

Chromate reduction by waste iron from electroplating wastewater using plug flow reactor

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Abstract

Waste iron was used to treat high concentration chromate (534 mg/L as Cr) from electroplating wastewater by plug flow reactor (PFR) due to the following reasons: (1) two wastes are treated simultaneously, (2) low pH of the electroplating wastewater (≈ 2) benefits the reaction between these two wastes, (3) effluent pH is elevated in the PFR, reducing the base requirement to meet the pH discharge standard for wastewater (pH 6–9). Complete chromate reductions were achieved at pH 1.7 for hydraulic retention time (HRT) of 98 min, pH 1.5 for HRT of 40 min and pH 1.3 for HRT of 20 min. Consequently, optimum HRT for complete chromate reduction was obtained for different pHs. Although more acids were used to lower influent pH to reduce HRT, effluent pH was higher due to more hydrogen ion reacting with chromate. Eventually, fewer bases are required to fulfill the discharge pH requirement of wastewater. Effluent pH 3–5 was observed with high turbidity, indicating the precipitations of chromium oxide and hydroxide were enhanced by the dissolved iron coagulation. X-ray diffraction was conducted to examine the remaining species. Other than chromium oxide and hydroxide species, an iron–chromium complex (Cr_2FeO_4) was also observed.
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Keywords: Waste iron; Chromate; Electroplating wastewater; Plug flow reactor; XRD

1. Introduction

Chromate is a potential carcinogen and is widely used in the electroplating industry. The traditional procedures of chromium reduction in the electroplating industry are to use a reducing agent such as sodium bisulfite (HNaSO_3) to reduce Cr(VI) to Cr(III). Coagulant, such as ferric salt, is then used to enhance the precipitation of either $\text{Cr}_2\text{O}_3(\text{s})$ or $\text{Cr}(\text{OH})_3(\text{s})$ around pH 8. Since the effluent chromate concentration in the electroplating industry could be as high as several hundreds mg/L as Cr, significant amounts of sodium bisulfite and coagulant are needed. Another method by zero valent iron (ZVI) to treat chromate in electroplating wastewater has been reported [1–4], where chromium was successfully removed by ZVI. However, the downside for using ZVI for high concentration chromate is very costly and not accepted by most of the electroplating factories. Waste iron is a good alternative, but most of these waste irons

are either discarded or sold for very cheap price and should be used for more effective purposes. For example, these waste irons can be used for wastewater treatment as reducing agents to remove the potential oxo-anion pollutants, such as chromate in this study. Therefore, the intention of the research reported in the present work is to reuse these low-priced waste irons to reduce the high concentration of chromate from electroplating effluent.

There are many researches in which ZVI particle is used to treat chromate for groundwater and wastewater in medium pH through batch modes [2,5–14]. These researches all concluded that chromate reduction efficiencies could be enhanced through increase in acidity. Consequently, the low pH (≈ 2) of electroplating wastewater in this study would favor the waste iron/chromate reaction. Three studies reported ZVI/chromate reaction in continuous modes. Guha and Bhargava [1] conducted a column study for 17 mg/L of chromate with hydraulic retention time (HRT) of 1.2 ± 0.2 h and showed that only 30% chromate was removed at initial pH 2.6. Lo et al. [10,15] reported that complete chromate reduction was achieved for 25 mg/L of chromate using column reactors with seepage velocity of 400 m/year.

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However, all these studies were conducted under low concentration of chromate with long HRT and the results cannot directly apply for electroplating wastewater with high concentration of chromate.

One study has used waste iron for chromate reduction for synthetic water, but was conducted in a batch mode at medium pH [16]. Since none of the study reported for waste iron to remove high concentration chromate from electroplating wastewater, this study demonstrates chromate reduction using wasted cast iron under low pH (≤ 2) and obtains the minimum HRT at different pHs. Moreover, a plug flow regime column reactor was selected in this study. A plug flow reactor (PFR) has the advantage over complete stirred tank reactor (CSTR) in this process. In PFR, the waste iron would be in direct contact with the low pH influent, but in CSTR, the waste iron would be in direct contact with the higher pH effluent unless acidity is consistent. Since lower pH favors the waste iron/chromate reaction, PFR would have faster reaction rate than that of CSTR. Accordingly, the objectives of this study are to examine the chromate reduction from electroplating wastewater by waste iron using PFR. Effects of pH and HRT, capacity of the waste iron, speciation for waste iron/chromate reaction and comparison of un-reacted and reacted waste iron species by X-ray diffraction (XRD) are investigated in this study.

2. Methods and materials

The waste iron (wasted cast iron) particles in this research were obtained from Li-Xiang Mechanic & Electronic Company, located in Northern Taiwan. These waste irons are generated during the cutting of billets after casting. The edges of billets are cut to make the surface smooth. The waste iron particles were washed with methanol several times to remove the oil residues. The washed waste iron was then stored in a dessicator filled with nitrogen gas. Waste iron particles passing through sieve #10 and remaining on sieve #20 were used in this study, representing size range of 0.85–2 mm.

The raw wastewater qualities are listed in Table 1. At this concentration and pH, Cr(VI) is presented as HCrO_4^- instead of $\text{Cr}_2\text{O}_7^{2-}$ according to Stumm and Morgan [17]. The treatment goal obedient to effluent standard in Taiwan is to reduce the Cr(VI) and total chromium to 0.5 and 2 mg/L, respectively. All chemicals used are of reagent grade. Methanol cleaned waste iron particle was packed in glass columns with diameter of 1.1 cm and length of 45 cm. A peristaltic pump (Firstek Sci-

entific, Model Ps-50) was used to control the upward flow. The column was a low dispersion plug flow type reactor with dispersion number of 0.0147 determined by a tracer study using NaCl. The packed columns have porosity of approximately 63%. Therefore, empty bed contact time (EBCT) was 160% higher than actual HRT which was changed by either varying the waste iron dosage or the flowrate of the influent. Three different flowrates (7, 13 and 25 mL/h) or flux (7.4, 13.7 and 26.3 cm/h) and three different weights of waste iron (3.5, 7 and 14 g) were tested for the four different pHs: 1.3, 1.5, 1.7 and 2.0. Therefore, overall of 36 experiments were conducted.

Dissolved nickel, copper and total chromium (Cr(VI)+Cr(III)) were measured by a flame atomic adsorption spectroscopy (GBC 932, GBC Scientific Equipment, Australia). Hexavalent chromium was measured colorimetrically according to the methods 3500-Cr listed in the 20th edition of the Standard Methods [18] using a UV-vis spectrophotometer (HACH Model DR-4000). Trivalent chromium was acquired by deducting hexavalent chromium from total chromium. The total iron content was analyzed also using the flame atomic adsorption spectroscopy. Ferrous ions were analyzed colorimetrically at 510 nm after forming colored complexes with 1,10-phenanthroline according to the Standard Methods 3500-Fe. The quantitative analysis of Fe^{3+} was obtained by subtracting Fe^{2+} concentration from total iron concentration. Crystal structures of the iron species before and after use were analyzed by an XRD (DMAX 2200 type VK, Rigaku Co., Japan).

3. Results and discussion

3.1. Effects of influent pH and HRT on chromate reduction and capacity for the waste iron

Fig. 1 presents effluent chromate concentration for the four different influent pHs versus time for HRT of 26 min (waste iron 7.0 g and flowrate 13 mL/h). From Fig. 1, operating at both pH 1.5 and pH 1.3 is capable of reducing chromate completely. Complete reduction here indicated that the effluent concentration is not detected by Method 3500-Cr with method detection limit (MDL) of 0.01 mg/L. For pH 1.3, the breakthrough time

Table 1
The chemical analysis of the raw electroplating wastewater

Cr(VI)	534
Ca^{2+}	7.4
Mg^{2+}	2.3
Ni^{2+}	94.2
Cu^{2+}	20.3
SO_4^{2-}	19.8
TOC	4.2
pH	2.0

Unit: mg/L except for pH is unitless.

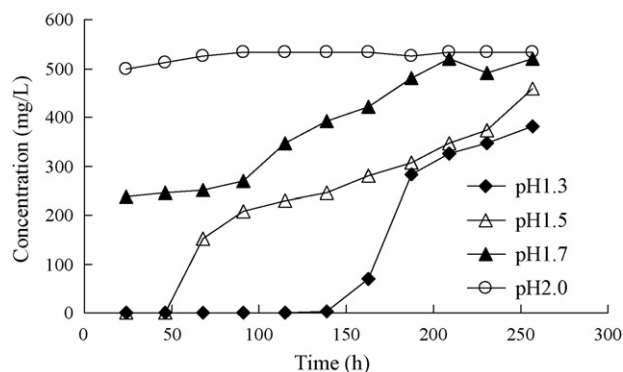


Fig. 1. Effluent chromate concentration vs. time for HRT of 26 min for different influent pH (waste iron 7.0 g and flowrate 13 mL/h).

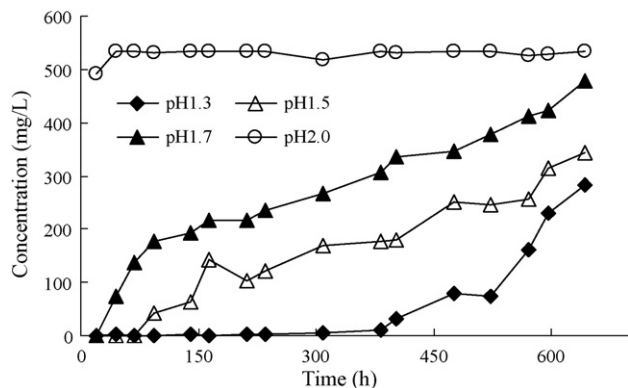


Fig. 2. Effluent chromate concentration vs. time for HRT of 98 min (waste iron 14.0 g and flowrate 7 mL/h).

can last for 145 h, but for pH 1.5, the breakthrough time can only last for 50 h. The breakthrough time or operation time is defined when the effluent concentration is higher than the allowable concentration, which is commonly 5% of the influent concentration. Chromate reduction was enhanced by increasing HRT by either increasing the waste iron dosage or decreasing the flowrate. Fig. 2 again presents effluent chromate concentration for different influent pH versus time but increasing the HRT to 98 min by increasing the waste iron to 14 g but reducing the flowrate to 7 mL/h. In this circumstance, complete chromate reductions were all achieved for pH 1.3, pH 1.5 and pH 1.7. For pH 1.3, the breakthrough time was increased to 330 h and for pH 1.5, the breakthrough time was increased to 65 h. Moreover, chromate was not completely removed for pH 1.7 in Fig. 1 but was completely removed after 20 h in Fig. 2 due to longer HRT. Besides, although some nickel, copper and sulfate from the plating process still presented in the wastewater, they did not affect the results since due to their low concentrations and un-favorable thermodynamics.

A minimum HRT to achieve complete reduction for different pHs was determined in Fig. 3. The dashed lines for pH 1.3, 1.5 and 1.7 are the regression lines from Langmuir type saturation curve equation in Eq. (1) since the chromate reduction efficiency increased sharply in the low HRT range but reached slowly to complete reduction. In Eq. (1), a and b are the empirical constants and can be obtained from linear plot of $1/\text{removal}$

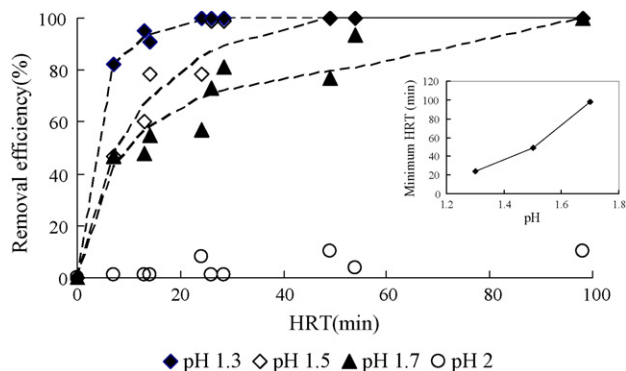


Fig. 3. Chromate reductions vs. HRT for different pHs.

efficiency and $1/\text{HRT}$:

$$\text{removal efficiency (\%)} = \frac{a \times \text{HRT (min)}}{b + \text{HRT (min)}} \quad (1)$$

Minimum HRTs to achieve 100% reduction for different pHs were obtained and presented in the smaller figure in Fig. 3. For 26 min of minimum HRT at pH 1.3 or 49 min of minimum HRT at pH 1.5 or 98 min of minimum HRT at pH 1.7, complete chromate reduction was achieved. Capacity of waste iron for chromate reduction was calculated by the waste iron utilization on per gram basis (as $\text{mg Cr}^{6+}/\text{g waste iron}$), thus the optimum dosage as well as the breakthrough time can be properly determined for various conditions for future full scale operation. The actual chromate reduction for the waste iron for various conditions was calculated based on the flowrate, influent concentration of 534 mg/L as Cr^{6+} , effluent concentration and breakthrough time or from Eq. (2), where amounts of chromate reductions (W_{Cr} , as mg Cr) were determined based on the area above the breakthrough point. In Eq. (2), $b.t.$ is the breakthrough time, C_{in} is the influent concentration and C_{out} is the effluent concentration, Q is the flowrate:

$$W_{\text{Cr}} = \int_0^{b.t.} [C_{\text{in}} - C_{\text{out}}] (\text{mg/L}) \times Q (\text{L/min}) \times t (\text{min}) dt \quad (2)$$

Since pH and HRT are the most important parameters to determine the waste iron requirement, all the results from the 27 experiments (data for pH 2 was excluded due to low removals) were regressed by a multi-variable equation in Eq. (3). This equation can be used for determining the waste iron dosage since both F test (for the model) and student t -distributions (for the variables) were significant at 95% confidence level with a correlation coefficient (R^2) of 0.43 from the results of analysis of variance (ANOVA) on the following equation:

$$\begin{aligned} \text{capacity (mg Cr}^{6+}/\text{g waste iron)} \\ = 259.8 + 0.42 \times \text{HRT (min)} - 165.0 \times \text{pH} \end{aligned} \quad (3)$$

The minus sign for pH indicates that higher pH had lower waste iron capacity, and the plus sign in HRT represents that higher HRT had higher waste iron capacity. Low correlation coefficient in this equation is resulted from some zero capacity data in the shorter HRT and higher pH. Nevertheless, the equation is still capable of estimating water iron capacity for chromate reduction for different operating conditions.

3.2. Speciation for waste iron/chromate reaction

Fig. 4 presents the dissolved chromium speciation versus time for chromium species for HRT of 98 min (waste iron 14.0 g and flowrate 7 mL/h) at pH 1.3. Initially, some of the total chromium were lost, then gradually increased and reached a constant influent concentration (534 mg/L as Cr^{6+}), indicating that some chromium (either Cr(VI) or Cr(III)) were adsorbed. From visual observation during the operation, in the beginning, the effluent was colorless instead of green, the color of triva-

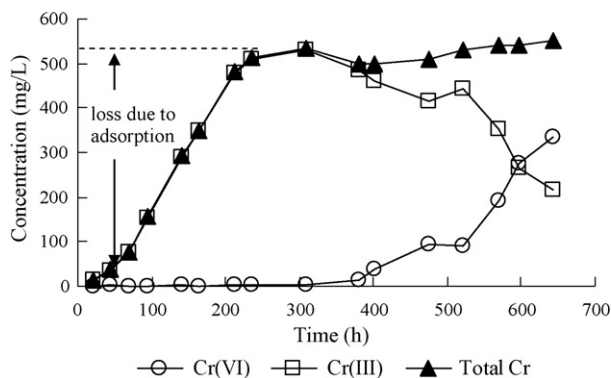


Fig. 4. Effluent concentrations vs. time for chromium species for HRT of 98 min at pH 1.3 (waste iron 14.0 g and flowrate 7 mL/h).

lent chromium. After some times, the green color was present, representing the trivalent chromium was observed at end of adsorption. The chromium loss could also contribute to the formation of a complex from waste iron and trivalent chromium. Erdem and Tumen [19] reported that a chromium-iron oxide compound, Cr_2FeO_4 , was observed by using ferrite to remove trivalent chromium. It is possible that similar compound can be observed and XRD was used to exam the reacted product and presented in the later section.

Fig. 5 presents effluent chromate concentrations versus time for ferrous and ferric ion to compare with chromate for HRT of 98 min (waste iron 14.0 g and flowrate 7 mL/h) at pH 1.3. Ferrous ion was produced initially due to either iron reacting with water or chromate under acidic condition, as indicated in Eqs. (4) and (5) [2,4,12]. Since strong oxidizing agent (chromate) was still presented, ferric ion was observed instead of ferrous ion afterward as shown in Eq. (6) [2], so ferric ion was increased but ferrous ion was decreased. Effluent pH was 3–5 with high turbidity due to the occurrence of iron coagulation, causing loss of ferric ion due to coagulation in Fig. 5. Hence two mechanisms (reduction and coagulation) were achieved by adding just one chemical (waste iron), where the formation of ferric ion was able to save the amount of coagulation chemicals

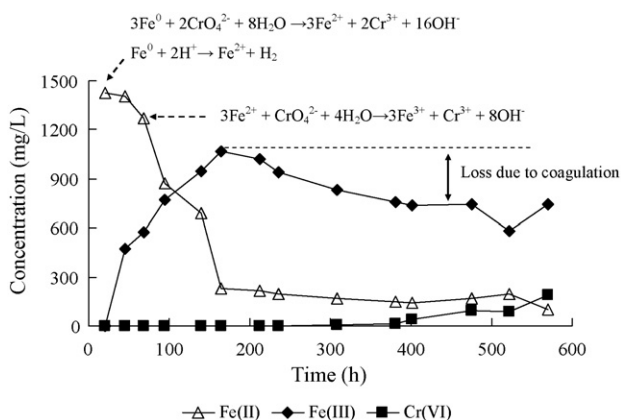
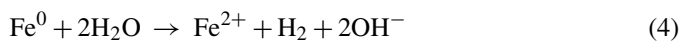


Fig. 5. Effluent concentration for HRT of 98 min at pH 1.3 (waste iron 14.0 g and flowrate 7 mL/h).

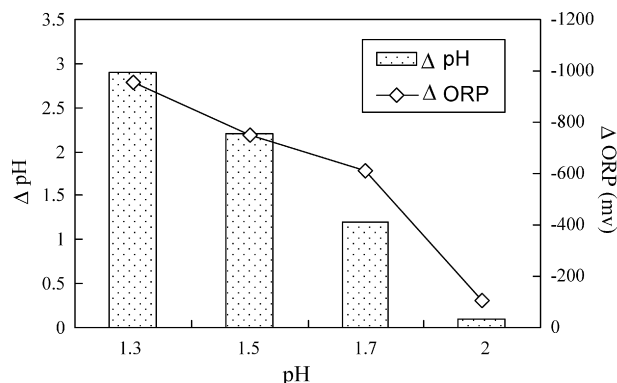


Fig. 6. ΔpH and ΔORP vs. four of the different pHs for HRT of 98 min (waste iron 14.0 g and flowrate 7 mL/h).

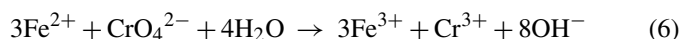
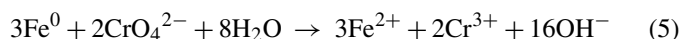


Fig. 6 presents ΔpH and ΔORP (oxidation–reduction potential) for the four different pHs for HRT of 98 min before breakthrough, where ΔpH is the difference between effluent pH and influent pH and ΔORP is the difference between effluent ORP and influent ORP. During the chromate reduction, pH was increased but ORP was decreased. Therefore, ΔpH is positive but ΔORP is negative. The result shows, when the influent pH is lower, the effluent pH or ΔpH is higher, ascribed to more hydrogen iron was reacted with chromate. Decrease of ORP or ΔORP (absolute value) was also higher for the lower influent pH since more reducing agent trivalent chromium was generated in lower pH, as illustrated in the E –pH diagram in Fig. 7. In Fig. 7, the thick line is the equal concentration line of HCrO_4^- and Cr^{3+} and the dashed lines are between O_2 , H_2O and H_2 . More downward of that thick line indicates more dominant of the Cr^{3+} . Therefore, more chromate reduction with more Cr^{3+} generation resulted in more ORP drop. Consequently, the values of ΔpH and ΔORP in Fig. 6 are able to represent the potential of chromate reduction by the waste iron.

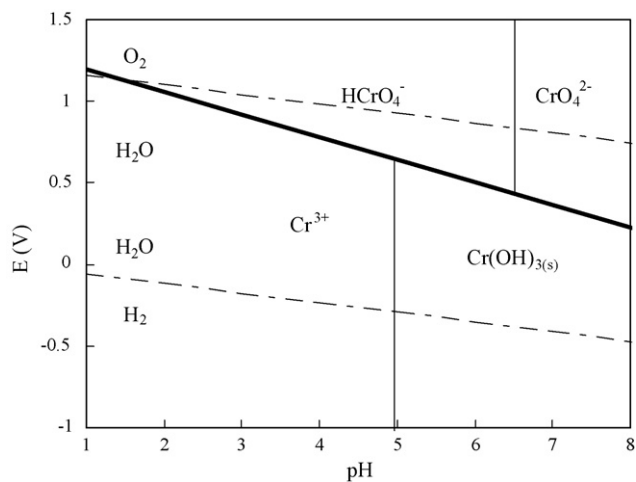


Fig. 7. E –pH diagram for chromium species of HCrO_4^- , CrO_4^{2-} , Cr^{3+} and $\text{Cr}(\text{OH})_{3(s)}$ for $\text{Cr} = 543 \text{ mg/L}$ based on thermodynamic data source from Stumm and Morgan [17] and Snoeyink and Jenkins [22].

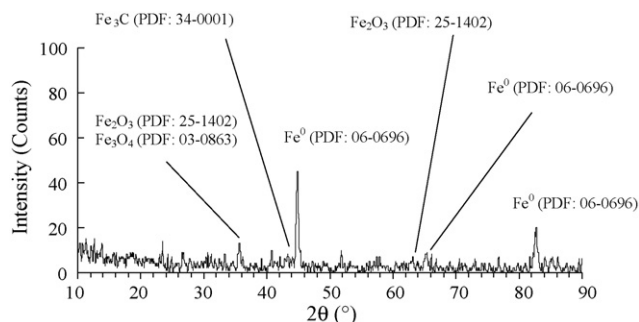


Fig. 8. XRD analyses (wavelength=copper K-alpha 1.54 Å) for waste iron before use.

3.3. Comparisons of the un-reacted and reacted waste iron by XRD

Fig. 8 presents the XRD analyses for the un-reacted waste irons. According to the powder diffraction file (PDF) based on the XRD database obtained from a PCPDFWIN software [20], major peaks in Fig. 8 were identified as Fe^0 (PDF: 06-0696, $2\theta=44.67$, and 82.42), $\text{Fe}_2\text{O}_3(\text{s})$ (PDF: 25-1402, $2\theta=35.68$), $\text{Fe}_3\text{O}_4(\text{s})$ (PDF: 03-0863, $2\theta=35.45$) and $\text{Fe}_3\text{C}(\text{s})$ (PDF: 34-0001, $2\theta=43.73$). The presence of $\text{Fe}_3\text{C}(\text{s})$ in the waste iron is typical since coal is used from steel production process. $\text{Fe}_2\text{O}_3(\text{s})$ or $\text{Fe}(\text{III})$ cannot react with chromate but would be a good source for the subsequent coagulation or precipitation process typically used in the electroplating plant. Fig. 9 presents the XRD analyses for the reacted waste irons for experimental condition of HRT 49 min for pH 1.5 and waste iron 7 g. The differences between these two were used to distinguish the mechanism of the reaction between waste iron and chromate. Major peaks in Fig. 9 were identified as Fe^0 (PDF: 06-0696, $2\theta=44.67$ and 82.42), $\text{Fe}_2\text{O}_3(\text{s})$ (PDF: 25-1402, $2\theta=35.68$), $\text{Fe}_3\text{O}_4(\text{s})$ (PDF: 03-0863, $2\theta=35.45$), $\text{Cr}_2\text{O}_3(\text{s})$ (PDF: 03-1124, $2\theta=54.93$), FeOOH (PDF: 34-1226, $2\theta=26.72$) and $\text{Cr}_2\text{FeO}_4(\text{s})$ (PDF: 34-0140, $2\theta=35.50$). Fe_3C was seen in un-reacted waste iron (Fig. 8) but not seen here probably due to the reduction of iron from Fe_3C . Therefore, from the results in Fig. 9, chromate was converted to trivalent chromium which could be either in the form of $\text{Cr}_2\text{O}_3(\text{s})$ or $\text{Cr}(\text{OH})_3(\text{s})$. For iron species, oxidation reaction had occurred on the waste iron species to form Fe_2O_3 , where oxidation num-

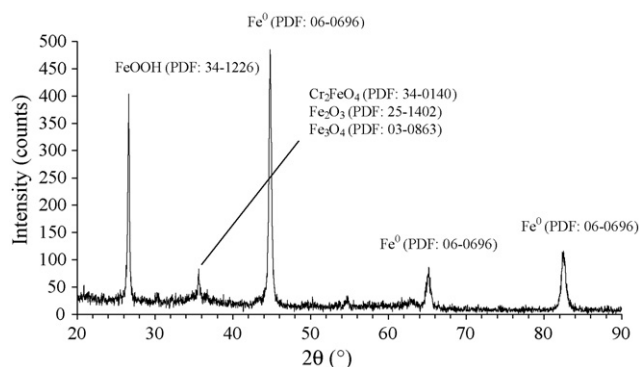
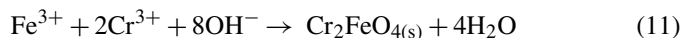
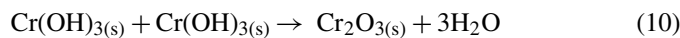
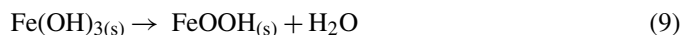
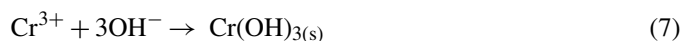


Fig. 9. XRD analyses (wavelength=copper K-alpha 1.54 Å) for reacted waste iron (HRT: 49 min for pH 1.5, waste iron 7.0 g).

ber of iron was increased from 0 (Fe^0) to 3 (Fe_2O_3). Formation of iron oxide, iron hydroxide and chromium oxide have occurred since the effluent pH was above 4. A chromium iron oxide compound, $\text{Cr}_2\text{FeO}_4(\text{s})$, was also observed, resulting from adsorption of $\text{Cr}(\text{III})$ species on to the waste iron. Similar result was reported by Erdem and Tumen [19] by using ferrite to remove trivalent chromium species. Previous discussion indicates total chromium was lost during the initial stage of the waste iron/chromium reaction and the formation of $\text{Cr}_2\text{FeO}_4(\text{s})$ is one of the possibilities. Consequently, the chemical reactions between waste iron and trivalent chromium based on the XRD analyses were described in Eqs. (7)–(11), where dissolved chromium and iron were precipitated as $\text{Cr}(\text{OH})_3(\text{s})$ ($K_{\text{sp}}=6.3 \times 10^{-31}$) and $\text{Fe}(\text{OH})_3(\text{s})$ ($K_{\text{sp}}=4 \times 10^{-38}$) [21], $\text{FeOOH}(\text{s})$ was resulted from the dewatering of $\text{Fe}(\text{OH})_3(\text{s})$. $\text{Cr}_2\text{O}_3(\text{s})$ was obtained from deducting three H_2O out of two $\text{Cr}(\text{OH})_3(\text{s})$, and $\text{Cr}_2\text{FeO}_4(\text{s})$ was the combination of ferric ion, trivalent chromium and hydroxide ion



4. Conclusions

Chromate was successfully removed by waste iron from electroplating wastewater in the plug flow type column reactors for $\text{pH} \leq 2$ in this work. For the four different tested pHs 1.3, 1.5, 1.7 and 2.0, complete chromate reduction was achieved at pH 1.7 for HRT of 98 min. HRT was reduced to 40 min if pH was reduced to 1.5 or 20 min if pH was reduced to 1.3 for complete chromate reduction. As either pH decreased or HRT was increased, both chromate reduction and the breakthrough time increased. When chromate reduction was increased, ferrous ion was produced and ORP was decreased. The effluent pH was 4.2 for the influent pH of 1.3 ($\Delta\text{pH} 2.9$), but the effluent pH was only 3.7 for the influent pH of 1.5 ($\Delta\text{pH} 2.2$), representing lower influent pH resulted in higher effluent pH. The result indicates the additional acid can not only enhance the chromate reduction efficiency, but also save the usage of base to fulfill the discharge pH requirement (pH 6–9). Effluent pH 3–5 was observed with high turbidity due to the occurrence of iron coagulation, indicating the precipitation of chromium oxide and hydroxide were enhanced by the dissolved iron. Ferrous ion was increased in the beginning due to the dissolution from the waste iron, but decreased coupling with the reduction of chromate. XRD was conducted to examine the remained species at pH 1.5. Other than trivalent chromium oxide and chromium hydroxide species, an adsorbed iron-chromium complex (Cr_2FeO_4) was also observed.

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