



The effectiveness of four organic matter amendments for decreasing resin-extractable Cr(VI) in Cr(VI)-contaminated soils

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ABSTRACT

This paper compared the effectiveness of four organic materials for decreasing the amounts of soil extractable Cr(VI) in Cr(VI)-contaminated soils using the DOWEX M4195 resin-extraction method. Organic matters were added into Cr(VI)-spiked soils [$500 \text{ mg Cr(VI)} (\text{kg soil})^{-1}$] in the form of sugarcane dregs compost (SCDC), cattle-dung compost (CDC), soybean meal (SBM) and rice bran (RB), in the amounts of 0, 1%, and 2% by dry weight, respectively. The results indicated that adding only 1% organic matter to the studied soils could effectively decrease the amount of soil resin-extractable Cr(VI) after 12 days of incubation. The decrease of resin-extractable Cr(VI) by organic materials was mainly the result from the reduction of Cr(VI) to Cr(III) supported by the XANES spectroscopy. Among the four tested organic materials, SBM and RB had higher effectiveness in decreasing soil resin-extractable Cr(VI) than CDC and SCDC. This result may be due to the fact that SBM and RB have more dissolved organic carbon (DOC) and protein than CDC and SCDC. Therefore, it was concluded that the contents of DOC and protein are the main factors that determine the effectiveness of organic materials for decreasing the amounts of soil available Cr(VI) in Cr(VI)-contaminated soils.

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1. Introduction

Soil contaminating chromium is released into the environment through various industrial activities, including electroplating, mining, pulp and paper production, timber treatment and petroleum refining [1,2]. Chromium exists in soils in two stable oxidation states, Cr(III) and Cr(VI). These two oxidation states of Cr have very different behaviors [3,4]. Chromium(VI) exists in oxyanion forms, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, under most conditions, and therefore it has high mobility in soils. Even at low concentration, Cr(VI) is considered carcinogenic and mutagenic to humans [5,6]. On the other hand, cationic Cr(III) is highly adsorbable by soil particles and is an essential human nutrient [7]. Since Cr(III) is considered less mobile, less soluble and less toxic than Cr(VI) [8,9], the existing remediation of Cr(VI)-contaminated sites usually involves the reduction of Cr(VI) into Cr(III) to reduce its mobility and toxicity [10–12].

Adding organic materials to Cr(VI)-contaminated soils to promote Cr(VI) reduction is a commonly used method. In addition

to accomplishing the intended remediation, this method is also environmentally friendly, inexpensive, and can reuse agricultural organic residues. Several researches have demonstrated that various organic materials, such as powdered leaves, biosolid composts, farm yard manure and brown seaweed can enhance the Cr(VI) reduction because of the dissolved organic carbon (DOC) and the small organic compounds released from the organic materials [1,5,13,14]. In our previous study, we demonstrated that adding cattle-dung and hog-dung composts enhance the reduction of Cr(VI) into Cr(III) in soils. However, the effectiveness is not very high, especially under high pH condition [15]. The effectiveness of Cr(VI) reduction is influenced by the decomposition rate of the added organic materials. In order to facilitate the reduction of Cr(VI) in a soil, it is certainly worthwhile to test the effectiveness of the reduction of Cr(VI) by organic materials that are more readily decomposed than cattle-dung and hog-dung composts. In Taiwan, sugarcane dregs compost (SCDC), cattle-dung compost (CDC), soybean meal (SBM), and rice bran (RB) are the major agricultural organic residues or composts. Among these four organic materials, RB and SBM can be decomposed more easily in soils than SCDC and CDC [16], and to the best of our knowledge their ability to reduce Cr(VI) has not been investigated. Therefore, in this study, RB and SBM are used to amend Cr(VI)-contaminated

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soil and to investigate their effectiveness to reduce Cr(VI) compared with that of SCDC and CDC, both of which are less readily decomposed.

Since the amount of soil available Cr(VI) is a better index than the total amount of Cr(VI) for evaluating the mobility and toxicity of Cr(VI), the effectiveness of organic materials in remediating Cr(VI)-contaminated soils in this study is assessed by examining the decrease in soil available Cr(VI) after adding organic materials. In our previous study, we demonstrated that the DOWEX M4195 resin-extraction method is feasible for extracting soil available Cr(VI) [2,15]. However, it is difficult to interpret whether the decrease of resin-extractable Cr(VI) in soils after being amended by organic matter is due to the reduction of Cr(VI) into Cr(III) or the sorption of Cr(VI) by the soil components. X-ray adsorption near edge structure (XANES) spectroscopy is a useful tool to distinguish between the species of Cr, Cr(VI) or Cr(III), in soils [15,17]. Therefore, in addition to the resin-extraction method, XANES spectroscopy was used to examine the extent of Cr(VI) reduction after amendment by organic materials.

The purpose of this study was to apply the DOWEX M4195 resin-extraction method to evaluate the effectiveness of various organic materials (i.e. SCDC, CDC, SBM, and RB) for decreasing the amounts of available Cr(VI) in Cr(VI)-contaminated soils. In addition, the XANES method was used to examine the extent of the reduction of Cr(VI) by adding organic materials.

2. Materials and methods

2.1. Preparation of resins

The purchased resins (DOWEX M4195, particle size >40 mesh) were first immersed in distilled water for 2 days and washed with 1N HCl for 1 day. The resins were then rinsed thoroughly with distilled water and transferred to a column to be converted into Cu-saturated form by eluting with 500 mg L^{-1} CuCl_2 . The Cu-saturated resins were then rinsed thoroughly with distilled water, oven-dried, and stored for further use [2,15].

A 60-mesh polypropylene net was used to make the resin bag. The Cu-saturated resins were retained in the bag for separating the resins from the soil particles. The resin bags were washed with 1N HCl and then rinsed with distilled water and oven dried before using it.

2.2. Preparation of Cr(VI)-contaminated soil

Three soils of Taiwan [Pinchung (Pc), Chingchung (Cf), and Taikang (TK)] were used in this study. Soil pH was determined by a pH meter (soil:H₂O = 1:1). Soil texture was measured using the hydrometer method [18]. Soil total nitrogen was analyzed by the Kjeldahl method [19]. Soil organic carbon content was determined using the Walkley-Black method [20], and the content of free iron oxides was analyzed by the DCB method [21].

One and 1/2 kg of air-dried soils were first added with 300 mL distilled water and then with or without 75 mL $\text{K}_2\text{Cr}_2\text{O}_7$ solution which had $10,000 \text{ mg Cr(VI) L}^{-1}$. After that, soils were again supplied with distilled water to reach their water holding capacity. The levels of Cr(VI) addition to the soils were 0 and $500 \text{ mg (kg soil)}^{-1}$, respectively. Then the Cr(VI)-spiked soils were mixed thoroughly and air-dried at room temperature. The air-dried Cr(VI)-spiked soils were then ground and passed through a 10-mesh sieve. Distilled water was then added again to the soils to reach the water holding capacity. The wetting and air-drying procedures were repeated three times to mimic field conditions, and each cycle lasted for around 4 weeks.

After three wetting- and air-drying cycles, the Cr(VI)-spiked soils were digested by aqua regia to determine the total concentration of Cr in Cr(VI)-spiked soils, using the following procedures. Soil samples (0.5 g) were added into 100 mL digestion tubes and rinsed with 0.5 mL H₂O. The aqua regia (10 mL, $\text{HNO}_3:\text{HCl} = 1:3 \text{ v/v}$) was then added slowly into the digestion tubes. After standing for 16 h, soil samples were heated on a hot plate at 140°C for 2 h and then the cooled digests were filtered through Whatman No. 42 filters and diluted to 100 mL with 0.5 M nitric acid. The Cr concentration in the digests was determined by using ICP-OES (PerkinElmer, Optima 2000). The Cr concentration of a certified reference soil sample (BCR 143R) was also determined by the same procedure to confirm the reliability of the digestion method. The recovery of Cr for the certified reference soil sample by using the aqua regia digestion method was 98%.

2.3. Properties of amending organic materials

Four organic materials, SCDC, CC, SBM and RB were used in this study. The pH of the organic materials was measured using the same methods as used for the soil samples. The organic matter content of the tested materials was determined using the loss-on-ignition method [22]. The DOC was extracted using distilled water (1:50, organic material:water ratio) for 24 h, filtered through a $0.45 \mu\text{m}$ membrane and then determined by TOC analyzer, O.I. analytical, Model 1010. The organic carbon and total nitrogen content were analyzed by CNS analyzer, LECO, CNS 2000, and the 6.25-folds of total nitrogen were regarded as the crude protein content of the organic materials. The amount of crude lipid was determined by using the Soxhlet extraction with *n*-hexane for 24 h. After the Soxhlet extraction, the samples were extracted with H₂O in a 75°C water bath for 24 h to determine the soluble sugar content. After the soluble sugar extraction, the contents of hemicellulose and cellulose were determined by the Nelson–Somogyi method [23]. The lignin content was estimated by subtracting the crude protein, crude lipid, soluble sugar, hemicellulose, cellulose, and ash from the total weight of the organic materials [16].

2.4. Cr(VI)-spiked soils amended with organic material and Cr(VI) extraction using resins

Organic matter was added into Cr(VI)-spiked soils with 0, 1% and 2% by dry weight in the form of SCDC, CDC, SBM and RB, respectively. The treatment without adding organic materials was used as the control. The soils amended by organic materials as well as the control were then incubated at field capacity at 20°C . Soils were taken out after 0, 4, 8, 12, 20, 30 and 40 days of incubation, then air-dried and ground to pass through a 80-mesh sieve for resin extraction.

Five grams of Cr(VI)-spiked soils amended by organic materials were placed in a 250 mL flask. One polypropylene bag containing 0.5 g of Cu-saturated resins and 100 mL of distilled water were added into the flask and were then shaken for 24 h to extract soil Cr(VI). At the end of the shaking period, the resin bag was taken out and rinsed thoroughly with distilled water. The resin bag was transferred into another flask, which contained 100 mL of 10% NaCl solution (pH 4.5) and shaken for 24 h to desorb the Cr(VI) from the resin. The desorption process was repeated twice, and the amounts of Cr(VI) in the desorption solution was determined by ICP-OES, PerkinElmer, Optima 2000.

2.5. XANES Analysis

Due to the XANES beam time arrangement and preventing the Cr species change during the sample storage period, another set of Cr(VI)-spiked soils with and without added organic matters in the

form of CDC and SBM incubated for 20 days were prepared and used to examine the degree of Cr(VI) reduction to Cr(III) by XANES. The soils were ground to pass through a 230-mesh sieve, and stored in sealed glass bottles for 1 week before XANES analysis. The Cr standards were obtained by mixing CrCl₃, K₂Cr₂O₇ and boron nitride powder. All of the standards contained 5% total chromium by weight but with various Cr(VI) percentages (10%, 20%, 30%, and 40%, respectively) [15]. Since the soil samples had low Mn [$<600 \text{ mg (kg soil)}^{-1}$] and water content ($<4\%$) and were stored only for 1 week prior to XANES analysis, the possibility of Cr(III) re-oxidation to Cr(VI) was low [24]. The XANES experiments were performed at the Wiggler beam line BL17C1 of the National Synchrotron Radiation Research Center in Taiwan. The electron storage ring was operated with 1.5 eV energy and 200 mA current. The Cr standards and soil samples were then fixed on the plastic sample holder with transparent tape for XANES analysis. Because of the low Cr concentration in the soil samples, the Cr standards and the soil samples were analyzed in the transmission mode and fluorescence mode respectively for enhancing the absorption intensity. The experiment data were normalized and plotted using the software program of Origin Pro 7.0.

3. Results and discussion

3.1. Properties of the studied soils and the added organic materials

The pH in the studied soils of Pinchung (Pc), Chingchung (Cf) and Taikang (Tk) represented an acid, neutral and alkaline condition, respectively (Table 1). The textures of the Pc and Tk soils were classified as clay soils and the Cf soil as loam. The Tk soil had a higher content of organic matter and total nitrogen than the Pc and Cf soils. In addition, the Pc soil had the highest content of free iron oxides among the three studied soils. The clay mineralogy of the three studied soils was quoted from Chen et al. [25] and FFTC/ASPAC [26] and shown in Table 1. The properties of the added organic materials are shown in Table 2. The pH range of these four kinds of organic materials ranged from 4.9 to 6. Among the four kinds of added organic materials, SBM had the highest amounts of DOC and protein, and SCDC had the lowest amounts. The difference in the properties of the soils and the added organic materials might affect the reduction of Cr(VI), resulting in different amounts of soil resin-extractable Cr(VI) after the wetting and drying cycles, and after the addition of various amending organic materials.

3.2. The effect of native and added organic materials on soil resin-extractable Cr(VI)

The total Cr concentration and resin-extractable Cr(VI) of Cr(VI)-spiked soils that went through three wetting and drying cycles is shown in Table 3. The total Cr concentration in Cr(VI)-spiked soils

without amending organic matters were confirmed to be close to $500 \text{ mg Cr (kg soil)}^{-1}$, indicating that the desired amounts of Cr(VI) were accurately spiked into the soils. It also shows that the resin-extractable Cr(VI) in all three Cr(VI)-spiked soils decreased after three wetting and drying cycles, without adding any organic materials. Among the three soils, the resin-extractable Cr(VI) of the Pc soil was the lowest, and only about 7% of spiked Cr(VI) could be extracted by the resins. It was demonstrated in our previous study that there was no detectable Cr(VI) peak in the XANES spectra of Cr(VI)-spiked Pc soil (Fig. 4 in Ref. [15]), and the decrease in resin-extractable Cr(VI) was as a result of the reduction of Cr(VI) to Cr(III) by native soil organic matter. Therefore, the low amounts of resin-extractable Cr(VI) in Pc soil may be mainly due to its low pH which favors the reduction of Cr(VI) into Cr(III) [8] (Table 1). In addition, due to the high content of iron oxide in Pc soil, the presence of Fe may enhance Cr(VI) reduction into Cr(III) through biotic and abiotic pathways [10,27]. Because the amount of resin-extractable Cr(VI) in Pc soil, without adding organic material, was very small and not detectable after adding organic materials (data not shown), the effectiveness of adding organic materials to decrease the extractable Cr(VI) in Pc soil is not presented and not discussed. The effect of adding organic materials on resin-extractable Cr(VI) of the Tk and Cf soils are shown in Table 4. It indicates that adding organic materials to Cr(VI)-spiked soils significantly ($p < 0.05$) decreases the resin-extractable Cr(VI). Less than 11% of the spiked-Cr(VI) could be extracted from the Cf and Tk soils after adding 1% organic matter of the tested organic materials, after they had been incubated for 40 days. When the addition of organic matter increased to 2%, less than 6% of the spiked-Cr(VI) could be extracted by resins. Adding organic materials into soils can also increase the activity of microbes in the soil, thereby promoting Cr(VI) reduction [5]. Therefore, adding any of these four organic materials to Cr(VI)-spiked soils can significantly decrease the extractable Cr(VI).

3.3. Comparing the effectiveness of these four organic materials to decrease soil resin-extractable Cr(VI)

A comparison of the effectiveness of these four organic materials to decrease soil resin-extractable Cr(VI) in Cf soil, shows that the extractable Cr(VI) decreased to 13.1 and 6.4 mg (kg soil)^{-1} after adding 1% organic matter in the form of SBM and RB respectively after 8 days of incubation. However, the same length of incubation and the same amounts of organic matter, but in the form of SCDC and CDC, resulted in a smaller decrease of resin-extractable Cr(VI). A similar result was also found in the Tk soil. These results suggest that SBM and RB are more effective for decreasing soil resin-extractable Cr(VI) than SCDC and CDC. The rate of decreasing resin-extractable Cr(VI) when adding 1% of organic matter of any of the four organic materials were fitted by the first-order kinetics

Table 1
Properties and clay mineralogy of the studied soils

| | Pinchen (Pc) | Chengchung (Cf) | Taikang (Tk) |
|--|--|--------------------------------|-----------------------------|
| pH (soil:H ₂ O = 1:1) | 4.2 | 7.7 | 8.1 |
| Particle size fraction | | | |
| Sand (g kg ⁻¹) | 58 | 364 | 101 |
| Silt (g kg ⁻¹) | 387 | 404 | 226 |
| Clay (g kg ⁻¹) | 555 | 232 | 673 |
| Texture | Clay | Loam | Clay |
| Organic carbon (g kg ⁻¹) | 8.80 | 8.50 | 16.3 |
| Total N (g kg ⁻¹) | 0.73 | 1.2 | 1.6 |
| Free iron oxides (g kg ⁻¹) | 37.1 | 13.9 | 24.1 |
| Clay mineralogy | Illite (30%), kaolinite (30%), vermiculite (30%) | Illite (>40%), kaolinite (20%) | Mica (30%), kaolinite (30%) |

Table 2
Properties of the added organic materials (g kg⁻¹)

| | Sugarcane dregs compost | Cattle-dung compost | Soybean meal | Rice bran |
|----------------------------------|-------------------------|---------------------|--------------|-----------|
| pH (O.M.:H ₂ O = 1:5) | 4.9 | 5.6 | 5.7 | 6.0 |
| Ash | 485 | 152 | 82.2 | 109 |
| Organic matter | 514.6 | 849.2 | 917.8 | 891.0 |
| Protein | 56.0 | 360 | 491 | 162 |
| Crude lipid | 8.70 | 7.60 | 11.0 | 150 |
| Soluble sugars | N.D. ^a | 0.9 | 2.5 | 3.1 |
| Hemicellulose | N.D. | 1.5 | 50 | 30 |
| Cellulose + lignin | 450 | 479 | 363 | 545 |
| Dissolved organic carbon (DOC) | 5.6 | 12.3 | 54.6 | 38.8 |
| Organic carbon | 241.0 | 446.9 | 434.0 | 440.0 |
| Total N | 9.0 | 58 | 79 | 26 |
| C/N ratio | 27 | 7.8 | 5.5 | 17 |

^a N.D.: not detectable (≤ 0.5 g kg⁻¹).

Table 3
Total Cr concentration and soil resin-extractable Cr(VI) of Cr(VI)-spiked soils after three wetting–drying cycles (mg (kg soil)⁻¹)

| Soil | Cr(VI)-spiked | Total Cr concentration ^a | Resin-extractable Cr(VI) |
|-----------------|---------------|-------------------------------------|--------------------------|
| Pinchen (Pc) | 0 | 42.6 ± 10 | N.D. ^b |
| | 500 | 481 ± 7 | 33.3 ± 0.9 |
| Chengchung (Cf) | 0 | 22.7 ± 2 | N.D. |
| | 500 | 494 ± 4 | 161 ± 8 |
| Taikang (Tk) | 0 | 48.4 ± 6 | N.D. |
| | 500 | 482 ± 5 | 150 ± 12 |

^a Soil samples were digested by aqua regia.

^b N.D.: not detectable (≤ 6 mg (kg soil)⁻¹).

equation as follows:

$$Y(t) = Y_0 e^{-kt} \quad (1)$$

where $Y(t)$ is the soil resin-extractable Cr(VI) concentration [mg (kg soil)⁻¹] after adding organic materials for the incubation times, t (days), Y_0 is the soil resin-extractable Cr(VI) concentration [mg (kg soil)⁻¹] before adding organic matters, k is the rate coefficient (day⁻¹). The rate coefficients are shown in Table 5, and

indicate that they follow the order of RB \approx SBM > CDC > SCDC. The results suggest that the rate of decreasing soil resin-extractable Cr(VI) by adding RB and SBM is faster than by adding CDC and SCDC. The difference in rate coefficients among tested organic materials can be explained by the different contents of DOC, composition, and C/N ratio of the added organic materials. Previous research has indicated that the amount of DOC in organic materials has a positive correlation to the Cr(VI) reduction rate [1]. As shown in Table 2, the

Table 4
The amounts of resin-extractable Cr(VI) (mg (kg soil)⁻¹) in Chengchung (Cf) and Taikang (Tk) Cr(VI)-spiked soils (500 mg Cr(VI) (kg soil)⁻¹) after amending 1% or 2% organic matter in the form of SCDC, CDC, SBM, and RB for various incubation times

| Soil | Organic materials added | Incubation time after organic materials addition (days) | | | | | |
|---------|-------------------------|---|-------------|-------------------|-------------|-------------------|-------------|
| | | 4 | 8 | 12 | 20 | 30 | 40 |
| Cf | 0 (control) | 116a ^a ± 1 | 125a ± 1 | 120a ± 2 | 112a ± 1 | N.A. ^b | 114a ± 2 |
| | SCDC 1% | 65.8b ± 1 | 65.9b ± 0.8 | 58.3b ± 0.4 | 45.0b ± 0.3 | 27.3a ± 2 | 34.4b ± 3 |
| | CDC 1% | 51.2c ± 0.2 | 40.9c ± 0.6 | 44.6c ± 1 | 31.3c ± 0.9 | 17.6b ± 0.7 | 18.3c ± 0.3 |
| | SBM 1% | 57.0c ± 2 | 13.1d ± 0.4 | N.D. ^d | N.D. | N.D. | N.D. |
| | RB 1% | 27.7d ± 0.5 | 6.4e ± 0.3 | N.D. | N.D. | N.D. | N.D. |
| | SCDC 2% | 26.6c ± 1.2 | 36.1b ± 0.2 | 37.3b ± 0.7 | 21.1b ± 2 | 11.0a ± 0.3 | 11.9b ± 0.1 |
| | CDC 2% | 17.6d ± 0.4 | 14.9d ± 0.2 | 15.2d ± 0.3 | 8.9d ± 0.1 | N.D. | N.D. |
| | SBM 2% | 41.0b ± 0.5 | 23.1c ± 1.9 | 19.0c ± 0.3 | 12.4c ± 0.3 | 6.8b ± 0.2 | 6.9c ± 0.1 |
| | RB 2% | 6.9e ± 0.2 | N.D. | N.D. | N.D. | N.D. | N.D. |
| | Tk | 0 (control) | 125a ± 6 | 95.7a ± 7 | 104a ± 1 | 108a ± 5 | 101a ± 1 |
| SCDC 1% | | 84.1b ± 3.1 | 56.3b ± 2.1 | 80.6b ± 2 | 63.7b ± 1 | 46.2b ± 2 | 53.1b ± 5 |
| CDC 1% | | 52.3d ± 2 | 22.7c ± 0.7 | 42.3c ± 0.3 | 30.0c ± 0.4 | 11.8b ± 0.4 | 24.9c ± 0.3 |
| SBM 1% | | 23.7c ± 0.6 | N.D. | N.D. | N.D. | N.D. | N.D. |
| RB 1% | | 18.0e ± 0.2 | 6.7d ± 0.1 | 9.7d ± 0.5 | N.D. | N.D. | N.D. |
| SCDC 2% | | 62.4b ± 7 | 36.4b ± 0.4 | 56.8b ± 1 | 38.4b ± 2 | 29.1b ± 0.2 | 28.7b ± 0.6 |
| CDC 2% | | 21.9c ± 3 | 9.30c ± 0.5 | 13.6c ± 0.5 | 6.10c ± 0.2 | N.D. | N.D. |
| SBM 2% | | 9.4d ± 0.8 | N.D. | N.D. | N.D. | N.D. | N.D. |
| RB 2% | | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |

^a Values followed by the same letter within each treatment of organic materials addition and control at same incubation time of each soil mean no statistically significant difference at 5% level according to Duncan's multiple range test.

^b N.A.: not available.

^c SCDC: sugarcane dregs compost; CDC: cattle-dung compost; SBM: soybean meal; RB: rice bran.

^d N.D.: not detectable (≤ 6 mg (kg soil)⁻¹).

Table 5

The first-order kinetics rate coefficients of decreasing soil resin-extractable Cr(VI) of the Chengchung (Cf) and Taikang (Tk) Cr(VI)-contaminated soils after amending with 1% organic matter

| Organic material added | Cf soil | | Tk soil | |
|------------------------|---------|-------|---------|-------|
| | | R^2 | | R^2 |
| SCDC ^a | 0.090 | 0.368 | 0.052 | 0.680 |
| CDC | 0.17 | 0.810 | 0.19 | 0.810 |
| SBM | 0.28 | 0.994 | 0.50 | 0.997 |
| RB | 0.44 | 0.999 | 0.47 | 0.999 |

^a SCDC: sugarcane dregs compost; CDC: cattle-dung compost; SBM: soybean meal; RB: rice bran.

RB and SBM had larger contents of DOC than did CDC and SCDC, and the rate coefficients for decreasing soil extractable Cr(VI) of RB and SBM were higher than those for CDC and SCDC. In addition, several researches have demonstrated that the DOC and the small organic compounds released from the decomposition of organic materials can enhance the reduction of Cr(VI) [1,5,13,14]. Stevenson [28] indicated that protein is the most easily decomposed fraction among the components of plant residues, followed by carbohydrate, hemicellulose, cellulose and lignin. As indicated in Tables 2 and 3, SBM contains higher levels of easily decomposed substances such as protein than those of SCDC. As a result the amount of soil resin-extractable Cr(VI), of the soil amended with SBM, were lower than those amended with SCDC at the same rate of organic matter application and incubation time. Although the quantity of protein for CDC and SBM were similar, the amounts of DOC of the SBM were far higher than those of the CDC. In addition, the higher contents of DOC in SBM, and the easily decomposed substances of SBM compared to those of CDC result in smaller amounts of resin-extractable Cr(VI). Although the easily decomposed fractions of SBM and RB in soils were similar, the higher C/N ratio of RB compared to that of SBM can result in more Cr(VI) in soils being reduced into Cr(III). As a result, the effectiveness of decreasing soil resin-extractable Cr(VI) by adding RB was higher than when adding SBM in the studied soils.

As mentioned above, the soil resin-extractable Cr(VI) was decreased significantly by adding any of the four organic materials. The reduction of Cr(VI) into Cr(III) by adding organic materials results in a decrease of soil resin-extractable Cr(VI) was confirmed by the XANES spectra. The XANES spectra of soil samples showed that the heights of the peak at 5992 eV, a characteristic that is unique to Cr(VI) and not to Cr(III), after adding 1% organic matter in the form of SBM and CDC respectively for 20 days of incubation, were lower than those without organic matter amendment (Fig. 1(b) and (c)). According to the calibration curve of the Cr(VI) peak height vs. the Cr(VI) percentage (Fig. 1(a)), there were about 12% and 24% Cr(VI) in Cr(VI)-spiked Cf and Tk soils without adding organic matter, respectively. With 1% CDC amendment, the Cr(VI) percentage was decreased to about 5% in Cf and Tk soils, and both the Cr(VI) percentages in 1% SBM amended Cf and Tk soils were decreased below the detection limit (Fig. 1). The results of the XANES spectra indicated that the Cr(VI) in the soil was reduced into Cr(III) after organic materials amendment, and that the decrease in extractable Cr(VI) after being amended by organic materials was mainly due to the reduction of Cr(VI) into Cr(III) instead of the sorption of Cr(VI) by soil solids. However, when comparing the results of XANES spectra with the amounts of resin-extractable Cr(VI), it showed that the resin-extraction method was more sensitive than the XANES method. Besides, the XANES analysis was used to determine the total amount of Cr(VI) in the soils, but the resin-extraction method was used to extract soil available Cr(VI) in Cr(VI)-spiked soils [2,15].

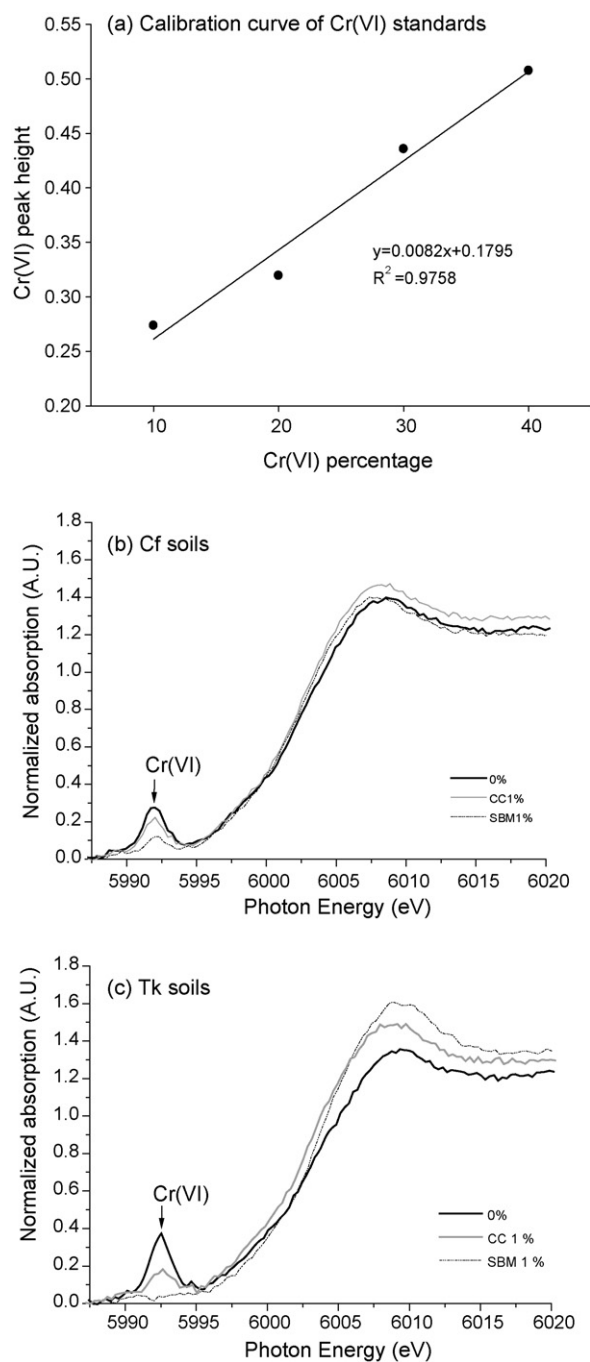


Fig. 1. The calibration curve of Cr(VI) peak height in XANES spectra vs. Cr(VI) percentage of Cr standard samples and the XANES spectra of Cr(VI)-spiked soils [$500 \text{ mg Cr(VI)} (\text{kg soil})^{-1}$] without and with adding 1% organic matter in the form of cattle-dung compost (CC) and soybean meal (SBM) for 20 days incubation.

Therefore, the effectiveness of four organic matter amendments in remediating Cr(VI)-contaminated soils was mainly assessed by using resin-extraction method rather than by using XANES analysis in this study. Several studies have demonstrated that both biotic and abiotic processes were involved in the reduction of Cr(VI) into Cr(III) in the natural environment [5,10,14,29,30]. Since we did not sterilize these studied soils, it is difficult to confirm whether the biotic or abiotic process was the main pathway for Cr(VI) reduction into Cr(III) in the organic matter amended soils.

4. Conclusion

The amounts of resin-extractable Cr(VI) in Cr(VI)-contaminated soils was effectively decreased by adding 1% organic matter of tested organic materials. The results of the XANES spectra indicated that the decrease of resin-extractable Cr(VI) was mainly due to the reduction of Cr(VI) by the added organic matter. Among the tested organic materials, SBM and RB contained a higher amount of DOC and easily decomposed substances. As a result they were more effective in decreasing resin-extractable Cr(VI) in Cr(VI)-contaminated soils than SCDC and CDC for the same amounts of organic matter applied and the same incubation time. Therefore, it is suggested that organic materials containing large amounts of DOC and consisting of easily decomposed matter are good candidates for amending Cr(VI)-contaminated soils by effectively decreasing the amount of soil resin-extractable Cr(VI).

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