Designing an Electrochemical System for Efficient Removal of Chromium from Leachate by Electrocoagulation Using a Solar Panel as the Power Supply

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Here, we report the removal of chromium from landfill leachate by electrocoagulation (EC) using iron and aluminum electrodes and a solar panel as the electrical energy source. Two rectangular plates of aluminum and iron were used as cathode and anode, respectively. Different kinds of operational parameters such as contact time, pH, inter-electrode distance and current density were investigated and optimized to obtain the best process function. Based on the findings, the removal efficiency of chromium increased by increasing the current density and the reaction time and decreasing the distance between the electrodes. The experimental results indicated that the removal efficiency of chromium of 98.0% from raw leachate was obtained under the optimized conditions of current density 4.5 A/m^2, initial pH of 3, contact times 27.0 min and the electrode-distance of 0.5 cm.

1. INTRODUCTION

As the world population is growing quickly, the levels of contaminations are expanding so the nonstop requirements for energy and nourishment are driving the investigation of the wastewaters reusing and retrieval of sources. The reality is that if water, as a restricted and crucial resource, is not saved after having been used in industrial forms, the world will face a crisis [1]. In accordance with the rapidly growing world's population and increasing level of pollution, water paucity is one of the greatest concerns that humankind will face [2]. New disaster, especially in developing countries, arisen by the industrial factories such as tanneries, batteries, metal-plating facilities, etc. is that they are releasing heavy metals wastewaters, directly or indirectly, into the environment increasingly. The problem is that these heavy metals, unlike natural pollutants, are not biodegradable, and unfortunately, almost all of the heavy metal ions are extremely poisonous or carcinogenic such as Hg, Cr, Cd, Ni, etc. [3]. Up to the

present time for all the nations, the potential hazards about the filtration landfill leachates into the groundwater substrates and aquifer models are serious concerns for the public health and ecosystems [4]. Abundant persistent organic contaminations in the various compositions of landfill leachates are the most serious problem, which should be eliminated before being entered into the environment [5]. Today, in most countries, the most common way to remove urban solid wastes is sanitary landfilling. Despite some benefits, such as low cost, this method has so many disadvantages such as producing intensely contaminated leachates, giving critical changes in both chemical compounds and volumetric stream that eventually cause the main problem [6]. Most of the wastewaters and leachates contain different sorts of poisonous substances such as heavy metals, and since heavy metal ions cannot be decomposed and mostly are aggregated in living organisms, they are known to be carcinogenic and hazardous [5, 7]. Heavy metals, in the form of composed of enzymes, enter the human body are transported by proteins or dissolved in body fat and cause insecure effects in the body [8]. These pollutants can attach to the carriers and macromolecules, pass through the membranes and consequently into the cells and leave their effects intact [9].

To treat wastewaters and leachates, some techniques based on physical or chemical properties such as developed oxidation, biological and electrochemical properties are applied. Electrocoagulation (EC) is a useful technique used to remove heavy metal ions from sewage that has good compatibility with the environment [10]. In fact, various techniques have been suggested for the removing of heavy metals in sewage or leachates such as ion exchange, resin adsorption [11], membrane filtration, sedimentation of chemicals [12] and EC [13].

EC is an efficient electrochemical technique that is highly effective in sewage treatment. In EC treatment of contaminated waters, sacrificial anodes corrode and release active coagulant precursors (metal ions) into the solution. At the same time, electrolytic reactions create gas (usually as hydrogen bubbles) at the cathode [14]. In comparison to traditional chemical treatment, electrochemical methods have some advantages: less coagulant ion is needed, less sludge is created and the compact equipment of EC makes the installation easier where the available space is limited [15]. The EC process has been used as an efficient way for the elimination of some pollutants, particularly heavy metal ions, from water and effluents. Furthermore, EC is a cheap and green method used to eliminate heavy metals specifically chromium from industrial wastes such as electroplating, metallurgy, chemical catalysts, leather tanning, pigments, printing inks and corrosion inhibitors [16].

According to the world health organization (WHO), a number of heavy metals such as chromium and cadmium, if introduced into the environment at a concentration level above the permissible limit, can cause serious and unsettling problems for the health of humans and other living organisms [17]. Chromium, in two six and trivalent oxide forms, has notable mobility in the environment, highly soluble in water and is toxic to many living organisms. Cr(III) easily undergoes as $Cr(OH)_3$ with low solubility in water. However, it is 1000 times less toxic than Cr(VI) is [18]. Hence, reducing the concentrations of heavy metals in drinking water, sewage and leachate are very necessary. Precipitation and adsorption processes are costly and time-consuming hence they have low efficiency. To overcome the weaknesses of the conventional water and wastewater treating techniques, EC as an electrochemical technique was developed [19, 20].

Here, we used the EC technique with two different iron and aluminum couple electrodes for chromium removal from leachate and optimized the conditions under which the highest removal efficiency could be achieved.

2. EXPERIMENTAL

2.1. Sampling of the leachate

The samples of the leachate used in this work were collected from an Iranian landfill located in the south of Kahrizak city, which was established 62 years ago. An average of 8000 tons of waste, which is produced in different sources including 22 districts of Tehran, suburbs and the townships are dispatched to this center daily for disposal and destruction. The leachate lake area of Kahrizak is about 12 hectares. The samples were immediately stored in a fridge at 5 °C. Before removal processing the leachate by the proposed EC method, the sample was analyzed for chromium and some other majors metal contents, the results are listed in Table 1. Also, some other characteristics of the leachate were analyzed (Table 1). The pH of the solution was measured by using a Lovibond Senso direct 150 (Germany). The ECD and TDO were measured by conductometer (IRSANAT, Iran) and TDO metered by a TDO-meter Hm-Digital (China).

Table 1. Some characteristics of the leachate of the Kahrizak landfill site (the metals are in mg/l)

Parameter	pH	Cd	Cr	Pb	Zn	TDS	EC	BOD	COD	BOD5	Color(pt-co)
Raw leachate	6.9	1.21	2.46	2.35	1.66	34	39.6	627	58500	5050	17800(black)

TDS, total dissolved solids; EC, electrical conductivity (dS/m); BOD, biological oxygen demand; COD, chemical oxygen demand; BOD5, BOD after 5 days

2.2. Setup of the EC reactor

The setup of the desired EC system with the electrochemical reactor as the heart of the system was made of a cubic glass box with the dimensions of $25 \times 20 \times 15$ cm^3 consisting of two tanks with a dual outlet (one for outflow of refined water and the other for sludge removal). Then, two rectangular plates of iron and aluminum at the sizes of $15 \times 10 \times 0.2$ and $15 \times 10 \times 0.1$ cm^3, respectively, were employed as the working electrodes. The aluminum plate was prepared from the Arak Alopars company (Iran) with total purity of 98 % and the iron plate was purchased from a valid market in Tehran. A 9×4 solar panel was used as the electrical energy source including a rectifier and a volt-ampere controller set.

2.3. Procedure

Prior to each experiment, the surface of the electrodes was abraded with sandpaper to clean, they were put in HNO$_3$ (0.15 M) for 15 min and then washed with distilled water. They were then placed in an oven at 100 °C for 15 min. A 1000 ml of the leachate sample was transferred to the reactor. The initial pH of the solution was adjusted using NaOH (0.1 M) or HCl (0.1 M) (Merck Company). After that, the

initial solution conductivity was adjusted by NaCl (Merck, 99.9% purity). The experiment process started only when that simultaneous aeration, voltage and the current density reached the desired values. The sample was then filtered with a Whatman filter paper and the concentration of the chromium content of the leachate was analyzed with an atomic absorption spectrometer (AAS, Perkin Elmer 4100 Germany). All experiments were repeated three times to trust enough the accuracy of the results. After the EC process, the removal efficiency of the chromium consistent was evaluated via the following equation.

$$\%R_f = (C_0-C)/C_0 \times 100 \tag{1}$$

where R_f, C_0 and C denote the removal efficiency percent, initial chromium concentration and the final chromium concentration after treatment, respectively.

3. RESULTS AND DISCUSSION

The EC process is based on the in-situ production of a coagulant by dissolution and consequently the production of anodic or cathodic hydroxides in the polluted water. Furthermore, cathodic reactions allow for removal of pollutant either by deposition on the cathode or by the evolution of hydrogen at the cathode. In an EC process, when a direct current source connects metal electrodes submerged in leachate or wastewater, oxidation and reduction reactions take place at the anode and cathode surfaces, respectively [16, 20].

If iron is used as an anode, its electrochemical oxidation will produce Fe^{2+} ion.

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2}$$

On the other hand, when the anode potential is adequately high, secondary reactions may take place at the anode surface including the oxidation of H_2O and Cl^- ions:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{3}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{4}$$

If chloride ion presents in the solution that increases the conductivity and the energy consumption, were minimized will prevent the iron anode from passivation by chromium as the Cl^- ion catalyze the iron dissolution by pitting corrosion. Thus, the presence of Cl^- ion improves the elimination efficiency of chromium. On the cathode, at the same time, the reduction of water and chromium can occur in the form of dichromate:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{5}$$

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

As previously noted, Fe^{2+} ion, which is produced in the anode can directly convert Cr(VI) into Cr(III) based on the following reaction.

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

The generated Fe^{3+} ions, depending on the solution pH, will immediately be subjected to further spontaneous reactions to generate different monomeric and/or polymeric metal hydroxide complexes such as $Fe(OH)_3$, $Fe(OH)_4^-$, $Fe[(H_2O)_3(OH)_3]$, $Fe(H_2O)_6^{3+}$, $Fe[(H_2O)_5(OH)]^{2+}$, $Fe[(H_2O)_4(OH)]^{2+}$, $Fe_2[(H_2O)_8(OH)]_2^{4+}$ and $Fe_2[(H_2O)_6(OH)_4]^{2+}$ [22].
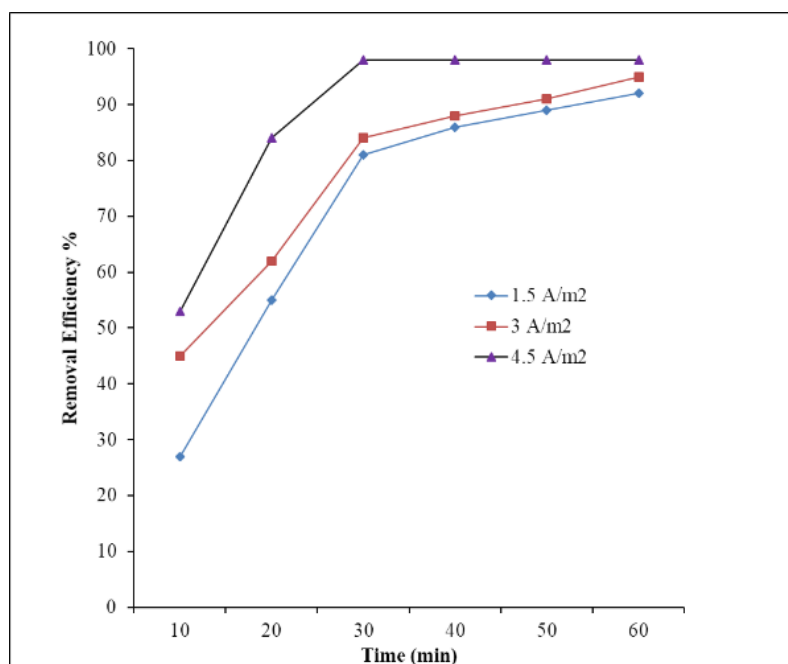
3.1. Effect of current density on the removal of the chromium content

Current density is an important parameter known in the EC method [23]. In electrochemical methods, current density controls the rate of the coagulant production as well as the amount and the rate of the bubble production. Therefore, it affects the growth of floccules on the EC. The relationship between the values of the hydroxide ion (m), at a certain time, is explained by the Faraday's law within the EC cell and the current flow:

$$m = ItM/zF \qquad\qquad (8)$$

where I, t, M, z and F denote current, consumed time, the molecular weight of the ion (g/mol), the number of electrons that are transferred in the reaction and the Faraday's constant, respectively [18, 24].

In order to examine the current density effect on the chromium removal efficiency, the EC process was performed with different current densities 1.5, 3.0 and 4.5 A/m^2. Fig. 1 shows that the efficiency of chromium removal increases with increasing current density. As shown in this figure, the removal efficiencies of chromium increase by 81.0, 84.0 and 98.0 %, respectively, during 27.0 min. Then the efficiency at the current density rate of 4.5 A/m^2 remains almost constant.


Figure 1. Effect of the current density on chromium removal at pH of 3, at different times on the Fe-Al couple electrode with a 0.5 cm spacing between the electrodes.

### 3.2. Effect of initial pH on the removal efficiency of chromium

The pH of the electrolyte solution plays an important role in the EC process [25]. To investigate the effect of pH, different initial pH was adjusted to 2.0, 3.0, 4.5, 5.5 and 6.5. The related removal efficiencies of chromium are shown in Fig. 2, at current densities of 1.5, 3.0 and 4.5 A/m^2, an inter-electrode distance of 0.5 cm and constant contact time of 27.0 min. The initial sample chromium concentration of 2.46 mg/l was decreased to 0.05 mg/l and the optimum removal of chromium was

obtained at initial pH 3, with the efficiencies value of 98.0%. When the pH tended towards acidic or basic amounts, the drop-in removal efficiency took place. Moreover, the effluent pH raised to 7.2 caused by releasing hydroxide ions from the produced iron hydroxides [26].
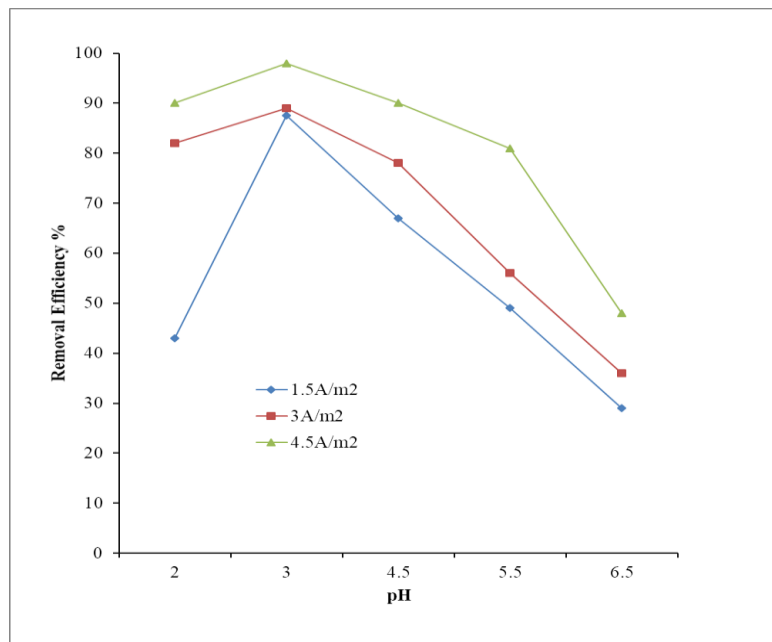
Figure 2. Effect of initial pH on the removal efficiency of chromium at difference current densities, contact time of 27.0 min, inter-electrode distance of 0.5 cm.

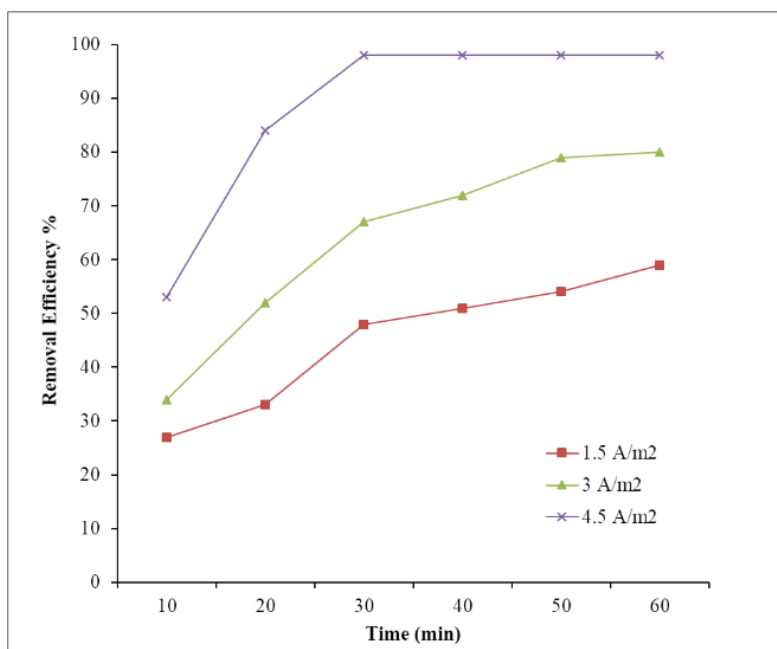*3.3. Effect of inter-electrode distance on removal efficiency of chromium*
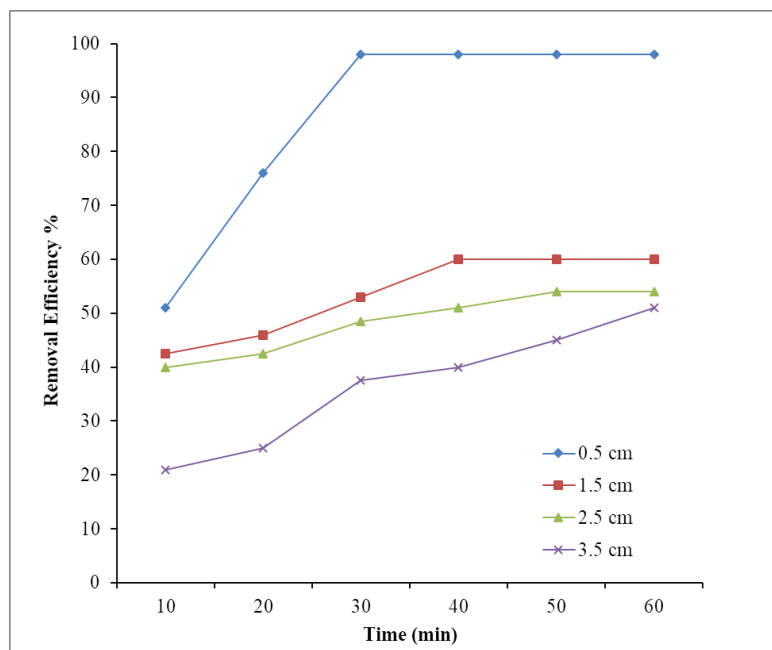
Figure 3. Effect of inter-electrode distance on chromium removal at pH of 3.0, current density of 4.5 A/m^2, at difference time.

How the distance between the electrodes can affect the removal of the selected metal from the raw leachate was investigated under the conditions the fixed current of 4.5 A/m^2, electrolysis time of 10.0 to 60.0 min, the initial pH of 3.0 with the Fe-Al electrodes system. As demonstrated in Fig. 3, when the distance between the Fe-Al electrodes was increased from 0.5 to 3.5 cm the removal efficiency of chromium was affected negatively. Finally, about the total of the removal efficiency of EC methods, the best results were obtained, when the distance between the Fe-Al electrodes was 0.5 cm.

3.4. Effect of the reaction time on the removal efficiency of chromium

The effect of contact time, ranging from 10.0 to 60.0 min, was examined under the conditions that were optimized so far: current density 4.5 A/m^2, initial pH 3.0 and distance between the electrodes of 0.5 cm. As shown in Fig. 4, up to 25 min increase in time the efficiency of chromium elimination reached 98.0% and no significant change was observed beyond this time. If the time of contact increases, the iron ion concentration and their hydroxide floccules will increase, also an increase will occur in the rate of bubble generation. The contaminants in leachate were eliminated by the effect of coagulation and flotation. As time is increased, high electrical energy was consumed so the optimum time of contact 27.0 min was used subsequently.

Figure 4. Effect of reaction time on chromium removal at difference current densities, at pH of 3.0, inter-electrode distance of 0.5 cm.

3.5. The Leachate chromium characteristics

The researchers who have already worked on Kahrizak waste sites believe that the Kahrizak Lake is the most polluted leachate in the world. After treatment of the leachate sample with the EC

method, the initial chromium content 2.46 mg/l diminished to 0.05 mg/l indicative a high efficiency for removal of chromium from the sample about 98.0%. Table 2 gives the results.

Table 2. Determination of chromium concentration (mg/l) in the sample by the EC method.

Heavy metal	MCL[a]	Before treatment	After treatment	%Removed
chromium	0.05	2.46	0.05	98.0

[a]Maximum Concentration Level

Fig. 5 clearly shows the performance of the proposed EC method for the contaminants removal of the tested waste sample before (left) and after (right) the EC operation. In this image, it is illustrated that a large part of the contaminants has been removed.
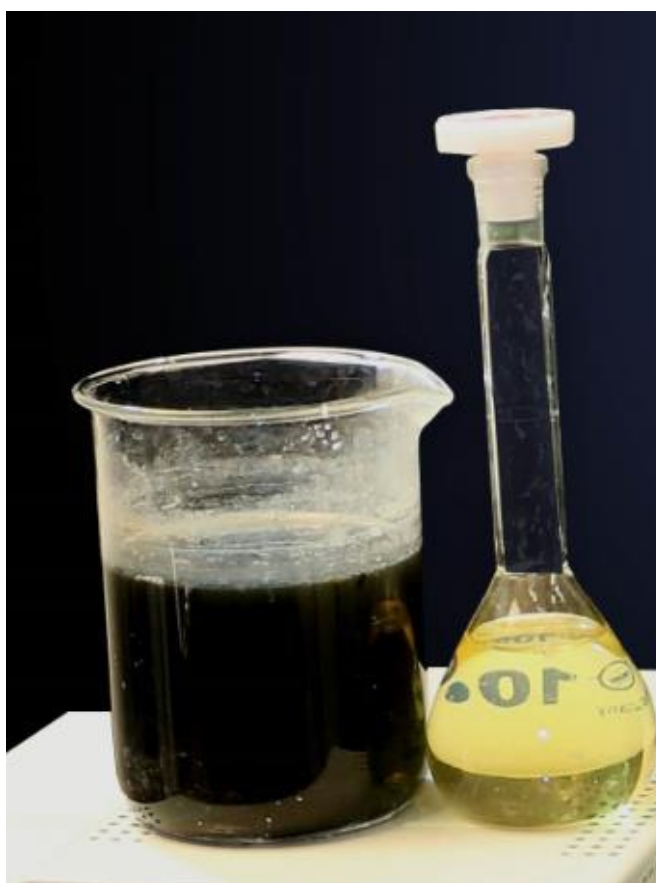
Figure 5. The contaminants removal of the tested waste sample before (left) and after (right) the EC operation.

In order to compare the performance of the proposed EC method with some recently other works, three indexed parameters including contact time, current destiny and removal efficiency percentage are compared and listed in Table 3. As seen, the performance of the proposed EC method is reasonable.

Table 3. Comparison the performance of the proposed EC method with some recently other works for chromium removal from wastes.

Pollutant source	Contact time (min)	Current (DC)	Electrode	Removal efficiency %	Ref.
Leachate	60	2.5 V	Al- stainless steel	88.35	[27]
Leachate	90	40 V	Fe-Al	70	[28]
Leachate	60	1000 mA	Fe-Fe	84	[29]
Wastewater	60	40 mA/cm^2	Fe-Fe	80	[30]
Wastewater	30	25 mA/cm^2	stainless steel	97	[31]
Industrial wastewater	30	8 V	Fe-Fe	96.2	[32]
Synthetic wastewater	48	3.5 mA/cm^2	Al-Al	90	[33]
Industrial wastewater	60	10 mA/cm^2	Al-Al	40	[34]
Leachate	27	0.45 mA/cm^2	Al-Fe	98.0	This work

4. CONCLUSIONS

The highly capable proposed electrocoagulation method was used as an efficient way for the elimination of some pollutants, particularly poising heavy metal ion hexavalent chromium, from an extremely contaminated source. We provided the best conditions for removal of chromium in leachates such as current density and the best electrode distance that resulted in a high chromium removal efficiency (98%) with a low 0.45 mA current consumption, which are outstanding performances toward other previously reported works. As a novelty, KCl was used as an electrolyte, by which the presence of the chloride ion in the solution increases the conductivity and prevents the iron anode from passivation by chromium so improves the elimination efficiency of chromium. On the other hand, the use of solar energy is an economic parameter that have been considered in the proposed electrochemical system.

References

1. A.A. Chopra, A.K. Sharma and V. Kumar, *Archi. Appl. Sci. Res.,* 3 (2011) 191.
2. D.T. Moussa, M.H.E. Naas, M. Nasser and M.J. A-Marri, *J. Environ.,* 186 (2017) 24.
3. F. Fenglian and Q. Wang, *J. Environ. Manage.,* 92 (2011) 407.
4. K.Y. Foo and B.H. Hameed, *J. Hazard. Mater.,* 171 (2009) 54.
5. N. Huda, A.A.A. Raman, M.M. Bello and S. Ramesh, *J. Environ. Manage.,* 204 (2017) 75.
6. S. Renou and J.G. Givaudan, *J. Hazard. Mater.,* 150 (2008) 468.
7. B.A. Aji, Y. Yavuz and A.S. Koparal, *Separ. Purif. Technol.,* 86 (2012) 248.
8. J.H. Kaegi and A. Schaeffer, *Biochemistry,* 27 (1988) 8509.
9. M.H. Moghadasian, *Crit. Rev. Food Sci. Nutri.,* 48 (2008) 402.
10. M. Mohammadizaroun and M.S. Yusoff, *J. Int. Scientific,* 2 (2014) 497.

11. R. Vinodh, R. Padmavathi and D. Sangeetha, *Desalination,* 267 (2011) 267.
12. T.A. Kurniawan and G.Y. Chan, *J. Chem. Engin.,* 118 (2006) 83.
13. P.M. Lakshmi and P. Sivashanmugam, *Separ. Purif. Technol.,* 116 (2013) 378.
14. R. Katal and H. Pahlavanzadeh, *Desalination,* 265 (2011) 199.
15. P.K. Holt, G.W. Barton and C.A. Mitchell, *Chemosphere,* 59 (2005) 355.
16. I.L. Hernández, C.B. Diaz and G.R. Morales, *J. Chem. Engin.,* 148 (2009) 97.
17. Guidelines for drinking-water quality, fourth edition*, World Health Organization* (*WHO)*, (2011).
18. A. Shafaei, M. Rezayee, M. Arami and M. Nikazar, *Desalination,* 260 (2010) 23.
19. E. Keshmirizadeh, S. Yousefi and M.K. Rofouei, *J. Hazard. Mater.,* 190 (2011) 119.
20. Y. Zhao, D. Kang, Z. Chen, J. Zhan and X. Wu, *Int. J. Electrochem. Sci.,* 13 (2018) 1250.
21. G.J. Rincon and E.J.L. Motta, *J. Environ. Manage.,* 144 (2014) 42.
22. M.G. Arroyo, V.P. Herranz, M.T. Montanés, J.G. Anaton and J.L. Guinon, *J. Hazard. Mater.,* 169 (2009) 1127.
23. R. Kamaraj, P. Ganesan, J. Lakshmi and S. Vasudevan, *Environ. Sci.,* 20 (2013) 399.
24. E. Gatsios, J.N. Hahladakis and E. Gidarakos, *J. Environ. Manage.,* 154 (2015) 117.
25. X. Li, J. Song, J. Guo, Z. Wang and Q. Feng, *Procedia Environ. Sci.,* 10 (2011) 1159.
26. C. Phalakornkule, P. Chantaraporn, P. Suprangpak, T. Warangkana, K. Benjawan and N. Thanawin, *J. Environ. Manage.,* 91 (2010) 918.
27. M.K.N. Mahmad and M.R. Rozainy, *Procedia Chem.,* 19 (2016) 681.
28. G. Hassani, A. Alinejad, A. Sadat, A. Esmaeili, M. Ziaei, A.A. Bazrafshan and T. Sadat, *J. Electrochem. Sci.,* 11 (2016) 6705.
29. D. Rabbani, G. Mostafaii, N. Roozitalab and A. Roozitalabs, *J. World. Appl. Sci.,* 17 (2012) 442.
30. K. Dermentzis, A. Christoforidis and E. Valsamidou, *Int. J. Environ. Sci.,* 1 (2011) 697.
31. K. Thirugnanasambandham and K. Shine, *Int. J. Chem. Reactor Engin.,* 16 (2018) 5.
32. D. Bhagawan, S. Poodari, T. Pothuraju, D. Srinivasulu, G. Shankaraiah, M.Y. Rani, V. Himabindu and S. Vidyavathi, *Environ. Sci. Pollut.,* 21 (2014) 14166.
33. E.S. El-Ashtoukhy, M. Abdel-Aziz and G. Sedahmed, *Water Air Soil Pollut.,* 229 (2018) 229.
34. I. Zongo, J.P. Leclerc, H.A. Maïga, J. Wéthé and F. Lapicque, *Separ. Purif. Technol.,* 66 (2009) 159.