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The study of Fenton oxidation process efficiency in the simultaneous removal of phenol, cyanide, and chromium (VI) from synthetic wastewater

Somayeh Golbaz[a], Ahmad Jonidi Jafari[b,]*, Roshanak Rezaei Kalantari[c]

[a]*Faculty of Health, Department of Environmental Health Engineering, Tehran University of Medical Sciences, Tehran, Iran*
[b]*Faculty of Medical Sciences, Department of Environmental Health, Tarbiat Modares University, P.O. Box 14115-331, Tehran, Iran*
Tel. +98 9367254535; Fax: +98 2182883825; email: a.jonidi@modares.ac.ir
[c]*Faculty of Health, Department of Environmental Health, Tehran University of Medical Sciences, Tehran, Iran*

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ABSTRACT

Background and objectives: phenol, cyanide, and chromium (VI) are toxic pollutants. They can be discharged from different industries simultaneously such as iron and steel industry, coal mining, automobile manufacturing of parts. Presence of these pollutants in water and wastewater is a serious hazard and these substances lead to undesirable effects on both the environment and human. Thus, control of these contaminants is essential for human health and environment. The main objective of this study was to assess the efficiency of Fenton process for simultaneous removal of phenol, cyanide, and chromium (VI) from synthetic wastewater. *Materials and methods*: This study is an experimental study in lab scale that was carried out in a batch system. Variations of this study including pH, chemicals concentration (Fe^{2+} and H_2O_2 and molar ratio Fe^{2+}/H_2O_2), and reaction time were investigated. Cyanide, phenol, and total chromium were determined respectively by colorimetric method (spectrophotometer), high-performance liquid chromatography, and atomic absorption spectrophotometer. *Results*: The results of this research showed that simultaneous removal efficiency of phenol, cyanide, and chromium (VI) from synthetic wastewater by Fenton process were 88, 86 and 92%, respectively (conditions: pH = 4, Cr^{6+} and $CN^- = 10\,mg\,l^{-1}$, Phenol = $150\,mg\,l^{-1}$, $H_2O_2 = 150\,mg\,l^{-1}$, $Fe^{2+} = 140\,mg\,l^{-1}$ ($Fe^{2+}/H_2O_2 = 0.58$) after 30 min reaction time). *Conclusion*: According to the results, it can be concluded that Fenton process can be considered as a suitable process for cyanide, phenol, and chromium (VI) removal to achieve environmental standards.

Keywords: Advanced oxidation; Fenton; Wastewater treatment; Toxic pollutants

1. Introduction

Toxic pollutants such as phenol, cyanide, and chromium (VI) can be present at the same time in various industries wastewater such as iron and steel industry, coal mining, automobile manufacturing of parts, photography, pharmaceuticals, ore leaching, plastics, manufacturing nonferrous metals, and metal plating [1,4]. Because of the high toxicity of these pollutants, their presence in sources of water and wastewater is a

*Corresponding author.

serious threat to the health and life of living beings [5,6]. Effects of the human exposure to cyanide include rapid breathing, tremors, neurological effects, weight loss, effects on thyroid, nerve damage, and death [6,7]. The effect of human exposure to phenol leads to mucosal irritation disease, skin irritation and burns, poisoning, along with a reduction in systemic blood pressure, increased heart rate, and coma [8]. Complications of exposure to chromium include chronic hepatitis disease, reduction of red blood cells, genetic damage, lung, and gastrointestinal cancers [9,10]. Therefore, standards have been imposed for wastewater discharges to the environment by these industries. Allowed concentration of cyanide and chromium for effluent disposal in accordance with the USEPA standards is 0.2 [11,12], and less than $0.05\,mg\,l^{-1}$ [10], respectively. However, the maximum concentration of phenol allowed in drinking water was $0.005\,mg\,l^{-1}$ [13].

Many physical (dilution, membranes) and chemical methods (adsorption, coagulation, precipitation and filtration, addition of metal and advanced oxidation methods (biological, catalytic, electrolytic, chemical, and photolytic methods)) have been used to remove these contaminants [6,12,14–24]. But the use of conventional water treatment processes due to the relatively high cost, need to highly control the process for additional water treatment, and the formation of dangerous waste products (especially Phenol), adds potentially objectionable cations/anions to water, low efficiency, sludge disposal, need for pretreatment, and application for limited concentration of pollutants is faced with limitations [7,11,13–15,18–22,25–28]. But during the recent years, advanced chemical oxidation process such as photocatalyst, ozonation, ultrasound, Fenton, and Photo-Fenton oxidation has been suggested for wastewater treatment containing nonbiodegradable materials or toxic substances, with high concentration of pollutants [29]. Two major advantages of Fenton, over other advanced oxidation process include: lack of sophisticated equipment and facilities requirement and lack of limitation effects on mass transfer [30]. In addition, it is more cost effective, environmental friendly. Fenton agent is a combination of Fe^{2+} and H_2O_2, which is used in acidity condition [31]. Hydroxyl radicals and ferrous ions, both play a part in the progression of reaction, and one of them play a significant role according to the operating conditions such as type of wastewater, Fe^{2+}/H_2O_2 ratio, and the presence of inhibitory substance. On the other hand, this process is mixture of oxidation and coagulation that resulting in less sludge production in comparative to coagulation and flocculation processes, and this can be considered as the advantage of this process [29]. Several studies on the Fenton process efficiency in wastewater treatment containing toxic and organic compounds have been conducted [32–35]. Results of these studies showed that the Fenton process in addition to the destruction of organic matter [34] is also effective in the removal of some toxic elements [32,33,35]. In some cases, it is also used as a pretreatment before biological processes [36]. Thus, Fenton is considered as an option for toxic wastewater treatment.

In the present study, phenol, cyanide and chromium (VI) removal efficiency from synthetic wastewater by Fenton process was studied and the influence of various parameters such as pH, optimum amounts of Fe^{2+} and H_2O_2, and reaction time were investigated.

2. Material and methods

2.1. Material

In this study, chemical materials including cyanide (KCN, purity > 99%), phenol (C_6H_5OH, purity > 99%), chromium (VI) (CrO_3, purity > 99%), hydrogen peroxide (H_2O_2, purity 30%), and iron (II) sulfate ($FeSO_4.7H_2O$, purity > 99.5%) were used. Stock solution of each of the pollutants was prepared by using deionized and distilled water and stored in dark Pyrex bottles kept refrigerated at −4˚C. Moreover, sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used for the pH adjustment of experiments, and methanol and buffer acetate (water soluble) was used for the regulation of high-performance liquid chromatography (HPLC). It should be noted that all the materials were manufactured by Merck (Germany).

2.2. Analysis of pollutants

Colorimetric method by UV–Vis spectrophotometer (CECIL-model 7100) with a wavelength of 578 nm was used for measurement of cyanide concentration [37]. All cyanide analyses were based on 4500-CN^- part of Standard Methods for Examination of Water and Wastewater [37].

Atomic flame absorption models A ANALYST 200 (with a wavelength of 357 nm) and the flow of fuel and acetylene with 10 and 3/31/min (respectively) was used for measurement of total chromium concentration. All chromium analyses were according to 3111-B part of Standard Methods for Examination of Water and Wastewater [37].

Analysis of Phenol concentration was performed by HPLC, (CECIL company), 4100 Model equipped with a UV–visible detector (CE 4200 model) at a wavelength of 270 nm. Samples were injected in the equipment fitted with a C18 column with internal diameter (4/2 mm) and length of 250 cm. Carrier phase contained methanol and ammonium acetate buffer (70:30, v/v) with pH = 4 [38]. Samples were filtered prior to injection into the apparatus by a 0.45 μm syringe filter with cellulose acetate material, so that the particles were completely removed. Read values stand in calibration curve of phenol and its concentration in each sample was calculated.

2.3. Procedure

This experimental study was designed to remove pollutants such as phenol, cyanide and chromium (VI), by using Fenton process and the laboratory scale in a closed system. During the Fenton process, effects of pH, optimal amounts of Fe^{2+}, H_2O_2 and the reaction time for removal of these pollutants from synthetic wastewater was studied. For performing the test, flask with 1.5 l capacity covered with aluminum foil was used (to prevent the exposure to light and the decomposition of pollutants). In this way, one liter of synthetic wastewater containing cyanide, chromium (VI) with initial concentration of 10 mg/l and Phenol with concentration of 150 mg l^{-1} was prepared. The effluent pH varied in the range of 3–11 by adding amounts of 1 N NaOH or H_2SO_4. Thus, a certain amount of Fenton's reagent dosage consisting of H_2O_2 (115 mg l^{-1}) and Fe^{2+} (140 mg l^{-1}) was added to the solution. After 60 min, optimal pH of the reaction was determined. By using one factor at a time, the impact of different variables such as Fe^{2+} (in the range of 100–180 mg l^{-1}) and H_2O_2 (from 50 to 350 mg l^{-1}), and time (0–120 min) on the simultaneous removal efficiency of the pollutants were investigated. Also, to ensure complete mixing of the reagents, was used a magnetic device with stirring rate of 100 rpm. At the end of the experiment, increasing the pH of the solution by sodium hydroxide to stop the Fenton reaction and to maintain pollutants was essential. Finally, the concentration of remaining pollutants was determined. To reduce the errors and increase accuracy, all experiments were repeated at least two times and finally a mean was obtained from the data.

3. Results and discussion

3.1. Effect of pH on Simultaneous removal efficiency of phenol, cyanide and chromium by Fenton reaction

As is evident from Fig. 1, highest pollutant removal efficiency of phenol, cyanide and chromium (VI) at pH = 4 was 82, 87, and 92%, respectively. pH has strong effects on the Fenton process and plays an important role in the mechanism of $OH^{\cdot}$ and Fe^{3+} production [39]. So that, the oxidizing property of hydroxyl radicals and the solvent ferrous ions in a very acidic pH (pH < 3) is greater than a higher pH. While, the iron ions are precipitated at pH of 3–5 as colloid particles and at pH above 5 as ferric ions (Fe $(OH)_3$ or $Fe_2O_3 + H_2O$) [31,40,41]. Above mentioned reasons, lead to slower and more limited decomposition of H_2O_2 and lesser generation of $OH^{\cdot}$. So it is evident that with increasing pH to above 4, removal rate of Phenol slightly decreases. On the other hand, slower and more limited decomposition of H_2O_2 has positive effects in removal of chromium. Therefore, pH = 4, was chosen as the optimum pH in this study.

In parallel to the above mentioned literature findings, pH 3–4 resulted in the highest removal efficiency of pollutants such as cyanide [31], chromium [42], mature landfill leachate [43], landfill leachate [44], hazardous industrial wastewater [32], Degradation of phenol combinations (4-nitrophenol [45], 2,4,6-trichlorophenol [46], 4-chlorophenol, and 2,4-dichlorophenol [47]), which is similar to this survey results.

3.2. Effect of various Fe^{2+} dosage on Simultaneous removal efficiency of phenol, cyanide and chromium in Fenton reaction

Results of the simultaneous removal of pollutants showed that in a condition with constant concentration of 115 mg l^{-1} H_2O_2, and pH = 4, and increasing Fe^{2+} concentration from 20 to 140 mg l^{-1}, lead to the increased efficiency for removal of each of the three pollutants (Fig. 2). By increasing the amount of

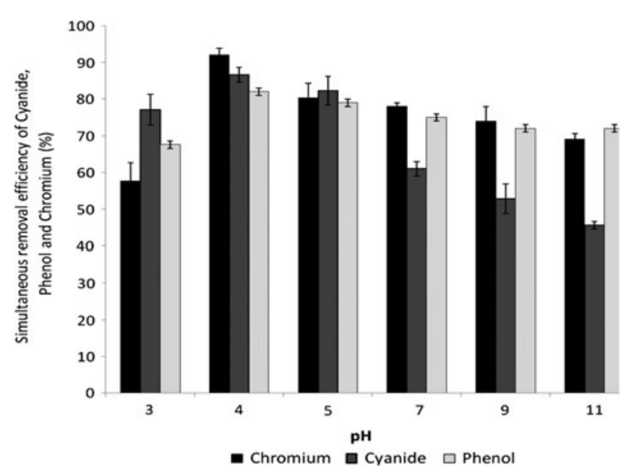

Fig. 1. Simultaneous removal efficiency of phenol, cyanide, and chromium according to pH in Fenton reaction (Conditions: CN^- and Cr (VI) = 10 mg l^{-1} and phenol = 150 mg l^{-1}, Fe^{2+} = 140 mg l^{-1}, H_2O_2 = 115 mg l^{-1} (mole ratio ofFe^{2+}/ H_2O_2 = 0.86) and time = 60 min).x

ferrous ions, efficiency of cyanide and chromium removal was increased and the rate of phenol removal was decreased.

Presence of Fe^{2+} along with H_2O_2 leads to increased production of hydroxyl radicals. Thereby, the phenol and cyanide concentration decrease rapidly (Reaction (1)). In this way, the hydroxyl radicals ($OH^{\cdot}$) attacked the organic compounds (RH) and by accepting a proton became oxidized into highly active organic radicals, which lead to their further oxidation (Reaction (2)) [31]. Besides, these radicals reduced the concentration of cyanide by breaking the carbon and nitrogen triple bond. Under the conditions of a strong oxidant such as hydrogen peroxide and a catalyst, cyanide was converted into cyanate (less toxic) (Reaction (3)) [33,48].

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^{\cdot} \quad (\textit{Reaction } 1)$$

$$OH^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \rightarrow \text{Further oxidation} \quad (\textit{Reaction } 2)$$

$$CN^- + OH^{\cdot} \rightarrow CNO^- + OOH^{\cdot} \quad (\textit{Reaction } 3)$$

By increasing the concentration of Fe^{2+} ions to more than $140\,mg\,l^{-1}$ (increasing the molar ratio Fe^{2+}/H_2O_2 to more than 0.57) significantly reduced the phenol removal. But it was not effective for the removal of cyanide. Presence of excess ferrous ions with hydroxyl radicals lead to the removal of them from the wastewater by the following reaction [39]:

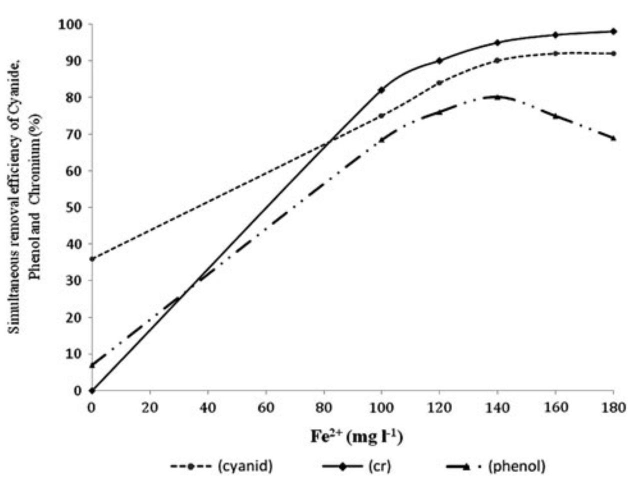

Fig. 2. Simultaneous removal efficiency of phenol, cyanide, and chromium at various dosage of ferrous sulfate (Conditions: CN^- and Cr $(VI) = 10\,mg\,l^{-1}$ and phenol $= 150\,mM\,l^{-1}$, pH = 4, $H_2O_2 = 115\,mg\,l^{-1}$ and time = 60 min).

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^- \quad (\textit{Reaction } 4)$$

So that, Wu et al. reported that Fe^{2+} dosage beyond the certain optimum point lead to scavenging effect of hydroxyl radicals generated in Fenton reactions and consequently, the decrease in pollutants degradation [49].

It was shown by other researches that the concentration of iron at the catalyst level ($Fe^{2+}/H_2O_2 < 1$) must be maintained so that the formation and inhibition of hydroxyl radicals and any other form of coagulation is prevented [31,50]. Lopez et al. also used the 0.5 and $0.27\,mM\,l^{-1}$ Fe^{2+} concentrations for elimination of 4-chloro,3-methyl phenol [50] and color removal [39] by Fenton process, respectively.

It should be noted that the Fenton reaction is performed at pH = 4 and at pH between 2 and 6 chrome oxide (CrO_3) is seen in the form of dichromate. Thus, we can expect that the reaction proceeds through the dichromate and bivalent iron reaction. Therefore, Fe^{2+} (Ferro) ion helps in the conversion of dichromate into trivalent chrome (Reaction (5)) [51,52].

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} \quad (\textit{Reaction } 5)$$

Fenton process is a combination of coagulation and oxidation process [53,54]. Therefore, when the amount of iron is more than hydrogen peroxide, ferrous ion can be used as a reactant (and not as a catalyst) in the Fenton reaction. Therefore, in hexavalent chromium removal by Fenton, coagulating properties were dominant; and Fenton oxidation properties had no effect on the removal of this pollutant. This process can lead to the consumption of hydroxyl radicals produced by trivalent iron ions (Fe^{3+}), and oxidize them into bivalent iron (Fe^{2+}) leading to the non beneficial degradation of hydrogen peroxide. This process is effective in reducing the removal efficiency of phenol. In addition to it, coagulation ability of Fenton at pH 3–7 occurred as per the Reactions (6)–(8) and the suspected solids were trapped by the compounds, finally leading to their precipitation [31].

$$2[Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe(H_2O)_8(OH)_2]^{4+} + 2H_2O \quad (\textit{Reaction } 6)$$

$$[Fe(H_2O)_8(OH)_2]^{4+} + H_2O \leftrightarrow [Fe_2(H_2O)_7(OH)_3]^{3+} + H_3O^+ \quad (\textit{Reaction } 7)$$

$$[Fe_2(H_2O)_7(OH)_3]^{3+} + [Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe_2(H_2O)_7(OH)_4]^{5+} + 2H_2O \quad (\textit{Reaction } 8)$$

3.3. Effect of various H_2O_2 dosages on simultaneous removal efficiency of phenol, cyanide, and chromium in Fenton reaction

The highest simultaneous removal efficiency of cyanide, phenol, and chromium (VI) pollutants at H_2O_2 concentration of 150 mg/l was 90, 88, and 92%, respectively (at constant concentration of 140 mg l^{-1} ferrous ion and pH = 4) (Fig. 3). Increasing the concentration of H_2O_2 to 350 mg/l greatly reduced the removal of chromium but the removal efficiency of cyanide and phenol was increased. The removal of phenol increased from 82 to 98% in the changes H_2O_2 concentration from 150 to 350 mg l^{-1}, respectively. However, removal efficiency of phenol at this increased amount, despite production of H_2O_2 at high concentration was not substantially reduced. Haung and his colleagues also showed that, 4-nitrophenol was removed after two hours to about 99% at the condition with Fe^{2+} = 5 mg l^{-1}, H_2O_2 = 170 mg l^{-1} [45].

But decreased removal efficiency of chromium with the increasing amount of hydrogen peroxide from 150 to 350 mg l^{-1}, can be due to the competition of hydrogen peroxide with hexavalent chrome for accepting an electron that leads to the reduction of ferrous ions in the solution. On the other hand, this reaction can be due to the reversible conversion of hexavalent chromium into trivalent chromium (in acidic pH), and because of the presence of excess hydrogen peroxide, the rate of chromium removal was reduced (Reaction (9)).

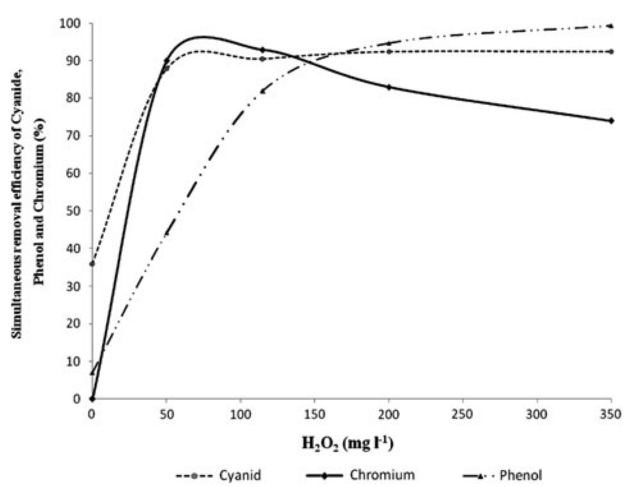

Fig. 3. Efficiency of simultaneous removal of phenol, cyanide, and chromium at various dosage of H_2O_2 (Conditions: CN^- and Cr (VI) = 10 mg l^{-1} and phenol = 150 mg l^{-1}, pH = 4, Fe^{2+} = 140 mg l^{-1} and time = 60 min).

$$2[Cr(OH)_6]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 2OH^- + 8H_2O \quad (Reaction\ 9)$$

Overall in this study, regarding the optimal amounts of Fe^{2+} and H_2O_2, and the molar ratio, Fe^{2+}/H_2O_2 = 0.58 was chosen as the optimal ratio. Lopez et al. reported that molar ratio of Fe^{2+}/H_2O_2 was almost 0.05, for treatment of a raw leachate in batch tests [43]. Also, Deng and Englehardt found an optimal Fe^{2+}/H_2O_2 molar ratio of 0.667 and 0.333 in batch mode and continuous mode operation, respectively; and, other researches on the efficiency of Fenton for the removal of insecticides, dangerous industrial wastewater treatment were in the molar ratio (Fe^{2+}/H_2O_2) lesser than one, and was in the range of 0.46–0.12 [36], 0.4 [48], 0.077 [32], 0.1 [33], 0.040–0.1 [35]. This difference in ratio was due to different concentration and types of pollutants [44]. However, the best removal efficiency was less than one (molar ratio of Fe^{2+}/H_2O_2).

With regard to low hydrogen peroxide consumption, the Fenton process is very economical and more cheaply than other processes such as membrane-based separation processes [55–57]; and in developing countries, there is a possibility of it being localized.

3.4. Effect of reaction time on simultaneous removal efficiency of phenol, cyanide, and chromium in Fenton reaction

Fig. 4 shows the effects of the removal of pollutants at optimal conditions from the previous stage by Fenton reaction. At 30 min times, removal effi-

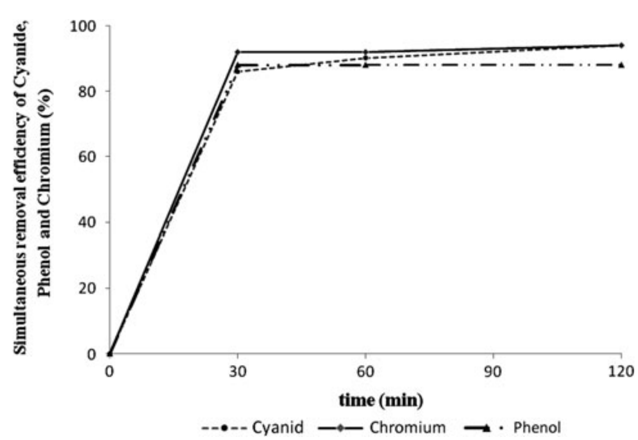

Fig. 4. Efficiency of simultaneous removal of phenol, cyanide, and chromium according to reaction time in Fenton reaction (Conditions: CN^- and Cr (VI) = 10 mg l^{-1} and phenol = 150 mg l^{-1}, pH = 4, Fe^{2+} = 140 mg l^{-1} and H_2O_2 = 150 mg l^{-1}).

ciency of chromium (VI), cyanide, and phenol pollutants were observed about 92, 86, and 88%, respectively. The studies on Fenton process showed that the Fenton reaction time depends on the concentration of iron (II) sulfate, hydrogen peroxide and the type, and concentration of pollutants. For instance, oxidation of phenol in concentrations below 250 mg/l required 30–60 min. While more concentrated wastewater may take several hours reaction time mainly because of the formation of intermediate compounds [58]. These intermediate compounds act as a primary competitor for hydroxyl radicals and a raptor of it. It is evident from the study that simultaneous presence of contaminants speed the elimination reaction time. Perhaps one of the reasons may be that chromium in water bed act as a powerful oxidizing agent, which can react with any other organic or reducing matter converting it into trivalent chromium [59]. This results in the removal of phenol and chromium.

4. Conclusions

In general, the efficiency of Fenton process for the simultaneous removal of phenol, cyanide, and chromium (VI) pollutants was 88, 86, and 92%, respectively. At optimal conditions, the initial concentration of chromium (VI), and cyanide was equivalent to 10 mg/l and initial concentration of phenol was 150 mg/l, respectively.

On the other hand, this study clearly showed that both hydroxyl radicals and ferrous ions are involved in the progression of Fenton reaction. In cyanide and phenol removal, the oxidation property of Fenton was more dominant than the coagulation property of Fenton for the removal of chromium (VI).

Finally, it can be said that Fenton process can be considered to be a good option for designing and selecting the simultaneous removal method for pollutants such as chromium (VI), cyanide, and phenol in order to achieve environmental standards.

Acknowledgments

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