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Improvement of electrocoagulation process on hexavalent chromium removal with the use of polyaluminum chloride as coagulant

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ABSTRACT

In the first phase of this study, effects of different parameters, including initial pH, applied current density, reaction time and initial chromium concentrations on the chromium removal efficiency, were investigated in electrocoagulation process. The results showed that the maximum removal efficiency of 78.8% was achieved at pH 3, current density of 12.5 mA/cm^2, and initial concentration of 50 mg/L. In the next phase, effect of adding polyaluminum chloride—as a conventional coagulant—to electrocoagulation process in order to have higher chromium removal efficiency and lower energy and electrode consumption was assessed. According to the results of this phase, the increase in polyaluminum chloride dosage to 1250 mg/L was beneficial for enhancing hexavalent chromium removal efficiency from 60.2 to 96.4% at pH 7, current density of 8.33 mA/cm^2 and initial concentration of 50 mg/L. Furthermore, adding PACl to the process led to reduction of considerable amount of energy and electrode mass depletion in comparison with the electrocoagulation process. In the last phase, response surface methodology (RSM) was employed to optimize five operating variables. According to the analysis of variance results, the R^2 values of 99.3% for chromium removal efficiency indicating that the accuracy of the polynomial model is acceptable. The optimum value of initial pH, current density, initial chromium concentration, reaction time and dosage of polyaluminum chloride were 5, 8.33 mA/cm^2, 50 mg/L, 40 min and 1000 mg/L, respectively. Chromium removal of 93% was observed in the experiment at optimum conditions, which was close to the model predicted result of 87.27%.

Keywords: Chromium removal; Electrocoagulation process; Synthetic wastewater; Aluminum electrodes; Polyaluminum chloride; Response surface methodology

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1. Introduction

Wastewater effluents containing hexavalent chromium (Cr^{6+}) come from different industrial activities such as plating facilities, power plants, mining, electrical equipment manufacturing, leather and wood industry, chemistry, surface treatment or production of fertilizers [1,2]. Hexavalent chromium which is primarily present in the form of dichromate

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$Cr_2O_7^{2-}$ and chromate CrO_4^{2-} poses significantly higher level of toxicity than the other valence states [3], and they have become a serious health concern due to its release into the environment. Exposure to chromium can cause cancer in lungs and may cause epigastria pain, vomiting, and severe diarrhea [4]. In animals, chromium can also cause respiratory problems, a lower ability to fight disease, birth defects, infertility, and tumor formation [5].

The chromium concentration in various wastewaters is variable from 50 to 700 mg/L [6–9], and in some areas which support many industrial activities, concentrations of chromium were found in the range of 0.033–5.25 mg/L in surface waters and ground waters [10,11]. According to WHO and EPA's standard limit, allowable amount of hexavalent chromium in drinking water is 0.05 [12] and 0.1 mg/L [13], respectively.

There are many techniques for the treatment of Cr^{6+}-containing industrial wastewater such as membrane separation [14], electro-flotation [15], adsorption [16], and nanofiltration [17]. Some of these techniques have limitations in selective separation and they have problems associated with high investment and operation costs [14]. Another method that has attracted great attention in wastewater treatment is electrocoagulation (EC), which has been successfully used to remove different kinds of pollutants [18–21]. Electrocoagulation method using Al electrode has attracted significant attention for chromium removal process because of its operational simplicity [22].

The mechanism of electrocoagulation is especially dependent on the chemistry of the aqueous medium, include particle size, pH, and chemical constituent concentrations. The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as Al^{3+} and $Al(OH)_2^+$ at low pH, which at appropriate pH values are transformed initially into $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$ according to the following reactions:

$$Al \rightarrow Al^{3+}(aq) + 3e^- \tag{1}$$

$$Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+(aq) \tag{2}$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \tag{3}$$

However, depending on the pH of the aqueous medium, other ionic species such as $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ and polymeric Al^{3+} hydroxo complexes may also be present in the system. Hydroxo cationic complexes can effectively remove pollutants by enmeshment in a precipitate and by adsorption to produce charge neutralization [23].

Polyaluminum chloride as a conventional coagulant uses in water/wastewater treatment plants in some countries [24–28]. The PACl contains a range of large hydrolysis and polymeric species, which carry a high cationic charge [29]. Surface activity and charge-neutralizing capacity of PACl may make it effective in electrocoagulation process. The greater size of particles and better settleability are other advantages of PACl application [30].

Response surface methodology (RSM) is an intelligent technique for developing, improving, and optimizing the process that can be eliminated limitations of classical experiments such as time-consuming and large number of experiments [31–33]. RSM for process optimization with coagulant such as PACl in conjunction with electrocoagulation process in an attempt to reach higher chromium removal efficiency and lower energy consumption has been rarely intended in the recent researches.

The study was performed in three phases. In phase 1, electrocoagulation was used alone for the removal of hexavalent chromium. For this purpose, the effect of different parameters including initial pH, applied current density, reaction time, and initial chromium concentrations on the chromium removal efficiency was examined. In the second phase, the performance of PACl as a coagulant in conjunction with electrocoagulation process was assessed. Finally, in phase 3, optimization through RSM was applied for chromium removal efficiency with the aid of PACl.

2. Materials and methods

A plexiglas tank having dimensions of 13 × 15 × 18 cm with the effective volume of 2.5 L was employed for present study. Four Al plate electrodes (Arak Co. (Iran), 99% purity) with total effective area of 240 cm^2 were used as electrodes. Thickness of aluminum plates was 3 mm and interelectrodes distance was maintained at 2 cm in each experiment. Electrodes were connected to a DC power supply (Micro, PW4053R, 0–5 A, 0–40 V) in a monopolar mode. The batch electrocoagulation cell with monopolarelectrode connection is shown in Fig. 1.

Chromium solutions were prepared by dissolving the required amounts of potassium dichromate (Merck, 99.9% purity) in distilled water and PACl (30% w/w Al_2O_3) in powder was used as coagulant. Sodium chloride salt (Merck) was used to adjust the initial solution conductivities (2.5 mS/cm). The selection of NaCl as supporting electrolyte is because

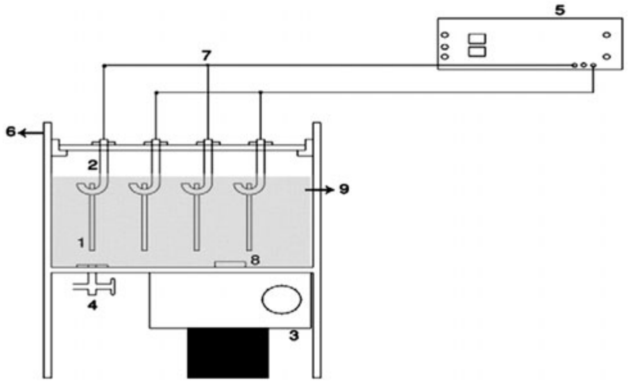

Fig. 1. Schematic diagram of EC cell used in this study. (1) aluminum plate electrode; (2) copper hook; (3) magnetic stirrer; (4) release valve; (5) DC power supply; (6) plexiglass vessel; (7) cables; (8) magnet; (9) sample.

of its ability to improve solution conductivity and eliminate the passive films of aluminum electrodes according to corrosion pitting phenomenon [34]. The initial pH of solutions was adjusted by NaOH and H_2SO_4 (4 N) before the experiments and pH values were measured using pH meter (340i, WTW, Germany).

In phase 1, the amount of chromium ions removal was measured at pH 3, 7, and 10 in initial chromium concentrations of 50, 150, and 500 mg/L and current densities of 4.16, 8.33, and 12.5 mA/cm^2. In phase 2, different amounts of PACl were dosed to the electrocoagulation tank at pH 7, and the best PACl dosage was selected for the removal of chromium in initial Cr^{6+} concentrations of 50, 150, and 500 mg/L at current densities of 4.16, 8.33, and 12.5 mA/cm^2. Optimization through RSM was used for chromium removal efficiency with the aid of PACl, by Minitab version 14.1 software for contour and main effect plots.

The desired samples were taken from solution every 20, 40, and 60 min. During the experiments, the direction of the current was reversed every 20 min to prevent the formation of passivation layer. All experiments were accomplished at room temperature. Mass depletion of the electrodes was calculated by subtracting the weight of the electrodes at the end of each experiment from the weight at the beginning of each experiment of the same electrodes. Sludge Volume Index (SVI) was determined by settling 1 L effluent in a graduated cylinder for 30 min, and the volume of the settled sludge was used to calculate the SVI from the standard methods (2710 D) [35]. The analysis of chromium was carried out using UV-visible spectrophotometer (HACH, DR 4000, USA) adopted from the standard methods (3500-Cr B) [35] for examination of water and wastewater.

3. Results and discussion

3.1. Phase 1: effect of different parameters on chromium removal by electrocoagulation process

The mechanism of chromium removal can be explained as follows: aluminum is dissolved by anodic dissolution, and a range of coagulant species and hydroxides are formed which destabilize and coagulate the suspended particles. This process leads to precipitate and adsorb dissolved Cr^{6+} [36]. Higher oxidized Cr^{6+} may also be reduced to Cr^{3+} in contact with the cathode:

$$Cr_2O_7^{2-} + 6e^- + 7H_2O \rightarrow 2Cr^{3+} + 14OH^- \quad (4)$$

Furthermore, the hydroxide ions formed at the cathode increase the pH of the wastewater and thereby induce precipitation of metal ions as corresponding hydroxides and co-precipitation with aluminum hydroxides:

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_{3(s)} \quad (5)$$

The suspended aluminum hydroxides can remove Cr^{6+} ions from the solution by sorption, co-precipitation or electrostatic attraction, followed by coagulation [37].

3.1.1. Effect of pH

One of the important parameters in the electrocoagulation process is the initial pH of the solution [38,39]. In this stage, the pH of the samples was adjusted to 3 (acidic condition), 7 (neutral condition), and 10 (alkaline condition) to study the effect of this parameter on the removal of chromium. Chromium removal efficiency versus time at different initial pH is shown in Fig. 2. As can be obtained from Fig. 2, the highest Cr^{6+} removal efficiency (about 78.8%) was observed at pH 3. Bazrafshan study group reported similar results for the removal of Cr^{6+} in a biopolar mode with changing the voltage in the range of 20–40 V and at different chromium concentrations of 5-50-500 mg/L [22]. Keshmirzadeh study group were also observed the maximum removal efficiency of Cr^{6+} occurred in acidic mediums (pH 3–5), at initial experimental conditions of KCl as electrolyte, chromium concentration of 100 mg/L, and current density of 153 A/m^2 [40].

At the acidic pH, all aluminum cations produced at the anode formed polymeric species and precipitated $Al(OH)_3$ leading to better removal efficiency [4,41]. Decreasing in removal efficiency at alkaline pH

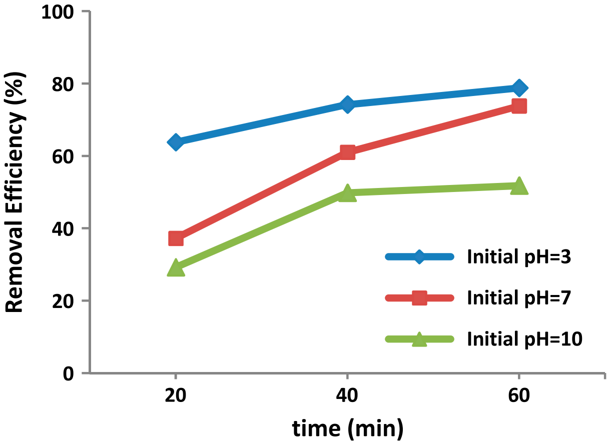

Fig. 2. Effect of pH on Cr^{6+} removal efficiency (Conductivity = 2.5 mS/cm, initial Cr^{6+}concentration = 50 mg/L, current density = 12.5 mA/cm^2).

was attributed to an amphoteric behavior of $Al(OH)_3$ which led to soluble monomeric anions $Al(OH)_4^-$.

3.1.2. Effect of current density

According to the Faraday's law, the amount of chromium removal depended on the quantity of aluminum hydroxide generated, which was related to the time and current density (Eq. (6)). Therefore, higher current density will generate significant amount of flocs and enhance the chromium removal efficiency. Furthermore, the current density adjusts the rate and size of bubble production, and the growth of flocs determines the coagulant production rate and results in a faster removal of pollutants [6,40,42].

$$m = \frac{ltM}{zF} \tag{6}$$

where I is the current intensity (A), t is the time (sec), M is the molecular weight of aluminum ion (g/mol), z is the number of electrons transferred in the reaction (3 for aluminum), and F is the Faraday's constant (96486 C/mol).

To evaluate the effect of current density on Cr^{6+} removal efficiency, three different currents (1 ,2, 3 A) that produce current densities of 4.16, 8.33, and 12.5 mA/cm^2 were examined. Hexavalent Chromium removal efficiency versus time at different currents is shown in Fig. 3. The results indicated that as the applied currents increased, the Cr^{+6} removal efficiency increased. This similar trend was also observed by other authors for boron [43], Mn^{2+} [39], Co^{2+} [41], and Cr removal [44]. As shown in Fig. 3, at the beginning of the process, current density has had a significant effect on the chromium removal, but in course of time this effect has decreased gradually so that the maximum removal efficiency was obtained 78.8% at current value of 3 A.

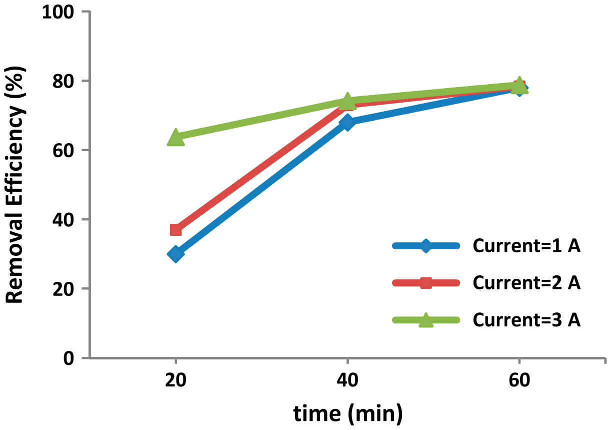

Fig. 3. Effect of current values on the Cr^{6+} removal efficiency (Conductivity = 2.5 mS/cm, initial Cr^{6+}concentration = 50 mg/L, initial pH = 3).

3.1.3. Effect of operation time

To investigate this effect, pH, and current density were constant at 3 and 12.5 mA/cm^2, respectively. Results revealed that at the beginning of process, the chromium removal rate was rapid and later it decreased gradually. This result was also observed by Bazrafshan study group for cadmium removal [45]. This is related to the fact that chromium ions are more abundant at the beginning of the EC process, and the generated aluminum hydroxides will form complexes with chromium resulting in rapid removal of Cr^{6+}.

3.1.4. Chromium Removal Kinetics

The influence of reaction time on chromium removal at different initial concentrations is shown in Fig. 4. It appears that at lower concentrations, less amount of chromium remained in the treated solution. The chromium removal can be modeled by adsorption phenomenon. During electrocoagulation, the insoluble Al hydroxides ($AlOH_3$) remove pollutants by surface adsorption [46]. The kinetic equation is further extended with pseudo-first-/second-order kinetic models. The pseudo-first-order kinetic model can be given as:

$$\frac{dqt}{dt} = k_1(q_e - q_t) \tag{7}$$

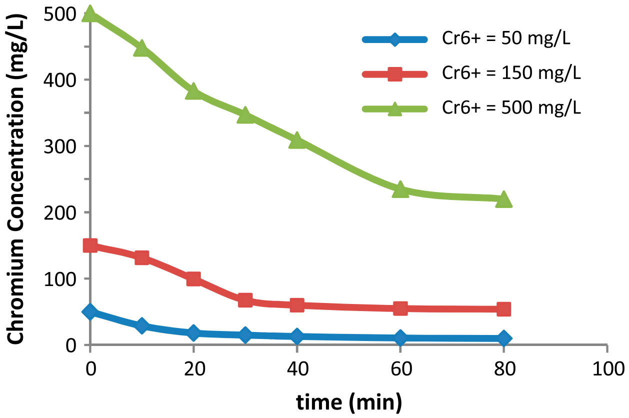

Fig. 4. Effect of reaction time on the Cr^{6+} removal efficiency at different initial concentration (Current density = 12.5 mA/cm^2, initial pH = 3).

where q_e and q_t refer to the amount of chromium adsorbed at equilibrium and at any time, t, respectively, and k_1 refer the equilibrium rate constant. Eq. (7) with boundary condition $t = 0$ to t and $q_t = 0$ to q_t can be arranged by simple integration to give:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{8}$$

In many cases, the first-order equation does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes. The pseudo-second-order kinetic equation can be given as:

$$\frac{dqt}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption. Integrating the Eq. (9) for the boundary condition $t = 0$ to t and $q_t = 0$ to q_t gives:

$$t/q_t = (1/k_2q_e^2) + (1/q_e)t \tag{10}$$

Table 1 depicts the computed results obtained from first- and second-order models. From the results, it is observed that the correlation coefficients for the second-order kinetic model were relatively higher than those obtained for the first-order kinetic model (except in Cr^{6+} Concentration of 50 mg/L). These results indicate that the second-order kinetic model can be applied suitably to predict the Cr^{6+} adsorption process onto aluminum hydroxides.

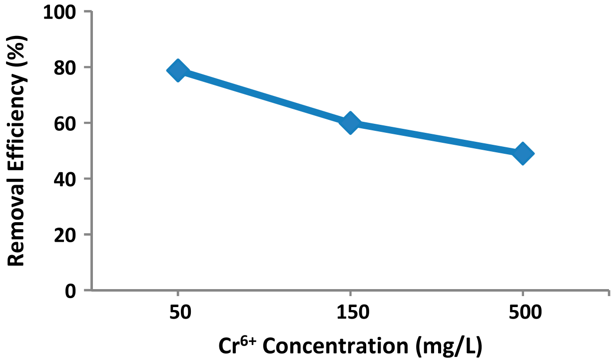

Fig. 5. Effect of initial concentration of Cr^{6+} on removal efficiency (Conductivity = 2.5 mS/cm, initial pH = 3, current density = 12.5 mA/cm^2, T_{EC} = 60 min).

3.1.5. Influence of initial chromium concentration

To study the effect of initial concentration, experiments were conducted in varying initial concentrations in the range of 50–500 mg/L (Fig. 5).

As shown in Fig. 5, the removal efficiencies were 78.8, 60, and 49%, in initial Cr^{6+} concentrations of 50, 150, and 500 mg/L, respectively. Therefore, the Cr^{6+} removal efficiency is reduced by increasing the initial Cr^{6+} concentrations. This similar trend was observed by other authors for boron [43], Mn^{2+} [39] and Co^{2+} removal [41]. However, different trend obtained by Keshmirzadeh study group that they found removal efficiency of 98 and 99.4% for Cr^{6+} concentrations of 100 and 500 mg/L, respectively, with the constant pH and current density of 10 and 153 A/m^2, while operating time increased from 25 to 55 min [40].

3.2. Phase 2: effect of adding PACl on electrocoagulation process

In this phase, the main aim was to investigate the performance of polyaluminum chloride as a coagulant

Table 1
Pseudo-first- and Pseudo-second-order adsorption kinetics of chromium (initial pH = 3, current density = 12.5 mA/cm^2)

Chromium conc. (mg/L)	First order adsorption			Second order adsorption		
	q_e	k_1	R^2	q_e	k_2	R^2
50	39.6188	0.0766	0.9985	49.5401	0.0016	0.9968
150	134.8239	0.0369	0.8850	513.0251	1.0355	0.9885
500	381.738	0.0177	0.9934	616.0329	1.783	0.9964

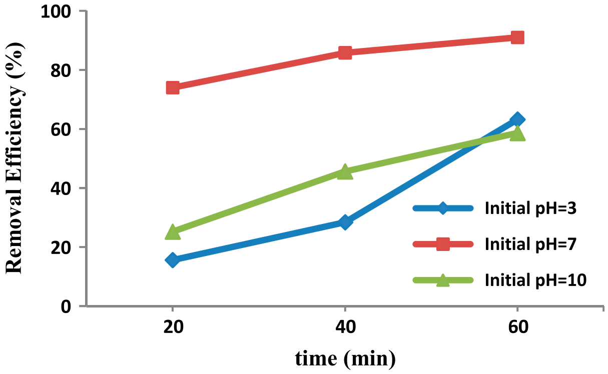

Fig. 6. Effect of pH on removal efficiency (Conductivity = 2.5 mS/cm, PACl dosage = 1,000 mg/L, initial Cr^{6+}concentration = 50 mg/L, current density = 8.33 mA/cm^2).

in conjunction with electrocoagulation process. For this purpose, it is necessary to determine the optimum pH value and coagulant dose for the best removal efficiency of chromium. Fig. 6 indicates that the maximum removal efficiency occurred at pH 7. Also as reported in Table 2, appropriate dosage of PACl obtained at 1,250 mg/L.

PACl generally contain significant amounts of polynuclear aluminum hydrolysis products, including $Al(OH)_4^-$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (Al_{13} species), and aluminum hydroxide ($Al(OH)_3$). The Al_{13} species was claimed as the most active species responsible for coagulation. Additionally, the floc properties including floc size, strength, and fractal dimension play an important role in pollutant removal efficiency [47]. The bridging or/and adsorption of pollutant onto amorphous precipitates in PACl coagulation substantially increased the floc size and led to improve removal efficiency [25,47].

In Table 3, the results obtained in phase 2 of study are compared with the data of phase 1. As presented in the table, PACl considerably enhanced the chromium removal efficiencies (especially in concentrations of 50, 150 mg/L) in comparison with the data of phase1. For an example, the variations of removal efficiency with PACl were compared with those of electrocoagulation without PACl addition in Fig. 7.

Table 2
Effect of PACl dosage on Cr^{6+} removal efficiency (pH = 7, initial Cr^{6+}concentration = 50 mg/L, current density = 8.33 mA/cm^2)

PACl dosage (mg/L)	Cr^{6+} removal efficiency (%) Time (min)		
	20	40	60
500	52.2	70.2	85.2
750	60	78.4	89.4
1,000	74	85.8	91
1,250	86.4	93.8	96.4
1,500	83	86.66	91.2

As can be seen in the figure, electrocoagulation process could not remove the hexavalent chromium more than 60.2% in current density of 8.33 mA/cm^2. So, it is interesting that adding 1,250 mg/L PACl improved the removal efficiency more than 96%. Increase in removal efficiency with adding PACl was also observed by Saeedi and Khalvati-Fahlyani study group for the removal of COD from oily wastewater of a gas refinery [30]. Ait Ouaissaa study group also demonstrated that the hexavalent chromium removal efficiency was significantly improved when electrocoagulation and adsorption (with activated carbon) processes were coupled [48].

In addition, as reported in Table 3, it can be concluded that mass depletion decreased after adding PACl to the electrocoagulation process. The range of mass depletion is varied from 0.630 to 2.751 gr for EC process and 0.41 to 1.647 gr for EC process in conjunction with PACl.

3.2.1. Energy consumption

Electrical energy consumption is a very important economical parameter in the electrocoagulation process [44]. The energy consumption in EC process at a constant voltage and current is calculated by the following Equation:

$$E = \frac{U.I.t}{V} \tag{11}$$

where E is the energy consumption (kWh/m^3), U is the applied voltage (V), I is the current intensity (A), t is the electrocoagulation time (h), and V is the volume of the wastewater (L).

The amounts of electricity consumption are compared for both processes after 60 min reaction time with the current density of 8.33 mA/cm^2 at pH 7. As a result of the experimental data, consumed energy for electrocoagulation process was about 8, 9.6, and 6.88 kWh/m^3, and for electrocoagulation process in conjunction with PACl was about 4.3, 5.06, and 5.44 kWh/m^3, in initial chromium concentrations of 50, 150, and 500 mg/L, respectively. So, it can be concluded that the energy consumption decreased noticeably after adding PACl to the process. This trend agrees with the observed data of Saeedi and

Table 3
Comparisons of the obtained data from electrocoagulation process/electrocoagulation in conjunction with PACl (Initial pH = 7, dosage of PACl = 1250 mg/L)

Current density (mA/cm^2)	C_0 (mg/L)	Cr^{6+} removal efficiency (%)						Final pH		Electrode mass depletion (gr)	
		Time (min)						EC	EC with PACl	EC	EC with PACl
		20		40		60					
		EC	EC with PACl	EC	EC with PACl	EC	EC with PACl				
4.16	50	23.8	76.2	39	77.8	53.4	81.4	9.45	8.16	0.797	0.419
	150	8.66	36.66	17.33	45	21.33	46	10	8.73	0.641	0.41
	500	7.6	10.8	12.8	16	17.8	21.4	8.8	8.8	0.630	0.442
8.33	50	27.6	86.4	50	93.8	60.2	96.4	9.6	8.9	1.495	0.839
	150	17.33	36.66	28	55	38	63	9.24	8.84	1.412	0.865
	500	12.8	10.8	17.2	23.2	22.8	28.6	9.8	8.8	1.090	0.873
12.5	50	37.2	80.8	61	91	73.8	96	9.33	8.9	2.751	1.647
	150	22.66	45.33	36.66	57.33	41	64	9.95	8.8	1.971	1.309
	500	19.8	27	26.8	29.6	29.8	39	10.5	8.68	2.380	1.338

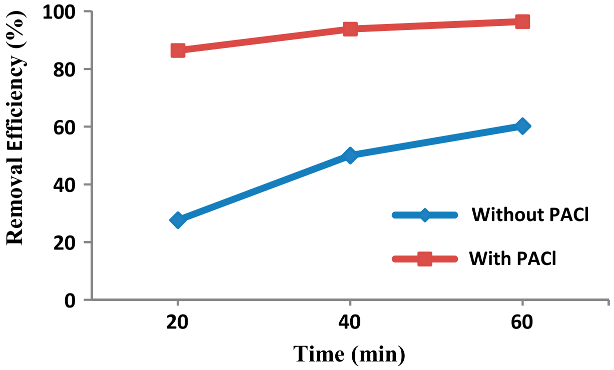

Fig. 7. Effect of adding PACl on removal efficiency (Conductivity = 2.5 mS/cm, initial pH = 7, initial Cr^{6+}concentration = 50 mg/L, current density = 8.33 mA/cm^2).

Khalvati-Fahlyani for removal of COD from oily wastewater of a gas refinery [30].

3.2.2. Sludge generated

Identification of sludge constituents that is produced in electrochemical treatment is an important part of each method evaluation [34]. The XRF analyses of sludge produced before and after adding PACl to the process are reported in Table 4.

As presented in Table 4, XRF analysis provided direct evidence that the quantity of sacrificed aluminum was decreased with the addition of PACl. The ratio of Cr to Al in electrocoagulation with PACl was also observed more than the ratio of Cr to Al in electrocoagulation without PACl. Other elements detected in the sludge may come from impurities of the anode and supporting electrolyte.

The sludge volume index (SVI) is an important part of electrocoagulation process because this parameter has a significant impact on the management and final disposal of the sludge. In this study, the SVI values were measured for both processes at the optimum operating conditions (initial Cr^{6+} concentration of 50 mg/L, current density of 8.33 mA/cm^2 for both processes and initial pH 3 and 7 for electrocoagulation

Table 4
XRF analysis of sludge produced (wt.%) in electrocoagulation/electrocoagulation process in conjunction with PACl at the optimum conditions

Constituents	Process		Constituents	Process	
	EC	EC with PACl		EC	EC with PACl
Al	21.1	18.6	Mn	0.013	0.021
Cr	5.6	5.6	Mg	0.125	0.15
Na	11.1	16.5	PO_4^-	0.59	1.03
Cl	20.9	24.9	SO_4^-	10.3	2.07
Fe	0.129	1.83	K	0.90	0.75
Cu	1.13	1.34	L.O.I[a]	27.93	24.35

Note: [a]L.O.I = Lost on Ignition.

process and electrocoagulation in conjunction with PACl, respectively). The SVI values were found as 281 and 322 mL/g for electrocoagulation process and electrocoagulation with PACl, respectively. The results demonstrate that the SVI value increased after adding PACl to the process. Olmez reported much lower SVI value (80 mL/g) in electrocoagulation process using stainless steel electrodes for Cr^{6+} removal [49].

Table 5
ANOVA results for Cr^{6+} removal efficiency (%)

Source	DF	Seq SS	Adj MS	*F*	*P*
Model	20	16751.9	837.60	235.58	0.000
Residual error	31	110.2	3.56	–	–
Lack-of-fit	22	83.1	3.78	1.25	0.378
Pure error	9	27.1	3.01	–	–

Note: $R^2 = 99.3\%$, R^2 (adj) = 98.9%.

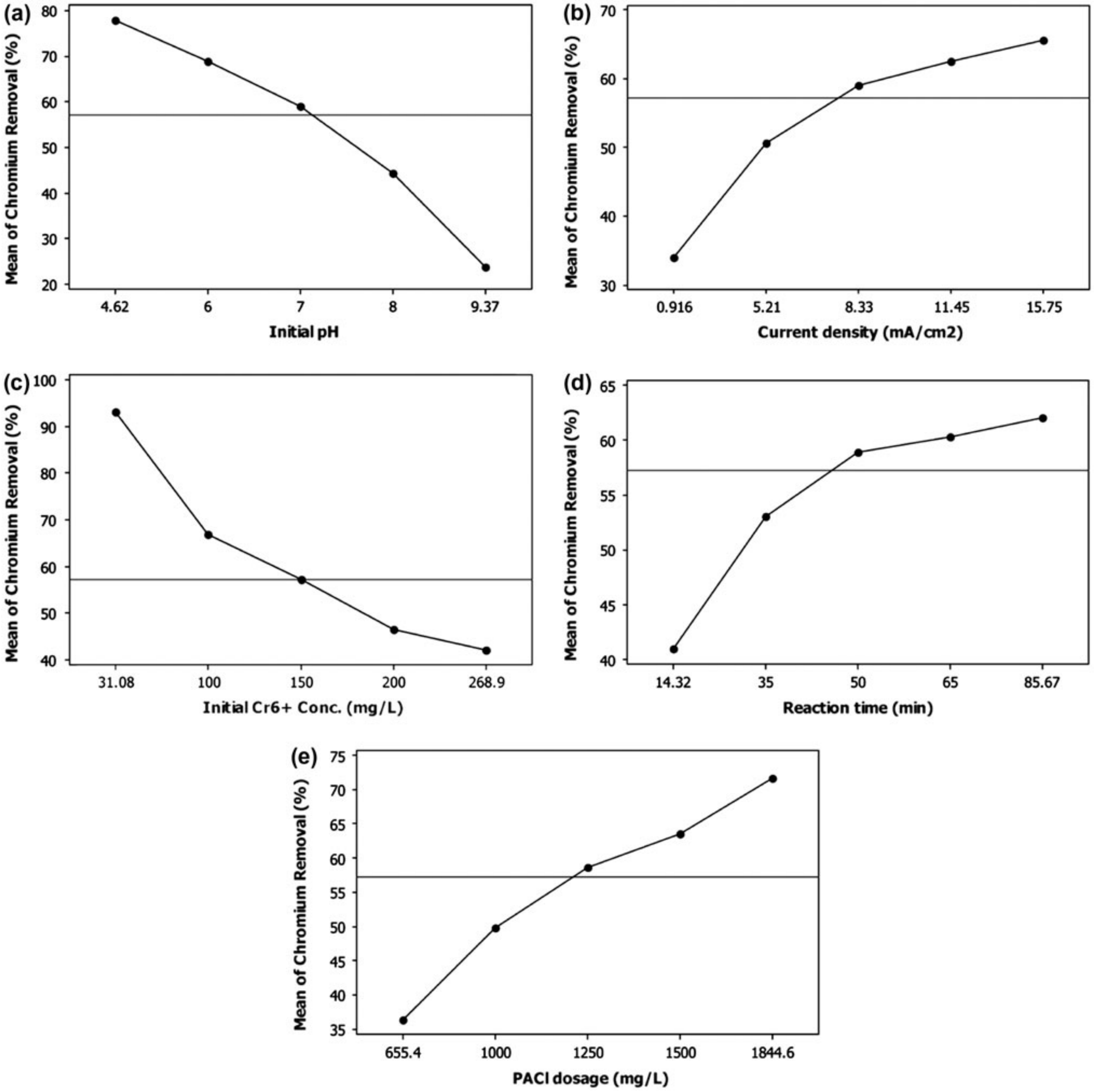

Fig. 8. Main effect plots of (a) initial pH (b) current density (c) initial Cr^{6+} concentration (d) reaction time (e) PACl dosage for chromium removal efficiency.

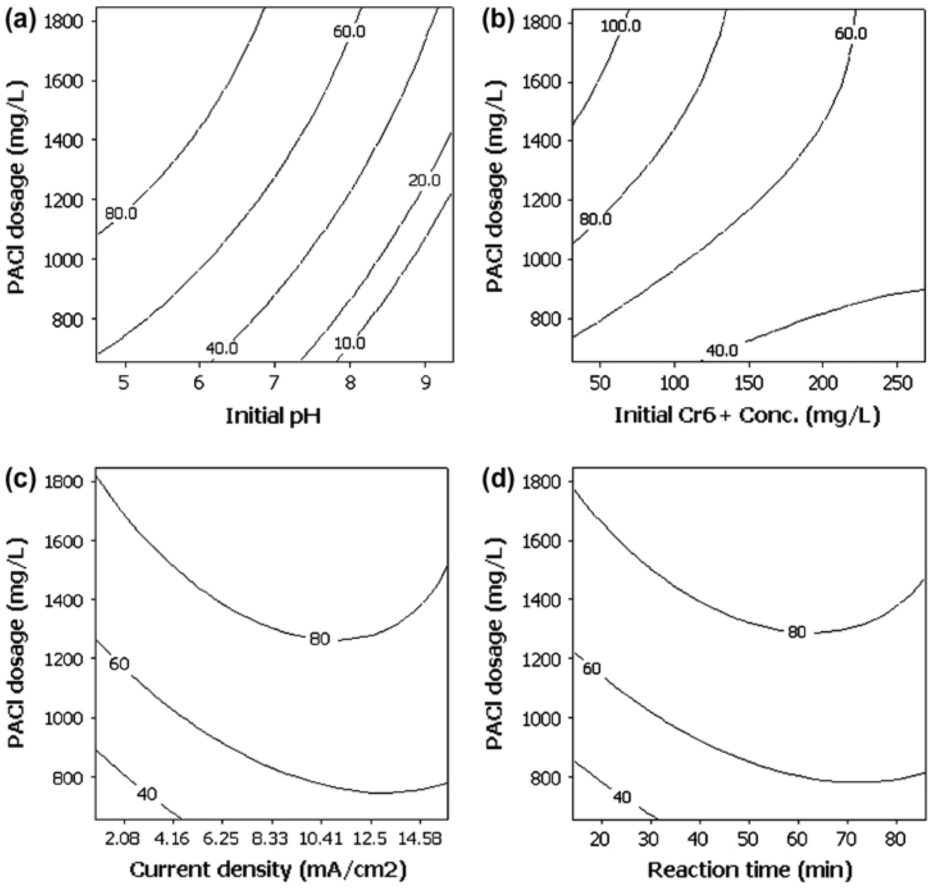

Fig. 9. Contour plots as a function of: (a) initial pH and PACl dosage at initial Cr^{6+} concentration of 100 mg/L, reaction time of 35 min and current density of 5.21 mA/cm^2; (b) initial Cr^{6+} concentration and PACl dosage at initial pH of 6, reaction time of 35 min and current density of 5.21 mA/cm^2; (c) Current density and PACl dosage at initial pH of 6, initial Cr^{6+} concentration of 100 mg/L and reaction time of 35 min; (d) reaction time and PACl dosage at initial pH of 6, initial Cr^{6+} concentration of 100 mg/L and current density of 5.21 mA/cm^2.

3.3. Phase 3: optimization through RSM for hexavalent chromium removal with the aid of PACl

In this stage, the selective parameters for the removal of hexavalent chromium were studied with a standard response surface methodology design (central composite design (CCD)). This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments. The effect of five variables in the process, including initial pH, current density, reaction time, initial chromium concentration and dosage of polyaluminum chloride, was investigated. A total of 52 experiments according to a 2^5 full factorial CCD, consisting of 32 factorial points (coded to the usual ± 1 notation), 10 axial points ($\pm\alpha$, 0, 0), (0, $\pm\alpha$, 0), (0, 0, $\pm\alpha$) ($\alpha = 2.38$), and 10 replicates at the center points (0, 0, 0) were conducted.

The results of the experimental design and graphical analysis of the obtained data were analyzed, and the statistical significance of the polynomial models was expressed by analysis of variance (ANOVA) with 95% confidence level and the coefficient of determination R^2. Finally, optimum values of parameters were obtained by determining a target in dedicated RSM program (response optimizer).

Based on RSM results, the second-order polynomial equations for Cr^{6+} removal efficiency is expressed by Eq. (9):

$$Y1 = 61.6804 - 12.0920\ x_1 + 6.1389\ x_2 + 3.8428\ x_3 - 10.3524\ x_4 + 6.9731\ x_5 - 1.7593\ x_1^2 - 1.9396\ x_2^2 - 1.6444\ x_3^2 + 1.1840\ x_4^2 - 1.2034\ x_5^2 + 2.4844\ x_1x_2 + 2.5000\ x_1x_3 - 1.2937\ x_1x_4 + 0.8906\ x_1x_5 - 0.5437\ x_2x_3 + 0.8563\ x_2x_4 - 1.2656\ x_2x_5 - 1.0469\ x_3x_4 - 1.0438\ x_3x_5 - 1.6875\ x_4x_5 \quad (9)$$

The adequacy of the model was justified through ANOVA. The results of the ANOVA for Cr^{6+} removal efficiency is given in Table 5. ANOVA results of this model indicated that this quadratic model could be used to navigate the design space. According to the table, the *P* value for the Cr^{6+} removal is lower than 0.05 indicating that quadratic model was significant. The *P* value of lack of fit greater than 0.05 implies that lack of fit for the model was insignificant.

Additionally, high R^2 value of 99.3% for chromium removal efficiency depicts a high correlation between the observed and predicted values. The main effects plot of each parameter on Cr^{6+} removal efficiency is shown in Fig. 8. According to Fig. 8, by decreasing initial pH and initial chromium concentration, and with the increase in applied current, reaction time, and PACl dosage, Cr^{6+} removal efficiency improved. In order to better explain the independent parameters and their interactive effects on the Cr^{6+} removal, contour plots are shown in Fig. 9.

3.3.1. Process optimization

The main aim of the optimization is to find the optimum values of variables for hexavalent chromium removal efficiency by dedicated RSM program. The optimum values of the process and the results of experiment under these optimum conditions are shown in Table 6. Response optimizer under these conditions estimated the hexavalent chromium removal efficiency of 87.27%. As shown in table, the response obtained from the experiments and as estimated by the models were in close agreement.

3.3.2. Determination the amounts of aluminum remained in the treated solution in the optimum condition obtained from RSM

The amounts of aluminum remained in the treated solution were measured after 60 min reaction time for EC process with PACl and EC process alone, in optimal conditions obtained from RSM. The results indicated that 2.1 and 18.1 mg/L aluminum was remained in treated solutions for EC with PACl and EC alone, respectively. So, after adding PACl the amount of aluminum has reduced to less than its allowable amount in the national (Iranian) effluent discharge standard limit (5 mg/L) [50], while for EC process alone we had much higher aluminum (18.1 mg/L) than the above-mentioned standard.

Table 6
Optimum values for hexavalent chromium removal efficiency

Variables	Unit	Optimum values(x_i)
Initial pH	–	5
Current density	mA/cm^2	8.33
Initial Cr^{6+} concentration	mg/L	50
Reaction time	min	40
PACl dosage	mg/L	1,000
Predicted Cr^{6+} removal efficiency	%	87.27
Experimental Cr^{6+} removal efficiency	%	93

4. Conclusions

According to the observed data of the present research, in phase 1, removal of Cr^{6+} was absolutely pH dependent in electrocoagulation process. The maximum removal of 78.8% occurred at pH 3, initial concentration of 50 mg/L and 12.5 mA/cm^2 current density after treatment time. In EC process, with the increase of initial Cr^{6+} concentration (in the range of 50 to 500 mg/L), the values of removal efficiencies were decreased from 78.8 to 49%. In phase 2, polyaluminum chloride was added to electrocoagulation process in order to have higher chromium removal efficiency and lower energy and electrode consumption. The results showed that increase in polyaluminum chloride dosage to 1,250 mg/L was beneficial for enhancing hexavalent chromium removal efficiency from 60.2 to 96.4% at pH 7, initial concentration of 50 mg/L and 8.33 mA/cm^2 current density. Addition of PACl to the process also led to decrease the considerable amount of energy consumption and electrode mass depletion. In the third phase, RSM was applied as an experimental design tool to describe the effect of main operating parameters on the Cr^{6+} removal efficiency. According to the ANOVA results, high R^2 values of 99.3% for chromium removal efficiency, depicts a high correlation between the observed and predicted values for model. The optimum values for treatment of Cr^{6+} was 87.27%, at initial pH of 5, current density of 8.33 mA/cm^2, initial Cr^{6+} concentration of 50 mg/L, reaction time of 40 min and initial PACl concentration of 1,000 mg/L. The response obtained from the experiments (93%) confirmed that the model and experimental results were in close agreement.

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