82.5% | 0.455 |
| 7 | 25 | 10 | 0.3 | 20 | 78.3% | 82.5% | 0.465 |
| 8 | 25 | 10 | 0.3 | 60 | 81.6% | 85% | 0.501 |
| 9 | 15 | 15 | 0.2 | 40 | 76.6% | 81.25% | 0.586 |
| 10 | 15 | 20 | 0.2 | 30 | 58.3% | 80% | 0.443 |
| 11 | 15 | 20 | 0.2 | 40 | 63.3% | 82.25% | 0.474 |
| 12 | 15 | 20 | 0.2 | 50 | 66.6% | 85% | 0.48 |
| 13 | 15 | 20 | 0.15 | 40 | 60% | 82.5% | 0.617 |
| 14 | 15 | 20 | 0.25 | 40 | 63.3% | 85% | 0.607 |
| 15 | 10 | 20 | 0.2 | 40 | 55% | 77.5% | 0.486 |
| 16 | 20 | 20 | 0.2 | 40 | 65% | 86.2% | 0.477 |
| 17 | 15 | 25 | 0.2 | 40 | 61.6% | 85% | 0.584 |
| 18 | 5 | 30 | 0.1 | 20 | 70% | 76.2% | 0.305 |
| 19 | 5 | 30 | 0.1 | 60 | 73.3% | 78.75% | 0.39 |
| 20 | 5 | 30 | 0.3 | 20 | 68.3% | 78.75% | 0.334 |
| 21 | 5 | 30 | 0.3 | 60 | 73.3% | 82.5% | 0.434 |
| 22 | 25 | 30 | 0.1 | 20 | 71.6% | 80% | 0.831 |
| 23 | 25 | 30 | 0.1 | 60 | 78.3% | 88.75% | 0.861 |
| 24 | 25 | 30 | 0.3 | 20 | 70% | 87.5% | 0.732 |
| 25 | 25 | 30 | 0.3 | 60 | 76.6% | 93.75% | 0.869 |
| 26 | 15 | 20 | 0.2 | 40 | 63.3% | 82.5% | 0.474 |
| 27 | 15 | 20 | 0.2 | 40 | 63.3% | 81.25% | 0. 47 |
| 28 | 15 | 20 | 0.2 | 40 | 63.3% | 80% | 0.472 |
| 29 | 15 | 20 | 0.2 | 40 | 65% | 81.25% | 0.471 |
| 30 | 15 | 20 | 0.2 | 40 | 65% | 82.5% | 0.474 |

## 2.5 Mathematical modeling

RSM involves screening and codification of the variables, mathematical-statistical treatment of data, and evaluation of the fitted model and the determination of the optimal conditions. RSM describes a model in the form of Eq. (1) to fit the experimental data and by optimization; the coefficients for the model were calculated. The relationship between the responses, input and the quadratic equation model for predicting the optimal variables were identified using the following:

$$Y = \beta_0 + \beta_i X_i + \beta_j X_j + \beta_{ii} X_i^2 + \beta_{jj} X_j^2 + \beta_{ij} X_i X_j + \ldots$$

where, Y, i, j, ., X are process response, linear coefficient, quadratic coefficient, regression coefficient and coded independent variables, respectively. All these coefficients variables are analyzed using multiple regression analysis. The response contour plot will be generated using DOE. Model terms are selected or neglected based on the probability of error (P) value with 95% of confidence level. The results obtained from CCD were examined by the analysis of variance (ANOVA). Three-dimensional (3D) plots and their respective contour plots were obtained based on the effect of the levels of the two factors. Therefore, the results of CCD can be presented in 3D

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presentations with contours. This will help to study the simultaneous interaction of the 2 variables on the responses. The experimental conditions and results are depicted in table 3.

## RESULTS AND DISCUSSION

### 3.1. RSM model fitting
The results of iron and manganese removal were described with quadratic and linear polynomial model. In this study, according to the P-values, significant model terms for iron and manganese removal are coded variables (A, B, C, D).

The regression equations based on the coded factors are equations (1), (2) and (3):

$$Mn\ removal,\ \% = +82.16 + 3.90A + 1.93B + 1.44C + 1.67D \tag{1}$$

$$Iron\ removal\ \% = 64.26 + 1.76\ A - 2.16B + 0.30C + 2.06D - 8.27A^2 + 38.93B^2 - 11.67C^2 - 8.47D^2 - 0.83B\ C + 0.83\ BD \tag{2}$$

$$Al\ residual,\ mg/l = +0.51 + 0.17\ A + 0.13B + 0.041D + 0.28\ C^2 - 0.32D^2 + 0.056A\ B \tag{3}$$

ANOVA results of the linear and Quadratic model in Table 4 showed that the model could describe the manganese and iron removal under operating conditions. This Table demonstrates that the linear model was significant at 95% confidence level with P-values (0.0001). P-values less than 0.05 shows that model terms are significant. In this case A, B, C, D are significant model terms for manganese and iron removal. In the present study, correlation coefficient ($R^2 = 0.86$) and ($R^2 = 0.96$) were obtained for manganese and iron removal, respectively. Correlation coefficient or $R^2$ explained good fit of the model. In the model, the measure of the signal to noise ratio is Adeq Precision. A ratio greater than 4 was desirable. In this study, Adeq Precision was desirable for both responses in the model, and ratio of 27.56 and 21.4 for manganese and iron removal indicate an adequate signal. In the model, the low value of the coefficient of variation indicated high precision and a good reliability of the experimental results (for manganese CV=1.93 %), (for iron CV = 2.2%).

**Table 4. The results of ANOVA for fit of resposes removal efficiency using central composite design**

| Model | Significant model terms | P-value | F-value | F-value Probability for lack of fit | standard deviation | CV | $R^2$ | adjusted $R^2$, | Adeq. precision | PRESS |
|---|---|---|---|---|---|---|---|---|---|---|
| Mn removal % Linear Model | A, B, C, D | < 0.0001 | 38.90 | 0.13 | 1.59 | 1.93 | 0.86 | 0.83 | 27.56 | 93.51 |
| Fe removal % Quadratic Model | A, B, C, D | < 0.0001 | 90.75 | 0.073 | 1.54 | 2.2 | 0.96 | 0.94 | 21.4 | 139.88 |
| Al residual mg/L Quadratic Model | A, B, C, D | < 0.0001 | 49.03 | < 0.05 | 0.053 | 10.97 | 0.92 | 0.90 | 25.92 | 0.097 |

### 3.2. Reactions during the electrocoagulation process
According to Faraday's law, reaction time and current density have direct effect on the amount of metal ions delivered into the system [23, 26]. In Table 3, it has been reported that an increase in the voltage and reaction time leads to an increase in the aluminum dissolving. Fig 3 indicates the amount of dissolving aluminum into the system after treatment by different temperatures. It is observed that as temperature increases aluminum dissolving increases, and also iron and manganese removal are affected.

### 3.3. Effect of the variables studied
### 3.3.1. Effect of current density and operation time
The current density is an operational parameter in electrocoagulation process that can be controlled directly. This parameter determines coagulant production dosage and the rate of the bubble generation [13]. In the literature, it has been reported that in the EC process, current density is an affecting factor in the treatment [23]. It has also been found that current density does not have an effect on pollutant removal [18]. Therefore, in order to investigate the

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effects of this factor in the present study, the design of the experiments were carried out with a voltage in the range of 5 to 25V. The Voltage had an important effect on the energy consumption and operational cost.

Fig 2(a,c) and fig 3(a) shows the removal of Fe (II), Mn (II) and aluminum residual from surface water as a function of voltage and time. Fig 2(a) shows that an increase in the voltage and reaction time increases iron removal efficiency. Fig 2(c) shows that an increase in the voltage and reaction time increases manganese removal efficiency. This figure also indicates that the higher current density has greater effect on manganese removal. Similar results for the effect of current density on removal efficiency were found by Kobya et al. during the treatment of potable water containing low concentration of arsenic [23] and Ghosh and et al in the removal of Fe(II) from tap water [27]. According to Table 3, a maximum manganese and iron removal was obtained 93.75%, 81.6% respectively. when using voltage 25 V and the reaction time of 60.
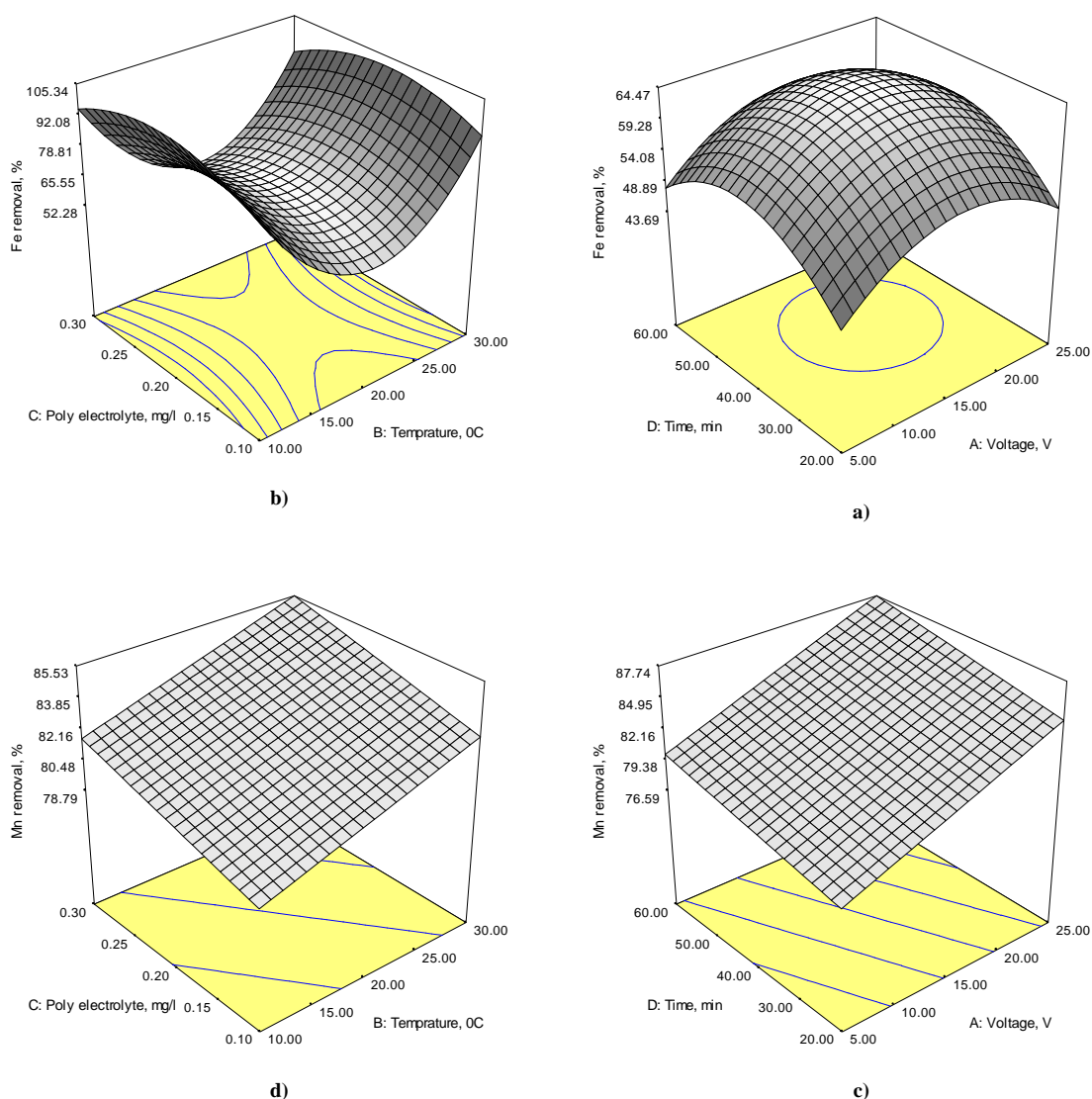


**Fig 2.(a, c) The response surface of iron and manganese removal efficiency (%) as the function of voltage (volt) and reaction time (min). (b,d) as the function of temperature (°C) and polyelectrolit (mg/L)**
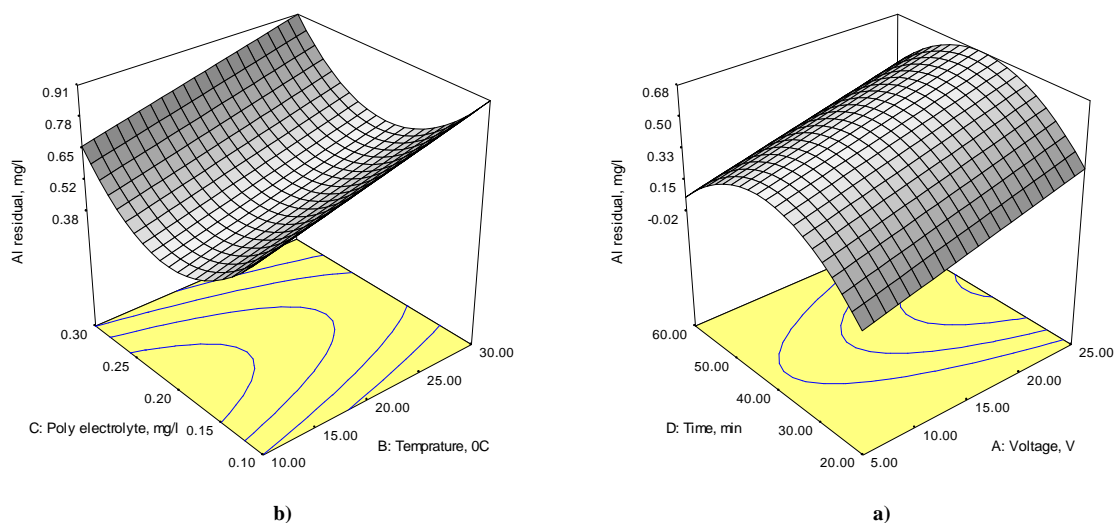
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**Fig 3.(a) The response surface of aluminum residual (mg/L) as the function of voltage (volt) and reaction time (min). (b) as the function of temperature (°C) and polyelectrolit**

### 3.3.2. Effect of anionic polyelectrolit
The results of Table 3 show that the removal efficiency of iron and manganese, increased with an increase in the anionic polyelectrolit. Also aluminum residual decreased. In the model, anionic polyelectrolit was a significant term at iron and manganese removal from surface water and decrease of aluminum residual.

### 3.3.3. Effect of temperature
The water temperature has an influence on the electrocoagulation process.The temperature was one of the significant terms of this study. In this model, the rate of anode dissolving at the range of temperatures (10 to 30Ċ) was investigated. The significant effect of temperature on the dissolving aluminum is presented in Table 3. As temperature increased aluminum dissolving increased during the experiments. Fig 2(b,d) indicate the removal of Fe (II) and Mn (II) as a function of temperature and anionic polyelectrolit. It is observed that the manganese removal efficiency, increased with an increase in the temperature, but decreased the iron removal efficiency . Because of that dissolved oxygen decreased with an increase in the temperature and decreased oxidation of $Fe^{+2}$ to $Fe^{+3}$. Similar results were found by Mikko Vepsalainen et al. In an investigation of the effects of temperature and initial sample pH on the natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM). In this research temperature had significant effects on aluminum dissolving and DOC removal [28].

## CONCLUSION

In this study, using RSM model, the effects of variables (voltage, temperature, anionic polyelectrolit and reaction time) on the removal of iron and manganese from surface water by electrocoagulation method have been investigated. ANOVA results of the model showed that there is a satisfactory adjustment between the experimental data and model for iron and manganses ($R^2$=0.96), ($R^2$=0.86) respectively. Maximum iron and manganese removal from surface water were obtained as 81.6%, 93.75% respectively. In this condition, aluminum residual in the treated water was greater than the drinking water standard. According to WHO standard for drinking water, the residual aluminum rate in drinking water should be less than 0.2 mg/L. Therefore, in order to achieve an optimized condition, both the rate removal of Fe (II) and Mn (II), and dissolving aluminum value in water from anode electrode are important. Optimum condition for iron and manganese removal from surface water was voltage of 5 V, reaction time of 20 min, anionic polyelectrolit 0.3 mg/L and temperature of 10 Ċ. In this condition, iron and manganese removal were 75%, 77.5% respectively, and the aluminum residual in the treated water was 0.154 mg/L. In this regard, basin system is in the bottom part of dam, the water temperature of the bottom of dam is always less than 10 Ċ, since the optimum temperature of water during all the seasons of year is 10 Ċ.

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This condition was appropriate for cold weather. Aluminum residual of this condition in warm weather was 0.3mg/L, thus in warm weather reaction time should be less than 20 min.

Electrocoagulation process with anionic polyelectrolit is an adequate method for pollution water to iron and manganese with low turbidity .

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