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ORIGINAL ARTICLE

Removal of Chromium (VI) from Aqueous Solution Using Electro-Fenton Process

Ali reza Rahmani · Elham Hossieni ·
Ali Poormohammadi

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Abstract Chromium (Cr) is considered to be mutagenic and carcinogenic, and is one of the most important pollutants that have been widely used in various industrial applications. Due to its adverse health impacts, Cr must be removed from effluents before being released into the water environments. The objective of the present study was to investigate the effect of electro-Fenton process (EFP) using iron electrodes in presence of sodium sulfate salt on the elimination of Cr(VI) from aqueous solution. The effect of various parameters such as pH, voltage, initial Cr(VI) concentration, hydrogen peroxide dosage and cyanide concentration (as interference ion), on the process efficiency of Cr(VI) removal have also been tested. The results indicate that the optimum pH, voltage and hydrogen peroxide dosage in EFP were determined to be 3, 30 V and 50 mL/L, respectively. The results of this research also demonstrated that EFP efficiency decreased with increasing initial Cr(VI) concentration. Moreover, EFP efficiency Cr(VI) removal decreased with increasing cyanide concentration; accordingly, the cyanide acts as interference ion in EFP and can reduce the removal efficiency of Cr(VI). According to the obtained results, the maximum removal efficiency of Cr(VI) at optimum condition was 97 % after 25 min. These findings suggest that EFP is suitable option for removing Cr(VI) from aqueous solution.

Keywords Chromium (VI) · Electro-Fenton · Iron electrodes · Cyanide · Interference ion

1 Introduction

In recent years, the discharge of untreated industrial wastewater into the aquatic systems has become a major concern (Samarghandi et al. 2014). Industrial wastewater may contain a significant number of heavy metals (Di et al. 2006). Chromium (Cr) is widely used in leather,

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A. r. Rahmani · E. Hossieni
Department of Environmental Health, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran

A. Poormohammadi (✉)
Social Development & Health Promotion Research Center, Kermanshah University of Medical Sciences, Kermanshah, Iran
e-mail: apoormohammadi000@yahoo.com

paint, petroleum, wood, electroplating and textile industries whose effluents are considered to be significant sources of Cr. The most common forms of Cr found in the aquatic environment are Cr (III) and Cr(VI) (Hu et al. 2009). Trace amounts of Cr (III) are beneficial to human organisms as an essential micro-nutrient (Khazaei et al. 2011). By contrast, Cr(VI) is considered to be mutagenic and carcinogenic. In addition, strong exposure of Cr(VI) causes nausea, vomiting, severe diarrhea and hemorrhage. Also, Cr(VI) has been classified in the group 1 of carcinogen substances by the International Agency for Research on Cancer (IARC) (Romero-González et al. 2006; Krishna and Siva Krishna 2013). The Environmental Protection Agency (EPA) has established 0.1 mg/L as maximum concentration of Cr in drinking water (Rafati et al. 2010). Due to various adverse effects of this compound, Cr (VI) must be treated before being released into the environment. It has been reported that Cr(VI) can be removed by chemical reduction, ion exchange, filtration, reverse osmosis and adsorption technology (Gao et al. 2005; Hasan et al. 2008; Baral et al. 2006). However, these technologies have some disadvantages, such as high reagent requirements, annual high operation costs, increased sludge production, costly adsorbent regeneration and clogging filter (Asgari et al. 2014; Malakootian et al. 2011). Therefore, alternative technologies have been developed to solve these problems. Nowadays, more and more attention has been paid to the use of electro-Fenton process (EFP) in treatment of various industrial wastewaters. In EFP, H_2O_2 is continuously generated on the cathode electrodes surface. The oxidizing power of the hydrogen peroxide is highly enhanced by the addition of Fe^{+2} generating from the Fenton reaction (Jiang and Mao 2012; Priambodo et al. 2011). In this process, Fe^{+2} or Fe^{+3} is added to the reactor solution to permit the oxidation of pollutants by hydroxyl radical generated from Fenton reaction according to Eq. (1). Moreover, Fe^{+3} can be reduced to Fe^{+2} according to Eq. (2) (Zarei et al. 2012; Bernardo-Bricker et al. 2014).

$$Fe^{+2} + H_2O_2 + H^+ \rightarrow Fe^{+3} + OH^{\circ} + H_2O \tag{1}$$

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \tag{2}$$

On the other hand, in EFP metal precipitates play an important role in removing inorganic compounds. Previous studies demonstrated that EFP was an effective method for the removal of broad range of wastewater pollutants such as phenol, dye and other recalcitrant organic compounds (Zarei et al. 2012; Zhang et al. 2006). Accordingly, the present study explored EFP efficiency in Cr(VI) removal from aqueous solution as an inorganic substance. The effect of pH, voltage, H_2O_2 and initial Cr(VI) concentration on the process efficiency were also investigated. Due to the fact that industrial wastewaters often contain different ions, from a practical point of view, in this research, the effect of various concentration of cyanide as an interference ion was also studied in relation to the performance of EFP in Cr(VI) removal.

2 Materials and Methods

2.1 Materials

Potassium dichromate ($K_2Cr_2O_7$, with a purity of 98 %), sodium cyanide (NaCN, with a purity of 98.8 %), (H_2O_2, 30 %), sulfuric acid, hydroxide sodium, 1, 5-Diphenylcarbazide and sodium sulfate salt (98 %) were purchased from Merck and Sigma-Aldrich Co (Germany).

To produce various amounts of voltage, a power supply device (SANJESH TEK, 8051, made of irannovin Co) was used. Moreover, solution pH was measured using a pH meter (Hatch Sinsion1). The samples were centrifuged using Centrifuge device (Sigma).

2.2 The EFP System

Experiments were carried out in a batch Plexiglas reactor with an effective volume of 1 L. A sketch of the reactor is shown in Fig. 1. Iron was used as the electrodes material, placed in the reactor in a nonpolar mode (at a distance of 2 cm from each other). Two electrodes as anode and two other electrodes as cathodes were connected to the power supply device. Also, a magnetic stirrer was used to stir the contents of the reactor. According to submergence depth and electrode dimensions, the ratio of surface area of electrodes to reactor volume was equal to 3.2 m^2/m^3. All the experiments were performed at lab temperature.

2.3 Experimental Procedure

Potassium dichromate was used in preparing the Cr(VI) stock solution for all the experiments. Then, different initial concentrations of Cr(VI) were prepared by dissolving proper amounts of stock solution in distilled water. The effect of some parameters such as pH, voltage, initial concentration of Cr(VI), hydrogen peroxide concentration and cyanide concentration as interference ion were studied on EFP. In the first step of experiments, the effect of pH on EFP efficiency was tested in the range 3–9. Solution pH of the samples was adjusted using hydroxide sodium (1 N) and sulfuric acid (1 M). Finally, optimum pH was chosen. In the next step, experiments were performed under three voltage values (10, 20 and 30 V). After determining optimum pH and voltage, the effect of initial Cr(VI) concentration on EFP efficiency was assessed in the range 100 to 1000 mg/L. Moreover, in order to determine optimum concentration of hydrogen peroxide in EFP, various concentrations of hydrogen peroxide (in the range 10 to100 mL/L) were tested under similar conditions. Finally, in order to determine the influence of cyanide as interference ion on EFP, experiments were carried out in absence and presence of cyanide at different concentrations in the range 100 to 500 mg/L. Sodium sulfate salt (500 mg/L) has been added as supporting electrolytes in EFP to increase the electric current diffusion in the reactor. Also, samples were withdrawn from the middle of the reactor at time intervals of 5, 10, 15, 20 and 25 min. All analyses were conducted in duplicate.

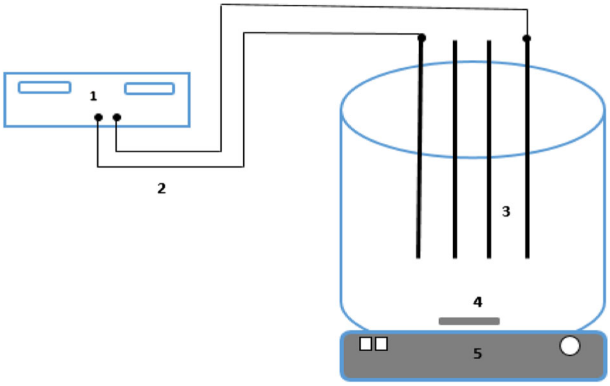

Fig. 1 EF reactor schematic: *1*. Power supply; *2*. Wires; *3*. Iron electrodes; *4*. Magnet; *5*. Stirrer

2.4 Analysis

Cr(VI) concentrations were measured by 1, 5-diphenylcarbazide method using UV-visible spectrophotometer (DR 5000) at 540 nm wave length. In order to avoid the effect of interference agents such as residual iron in the samples and produced sludge, all samples were centrifuged for 3 min (4000 rpm) using Centrifuge device (Hasan et al. 2008; Anota et al. 2006; Pazos et al. 2010). The Cr(VI) removal was determined by the following Eq. (3):

$$\mathrm{Cr(VI)\ removal\%} = \frac{C_0 - C}{C_0} \times 100 \tag{3}$$

where C_0 and C are Cr(VI) concentration (mg/L) before and after experiments, respectively.

3 Results and Discussion

3.1 Effect of pH

The initial pH of the solution is one of the most important factors in EFP. In the present study, the effect of pH in EFP on Cr(VI) removal was studied in the range 3–9. As shown in Fig. 2a,

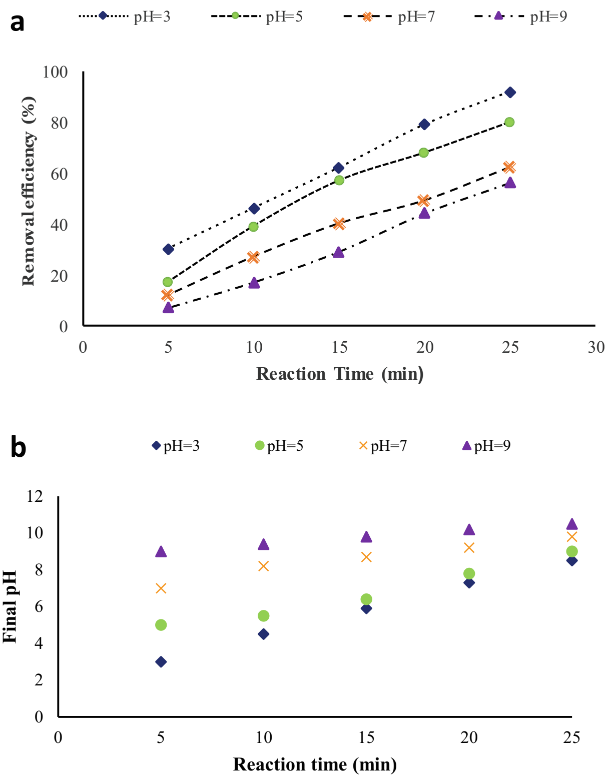

Fig. 2 **a** The effect of solution initial pH on the EF process efficiency **b** The final pH values of the solution during the EF process (Voltage: 20 V, initial Cr VI concentration: 100 mg/L, H_2O_2: 25 mL/L, electrolyte concentration: 0.5 g/L of sodium sulfate)

the EFP efficiency decreased with increasing pH. The maximum removal efficiency was achieved at pH 3. This is attributed to the role of pH on EFP, because in this process main species like $Fe(OH)^{+2}(H_2O)_5$ at strong acidic conditions have the largest light absorption coefficient (Zarei et al. 2010; Priambodo et al. 2011). Also, at strong acidic conditions, sodium sulfate salt yield sulfate ions; sulfate and Fe^{2+} ions in EFP can cause reduction of Cr(VI) to Cr (III). Therefore, the EFP using iron electrodes can cause first the reduction of Cr(VI) to Cr (III), and then, removal the total Cr (III) from the water solution through precipitation (Souza et al. 2012). This finding is consistent with the results of many authors about optimum pH range in EFP (e.g., Jiang and Mao 2012; Priambodo et al. 2011). Moreover, some previous studies revealed that the values of pH in Fenton oxidation should be in the range 2 to 4 (Priambodo et al. 2011; Zhang et al. 2006). Therefore, in the present study, pH of 3 was chosen as the optimum condition in the following experiments. In addition, the final pH values of the solution were measured during the reaction. As can be observed in Fig. 2b, the pH values increased with increasing reaction time; the increase in solution pH may be beneficial for the coagulation of the precipitates of $Cr(OH)_3$ and $Fe(OH)_3$.

3.2 Effect of Applied Voltage

One of the other important factors in EFP is the applied voltage, because the hydrogen peroxide generation in this process is directly related to the applied voltage. In the present study, the effect of various voltage values on EFF efficiency was studied. Figure 3, shows the efficiency of removing Cr(VI) for electrical potential values of 10, 20 and 30 V and pH of 3. As shown in Fig. 3, the maximum removal efficiency of Cr(VI) by EFP was equal to 95 % and was achieved at voltage of 30 V after 25 min. According to the results, the EFP efficiency increased with the increase of the applied voltage. This increase in the removal efficiency can be attributed to the fact that in EFP the electro-regeneration of iron ions increased with the increasing applied voltage. Consequently, Cr(VI) may be reduced to Cr (III) by means of Fe^{2+} ions, then Cr (III) can be removed by the coagulation of the precipitates of $Cr(OH)_3$ and $Fe(OH)_3$ (Souza et al. 2012). Moreover, by increasing the applied voltage, a higher rate of hydroxyl radicals are generated by the degradation of hydrogen peroxide (Samarghandi et al. 2014); the increase in hydrogen peroxide concentration will be beneficial for the coagulation of the precipitates of $Cr(OH)_3$ and $Fe(OH)_3$ (Souza et al. 2012). Also, similar results were obtained by Jiang and Mao (2012) on the removal of phenol using EFP, however, the results of

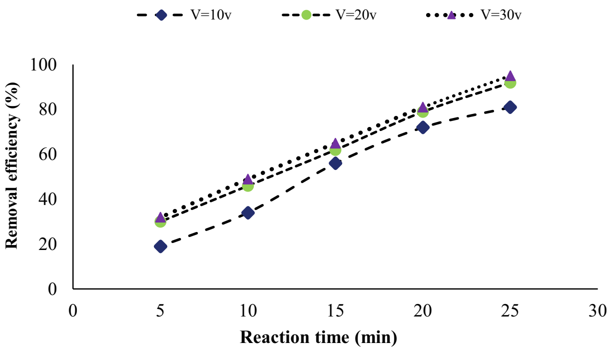

Fig. 3 The effect of voltage on the EF process efficiency (pH: 3, initial Cr(VI) concentration: 100 mg/L, H_2O_2: 25 mL/L, electrolyte concentration: 0.5 g/L of sodium sulfate)

the mentioned study indicated that further increase of the electrical current led to decrease in the COD removal efficiency (Priambodo et al. 2011).

3.3 Effect of Hydrogen Peroxide

In this part of the study, the effect of hydrogen peroxide dosage (10, 25, 50, 75 and 100 mL/L) on EFP was investigated. As revealed in Fig. 4, in EFP the maximum removal efficiency of Cr(VI) in presence of 25 and 50 mL/L of hydrogen peroxide was 95 and 97 %, respectively. On the contrary, the minimum removal efficiency was obtained at 10 and 100 mL/L of hydrogen peroxide, which was 76 and 72 %, respectively. Therefore, in EFP with the increase of hydrogen peroxide from 10 to 50 mL/L, the process efficiency in removal of Cr(VI) was enhanced. This can be related to the increase of hydrogen peroxide concentration. According to Eq. (1), the presence of hydrogen peroxide in EFP can lead to a faster production of Fe^{3+}. On the other hand, when an iron anode is used in EFP, Fe^{2+} is dissolved in the reactor from the iron anode electrode, whereas hydroxide ions and H_2 gas are generated at the cathode according to Eq. 4 (Souza et al. 2012; Seid-Mohammadi et al. 2014):

$$2\,H_2O + 2\,e^{\circ} \rightarrow 2\,OH^{\circ} + H_2 \tag{4}$$

In the presence of O_2, dissolved Fe^{2+} is oxidized to $Fe(OH)_3$, according to the Eq. 5(Souza et al. 2012):

$$4\,Fe^{2+} + 10\,H_2O + O_2 \rightarrow 4\,Fe(OH)_3 + 8\,H^+ \tag{5}$$

Once the insoluble flock of $Fe(OH)_3$ are produced, they can remove Cr by surface attraction (Souza et al. 2012; Seid-Mohammadi et al. 2014). Consequently, the Cr(VI) removal efficiency by EFP increases. In contrast, as the hydrogen peroxide dosage increase from 50 to 100 mL/L, the process efficiency decreased. This result is due to over-dosage of hydrogen peroxide in the reactor, which can lead to the faster consumption of hydrogen peroxide. Finally, the hydroperoxyl radical generated from the hydrogen peroxide decomposition (according to Eq. 6), is a weak oxidant compared with the hydroxyl radical (Zarei et al. 2012).

$$OH^{\circ} + H_2O_2 \rightarrow H_2O + HO_2^{\circ} \tag{6}$$

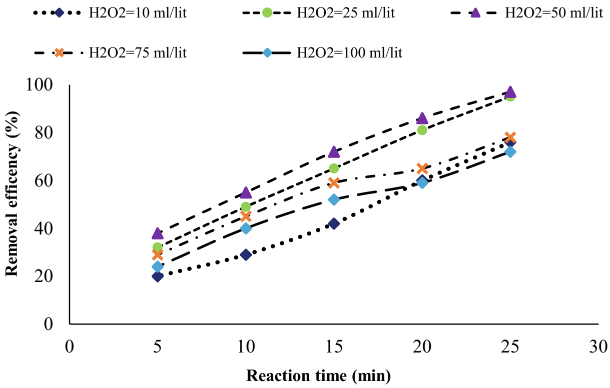

Fig. 4 The effect of hydrogen peroxide dosage on the EF process efficiency (pH: 3, voltage: 30V, initial Cr(VI) concentration: 100 mg/L, electrolyte concentration: 0.5 g/L of sodium sulfate)

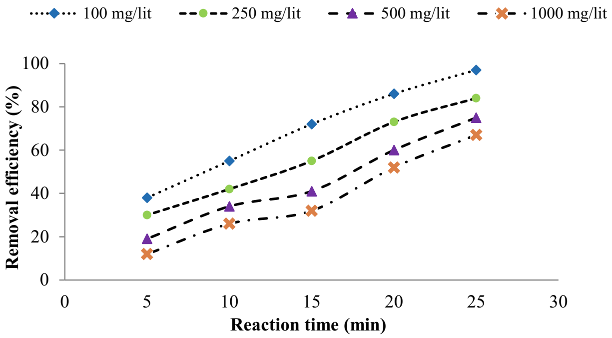

Fig. 5 The effect of initial Cr(VI) concentration on the EF process efficiency (pH: 3, voltage: 30 V, H_2O_2: 50 mL/L, electrolyte concentration: 0.5 g/L of sodium sulfate)

3.4 Effect of Initial Cr(VI) Concentration

Due to the fact that industrial wastewaters often contain various concentration of pollutants, in this step of experiments, the effect of different initial concentrations of Cr(VI) on EFP were studied. Figure 5 presents EFP efficiencies at different initial concentrations of Cr(VI), e.g., 100, 250, 500 and 1000 mg/L. The results indicate that the removal efficiencies of 100 and 1000 mg/L Cr(VI) were 97 and 67 % after 25 min, respectively. So, the efficiency of EF process decreased with increasing Cr(VI) concentration. This can be attributed to this fact that EFP produced only a limited amount of coagulant agents and hydroxyl radicals, thus the removal efficiency reduced with the increase of Cr(VI) concentration. This result is in accordance with the findings on Fe (III) removal by Ghosh et al. (2003). Seid-Mohammadi et al. (2014) also observed that in the electrocoagulation process using iron electrode, as the initial concentration of humic acid increased, its removal efficiency decreased.

3.5 Effect of Interference Ion

Cyanide is one of the most toxic substances found in industrial wastewater such as gold extraction, metallurgical, coal power, petrochemical, oil, paint, photography, iron and steel industries. Therefore, most of industrial wastewaters can contain different concentrations of

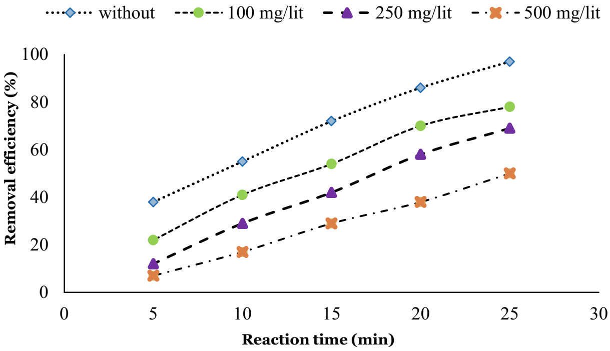

Fig. 6 The effect of initial cyanide concentration on the EF process efficiency (pH: 3, voltage: 30V, H_2O_2: 50 mL/L, initial Cr VI concentration: 100 mg/L, electrolyte concentration: 0.5 g/L of sodium sulfate)

Table 1 The parameters obtained from various kinetics models using different Cr(VI) concentrations

Initial Cr(VI) concentration (mg/L)	Zero-order		First-order		Second-order	
	k_0	R^2	k_1	R^2	k_2	R^2
100	14.9	0.99	0.72	0.90	1.3×10^{-3}	0.85
250	34.7	0.99	0.37	0.95	4.6×10^{-3}	0.85
500	69	0.98	0.28	0.93	5×10^{-4}	0.87
1000	136	0.97	0.23	0.93	6.8×10^{-2}	0.64

cyanide, which can affect the treatment process. In this research, to study the effect of cyanide ion on EFP efficiency in removal of Cr(VI), experiments were performed at various concentrations of cyanide (100, 250 and 500 mg/L) as an interference ion. The results are shown in Fig. 6. As shown, the maximum removal efficiency of Cr(VI) was obtained in absence of cyanide. The results also indicate that the EFP efficiency in Cr(VI) removal decreases with increasing cyanide concentration, with removal efficiency of Cr(VI) for cyanide concentrations of 100, 250 and 500 mg/L being 78, 69 and 50 %, respectively, after 25 min. Thus, it is concluded that the presence of cyanide ions has adverse impact on EFP efficiency and can reduce the removal efficiency of Cr(VI) by this process. This can be associated to the fact that in EFP the hydroxyl radicals produced by decomposition of hydrogen peroxide react with cyanide, so this phenomenon leads to increase in oxidation of cyanide and reduction of EFP efficiency in Cr(VI) removal (Jiang and Mao 2012; Asgari et al. 2014). Xue et al. (2008) also observed that the presence of anions in the adsorption process has inhabitant effects on adsorption of dye. There are no another similar published studies which can be compared with this part of our findings.

3.6 Kinetic Study

In this study, the kinetics of Cr(VI) removal using EFP were also investigated to select the optimum conditions for greater scales. Therefore, to achieve this goal, zero-order, first-order and second-order kinetics were investigated.

The results obtained revealed that the removal process followed the zero-order kinetic model with a correlation coefficient values of 0.99 (Table 1). Fig. 7 shows the kinetic curves

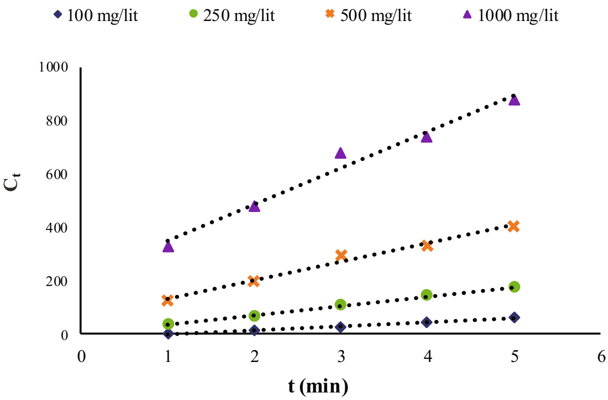

Fig. 7 The results of kinetic study (zero-order kinetic model)

obtained from zero models. Therefore, the zero-order kinetic model gave better results than other models in removal of Cr(VI) using EFP. The reaction is very likely to take place on the surface of the electrode. Therefore, zero order is observed.

4 Conclusion

The present study has explored the efficiency of EFP in removal of Cr(VI) from synthetic wastewater. The effect of pH, voltage, H_2O_2 and initial Cr(VI) concentration were tested. The results indicated that, the optimum pH, voltage and hydrogen peroxide dosage in EFP were 3, 30 V and 50 mL/L, respectively. The results also demonstrated that the EFP efficiency decreased with the increasing initial Cr(VI) concentration. Moreover, the EFP efficiency in Cr(VI) removal decreased with increasing cyanide concentration, accordingly cyanide acts as interference ion in EFP and can reduce the removal efficiency of Cr(VI). The results of the kinetic study indicated that the zero-order kinetic model gave better results than other models in removal of Cr(VI) using EFP. Based on the results obtained, EFP is a suitable option in removing Cr(VI) from an aqueous solution.

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