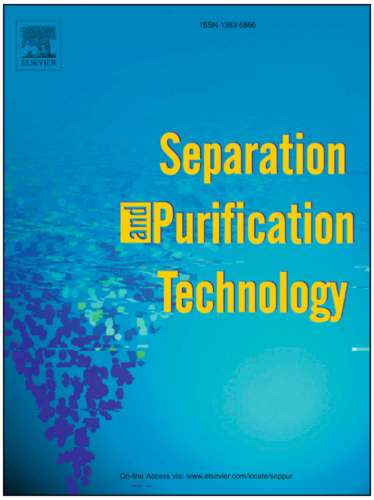

Chromium removal from drinking water by redox-assisted coagulation: Chemical versus electrocoagulation

A. Martín-Domínguez, M.L. Rivera-Huerta, S. Pérez-Castrejón, S.E. Garrido-Hoyos, I.E. Villegas-Mendoza, S.L. Gelover-Santiago, P. Drogui, G. Buelna

PII: S1383-5866(17)32971-4
DOI: https://doi.org/10.1016/j.seppur.2018.02.014
Reference: SEPPUR 14378

To appear in: *Separation and Purification Technology*

Received Date: 11 September 2017
Revised Date: 5 February 2018
Accepted Date: 6 February 2018

Please cite this article as: A. Martín-Domínguez, M.L. Rivera-Huerta, S. Pérez-Castrejón, S.E. Garrido-Hoyos, I.E. Villegas-Mendoza, S.L. Gelover-Santiago, P. Drogui, G. Buelna, Chromium removal from drinking water by redox-assisted coagulation: Chemical versus electrocoagulation, *Separation and Purification Technology* (2018), doi: https://doi.org/10.1016/j.seppur.2018.02.014

Chromium removal from drinking water by redox-assisted coagulation: chemical versus electrocoagulation

A. Martín-Domínguez [1], M.L. Rivera-Huerta [1], S. Pérez-Castrejón [1], S.E. Garrido-Hoyos[1], I.E. Villegas-Mendoza[1], S.L. Gelover-Santiago[1], P. Drogui*[2], G. Buelna[3]

[1] Instituto Mexicano de Tecnología del Agua (IMTA) Paseo Cuauhnáhuac 8532, Colonia Progreso, Jiutepec, Morelos. C.P. 62550, Tel. 01 777 319 3600

[2] Institut National de la Recherche Scientifique (INRS-Eau Terre et Environnement), Université du Quebec, 490 rue de la Couronne, Quebec, Qc, Canada, G1K 9A9, Phone : (418) 654-3119, Fax : (418) 654-2600.

[3] Centre de Recherche Industrielle du Québec (CRIQ), 333 rue Franquet, Québec, QC, Canada, G1P 4C7, Phone : (418) 659-1550, Fax : (418) 652-2251.

*Corresponding author (email): patrick.drogui@ete.inrs.ca

August, 2017

Separation and Purification Technology

Abstract

Chemical Coagulation (CC) and Electrocoagulation (EC) processes using iron as coagulating agent were compared while treating aquifer water contaminated by a relatively high concentration of total chromium (CrT =19.0 mg L^{-1}). A continuous semi-pilot comprising of EC (or CC), followed by flocculation, sedimentation and sand-filtration steps was used to remove CrT from water in order to get drinking water. A ratio of Fe/CrT ≥ 3 was required to reach the best efficiency of treatment using EC and CC. More than 99% of CrT was removed and residual CrT concentration below 0.05 mg L^{-1} (the limiting value recommended by WHO) could be obtained using the both configurations. However, CC increased the concentration of dissolved solids above the guideline recommended for drinking water.

Key works:

Chromium; chemical coagulation; electrocoagulation; drinking water; semi-pilot scale.

NOMEMCLATURE

CC = Chemical coagulation

EC = Electrocoagulation

Fe II = Iron in reduced ionic form

CrT = Total chromium (Cr(VI) + Cr(III))

CrTsed = Total concentration of Cr to the output of the sedimentation

CrTfilt = Total concentration of Cr to the output of the sand filtration

CrTD = Total chromium dissolved

FeT = Total iron (Fe(II)+ Fe(III))

FeTt = Total theoretical concentration of Fe

FeTreact = Total concentration of Fe to the output of the reactor

FeTsed = Total concentration of Fe to the output of the sedimentation

FeTfilt = Total concentration of Fe to the output of the sand filtration

FeTD = Total iron dissolved

MCL = Maximum Concentration Level

MF = Microfiltration

NOM = Mexican Official Standards

WHO = World Health Organization

1 Introduction

In aquatic environments, chromium is mainly found in two states of oxidation: hexavalent Cr(VI) and trivalent Cr(III). Under typical pH and potential redox conditions found in underground water; hexavalent chromium exists in solution as bichromate ($HCrO_4^{-}$), chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). Generally, the salts containing the ionic form of Cr(VI) are more soluble than those containing Cr(III). It is required to reduce the oxidation state of chromium in order to easily remove it from water [4]. On the other hand, Cr(VI) is also the most toxic form for microorganisms, plants, animals and humans [11]. Due to the health risks from the presence of this element in drinking water, its maximum concentration is regulated in Mexico by the Mexican Official Standard NOM-127-SSA1-1994 (modified in the year 2000) [22] to a limiting value of 0.05 mg L^{-1} of total chromium (CrT). The guideline from World Health Organization for drinking water is 0.05 mg L^{-1} [11].

Abundant literature currently exists on the treatment of water with highly toxic chromium species. Water treatment processes for chromium removal can mainly be divided into four groups: a) reduction-coagulation (chemical or electrochemical) of Cr(VI) to Cr(III) followed by flocculation, precipitation and filtration [1, 2]; b) adsorption or bioadsorption on different types of materials macro or nanoparticles [10, 15, 16]; c) ion exchange [21] and d) membrane filtration technology [18].

The most appropriate technology to remedy an aquifer contaminated with chromium depends on a variety of factors, including: the area and depth of the contaminated aquifer, the flow velocity, the volume to be treated, the conductivity of the contaminated soil, the geochemical properties, the organic material available in the soil, the concentration of the contaminant, the presence of other ions in the matrix, the pH, as well as the availability of land to implement some type of *ex-situ* treatment.

A treatment *ex-situ* for the removal of chromium is chemical coagulation with ferrous sulfate ($FeSO_4$). This approach is used to reduce Cr(VI) to Cr(III) through the oxidation of Fe(II) to Fe(III). Fe(III) can react with water to forms ferric hydroxides having large surface area that can be used as sorption agents for chromium [14]. Chromium can be completely remove from water when this method is combined with sedimentation followed by filtration.

Hexavalent chromium was not removed by alum or ferric coagulation or by lime softening, this can be attributed to high solubility of chromate and dichromate ions [1]. Lee and Hering [17] indicated that at pH values higher than 6.5 the global redox reaction between the Cr(VI) and Fe(II) takes place as follows (Eq. 1):

$$CrO_4^{-2} + 3Fe^{+2} + 8H_2O \rightarrow 4Fe_{3/4}Cr_{1/4}(OH)_{3(s)} + 4H^+ \qquad (1)$$

The required dose of Fe(II) is 3 to 5 times the molar concentration of Cr(VI). This process is efficient, but it has the disadvantage of requiring high doses of coagulant at elevated chromium concentrations. Large amounts of coagulant increase the dissolved salts in treated water and produce a large amount of sludge that has to be disposed of as hazardous waste.

An alternative method of chemical coagulation (CC) is electrocoagulation (EC), in which the production of the coagulant is performed through the electrochemical oxidation of sacrificial electrodes without the need of added chemical salts. Similar to chemical methods, electrocoagulation electrodes (made either iron, aluminum, or an alloy) reduce Cr(VI), followed by $Cr(OH)_3$ precipitation [9]. Batch adsorption experiments [25] in which Cr(VI) was contacted with preformed solids produced by electrocoagulation indicated that Cr(VI) adsorption is not a dominant mechanism for Cr(VI) removal in EC and that the reduction to Cr(III) is critical to successful treatment.

The main advantages of using EC to remove chromium from water can be summarized as follows: i) EC does not increase the concentration of dissolved salts and produces up to 50% less sludge than redox-assisted CC [3]; ii) EC involves successive stages of coagulant formation and subsequent reduction of hexavalent chromium to trivalent chromium, mainly with iron electrodes [29]. The theoretical reactions in the EC reactor, is shown in Eq.2, Eq.3 and Eq.4 [5]:

Anode $$Fe(s) \rightarrow Fe(II) + 2e^-$$
$$Cr^{6+} + 3Fe^{2+} \leftrightarrow Cr^{3+} + 3F \leftrightarrow e^{3+} \quad (2)$$

Cathode $$2H_2O + 2e^- \rightarrow 2OH^-(aq) + H_2(g) \quad (3)$$

Overall reaction in bulk solution (pH between 6 and 8) [7]:

$$CrO_4^{-2}(aq) + 8H^+(aq) + 6Fe(II)(aq) \rightarrow Cr(III)(aq) + 6Fe(III)(aq) + 4H_2O$$

$$Cr_2O_7^{-2}(aq) + 14H^+(aq) + 6Fe(II)(aq) \rightarrow 2Cr(III)(aq) + 6Fe(III)(aq) + 7H_2O$$

$$Cr(III)(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s) \quad (4)$$

Faraday Law states that the number of moles produced (N) in an electrochemical process is directly proportional to the amount of charge that passes between the electrodes. The production of iron (coagulant) in an electrochemical reactor that operates continuously depends directly on the current (I) and inversely on the flow (Eq. 5). Faraday's law is used to provide a theoretical amount for total iron:

$$m = \frac{I.t.M}{z.F} \qquad (5)$$

Where "m" is the amount (g) of iron ions generated, "z" is the number of electrons transferred in the reaction at the electrode, "M" is the molecular weight (g. mol^{-1}), "I" is the applied current (A), "t" is the treatment time (s) and "F" is Faraday's constant (96 500 C.mol^{-1}). The concentration of iron in g/L can be calculated as follows:

$$FeTt = \frac{m}{V} = \frac{I.t.M}{z.F.V} = \frac{I.M}{z.F.Q} \qquad (6)$$

Where "V" is the working volume (L) of water in the reactor and, "Q" is the flow rate of water (L.s^{-1}). The current to be applied to set the desired dose of iron can be determined from equation 5. The resulting voltage (V) depends on the resistance of the system by the passage of current intensity.

In a batch electrocoagulation system [12], the experimental results proved that EC can reach 100% removal of 0.2 mg L^{-1} of total chromium, from brackish groundwater, using iron electrodes arrangement with ACD of 7.94 mA cm^{-2}, initial pH of 8, and an operating temperature of 25 °C.

In batch cell removing chromium ions (Cr^{6+} & Cr$^{3+)}$ from synthetic wastewater solutions (from 100 to 300 ppm) by electrocoagulation [30], the study revealed that as current density increases, %Cr^{3+} removal slightly increases, whereas % Cr^{6+} removal slightly decreases. Maximum % Cr^{6+} removal occurs at pH 4.5, whereas maximum % Cr^{3+} removal occurs at pH 8.

An electrocoagulation column (ECC) in continuous operation was evaluated [13] for the treatment of the collected brackish groundwater water samples contained 0.2 mg L^{-1} of chromium and other ions. The optimum conditions in terms of initial pH, feed flowrate and applied current density (ACD) were found to be 8, 30 mL min^{-1} and 7.61 mA cm^{-2} respectively. The chromium removal efficiency was 100%.

When iron plates were used as sacrificial anodes [24], the electrocoagulation process was effective (99%) in removing chromium (18.1 ppm) when the solution pH was maintained in the range of 6.9 to 8.8.

Borghe-ei et al. [6] also studied Cr removal from a synthetic wastewater by using electrocoagulation process. Different voltages, treatment times and initial pH were tested to remove Cr having an initial concentration of 50 mg L^{-1}. They observe that lower pH, more contact time and higher voltages are required to efficiently remove Cr by electrocoagulation method.

Bazrafshan et al. [5] showed that electrocoagulation process achieved a fast and effective reduction of Cr (over 98%) in solutions containing an initial Cr concentration up to 500 mg L^{-1}. The best results were obtained when the pH was maintained at 3, with a voltage ranging from 20 to 40 V and a treatment time of 20 - 60 min.

According to Sadeghi et al. [27] the optimal values for treatment of 50 mg/L of Cr(VI) were 90.32% at initial pH of 5, current of 2 A, reaction time of 60 min and initial PACl concentration of 1010 mg/L.

Dans l'analyse par Patidar et al. [26], sur le potentiel du processus de l'électrocoagulation pour l'élimination des métaux lourds dans l'eau, ils concluent que la plupart des études qui existent dans la littérature sont en batch, et qu'il est nécessaire d'effectuer essais pilotes pour déterminer la faisabilité d'utiliser ce processus à l'échelle réelle.

The main objective of this study was to compare the efficiency of electrocoagulation (EC) with chemical coagulation (CC) in treating water contaminated by relatively high concentrations of chromium. To do this, a continuous semi-pilot comprising either of EC or CC, followed by flocculation, sedimentation and sand-filtration steps was used to compare the two technological approaches.

2. Material and methods

CC and EC experiments were carried out using the same initial water quality. The only difference consisted in the coagulant ion dose. Settling and sand-filtration operations were successively applied after physicochemical treatments (CC or EC). Besides, effluents from CC and EC were filtered through membranes with a pore size of 0.45 and 0.1 μm, respectively.

2.1. Quality of Water

The water samples used throughout this study were obtained from a well contaminated with chromium waste. Its principal physicochemical characteristics were the following: CrT=19.0 mg L^{-1}; Cr(VI)=18.5 mg L^{-1}; true color =150 UPt-Co; conductivity =1264 μS cm^{-1}; total dissolved solids (TDS)=872 mg L^{-1}; pH=6.21; total hardness (TH)=320 mg L^{-1} $CaCO_3$; sulphate (SO_4^{2-}) = 324 mg L^{-1}.

2.2. Chemicals

Monterrey brand analytical grade ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was used for chemical coagulation. For electrocoagulation, Fe(II) was produced by anodic dissolution of iron sacrificial electrodes. A KEMIRA A-100PWG Superfloc anionic polymer was used as flocculent agent in both processes. Reactive grade J.T. Baker brand sodium hydroxide (NaOH) and/or hydrochloric acid (HCl) were used for the pH adjustment. Basic and acidic solutions were prepared respectively at a concentration of 0.15 N and 0.1 N. Between two tests, the electrolytic reactor was cleaned with 30% hydrochloric acid solution and rinsed with tap water.

2.3. Experimental pilot unit

The pilot unit used in this study (Figure 1) was operated in continuous mode with a flow rate of 1.5 L min^{-1}. The treatment stages can be summarized as follows: a) chemical coagulation (in rapid agitation chamber) or electrochemical coagulation (with a tubular EC reactor of 1.44 L); b) mechanical flocculation in three chambers, each one of them having 10 L of working volume and mixing was achieved by an agitator with various-speed palettes driven by a ¼ HP motor (BALDOR, 90 V); c) ascending flow high-rate settling, with a set capacity of 60 L; d) filtration in a column with a diameter of 9 cm, packed with a gravel bed of 13 cm thickness and silica sand having 50 cm high, this with an equivalent diameter (Deq) = 0.65 mm and a uniformity coefficient (U.C.) = 1.5. The system was built in transparent acrylic in order to see inside of each treatment unit. To measure the flow rate of water, a rotameter industrial "Blue-White", model F400 was installed in the inlet pipe, which was verified periodically by the method volume-time, at the exit of the settler or filter unit.

EC reactor was built joining eight tubes of PVC schedule 40 with 3/4 inch in diameter and 1.17 m length, hydraulically connected between them with 90° elbows. Inside this housing were connected, concentrically, two electrodes manufactured with schedule 40, ASTM (Association for Testing Materials) 53/A 106 grade carbon steel, with nominal diameters of 1/2 and 1/4 inch. Concentric electrodes were connected electrically in monopolar configuration. When the water passes through the concentric electrodes, it was enriched with iron produced by the oxidation of the material. In addition to producing the Fe (II) required for coagulation, the electrochemical reactor ensures the optimal mixing in this stage of the process. A Sorensen brand DCM40-15 model was used as power supply, which allowed for the current to be set. A differential manometer was installed at the entrance and exit of the reactor to measure the head loss (ΔH) in centimeters of mercury.

2.4. Analytical methods and equipment

The methods and equipment used to determine water quality were the following: true color with spectrophotometer Hach, method 8025; electrical conductivity and TDS with WWW/340i equipment; CrT with Flame Atomic Absorption spectrometer [23] and Hach method 8024; Cr(VI) with spectrometer Hach, method 8023; TH with titration with EDTA; SO_4^{2-} with turbidimeter Hach, method 8051 and total iron (FeT) with spectrometer Hach, method 8008. Hach Company DR/2800 equipment was used for the spectrophotometry.

The validation of the method of measurement of total chromium used, took place preparing standards of concentration known from a stock solution of 50 mg/L of Cr(III) (Hach, lot A1188); these standards were analyzed by the Hach 8024 method and by Mass Spectrometry of Atomic-Flame Absorption (SAA) [23]. The adjusted correlation coefficients R^2 resulted: 0.9973 for Hach-Theoretical comparison, 0.9993 for SAA-Theoretical comparison and 0.9949 for Hach-SAA comparison.

2.5. Description of tests

Chemical Coagulation (CC)

The coagulant and pH modifier were added in the rapid mixing chamber for CC tests. Preliminary tests to determine the optimum dose, it allowed to check that the reduction reaction is very fast and a contact time of 15 seconds is sufficient to complete the reaction. The water passed directly from the rapid mixing to the flocculation, followed by settling and filtration stages. The polymer was added to the water at the entrance to the flocculation. The operating conditions during the CC tests are shown in Table 1.

Electrochemical Coagulation (EC)

The doses for iron and polymer at a laboratory scale, as well as the most efficient pH for CrT removal are summarized in Table 2. Once treated by EC reactor, the water passed into the rapid mixing chamber, where the polymer was added and the pH was adjusted. Only a fraction of water flow rate leaving the reactor was sent directly in the next process (flocculation-sedimentation-filtration), due to the capacity of these units. The EC reactor was chemically washed using a solution of 5% commercial descaling agent before and after every test. The wash lasted eight minutes in the direction of the flow and eight minutes against the flow, with the purpose of eliminating anything deposited and encrusted on the surface of electrodes and on the wall of the reactor that may have formed during the test. The reactor was then rinsed with clean water until the pH was neutral.

Clarification and filtration

The Fe (II) added to water (during CC or EC processes) reduces the Cr(VI) to Cr(III). The reduced form of chromium (Cr(III)) can be adsorbed onto the iron hydroxide formed or forming highly insoluble chromium hydroxide (Eq. 1) [19]. Both products can be agglomerated to form larger particles through flocculation, and separated from the water by sedimentation and filtration. The same stages of clarification, with the same operating conditions (Table 3), were used for CC as well as for EC tests. The mixing gradients, residence times and sedimentation and floculation velocities are those conventionally used [8] for this type of process. Samples were taken at the outlet of sedimentation as well as filtration to determine the CrT and FeT.

3. Results and discussion

3.1. Performances of Chemical Coagulation (CC)

Table 4 and Figure 2 show the results recorded by using CC, sedimentation and filtration steps. The treatment efficiency was obtained by measuring the total iron (FeT) and the total chromium (CrT) at the outlet of each experimental unit. The maximum percentages of Fe and Cr removal of 96.7% and 99.7% were respectively recorded at the outlet of the settling tank. After sand filtration, 99.9% Fe and >99.9% Cr were removed. Thus, CC treatment followed by flocculation, sedimentation and sand filtration allowed maintaining the residual CrT concentration below the maximum concentration level (MCL) (0.05 mg L^{-1}) recommended in water for human consumption in Mexico [22]. However, when the dose of iron reached 54.5 mg L^{-1} at the 6th hour of operation, the residual CrT concentration was above the limiting MCL value. This indicates that the FeT/CrT ratio must not be lower than three in order to guarantee a residual CrT concentration below the maximum concentration level (MCL). The average concentration of iron dosed was 63.8 ± 5.2 mgL-^{1} and the relationship of FeT/CrT was 3.4 ± 0.3. The erratic behaviour of iron in the sedimentation and filtration stages suggests the need for stabilization of sludge and "maturity" of the filter bed to achieve a system of separation stable of flocs.

Unlike what happens with the concentration of chromium, the iron in the filter effluent only meets the level recommended in water for human consumption in Mexico (0.3 mg L^{-1}) [22] when the FeT dose is 54.5 or 61.0 mg L^{-1}. It is necessary to remove iron from water due to the colorization of water when its concentration is higher than the MCL. The removal of iron from water contributes to reduce the operating costs and avoid maintenance problems caused in the distribution networks.

The pH values obtained in the treated water always fall within the interval of 6.5 to 8.5 established by quality standard. The high concentrations of sulfates in the filter effluent (450-470 mg L^{-1}) are due to the average initial concentration of sulfates in the raw water, and the contribution of sulfate anions (approximately 136 mg L^{-1}) from the ferrous sulfate used as a reducing agent and coagulant, which represents an increment in TDS. The final values of the sulfate ion exceed those indicated (400 mg L^{-1}) in the guideline from Mexico [22], so the system need to remove these dissolved compounds by using for instance nanofiltration process.

3.2. Performances of Electrocoagulation (EC)

The results from Table 5 and from Figure 3 show, with respect to the EC reactor operation, that there was no electrode passivation since the voltage did not increase during the duration of the test, however, there was a continuous increase in the head loss through the reactor; this indicates that the floc and/or the gas formed inside the reactor, formed a hydraulic blockage that decreased the transverse section of the flow. The average concentration of iron dosed was 59.95 ± 4.81 mgL^{-1} and the ratio FeT/CrT was 3.17 ± 0.26. Even though the ratio FeT/CrT> 3, this was not sufficient to meet the MCL for chromium (Cr). During the stage of filtration, iron particles that already contained Cr, could not be retained. Maximum removal efficiencies for Fe and Cr recorded at the outlet of the settling tank were 97.5% and the 99.1%, respectively. The efficiency of the EC system increases with the operating time and the concentration of CrT can meet the water quality standards with a ratio of FeT/CrT = 3.

The advantage of EC process (compared to CC) was mainly due to the fact that the residual concentrations of sulfates did not surpass the limit allowed by the water quality standard. Thus, additional process was not necessary to eliminate the dissolved solids. The configuration of the treatment including successively EC, flocculation, decantation and sand filtration steps appeared to be more effective and stable to remove CrT, compared to the configuration using CC, flocculation, decantation and sand filtration processes (Figure 2 and Figure 3). In fact, the process including EC system remained stable over third hours of treatment, even if the dose of iron decreased from 67.8 to 57 mg L^{-1}. The rapid precipitation of iron can be compared in Figure 2 and Figure 3. It can be observed that in the second hour, the concentration of iron recorded at the outlet of the settling tank was below 3 mg L^{-1} by using EC process, whereas a residual concentration of 5.55 mg L^{-1} was recorded at the same time using CC process. This indicates that the metallic floc produced by EC was heavier and had less water attached, leading to its rapid precipitation. In the case of CC, it can be observed that there was more residual iron concentration recorded at the outlet of the settling tank, compared to the value recorded in the case of the configuration using EC process. Nevertheless, the residual CrT concentrations were lower. In both cases, it was feasible to be able to produce an effluent with a residual CrT concentration less than or equal to 0.05 mg L^{-1}. Using electrocoagulation process, the system was more stable, but it need more time to reach a concentration suitable for CrT. However, it would be worthwhile to slightly increase the FeT/CrT ratio while using EC to take advantage of the stability of the system and not increase the dissolved solids in treated water.

3.3. Filtration in 0.1μm and 0.45 μm

To verify the efficiency of Cr(VI) reduction to Cr (III) form, as well as the association of the latter with the formed iron hydroxides, samples were taken at the outlet coagulation step during a period of 6 hours. Table 6 shows that the elimination of specific pollutants (Cr and Fe), is forming insoluble species from the stage of coagulation, in the two processes studied. However, in the EC, only after 4 hours of operation are managed properly to remove chromium, whereas with CC this was observed from the beginning.

Based on these results, if the iron passes through the sand filter and does not meet the quality standard, it is suggested using microfiltration membranes to ensure the quality of the water. However, it is not recommended to remove the sand filtration stage prior to the microfiltration, since the high amount of coagulant would lead to frequent washing of the membranes.

It is interesting to compare these results with those obtained to different experimental conditions by other authors.

The removal of hexavalent chromium from a synthetic solution using electrocoagulation process was studied by Verma et al. [28]. The best percentages of Cr removal (~100%) was recorded for an initial pH of 4.0 and a current density imposed of 50 mA cm^{-2} during a period of electrolysis of 15 min. They compared the chromium removal using ferric chloride as a coagulant and found that electrocoagulation is more efficient and relatively faster in comparison with chemical coagulation.

Mella and Glanert [20] studying the removal of the Cr from the tanning wastewater through chemical precipitation (CP) and electrocoagulation (EC) techniques obtained that, the highest removal efficiency of 97.76% was obtained with Al electrodes by conducting electrolysis at 3.0 V for 110 min. Electrocoagulation with iron electrodes at a current density of 10 mA cm^{-2}, electrocoagulation time of 20 min, and pH 3.0 resulted in 99.9 % removal efficiency of Cr.

By comparison, similar or better results were obtained in the present study, but with a reactor that requires pH of natural water, few seconds of residence time and low voltage.

4. Conclusion

This comparison study shows that EC is a viable alternative to CC for removing chromium, with the advantage of not adding other ions to the water and therefor avoiding the addition of another treatment stage to remove them. CC removal efficiencies recorded at the outlet of sand filter were 99.9% for FeT and >99.9% for CrT. By comparison, EC removal efficiencies were 99.7% for FeT and CrT. FeT/CrT ratios for CC and EC were 3.4 ± 0.3 and 3.17 ± 0.26, respectively. The system comprised of EC, flocculation, decantation and sand filtration showed better stability and flexibility to inject the reducing agent coagulant (iron). The EC process does not increase the sulfate concentration in water, while the CC process exceeds the water quality standard due to the addition of coagulant. Residual CrT concentration below 0.05 mg L^{-1} (the limiting value recommended by WHO and NOM) could be obtained using either the configuration of the treatment comprising of EC or CC process. However, the efficiency could be improved by using microfiltration membrane instead of sand filtration.

Conflict of interest

The authors declare no competing financial interest

Acknowledgements

The authors are grateful to the Mexican Institute of Water Technology (IMTA) and the Ministry of Environment and Natural Resources (SEMARNAT) for the support received in the accomplishment of this work.

References

[1] AWWA. Chromium in Drinking Water: A technical information primer. http://www.awwa.org/Portals/0/files/legreg/documents/UpdatedChromiumInDrinkingWaterSummaryFinal.pdf, 2013.

[2] S. Aoudj, A. Khelifa, N. Drouiche, R. Belkada and D. Miroud. Simultaneous removal of chromium(VI) and fluoride by electrocoagulation–electroflotation: Application of a hybrid Fe-Al anode. Chemical Engineering Journal 267 (2015) 153–162.

[3] C. Barrera-Díaz, M. Palomar-Pardavé, M. Romero-Romo, S. Martínez. Chemical and electrochemical considerations on the removal process of hexavalent chromium from aqueous media. Journal of Applied Electrochemistry. 33(1) (2003) 61-71.

[4] 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 (2012) 1– 12.

[5] E. Bazrafshan, A.H. Mahvi, S. Naseri, A.R. Mesdaghinia, Performance Evaluation of Electrocoagulation Process for Removal of Chromium (VI) from Synthetic Chromium Solutions Using Iron and Aluminum Electrodes. Turkish J. Eng. Env. Sci. 32 (2008) 59 – 66.

[6] S.M. Borghe-ei, J. Goodarzi, M. Mohseni, A. Amouei, Efficiency of Removing Chromium from Plating Industry Wastewater using the Electrocoagulation Method. *Int. Arch. Health Sci.*, 2(2) (2015) 83-87.

[7] M. S. Bhatti, A. K. Thukral, A. S. Reddy and R. K. Kalia (Chapter 1 RSM an ANN-GA Experimental Desing Optimization for Electrocoagulation removal of Chromium).

Capital Publishing Company, New Delhi, India. Trends in Asian Water Environmental Science and Technology, DOI 10.1007/978-3-319-39259-2_1. (2017).

[8] J. Bratby, Coagulation and Floculation in water and wastewater treatment. IWA Publishing (2006), London. Second edition.

[9] M. Chebeir. Occurrence and Transformation of Chromium in Drinking Water Distribution Systems. UC Riverside Electronic Theses and Dissertations. Powered by the California Digital Library. University of California. (2017).

[10] M. Ciopec, C.M. Davidescu, A. Negrea, I. Grozav, L. Lupa, P. Negrea and A. Popa. Adsorption studies of Cr(III) ions from aqueous solutions by DEHPA impregnated onto Amberlite XAD7 – Factorial design analysis. Chem. Eng. Res. Des. 90(10) (2012)1660–1670.

[11] Guidelines for Drinking-Water Quality - 4th ed. WHO Library Cataloguing-in-Publication Data. ISBN 978 92 4 154815 1. World Health Organization (2011).

[12] S.S. Hamdan and M.H. El-Naas. Characterization of the removal of Chromium (VI) from groundwater by electrocoagulation. J. Indus. Eng. Chem. 20(5) (2014) 2775–2781.

[13] S. S. Hamdan, M. H. El-Naas. An electrocoagulation column (ECC) for ground water purification. Journal of Water Process Engineering 4 (2014) 25–30.

[14] I. Kabdaşl, I. Arslan-Alaton, T. Ölmez-Hancı and O. Tünay. Electrocoagulation applications for industrial wastewaters: a critical review. Environmental Technology Reviews. 1(1) (2012) 2–45.

[15] M. Kumar, A. Pal, J. Singh, S. Garg, M. Bala, A. Vyas, Y.P. Khasa and U.C. Pachouri. Removal of chromium from water effluent by adsorption onto *Vetiveria zizanioides* and *Anabaena* species. Nat. Sci. 5(3) (2013) 341-348.

[16] K.C.K. Lai and I.M.C Lo. Removal of chromium (VI) by acid-Washed zero-valent iron under various groundwater geochemistry conditions. Environ. Sci. Technol. 42 (4) (2008) 1238-1244.

[17] G. Lee and J. G. Hering. Removal of chromium (VI) from drinking water by redox-assisted coagulation iron (II). Journal of Water Supply: Research and Technology - AQUA. 52.5 (2003) 319-332.

[18] V. Madhavi, A. V. Bhaskar Reddy, K. G. Reddy, G. Madhavi and T. N. K. Vara Prasad. An Overview on Research Trends in Remediation of Chromium. *Res. J. Recent Sci.* 2 (1) (2013)71-83.

[19] L. McNeill, J. McLean, M. Edwards and J. Parks. State of the science of hexavalent chromium in drinking water. Water Research Foundation. Denver, Co. USA (2012).

[20] B. Mella, A.C. Glanert and M. Gutterres. Removal of chromium from tanning wastewater and its reuse. Proc. Safe. Environ. Prot. 95 (2015) 195-201.

[21] D. Neshem, J. P. Hanson, C. Miller, K. Ivarson, N. Jaschke and P. Meyers. Efficiencies and Optimization of Weak Base Anion Ion-Exchange Resin for Groundwater Hexavalent Chromium Removal at Hanford – 14202. WM2014 Conference. March 2 – 6 (2014) 1-13. Phoenix, Arizona, USA.

[22] Norma Oficial Mexicana (NOM-127-SSA1-1994). Salud ambiental. Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización. *Diario Oficial de la Federación. 20 de junio de 2000, México*.

[23] Norma Mexicana NMX-AA-044-SCFI-2014. Water Analysis - Measurement of Hexavalent Chromium in Natural Waters, Saline Waters, Wastewaters And Treated Wastewaters–Test Method. https://www.gob.mx/cms/uploads/attachment/file/166148/nmx-aa-044-scfi-2014.pdf

[24] I. E. Odongo and M. J. McFarland. Electrocoagulation Treatment of Metal Finishing Wastewater. Water Environment Research. 86(7) (2014) 579-583.

[25] C. Pan, L. D. Troyer, J. G. Catalano and D. E. Giammar. Dynamics of Chromium(VI) Removal from Drinking Water by Iron Electrocoagulation. Environ. Sci. Technol. 50 (2016) 13502−13510.

[26] K. Patidar, A. Chouhan, L. S. Thakur. Removal of Heavy Metals from Water and Waste Water by Electrocoagulation Process –A Review. International Research Journal of Engineering and Technology (IRJET). 4(11) (2017) 16-25.

[27] S. Sadeghi, M. R. A. Moghaddam and M. Arami. Techno-economical evaluation of hexavalent chromium removal by electrocoagulation process with the aid of polyaluminum chloride as coagulant: optimization through response surface methodology. Environmental Engineering and Management Journal 16(1) (2017) 93-104.

[28] S.K. Verma, V. Khandegar, A.K. Saroha. Removal of Chromium from Electroplating Industry Effluent Using Electrocoagulation. Journal of Hazardous, Toxic, and Radioactive Waste. 17(2) (2013).

[29] A.E. Yehia, N. Ehssan, E. Iman, S. Doaa. Removal of Cr(VI) ions from waste water by electrocoagulation using iron electrode. Egypt. J. Petr. 24(2) (2015) 183-192.

[30] T.M. Zewail, N.S. Yousef. Chromium ions (Cr^{6+} & Cr^{3+}) removal from synthetic wastewater by electrocoagulation using vertical expanded Fe anode. Journal of Electroanalytical Chemistry 735 (2014) 123–128.

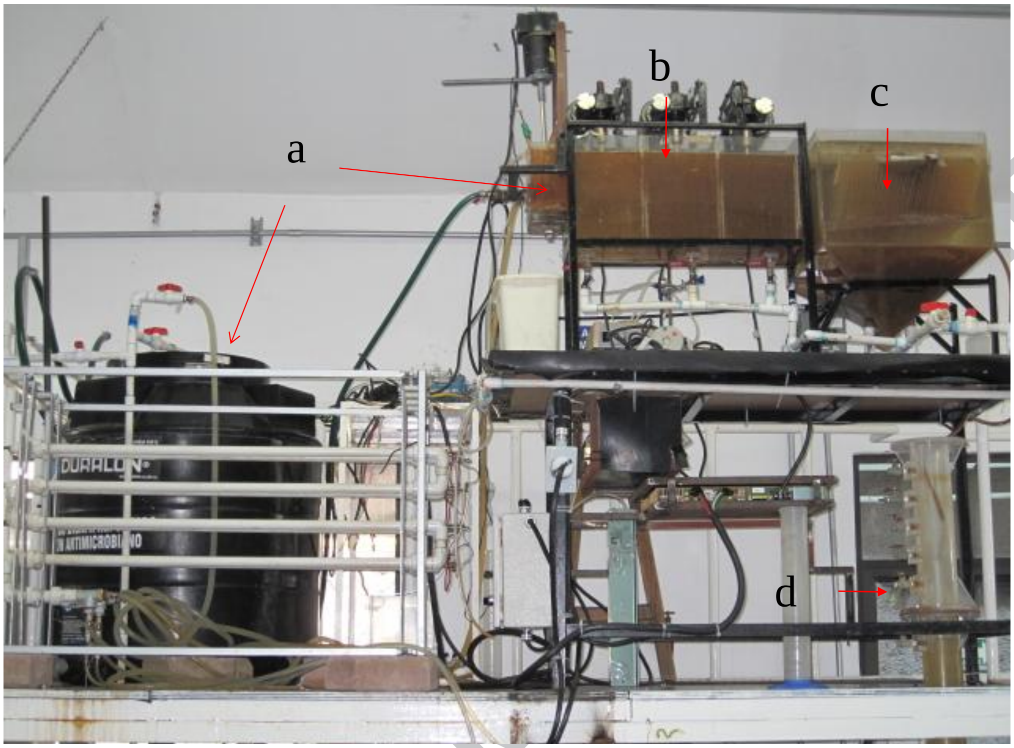

Fig.1 **Semi-pilot plant: a) EC reactor and rapid agitation chamber for CC, b) three-chamber of flocculation, c) high-rate settler and d) silica sand filter.**

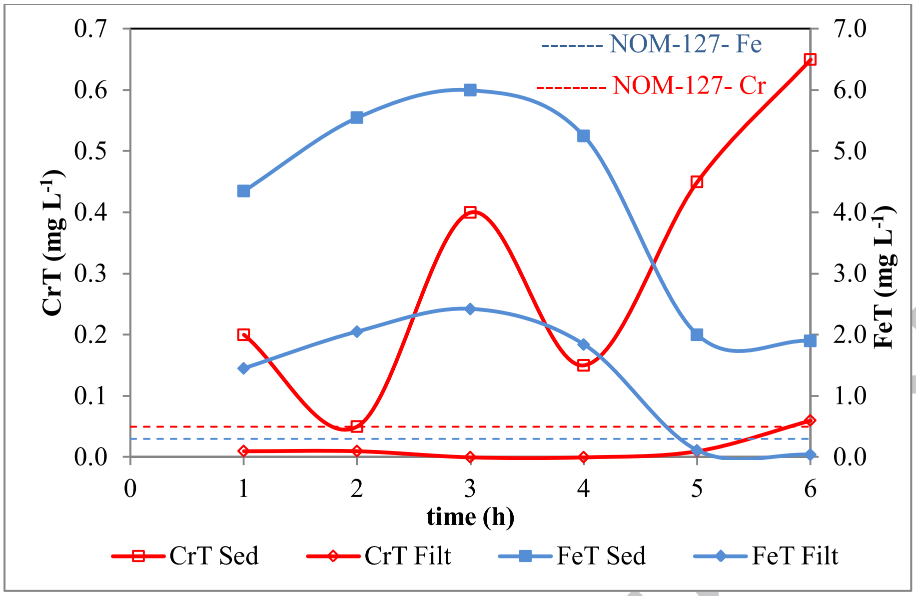

Fig.2 Variation of CrT and FeT in water during chemical coagulation (CC) treatment.

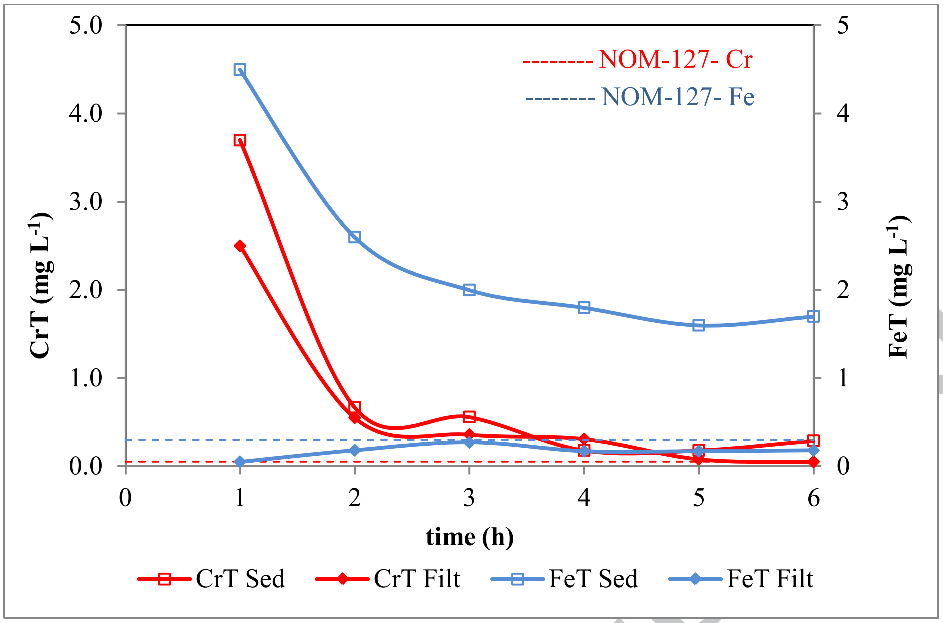

Fig.3 **Variation of CrT and FeT in water during electrocoagulation (EC) treatment.**

Table 1: **Operating conditions in the CC system**

Parameters	**Values**
Flow in the coagulation stage (Q_{CC})	1.5 L min^{-1}
pH	7.0

Dose of polymer	1.0 mg L^{-1}
Dose of Fe	~ 60 mg L^{-1}
Velocity gradient in the rapid mix stage	600 s^{-1}
Residence time in the rapid mix stage	1 min

Table 2: Operating conditions of the EC system

Parameters	**Values**
Flow in the EC reactor (Q_{EC})	3.5 L min^{-1}
Current applied (I)	12.5 – 12.7 A
Current density (i)	30 A m^{-2}
Voltage (V)	3.5- 4.3
pH	~ 7,0
Dose of polymer	1 mg L^{-1}
Dose of coagulant Fe	~ 60 mg L^{-1}
Velocity gradient in the reactor	325 s^{-1}
Residence time in the reactor	24.6 s
Velocity gradient in the mixing chamber (pH adjustment/polymer addition)	600 s^{-1}
Residence time in the mixing chamber (pH adjustment/ addition of	1 min

polymer)	

Table 3: Operating conditions for the clarification and filtration stages

Parameters	**Values**
Flow rate in the clarification stage	~1.5 L min^{-1}
Successive velocity gradients in the flocculation tank	60 s^{-1}; 40 s^{-1}; 20 s^{-1}
Residence time in the flocculation tank	21 min
Settling rate (settling tank)	16 m h^{-1}
Residence time in the settling tank	45 min
Filtration rate	14 m h^{-1}

Table 4: Performances during chemical coagulation (CC) process

Effluent from coagulation			
Time (h)	Conductivity (µS cm^{-1})	FeT (mg L^{-1})	FeT/CrT
1	1241	68.0	3.6
2	1235	66.5	3.5
3	1235	67.5	3.6

4	1301	65.5	3.4
5	1285	61.0	3.2
6	1274	54.5	2.9
Average	1262	63.8	3.4
SD	31	5.2	0.3

Effluent from settling

Time (h)	pH	Conductivity (µS cm^{-1})	FeT$_{Sed}$ (mg L^{-1})	CrT$_{Sed}$ (mg L^{-1})	FeT$_{sed}$ Remov (%)	CrT$_{sed}$ Remov (%)
1	6.89	1270	4.35	0.20	93.6	98.9
2	6.83	1292	5.55	0.05	91.7	99.7
3	6.81	1298	6.00	0.40	91.1	97.9
4	6.81	1320	5.25	0.15	92.0	99.2
5	7.07	1367	2.00	0.45	96.7	97.6
6	7.22	1367	1.90	0.65	96.5	96.6
Average	6.94	1319	4.18	0.32	93.6	98.3
SD	0.11	40	1.81	0.22	2.5	1.2

Effluent from filtration

Time (h)	pH	Sulfates (mg L^{-1})	FeT$_{Filt}$ (mg L^{-1})	CrT$_{Filt}$ (mg L^{-1})	FeT$_{Filt}$ Remov (%)	CrT$_{Filt}$ Remov (%)
1	7.14	460	1.45	0.01	97.9	99.9
2	6.87	450	2.05	0.01	96.9	99.9
3	6.80	470	2.42	≤ 0.01	96.4	≥ 99.9
4	6.87	470	1.84	≤ 0.01	97.2	≥ 99.9
5	7.13	460	0.11	0.01	99.8	99.9
6	7.34	450	0.04	0.06	99.9	99.7
Average	7.03	460	1.32	0.02	98.0	99.9
SD	0.21	8,94	1.01	0.02	1.5	

SD= Standard Deviation

Table 5: Performances during electrocoagulation (EC) process

EC reactor (Operating Conditions)

Time (h)	V (Volts)	ΔH (cm Hg)
1	3.9	9.4
2	3.8	11.6
3	3.5	13.2
4	3.6	14.6
5	3.7	17.6
6	3.8	20.4
Average	3.72	14.47
SD	0.15	4.01

Effluent from EC reactor

Time (h)	Cond. (μS cm^{-1})	pH	FeT_t (mg L^{-1})	FeT_{react} (mg L^{-1})	FeT/CrT
1	1327	7.0	63.8	67.8	3.6
2	1350	7.1	62.0	55.0	2.9
3	1320	6.9	62.0	56.3	3.0
4	1325	7.0	63.4	61.3	3.2
5	1322	7.0	64.1	62.3	3.3
6	1317	7.1	64.9	57.0	3.0
Average	1327	7.02	63.37	59.95	3.17
SD	12	0.08	1.17	4.81	0.26

Effluent from settling

Time (h)	Cond. (μS cm^{-1})	pH	FeT_{sed} (mg L^{-1})	CrT_{sed} (mg L^{-1})	FeT_{sed} (%)	CrT_{sed} (%)
1	1309	6.9	4.5	3.70	92.9	80.5
2	1335	7.0	2.6	0.67	95.8	96.5
3	1317	7.0	2.0	0.56	96.8	97.1
4	1310	7.2	1.8	0.18	97.2	99.1
5	1267	7.1	1.6	0.18	97.5	99.1
6	1304	7.2	1.7	0.29	97.4	98.5
Average	1307	7.07	2.37	0.93	96.3	95.1
SD	22	0.12	1.10	1.37	1.74	7.22

Effluent from filtration

Time (h)	SO_4 (mg L^{-1})	Cond. (μS cm^{-1})	pH	FeT_{filt} (mg L^{-1})	CrT_{filt} (mg L^{-1})	FeT_{filt} (%)	CrT_{filt} (%)
1	350	1302	6.74	0.05	2.50	99.9	86.8
2	350	1303	7.08	0.18	0.55	99.7	97.1

3	360	1317	7.23	0.27	0.36	99.6	98.1
4	365	1317	7.18	0.17	0.31	99.7	98.4
5	360	1293	7.26	0.17	0.08	99.7	99.6
6	380	1290	7.20	0.18	0.05	99.7	99.7
Average	361.8	1304	7.12	0.17	0.64	99.7	96.6
SD	11	11.48	0.19	0.07	0.93	0.11	4.89

SD= Standard Deviation

Table 6: **Total chromium dissolved (CrTD) and Total iron dissolved (FeTD) upon leaving the EC reactor and the mixing chamber for CC**

Time (h)	**EC reactor effluent (filtered by 0.1** μm)		**CC Mixing chamber effluent (filtered by 0.45** μm)	
	FeTD (mg L^{-1})	CrTD (mg L^{-1})	FeTD (mg L^{-1})	CrTD (mg L^{-1})
1	0,02	3,30	0,01	0,03
2	0,01	0,50	0,02	0,04
3	0,01	0,40	0,01	0,02
4	0,04	0,05	0,01	0,02
5	0,04	0,05	0,02	0,03
6	0,05	0,01	0,01	0,03

Research Highlights

- A semi-pilot comprising either of EC or CC was used to remove CrT from water.
- EC and CC using Fe as coagulating agent are effective in removing CrT from water.
- The best performances were established using a ratio of Fe/CrT > 3
- CrT concentration ($C_0 = 19.0$ mg L^{-1}) could be optimally diminished by up to 99 %.
- Residual CrT concentrations were below the limiting value recommended (0.05 mg L^{-1})