Adsorption and mobility of Cr(III)–organic acid complexes in soils

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ABSTRACT

The soluble Cr(III) is likely to be complexed with organic ligands in ligand-rich soil. Cr(VI) chemical reduction by organic acids and bioreduction by microorganisms can produce soluble Cr(III)–organic acids complexes. Thus, it is of great significance to investigate the absorption and mobility of Cr(III)–organic acid complexes in soils. In this study, Cr(III)–EDTA and Cr(III)–cit were prepared and purified, and then were examined for adsorption and mobility. The results demonstrated that Cr(III) was strongly bound to soil, while Cr(III)–organic acid complexes had no or slight interaction with soils since Cr(III)–EDTA and Cr(III)–cit complexes mainly existed as the forms of [Cr(III)–EDTA]$^-$ and [Cr(III)–cit], respectively, under the tested conditions with initial pH 4.0–9.0. The adsorption of Cr(III) increased but that of Cr(III)–organic acid complexes decreased with the content of soil organic matter. Compared with Cr(III)–EDTA, the mobility of Cr(III)–cit in soil columns was reduced, due to the specific adsorption between soils and Cr(III)–cit which contained one free hydroxyl group.

1. Introduction

Chromium has multiple oxidation states, but only trivalent and hexavalent are stable under physiological conditions [1]. Of the two environmentally available forms, hexavalent chromium (Cr(VI)) is generally more soluble, mobile, and toxic than the trivalent form (Cr(III)) [2]. In contrast, Cr(III) exhibits positive effects such as potentiating insulin action, and improving normal lipid and carbohydrate metabolism [3–5]. Due to the threat of Cr(VI) to environment, the conversion of Cr(VI) to Cr(III) is a significant process to limit its toxic effects [6].

There are some chemical and biological approaches for the removal of Cr(VI). Various organic acids have been extensively studied for the reduction of Cr(VI), demonstrating that some of them can effectively transform Cr(VI) to Cr(III) in the presence of Mn(II) [7–9] or Fe(III) under irradiation [10]. Soils or minerals can markedly enhance the reduction of Cr(VI) by organic acids due to the catalysis of Mn(II) or Fe(III) on the soil surfaces [11]. Bioremediation, a clean-up approach with low cost, can be an alternative to the existing methods. It has been reported that a number of aerobic and anaerobic microorganisms are capable of transforming Cr(VI) to Cr(III) [6,12–15].

However, both Cr(VI) chemical reduction by organic acids and bioreduction by microorganisms can produce soluble Cr(III)–organic acids complexes, which lead to increasing mobility of Cr(III) in soils as compared with free Cr(III) [6,16–19]. Also, the free Cr(III) is likely to be complexed with organic ligands in ligand-rich environment. The Cr(III)–organic acid complex is relatively stable in the presence of manganese oxides [15]. But, it is easier to be photochemically oxidized to Cr(VI) under the alkaline condition than free Cr(III) [20,21]. Therefore, the Cr(III)–organic acid complex may result in a potential threat to the environment.

Although the adsorption and mobility of Cr(III) were widely reported [15,22,23], there is limited understanding on the behavior of Cr(III)–organic acid complex in soils. So it is necessary to comprehensively investigate the adsorption and mobility of Cr(III)–organic acid complexes in soils under approximate environmental conditions in a laboratory setting. In the present study, Cr(III)–EDTA and Cr(III)–cit were prepared and purified. Three typical soils from China, Red Soil, Yellow Brown Soil and Chernzem, were selected and the effects of pH and soil organic matter on the adsorption and mobility of Cr(III)–organic acid complexes were investigated.

2. Materials and methods

2.1. Materials

The stock solution of Cr(III) (0.1 M) was prepared by dissolving CrCl$_3$·6H$_2$O(s) (Sinopharm Chemical Reagent Co., Ltd) in diluted HCl solution at pH < 2 in order to prevent hydrolysis. The stock solutions of citric acid (0.1 M) and ethylenediaminetetraacetic acid (EDTA) (0.1 M) were obtained by dissolving reagent-grade citric acid monohydrate (Shantou Xilong Chemical Factory) and reagent-grade EDTA (Sinopharm Chemical Reagent Co., Ltd.) in deionized

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Table 1
The selected properties of the soils.

Soil	pH	Organic matter (g/kg)	Specific surface area (m²/g)	CEC (cmol/kg)
Chernzem	7.56 ± 0.07	32.06 ± 1.3	9.36	25.0[a]
Yellow Brown Soil	7.19 ± 0.04	16.23 ± 0.5	11.51	16.6[a]
Red Soil	4.62 ± 0.02	6.35 ± 0.24	26.73	8.6[b]

[a] Data from Ref. [27].
[b] Data from Ref. [28].

water, respectively. The other chemicals used in the study were at least of reagent grade.

Three typical types of soils from China, Red Soil from Yingtan, Jiangxi Province, Yellow Brown Soil from Nanjing, Jiangsu Province, and Chernzem from Heilongjiang Province, were selected in the present study. The air-dried soils were ground and passed through 100 mesh sieves for adsorption experiments. The soil particles with grain sizes of 30–60 mesh sieves were collected for mobility experiments. To investigate the effect of soil organic matter on the adsorption of Cr(III)–organic acid complex, the air-dried soils were treated with 30% H_2O_2 to remove organic matter [24]. The selected properties of these soils were analyzed [25–28] and listed in Table 1.

All the glassware used was cleaned by soaking in 1 M HCl for 12 h and thoroughly rinsed with tap water and then deionized water.

2.2. Preparation of Cr(III)–organic acid complex

Cr(III)–cit and Cr(III)–EDTA complexes were prepared by mixing 5 mL 0.1 M Cr(III) and 2.5 mL 0.1 M citric acid/EDTA solutions, respectively, at a molar ratio of Cr(III) to citric acid/EDTA of 2:1. Excessive Cr(III) was used to make citric acid and EDTA completely chelated at pH 6 and 25 °C for 48 h [20,21]. Then the mixture was filtered to remove the potential $Cr(OH)_3$ precipitates and finally purified by 732 cation exchange resin (Shanghai Qingxi Chemical and Technology Co., Ltd) to eliminate all the unchelated Cr(III). The effluent was collected, diluted to 250 mL by deionized water, and analyzed by high performance liquid chromatography (HPLC) for free organic acids. The analytical results showed that no free organic acids were detected. The concentrations of Cr(III) in Cr(III)–cit/EDTA stock solutions measured by atomic absorption spectrophotometer (HITACHI180 with 0.04 μM detection limit) were 1000 μM. And the ratio of Cr(III) to cit/EDTA in the complex was determined to be 1:1 according to a method by Dai et al. [20]. The stock solutions were stored in the dark to prevent any potential light-induced reactions prior to use.

2.3. Adsorption of Cr(III)–organic acid complex

The adsorption experiments were carried out through the batch equilibration method. Briefly, 100 mL of Cr(III) or Cr(III)–EDTA/Cr(III)–cit solutions of 100 μM were transferred to 250 mL glass bottles and the initial pH values were adjusted with NaOH or HCl to 4.0, 6.5, and 9.0. The change of solution volume due to pH adjustment (less than 5 mL) was neglected. Afterwards, 0.1, 0.2, 1.0 and 2.0 g soil samples were introduced into the glass bottles. The concentrations of the soils were 1, 2, 10 and 20 g/L, respectively. The suspensions were shaken at 180 rpm and 25 ± 0.5 °C. A 2 mL suspension was drawn out at a fixed interval with a 5 mL plastic syringe, and then filtered to a glass test tube with a 0.45 μm filter to remove the soil.

2.4. Mobility of Cr(III)–organic acid complex

The experiments for mobility of Cr(III)–organic acid complexes were performed in glass columns 40 cm in length, and 3.5 cm in diameter, with a piston at the bottom to control the flow velocity of

solution. A 500 mL separation funnel was put at the top of the glass column to keep the solution level in the soil column unchanged. Soil and quartz sand with the same particle sizes at a ratio of 4:1 by weight were homogeneously mixed to overcome high soil viscosity which hinders downward infiltration. Each column, approximate 10 cm in height, was gently packed with a 50-g mixture of soil and quartz sand. Quartz sand of 1 cm height was placed at the bottom and the top of the soil columns, respectively. Deionized water was then slowly added to each column to wet the soil thoroughly. Finally, the soil column was leached with 100 μM Cr(III)–organic acid complex at 40 ± 2 mL/h and the effluent was collected.

2.5. Analytical methods

The analyses of organic acids were performed using HPLC (Waters 2487). The mobile phase consisted of 25 mM diammonium phosphate at pH 2.8 with 3% (v/v) CH_3OH. The Lichrospher, C_{18} (5 μm, 250 mm × 4.6 mm), was used as the separation column and the components in the eluent were determined at 214 nm. The Cr(III) concentrations were measured by AAS. An Orion 868 pH meter, after two-point calibration, was used to determine pH values.

3. Results and discussion

3.1. Forms of Cr(III) and Cr(III)–organic acid

The distributions of Cr(III) and Cr(III)–EDTA forms were simulated by Visual MINTEQ with a span of pH from 3 to 10 at a regular interval of 1. The distributions of the main forms were listed in Table 2a for Cr(III) and Table 2b for Cr(III)–EDTA. Cr(III) ions mainly exist as free Cr(III) and $[CrOH]^{2+}$ at a pH range of 3–4 and as $Cr(OH)_3$(aq) at pH values from 7 to 10. Cr(III)–EDTA ions distribute as $[CrEDTA]^-$ and [CrHEDTA](aq) at pH 3 and as $[CrEDTA]^-$ and $[CrOHEDTA]^{2-}$ at pH values ranging from 6 to 10. No free Cr(III), $Cr(OH)_4^-$ and $Cr(OH)_3$(aq) are present in Cr(III)–EDTA solution.

The pH-dependant forms of Cr(III)–cit complexes were listed in Table 2c (the data from our previous study [20]). The results indicate that the Cr(III)–cit complexes mainly exist as $[Cr(III)–H–cit]^+$ and [Cr(III)–cit] at a pH range of 3–5, while $[Cr(III)–H–cit]^+$ disappears at higher pH. $[Cr(III)–OH–cit]^-$ coexists with [Cr(III)–cit] when pH rises to 9 or more.

3.2. Adsorption of Cr(III) and Cr(III)–organic acid complex onto soils

The adsorption of Cr(III), Cr(III)–EDTA and Cr(III)–cit with an initial concentration of 100 μM onto three typical soils from China was investigated at initial pH 4.0 and 25 °C. The ratio of water to soil by weight was 500:1 for Cr(III) adsorption and 50:1 for Cr(III)–organic acid complex adsorption. High soil loading was utilized due to low adsorption of Cr(III)–organic acid. As shown in Fig. 1a, Cr(III) was strongly adsorbed by three soils. In the present study, the soil suspension was not buffered to avoid the possible competition for adsorption sites with the ions from buffer solution. Therefore the solution pH values for adsorption finally shifted to approximately

Table 2a
The distribution of Cr(III) forms at different pH.

pH	Forms of free Cr(III)						
	Cr^{3+}	$[CrOH]^{2+}$	$[Cr_2(OH)_2]^{4+}$	$[Cr(OH)_2]^+$	$[Cr_3(OH)_4]^{5+}$	$Cr(OH)_{3(aq)}$	$[Cr(OH)_4]^-$
3.0	81.602	18.26	0.124	0	0	0	0
4.0	29.041	68.994	1.605	0.344	0.012	0	0
5.0	3.681	88.809	2.594	4.467	0.255	0.195	0
6.0	0.232	56.747	1.039	28.746	0.644	12.592	0
7.0	0	3.48	0	17.87	0	78.64	0
8.0	0	0.043	0	2.219	0	97.704	0.034
9.0	0	0	0	0.226	0	99.424	0.35
10.0	0	0	0	0.022	0	96.574	3.404

Table 2b
The distribution of Cr(III)–EDTA forms at different pH.

pH	Forms of Cr(III)–EDTA					
	Cr^{3+}	$[CrEDTA]^-$	$[CrHEDTA](aq)$	$[CrOHEDTA]^{2-}$	$[Cr(OH)_4]^-$	$Cr(OH)_3(aq)$
3.0	0	92.562	7.436	0	0	0
4.0	0	99.181	0.802	0.017	0	0
5.0	0	99.747	0.081	0.172	0	0
6.0	0	98.278	0	1.714	0	0
7.0	0	84.968	0	15.031	0	0
8.0	0	35.964	0	64.036	0	0
9.0	0	5.302	0	94.698	0	0
10.0	0	0.553	0	99.447	0	0

Table 2c
The distribution of Cr(III)–cit forms at different pH.[a]

pH	Forms of Cr(III)–cit		
	$[Cr(III)-H-cit]^+$	$[Cr(III)-cit]$	$[Cr(III)-OH-cit]^-$
3.0	33.84	66.16	0
4.0	13.21	86.79	0
5.0	7.04	92.96	0
6.0	0	100	0
7.0	0	100	0
8.0	0	100	0
9.0	0	60.41	39.59
10.0	0	38.93	61.07

[a] Data in this table are from our previous study [20].

soil pH values (see Table 1). Based on the results in Table 2a, we speculated that the major forms of Cr(III) were Cr^{3+} and $[CrOH]^{2+}$ in the suspension of Red Soil, and $[Cr(OH)_2]^+$ and $Cr(OH)_3(aq)$ in the suspensions of Yellow Brown Soil and Chernzem. These forms with positive charges are easily adsorbed by the three soils with net negative charges. The adsorption of Cr(III) by three soils mainly occurred within the first 20 min, and then the adsorption amounts kept constant, implying the soils were saturated by Cr(III) (Fig. 1). The maximum adsorption amounts of Cr(III) by Red Soil, Yellow Brown Soil and Chernzem under the tested conditions were 26, 47 and 49 μmol/g, respectively. The adsorption amounts of Cr(III) by Yellow Brown Soil and Chernzem were almost two times that of Red Soil. The high Cr(III) adsorption amount in Chernzem and Yellow Brown Soil may be due to the high cation exchange capacity (CEC) and high organic matter contents (see Table 1). The trend is just opposite to Cr(VI) adsorption by these three soils [11] since Cr(VI) exists as the forms of negative charge such as $HCrO_4^-$ or $Cr_2O_7^{2-}$, which was difficult to be adsorbed by the soils with net negative charges.

Compared with the adsorption of Cr(III), Cr(III)–organic acid complexes exhibited weaker adsorption by the soils (Fig. 1b). The adsorption amounts of Cr(III)–EDTA by Chernzem, Yellow Brown Soil and Red Soil at the end of 360 min was 0.06, 0.09 and 0.31 μmol/g, respectively, and 0.91, 1.64 and 2.92 μmol/g, respectively, for Cr(III)–cit. The adsorption amount of Cr(III) by the soils was ten to hundred times that of Cr(III)–organic acids.

We concluded that the weaker adsorption of Cr(III)–organic acid resulted from their form distribution. Cr(III)–EDTA mainly exists as $[CrEDTA]^-$ and $[CrOHEDTA]^{2-}$, and Cr(III)–cit mainly as $[Cr(III)-cit]$ in a pH range of 4–8 (Tables 2a–2c). Cr(III)–EDTA carried negative charges, and as a result it displayed lower adsorption by the soils than $[Cr(III)-cit]$. The adsorption of Cr(III)–organic acid complexes by the three soils was in the order of Red Soil > Yellow Brown Soil > Chernzem, which is just opposite to the trend of the contents of soil organic matter (Table 1).
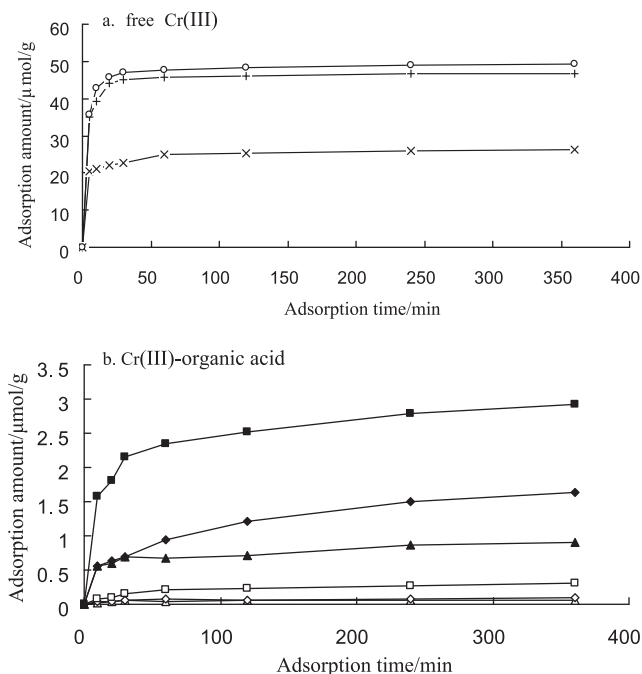
Fig. 1. Adsorption of Cr(III) by soils at a ratio of water:soil = 500:1 by weight (a) and the adsorption of Cr(III)–organic acid by soils at a ratio of water:soil = 50:1 by weight (b) at 25 °C and initial pH = 4.0: (○) Chernzem + Cr(III); (+) Yellow Brown Soil + Cr(III); (×) Red Soil + Cr(III); (▲) Chernzem + Cr(III)–cit; (♦) Yellow Brown Soil + Cr(III)–cit; (■) Red Soil + Cr(III)–cit; (△) Chernzem + Cr(III)–EDTA; (◊) Yellow Brown Soil + Cr(III)–EDTA; (□) Red Soil + Cr(III)–EDTA.

To verify whether Cr(III)–organic acid complex or free Cr(III) was adsorbed due to the possible replacement of Cr(III) in organic acid complex by Fe(III) from soils, Fe(III) in the solutions after the adsorption of Cr(III)–organic acid complex was detected by AAS. The results indicated that the amount of Fe with background correction obtained with the same pH solutions but without Cr(III)–organic acid complex was less than 5% of adsorption amount of Cr(III)–organic acid complex. Therefore, it is concluded that the amount of Cr(III) replaced by Fe(III) in this study was negligible and Cr(III) was adsorbed by soils mainly as the form of Cr(III)–organic acids, not as free Cr(III) in this study. The possible reason is that the Fe(III) in the soils has been fixed by adsorption, precipitate or complex with soil organic matter. As a result, it is more difficult for Fe(III) in soils to replace the Cr(III) to complex with EDTA/cit in spite of more stable Fe(III)–EDTA/cit complex.

3.3. Effect of soil organic matter on adsorption of Cr(III) and Cr(III)–organic acid complex

Based on the results in Section 3.2, we speculated that high contents of soil organic matter contribute to the adsorption of Cr(III), but are disadvantageous to the adsorption of Cr(III)–EDTA/cit. In order to verify the speculation, the soils were treated with 30% H_2O_2 to remove organic matter [24]. The adsorption of Cr(III) and Cr(III)–EDTA/cit with initial concentrations of 100 μM by the soils treated with H_2O_2 was examined at initial pH 4.0 and 25 °C. The ratio of water to soil by weight was also 500:1 for Cr(III) adsorption and 50:1 for Cr(III)–organic acid complex adsorption. Compared to the pristine soils, the adsorption amounts of Cr(III) by Chernzem, Yellow Brown Soil and Red Soil with organic matter removed decreased by 26%, 13% and 7%, respectively (Table 3). The extent of reduction in adsorption amount is quite in agreement with the contents of soil organic matter (Table 1). Part of negative charges of soil is generated by the dissociation of hydroxyl and phenolic hydroxyl [29]. Removal of organic matter leads to a decrease in the negative charges of soil. As previously discussed, the forms of Cr(III) are mainly Cr^{3+} and $[CrOH]^{2+}$ in the suspension of Red Soil, and $[Cr(OH)_2]^+$ and $Cr(OH)_3(aq)$ in the suspensions of Yellow Brown Soil and Chernzem. Therefore, the electrostatic adsorption was obviously weakened, resulting in a decrease of adsorption amounts of Cr(III) by soils.

In contrast, the adsorption amounts of Cr(III)–cit by Chernzem, Yellow Brown Soil and Red Soil markedly increased by 34%, 36% and 9%, respectively (Table 3), suggesting that removal of organic matter contributes to adsorption of Cr(III)–cit by soils. The result further explains why the adsorption amounts of Cr(III)–cit by pristine soils were in the order of Red Soil > Yellow Brown Soil > Chernzem. However, the removal of organic matter has little effect on adsorption amounts of Cr(III)–EDTA.

The enhancement of Cr(III)–cit adsorption by soils after the removal of soil organic matter was ascribed to an increase of specific adsorption between Cr(III)–cit and soils. The destruction of soil organic matter will expose more metal ions such as Fe(III) to complex with Cr(III)–cit. The trend in the soils with higher content of organic matter is more apparent. But, such a reaction is difficult to occur between Cr(III)–EDTA and soils (see Section 3.5 for the detail discussion).

3.4. Mobility of Cr(III)–organic acid in soil columns

The mobility of Cr(III)–organic acid complexes with an initial concentration of 200 μM was tested in soil columns with a continuous flow at initial pH 4.0 and 25 °C. The breakthrough profiles (Fig. 2) demonstrate different adsorption affinities between soil and Cr(III)–organic complexes. Cr(III)–EDTA in effluents was detected at a leaching volume of approximately 20 mL in Chernzem and
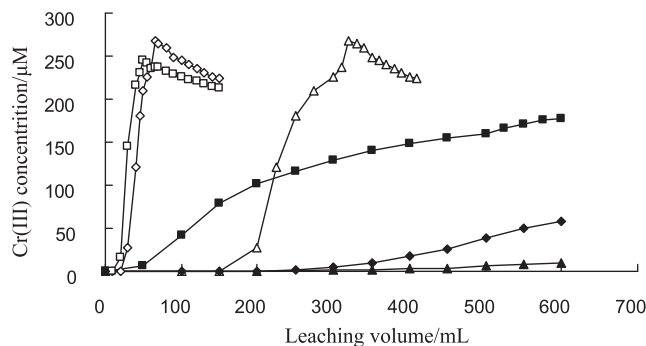

Fig. 2. Mobility of Cr(III)–cit and Cr(III)–EDTA in soils at initial pH = 4.0 and 25 °C. Initial concentration of Cr(III)–cit and Cr(III)–EDTA: 200 μM: (■) Chernzem + Cr(III)–cit; (♦) Yellow Brown Soil + Cr(III)–cit; (▲) Red Soil + Cr(III)–cit; (□) Chernzem + Cr(III)–EDTA; (◇) Yellow Brown Soil + Cr(III)–EDTA; (△) Red Soil + Cr(III)–EDTA.

approximately 30 mL in Yellow Brown Soil, indicating little adsorption to the two soils, while the leaching volume in Red Soil rose to approximately 200 mL, indicating more interaction with Red Soil. The results are consistent with the previous adsorption study. As shown in Fig. 2, the peak value of effluent concentration was higher than the initial concentrations of Cr(III)–EDTA in the three soil columns. The peak values of effluent concentrations were 237 μM in Chernzem, 264 μM in Yellow Brown Soil and 222 μM in Red Soil, respectively. The results may be due to the partial desorption of Cr(III)–EDTA adsorbed on soil surfaces at the initial phase. Then, the concentrations of Cr(III)–EDTA slowly decreased to the initial concentrations, implying that the adsorption of Cr(III)–EDTA by soils columns reached saturation. The leaching profiles for Cr(III)–EDTA in Chernzem and Yellow Brown Soil were quite similar but was significantly retarded in Red Soil, suggesting that the adsorption affinities of Cr(III)–EDTA by Chernzem and Yellow Brown Soil be almost the same and that by Red Soil be apparently larger.

Compared to Cr(III)–EDTA, mobility of Cr(III)–cit obviously decreased. The concentrations of effluents were 177.8 μM in Chernzem, 59.3 μM in Yellow Brown Soil and 10.3 μM in Red Soil, respectively, when the leaching volume was 600 mL, indicating that the adsorption of Cr(III)–cit by soils was stronger than that of Cr(III)–EDTA.

The saturated adsorption of Cr(III)–EDTA by Chernzem, Yellow Brown Soil and Red Soil in column experiments obtained by MAT-LAB software were 0.13, 0.16 and 1.6 μmol/g, respectively, which correspondingly increased by 2.2, 1.8 and 5.2 times compared with those obtained by batch experiments in Section 3.2. The differences were supported by our preliminary study (data not shown) which showed that adsorption amounts (Cr(III)–EDTA/cit μmol/g soil) in batch experiments increased with soil loading. The ratio of soil to solution by weight in soil column was much greater than that in batch experiment. Nevertheless, further experiments are needed to explain the increase of adsorption amounts with soil loading.

3.5. Effect of pH on mobility of Cr(III)–organic acids in soil columns

The effect of pH on the mobility of Cr(III)–organic acids in soil columns was conducted at initial pH values of 4.0, 6.5 and 9.0. As previously discussed, the leachate was not buffered to avoid the possible competition for adsorption sites with the ions from the buffer solution. Therefore, the solution pHs of effluents are different from those of eluents containing Cr(III)–organic acid complexes. For example, the pHs of the effluents shifted from 4.0 to 4.4, 6.5 to 4.6 and 9.0 to 4.8 in Red Soil column, from 4.0 to 7.4, 6.5 to 7.5 and 9.0 to 7.5 in Chernzem column, and from 4.0 to 7.1, 6.5 to 7.1 and

Table 3
Comparison of adsorption amounts ($\mu g/g$) for different Cr(III) forms by pristine soils and the soils treated with H_2O_2 for 360 min.

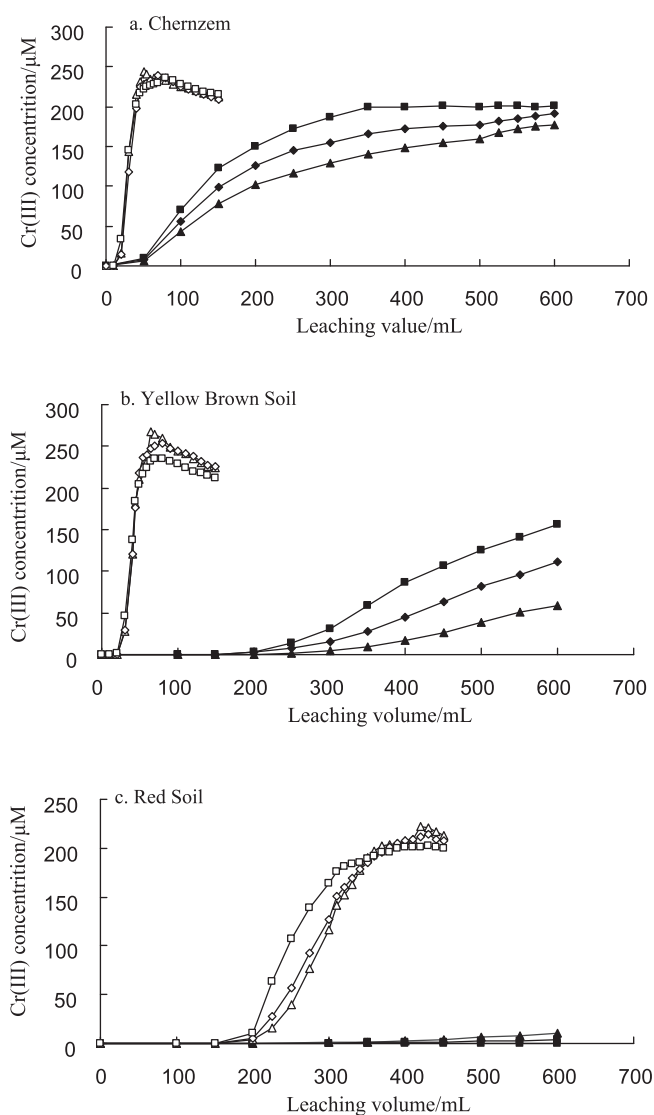| Forms of Cr(III)	Soils					
	Red Soil		Yellow Brown Soil		Chernzem	
	A	B	A	B	A	B
Cr(III)	25.99 ± 0.25	29.98 ± 0.29	47.17 ± 0.52	41.25 ± 0.44	49.64 ± 0.65	36.56 ± 0.08
Cr(III)–EDTA	0.32 ± 0.01	0.29 ± 0	0.09 ± 0	0.085 ± 0.01	0.06 ± 0	0.09 ± 0
Cr(III)–cit	2.88 ± 0.06	3.12 ± 0.08	1.62 ± 0.03	2.19 ± 0.08	0.93 ± 0.03	1.25 ± 0.06

Note: A, pristine soil; B, removal of organic matter.

9.0 to 7.2 in Yellow Brown Soil column, respectively, showing that the pHs of effluents were close to the soil pHs (see Table 1) and the pHs in soil columns changed gradually with the increasing depth of leachates.

As shown in Fig. 3a–c, the three leaching curves of Cr(III)–EDTA solution were almost overlapped, suggesting that initial pH should have no effect on the mobility of Cr(III)–EDTA in the three soils. We speculate that there are two reasons for this. First, Cr(III)–EDTA mainly exists as $[CrEDTA]^-$ and $[CrOHEDTA]^{2-}$ (Table 2b), which

could not be easily adsorbed by the three soils with negative charges. Second, the buffering capacities of soils weakened the effect of the initial pH.

Cr(III)–cit exhibited different mobilities at different initial pH values in soil columns (Fig. 3a–c). High pH values help Cr(III)–cit to mobilize in Chernzem and Yellow Brown Soil, but reduce the mobility of Cr(III)–cit in Red Soil. As previously discussed, Cr(III)–cit mainly exists as [Cr(III)–cit] in a pH range of 5–8 (Table 2c). So it is expected that electrostatic adsorption does not occur between soil and Cr(III)–cit. Based on the fact that the adsorption amounts of Cr(III)–cit by soils are much greater, especially in Red Soil, we suggest that specific adsorption might occur between soil and Cr(III)–cit. James et al. [30] pointed out that when pH was higher than 4.7, Cr(III)–cit was combined by two carboxyl groups and one hydroxyl group was free. Nowack et al. [31] found that Co(III)–EDTA was not adsorbed as strongly as Co(II)–EDTA by goethite and proposed that in the Co(III)–EDTA complex all carboxylate groups were coordinated to the metal center whereas for Co(II)–EDTA one carboxylate group coordinated freely with the surface of goethite. In the Cr(III)–EDTA complex, all carboxyl groups might be also combined with the Cr(III), which is another reason why Cr(III)–EDTA is less easily adsorbed by soils than Cr(III)–cit.

4. Conclusions

Free Cr(III) is strongly bound to soils, and the binding capacity of Cr(III) by soils are in the order of Chernzem > Yellow Brown Soil > Red Soil, directly proportional with the contents of organic matter and CEC. In contrast, the Cr(III)–organic acid complexes have no or slight interaction with soils, and the adsorption capacity for Cr(III)–organic acid complexes by soils decrease with the contents of organic matter. The forms of Cr(III) and Cr(III)–organic acid which greatly depend on pH affect their adsorption and mobility in soils. Cr(III) mainly exists as Cr^{3+}, $[CrOH]^{2+}$ and $[Cr(OH)_2]^+$, resulting in high adsorption and very low mobility in the three selected soils under the tested pH conditions. Cr(III)–EDTA and Cr(III)–cit exist as negatively charged and neutral molecules, respectively, leading to weak adsorption and high mobility in soils. Compared to Cr(III)–EDTA, Cr(III)–cit exhibits greater affinities with soils, which is attributed to the specific adsorption between soils and Cr(III)–cit with one free hydroxyl group. Thus, the results in the present study are environmentally significant regarding the elucidation of the effects of soil characteristics and types of Cr(III)–organic acid complexes on the adsorption and mobility of Cr(III) in soil.

Fig. 3. Effect of initial pH on the mobility of organic acid–Cr(III) ($200\,\mu M$) in soils at 25 °C: (▲) Cr(III)–cit, pH = 4.0; (♦) Cr(III)–cit, pH = 6.5; (■) Cr(III)–cit, pH = 9.0; (△) Cr(III)–EDTA, pH = 4.0; (◇) Cr(III)–EDTA, pH = 6.5; (□) Cr(III)–EDTA, pH = 9.0.

Acknowledgments

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