



## The effectiveness of ferrous iron and sodium dithionite for decreasing resin-extractable Cr(VI) in Cr(VI)-spiked alkaline soils

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### ABSTRACT

Ferrous iron, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and a mixture of Fe(II) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4:1 mol/mol) were tested for their effectiveness for decreasing resin-extractable Cr(VI) in alkaline Cr(VI)-spiked soils. The results indicated that adding those reductants greatly decreased the amount of resin-extractable Cr(VI) when the application rate of reductants equaled the number of equivalents of dichromate added to the Cr(VI)-spiked soils. This was mainly as a result of the Cr(VI) reduction into Cr(III), as supported by the XANES spectra. Among the tested reductants, a mixture of Fe(II) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was the most effective to decrease resin-extractable Cr(VI). The extent to which resin-extractable Cr(VI) and soil pH were decreased was affected by the pH of the reductants. Among the tested reductants at various pH, FeSO<sub>4</sub> at pH below 1 was the most effective in decreasing resin-extractable Cr(VI) in alkaline soils. However, the soil pH was the most decreased as well. On the other hand, the mixtures of ferrous iron and dithionite at a wide range of pH were all efficient (>70% efficiency) in decreasing resin-extractable Cr(VI). Moreover, the extent of the decrease in soil pH was much smaller than that by FeSO<sub>4</sub> (pH < 1) alone, and thus the possibility of the Cr(III) hazard can be avoided.

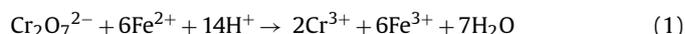
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### 1. Introduction

Chromium exists in two oxidation states, Cr(III) and Cr(VI), in the environment. Cr(III) is easily precipitated and adsorbed by soils while Cr(VI) exists as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> or CrO<sub>4</sub><sup>2-</sup> and is more soluble and mobile than Cr(III) [1,2]. It is known that Cr(VI) is a carcinogen to mammals, whereas, cationic Cr(III) is an essential nutrient for human [3–5]. Chromium is used in various industrial activities including electroplating, mining, pulp and paper production, timber treatment, and petroleum refining, and thus Cr is released into environment [6,7]. Since the toxicity and mobility of Cr(III) is less than that of Cr(VI) [8,9], the present remediation of Cr(VI)-contaminated sites usually involves the reduction of Cr(VI) into Cr(III) to reduce its mobility and toxicity [10–12]. However, Cr(VI) reduction is slowed down when the pH is increased due to the decrease of consumable protons [13]. Thus, the remediation methods that were feasible for Cr(VI)-contaminated sites in acid conditions may not be feasible for those in alkaline conditions [14].

Su and Ludwig [14] generalized that there are three groups of reductants that are commonly used to reduce Cr(VI) into Cr(III). The first group of reductants includes organic compounds

such as ascorbate [15], soil organic matter [6], and composts [16,17]. In our previous study, the reduction of Cr(VI) into Cr(III) by applying cattle-dung and hog-dung composts was a feasible method to decrease the amount of resin-extractable Cr(VI) in Cr(VI)-contaminated soils. However, the effectiveness of compost amendment on decreasing soil resin-extractable Cr(VI) concentration in alkaline soils is significantly lower than that in acid soils [16]. In addition, the reduction of Cr(VI) into Cr(III) with the amendment of organic matter in Cr(VI)-contaminated soils requires a long incubation time. The effectiveness of adding organic matter to decrease the Cr(VI) concentration in Cr(VI)-spiked soils is restricted by the low decomposition rate and dissolved organic carbon content of organic matter [16,17]. Therefore, due to the slow reaction, the amendment of organic matter is not the best method to decrease the risk of Cr(VI) contamination in those cases requiring immediate remediation. The second group of reductants includes iron-based compounds such as zero-valent iron [18], dissolved Fe(II), and Fe(II) associated with hematite and biotite. Dissolved Fe(II) is used in batch and column experiments to remediate Cr(VI)-contaminated waste water, sediments, and soils [10,11,19]. The reaction of ferrous irons with Cr(VI) in the environment is shown in the following equation [10]:

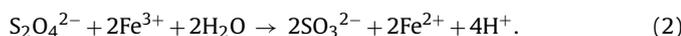


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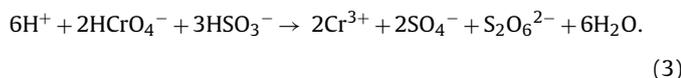
**Table 1**  
Properties of the studied soils

Soil	pH soil:H <sub>2</sub> O = 1:1	Particle size fraction			Texture	Organic carbon (g kg <sup>-1</sup> )	Free iron oxides (g Fe kg <sup>-1</sup> )
		Sand (g kg <sup>-1</sup> )	Silt (g kg <sup>-1</sup> )	Clay (g kg <sup>-1</sup> )			
Chengchung (Cf)	7.7	364	404	232	Loam	8.6	9.78
Taikang (Tk)	8.2	37	250	713	Clay	7.7	23.1

There is a concern that after injecting ferrous irons into an alkaline subsurface, clogging occurs resulting in the oxidation of Fe(II) by oxygen. This is more likely in an alkaline system and thus the effectiveness of reducing Cr(VI) into Cr(III) is decreased. Geelhoed et al. [20] found that the precipitation of iron took place when FeSO<sub>4</sub> was added into chromium ore processing waste, resulting from residues with high pH. In addition, the SO<sub>4</sub><sup>2-</sup> from FeSO<sub>4</sub> may also contribute to the increased leaching of CrO<sub>4</sub><sup>2-</sup>. The third group of reductants are reduced-sulfur compounds such as hydrogen sulfide [21], sodium metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>), and sodium dithionite [22,23]. Previous studies indicated that dithionite was useful for the in situ remediation of Cr(VI)-contaminated groundwater when accompanied with K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> buffer at pH 11 [22–24]. Istok et al. [22] indicated that Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was able to reduce Fe(III) to Fe(II) in the environment, and that the reaction occurred via the following equations:



The produced Fe<sup>2+</sup> can then be used to reduce Cr(VI) into Cr(III) based on Eq. (1). In addition, the decomposed products of dithionite, such as sulfite (SO<sub>3</sub><sup>2-</sup>), bisulfite (HSO<sub>3</sub><sup>-</sup>), and thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>), can reduce the Cr(VI) into Cr(III) directly in long-term groundwater treatment by the following reaction [25]:



However, the effectiveness of adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to decrease the concentration of Cr(VI) is limited due to the low contents of dithionite-reducible iron in Cr(VI)-contaminated sites [14]. In addition, the reaction rate of Cr(VI) reduction into Cr(III) by adding dithionite decomposed products decreases with the increasing pH [25]. These three groups of reductants were used effectively in some cases for reduction of Cr(VI) into Cr(III). However, their effectiveness and application are confined by the need of a long incubation time when organic matters amendments are used. Clogging occurs when ferrous iron is added. When dithionite is used, the effectiveness is confined by a low content of dithionite-reducible iron in Cr(VI)-contaminated sites.

Su and Ludwig [14] demonstrated that the effectiveness of decreasing the amount of Cr(VI) in the residue of alkaline ore processing was higher when adding a solution of 0.05 M FeSO<sub>4</sub> and 0.05 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (1:1 mol/mol, pH 3.5) than when adding a solution of 0.05 M FeSO<sub>4</sub> or 0.05 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> alone at similar pH, respectively. They hypothesized that ferrous iron could be stabilized by H<sup>+</sup> generated from the reaction of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and Fe(III) oxides. And, that by adding mixed reductants the Cr(VI) reduction is dominated by Fe(II) rather than by the contribution from Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. To the best of our knowledge, there are few studies in the literature that have investigated the effectiveness of adding a mixture of ferrous iron and dithionite to decrease the Cr(VI) concentration in alkaline Cr(VI)-contaminated soils. In addition, the extent of aqueous Fe(II) oxidation by dissolved O<sub>2</sub> and dithionite is affected by pH [26,27]. Thus, the effectiveness of ferrous iron, dithionite, and the mixture of ferrous iron and dithionite for decreasing Cr(VI) concentration in an alkaline condition may be affected by the solution pH.

Therefore, it is worthwhile to test the effectiveness of the reduction of Cr(VI) in alkaline soils by stoichiometrically adding reductants, FeSO<sub>4</sub>, Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and a mixture of ferrous iron and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, at various pH.

In our previous study, we demonstrated that the mobility and phytotoxicity of Cr(VI) were better evaluated by using the soil available Cr(VI) content than by using the total amount of Cr(VI). In addition, we demonstrated that the DOWEX M4195 resin extraction method is feasible for extracting soil available Cr(VI) [7,16]. Therefore, the effectiveness of reductants at various pH levels to decrease the amount of resin-extractable Cr(VI) in Cr(VI)-contaminated soils is assessed in this study. Moreover, in our previous experiments, the X-ray absorption near edge structure (XANES) spectroscopy was demonstrated to be able to examine the extent of Cr(VI) reduction after amendment by organic materials. The pre-edge peak at 5992 eV in Cr K-edge XANES spectra was a unique characteristic of Cr(VI), but not of Cr(III), and therefore the pre-edge peak was used to identify the speciation of Cr in our studies [28].

In this study, the DOWEX M4195 resin extraction method was used to evaluate the effectiveness of various reductants, FeSO<sub>4</sub>, Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and a mixture of ferrous iron and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4:1 mol/mol), to decrease the soil resin-extractable Cr(VI). The effect of the pH of the added reductants on the amounts of resin-extractable Cr(VI) in Cr(VI)-contaminated soils was also investigated. The XANES method was employed to examine the extent of the reduction of Cr(VI) into Cr(III) by the added reductants.

## 2. Materials and methods

### 2.1. Soil properties and the preparation of Cr(VI)-contaminated soils

Two representative alkaline soils from Taiwan, Chengchung (Cf) and Taikang (Tk), were selected in this study. The pH of these soils was measured in 1:1 soil/H<sub>2</sub>O suspension by using a pH meter (Table 1). The soil organic carbon and free iron oxide contents were determined by the Walkley-Black method [29] and the sodium dithionite–citrate–bicarbonate (DCB) method [30], respectively.

One kg of soil was spiked with 0, 50, 100, and 200 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution (5000 mg Cr(VI) L<sup>-1</sup>) to reach the level of 0, 250, 500, and 1000 mg kg<sup>-1</sup> Cr in soil, respectively. Then, distilled water was added to the soils to reach the soil water-holding capacity. They underwent three wetting–drying cycles at room temperature to mimic field conditions. Each cycle lasted for around 30 days. Afterwards, the soils were ground to pass through a 10-mesh sieve, and stored for further use.

### 2.2. Amending Cr(VI)-spiked soils with reductants

The 100 g Cr(VI)-spiked soils were mixed with the reductants, 0.2 M FeSO<sub>4</sub>, 0.2 M Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with 0.05 M K<sub>2</sub>CO<sub>3</sub>, and a mixture of 0.2 M Fe(II) and 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, respectively. Based on Eqs. (1) and (2), the application rate of the reductants (number of equivalents) was equal to the number of equivalents of dichromate added to 0, 250, 500, and 1000 mg kg<sup>-1</sup> in Cr(VI)-spiked soils. Since one mole of Fe(II) and S<sub>2</sub>O<sub>4</sub><sup>2-</sup> were

**Table 2**  
Amount of resin-extractable Cr(VI) in Cr(VI)-spiked soils after three wetting–drying cycles

Cr(VI) added (mg kg <sup>-1</sup> Cr(VI) in soil)	Chengchung (Cf) (mg kg <sup>-1</sup> Cr(VI) in soil)	Taikang (Tk) (mg kg <sup>-1</sup> Cr(VI) in soil)
0	N.D. <sup>a</sup>	N.D.
250	15.1 ± 0.6	113 ± 1
500	81 ± 1	265 ± 1
1000	334 ± 11	547 ± 14

<sup>a</sup> N.D.: not detectable ( $\leq 5$  mg kg<sup>-1</sup> Cr(VI) in soil).

equal to 1 and 2 equivalents, respectively, the mole ratio of Fe(II):Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> added into the Cr(VI)-spiked soils was set to be 4:1 for the mixture of Fe(II) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to fulfill the design that the equivalent of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was 1/3rd of the total equivalent of the mixture. The amount of reductants (in mole number) added into Cr(VI)-spiked soils were presented in Table 3. Then, distilled water was added to the soil samples till they reached their water-holding capacity. The soil samples were then air-dried at room temperature for around 1 week. They were then ground to pass through 10 and 80 mesh sieves to determine the soil pH and the amounts of resin-extractable Cr(VI), respectively.

### 2.3. Resin preparation and soil available Cr(VI) extraction by resin

The selected Dowex M4195 resins (particle size >425 μm, The Dow Chemical Company, Midland, MI, USA) were immersed in deionized water for 2 days and washed with 1N HCl. Then the resins were converted into Cu-saturated by continuously eluting 500 mg L<sup>-1</sup> CuCl<sub>2</sub> until the concentrations of Cu in effluent and in influent were equal. After that, the Cu-saturated resins were rinsed with distilled water and were oven-dried. Yu et al. [7] reported that 1 g Cu-saturated DOWEX M4195 resin can adsorb over 6.37 mg Cr(VI) in a solution. In addition, 60 mesh polypropylene (PP) bags were prepared to retain the air-dried Cu-saturated resins.

Ten grams of the treated soil (passed through an 80 mesh sieve) were placed in a 300-mL flask with 100 mL distilled water, and then 1 g Cu-saturated resin in a sealed PP bag was added. The flasks were then shaken at 150 rpm for 24 h. After that, the resin bags which had adsorbed Cr(VI) were transferred into different flasks and 100 mL 10% (w/w) NaCl solutions (pH 4) were used to desorb Cr(VI) by shaking at 150 rpm for 24 h. The desorption process was repeated twice, and the amounts of Cr(VI) in the NaCl solutions were determined by ICP-OES (PerkinElmer, Optima 2000). All experiments were carried out in triplicate.

### 2.4. XANES analysis

Because of the limitation of the XANES beam time, another 50 g of 500 mg kg<sup>-1</sup> Cr(VI) in Cr(VI)-spiked soils were treated without or with the same reductant solutions as described previously. However, the application rates of the reductants were 70% and 120% the number of equivalent of dichromate added into the Cf and Tk soils, respectively. The treated soils were air-dried at room temperature and ground to pass through a 230-mesh sieve, and then stored in sealed glass bottles for 1 week before XANES analysis. The Cr standards were obtained by mixing CrCl<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with boron nitride powder, respectively. All of the standards contained 5% total chromium by weight but with various Cr(VI) percentages (10, 20, 30, 40, 50 and 70, respectively) [16]. Standard and soil samples were sealed with transparent tape, and then mounted on sample holders for XANES analysis. The Chromium K-edge XANES analysis was implemented with the Wiggler beam line BL17C1 at the National Synchrotron Radiation Research Center in Taiwan. The energy and current of the electron storage ring was 1.5 eV and 200 mA, respectively. Due to the low Cr concentration in the soil samples the data of

the XANES analysis were collected in fluorescence mode to enhance the absorption intensity.

### 2.5. The effect of the application rate and the pH of the reductants on decreasing resin-extractable Cr(VI)

In order to investigate the effect of the application rate of reductants on the decrease of resin-extractable Cr(VI) in soils, the application rate of the reductants was decreased to half the number of equivalents of added dichromate. One hundred gram of 1000 mg kg<sup>-1</sup> Cr(VI) in Tk soils was mixed with 0.1 M FeSO<sub>4</sub>, 0.1 M Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with 0.05 M K<sub>2</sub>CO<sub>3</sub> and a mixture of 0.1 M Fe(II) and 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4:1 mol/mol), respectively. The amount of reductants (in mole number) added into Cr(VI)-spiked soils are shown in Table 4. Then the distilled water was added to the soils until they reached their water-holding capacity. After that, the soils were air-dried and ground to pass through an 80-mesh sieve, and then the amounts of resin-extractable Cr(VI) were determined. In addition, the pH of the reductant solutions was adjusted by H<sub>2</sub>SO<sub>4</sub> or NaOH to various pH in order to investigate the effect of pH on the amounts of resin-extractable Cr(VI) using the same procedures as described previously. The pH of the reductant-treated soils was then measured.

## 3. Results and discussion

### 3.1. Resin-extractable Cr(VI) of Cr(VI)-contaminated soils before adding reductants

The soil properties of Chengchung (Cf) and Taikang (Tk) are shown in Table 1. Both soils are alkaline soils. After adding Cr(VI) solutions into the studied soils and going through three wetting–drying cycles, the amounts of resin-extractable Cr(VI) in Cf and Tk soils are shown in Table 2. After three wetting and drying cycles, the resin-extractable Cr(VI) in all Cr(VI)-spiked soils decreased without adding any reductants. The amount of resin-extractable Cr(VI) in Tk soils without adding reductants was about 50% of the spiked Cr(VI) and was higher than those of the Cf soils with the same amount of Cr(VI)-spiked. Bartlett and Kimble [8] demonstrated that the Cr(VI) in the soil was favorably reduced by soil organic matter under acid and neutral conditions. The Tk soil had a lower content of organic carbon and a higher soil pH than the Cf soil. Therefore, the low amounts of resin-extractable Cr(VI) in Cf soils may be due to their lower soil pH and higher content of native organic matter. Although Tk soil had a higher content of free iron oxides, which could provide better adsorption sites for Cr(VI) anions than the Cf soil, the positive charge on the sorbents was decreased due to the increasing pH [31]. Consequently, the adsorption of Cr(VI) on free iron oxides surfaces was not emphasized in this study. Although the amounts of resin-extractable Cr(VI) decreased after three drying–wetting cycles, there were still significant amounts of extractable Cr(VI) remaining in the alkaline Cr(VI)-spiked soils. It should be worthwhile to add reductants into Cr(VI)-contaminated soils to enhance the reduction of Cr(VI) into Cr(III), and to

**Table 3**  
Amount of soil resin-extractable Cr(VI) and pH after adding reductants

Cr(VI) spiked (mg kg <sup>-1</sup> )	Reductant	Reductant added to 100 g soil <sup>a</sup> (mmol)	Reductant pH	Cf soil		Tk soil	
				mg kg <sup>-1</sup>	pH	mg kg <sup>-1</sup>	pH
500	Distilled H <sub>2</sub> O		5.4	81 a <sup>b</sup> ± 1	8.1	265 a ± 1	8.0
	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	1.5	8.6	N.D. <sup>c</sup>	8.6	20.6 b ± 0.3	8.3
	FeSO <sub>4</sub>	3.0	2.7	N.D.	7.1	21.0 b ± 2.3	7.6
	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	3.0	3.2	N.D.	5.6	6.0 d ± 0.2	7.6
	FeSO <sub>4</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	2.0 + 0.5	6.6	N.D.	7.3	15.6 c ± 0.8	7.8
	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	2.0 + 0.5	5.6	N.D.	7.2	9 d ± 1	7.7
1000	Distilled H <sub>2</sub> O		5.4	334 a ± 11	7.9	547 a ± 14	7.9
	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	3.0	8.6	8.0 b ± 0.1	8.2	21.9 b ± 0.5	8.2
	FeSO <sub>4</sub>	6.0	2.3	7.0 b ± 0.7	6.4	23.0 b ± 0.6	7.3
	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	6.0	2.0	N.D.	4.3	N.D.	5.3
	FeSO <sub>4</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	4.0 + 1.0	6.6	6.5 b ± 0.4	7.1	7.0 b ± 0.3	7.5
	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	4.0 + 1.0	5.6	N.D.	6.6	N.D.	7.5

<sup>a</sup> The application rate of the reductant in number of equivalents was equal to the number of equivalents of dichromate added into soils.

<sup>b</sup> Values followed by the same letter within the each sub-column mean not statistically significant difference ( $p < 0.05$ ) between the amount of Cr(VI) at 5% level according to Duncan's multiple range test.

<sup>c</sup> N.D.: not detectable ( $\leq 5$  mg kg<sup>-1</sup> in soil).

investigate the effectiveness of those reductants on decreasing resin-extractable Cr(VI).

### 3.2. Effectiveness of adding various reductants to decrease soil resin-extractable Cr(VI)

Since the amounts of resin-extractable Cr(VI) in 250 mg kg<sup>-1</sup> Cr(VI)-spiked Cf and Tk soils were too small for comparing the effectiveness of adding reductants to decrease the contents of resin-extractable Cr(VI), the results of adding reductants in 250 mg kg<sup>-1</sup> Cr(VI) in soil are not presented and are not discussed in this paper. The amount of soil resin-extractable Cr(VI) in 500 and 1000 mg kg<sup>-1</sup> in Cr(VI)-spiked soils without or with adding reductants, when the application rates of the reductants equal the number of equivalents of dichromate added into soils, are given in Table 3. After adding the reductants, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with 0.05 M K<sub>2</sub>CO<sub>3</sub>, FeSO<sub>4</sub>, Fe(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, a mixture of FeSO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4:1 mol/mol), and a mixture of Fe(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4:1 mol/mol), respectively, into 500 mg Cr(VI)-spiked soils, the amounts of resin-extractable Cr(VI) in Cf soils were below the detection limit. They were less than 5% of the spiked-Cr(VI) that could be extracted from the Tk soils. In the reductants-added 1000 mg kg<sup>-1</sup> Cr(VI) in soils, less than 1% and 2% of the spiked-Cr(VI) could be extracted from the Cf and Tk soils, respectively. The effectiveness of adding reductants to decrease resin-extractable Cr(VI) is shown mainly by the result of the reduction of Cr(VI) into Cr(III). This is supported by the XANES spectra of reductant-added Cr(VI)-spiked soils (Fig. 1). Based on the calibration curve of the Cr(VI) peak height vs. the Cr(VI) percentage (Fig. 1(a)), there were about 5% and 56% Cr(VI) in Cr(VI)-spiked Cf and Tk soils without adding reductants, respectively. For the peak at 5992 eV, the unique characteristics of Cr(VI) (but not from Cr(III)), reductant-treated soil samples were below the detection limit in

the XANES spectra. This indicates that the decrease of soil resin-extractable Cr(VI) by adding reductants was mainly due to Cr(VI) reduction into Cr(III) rather than the Cr(VI) sorption by soils.

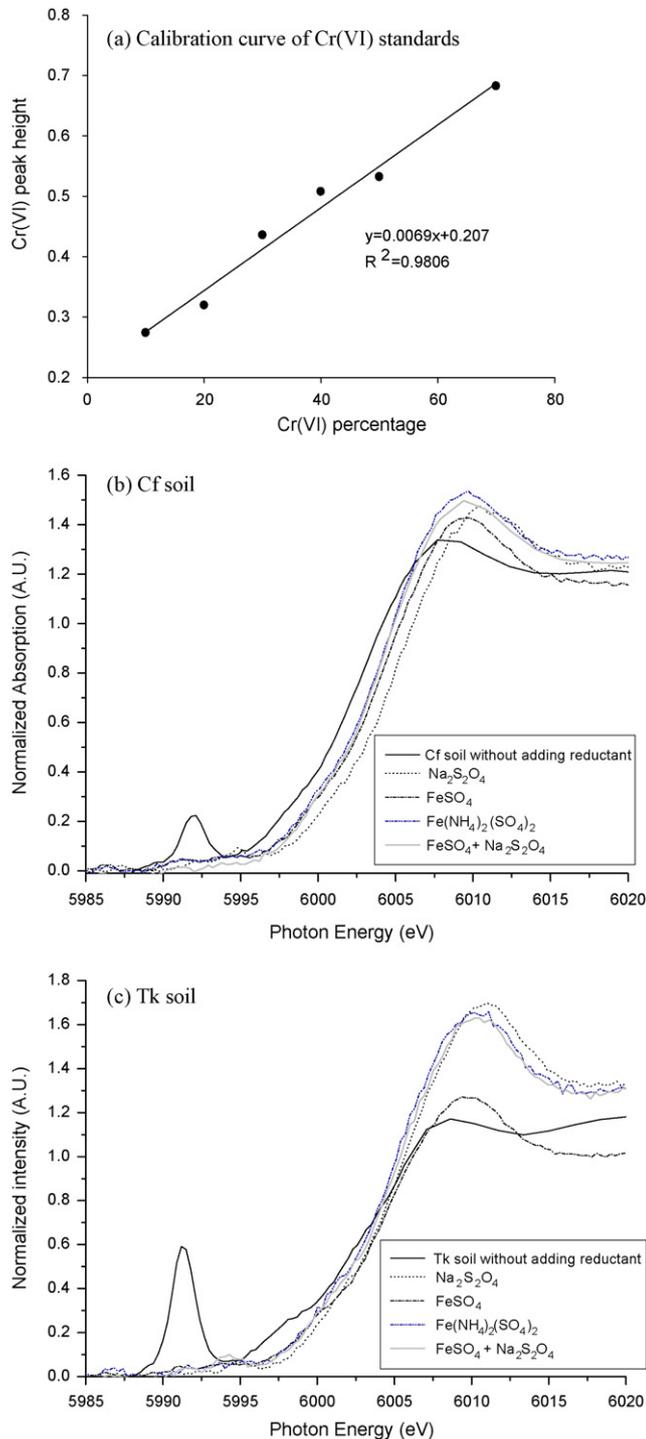
There were no significant differences ( $p < 0.05$ ) in the amounts of resin-extractable Cr(VI) among all the reductant treatments, except in the 500 mg kg<sup>-1</sup> Cr(VI) in Tk soils when the application rate of reductants was equal to the number of equivalent of added dichromate in soils. Therefore it is difficult to compare the effectiveness of the tested reductants to decrease the amounts of resin-extractable Cr(VI). In order to compare the effectiveness of added reductants in decreasing the contents of resin-extractable Cr(VI) in soils, the application rate of reductants was decreased to 1/2 the number of equivalents of added dichromate in 1000 mg kg<sup>-1</sup> in Cr(VI)-spiked Tk soils in this study. The amounts of resin-extractable Cr(VI) of Tk soils are shown in Table 4. Among the five reductants, the effectiveness of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with 0.05 M K<sub>2</sub>CO<sub>3</sub> was the lowest, and that of the mixture of ferrous iron and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4:1 mol/mol) for decreasing resin-extractable Cr(VI) were the highest. The low effectiveness of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to decrease resin-extractable Cr(VI) might be due to the fact that even though the Tk soil has significant amounts of free iron oxides, only a small portion of Fe(III) in the studied soils could be reduced into Fe(II) by the added Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Consequently the Fe(II) could react with Cr(VI) to form the precipitates [15,22]. On the other hand, if most of the Fe(III) in Cr(VI)-spiked soil could be reduced into Fe(II), the precipitation of FeS might occur in alkaline soil [30,32], and thus the extent of the Cr(VI) reduction into Cr(III) could be inhibited. Su and Ludwig [14] considered that ferrous iron could be stabilized by H<sup>+</sup> from the reaction of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with Fe(III) oxides. They hypothesized that the Cr(VI) reduction by adding the mixed reductant of Fe(II) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, is dominated by Fe(II) rather than by the contribution from Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. In this study, we found that the extent of decreasing soil resin-extractable Cr(VI)

**Table 4**  
The amount of resin-extractable Cr(VI) in Taikang 1000 mg kg<sup>-1</sup> Cr(VI)-spiked soils after adding the reductants

Reductant	Reductant added to 100 g soil <sup>a</sup> (mmol)	Reductant pH	Soil pH (soil:H <sub>2</sub> O = 1:1)	Resin-extractable Cr(VI) mg kg <sup>-1</sup>
Distilled H <sub>2</sub> O		5.4	7.9	547 a <sup>b</sup> ± 14
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	1.5	8.6	8.3	237 b ± 9
FeSO <sub>4</sub>	3.0	2.3	7.6	203 c ± 8
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	3.0	2.9	7.7	205 c ± 10
FeSO <sub>4</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	2.0 + 0.5	5.2	7.8	167 d ± 8
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	2.0 + 0.5	6.3	7.8	167 d ± 6

<sup>a</sup> The application rate of reductant in number of equivalents was 1/2 the number of equivalents of dichromate added into soils.

<sup>b</sup> Values followed by the same letter within the column mean not statistically significant difference ( $p < 0.05$ ) between the amount of Cr(VI) at 5% level according to Duncan's multiple range test.



**Fig. 1.** (a) The calibration curve of Cr(VI) peak height in XANES spectra vs. Cr(VI) percentage of Cr standard samples and (b) Cf soil and (c) Tk soil, the XANES spectra of 500 mg Cr(VI) kg<sup>-1</sup> spiked-soils without and with adding the reductants for Chengchung (Cf) and Taikang (Tk) soils, respectively. The application rates of the reductants were 70% and 120% of the number of equivalents of dichromate added into the Cf and Tk soils, respectively. (a)

by adding mixed reductants of Fe(II) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was higher than by adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> or ferrous iron alone (Table 4). When adding Fe(II) only, the ferrous iron might be unstable because the ferrous iron might be hydrolyzed or oxidized by oxygen, which may greatly decrease the amount of ferrous iron that could reduce Cr(VI) into Cr(III). According to Eqs. (1) and (2), the effectiveness of Fe(II) in the

mixture of Fe(II) and dithionite for reducing Cr(VI) into Cr(III) might increase when the H<sup>+</sup> was produced by the reaction of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and Fe(III) oxides to stabilize Fe(II). When we compare the results of the decrease in resin-extractable Cr(VI) by adding the mixture of ferrous iron and dithionite (4:1 mol/mol) with the results of adding Fe(II) or Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> alone, it suggests that the higher effectiveness of the mixture of ferrous iron and dithionite on the reduction of Cr(VI) into Cr(III) might be mainly due to Fe(II) from the added ferrous iron instead of from the soil dithionite-reducible Fe(III).

### 3.3. Effectiveness of decreasing resin-extractable Cr(VI) by reductants with various pH

As mentioned above, the effectiveness of reductants to decrease resin-extractable Cr(VI) can be influenced by the pH condition which can alter the species of Fe and S and thus affect the extent of the Cr(VI) reduction. The effect of the pH of the added reductant solutions on decreasing the amounts of resin-extractable Cr(VI) in Tk 1000 mg kg<sup>-1</sup> soil are shown in Table 5. The amounts of soil resin-extractable Cr(VI) by adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (pH 6.1–10.3) were 44–66% compared to those of adding water only. Both the soil pH and the contents of the resin-extractable Cr(VI) decreased as the pH of the added Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> solutions decreased. This indicates that the effectiveness of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> on decreasing resin-extractable Cr(VI) decreases when the pH of the added Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> solution is increased from 6 to 10. This might be due to the fact that there were fewer amounts of Fe(II) produced from dithionite-reducible iron in Tk soil for reducing Cr(VI) into Cr(III). On the other hand, the FeS might precipitate when the solution pH was increased. Moreover, according to Eq. (3), the extent of the reduction of Cr(VI) into Cr(III) by dithionite decomposed products such as sulfite, bisulfite, and thiosulfate, decreases as the solution pH increases. When adding FeSO<sub>4</sub> or Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> at pH < 1–4.4, the amounts of soil resin-extractable Cr(VI) decreases as the pH decreases. When the pH of the added FeSO<sub>4</sub> is below 1, the contents of the resin-extractable Cr(VI) is far less than in other treatments. Based on Eq. (1), the reduction of Cr(VI) into Cr(III) will be enhanced as the pH of the ferrous iron solution decreases. In addition, a lower pH will prevent the precipitation of iron in soils, thus there is more soluble Fe<sup>2+</sup> to react with Cr(VI) with a lower pH than with a higher pH. The amounts of soil resin-extractable Cr(VI) in Tk soils by adding sulfuric acid (pH 1.1) were similar to the results of adding distilled water at the same application volume (data not shown). This confirms that the decrease of resin-extractable Cr(VI) by adding Fe(II) at pH 1.4–4.4 is due to Cr(VI) reduction into Cr(III) by added ferrous iron instead of added H<sup>+</sup>. However, the contents of the resin-extractable Cr(VI) by adding the blend of ferrous iron and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4:1 mol/mol) at various pH (pH 1.4–6.3) in Cr(VI)-spiked soils were not affected by the solution pH. Although the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was unstable and white precipitate formed in the acid condition, the effectiveness of the mixed reductants for decreasing resin-extractable Cr(VI) remained. This suggests that in acid conditions, the reduction of Cr(VI) into Cr(III) is mainly due to the involvement of ferrous iron rather than that of dithionite.

Table 5 also shows that the soil pH decreased as the pH of the added reductant solutions decreased. Since the contents of the soluble Cr(III) and total dissolved-phase Cr in the soil will be enhanced when the soil pH is at 4 or below [8], there is a concern that the hazard of Cr(III) in soil might be increased by lowering the soil pH through the addition of reductants. Although there were the least amounts of resin-extractable Cr(VI) after adding FeSO<sub>4</sub> at pH < 1 among these treatments, the soil pH was decreased to 3.5. The decrease of soil pH by added Fe(II) might be attributed to the H<sup>+</sup> in solution and the hydrolysis of Fe<sup>2+</sup>. However, the soil pH was changed by less than 1 pH unit after adding the mixture of ferrous

**Table 5**The amount of resin-extractable Cr(VI) ( $\text{mg kg}^{-1}$  Cr(VI) in soil) in  $1000 \text{ mg kg}^{-1}$  Cr(VI)-spiked Tk soil after adding reductants with various pH

Reductant <sup>a</sup>	Reductant pH	Resin-extractable Cr(VI)	Soil pH
Distilled H <sub>2</sub> O	5.4	547 ± 14	7.9
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	6.1	185 c <sup>b</sup> ± 5	7.9
	8.6	237 b ± 9	8.3
	10.3	305 a ± 9	8.3
FeSO <sub>4</sub>	0.9	21 d ± 2	3.5
	1.4	180 c ± 2	6.7
	2.3	203 b ± 8	7.6
	4.4	218 a ± 9	7.8
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	1.4	185 b ± 3	6.8
	2.9	205 a ± 10	7.7
	4.4	197 a ± 2	8.1
FeSO <sub>4</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	1.4	169 a ± 2	7.2
	5.2	167 a ± 8	7.8
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (4:1 mol/mol)	1.4	178 a ± 2	7.0
	6.3	167 b ± 6	7.8

<sup>a</sup> The application rate of reductant in number of equivalents was 1/2 the number of equivalents of dichromate added into soils.

<sup>b</sup> Values followed by the same letter within each reductant mean not statistically significant difference ( $p < 0.05$ ) between the amount of Cr(VI) at 5% level according to Duncan's multiple range test.

iron and dithionite (4:1 mol/mol) at pH 1.4–6.3. This suggests that the mixture of ferrous iron and dithionite in a wide range of pH were all efficient for decreasing the amounts of resin-extractable Cr(VI) in alkaline Cr(VI)-spiked soils, without decreasing the soil pH. Thus the possible risk from soluble Cr(III) and total dissolved Cr in soils might be minor when adding a mixture of ferrous iron and dithionite rather than by adding FeSO<sub>4</sub> at pH < 1 alone for remediating alkaline Cr(VI)-contaminated soils. The long-term fate of the stabilized soil Cr after amending the reductants needs to be further studied. The possibility of Cr(III) re-oxidizing into Cr(VI) was not expected except in soils with high amount of Mn oxides [33].

#### 4. Conclusion

The amount of resin-extractable Cr(VI) in the tested Cr(VI)-spiked alkaline soils was decreased to less than 5% of spiked-Cr(VI) by adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with K<sub>2</sub>CO<sub>3</sub>, FeSO<sub>4</sub>, Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, and a mixture of ferrous iron and dithionite (4:1 mol/mol), respectively, when the application rate of the reductants (number of equivalent) was equal to the number of equivalent of dichromate added into the soils. The decrease of intensities of the XANES Cr(VI) peak in the spectra of the Cr(VI)-spiked soil samples with reductants treatments proved that the decrease of resin-extractable Cr(VI) by added reductants was due to Cr(VI) reduction into Cr(III). When the application rate of the reductants was decreased to 1/2 the number of equivalent of dichromate added into the soils, the mixture of ferrous iron and dithionite was the most effective to decrease the soil resin-extractable Cr(VI) among the tested reductants. The reduction of Cr(VI) into Cr(III) was mainly due to the Fe(II) from the added ferrous iron instead of from the soil dithionite-reducible Fe(III). Adding reductants with various pH, FeSO<sub>4</sub> at pH below 1 was the most effective for decreasing resin-extractable Cr(VI) in alkaline soils. However, this decreased the soil pH the most (from 7.9 to 3.5) among the tested reductants. On the other hand, the mixture of ferrous iron and dithionite with a wide pH range was very efficient in decreasing the resin-extractable Cr(VI) into Cr(III) in the studied Cr(VI)-spiked soil. This also decreased the soil pH to a much lesser degree compared to the added FeSO<sub>4</sub> (pH < 1) alone, thereby avoiding the possibility of the Cr(III) hazard.

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