Treatment of hexavalent chromium by using a combined Fenton and chemical precipitation process
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ABSTRACT
This work aimed to remove hexavalent chromium and three treatment schemes were examined based on a laboratory scale design: (a) Fenton process, (b) precipitation process, and (c) Fenton process followed by precipitation process. Variations of this study including pH, Fenton and precipitation reagents (molar ratio of Fe²⁺/H₂O₂ and FeCl₃), contact time, and initial concentration of chromium were investigated. The results showed that about 98% of Cr⁶⁺ is removed by the coagulation property of the Fenton process, and the ideal conditions for its removal included Cr⁶⁺ = 10 mg/L, pH = 4, molar ratio Fe²⁺/H₂O₂ = 2.4 with a time duration of 30 min. Maximal removal efficiency of Cr⁶⁺ in the precipitation process was equivalent to 97% in the following optimum conditions: Cr⁶⁺ = 5 mg/L, pH = 7, FeCl₃ = 0.7 g/L and deposition time of 20 min. Combination of these two methods can remove greater concentrations of chromium (15 mg/L) to about 99.99%. Therefore, removal of Cr⁶⁺ by the combined Fenton and precipitation process was better than any of the methods alone (Kruskal-Wallis, P value ≤0.05). Consequently, the Fenton process followed by precipitation process can be considered as a suitable process for Cr⁶⁺ removal to achieve environmental standards.

Key words | chemical precipitation, Fenton oxidation, hexavalent chromium, industrial wastewater

INTRODUCTION
The chromium element is seen most commonly in aquatic solutions as Cr³⁺ and Cr⁶⁺. However, the problems caused by chromium in the environment are mostly due to the Cr⁶⁺ ion being one of the most toxic polluters in aquatic environments. This pollutant is present in the wastewater of various industries, such as textile (Rengaraj et al. 2003), coal mining, ore leaching (Park et al. 2007), plastics and metal plating industries (Rengaraj et al. 2003). The amount of chromium differs in industrial wastewater depending on the type of industry. For example, the amount in electronic process wastewater is 10 mg/L (Rengaraj et al. 2003). This element causes chronic hepatitis disease, hematological side effects, lung and gastrointestinal cancers, and genetic damage. The US Environmental Protection Agency has also classified Cr⁶⁺ in group A (carcinogenic to humans) (Pontius 1990) and recommended a maximum level of 0.05 mg/L Cr⁶⁺ for effluent discharge into the environment (Baral & Engelken 2002).

Due to the adverse effects of chromium, various techniques are used for its removal from industrial wastewater, such as absorption, reverse osmosis, ion exchange, electrodialysis (Suksabye et al. 2007), biodegradation, adsorption by natural biomaterials such as fungi and algae (Park et al. 2007), electrochemical deposition, solvent extraction (Baral et al. 2006), and membrane separators (Golder et al. 2007). However, these conventional water treatment processes are limited due to the relatively high cost, low efficiency, and application for limited concentration of chromium (Eckenfelder 1989; Ranganathan 2000; Chaudhary et al. 2003; Baral et al. 2006; Suksabye et al. 2007). In recent years, advanced chemical processes such as photocatalyst, ozonation, ultrasound, Fenton, and photo Fenton have been proposed as the most conventional methods for the treatment of wastewater containing nonbiodegradable or toxic substances and also containing higher concentrations...
of pollutants (Meri et al. 2005). Lack of the need for advanced equipment and facilities, and lack of limitations related to mass transfer, are two major advantages of Fenton compared to other advanced oxidation processes (Suthersan 2002). Fenton’s reagent is a combination of divalent iron salts (ferrous ions) and hydrogen peroxide. Depending on the operating conditions, such as type of wastewater, ratio of Fe$^{2+}$/H$_2$O$_2$, and inhibitory substances, any of these reagents may play a more important role in the progression of the reaction under acidic conditions (Neyens & Baeyens 2003). During the Fenton process, many colloidal particles are formed. These tiny particles require a long time to settle and it seems to be necessary to use coagulants (Neyens & Baeyens 2003). On the other hand, application of a coagulation process alone generates large volumes of sludge and results in high costs for sludge disposal, and its limited ability to reduce and eliminate all toxic materials, metals, and dissolved substances to the desired amount and environmental standards have not been recommended. Furthermore, in the case of some metals, such as Cr$^{6+}$, it is necessary that the degree of metal oxidation is changed by other processes before settling down. The objective of this study was to evaluate the effectiveness of the combined Fenton and precipitation (ferric chloride) process for the treatment of Cr$^{6+}$ from synthetic wastewater. During these processes, the effects of various parameters, such as pH, reagent concentrations and precipitation (Fe$^{2+}$, H$_2$O$_2$, and FeCl$_3$), contact time, and initial concentration of chromium were investigated.

**MATERIALS AND METHODS**

**Materials**

Chemical materials including chromium trioxide (CrO$_3$), hydrogen peroxide (H$_2$O$_2$), iron (II) sulfate (FeSO$_4$.7H$_2$O) and ferric chloride (FeCl$_3$) were used. A stock solution of chromium was prepared by using deionized water and stored in dark Pyrex bottles kept in a refrigerator. Moreover, sulfuric acid (H$_2$SO$_4$) and sodium hydroxide (NaOH) were used for the pH adjustment of experiments. It should be noted that all the materials were manufactured by Merck (Germany).

**Experimental procedure**

Three treatment schemes were examined based on a laboratory scale design: (a) Fenton process, (b) precipitation process, and (c) Fenton process followed by precipitation process.

In order to determine the optimum conditions for the removal of Cr$^{6+}$ several experimental parameters were varied during Fenton and precipitation processes. In the Fenton process, effect of changing pH, molar ratio of Fe$^{2+}$/H$_2$O$_2$, contact time and effects of initial chromium concentration on its elimination from the aqueous solution were studied. For conducting the tests, flasks with 1.5 L capacity covered by aluminum foil were used. In this way, 1 L of synthetic wastewater containing 10 mg/L Cr$^{6+}$, from the combination of CrO$_3$ and HNO$_3$, were obtained. For determining the optimum pH, the pH was set in the range of 3–11 by NaOH or H$_2$SO$_4$. Then, the desired amounts of FeSO$_4$.7H$_2$O and H$_2$O$_2$ with a molar ratio of Fe$^{2+}$/H$_2$O$_2$ = 0.6 (Fe$^{2+}$ = 0.9 mM/L) were added to the solution. A magnetic device with stirring rate of 100 rpm was used to ensure complete mixing of the reagents. The pH of the sample after the completion of reaction time with sodium hydroxide reached 13. Then the samples were prepared to measure the total chromium. Similarly, in the next phases by using one factor at a time method, effect of Fe$^{2+}$ (0.9–3.6 mM/L), H$_2$O$_2$ (1.5–10.3 mM/L), contact time (15–90 min), and initial concentration of Cr$^{6+}$ (5–15 mg/L) in the treatment of it were investigated.

All experiments for the precipitation process were carried out by using a conventional Jar-test apparatus, equipped with six beakers of 1 L volume. Considering the importance of pH in the precipitation process, pH of a solution containing 10 mg/L Cr$^{6+}$ was adjusted in the range of 3–11 by adding amounts of NaOH or H$_2$SO$_4$. Thus, ferric chloride was added to every beaker at a concentration of 0.7 g/L. After performing the Jar-test (60 s with a speed of 200 rpm, 20 min with a rate of 30 rpm, and 60 min deposition time), samples from each beaker were taken and prepared to measure the remaining total
chromium. Similarly, in the next phase by using one factor at a time method, effect of FeCl₃ (0.4–1.8 g/L), deposition time (30–90 min), and initial concentration of Cr⁶⁺ (5, 10, 15 mg/L) on the removal efficiency of chromium were studied.

In the final stage, the effectiveness of combined Fenton and precipitation processes in removal of Cr⁶⁺ (in the optimum conditions obtained from each of the Fenton and precipitation processes) was also studied. In order to reduce the errors and increase accuracy, all experiments were repeated at least twice and, finally, a mean was obtained from the data.

Also, the Kruskal-Wallis H test was used in order to find a significant difference (5% level) between the performances of the three methods of Fenton, precipitation, and their combination for the removal of different concentrations of Cr⁶⁺.

Analysis of pollutant

Atomic flame absorption (A ANALYST 200) was used for measuring total chromium concentration. All chromium analyses were in accordance with 3111-B part of Standard Methods for Examination of Water and Wastewater (Eaton et al. 2005).

RESULTS AND DISCUSSION

Determining the optimal conditions of Fenton for removal of chromium

Effect of initial pH

Figure 1 shows the results for determining the appropriate pH for Fenton’s process. It is observed that the highest removal efficiency of Cr⁶⁺ is achieved at pH = 4 (52%) and the removal efficiency decreases by increasing the pH; whereas, the minimum Cr⁶⁺ removal efficiency (35%) was observed at pH = 11. Several researchers have shown that the optimum pH in the Fenton’s reagent is in the pH range of 3–4, as reported for the removal of cyanide (Kun-Woo & Hyung-joon 1999), recalcitrant compounds (Xing et al. 2006), mature landfill leachate (Lopez et al. 2004), and landfill leachate (Deng & Englehardt 2006). At pH < 3, iron ions are completely solvable. However, at pH between 3 and 5, iron ions are seen in the form of colloidal particles; and at higher pH ferric ions are deposited in the form of Fe₂O₃ with Fe(OH)₃ (Sedlak & Andren 1994; Neyens & Baeyens 2005; Al-Momani et al. 2006). The above-mentioned reasons lead to the slower and more limited decomposition of H₂O₂ that is effective in the removal of Cr⁶⁺. Therefore, pH = 4 was chosen as the optimum condition in this study.

Effect of molar ratios of Fe²⁺/H₂O₂

Table 1 illustrates that by increasing the molar ratio of Fe²⁺/H₂O₂ from 0.1 to 2.4 leads to an increase of the removal efficiency of Cr⁶⁺. Thus, the removal rate is increased from 29% at a molar ratio of Fe²⁺/H₂O₂ = 0.1 to more than 97% at a molar ratio of Fe²⁺/H₂O₂ = 2.4. When the molar ratio of Fe²⁺/H₂O₂ is equal to or greater than 2 (Fe²⁺/H₂O₂ ≥ 2),
ferrous ions can act as a reactor in the Fenton reaction (Neyens & Baeyens 2003). Removal of hexavalent chromium occurs mostly by the coagulation property of Fenton’s method. Produced hydroxyl radicals are consumed by the trivalent iron ions, and by forming divalent iron ions lead to the decomposition of hydrogen peroxide that is effective in the removal efficiency of Cr⁶⁺. Therefore, considering the fact that at pH = 2–6, chromium oxide is found in the form of dichromate (Cr₂O₇²⁻, orange) and Fenton’s reaction is performed at pH = 4, it can be expected that the process proceeds by the reaction between dichromate and divalent iron in a way that dichromate requires six electrons to be converted into trivalent chromium (Reaction (1)). When ferrous ions are converted into ferric ions, they lose their electron and help in the conversion of dichromate into trivalent chromium (Reactions (2) and (3)).

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (1)
\]

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad (2)
\]

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+} \quad (3)
\]

Another finding of the present study is that by reducing the molar ratio of Fe²⁺/H₂O₂ (by increasing the amount of hydrogen peroxide), the Cr⁶⁺ removal efficiency decreases. It is possible that, on one hand, hydrogen peroxide competes with hexavalent chromium for accepting an electron and as a result reduces the ferrous ions present in the solution. On the other hand, excess of hydrogen peroxide leads to the reversible reaction between hexavalent and trivalent chromium (at acidic pH) and reduces the elimination of Cr⁶⁺. Thus, the trivalent chromium formed reacts with hydrogen peroxide to form the hexavalent chromium (Reaction (4)).

\[
2[\text{Cr(OH)}_6]^{3-} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{CrO}_4^{2-} + 2\text{OH}^- + 8\text{H}_2\text{O} \quad (4)
\]

Research by Alaton and co-workers (2007) about the effect of Fenton’s treatment on the biodegradability of chromium-complex azo dyes, also showed that the molar ratio of Fe²⁺/H₂O₂ = 0.06 removes only 30% of COD and total color (Arslan-Alaton et al. 2007). Therefore, at lower molar ratios of Fe²⁺/H₂O₂ the rate of Cr⁶⁺ removal is reduced, which is consistent with our results.

Effect of time and initial concentration of chromium

In order to determine the appropriate time for the removal of Cr⁶⁺ by Fenton’s method, several tests were performed in the time period of 15–90 min (Figure 2). The obtained result shows that Cr⁶⁺ was removed rapidly during the first 30 min and then it leveled off at further times. Thus, 30 min time was chosen in the later stage as the appropriate reaction time since better removal performance was obtained. Results also showed that by increasing the concentration of Cr⁶⁺ from 10 to 15 mg/L, the percentage removal efficiency of chromium at a molar ratio of Fe²⁺/H₂O₂ = 2.4 was reduced from 98 to 88% (Figure 3). Optimal ratio of
(Fe²⁺/H₂O₂)/(Cr⁶⁺) = 6 was obtained. Therefore, by reducing the amount of ferrous sulfate on one hand and increasing the concentration of peroxide hydrogen and chromium on the other, decreases the removal efficiency of Cr⁶⁺.

**Determining the effect of precipitation process on chromium removal**

**Effect of the initial pH**

The result obtained in this process is depicted in Figure 4. At pH = 7 most of the Cr⁶⁺ removed was equivalent to 90% and the least amount of chromium removed at pH = 11 was equivalent to 35%. Song et al. (2004) performed the treatment of tannery wastewater by chemical coagulation (alum and ferric chloride) and reported that this method was effective in reducing chromium and its removal efficiency is dependent on pH and the amount of coagulant. These authors also reported that the removal of 12.5 mg/L of chromium at pH = 7.5 and 0.8 g/L of coagulant was equivalent to 74–99%. Also, the results obtained from their research showed that the performance of ferric chloride was better than alum (Song et al. 2004).

**Effect of various concentrations of ferric chloride**

Table 2 shows the effect of amount of ferric chloride on the removal efficiency of chromium. It is observed that the highest removal efficiency of approximately 90% was related to ferric chloride equivalent to 0.7 g/L; and by increasing the amount of FeCl₃, there is no significant change in the removal efficiency. Barnes and co-workers also used ferric chloride equivalent to 0.8 g/L as a coagulant for the treatment of tannery wastewater containing chromium (Barnes et al. 1981). Unlike other hazardous metals, chromium is also found in the form of anion; and major anions related to Cr⁶⁺ are found in the form of chromate and dichromate. It should be noted that the most important compounds of this element include chromate, dichromate sodium, and potassium. In the reaction of ferric chloride with anions of Cr⁶⁺, precipitates of iron dichromate (Fe₂(Cr₂O₇)₃) and iron chromate (Fe₂(CrO₄)₃) are formed. Since chromium trioxide at neutral pH exists in the form of chromate, the possibility of precipitation of iron chromate is higher than iron dichromate. Therefore, it is important to consider the volume of produced sludge and the hazards of the sediment.

However, chromate at alkaline pH and dichromate at acidic pH can also react with chloride ions to form trivalent chromium (Reactions (5) and (6)):

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (5)
\]

\[
\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3 + 5\text{OH} \quad (6)
\]

**Effect of time and initial concentration of chromium**

Figures 5 and 6 show the effect of deposition time and initial concentration of pollutant on the removal efficiency of Cr⁶⁺. The most effective removal efficiency was found at a duration of 20 min with an initial concentration of chromium equivalent to 5 mg/L; then it leveled off at further times. Also, the removal efficiency of Cr⁶⁺ decreased from 97 to 77% when the concentration changed from 5 to 15 mg/L.
Combined treatment by Fenton process followed by precipitation process

Effects of the combined method of Fenton’s oxidation and precipitation on the removal efficiency of different concentrations of Cr$^{6+}$ showed that the best removal efficiency of chromium was equivalent to 99.99% at concentrations equal to and less than 15 mg/L (Figure 7). The removal efficiency of chromium at optimal conditions of Fenton and precipitation processes separately was about 98 and 97%, respectively. However, results of the Kruskal-Wallis H test at a significance level of 5%, showed a significant difference (5% level) between the performances of the three methods (Fenton, precipitation, and their combination) for the removal of the selected concentrations of Cr$^{6+}$ ($P$ value $\leq 0.05$). In other words, at three concentrations of Cr$^{6+}$, the performance of the combined method was significantly greater than the Fenton and precipitation methods’ efficiency separately for the removal of chromium. Moreover, higher concentrations of chromium (15 mg/L) were removed.

During the Fenton’s process, hexavalent chromium is converted into trivalent chromium by reacting with divalent iron. As the Fenton’s reaction takes place at pH $= 4$, trivalent chromium is seen in the form of very small suspended particles in the solution. A small proportion of the suspended particles can be trapped in iron complexes such as $[\text{Fe}_2(\text{H}_2\text{O})_7\text{OH})_4]^{3+}$, $[\text{Fe}_2(\text{H}_2\text{O})_7\text{OH})_3]^{3+}$, and $\text{[Fe(H}_2\text{O})_3\text{(OH})_3]^{4+}$ (at pH between 3 and 5 iron ions are seen in the form of colloidal particles) and are removed.

However, the bulk of the particles are removed during the precipitation process because this process makes it possible for the trivalent chromium (Cr(OH)$_3$) formed during the Fenton process along with deposits formed, (Fe(OH)$_3$), to be precipitated together and settle at the bottom of the container in a very short time. Thus the final product formed by the hydrolysis of ferric chloride is ferric hydroxide which leads to the formation of gelatinous flocs without any shape. These flocs are heavier than water and settle because of their own weight. With the formation of these flocs, colloids may be trapped inside or become attached to the adhesive surface of flocs by the time of settling. Therefore, it seems that during the precipitation process, sweep floc mechanism is effective.
in the removal of trivalent chromium formed during the Fenton process. Therefore, by using the two methods in an integrated form, both the hexavalent chromium and trivalent chromium are removed.

It should be noted that during the Fenton’s process, hexavalent chromium is converted into trivalent chromium. During the precipitation process also chromium anion with ferric chloride leads to the formation of iron chromate precipitates. However, during the combination of these two methods, initially hexavalent chromium is converted into trivalent chromium and it is trivalent chromium that gets deposited. Therefore, the sludge formed during the integrated process is less toxic.

CONCLUSION

About 98% of Cr$^{6+}$ is removed by the Fenton process, and the ideal conditions for its removal included Cr$^{6+} = 10$ mg/L, pH = 4, molar ratio Fe$^{2+}/\text{H}_2\text{O}_2 = 2.4$ with a time duration of 30 min. Maximal removal efficiency of hexavalent chromium in the precipitation process was equivalent to 97% in optimum conditions: Cr$^{6+} = 5$ mg/L, pH = 7, FeCl$_3 = 0.7$ g/L and deposition time of 20 min. The combination of these two methods can remove greater concentrations of chromium (15 mg/L) to about 99.99%, while the precipitation process after the Fenton’s method leads to the removal of suspended particles and the deposits are less toxic than the iron chromate.

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