

Chromium removal from aqueous solution by the ferrite process

Mehmet Erdem^{a,*}, Fikret Tumen^b

^a Department of Environmental Engineering, Firat University, 23279 Elazığ, Turkey

^b Department of Chemical Engineering, Firat University, 23279 Elazığ, Turkey

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Abstract

This research summarises the results of the study on the removal of chromium by applying the ferrite process to the solutions obtained from two different Cr(VI) reduction processes utilising sodium sulphite and ferrous sulphate as reducing agents. For both solutions containing trivalent chromium ions, the optimum treatment conditions were determined. The generated sludges were characterised by XRD analysis and physical tests. In addition, to explore the dissolution properties of the sludges obtained, they were contacted with the solutions of sulphuric, citric, tartaric, oxalic and ascorbic acids and EDTA. Also, the sludge samples were subjected to standard toxicity characterisation leaching procedure (TCLP) test of USEPA in order to determine the pollution potential. An efficient Cr(III) removal (about 100%) in the solution from the Cr(VI) reduction process utilising sodium sulphite as reducing agent was achieved when the solution was treated at pH 9 and 50 °C for 60 min in the presence of Fe²⁺/Cr³⁺ weight ratio of 16. For the other Cr(III) solution prepared from Cr(VI) reduction by ferrous sulphate, a Fe²⁺/Cr³⁺ weight ratio of 17.9 at the same conditions was found to produce complete removal of Cr(III). It was determined that the spynel chromium–iron compounds obtained in the process were in the form of chromite (Cr₂FeO₄). Dissolution experiments and TCLP tests show that the concentrations of the chromium dissolved from both sludges were below the limit given as 5 mg l⁻¹ by USEPA. The results showed that Cr(III) removal through ferrite process provides the advantages that the sludges generated are non-voluminous, easily separable and environmentally stable.

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Keywords: Wastewater treatment; Chromium removal; Ferrite process; Dissolution; TCLP

1. Introduction

The ores and compounds of chromium have widespread use in alloy preparation, electroplating, leather tanning, pigment preparation, corrosion inhibition, glass, ceramic and refractory making etc. Industries using chromium often discharge toxic wastewater that may endanger natural life and public health. Because of its mutagenic and carcinogenic nature [1], the presence of hexavalent chromium in aqueous streams is one of the most important environmental issues.

To remove the toxic metal ions from wastewater, current methods are based on precipitation, ion exchange, solvent extraction, adsorption, and reverse osmosis techniques [2]. Chemical precipitation, especially as metal hydroxide or sulphide, is widely practised, having the advantages of simplicity and inexpensive chemicals. In chemical precipitation, however, generation of a voluminous toxic waste

sludge is a major problem encountered. The finely dispersed and low density sludges formed necessitates careful disposal in further steps. In our recent study, it has been found that chromium can be released at undesired levels from a hydroxide precipitate in the presence of complexing agents. Further, toxicity characterisation leaching procedure (TCLP) tests have confirmed that hydroxide sludge may pose the environmental risk [3]. These findings show that a further stabilisation is needed for chromium hydroxide sludges formed in the chromium removal process.

The heavy metal ions can also be removed from a solution by situating at the lattice point in a spynel structure. The incorporated heavy metal is less mobile than in the hydroxide form, and thus more stable in the environment. The method, called the “ferrite process”, has other advantages in that the ferrite sludges is formed in a dense structure, easily separated in a magnetised field and used commercially in various applications [4].

In the ferrite process, heavy metal ions in aqueous solution are first coprecipitated with ferrous iron added at a suitable

* Corresponding author.

E-mail address: merdem@firat.edu.tr (M. Erdem).

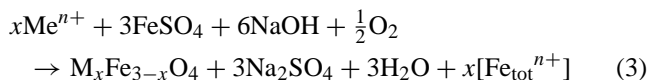
alkaline pH according to following reaction.



Then, the mixture of hydroxides formed is oxidised with air at a temperature above 50 °C until a metal ferrite-bearing precipitate having a black colour and magnetic properties forms (Eq. (2)) [4–6].



Barrado et al. [7] have suggested following mechanism for metal ions having divalent and polyvalent metal ions.

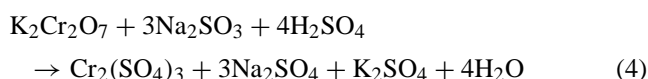


Currently, a few studies on the removal of heavy metal ions from aqueous solution by the ferrite process have been reported. These studies have been generally focused on the removal of divalent heavy metals [8–16]. There is very limited information available on the chromium(III) removal by ferritisation and the stability of its sludge [6,13,17]. Therefore, in this study, the chromium removal was examined by applying the ferrite process to Cr(III) solutions prepared by reducing the Cr(VI) solution using sodium sulphite and ferrous sulphate. For this purpose, some parameters such as aeration rate and $\text{Fe}^{2+}/\text{Cr}^{3+}$ weight ratio affecting the chromium removal from the solutions by the ferrite process were optimised. In addition, spynel-bearing sludges formed in the process were chemically and mineralogically characterised and their dissolution properties in the various media were determined.

2. Materials and methods

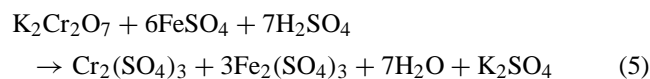
2.1. Preparation of solutions

In this study, two Cr(III) solutions having different composition were used. Solution (S1) was prepared by the reduction of Cr(VI) using sodium sulphite. First, Cr(VI) solution in the concentration of 2000 mg Cr(VI) l^{-1} was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck-1.04862) in distilled water. The pH of this solution was adjusted to 2 ± 0.1 by a H_2SO_4 solution. A stoichiometric amount of sodium sulphite, calculated from Eq. (4), was added to this solution and the Cr(VI) was reduced by shaking the mixture for a period of 15 min. Completion of reduction was followed by a colour test applying 1,5-diphenyl carbazide which is specific for Cr(VI) [18].



Solution (S2) was prepared in the same way by using ferrous sulphate (Merck-1.03926) as reducing agent. It has been reported that an excess dosage of the theoretical amount of ferrous sulphate (approximately 2.5 fold) is required in

order to obtain a complete reduction of Cr(VI) according to Eq. (5) in a short reaction period [19]. Therefore, 2.5-fold of theoretical amount of ferrous sulphate was used in the Cr(VI) reduction step.



In the dissolution experiments, sulphuric (Merck-1.00713), citric (Merck-242), tartaric (Merck-802), oxalic (Riedel-de Haën-33506), and ascorbic (Aldrich-25,556-4) acids, and EDTA (di sodium salt) (Pan Reac) solutions having the concentrations of 10^{-2} M with initial pH values of 3, 4 and 5 (± 0.1) were used as dissolution agents.

H_2SO_4 and NaOH (Merck-1.06462) solutions were used to adjust the pHs of the solutions.

2.2. Apparatus

The Cr(III) solutions were treated in an experimental system consisting flask shaker (Clifton), 250 ml erlenmayer, temperature controlled water bath, pH-meter, air pump, rotameter, and gas-washing bottle (Fig. 1).

2.3. Experimental procedure

2.3.1. Chromium removal experiments

The Cr(III) solution in a concentration of 100 mg l^{-1} was mixed with the required amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in a 250 ml erlenmayer. After complete mixing, the pH of the solution was adjusted to 9 by adding NaOH solution. The content of the erlenmayer was heated at 50 °C and shaken at 300 cycle min^{-1} while air was simultaneously passed into the solution at various flow rates for 60 min until a black magnetic spynel precipitate was formed.

The precipitate was separated from the solutions by filtration and then dried at room temperature. While solid samples were subjected to XRD analysis and magnetic test, filtrates were analysed for residual metal ions.

2.3.2. Dissolution experiments

The air-dried sludge sample of 0.5 g and a 50 ml solution with desired concentration and pH were mixed in a flask and shaken at 300 cycle min^{-1} for a contact time of 8 h. All of the experiments were carried out at 25 °C. In addition, to determine the pollution potential, sludge samples were subjected to the TCLP [20].

At the end of each run, the reaction mixture was centrifuged at 7000 rpm for 15 min and the pH of filtrate was measured by pH meter (Shot CG 840). The supernate was acidified with HNO_3 (Merck-1.00443) to prevent precipitation, and retained for chromium and iron analyses.

2.4. Methods of analyses

Mineralogical compositions of precipitates obtained from ferritisation experiments were determined by X-ray

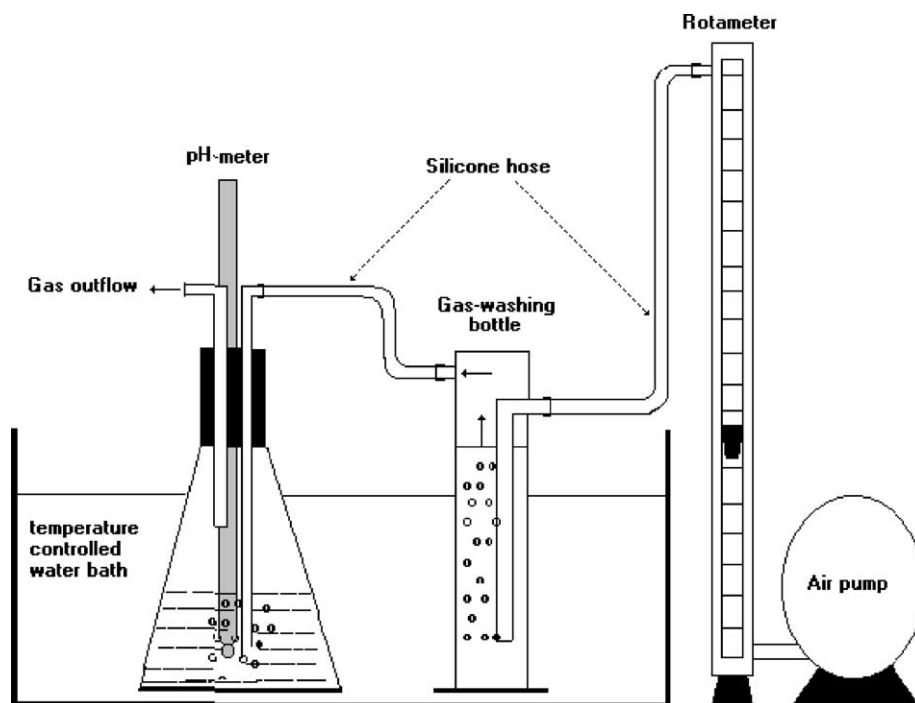


Fig. 1. Schematic diagram of experimental apparatus.

diffractometer (Siemens, D-5000). In order to determine the chromium and total iron content of the ferrite-bearing residues, 0.25 g of solid sample was dissolved in 20 ml of 37% HCl and diluted to 50 ml with distilled water. The iron and chromium concentrations were determined using a Perkin–Elmer (PE 370) atomic absorption spectrophotometer. In addition, the precipitates were tested for a response to a magnet applied outside the glassware.

3. Results and discussion

The results of the study on the removal of chromium by applying the ferrite process to the solutions obtained from two different Cr(VI) reduction processes utilising sodium sulphite and ferrous sulphate as reducing agents, dissolution properties of the sludges containing spinel chromium–iron compounds formed in the process and TCLP test applied to the sludges are presented in the following sections.

3.1. Chromium removal study

The most important parameters affecting formation of metal ferrites in aqueous solutions are pH, temperature, amount of Fe^{2+} and aeration rate. The first stage in the ferrite formation is coprecipitation of metal and ferrous ion. This process generally occurs at the pH for ferrous ion precipitation (approximately pH 8.5). Taking into consideration the above knowledge, and the amphoteric character of chromium, precipitation pH was selected as 9.

In some studies, various temperatures in the ranges of 25–200 °C have been tested to form metal ferrites in solution [6,8,10,17]. It has been stated that the completion period is shorter for higher temperature. In preliminary studies carried out at 50 °C for 60 min, all the chromium was removed from solution by the ferrite process. Therefore, subsequent experiments were carried out at 50 °C for 60 min of contact time.

After the suitable conditions for the parameters of pH, temperature and contact time were determined, the effect of the aeration rate on the ferrite formation was examined in the solution (S1) from Cr(VI) reduction process using sodium sulphite as a reducing agent. For this purpose, the aeration rate was varied between 0 and 250 ml min^{-1} , while the weight ratio of $\text{Fe}^{2+}/\text{Cr}^{3+}$ was 16. The results are presented in Table 1.

It has been observed that the precipitates obtained from the non-aerated solution, and the solution aerated at the rates of 25 and 50 ml min^{-1} , have the common ferrite properties given in literature [4]. Under these conditions, concentrations of the chromium and iron remaining in the solutions were below the detection limits. In some studies related to formation of divalent metal ferrites, it has been noted that the divalent metal ferrites form in the aerated solutions [12,14,15]. In the present study, the formation of a ferrite type compound at the higher air flow rates above 50 ml min^{-1} was not observed. This situation can be explained by the structural properties of the spinel ferrites, which are the oxides containing divalent metal and ferric ions together. The formula of these compounds is MeFe_2O_4 [4]. When the formula of the chromium–iron spinel is ex-

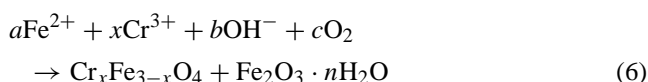
Table 1

The effect of air flow rate on the removal of chromium from S1 by ferritisation (weight ratio of $\text{Fe}^{2+}/\text{Cr}^{3+}$: 16, temperature: 50 °C, pH 9, contact time: 60 min)

Air flow rate (ml min^{-1})	Properties of the precipitates	The concentration of metals remaining in the solution (mg l^{-1})	
		Cr	Fe
0	Black, fine crystalline, strongly magnetic	ND	ND
25	Black, fine crystalline, strongly magnetic	ND	ND
50	Black, fine crystalline, strongly magnetic	ND	ND
100	Dark brown, weakly magnetic	ND	ND
150	Dark brown, weakly magnetic	ND	ND
200	Dark brown, weakly magnetic	ND	ND

ND: not detected.

aminated, it can be seen that the structure is inverse, that is, Me_2FeO_4 . Therefore, to form ferrite type compound with a trivalent metal, the iron must be situated in the structure of the spinel as ferrous ion, before oxidation. The XRD pattern of the precipitate obtained from non-aerated solution also confirms this result, since chromium–iron compound formed under these conditions is in the form of chromite (Cr_2FeO_4). Beside the chromite, hematite and goethite formed under the same experimental conditions. These compounds have been identified by Barrado et al. [21], who have investigated the characterisation of solid residues obtained from Cr removal from aqueous solutions by a ferrite process. This situation occurred in the presence of excess Fe(II) and OH^- has been explained in the following reaction [21].



The effect of weight ratio of $\text{Fe}^{2+}/\text{Cr}^{3+}$ on the removal of chromium by ferritisation was investigated in two stages. In the first stage, this effect was examined by varying the $\text{Fe}^{2+}/\text{Cr}^{3+}$ weight ratio in the range of 10–18 for S1 solution. The obtained results are shown in Table 2. It was determined that all the chromium in S1 was removed for all $\text{Fe}^{2+}/\text{Cr}^{3+}$ ratios, except for the ratio 10. However, the pre-

Table 2

The effect of $\text{Fe}^{2+}/\text{Cr}^{3+}$ weight ratio on the removal of chromium from S1 by ferritisation (temperature: 50 °C, pH 9, contact time: 60 min)

Weight ratio of $\text{Fe}^{2+}/\text{Cr}^{3+}$	Properties of the precipitates	The concentration of metals remaining in the solution (mg l^{-1})	
		Cr	Fe
10	Brown, non-magnetic	0.96	2.30
12	Dark brown, weakly magnetic	ND	2.11
14	Dark brown, weakly magnetic	ND	ND
16	Black, fine crystalline, strongly magnetic	ND	ND

ND: not detected.

cipitate in the spinel character formed at the weight ratios of $\text{Fe}^{2+}/\text{Cr}^{3+}$ higher than 14. It was observed that the properties of the precipitates formed at lower weight ratios were different from those of the ferrites in colour and magnetisation. XRD analyses of the precipitates obtained at lower ratios showed that the chromium and iron were in the form of their individual oxides.

In the second stage, the effect of $\text{Fe}^{2+}/\text{Cr}^{3+}$ weight ratio was investigated for the S2 solution. As seen from Eq. (5), when Cr(VI) is reduced with FeSO_4 , divalent iron ions in equivalent amount are oxidised to the trivalent state. It has been stated that 2.5 fold of theoretical amounts of FeSO_4 is recommended for this reaction. In this study, FeSO_4 corresponding to 807 mg Fe^{2+} , which is 2.5 fold of the theoretical amount, was used in order to reduce 1 l of 100 mg l^{-1} Cr(VI) solution. Since the experiments were carried out in closed vessels, in this case, by neglecting the presence of oxidising agents except for Cr(VI) , it can be calculated that 323 mg l^{-1} ferric ions form. It is plausible that the ferrous ions remaining in the solution may participate to the ferrite formation. Starting from this idea, in the first ferritisation experiments, the difference of initial and oxidised amounts of iron ($807 - 323 = 484 \text{ mg l}^{-1}$) was assumed as Fe^{2+} . The conditions of chromium removal by ferritisation were examined by varying the weight ratio of (total iron)/ Cr^{3+} in the range of 10–26. The term of total iron expresses sum of the ferrous iron added to form a ferrite type compound and present iron in reduced solution. The results are given in Table 3.

Under the conditions investigated, concentrations of chromium remaining in the solutions were below the detection limits. But, precipitates having ferrite character formed at the (total iron)/ Cr^{3+} weight ratio of 24 and 26. These ratios correspond to (added Fe^{2+})/ Cr^{3+} values of 15.93 and 17.93, respectively. When it is compared with the weight ratio of $\text{Fe}^{2+}/\text{Cr}^{3+}$, 16 found for S1, it can be seen that the ferrite forms in similar conditions for S2. This situation

Table 3

The effect of $\text{Fe}^{2+}/\text{Cr}^{3+}$ weight ratio on the removal of chromium from S2 by ferritisation (temperature: 50 °C, pH 9, contact time: 60 min)

Weight ratio of (Fe^{2+} added + 484)/ Cr^{3+}	Properties of the precipitates	The concentration of metals remaining in the solution (mg l^{-1})	
		Cr	Fe
10	Brown, non-magnetic	ND	2.84
12	Brown, non-magnetic	ND	ND
14	Brown, weakly magnetic	ND	ND
16	Brown, weakly magnetic	ND	ND
18	Brown, weakly magnetic	ND	ND
20	Brown, weakly magnetic	ND	2.58
22	Black, weakly magnetic	ND	2.14
24	Black, fine crystalline, strongly magnetic	ND	4.40
26	Black, fine crystalline, strongly magnetic	ND	6.12

ND: not detected.

shows that the excessive iron ions assumed as Fe^{2+} in S2 do not participate to the ferrite. However, it may be stated that ferrous iron remaining in the solution after Cr(VI) reduction may be partially oxidised to ferric form by air-oxygen dissolved in the solution. Further, during the ferritization, ferrous ions in the solution may participate as amorphous $\text{Fe}(\text{OH})_2$, because the pH of the medium is suitable for Fe^{2+} precipitation.

In the second ferritisation experiments, the iron ions in the solution (S2) from Cr(VI) reduction process were assumed as Fe^{3+} . To precipitate total trivalent metal ions (Cr^{3+} and Fe^{3+}) in the form of ferrite type compound, the $\text{Fe}^{2+}/\text{Me}^{3+}$ weight ratio was varied in the range of 2–7. While the concentration of chromium ions in the solution was found to be below the detection limits under the all conditions studied, ferrite type compound formed for a $\text{Fe}^{2+}/\text{Me}^{3+}$ weight ratio of 3 and higher. One may think that iron ferrite (magnetite) simultaneously forms in this application. However, XRD analysis showed that chromite was formed only as a spinel compound. This situation may be attributed to a process pH of 9. It is in agreement with the results of some earlier studies that magnetite forms at pHs above 11 [22,23].

Although the amount of Fe^{2+} needed to remove whole chromium from S2 solution by ferritisation was higher than that from S1, the filtration of precipitate containing chromite, maghemite and goethite by a simple filtration was rather easy due to their magnetic properties. Ferrous sulphate is the cheapest reducing agent for Cr(VI). But, it is rarely used in practise since filtration of voluminous sludges formed in precipitation step of Cr(III) is rather difficult. In this study, it has been observed that easily filterable sludges form in ferrite process. This advantage may lead to the widespread use of ferrous sulphate.

3.2. Dissolution properties of sludges

The sludges obtained from S1 and S2 solutions by the Ferrite process contain 5.93% Cr, 53.07% Fe and 5.11% Cr, 54.57% Fe, respectively, in dry basis. Dissolution properties of these sludges containing spinel chromium–iron compounds formed in the process were investigated in sulphuric, citric, ascorbic, oxalic, tartaric acids and EDTA (di sodium

salt) solutions having different pH. These complex forming agents (particularly organic acids with low-molecular weight) may be in contact with such sludges in the environment. These acids are secreted into the soil solution by plant roots and are also generated during decay of organic substances such as residues of animals and plants, fungus and organisms [24,25]. It has been reported that the concentration of these acids in soil solutions are in the range of 10^{-2} to 5×10^{-4} M [24,26,27]. These acids may increase the mobility of the heavy metals in soils and water ecosystems by forming soluble complexes. Therefore, dissolution of metals from the chromium–iron spinel bearing sludges was investigated in the 10^{-2} M solutions with initial pH values of 3, 4 and 5 prepared from substances mentioned above. The results are presented in Figs. 2 and 3.

It was seen that the concentrations of the metals released from both sludges increased with decreasing pH. While the concentrations of the chromium released from the sludge obtained from S1 were detected in the range of $0.8\text{--}1.52 \text{ mg l}^{-1}$, it was found to be $0.56\text{--}1.05 \text{ mg l}^{-1}$ for S2. Although the pHs of the sulphuric acid solutions were the same as for the solutions containing organic substances, the concentration of the metals dissolved in the sulphuric acid solutions were below the detection limits. This situation shows that the presence of organic substances accelerates the dissolution of the metals from sludges, probably due to the complex formation. Iron dissolution exhibited similar behaviour, but, its concentration for both sludges obtained from S1 and S2 were found in the range of $1.87\text{--}38.7 \text{ mg l}^{-1}$ and $6\text{--}57.41 \text{ mg l}^{-1}$, respectively.

3.3. TCLP test

In order to determine the pollution potentials of both sludges, the TCLP test was applied to the samples. But, it was observed that the concentrations of chromium were below the detection limits.

Data obtained from dissolution experiments and TCLP test show that the concentration of the chromium dissolved from both sludges is below the 5 mg l^{-1} limit for TCLP specified by USEPA. In our recent study, it was found that the chromium concentrations released from the hydroxide

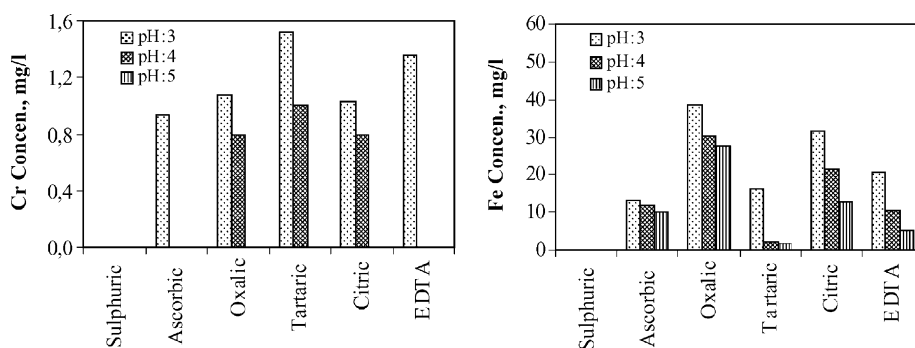


Fig. 2. Dissolution properties of chromium ferrite-bearing sludge obtained from S1 in various solutions (liquid/solid: 100, concentration of the dissolution agent: 10^{-2} M, contact time: 8 h, temperature: 25°C).

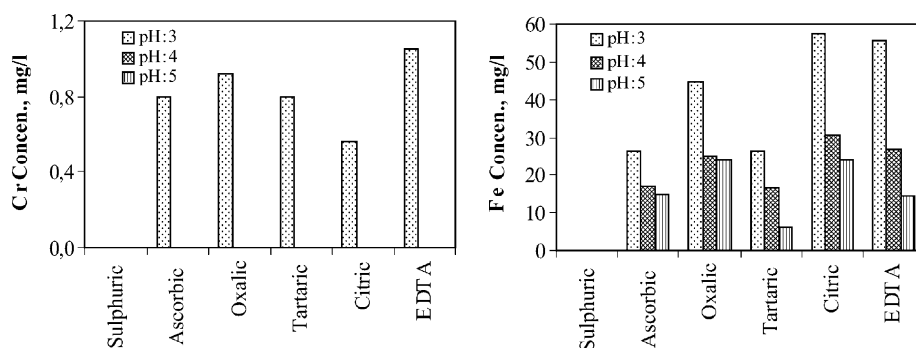


Fig. 3. Dissolution properties of chromium ferrite-bearing sludge obtained from S2 in various solutions (liquid/solid: 100, concentration of the dissolution agent: 10^{-2} M, contact time: 8 h, temperature: 25°C).

sludges of a conventional precipitation, which were obtained from S1 and S2 solutions, were 8.87 and 4.27 mg l^{-1} , respectively [3]. When these concentration values are compared with the chromium concentrations released from sludges in the form of spinel, it can be seen that the chromium levels released from hydroxide sludges are higher about four–six-fold. As a consequence, it can be concluded that the sludges obtained in spinel form are environmentally more stable than that in hydroxide form.

4. Conclusion

This work shows viable solution to chromium removal from wastewater by conversion of the chromium into chromium–iron spinel compounds. The dissolution study shows that the fixation of chromium by spinelisation is more effective compared to that by precipitation as individual hydroxides. Also, the result of the TCLP test meets the USEPA limit. The major advantages of the process are: (1) effective chromium removal; (2) densified particles or small volumes of sludges obtained; (3) separation ease due to magnetic property of sludges; and (4) low dissolution levels of sludges formed even in complexing media compared to those of hydroxide sludges formed in the conventional method. Thus, cheaper ferrous salts can be used in the Cr(VI) reducing step, because excessive ferrous ions remained in solution could be utilised as iron component in the spinelisation stage. Sludge formed in this process is not as voluminous as that in hydroxide precipitation technique. Moreover, spinel compound formed as chromite in the removal process could be completely removed from the environment by adding this sludge to the chromite ores that are used as raw materials in sodium dichromate, fire–brick, and ferrochrome alloy etc. production.

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