

Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero valent iron process

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Received 6 May 2006; received in revised form 11 August 2006; accepted 14 August 2006

Available online 18 August 2006

Abstract

Fluidized zero valent iron (ZVI) process was conducted to reduce hexavalent chromium (chromate, CrO_4^{2-}) to trivalent chromium (Cr^{3+}) from electroplating wastewater due to the following reasons: (1) Extremely low pH (1–2) for the electroplating wastewater favoring the ZVI reaction. (2) The ferric ion, produced from the reaction of Cr(VI) and ZVI, can act as a coagulant to assist the precipitation of $\text{Cr}(\text{OH})_{3(s)}$ to save the coagulant cost. (3) Higher ZVI utilization for fluidized process due to abrasive motion of the ZVI. For influent chromate concentration of 418 mg/L as Cr^{6+} , pH 2 and ZVI dosage of 3 g (41 g/L), chromate removal was only 29% with hydraulic detention time (HRT) of 1.2 min, but was increased to 99.9% by either increasing HRT to 5.6 min or adjusting pH to 1.5. For iron species at pH 2 and HRT of 1.2 min, Fe^{3+} was more thermodynamically stable since oxidizing agent chromate was present. However, if pH was adjusted to 1.5 or 1, where chromate was completely removed, high Fe^{2+} but very low Fe^{3+} was present. It can be explained that ZVI reacted with chromate to produce Fe^{2+} first and the presence of chromate would keep converting Fe^{2+} to Fe^{3+} . Therefore, Fe^{2+} is an indicator for complete reduction from Cr(VI) to Cr(III). X-ray diffraction (XRD) was conducted to exam the remained species at pH 2. ZVI, iron oxide and iron sulfide were observed, indicating the formation of iron oxide or iron sulfide could stop the chromate reduction reaction.

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Keywords: Fluidized bed; Zero valent iron; Chromate; Electroplating wastewater; XRD

1. Introduction

Chromium is a carcinogenic, non-biodegradable and highly toxic pollutant, which is widely used in the electroplating industry and greatly affects our environments. The typical procedures of chromium reduction for the electroplating industry are to use a reducing agent, sodium bisulfite (HNaSO_3), to reduce Cr(VI) to Cr(III). pH is then adjusted to around 8, allowing $\text{Cr}_2\text{O}_{3(s)}$ or $\text{Cr}(\text{OH})_{3(s)}$ to precipitate afterwards. Coagulant is typically used to assist the precipitation of $\text{Cr}_2\text{O}_{3(s)}$ or $\text{Cr}(\text{OH})_{3(s)}$. Therefore, significant amounts of sodium bisulfite and coagulant are needed in these procedures. Lately there has been considerable interest in using ZVI to treat inorganic chemicals, including chromate. Many types of reactive barriers or permeable walls were constructed for groundwater remediation sites for chromium

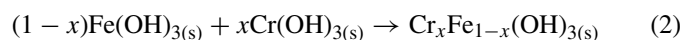
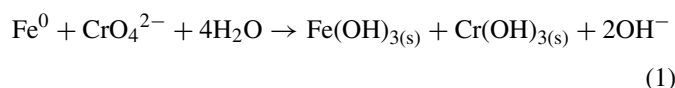
removal [1–11], the downside for using such technology on soil or groundwater is the elevated pH which causes the slower reactivity of ZVI.

ZVI has also been used in batch type reaction for chromate reduction for industrial wastewater [12–14]. Chang [12] reported when the sample with low level of chromium (<14 mg/L) was mixed with thin iron wire at pH 3–8, 50–90% of the total chromium were reduced in 4 h. They also found out that the initial reduction efficiency was pH dependent; the lower the pH, the higher the reduction rate. Guha and Bhargava [13] conducted 24-h batch studies using synthetic plating wastewater to demonstrate that ZVI is a good technology for high chromate concentration (325 mg/L) but not for low chromate concentration (17 mg/L). They also conducted a column study with two sand and iron mixed columns (volume of iron was 30 and 50%, respectively) for 17 mg/L chromate with HRT of 1.2 ± 0.2 h. Their results showed that only 30% chromate was removed even at initial pH 2.6 and such a long detention time. There was no explanation for low chromate removal in this article, but it can be

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contributed to several reasons (1) iron–chromium or iron oxide precipitation on the iron surface to limit the capabilities of ZVI. (2) The end pH was elevated to pH 6.3 due to the exhaustion of hydrogen ion, but high pH is not favored to the ZVI/chromate reaction thermodynamically. (3) Since the reduction of chromate using ZVI is also dependent on the diffusion of chromate from bulk solution onto the ZVI surface [14], mixing is an important parameter to achieve efficient nitrate reduction. However, no mixing intensity can apply for packed column to increase the diffusion transport of chromate on ZVI.

Several chemical equations between ZVI and chromate are proposed in several literatures. Among these chemical equations, Eqs. (1) and (2) reported by Chang [14] are the most significant equations for electroplating wastewater since the residual iron and chromium are required to precipitate out by optimizing the pH level to fulfill the requirement discharge standard of total chromium in Taiwan (2 mg/L as Cr) by optimum coagulation



Since the optimum precipitation pH range for $\text{Cr}(\text{OH})_{3(s)}$ and $\text{Fe}(\text{OH})_{3(s)}$ are both around 8, which make iron salt a perfect coagulant instead of aluminum salt, indicating the dissolved iron after the ZVI/chromate reaction can be utilized for the coagulation reagent. Therefore, the cost of coagulant can be saved and only one chemical is needed instead of two if enough dissolved iron is generated. Consequently, the resulting species, ferric ion, can be utilized as an excellent source of coagulant since most of the electroplating wastewater treatment facilities have coagulation process before discharge to assist the precipitation of $\text{Cr}(\text{OH})_{3(s)}$ to conform the discharge regulation requirement of color and turbidity.

From above discussions, all the studies showed at least 1 h HRT are required to achieve 90% chromate. However, the long HRT is not acceptable for most of the electroplating plant, causing more land space requirement. To achieve these goals, in this experiment, pH levels from 1 to 2 was conducted since previous study was only operated as low as pH 2.6. Moreover, some wastewater pH for electroplating wastewater could be less than 2. Besides, only one study has conducted a continuous study by ZVI packed columns. However, there are two disadvantages for packed column systems: (1) pH would be increased but it is impossible to maintain constant pH for packed columns, (2) mixing mechanism cannot be applied on packed columns, so chromate reduction in these processes is potentially limited by the transport of chromate from bulk solution to the surface of ZVI. The designed fluidized ZVI process can overcome the above disadvantages. The process makes pH control and mixing possible through addition of acidity [15], i.e. controlling pH, and achieve adequate mixing intensity [16] among the fluidized ZVI. Besides, the proposed fluidized process prevents the possible clogging problem resulting from oxidized iron compounds, which often occurs in the packed column ZVI system to decrease

the porosity and the permeability [17]. Moreover, utilization of ZVI for fluidized process would be higher due to abrasive motion of the ZVI to remove the possible precipitated layer on ZVI [16]. Due to the above advantages, a fluidized ZVI treatment system was proposed to investigate for chromium reduction for the low pH electroplating waster in this study. Moreover, X-ray diffractometry (XRD) was conducted for chemical analysis for the reacted species since it was not yet identified in the previous studies. Therefore, the objectives of this study are to investigate the followings: (1) the effects of pH, HRT and ZVI dosages, (2) speciation and mechanism of the ZVI/chromate reaction, (3) lifetime of ZVI and capacity of ZVI, (4) determination of reacted ZVI species by XRD.

2. Methods and materials

The raw wastewater was acquired from a local electroplating facility in northern Taiwan with water qualities listed in Table 1. Since the plating process includes three procedures: first copper, then nickel and chromium; therefore, some Cu^{2+} and Ni^{2+} were still presented in the wastewater, but these two metals did not significantly affect the results in the oxidation–reduction process due to their low concentrations comparing to chromate. The dominant species for chromium species for the influent concentration is CrO_4^- instead of $\text{Cr}_2\text{O}_7^{2-}$, ascribing to this equation ($2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$, $\log K = 1.52$). The only other oxidizing species, which might compete with ZVI in this water is sulfate, but the concentration of sulfate is pretty low comparing to chromate. The treatment goal for chromate is to reduce the Cr(VI) and total Cr to 0.5 and 2 mg/L, respectively.

All chemicals used are of reagent grade. Laboratory grade ZVI powder (40 mesh, about 212 μm in diameter, purchased from RDH Chemical Co.) with surface area of 0.183 m^2/g measured by BET analysis. Fig. 1 is a schematic setup of the experimental system. A glass column with diameter of 130 mm and length of 600 mm was employed as the reactor. The total volume of 73 mL was controlled by a fluid level controller. A circulation pump was installed for maintaining the upflow velocity of at least 72 m/h to fluidize the ZVI. HRT was changed by varying the flow rate of the influent and effluent pumps. The system pH was controlled by a glass electrode and a pH controller, which controls the dosing of sulfuric acid (0.5N). Effluent was withdrawn continuously from the top of the effluent is around 2 cm above that of the circulation pump to avoid the carryover of ZVI.

Table 1
The chemical analysis of the raw electroplating wastewater

Cr(VI)	418
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.

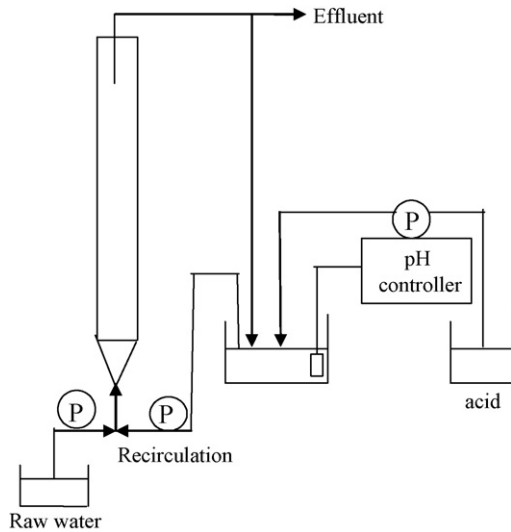


Fig. 1. Schematic diagram for fluidized ZVI process.

The total chromium concentration was 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 deduced 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 [18]. The quantitative analysis of Fe^{3+} was obtained by subtracting Fe^{2+} concentration from total iron concentration. Crystal structures of the reacted ZVI species were analyzed by an X-ray diffraction, a DMAX 2200 VK type manufactured by Rigaku Co., Japan.

3. Results and discussion

3.1. Effects of pH, HRT and ZVI dosage

Three different pHs were tested in the designed fluidized ZVI system where pH 2 was the raw water pH without acid addition. Fig. 2 plots the ratio of effluent/influent (C/C_0) versus time at short HRT of 1.2 min with ZVI of 3 g or 41 g/L. As shown in Fig. 2, when the pH was controlled at 2, only 30% of chromate was removed. When the pH was reduced to 1.5 or 1, more than 99.9% removal was achieved. Therefore, simply by reducing pH to 1.5 or 1, the effluent chromate concentration of 0.21 mg/L (as Cr^{6+}) can meet the effluent standard of 0.5 mg/L (as Cr^{6+}) in Taiwan. Moreover, the exhaustion time for ZVI was occurred at 115 min for pH 1.5 but at 75 min for pH 1. Theoretically, lower pH would favor the ZVI/chromate reaction [12,14]. However, reaction at pH 1 had earlier exhaustion time, or less ZVI utilization. It can be contributed to when pH is 1, ZVI also have high reactivity with hydrogen ion in the water to produce hydrogen

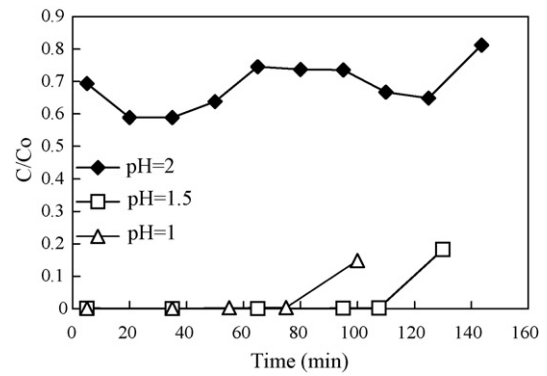


Fig. 2. C/C_0 vs. time for three pHs for HRT of 1.2 min with ZVI of 3 g or 41 g/L in the reactor.

gas to reduce the lifetime of the ZVI. Consequently, optimum pH was shown at pH 1.5 instead of pH 1 in this HRT.

The chromate removal can be increased also by increasing the HRT without pH adjustment (controlled at pH 2). Fig. 3 plots the C/C_0 versus time for HRTs of 1.2 and 5.6 min with ZVI of 3 g or 41 g/L in the fluidized reactor. As shown in Fig. 3, when the HRT was 1.2 min at pH 2, only 30% chromate was removed. But when the HRT was increased to 5.6 min, complete removal (99.9%) was achieved. Therefore, simply by increasing HRT to 5.6 min, the effluent chromate concentration of 0.26 mg/L (as Cr^{6+}) can also meet the effluent standard of 0.5 mg/L (as Cr^{6+}) in Taiwan. Comparing to previous ZVI/chromate studies where HRT was 24 h for batch studies to reach 90% chromate removal [12] or HRT was 1.2 ± 0.2 h for column studies to reach 30% chromate removal [13], the proposed fluidized system can completely remove the 416 mg/L chromate for HRT only 5.6 min at pH 2. The results indicate the efficiency of chromate removal by ZVI can be significantly improved by acidity control and mixing intensity through the designed fluidized ZVI system.

Fig. 4 plots the C/C_0 versus time at HRT of 1.2 min with three ZVI dosages at pH 1.5 since pH 1.5 was previously determined as the optimum operating pH at such a HRT. Complete removals were achieved in these three conditions. When the ZVI dosage was 1 g or 13.7 g/L, the ZVI was capable of removing chromate for ZVI exhaustion time of 30 min; when the dosage was 2 g or 27.4 g/L, the ZVI was capable of removing chromate for exhaustion time of 67 min; when the dosage was 3 g or 41.1 g/L, the

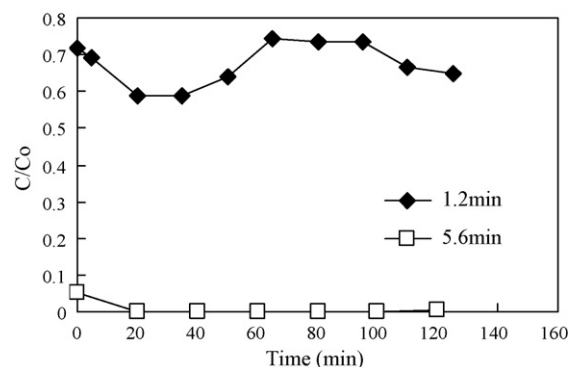


Fig. 3. C/C_0 vs. time for two different HRT (pH 2 with ZVI of 3 g or 41 g/L in the reactor).

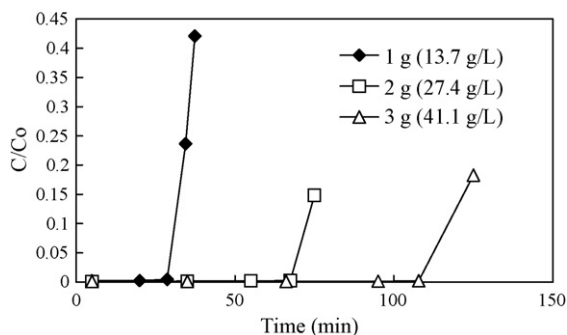


Fig. 4. C/C_0 vs. time for three different ZVI dosages (HRT: 1.2 min for pH 1.5).

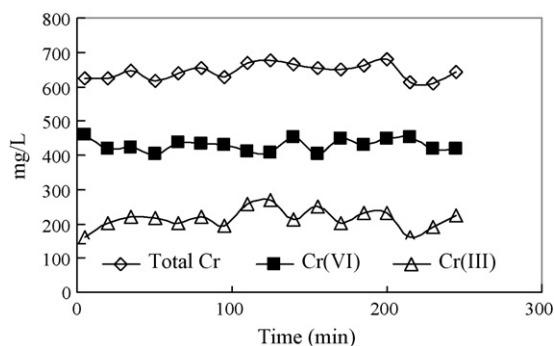


Fig. 5. Effluent concentrations vs. time for chromium species (HRT 1.2 min, pH 2 and ZVI = 3 g (41 g/L)).

ZVI was capable of removing chromate for exhaustion time of 111 min. On per gram basis, the addition of ZVI was capable for 35 min lifetime averagely. It was a little bit lower for the lifetime of the first gram and might result from small portion of ZVI reacting with either dissolved oxygen or hydrogen ion in the acidic condition.

3.2. Speciation and mechanisms for ZVI/chromate reaction

According to Eqs. (1) and (2), $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Fe}(\text{OH})_3(\text{s})$ are the resulting species, but in acidic condition, Cr^{3+} , Fe^{3+} and also ferrous ion (Fe^{2+}) are possibly presented in the solution. Figs. 5 and 6 present the dissolved chromium and iron speciation at pH 2. From Fig. 5, only partial removal ($\approx 30\%$) of chro-

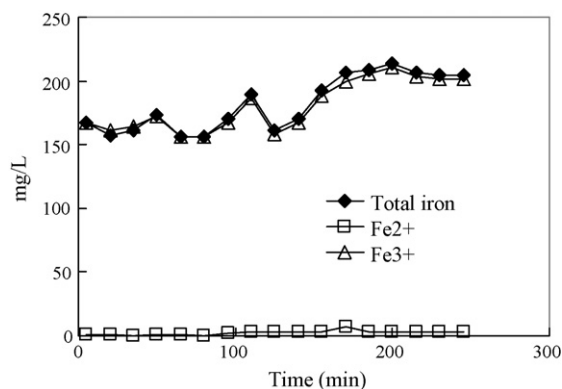


Fig. 6. Effluent concentration vs. time for iron species (HRT 1.2 min, pH 2 and ZVI = 3 g or 41 g/L).

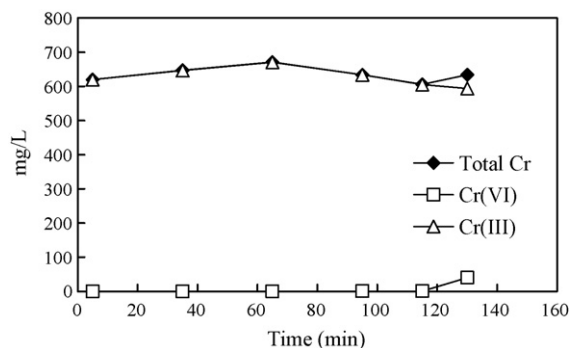


Fig. 7. Effluent concentrations vs. time for chromium species (HRT 1.2 min, pH 1.5 and ZVI = 3 g (41 g/L)).

mate was seen. No obvious change for total chromium indicates no chromium loss due to chromium hydroxide precipitation in such a low pH. Chromate was reduced from 418 mg/L (as Cr^{6+}) to 287 mg/L, and trivalent chromium was around 131 mg/L. It demonstrates steady state was quickly reached and no speciation variation was seen. From Fig. 6, total dissolved iron was gradually increased due to dissolution of ZVI, Fe^{3+} was dominant and Fe^{2+} was very low. Since there was still a lot of strong oxidizing agent, chromate, was still presented, Fe^{3+} was observed instead of Fe^{2+} since Fe^{3+} is more thermodynamically stable at such high ORP condition (around 550 mV). These observations conform the results from previous research [14].

However, speciations were different for pH 1.5 comparing to pH 2. Figs. 7 and 8 present the chromium and iron speciation at pH 1.5. Firstly from Fig. 2, chromate was completely removed at pH 1.5, therefore all the chromium species was presented as Cr^{3+} . From Fig. 7, all the chromium was converted to trivalent chromium at pH 1.5 instead of only partial removal of chromate for pH 2. In Fig. 8, Fe^{2+} was observed instead of Fe^{3+} . It can be contributed that unlike for pH 2, where chromate was still presented, there is no chromate at pH 1.5. Therefore, no oxidizing agent chromate was available to convert Fe^{2+} to Fe^{3+} so high Fe^{2+} was observed. Another explanation is in such a low ORP condition (ORP = 150 mV), where no presence of oxidizing agent chromate was observed, Fe^{2+} is more thermodynamically stable. Afterwards (about 60 min), Fe^{2+} was gradually decreased but Fe^{3+} was gradually increased when ZVI was gradually used

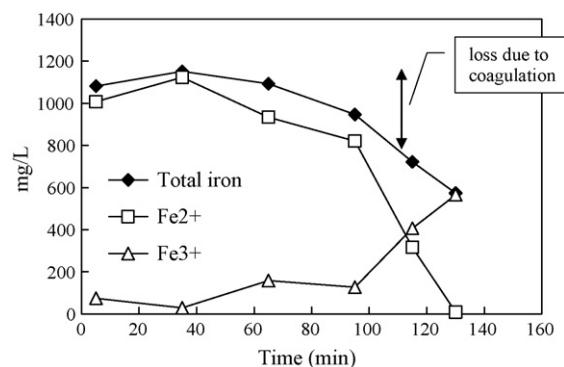
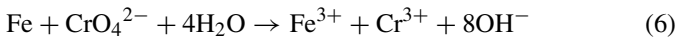
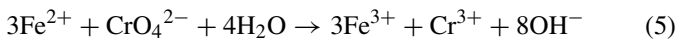
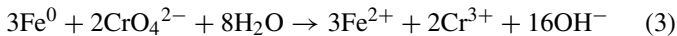


Fig. 8. Effluent concentration vs. time for iron species (HRT: 1.2 min for pH 1.5 ZVI = 3 g (41 g/L)).

up and chromate was gradually increased. Slight coagulation was observed close to breakthrough point due to the increase of Fe^{3+} . Therefore, Fe^{2+} is an indicator for complete reduction from chromate to trivalent chromium. Moreover, higher dissolved iron concentration for pH 1.5 was observed comparing to pH 2, resulting from (1) more chromate reduction by ZVI, (2) some hydrogen ion reacting with ZVI to generate dissolved iron and hydrogen gas. Evidence of hydrogen gas generation was seen by observation of some gas bubble in the reactor. Consequently, the following mechanisms were proposed for the low pH reaction. ZVI was firstly reacted with chromate to form Fe^{2+} , as indicated in Eq. (3). Some ZVI would react with hydrogen ion to generate hydrogen gas, as indicated in Eq. (4). If chromate is not completely removed, the Fe^{2+} would keep reacting with chromate to produce Fe^{3+} in Eq. (5), or combining Eqs. (3) and (5) to form Eq. (6), so no Fe^{2+} was observed in the system. But if chromate is completely removed, since no chromate is available, only Eq. (3) or (4) would occur. Unlike specified in the previous study, the precipitation of $\text{Fe}(\text{OH})_{3(s)}$, $\text{Cr}(\text{OH})_{3(s)}$ or $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_{3(s)}$ was observed since they can only occur at higher pH



3.3. Capacity of ZVI for chromate removal and lifetime analysis

Capacity of ZVI was calculated by the ZVI utilization on per gram basis so the optimum dosage as well as the operation time can be properly determined for various conditions for future full scale operation. Theoretically, according to the stoichiometric ratio in Eq. (6), 1 g of ZVI is capable of reacting 2.25 g CrO_4^{2-} or 1.107 g Cr^{6+} . The actual chromate reduction for ZVI for various conditions can be calculated based on the flowrate (for example, 60 mL/min for detention time 1.2 min), influent concentration of 418 mg/L as Cr^{6+} , effluent concentration and operational time or from Eq. (7), where amounts of chromate reductions (as mg Cr) were determined based on the area above the breakthrough point. In Eq. (7), b.t. is the breakthrough time, C_{in} is the influent concentration and C_{out} is the effluent concentration, Q is the flowrate

$$W_{\text{Cr}} = \sum_{\text{time}=0}^{\text{time}=\text{b.t.}} [C_{in} - C_{out}] (\text{mg/L}) \times Q (\text{L/min}) \times \text{time} (\text{min}) \quad (7)$$

Table 2
Actual and theoretical capacity for chromate reduction by ZVI at breakthrough

pH	Dosage of ZVI	Chromate removal (%)	Actual ZVI capacity (mg Cr^{6+} /g ZVI)	Theoretical ZVI capacity (mg Cr^{6+} /g ZVI)	ZVI utilization for chromate (%)
1	3 g (41.1 g/L)	99.9	627	1107	56.6
1.5	3 g (41.1 g/L)	99.9	961	1107	86.8
2	3 g (41.1 g/L)	$\cong 30$	263	1107	23.8

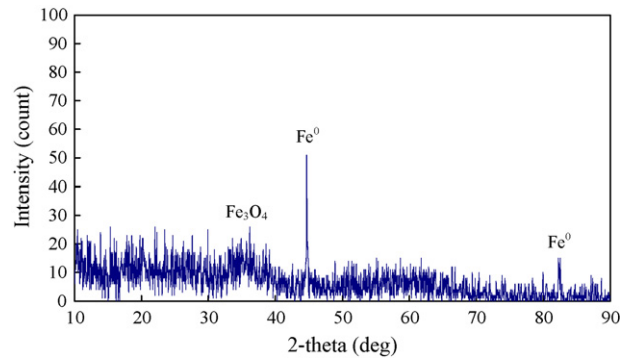


Fig. 9. XRD analyses (wavelength = copper K-alpha 1.54 Å) for reacted iron species (HRT: 1.2 min for pH 2, ZVI = 3 g (41 g/L)).

Table 2 presents the capacity and utilization percent of ZVI for chromate reduction for three pHs. In this case, since both low pH and fluidized reactor were utilized, higher capacity and utilization percent for ZVI were achieved and the rank for three pHs is $1.5 > 1 > 2$. The reason for higher capacity for pH 1.5 was mentioned previously that when pH was 1, fresh ZVI could react with hydrogen ion to produce hydrogen gas, causing waste of ZVI. Consequently, pH 1.5 was shown better capacity comparing to pH 1. Moreover, from visual inspection, there was no remained ZVI, resulting from all ZVI was reacted due to either hydrogen ion or chromate but some ZVI remained for pH 2 condition.

3.4. Characterization of reacted ZVI by XRD

Since some of the ZVIs were not used for operation condition of either pH 2 or shorter HRT, indicating some surface coating formed onto the ZVI surface may deactivate the ZVI. XRD was conducted to analyze the crystal structure of the reacted ZVI for experimental condition of HRT: 1.2 min for pH 2 and ZVI = 3 g (41 g/L). Fig. 9 presents the XRD analyses for the reacted iron species. According to the powder diffraction file (PDF) based on the XRD database obtained from PCPDFWIN software [19], three major peaks in Fig. 9 were identified as Fe^0 (ZVI) (PDF #: 06-0696, $2\theta = 44.67$ and 82.32), Fe_3O_4 (PDF #: 19-0629, $2\theta = 35.428$). The rest weaker peaks could be resulted from either noise or some other species such as iron sulfide (FeS or FeS_2) due to the reduction of sulfate to sulfide. Therefore, from the results in Fig. 9, since oxidation reaction was occurred on the ZVI species to form Fe_3O_4 , where oxidation number of iron was increased from 0 (ZVI) to $8/3$ (Fe_3O_4), indicating the formation of iron oxide stopping the chromate reduction reaction if pH is not low or HRT is not long enough. However, when the pH was 1 or 1.5, the iron oxide layer was not formed since iron

was dissolved in solution instead of forming precipitated layer in such as a low acidity. Consequently, the partial chromate reduction was achieved due to some of the iron was converted to iron oxide.

4. Conclusions

Fluidized zero valent iron (ZVI) process successfully reduced hexavalent chromium (chromate, CrO_4^{2-}) to trivalent chromium (Cr^{3+}) from electroplating wastewater for $\text{pH} < 2$. For influent chromate concentration of 418 mg/L as Cr^{6+} , $\text{pH} 2$ and ZVI dosage of 3 g (41 g/L), chromate removal was only 29% with hydraulic detention time (HRT) of 1.2 min, but was increased to 99.9% by either increasing HRT to 5.6 min or adjusting pH to 1.5. For iron species at $\text{pH} 2$ and HRT of 1.2 min, Fe^{3+} was more thermodynamically stable since oxidizing agent chromate was present. However, if pH was adjusted to 1.5 or 1, where chromate was completely removed, high Fe^{2+} but very low Fe^{3+} was present. It can be explained that ZVI reacted with chromate to produce Fe^{2+} first and the presence of chromate would keep converting Fe^{2+} to Fe^{3+} . Therefore, Fe^{2+} is an indicator for complete reduction from Cr(VI) to Cr(III). XRD was conducted to exam the remained species at $\text{pH} 2$. ZVI, iron oxide and iron sulfide were observed, indicating the formation of iron oxide or iron sulfide can stop the chromate reduction reaction at $\text{pH} 2$.

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