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The effect of low-molecular-weight organic-acids (LMWOAs) on treatment of chromium-contaminated soils by compost-phytoremediation: Kinetics of the chromium release and fractionation

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ABSTRACT

A soil–plant biological system was developed from chromium (Cr) polluted soil treated by the compost-phytoremediation method. The transformation and migration of the Cr in this system is comprehensively studied in this research. The results illustrated that the co-composting treatment can reduce the Cr availability from 39% (F1 was about 31% of total, F2 was about 8% of total) to less than 2% by stabilizing the Cr. However, herbaceous plants can accumulate the concentrations of Cr from 113.8 to 265.2 mg/kg in the two crops, even though the concentration of soluble Cr in the substrate soil was below 0.1 mg/L. Cr can be assimilated and easily transferred in the tissues of plants because the low-molecular-weight organic-acids (LMWOAs) derived from the plant root increase the bioavailability of Cr. The amount of extracted Cr dramatically increased when the organic acids were substituted in this order: citric acid > malic acid > tartaric acid > oxalic acid > acetic acid. On average the maximum (147.4 mg/kg) and the minimum (78.75 mg/kg) Cr were extracted by 20 mmol/L citric acid and acetic acid, respectively. The desorption of Cr in different acid solutions can be predicted by the pseudo second-order kinetics. The exchangeable Cr, carbonate-bound Cr, and residual Cr decreased, while Fe–Mn oxide bound Cr and organic bound Cr increased in the soil solid phase. According to the experimental results, the organic acids will promote the desorption and chelation processes of Cr, leading to the remobilization of Cr in the soil.

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Introduction

Chromium is an important basic material for the chemical industry due to its corrosion resistance and aesthetic properties (Baikousi et al., 2012). It is applied in various processes such as

electroplating process, leather tanning, pigment manufacture, steel making, wood preservative, and textile dyeing (Zhou and Song, 2004). Chromium-contaminated soil is mainly caused by the discharge of chromium containing waste. The dissolvable hexavalent chromium Cr(VI), which ranges from 0.3% to 1.5%

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in chromium slag, can lead to severe contamination of the environment by flowing into soil, surface water and ground water with rainfall. It was reported that the content of total Cr in soils near chromium residue stockpiles was in the range of 656.1 to 3500.1 mg/kg, and the soluble Cr(VI) in soils near slag heaps were in the range of 49.5 to 252.7 mg/kg (Sunhong et al., 2009). Obviously, the development of remediation technologies for soils contaminated by chromium residue is one of the more important and urgent tasks for the chromium industry.

Compared with traditional methods, biological remediation has some distinctive advantages such as low investment/expense and the variety of treatment methods. Compost-phytoremediation technology is an attractive alternative because the metal toxicity of soil is lower and nutrient sources are supplied to the plant growth (Chiu et al., 2006; Elouear et al., 2016; Kumpiene et al., 2008). It was noted that organic amendments are considered especially effective in Cr stabilization (Wiszniewska et al., 2016), through Cr(VI) oxy-anions are readily reduced to Cr(III) by electron donors such as organic matter (Loubna et al., 2015). Hanc et al. reported that waste compost could convert water soluble Cr change into crystalline-precipitated Cr. As a consequence, the ultimate goal of biological remediation is to realize true sustainable land use, especially in agriculture and forestry (Hanc et al., 2012; Kovacs and Szemmelveisz, 2017).

Low-molecular-weight organic-acids (LMWOAs) include oxalic, succinic, tartaric, formic, malic, acetic, butyric, lactic, fumaric, maleic, and citric acids (Xiao and Wu, 2014), all of which can derive from the decomposition of soil matter, plant root exudates, microbial metabolites, etc. within the rhizosphere soils (Qin et al., 2004; Taghipour and Jalali, 2013). Concentrations of LMWOAs in soils are quite low, and the concentration of LMWOAs in rhizosphere soils is 0.2–0.5 hydrogen ion concentration (pH) units higher than that in non-rhizosphere soil (Lu et al., 2007; Taghipour and Jalali, 2013). High amounts of LMWOAs that are concentrated in rhizosphere soils can alter the heavy metal chemical process through chelation, precipitation and oxidation–reduction reactions (Afshan et al., 2015; Taghipour and Jalali, 2016). It has been shown that desorption efficiency was dependent on molecular compositions and LMWOAs and the stability constant of the LMWOA–metal complexes (Qin et al., 2004). Some studies have reported that the complexation of metals and LMWOAs can strongly alter the fixation of metals by soil organic matter, oxides, and clays, while increasing the total amounts of dissolved cations in soil (Banks et al., 2006; Malek et al., 2009). Thus such properties can be used in phytoremediation to increase metal bioavailability, impact the metal solubility, uptake into plants, and minimize the environmental risk (Afshan et al., 2015; Lu et al., 2007).

Most previous researchers have focused on promoting the solubility of metals in the presence of organic acids and accumulating high levels of metals in plant biomass (Balseiro-Romero et al., 2014; Kim et al., 2010; Wiszniewska et al., 2016). But little research had investigated the relationship among Cr, organic acids, and Cr polluted soils treated by co-compost. Studies on the effect of organic acids on the kinetic release of Cr from Cr polluted soils treated by co-compost are scarce. Based on the above considerations, a soil–plant biological system was created from Cr polluted soil treated by the compost-phytoremediation method. The transformation and

migration of the Cr in this system is comprehensively studied in this research. The objectives of the present work were to (1) evaluate the effects of chicken manure co-composting on the growth and the heavy metal accumulation of herbaceous plants (*Cynodon dactylon* (L.) Pers. and *Festuca arundinacea* Schreb.) in Cr polluted soil; (2) compare the amount of Cr release from chicken manure compost biomass treated soil under different concentrations of organic acids; (3) explore the mechanism of organic acids on Cr desorption in treated soil; and (4) illustrate the kinetics of Cr release in the treated soil under the presence of organic acids (citric acid and acetic acid). The results of this study can be used to predict the fate and transport in the Cr polluted soil by treated compost-assisted phytoextraction.

1. Materials and methods

1.1. Cr contaminated soil treated by co-composting

The origin and composition of the feedstocks used in the co-composting experiment were as follows. The Cr polluted soil samples were collected from over-20-year-old chromate plants located in Yima City of HeNan Province. Chicken manure was obtained from livestock farms in suburban areas of Beijing, China. Maize straw was obtained from farmland in the rural outskirts of Beijing, and the straw was air-dried and cut into 10–20 mm lengths before composting. An experimental composting system (self-made experimental equipment) with a dry weight of approximately 10 kg materials was set up indoors. The stock materials for the compost heap consisted of chicken manure and dry maize straw with an adjusted C/N ratio of 30:1. The moisture content of the stock material was initially adjusted to approximately 60%. After sampling, the moisture content was monitored and adjusted to approximately 50%–60% by the addition of sterile deionized water throughout the composting period. The mixture was packed loosely in a closed fermentation tank with dimensions of 0.25 m × 0.25 m × 0.5 m (length × width × height). The fermentation tank is made of a double stainless steel shell, and can be heated using a water bath to simulate regularity of temperature change. Aeration of the compost pile relied on natural ventilation and turning. The mixture was turned three times a week during the first 3 weeks, after which it was turned once a week. A perforated metal plate was equipped at the bottom to distribute the air supplied from air compressors, and air was discharged from a fermentation tank through the top of composting materials to a collection bottle with boric acid solution. In this study, six barrels were divided into three groups (each group containing two repeats). Mixture of chicken manure and Cr polluted soil with various dry weight ratios (C0 (1:0), C1 (1:1), C2 (1:2)) was carried out. After 50 days, the sample was prepared for the phytoremediation experiments. At each sampling occasion, three samples were periodically taken from the surface, center, and bottom depths of the entire pile and mixed together for parameter analysis.

1.2. Batch experiments for Cr(VI) phytoremediation

A glasshouse growth experiment was set up to investigate the stabilization effect of Cr polluted soil treated by co-composting.

The concentrations of total Cr in the soil treated by composting were studied in pot and germinating experiments. There were eight groups. CK denotes chicken manure composting sample without soil, and others were mixtures of chicken manure and soil co-composting samples at different ratios, as follows: T₁ (T_{Cr} 300 mg/kg, Cr(VI) 1.23 mg/L); T₂: (T_{Cr} 600 mg/kg, Cr(VI) 2.45 mg/L); T₃: (T_{Cr} 900 mg/kg, Cr(VI) 3.68 mg/L); T₄: (T_{Cr} 1200 mg/kg, Cr(VI) 4.90 mg/L); T₅: (T_{Cr} 1500 mg/kg, Cr(VI) 6.13 mg/L); T₆: (T_{Cr} 2400 mg/kg, Cr(VI) 9.81 mg/L); and T₇: (T_{Cr} 3000 mg/kg, Cr(VI) 11.25 mg/L). Herbaceous plants (*Cynodon dactylon* (L.) Pers. and *Festuca arundinacea* Schreb.) were used as the test plants. Each pot contained 1 kg soil (dry weight). Two hundred seeds were sown in each pot. Each treatment was three replicates. During the germination period, the moisture content of the soil was maintained at 80% of field capacity. The plants were harvested 12 weeks after sowing and dried at 70°C with a forced draft oven. The dry weights were recorded, the plant materials were ground and digested with concentrated HNO₃ (Afshan et al., 2015), and the concentration of Cr in the plant digest was determined with Inductively Coupled Plasma Mass Spectrometry (ICP–MS) (NeXION 300X, PerkinElmer, USA). Two crop harvests were conducted in the pot experiments within a year in this study. After the first batch of plants was harvested, the second batch of plants continued to grow in the same substrate soils.

1.3. Release of Cr

LMWOAs are compounds of unsaturated carbon and hydroxyl groups that consist of mono-, di-, and tricarboxylic acids (Lu et al., 2007). In this study, five organic acids (citric acid, tartaric acid, oxalic acid, acetic acid, and malic acid) and CaCl₂ were chosen as organic chelates in order to investigate the release of Cr from contaminated soil treated by chicken manure co-composting. It was indicated that the average concentration of these organic acids was approximately 1–100 μmol/L in the soil solution (Xiao and Wu, 2014). They also have various pK_a, ligand forms and numerous functional groups, as shown in Table 1 (Serjeant and Dempsey, 1979). CaCl₂ has often served to represent soil background electrolytes in soil desorption research (Qin et al., 2004; Taghipour and Jalali, 2016). In this study, it was selected to be a comparative extractant.

Cr extractions were performed at room temperature. The soil samples (1 g) were extracted with 10 mL of 5, 10, 15, and 20 mmol/L of citric acid, tartaric acid, oxalic acid, acetic acid, malic acid and CaCl₂ solutions. The suspensions were shaken for 2 hr at 220 r/min in a shaking machine (HT-2102, HerryTech, Shanghai, China) and, centrifuged at 5000 r/min

for 10 min; then, the Cr concentration in the supernatant was analyzed by ICP–MS.

The kinetic experiments were performed in 5, 10, 15, and 20 mmol/L citric acid, acetic acid and 10 mmol/L CaCl₂ solution, and the suspensions were shaken for 0.5 hr, 1 hr, 2 hr, 4 hr, 8 hr, 16 hr, 24 hr, and 48 hr at 25°C, and then treated the same as those in the Cr extraction experiments. Two equations, namely pseudo-second-order kinetics (Eq. (1)) and Elovich kinetics (Eq. (2)), were used to study the release of Cr with time.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{1}$$

$$q_t = A \ln t + B \tag{2}$$

where q_t (mg/kg) is the amount of Cr released at different desorption times, t (hr) is the desorption time, q_e (mg/kg) is the cumulative amount of Cr released at different desorption times, k is the pseudo-second-order rate constant, and A and B are the Elovich kinetic rate constants. These kinetic models were tested by coefficient of determination (R²), and the standard errors (SE), which could be calculated by the following equation:

$$SE = \sum \frac{(q_{e, \text{exp.}} - q_{e, \text{cal.}})^2}{q_{e, \text{cal.}}} \tag{3}$$

where, q_{e,exp.}, and q_{e,cal.}, represent the measured and predicted Cr released to the experimental data, respectively. The smaller the SE, the better the equation describes the kinetics.

Metal Cr speciation analyses were carried out before and after release of Cr from soils. The sequential extraction of Tessier et al. with modification was used (Tessier et al., 1979; Zorpas et al., 2003). One gram of each sample was weighed and placed in a 50 mL polycarbonate centrifuge tube. The extraction steps were as follows:

- (1) Exchangeable (F1). The compost sample was extracted at room temperature with 8 mL of 1 mol/L MgCl₂ by shaking for 1 hr.
- (2) Carbonate-bound (F2). The residue from (1) was extracted with 8 mL of 1 mol/L CH₃COONa at pH 5.0 by shaking for 5 hr.
- (3) Fe–Mn oxide bound (F3). The residue from (2) was extracted with 20 mL of 0.04 mol/L (NH₂OH·HCl) in 25% acetic acid (V/V) at 96°C for 6 hr by shaking.
- (4) Organic matter bound (F4). To the residue from (3), 10 mL of 0.02 mol/L HNO₃ and 5 mL of H₂O₂ (30%) at pH 2.0 were added at 85°C for 2 hr of interval shaking. Then, an additional 3 mL of H₂O₂ (30%) at pH 2.0 was added at 85°C for 3 hr of interval shaking. After cooling, 5 mL of 3.2 mol/L NHOAc was added and agitated continuously for 30 min.
- (5) Residual (F5). The residue from (4) was digested with a mixture of HF and HClO₄ (5:1, V/V).

1.4. Chromium analysis

Water-soluble Cr was determined by ICP–MS after the samples had been mechanically shaken in water suspension at a ratio

Table 1 – Low-molecular-weight organic-acids used in this study.

Organic acid	Molecular formula	Ligand form	pK _a ^a
Citric acid	CH ₂ C(OH)CH ₂ (COOH) ₃	H ₃ L	3.13, 4.76, 6.40
Malic acid	CH ₂ CH(OH)(COOH) ₂	H ₂ L	3.46, 5.10
Oxalic acid	(COOH) ₂	H ₂ L	1.252, 4.266
Tartaric acid	HOCOCH(OH)CH(OH)COOH	H ₂ L	2.98, 4.34
Acetic acid	CH ₃ COOH	HL	4.76

Table 2 – Physicochemical properties of Cr polluted soil and chicken manure used in the pot experiment.

	Chicken manure	Dry straw	Soil	Chicken manure compost (C0, last)	Soil with compost (C1, initial)	Soil with compost (C1, last)	Soil with compost (C2, initial)	Soil with compost (C2, last)
Total Organic Carbon; TN Total Carbon (TOC) (g/kg)	148	542	4.5	312	214.35	127.15	186.5	112.45
TN (g/kg)	23.06	8.9	0.8	22.87	10.74	11.10	8.69	9.26
C/N	6.4	69.60	5.62	13.64	19.96	11.45	21.46	12.15
pH	8.8	–	7.2	10	8.8	9.7	8.2	9.5
T _{Cr} (mg/kg)	56	68	5458	38	1920	2022	2816	3104
Cr(VI) (mg/L)	0	0	257.9	0	60.45	8.26	90.85	11.36
Fe (g/kg)	–	–	355.84	–	125.18	136.45	200.27	218.32
Mn (g/kg)	–	–	68.66	–	24.15	28.46	38.64	45.54

Individual treatments are: chicken manure and polluted soil mixture compost with various dry weight ratios (C0 (1:0), C1 (1:1), C2 (1:2)). Values represent mean (n ≤ 3). (–) not detected.

of 1:10 (W/V) at 200 r/min for 24 hr. The total Cr concentrations in samples were determined by ICP–MS after the samples had been digested with a mixture of hydrofluoric (40.0%), nitric (68.0%), and perchloric (72.0%) acid.

1.5. Data analysis

To ensure the reliability of chemical analyses method and reproducibility of data, the blanks and control plants and soil reference materials in all extraction batches have been systematically used. Each extracted sample testing was conducted in triplicate and only results with a variation coefficient of less than 10% were kept for further handling. All testing samples were within limits of standard sample detection. The statistical analysis of data was applied to compute the mean and standard deviation. All statistical analysis was carried out using the IBM SPSS Statistics v.19.0 for Windows (IBM Corp.). The comparison of the averages was analyzed statistically with the Tukey Test, and the statistical significant differences of hypotheses were used at $p < 0.05$.

2. Results and discussion

2.1. Plant growth and chromium uptake

2.1.1. Characteristics of the Cr polluted soil and chicken manure
Basic physicochemical characteristics of the Cr polluted soil and chicken manure are shown in Table 2. The concentration of Cr in the F1, F2, F3, F4, and F5 fractions was 1717, 368.6, 291.5, 7.3, and 3100.6 mg/kg, respectively. A high content of Cr was found in the soil, especially in the exchangeable fraction, due to the contamination caused by the local production of chromium salts and the high content of Fe and Mn in the soil. Chicken manure contains much higher levels of total C and N (148 and, 23.06 g/kg, respectively). Concerning Cr in C1 co-composting, at the end of the composting period, the available fractions are reduced from 39% (F1 was about 31% of total, F2 was about 8% of total) to less than 2%. And the amount of Cr associated with the organic fraction rose from less than 1% of the total at the start of the composting period to 28% at the end. The water-soluble Cr(VI) content significantly

Table 3 – Effect of different concentrations of total Cr treated by composting on biomass of *Cynodon dactylon* (L.) Pers. and *Festuca arundinacea* Schreb.

			CK	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇
The first harvest	<i>Cynodon dactylon</i> (L.) Pers.	Germination rate (%)	90.06 ± 0.42a	88.5 ± 0.3b	86.9 ± 0.1c	88.4 ± 0.1bd	87.2 ± 0.1e	85.7 ± 0.15f	0	0
		Leaf weight (g)	6.7 ± 0.1a	5.05 ± 0.02b	4.61 ± 0.02c	9.61 ± 0.01d	9.04 ± 0.01e	4.92 ± 0.01f	0	0
		Root weight (g)	1.4 ± 0.2a	1.65 ± 0.03a	0.84 ± 0.01c	2.05 ± 0.00d	1.86 ± 0.0e	0.77 ± 0.01f	0	0
	<i>Festuca arundinacea</i> Schreb.	Germination rate (%)	94.8 ± 0.25a	92.4 ± 0.45a	93.4 ± 0.1c	94.6 ± 0.2a	89.4 ± 0.15e	12.6 ± 0f	0	0
		Leaf weight (g)	5.42 ± 0.07a	4.78 ± 0.03b	4.61 ± 0.01c	6.35 ± 0.03d	4.49 ± 0.02e	0.23 ± 0f	0.06 ± 0	0
		Root weight (g)	1.2 ± 0.06a	1.64 ± 0.03b	1.49 ± 0.03c	2.87 ± 0.03d	2.49 ± 0.02e	0.04 ± 0f	0.01 ± 0	0
The second harvest	<i>Cynodon dactylon</i> (L.) Pers.	Germination rate (%)	84.4 ± 0.2a	82.4 ± 0.0b	85.4 ± 0.15c	88.4 ± 0.1d	86.9 ± 0.06e	74.5 ± 0.15f	0	0
		Leaf weight (g)	4.12 ± 0.03a	3.4 ± 0.02b	4.3 ± 0.03c	9.3 ± 0.02d	8.8 ± 0.01e	2.3 ± 0.02f	0	0
		Root weight (g)	1.22 ± 0.02a	1.01 ± 0.04b	1.1 ± 0.03bc	2 ± 0.02d	1.2 ± 0.02a	0.8 ± 0.01f	0	0
			86.4 ± 0.58a	84.6 ± 0.2b		87.4 ± 0.2a		16.8 ± 0.1f	0	0

Table 4 – Effect of different concentrations of total Cr treated by composting on Cr concentration uptake by *Cynodon dactylon* (L.) Pers. and *Festuca arundinacea* Schreb.

		Cr (mg/kg)	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇
The first harvest	<i>Cynodon dactylon</i> (L.) Pers.	Leaf	37.16 ± 0.35a	45.76 ± 0.15b	51.9 ± 0.1c	65.8 ± 0d	55.2 ± 0.02e	–	–
		Root	90.8 ± 0.1a	133.8 ± 0.15b	154.7 ± 0.06c	144.9 ± 0.1d	120.8 ± 0.83e	–	–
		Total	128 ± 0.45a	179.6 ± 0.3b	206.6 ± 0.15c	210.6 ± 0.1d	176 ± 0.84e	–	–
	<i>Festuca arundinacea</i> Schreb.	Leaf	29.8 ± 0.3a	43.8 ± 0.06b	48.2 ± 0.1c	62.5 ± 0.02d	–	–	–
		Root	84 ± 0.25a	132.6 ± 0.15b	131.6 ± 0.12c	128.4 ± 0.06d	–	–	–
		Total	113.8 ± 0.55a	176.4 ± 0.21b	179.8 ± 0.21c	190.9 ± 0.08d	–	–	–
The second harvest	<i>Cynodon dactylon</i> (L.) Pers.	Leaf	12.8 ± 0.1a	20.82 ± 0.03b	21.12 ± 0.01c	28.8 ± 0.02d	25.6 ± 0.03e	–	–
		Root	123.4 ± 0.15a	153.6 ± 0.02b	176.4 ± 0.1c	216 ± 0.25d	207.4 ± 0.59e	–	–
		Total	136.2 ± 0.25a	174.42 ± 0.05b	197.52 ± 0.11c	244.8 ± 0.27d	232.67 ± 0.61e	–	–
	<i>Festuca arundinacea</i> Schreb.	Leaf	20.68 ± 0.01a	41 ± 0.12b	41.6 ± 0.15c	54.6 ± 0.03d	–	–	–
		Root	109.2 ± 0.06a	205 ± 0.1b	211.56 ± 0.02c	210.6 ± 0.03d	–	–	–
		Total	219.88 ± 0.06a	246 ± 0.2b	253.16 ± 0.17c	265.2 ± 0.06d	–	–	–

Values represent mean ± SD (n = 3). Different letters indicate that values are significant different at p < 0.05. (–) not detected.

decreased from 60.45 to 8.26 mg/L in the Cr polluted soil, indicating that the compost was effective in lowering the metal toxicity of the soil.

2.1.2. Effect of treatments on plant growth

Table 3 presents the germination rate and the final dried biomass of herbaceous plant matter after harvesting. There are no visual symptoms of metal Cr toxicity from T1 to T5 in the germination and growth of herbaceous plants, but very few plants can grow after T5. The heaviest of the total dry mass of herbaceous plant was T3 in two crops, even heavier than T1. These results showed that a high concentration of Cr was seriously harmful to plant growth and development, but only at or above in a certain range of concentration (1200 mg/kg of total Cr and 8.43 mg/kg of Cr(VI)). It has been reported that a low concentration of Cr can promote the growth of plants by promoting the growth of roots and root hairs, and by increasing the share of medulla and cortical tissue layers of the roots (Gupta et al., 2009; Shanker et al., 2004). Similar results were also found in the research of Cary et al. (Cary et al., 1977), but they postulated that Cr was not an essential element in plant nutrition such that it could accelerate plant growth. The reason for this may be that: when an appropriate amount of chromium elements was applied, the uptake of nutrients by plants and their transformation and utilization were promoted.

2.1.3. Cr concentration in plant shoots and roots

The total content of Cr accumulated in the entire plant tissues of two crops of herbaceous plants growing in seven test soils is shown in Table 4. The total Cr content in plants grown in the T4 (1200 mg/kg) was the highest, which indicates the accumulation in and high tolerance of the tested herbaceous plants. Accumulation of Cr is greatest in roots and lowest in leaves. The root is one of the most important plant organs, as it is also the main alimentative organ for the growth, transport and assimilation of nutriment. Some studies reported that root cells subjected to heavy metal stress develop metabolic disorders and exhibit decreased root activity (Wiszniewska et al., 2016). Table 4 shows that with increasing Cr concentration, the total Cr content in roots increases. When the concentration of Cr in soil was 900–1200 mg/kg, the content of Cr extracted by roots was the highest. If the Cr concentration was above 1500 mg/kg, there would be an active toxicity distinct to plant roots.

2.1.4. Cr concentration in the substrate soil

After the first harvest, the soluble Cr(VI) concentrations of the substrate soils in pots were below 0.1 mg/L, and in some samples, Cr(VI) could not even be detected. This result indicated that the soluble Cr content in the substrate soil was very low, which could be attributed to the efficient compost-assisted phytoremediation in the treatment of the Cr polluted soil. According to Table 4, the plants can also accumulate high concentrations of Cr in the second crops. It was reported that LMWOAs produced in the rhizosphere could increase the bioavailability of heavy metals so that they were extracted and easily taken up by in the tissues of plants (Oburger et al., 2009; Xiao and Wu, 2014). Citric acid enhanced the bio-adsorption of Cr by *Pseudomonas aeruginosa* (Puranik and Paknikar, 1999).

2.2. Release of Cr from soil treated by co-composting in the presence of organic acids

Cr was released by successive extraction with 5, 10, 15, and 20 mmol/L citric acid, tartaric acid, oxalic acid, acetic acid, malic acid and 10 mmol/L CaCl₂ solutions. Quantities of Cr released with LMWOAs (other than acetic acid) were higher

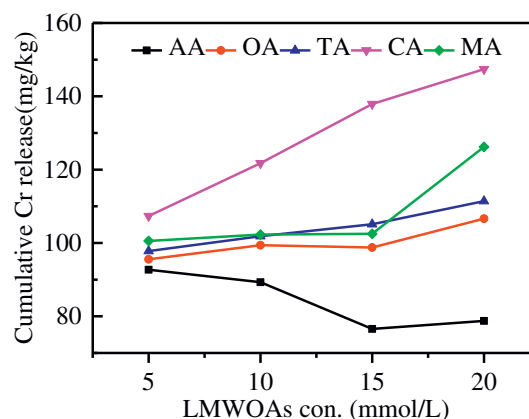


Fig. 1 – Mobilized Cr under different low-molecular-weight organic-acid concentrations (5, 10, 15, and 20 mmol/L citric acid, tartaric acid, oxalic acid, acetic acid, malic acid, respectively.) Values represent mean ± standard deviation (SD) (n = 3).

Table 5 – pH changes under different low-molecular-weight organic-acid concentrations.

Con. (mmol/L)	Citric acid		Malic acid		Tartaric acid		Oxalic acid		Acetic acid		CaCl ₂	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
5	8.91	9.45	9.04	9.50	9.02	9.48	9.10	9.42	9.12	9.35	–	–
10	8.25	9.06	8.36	9.10	8.33	9.02	8.41	9.15	8.86	9.24	8.36	8.84
15	7.16	8.58	7.35	8.69	7.29	8.66	7.26	8.54	7.86	8.52	–	–
20	6.54	7.98	6.50	8.26	6.65	8.31	6.75	8.42	7.54	8.26	–	–

(–) not detected. Con.: concentration.

than those with CaCl₂. Cumulative Cr released by CaCl₂ was 89.7 mg/kg, while that released by LMWOAs ranged from 106.65 to 147.4 mg/kg. Therefore, LMWOAs have a strong effect on the release of Cr in the soil. Fig. 1 shows the influence of the organic acids on the Cr release. The total amount of the Cr release was in this order: citric acid > malic acid > tartaric acid > oxalic acid > acetic acid. According to the results, the more carboxylic groups in the organic acid, the higher the release of Cr, which is consistent with previous reports (Taghipour and Jalali, 2013). When the organic acid concentration in the desorption solution increased from 5 to 20 mmol/L, the Cr released by citric acid increased from 107.35 to 147.4 mg/kg, and Cr released by malic acid ranged from 100.55 to 126.2 mg/kg. The trend in the amounts of Cr released by tartaric acid and oxalic acid was similar to that released by malic acid. The Cr released by acetic acid varied from 92.7 to 78.75 mg/kg. In addition, 5 mmol/L acetic acid extracted more Cr than the 20 mmol/L acetic acid.

It was proposed that two mechanisms can illuminate the effect of organic acids on the mobilization of Cr in contaminated soils (Taghipour and Jalali, 2016): (1) the dissolution of minerals that contained Cr by decreasing solution pH, and (2) organic ligands and Cr forming surface complexes through adsorption on the mineral surfaces. Table 5 shows that the pH in the soil solution decreased after Cr was released by organic acids. For instance, when 20 mmol/L organic acid was added into soils, the pH was 6.54, 6.50, 6.65, 6.75, and 7.54 using citric, malic, tartaric, oxalic, and acetic acids, respectively. At the end of Cr release, the pH levels were 7.98, 8.26, 8.31, 8.42, and 8.26, respectively. It was proposed that solution pH strongly influenced the activities of the metal, in accordance with the de/protonation of LMWOA (Debela et al., 2010).

It was reported that the soil pH after the release of P was observably different by using malic, citric, and oxalic acids in

the control sample (Taghipour and Jalali, 2013). However, the pH value of the solution cannot entirely explain the dissolution phenomenon observed in this study. For example, 20 mmol/L acetic acid has a lower pH (7.54) than 5 mmol/L acetic acid (9.12). After Cr was released by acetic acid, 5 mmol/L acetic acid extracted more Cr than the 20 mmol/L acetic acid. The pH value of the solution may be a significant factor in the dissolution of Cr polluted soil, but the specific affinity of acetic acid for Cr seems to be the major driving factor in this study. Some studies also reported that organic acids with different carboxylic groups have different abilities for releasing heavy metal, *e.g.*, the tricarboxylic (citric) and dicarboxylic acids (oxalic, malonic, fumaric, and tartaric) are more effective than monocarboxylic acids (acetic acid), because of their greater molecular weight and ability to carry more negative charges and they have more surface area. In addition, carboxylic groups and hydroxyl containing binding sites can react with heavy metal ions on a soil surface (Jing et al., 2007; Taghipour and Jalali, 2013).

2.3. Kinetic study

Cr released from soil by extraction with CaCl₂, citric acid and acetic acid is shown in Fig. 2. Similar to the trend observed in Cr released by CaCl₂, citric acid and acetic acid, the soluble Cr in all LMWOAs solution exhibited high concentration in the initial stages (8 hr) of dissolution followed by a slow decline. It was reported that nickel and lead in soils also had the same trend (Tabar and Sajadi, 2013). It was also proposed that the Cr release in the initial stages was the fraction easily extracted by all extractions, and then the less mobile fractions followed later. The releasing process is a complex combination of desorption and dissolution (Taghipour and Jalali, 2016). To investigate Cr release kinetics in soils, two kinetic equations (pseudo-second-order kinetics and Elovich kinetics) were used

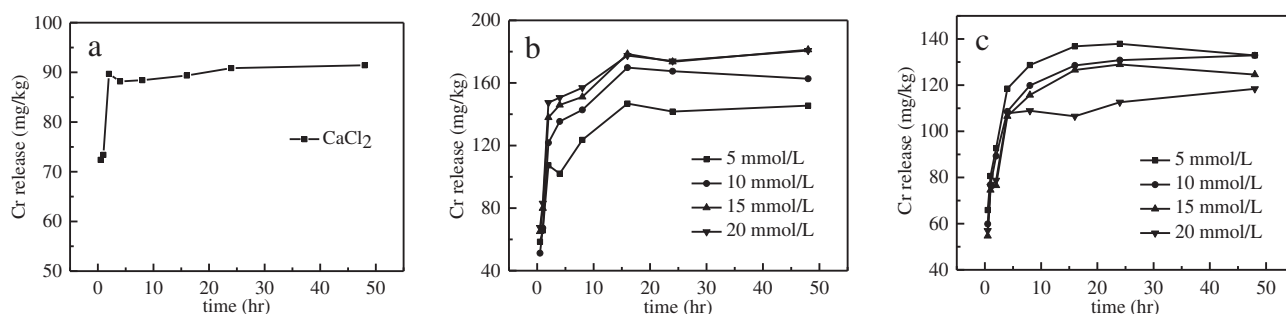


Fig. 2 – Kinetic release of Cr in treated soil by successive extractions with (a) CaCl₂ (10 mmol/L) (b) citric acid (5, 10, 15, and 20 mmol/L) and (c) acetic acid (5, 10, 15, and 20 mmol/L), respectively. Values represent mean ± SD (n = 3).

Table 6 – Kinetic parameters for the release of Cr.

Extraction media	Con. (mmol/L)	$t / y = 1 / (k * q_e^2) + t / q_e$				$y = A + B \ln t$	
		R ²	k (g/mg/hr)	q _{e,cal.} (mg/kg)	q _{e,exp.} (mg/kg)	R ²	B
Citric acid	5	0.9990	5.9060	149.25	145.5	0.9154	20.81
	10	0.9984	6.4479	169.49	162.7	0.8742	26.52
	15	0.9993	4.8866	185.15	181.2	0.8858	26.02
	20	0.9996	5.7179	185.18	180.7	0.8439	24.85
Acetic acid	5	0.9991	16.1047	135.14	132.86	0.8945	16.612
	10	0.9999	8.5556	135.14	132.9	0.9503	16.77
	15	0.9990	11.0600	128.21	124.58	0.9096	16.985
	20	0.9989	9.6669	119.04	118.4	0.8674	12.847
CaCl ₂	10	1.0000	5.400	91.743	91.43	0.6895	4.07

Values represent mean ± SD (n = 3). Con.: concentration; R²: coefficient of determination; k: pseudo-second-order rate constant; q_{e,cal.}: predicted Cr released to the experimental data; q_{e,exp.}: measured Cr released to the experimental data; B: Elovich kinetic rate constant.

in this study. The values of kinetic model parameters are shown in Table 6. A comparison of observed and model calculated for R² indicated that the equations can appropriately represent the cumulative Cr release. The results indicated that the pseudo-second-order kinetics can fit Cr desorption by different acid solutions. The R² values were in the range of 0.99–1.0 for all the treatments. Furthermore, there was good agreement between the q_{e,cal.} values and q_{e,exp.} values, as demonstrated by the lower SE values of <7.9794 (citric acid), <8.3057 (acetic acid), and <1.3936 (CaCl₂) in compost treated soils according to the pseudo-second-order model. The release rate of Cr was 5.400 g/mg/hr, from 4.8866 to 6.4479 g/mg/hr, and from 8.5556 to 16.1047 g/mg/hr for CaCl₂, citric acid, and acetic acid, respectively. The different k values indicated that the ability of Cr release differed by the organic acid used. In general, the mean release rate of Cr by citric acid (5.7396 g/mg/hr) was higher than that by acetic acid (11.3468 g/mg/hr). Table 6 also shows that the Elovich kinetics can describe Cr desorption by different acid solutions. It was reported that the desorption

process was a heterogeneous diffusion-reaction (Aharoni and Levinson, 1991).

2.4. The effect of organic acids on Cr fractionation

A continuous extraction method was adopted to analyze the chemical forms of Cr in the soil, and the change in Cr content with different forms was compared by different organic acid extractions. It is essential to understand the environmental implications and risks of organic acids on Cr polluted soil. The various Cr fractions exhibited great differences in mobility, bioavailability, and chemical behaviors in the soil. The results of the fraction analyses and the contributions of five fractions relative to total Cr before and after Cr release using different organic acids are shown in Fig. 3. Before release, the exchangeable Cr, carbonate-bound Cr, Fe–Mn oxide bound Cr, organic bound Cr, and residual Cr were 23.65, 12.95, 541.5, 445.15, and 976.75 mg/kg, respectively.

After release, as shown in Fig. 3, the exchangeable Cr, carbonate-bound Cr, and residual Cr decreased, while the Fe–Mn oxide bound Cr and organic bound Cr increased in the soil solid phase. The highest percentage of Cr was associated with the Fe–Mn oxide bound Cr with mean values of 732.15, 729.17, 678.25, 779.25, and 789.37 mg/kg in citric acid, malic acid, tartaric acid, oxalic acid, and acetic acid, respectively. These results may be attributed to high Fe/Mn content in the soil. Table 2 shows that the contents of Fe and Mn were approximately 125.18 and 24.15 g/kg, respectively. Additionally, the lowest percentage was found in the exchangeable fraction, with mean values of 7.98, 12.5, 8.77, 8.16, and 7.66 mg/kg in citric acid, malic acid, tartaric acid, oxalic acid, and acetic acid, respectively. This result indicated that the chelation and desorption processes of Cr by organic acids could lead to remobilization of Cr in the soil.

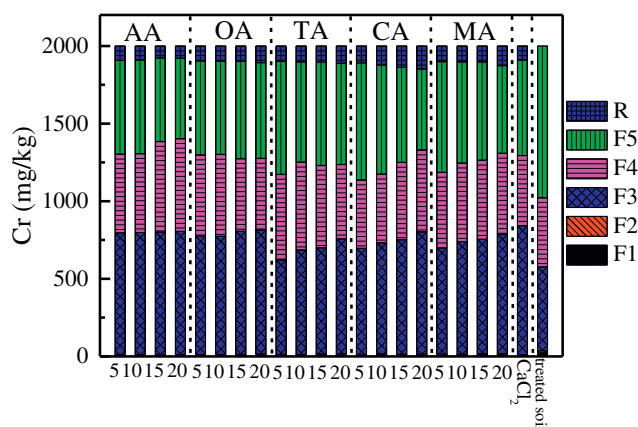


Fig. 3 – Fractionation of Cr in treated soil by co-composting, before and after Cr release with 5, 10, 15, and 20 mmol/L citric acid (CA), tartaric acid (TA), oxalic acid (OA), acetic acid (AA), malic acid (MA) and 10 mmol/L CaCl₂ solutions, respectively. (F1: exchangeable, F2: carbonate-bound, F3: Fe–Mn oxide bound, F4: organic matter bound, F5: residual, R: Cr release.) Values represent mean ± SD (n = 3).

3. Conclusion

This study provides a comprehensive discussion of the transformation law and migration features of the metal Cr in a soil–plant biological system obtained from Cr polluted soil treated by the compost-phytoremediation method. The

experimental results of chicken manure and Cr polluted soil co-composting proved that water-soluble Cr(VI) content significantly decreased. Composting can reduce Cr availability by making the Cr more stable and less mobile. The glasshouse growth experiment revealed that all the tested plants in the two crops were able to accumulate Cr to various degrees. This result indicated that LMOWAs derived from plant root increased the bioavailability of heavy metals so that they were able to assimilate and transfer easily in the tissues of plants. Kinetic release and fractionation of Cr were carried out using LMOWAs (citric, tartaric, oxalic, acetic, malic acids). After Cr was released by organic acids, the content of exchangeable Cr, carbonate-bound Cr, and residual Cr decreased, while Fe–Mn oxide bound Cr and organic bound Cr increased in all treatments. This result indicated that LMOWAs play an important role in the remobilization and migration of Cr in soils. Therefore, the ability of organic acids to desorb and transport Cr in natural systems should be considered together.

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