Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23762

157 (2019) 315–323
July

Hexavalent chromium removal from tunneling wastewater using chemical and electrochemical techniques

Joan A. Salvadó*, Enrique Ferrero, Susana Navea, Carme Repollés, Lidia Jimenez, Ana M. Climente, Jorge J. Malfeito

R&D Department of Acciona Agua S.A.U., 08820 El Prat de Llobregat, Barcelona, Spain, emails: jsalvado@acciona.com (J.A. Salvadó), enrique.ferrero.polo@acciona.com (E. Ferrero), susana.navea.vazquez@acciona.com (S. Navea), carmen.repolles.ramirez@acciona.com (C. Repollés), lidia.jimenez.carrion@acciona.com (L. Jimenez), anamaria.climente.luque@acciona.com (A.M. Climente), jorgejuan.malfeito.sanchez@acciona.com (J.J. Malfeito)

Received 9 October 2018; Accepted 8 January 2019

ABSTRACT

Hexavalent chromium (Cr^{6+}) is of particular environmental concern due to its toxicity and mobility and removing it from industrial wastewater is a challenging task. The present investigation deals with the removal of Cr^{6+} (~150 ppb) of tunneling wastewater, which has a very basic pH (11–12). For this purpose, batch experiments with wastewater samples were conducted to determine whether sub-ppb concentrations of dissolved Cr^{6+} could be achieved by chemical (using ferrous sulfate) or electrochemical reduction (iron electrodes). Cr^{6+} is chemically reduced to less soluble Cr^{3+} species by Fe^{2+}. The influence of pH, temperature, suspended solids, concentration of ferrous sulfate, current density and reaction time were evaluated in the removal of Cr^{6+}. Further, predictive equations were developed within the studied ranges. The results showed that ferrous sulfate is a good reducing agent of Cr^{6+} at very basic conditions and at short reaction times. Optimal conditions were at pH = 12°C and 22°C, with the presence of suspended solids and at molar ratios 15:1 (Fe^{2+}/Cr^{6+}); 97.8% of Cr^{6+} was removed under these conditions. On the other hand, electrocoagulation was better at reducing Cr^{6+} at lower pH; 99.3% of Cr^{6+} was removed at pH = 8, 0.5 mA cm^{-2}, and 8 min of reaction time. At very basic conditions, the removal of Cr^{6+} could be achieved by means of higher current density values. Overall, the removal of Cr^{6+} with ferrous sulfate was more efficient at higher pH and at reaction times lower than 5 min, while electrocoagulation showed enhanced removal at neutral pH and at longer reaction times.

Keywords: Hexavalent chromium; Ferrous sulfate; Electrocoagulation; Tunneling wastewater

1. Introduction

Hexavalent chromium (Cr^{6+}), which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), possesses significantly higher levels of toxicity, and has been recognized as a potential carcinogen, 100-fold more toxic than trivalent chromium, for both acute and chronic exposures because of its high water solubility and mobility, as well as its easy reduction [1]. In the environment, Cr^{6+} does not readily precipitate and becomes bound to components of soil. Cr^{6+} is considered to be a priority pollutant by the U.S. Environmental Protection Agency.

During the last years, several treatment technologies have been developed to remove Cr^{6+} from water or wastewater matrices. Common methods include chemical reduction with co-precipitation, adsorption, ion exchange, membrane separation, electro-dialysis, electro-coagulation, phytoremediation, flotation and solvent extraction [2–9]. Although there is extensive scientific literature on the aforementioned methods for the treatment of Cr^{6+} in wastewaters, none of them refer to their use at very basic conditions. The success

---

* Corresponding author.

Presented at the EDS conference on Desalination for the Environment: Clean Water and Energy, 3–6 September 2018, Athens, Greece

of the applied technologies, in terms of Cr^{6+} removal rate and efficiency, depends on the physicochemical conditions occurring in the aquatic environment. Thus, it is necessary to evaluate different technologies and investigate the best option to diminish Cr^{6+} concentrations easily and to a lower cost.

The present investigation deals with the removal of Cr^{6+} from tunneling wastewater with a very high pH (pH ~ 12), focusing on chemical reduction with ferrous sulfate and electrocoagulation. Chemical reduction is the most commonly used method for the reduction of Cr^{6+} to the trivalent state, followed by its precipitation as Cr^{3+} hydroxide. Cr^{6+} is readily reduced to Cr^{3+} through many processes. In general, the most practiced methods are the reduction of Cr^{6+} by iron salts (ferrous sulfate and ferrous ammonium sulfate), tin salts, metals (Fe°), sulfur compounds (sulfur dioxide, sodium bisulfite, sodium metabisulfite), calcium polysulfide and sodium nitrite [10–13]. Numerous observations indicate that iron salts, that is, ferrous sulfate, can be effective reductants of Cr^{+6} in water. It has been observed that the rates of aqueous Cr^{6+} reduction by highly soluble Fe^{2+} salts is significantly fast, with reduction being generally completed within the first minutes after the addition of ferrous iron [14,15]. The reduction of dissolved Cr^{6+} by Fe^{2+} can be described by the overall reaction:

$$Cr^{6+} + 3Fe^{2+} \rightarrow Cr^{3+} + 3Fe^{3+} \tag{1}$$

The products of Reaction (1) will co-precipitate as hydroxides in slightly acidic to alkaline solutions under the following Reaction (2):

$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \rightarrow Cr_xFe_{1-x}(OH)_3 \downarrow + 3H^+ \tag{2}$$

Temperature and pH strongly influence the reduction of Cr^{6+} by Fe^{2+}. The reaction rate is increased by increasing temperature and pH (in the range between 6 and 8) [2,16], but dissolved oxygen competes with Cr^{6+} in Fe^{2+} oxidation, especially at higher pH values [2,17]. In general, ferrous sulfate seems to be of great practical importance for Cr^{6+} reduction. It has been successfully used for Cr^{6+} removal in pilot scale and full scale drinking water treatment [2] and it has proven to reduce Cr^{6+} concentration to sub-ppb levels. The relatively short reaction time (<5 min) consents to the development of a process with acceptable fixed costs and significantly low operating costs. However, it is still unknown the removal efficiency of Cr^{6+} at pH ~ 12.

This study also focuses on electrocoagulation, a wastewater treatment with economical and environmental advantages that have attracted a great deal of attention during the last years [18,19]. Electrocoagulation is the electrochemical production of destabilization agents that neutralize the electric charge of Cr^{6+} present in solution. An electrocoagulation reactor consists of a reservoir in which the solution is contained in two electrodes: a cathode and an anode. An external source provides the energy required for dissolution of the anode called a sacrificial electrode, which is usually iron [19,20]. The electrochemical reduction of Cr^{6+} involves the liberation of Fe^{2+} ions into the solution due to the oxidation of the anode electrode. The reaction in bulk solution is as follows [21,22]:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 7H_2O \rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^- \tag{3}$$

The removal of Cr^{6+} by electrocoagulation involves two stages: the reduction of Cr^{6+} to Cr^{3+} at the cathode or by the Fe^{2+} ions generated from the oxidation of the iron anode and the subsequent co-precipitation of the Fe^{3+}/Cr^{3+} hydroxides:

$$Cr(aq)^{3+} + 3OH^- \rightarrow Cr(OH)_3(s) \tag{4}$$

Depending on the pH of the aqueous medium, different ionic species, such as $Fe(aq)^{3+}$, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_4^-$, may be present in the system. The suspended solid iron hydroxides can also remove pollutants from the solution by sorption, co-precipitation or electrostatic attraction, followed by coagulation [23]. However, the amount of sludge produced under the optimized conditions is lower than the amount generated by chemical treatment with ferrous sulfate [24]. The objectives of this research were to evaluate and optimize the feasibility of chemical reduction with ferrous sulfate and electrocoagulation in removing Cr^{6+} from tunneling wastewater at very basic pH. For this purpose, batch experiments and mathematical modeling were performed to examine the effects of the key process parameters.

2. Materials and methods

2.1. Materials

Tunneling wastewater with ~150 ppb of Cr^{6+} and pH ~ 12 (Table 1). Chemicals used were analytical reagents of high purity. Nitric acid 69% was purchased from Panreac (Barcelona, Spain). Ferrous sulfate ≥99% ($FeSO_4·7H_2O$) was purchased from Sigma-Aldrich (Darmstadt, Germany). Dissolved chromium used as quality control standards was from High-Purity Standards (Charleston, USA). Multi-elemental spike solution (IES-WWK) used in the isotopic

Table 1
Physicochemical properties of the tunneling wastewater

Parameters	Values
C-DOC, mg L^{-1}	54.17
Turbidity, NTU	5.6
Hardness, °dH	304.21
pH	12.1
Conductivity, mS m^{-1}	395
Cr^{3+}, mg L^{-1}	<0.0010
Cr^{6+}, μg L^{-1}	157
Ca, mg L^{-1}	2,050
K, mg L^{-1}	93
Mg, mg L^{-1}	74.5
Na, mg L^{-1}	147
Cl^-, mg L^{-1}	50.6
SO_4^{2-}, mg L^{-1}	17
NO_3^-, mg L^{-1}	<2.00

dilution was from ISC-Science (Oviedo, Spain). Powder pillows, ChromaVer® 3 (reference 1206628), were purchased from Hach Lange (Derio, Spain). Glass volumetric flasks and 0.5 L polypropylene reaction vessels were cleaned with 10% HCl and rinsed several times before use.

2.2. Batch experiments

2.2.1. Ferrous sulfate

Experiments were conducted to examine the removal of Cr^{6+} from tunneling wastewater under varying conditions. Parameters examined include different Fe^{2+}/Cr^{6+} molar ratios, pH values, presence and absence of suspended solids, temperatures and reaction times at low stirring (Table 2). The general procedure for all experiments was as follows. Tunneling wastewater (~500 mL) was added to a polypropylene reaction vessel and it was continuously mixed using a magnetic stirrer to facilitate the homogenization of the tunneling wastewater during the reaction time. Then, the reducing agent (ferrous sulfate), at different Fe^{2+}/Cr^{6+} molar ratios, was added to the wastewater. After 5 and 30 min reaction times, a sample volume was filtered through a 0.45 μm polyvinyl difluoride (PVDF) syringe filters in order to determine the dissolved chromium of the tunneling wastewater aliquot by means of ICP-MS. The pH of the wastewater was adjusted (at pH = 9) by adding sulfuric acid. Some experiments were performed with filtered wastewater (0.45 μm) to simulate the addition of ferrous sulfate after a coagulation–flocculation–decantation process.

2.2.2. Electrocoagulation

The bench-scale unit used for this study was designed to perform electrocoagulation in ~500 mL of tunneling wastewater. It consisted of a 0.5 L electrochemical reactor with two iron electrodes of rectangular shape (12.6 cm × 1.9 cm × 0.1 cm), installed horizontally in the middle of the reactor at 6 or 7 cm depth, which corresponds to $S = 24.19$ or $S = 28.19$ cm^2 electrode surface area. To remove the oxide and/or passivation layers from the electrodes, the electrode surfaces were abraded with sand paper, rinsed with Milli-Q water and dried. The electrodes were connected to a DC power supply (LABPS3005N, Velleman, Gavere, Belgium) providing 0–30 V (0–5 A) with galvanostatic operational options for controlling the current density. In each experiment, the direction of the current was reversed to limit the formation of passivation layers [25]. The tunneling wastewater was completely and continuously mixed by a magnetic stir bar at 425 rpm. The

Table 2
Results of Cr^{+6} removal using ferrous sulfate at different conditions: molar ratios (Fe^{2+}/Cr^{6+}), pH values, filtration, temperature and reaction times. Initial Cr^{6+} concentration of 138 μg L^{-1}

Molar ratio Fe^{2+}/Cr^{6+}	pH	Temperature	Filtration (0.45 μm)	Cr^{6+} (μg L^{-1}) 5 min	Cr^{6+} (μg L^{-1}) 30 min	% Cr^{6+} removed 5 min
3:1	9	22	Yes	134	132	2.8
3:1	9	22	No	92.8	90.7	32.8
3:1	12	22	Yes	83.4	83.0	39.6
3:1	12	22	No	88.1	85.9	36.2
3:1	12	7	No	100	97.6	27.6
6:1	9	22	Yes	132	129	4.3
6:1	9	22	No	72.8	73.1	47.2
6:1	12	22	Yes	61.4	61.2	55.5
6:1	12	22	No	56.4	56.4	59.1
6:1	12	7	No	62.2	62.7	54.9
10:1	9	22	Yes	114	110	16.2
10:1	9	22	No	46.1	45.0	66.6
10:1	12	22	Yes	31.4	31.2	77.2
10:1	12	22	No	18.9	19.3	86.3
10:1	12	7	No	35.1	34.9	74.6
15:1	9	22	Yes	5.2	4.5	96.2
15:1	9	22	No	11.6	12.4	91.6
15:1	12	22	Yes	9.9	11.5	92.8
15:1	12	22	No	3.0	3.2	97.8
15:1	12	7	No	11.8	11.9	91.4
30:1	9	22	Yes	2.8	3.2	98.0
30:1	9	22	No	4.8	4.7	96.5
30:1	12	22	Yes	5.0	8.1	96.4
30:1	12	22	No	4.3	4.5	96.9
30:1	12	7	No	0.56	0.80	99.6

pH of the wastewater was adjusted (at pH = 8 and pH = 9) by adding sulfuric acid. All experiments were performed at room temperature and samples were taken from the surface water and measured over time after filtration (times = 0, 1, 3, 5, 8, 10, 20 and 30 min).

2.3. Analysis

The wastewater samples were filtered (0.45 μm) and analyzed immediately after each experiment by means of spectrophotometric measurements using a specific method to determine only Cr^{6+} and by inductively coupled plasma mass spectrometry (ICP-MS). Spectrophotometric measurements were done with a DR 5000 Hach Lange Spectrophotometer using the proper Hach Lange Kits. For Cr^{6+} determination, the employed Hach Lange kit was reagent powder pillows, ChromaVer® 3 (reference 1206628) based on the USEPA 1,5-diphenylcarbohydrazide method, which can be applied to water and wastewater samples. The range of the kit was 0.010–0.70 mg L^{-1} of Cr^{6+}. Total dissolved chromium concentrations were measured by ICP-MS equipped with a collision chamber 7500-cx Agilent and a High Matrix Introduction (HMI) accessory using an on-line isotopic dilution mass spectrometry technique. This HMI accessory allows the analysis of samples with high salinity content, eliminates the external dilution of samples in many cases, significantly improves plasma robustness and also reduces oxide interferences to extremely low levels. The isotopic dilution technique involves the addition of a known amount of an enriched isotope element of interest to the sample. This addition was made prior to sample preparation during which the spiked addition of the enhanced isotope was 'equilibrated' with the sample. Although ICP-MS can only measure total dissolved chromium, the concordance in the results obtained with both techniques (spectrophotometry and ICP-MS) indicated that all dissolved chromium was found as Cr^{6+}. All Cr^{+6} results were the average of five samples, and each sample was analyzed in triplicate. Uncertainties of Cr^{+6} data were between 1% and 4%.

2.4. Data analysis

The obtained data were analyzed with Statgraphics Centurion XVI, version 16.1.07 (2009), in order to simulate the Cr^{6+} removal by chemical (ferrous sulfate) and electrochemical techniques. For each factor, the experimental range and the central point were based on the results of preliminary trials. Simulations were developed using a factorial and a Taguchi method. Then we obtained the Pareto charts to visualize the influential factors, the response surfaces to depict the significant factors vs. one response and the prediction equation. The precision of the models was evaluated by the coefficient of determination, R^2, which indicates how well the data fit the statistical model in the range of study; it is a relative measurement of the linear association between the experimental data and the predicted ones by the equation.

3. Results and discussion

3.1. Chemical reduction: ferrous sulfate

The efficiency of Cr^{6+} removal by chemical reduction using ferrous sulfate was examined under varying conditions, including Fe^{2+}/Cr^{6+} molar ratios (3:1, 6:1, 10:1, 15:1 and 30:1), pH values (9 and 12), presence and absence of suspended solids (to simulate before and after a coagulation–flocculation–decantation process), temperature (21°C and 7°C) and reaction times (5 and 30 min) at low stirring (Table 2).

3.1.1. Effect of ferrous sulfate dose

The influence of ferrous sulfate concentration on the removal efficiency of Cr^{6+} is shown in Table 2 and Fig. 1. At molar ratio of 3:1 (Fe^{2+}/Cr^{6+}), it was possible to achieve a Cr^{6+} removal of 39.6%, at 6:1 the maximum Cr^{6+} removal was 59.1%, at 10:1 it was possible to achieve the 86.3% removal, and at molar ratios of 15:1 and 30:1, the 97.8% and 99.6%, respectively. These results show a strong dependence of ferrous sulfate dose on the removal of Cr^{6+}. The molar ratio of Fe^{2+}/Cr^{6+} needs to be at least 15:1 to achieve >90% removal. Thus, the amount of ferrous sulfate should be in excess to the theoretical value of the 3:1 stoichiometric ratio. The incomplete Cr^{6+} removal cannot be attributed to insufficient reaction time since no change in the residual Cr^{6+} concentration was observed between 5 and 30 min (Table 2). This observation is consistent with previous reports of rapid reaction of Cr^{6+} with Fe^{2+} at circumneutral pH [17]. The incomplete reduction of Cr^{6+} at the 3:1 stoichiometric ratio most likely resulted from the competition between Cr^{6+} and O_2 for reaction with Fe^{2+}, which decreased the efficiency of Cr^{6+} reduction at low Fe^{2+} doses [17]. Thus, more efficient reaction of Cr^{6+} with Fe^{2+} would be anticipated in groundwater containing little or no dissolved oxygen. In these cases, Fe^{2+} could be added at concentrations closer to the stoichiometric dose.

3.1.2. Effect of pH and suspended solids

Ferrous sulfate experiments were performed at different pH (pH = 9 and 12) and in previously filtered (0.45 μm pore size) and not-filtered wastewater samples (Table 2 and Fig. 1). Similar results of Cr^{6+} removal were observed at 5 and 30 min reaction times (Table 2). Results at pH = 9 and 12 under the same conditions (not-filtered wastewater samples and 22°C) showed a slightly better Cr^{6+} removal at pH = 12 than at pH = 9 (Fig. 1c). For instance, results at 5 min reaction time and pH = 9, adding 10:1 and 15:1 molar ratios of Fe^{2+}/Cr^{6+}, showed a Cr^{6+} removal of 66.6% and 91.6%, respectively; and at pH = 12 we obtained a removal of 86.3% and 97.8%, respectively. Further, at pH = 9, there were wide differences between filtered and not-filtered samples, with much better Cr^{6+} removal in samples with suspended solids, and at pH = 12 the differences were almost negligible (Figs. 1a and b). All in all, there was better Cr^{6+} removal at pH = 12 and in not-filtered samples, and the influences of pH and suspended solids were higher at lower molar ratios than 30:1 (Fe^{2+}/Cr^{6+}). These results are consistent with previous studies showing that mineral surfaces and organic matter accelerate the Cr^{6+} reduction, enhancing the reactivity of adsorbed Fe^{2+} [26]. Other studies also recorded high reaction rates at high alkaline pH, due to the increase in concentration of the highly reactive hydroxylated species of Fe^{2+} [$Fe(OH)^+$ and $Fe(OH)_2$] [2,16,26,27]. Schlautman and Han [27] further explained that this can be attributed to the dissolved Fe^{2+} speciation with pH.

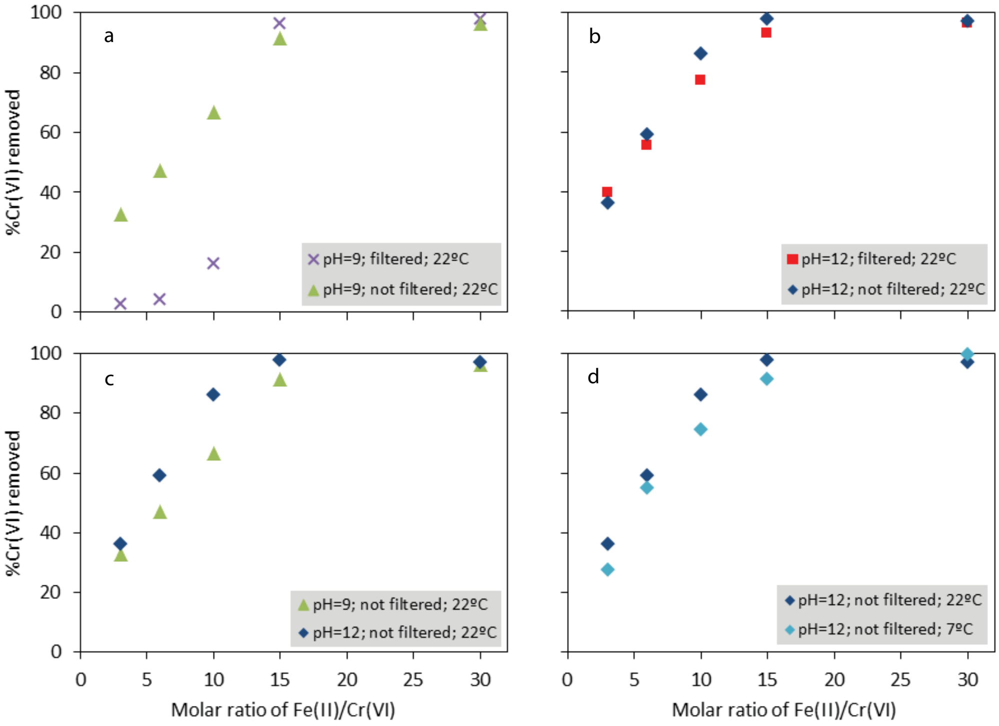

Fig. 1. Removal of Cr^{6+} by redox-assisted coagulation at 5 min reaction time with various molar ratios (Fe^{2+}/Cr^{6+}) at different conditions of pH, temperature and filtration of the sample: (a) pH = 9, 22°C with filtered and not-filtered samples, (b) pH = 9, 22°C with filtered and not-filtered samples, (c) not-filtered samples, 22°C at pH = 9 and pH = 12, and (d) pH = 12, not-filtered samples at 7°C and 22°C.

3.1.3. Influence of temperature

Experiments were performed at 7°C and 22°C under the above-mentioned optimal conditions of pH = 12 and with suspended solids (Table 2 and Fig. 1d). Similar results were observed at 5 and 30 min reaction times (Table 2). Results at 5 min reaction time and 7°C, adding 10:1 and 15:1 molar ratios of Fe^{2+}/Cr^{6+}, showed a Cr^{6+} removal of 74.6% and 91.4%, respectively; and at 22°C we obtained a removal of 86.3% and 97.8%, respectively. At a molar ratio of 30:1, the difference between 7°C and 22°C was almost negligible. Thus, the fraction of Cr^{6+} removed at 7°C was slightly lower than at 22°C, at molar ratios of Fe^{2+}/Cr^{6+} below 30:1. These results are in accordance with previous studies, showing that Cr^{6+} reduction increases with increasing temperature, confirming the endothermic character of the reaction [2].

3.1.4. Data analysis

The results of the factorial experimental design allowed discrimination of the influence of the studied variables inside the studied ranges: molar ratios (Fe^{2+}/Cr^{6+}) between 3:1 and 30:1, pH = 9 to pH = 12, presence and absence of suspended solids and temperatures between 9°C and 22°C. The obtained prediction equation was in the form of a second-order polynomial function for the Cr^{6+} removal (Eq. (5):

$$\begin{aligned}\mathrm{Cr}^{6+}\mathrm{removal}(\%) = {} & -47.8282 + 9.86939 \times A + 4.18243 \times B - 2.87595 \times \\ & C + 0.712866 \times D - 0.176346 \times A^2 - 0.110086 \times \\ & A \times B - 0.0065661 \times A \times C - 0.0263117 \times A \times D \end{aligned} \quad (5)$$

where A is the molar ratio (Cr^{6+}:Fe^{2+}), B is the pH, C is the filtration of the sample (1 = filtered or 0 = not filtered) and D is the temperature. The obtained model fit the data very well as R^2 was 98.84%. Thus, the prediction equation allowed to calculate the Cr^{6+} removal (%) considering the molar ratio (Fe^{2+}/Cr^{6+}), pH, temperature and filtration in other operation conditions inside the studied ranges, particularly from molar ratios between 3:1 and 15:1. A Pareto graph was used to show which of these variables and their interactions were more significant (Fig. 2a). Factors exceeding the blue line (the significant level at 5%) were considered statistically significant in the Cr^{6+} removal by ferrous sulfate. Based on the Pareto chart, molar ratio was the most important factor in the model, but pH was also significant. The higher molar ratio and pH led to the higher Cr^{6+} removal. Temperature and filtration were not significant factors in the model (Fig. 2a). According to the statistical method, a second-order polynomial function was obtained and molar ratio (Fe^{2+}/Cr^{6+}) presented a quadratic effect in the model. The interactions between molar ratio and the other factors (pH, temperature and previous filtration of the sample) were not significant in the model. Thus, the effect of molar ratio was so strong that it did not depend on the level of the other factors.

The relationship between molar ratios and pH can be assessed by examining the response surface generated by holding constant the filtration factor (0 = not filtered) and temperature (22°C). The estimated response surface (Fig. 2b) confirmed that molar ratio and pH had a positive effect on the Cr^{6+} removal. For instance, at pH = 12 and molar ratio of 15:1, we obtained a Cr^{6+} removal of 97.8%. To the best of our knowledge, this is the first study of Cr^{6+} removal at very high pH (pH = 12). Further, these results demonstrate that very basic conditions improve the removal of Cr^{6+} using ferrous sulfate as a reducing agent.

3.2. Electrocoagulation

Electrocoagulation experiments were performed in a tunneling wastewater of ~150 µg L^{-1} of Cr^{6+} at different current densities (0.05, 0.5, 1, 2, 5, 10 and 15 mA cm^{-2}), pH values (pH = 8, 9 and 12) and reaction times from 5 to 30 min (Figs. 3 and 4).

3.2.1. Effect of electrocoagulation time

The efficiency of electrocoagulation is influenced by the reaction time. It determines the rate of production of iron (II) ions from iron electrode [28]. To investigate the effect of electrocoagulation time on the residual concentrations of Cr^{6+} ions, a series of experiments were carried out at the studied current densities and pH. In all cases, by increasing the electrocoagulation time the residual Cr^{6+} concentrations decreased (Figs. 3 and 4). For instance, at pH = 12 and 10 mA cm^{-2}, the removal of Cr^{6+} at 10 and 30 min reaction times was 48% and 97%, respectively; or at pH = 9 and 1 mA cm^{-2}, the Cr^{6+} removal at 1 and 8 min reaction times was 56% and 99%, respectively. Thus, the reaction time that is necessary to obtain a complete removal of Cr^{6+} depends on the pH and the applied current density.

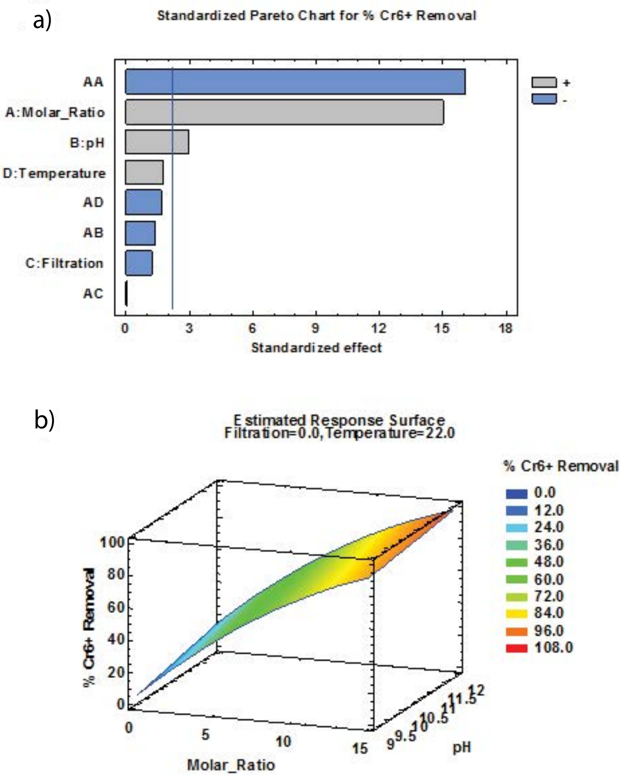

Fig. 2. Optimization results obtained for the Cr^{6+} removal (%). (a) Pareto chart (a = 5%) and (b) response surface.

3.2.2. Effect of applied current

To evaluate this effect, a series of experiments were conducted at different current densities. According to Faraday's law, increasing the current density leads to a higher coagulant dosage per time unit. The process should, therefore, be accelerated. Fig. 3 depicts Cr^{6+} removal under different current densities (0.05, 2, 5, 10 and 15 mA cm^{-2}) at the initial pH of the wastewater (pH = 12). These results show that increasing the current density led to an acceleration of the Cr^{6+} removal process. At 10 mA cm^{-2} it was necessary 30 min of electrocoagulation to achieve a complete Cr^{6+} removal, however, at 15 mA cm^{-2} it was necessary 10 min. Further, at 0.05, 2 and 5 mA cm^{-2}, the Cr^{6+} removal was only the 5%, 17% and 31%, respectively, after 30 min of electrocoagulation (Fig. 3). Previous studies also established that the applied current has a considerable influence on the performance of the electrocoagulation process [29–31]. However, results at pH = 8 showed a slightly better removal at 0.5 mA cm^{-2} than at 1 mA cm^{-2} (Fig. 4). The improved Cr^{6+} at low currents with neutral pH could be related to the increasing Fe^{2+} dissolution from the electrodes under these conditions [32].

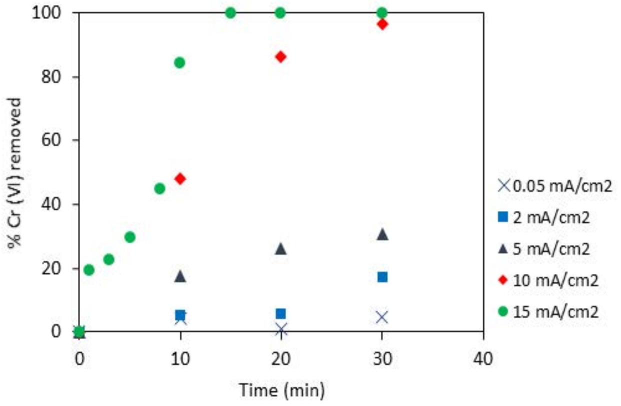

Fig. 3. Evaluation of Cr^{6+} applying different current densities (0.05, 2, 5, 10 and 15 mA cm^{-2}) to the raw tunneling wastewater (pH = 12). Reaction times from 0 to 30 min.

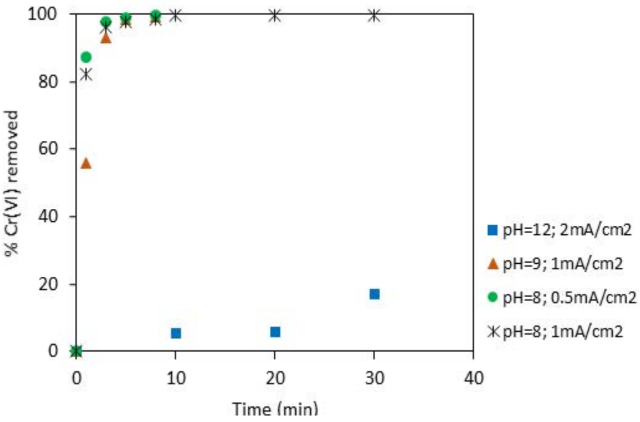

Fig. 4. Effect of pH (pH = 8, 9 and 12) on the removal of Cr^{6+} at similar current densities (0.5–2 mA cm^{-2}). Reaction times from 0 to 30 min.

3.2.3. Influence of pH

To examine the influence of pH on electrocoagulation, experiments were conducted over a range of initial pH values ($pH = 8$, 9 and 12), decreasing the pH by adding sulfuric acid. Results showed that at $pH = 12$ it was necessary a current density of 15 mA cm^{-2} during 15 min, or 10 mA cm^{-2} for 30 min to achieve a complete Cr^{6+} removal. However, at $pH = 9$ and $pH = 8$, the Cr^{6+} removal was completed after 5 min of electrocoagulation, with current densities of 1 and 0.5 mA cm^{-2}, respectively. The pH dependence of Cr^{6+} reduction is consistent with several reports in the literature showing an increasing reduction at $pH = 8$ [16,20,26,33]. However, this is the first clear quantification of the rate of Cr^{6+} removal at different pH higher than $pH = 8$.

The appearance of the orange color of the wastewater was related to the reduction of Cr^{6+}. The initial clear and whitish tunneling wastewater became a turbid orange suspension typical of Fe^{3+}(oxy)hydroxides. The dominant iron oxide formed during electrocoagulation was lepidocrocite (γ-FeOOH). It is a well-known product of Fe^{2+} oxidation by oxygen in the absence of strongly adsorbing ions [20,34]. Previous studies showed that the trend of total iron concentrations was consistent with Faraday's law with the assumption that Fe^{2+} is generated at the anode [20,35], and the difference between total and dissolved iron is the value consumed by reducing Cr^{6+} [20]. Fe^{2+} to Fe^{3+} oxidation was better and faster at $pH = 8$ than at lower pH. Thus, we suggest that at $pH = 12$, it is mainly formed $Fe(OH)_2$, instead of Fe^{2+}, and $Fe(OH)_2$ is slower oxidized to Fe^{3+}.

3.2.4. Design of experiments

A design of experiments was developed to visualize the most influential factors in the removal of Cr^{6+} by electrocoagulation, to obtain a response surface and a prediction equation inside the studied ranges. The obtained model was as follows:

$$Cr^{6+}\text{removal}(\%) = 30.7076 + 15.8236 \times A + 3.17783 \times B - 0.803189 \times C - 1.36173 \times A^2 + 1.12244 \times A \times C - 0.0666005 \times B^2 - 0.279572 \times B \times C - 0.549957 \times C^2 \tag{6}$$

where A is the pH (between 8 and 11), B is the reaction time (between 1 and 8 min) and C is the current density (from 0.5 to 10 mA cm^{-2}). The obtained model was in the form of a second-order polynomial function and fit the data very well as R^2 was 92.95%. To show the most influential factors and their interactions, a Pareto graph was performed (Fig. 5). Factors exceeding the blue line (the significant level at 5%) were considered statistically significant in the Cr^{6+} removal by electrocoagulation. Based on the Pareto chart, current density was the most important factor in the model, but pH and reaction time were also significant. The interactions between each factor were also significant revealing the complexity of this study. The relationship between current density and reaction time can be assessed by examining the response surface generated by holding constant the pH factor. The estimated response surfaces showed that the maximum Cr^{6+} removal (%) was obtained at high current density values when the pH of the water sample was high, while less

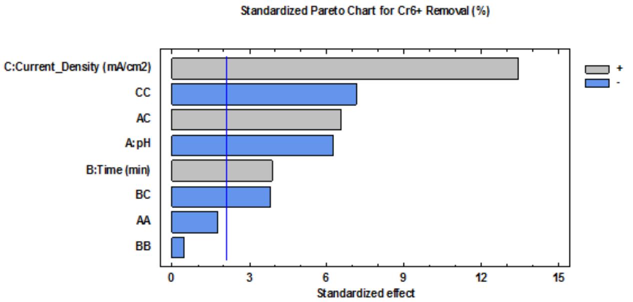

Fig. 5. Standard Pareto chart showing the effects of independent variables: (a) pH, (b) reaction time (min) and (c) current density (mA cm^{-2}), and their combined effects on the Cr^{6+} removal by electrocoagulation. The blue line depicts the significant level at 5%.

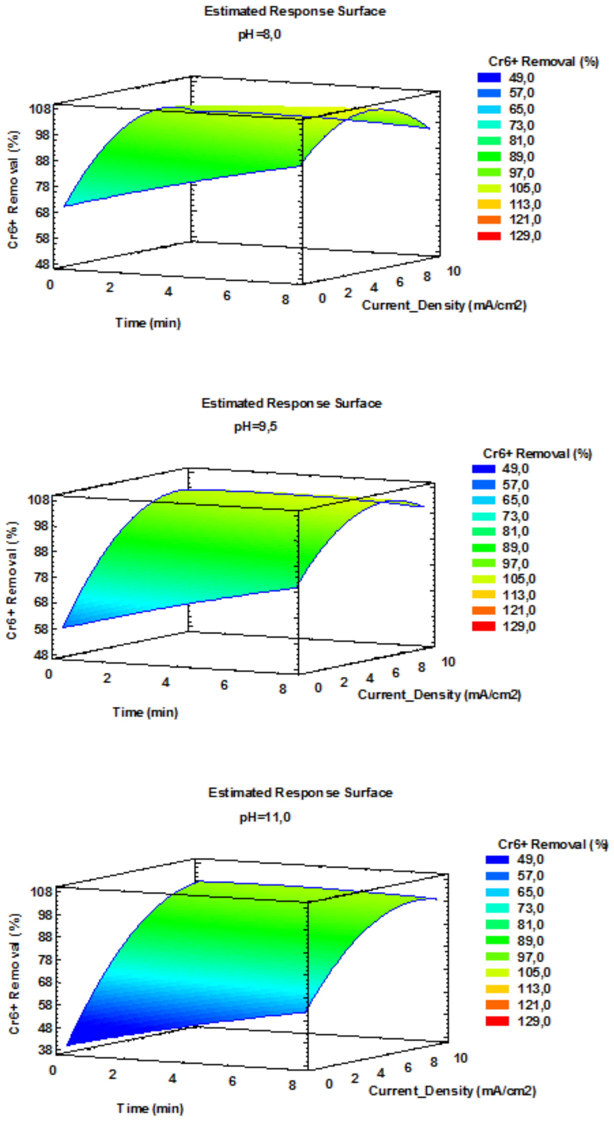

Fig. 6. Response surface plots showing the effect of current densities and reaction times at different constant pH values ($pH = 8$, 9.5 and 11).

current densities were needed at lower pH values (Fig. 6). This is the first clear quantification of the rate of Cr^{6+} removal on electrocoagulation at different pH higher than pH = 8.

4. Conclusions

The present study investigates the removal of Cr^{6+} from tunneling wastewater at very high pH. The results obtained in this study show that ferrous sulfate ($FeSO_4{\cdot}7H_2O$) removes Cr^{6+} in a short reaction time (at reaction times lower than 5 min), there is no need to lower the pH as it is more efficient at higher pH, and it should be used before coagulation–flocculation–decantation processes. Further, higher molar ratios enhance the redox reaction. The amount of ferrous sulfate should be in excess to the theoretical value of the 3:1 stoichiometric ratio, likely due to the competition between Cr^{6+} and O_2 for reaction with Fe^{2+}, which decreased the efficiency of Cr^{6+} reduction at low Fe^{2+} doses. The removal of Cr^{6+} is completed at a molar ratio of 1:15, indistinctly of pH, *Tª* and filtration. At lower molar ratios (below 1:15 molar ratio), Cr^{6+} removal is more effective at pH = 12°C, 22°C and in water samples that were not previously filtered. To the best of our knowledge, this is the first study of Cr^{6+} removal at very high pH (pH = 12). Further, these results demonstrate that very basic conditions improve the removal of Cr^{6+} using ferrous sulfate as a reducing agent.

The efficiency of electrocoagulation is influenced by the reaction time. In all cases, by increasing the electrocoagulation time the residual Cr^{6+} concentrations decreases. The reaction time that is necessary to obtain a complete removal of Cr^{6+} depends on the pH and the applied current density. The results in the removal of Cr^{6+} enhance at neutral pH (pH = 8 and 9). At higher pH, electrocoagulation requires much longer reaction times and higher current densities. The obtained prediction equations using chemical and electrocoagulation techniques allow us to calculate the Cr^{6+} removal (%), considering the different studied parameters and ranges.

References

[1] R. Saha, R. Nandi, B. Saha, Sources and toxicity of hexavalent chromium, J. Coord. Chem., 64 (2011) 1782–1806.

[2] M.G. Mitrakas, A.S. Pantazatou, R. Tzimou-Tsitouridou, C.A. Sikalidis, Influence of pH and temperature on Cr(VI) removal from a natural water using Fe(II): A pilot and full scale case study, Desal. Wat. Treat., 33 (2011) 77–85.

[3] C.E. Barrera-Díaz, V. Lugo-Lugo, B. Bilyeu, A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction, J. Hazard. Mater., 223–224 (2012) 1–12.

[4] A. Dabrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere, 56 (2004) 91–106.

[5] D. Mohan, C.U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater., 137 (2006) 762–811.

[6] N.K. Lazaridis, M. Jekel, A.I. Zouboulis, Removal of Cr(VI), Mo(VI), and V(V) ions from single metal aqueous solutions by sorption or nanofiltration, Sep. Sci. Technol., 38 (2003) 2201–2219.

[7] S.K. Nataraj, K.M. Hosamani, T.M. Aminabhavi, Potential application of an electrodialysis pilot plant containing ion-exchange membranes in chromium removal, Desalination, 217 (2007) 181–190.

[8] C. Cervantes, J. Campos-García, S. Devars, F. Gutiérrez-Corona, H. Loza-Tavera, J.C. Torres-Guzmán, R. Moreno-Sánchez, Interactions of chromium with microorganisms and plants, FEMS Microbiol. Rev., 25 (2001) 335–347.

[9] K.A. Matis, P. Mavros, Recovery of metals by ion flotation from dilute aqueous solutions, Sep. Purif. Methods, 20 (1991) 1–48.

[10] M. Chrysochoou, A. Ting, A kinetic study of Cr(VI) reduction by calcium polysulfide, Sci. Total Environ., 409 (2011) 4072–4077.

[11] M. Magistri, D. Padovani, M. Spa, Chromate Reducing Agents, Cement Standards, 2005.

[12] G. Pei, Z. Wei, H. Fu, J. Liu, F. Yu, Optimization of hexavalent chromium removal from wastewater by ferrite precipitation, J. Residuals Sci. Technol., 13 (2016), 85–91.

[13] E. Theologou, I. Panagiotakis, D. Dermatas, M. Chrysochoou, T. Toskos, Remediation technologies for hexavalent chromium contaminated aquifers, in: Proceedings of the 13th International Conference on Environmental Science and Technology, 2013.

[14] S.E. Fendorf, G. Li, Kinetics of chromate reduction by ferrous iron, Environ. Sci. Technol., 30 (1996) 1614–1617.

[15] M.J. McGuire, N.K. Blute, C. Seidel, G. Qin, L. Fong, Pilot-scale studies of hexavalent chromium removal from drinking water, J. Am. Water Works Assoc., 98 (2006) 34–143.

[16] D.L. Sedlak, P.G. Chan, Reduction of hexavalent chromium by ferrous iron, Geochim. Cosmochim. Acta, 61 (1997) 2185–2192.

[17] G. Lee, J.G. Hering, Removal of chromium(VI) from drinking water by redox-assisted coagulation with iron(II), J. Water Supply Res. Technol. AQUA, 52 (2003) 319–332.

[18] Y. Esfandyari, Y. Mahdavi, M. Seyedsalehi, M. Hoseini, G.H. Safari, M.G. Ghozikali, H. Kamani, J. Jaafari, Degradation and biodegradability improvement of the olive mill wastewater by peroxi-electrocoagulation/electrooxidation-electroflotation process with bipolar aluminum electrodes, Environ. Sci. Pollut. Res., 22 (2015) 6288–6297.

[19] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage., 90 (2009) 1663–1679.

[20] C. Pan, L.D. Troyer, J.G. Catalano, D.E. Giammar, Dynamics of chromium(VI) removal from drinking water by iron electrocoagulation, Environ. Sci. Technol., 50 (2016) 13502–13510.

[21] S.A. Martínez, M.G. Rodríguez, C. Barrera, A kinetic model that describes removal of chromium VI from rinsing waters of the metal finishing industry by electrochemical processes, Water Sci. Technol., 42 (2000) 55–61.

[22] A.K. Golder, A.N. Samanta, S. Ray, Removal of trivalent chromium by electrocoagulation, Sep. Sci. Technol., 53 (2007) 33–41.

[23] N. Meunier, P. Drogui, C. Gourvenec, G. Mercier, R. Hausler, J.F. Blais, Removal of metals in leachate from sewage sludge using electrochemical technology, Environ. Technol., 25 (2004) 235–245.

[24] T. Ölmez, The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology, J. Hazard. Mater., 162 (2009) 1371–1378.

[25] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Sci. Technol., 38 (2004) 11–41.

[26] I.J. Buerge, S.J. Hug, Kinetics and pH Dependence of Chromium(VI) Reduction by Iron(II), Environ. Sci. Technol., 31 (1997) 1426–1432.

[27] M.A. Schlautman, I. Han, Effects of pH and dissolved oxygen on the reduction of hexavalent chromium by dissolved ferrous iron in poorly buffered aqueous systems, Water Res., 35 (2001) 1534–1546.

[28] Z.R. Guo, G. Zhang, J. Fang, X. Dou, Enhanced chromium recovery from tanning wastewater, J. Cleaner Prod., 14 (2006) 75–79.

[29] N. Adhoum, L. Monser, N. Bellakhal, J.E. Belgaied, Treatment of electroplating wastewater containing Cu^{2+}, Zn^{2+} and Cr(VI) by electrocoagulation, J. Hazard. Mater., 112 (2004) 207–213.

[30] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A Physicochem. Eng. Asp., 211 (2002) 233–248.

[31] P. Gao, X. Chen, F. Shen, G. Chen, Removal of chromium(VI) from wastewater by combined electrocoagulation–electroflotation without a filter, Sep. Purif. Technol., 43 (2005) 117–123.

[32] I. Heidmann, W. Calmano, Removal of Cr(VI) from model wastewaters by electrocoagulation with Fe electrodes, Sep. Purif. Technol., 61 (2008) 15–21.

[33] M. Pettine, L. D'Ottone, L. Campanella, F.K. Millero, R. Passino, The reduction of chromium (VI) by iron (II) in aqueous solutions, Geochim. Cosmochim. Acta, 62 (1998) 1509–1519.

[34] K.L. Dubrawski, C.M. van Genuchten, C. Delaire, S.E. Amrose, A.J. Gadgil, M. Mohseni, Production and transformation of mixed-valent nanoparticles generated by Fe(0) electrocoagulation, Environ. Sci. Technol., 49 (2015) 2171–2179.

[35] Y.A. El-Taweel, E.M. Nassef, I. Elkheriany, D. Sayed, Removal of Cr(VI) ions from waste water by electrocoagulation using iron electrode, Egypt. J. Petrol., 24 (2015) 183–192.