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Isoyama, Masahiro
Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Wada, Shin-Ichiro
Faculty of Agriculture, Kyushu University

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Soil Chemistry Effect on Feasibility of Cr–decontamination by Acid–Washing

Masahiro ISOYAMA[1] and Shin–Ichiro WADA*

Laboratory of Soil Science, Division of Soil Science and Plant Production, Department of Plant Resources, Faculty of Agriculture, Kyushu–University, Fukuoka 812–8581, Japan
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Soil washing with simple acid has been proven to be effective for removal of cationic heavy metals from contaminated soils. Since the adsorption of anionic heavy metals is enhanced in acidic medium, the efficiency of acid–washing may not be guaranteed for soils that are doubly contaminated with cationic and anionic heavy metals. To evaluate the efficiency of acid–washing, nine soils were artificially contaminated with chromate and chromium was extracted with hydrochloric acid of 0.5 mmol L^{-1} to 1 mol L^{-1}. A part of spiked chromate was reduced to trivalent chromium and the remaining chromate ions were almost quantitatively extracted with the hydrochloric acid. However, increasing hydrochloric acid concentration was not effective for the extraction. Possible mechanisms underlying the observed low efficiency were considered to be the enhanced reduction in acidic solution, complexation by humic substance and adsorption via cation exchange reactions. We concluded that acid–washing satisfactorily works for chromate removal in non–allophanic soils but inefficient for removal of trivalent chromium particularly from soils having high effective cation exchange capacity and organic matter content.

INTRODUCTION

Contamination of soils by toxic heavy metals has been a serious environmental issue in industrial areas (Adriano, 1986). Heavy metals are retained by most of soils and the effect of pollution tends to be chronic. Typical counter measures to reduce the threat of toxicity of heavy metals are stabilization and decontamination. In the former, heavy metals are transformed into less soluble compounds or bound onto some adsorbents. In heavily contaminated soils, however, the performance of stabilization technology is usually insufficient and decontamination is needed.

Recently, many researchers tested washing with chelating agents to remove heavy metals from soils (Chen and Hong., 1995; Reed *et al.*, 1996; Abmaizer and Smith, 1999) and proved that they are effective for decontaminating cationic heavy metals like Pb^{2+} and Cd^{2+}. A problem of the method is that toxicity of the chelating agents and the increased solubility of the heavy metals that may remain in the treated soils after treatment (Page and Page, 2002). Thus the washing with simple inorganic acids is still worth further study. Isoyama and Wada (2005) washed Pb–contaminated soils having diverse chemical and mineralogical properties and found that it is basically effective for all types of soils. They also showed that the heavy metals that remained after acid treatment are easily stabilized (unpublished).

In some sites, soils are contaminated with more than two kinds of heavy metals. For two or more cationic heavy metals, the washing with acid is expected to be equally effective if operating conditions are suitably modified. However, the situation is quite different when contaminants are combinations of cationic and anionic heavy metals. Surface complexes of cationic metals stabilize as soil pH is increased and the trend is opposite for anionic metals (Sposito, 1984). The addition of acid increases the stability of anion–soil surface complexes. In the present study nine soils contaminated with chromate (Cr(VI)) were washed with hydrochloric acid (HCl) to remove these heavy metals. The objective of the study is to evaluate the performance of acid treatment for the removal of anionic heavy metals that may co–present with cationic heavy metals.

MATERIALS AND METHODS

Nine soil samples that differ in chemical and mineralogical properties were used in the present study. The collected soils were air–dried and passed through a 2–mm screen. Some chemical and mineralogical properties of the soils were analyzed with standard procedures (Standard Methods of Soil Analysis Committee, 1986) and summarized in Table 1. The contents of allophane and ferrihydrite were determined by the selective dissolution with a ammonium oxalate–oxalic acid buffered at pH 3.5 (Parfitt and Wilson, 1985). Crystallline minerals in the clay fraction was identified by X–ray diffraction according to the method described by Wada and Umegaki (2001).

The soil samples were artificially contaminated with Cr(VI) by spraying 0.0192 mol L^{-1} potassium dichromate solution and air–drying. The amount of the sprayed solution was adjusted to make the total chromium (Cr) content 1000 mg kg^{-1}. The contents of the total Cr and Cr(VI) were determined by hot HCl digestion (Asami and Kato, 1977) and Na_2CO_3–NaOH extraction and colorimetry (James *et al.*, 1995), respectively.

Batch–washing was employed in the present study. Two gram portion of a soil sample was placed in an 85–mL polycarbonate centrifuge tube and 10 mL of HCl

[1] Laboratory of Soil Science, Division of Soil Science and Plant Production, Department of Plant Resources, Graduate School of Bioresources and Bioenvironmental Sciences, Kyushu University

* Corresponding author (E–mail: wadasi@agr.kyushu–u.ac.jp)

Table 1. Selected properties of soil samples used.

Sample name	pH	Organic carbon	Clay	Allophane	Ferrihydrite	Specific surface area	ECEC	Major ion adsorbers
		g kg^{-1}				$m^2 g^{-1}$	$cmol_c kg^{-1}$	
Sasaguri1–A	5.1	70	593	0.4	2.9	367	42.59	Smectite, Humus
Sasaguri2–B	4.8	4	305	tr.	3.1	237	15.55	Kaolin
Yoshiki–A	4.9	55	56	tr.	3.9	70	5.15	Kaolin, Humus
Yoshiki–B	5.3	9	82	0.3	2.5	20	1.86	Kaolin
Chikugo–A	5.7	18	351	9.8	17	166	21.86	Smectite
Goshi–A	5.9	71	214	162	39	191	13.00	Allophane, Imogolite, Humus
Choyo–B	5.7	29	192	133	55	267	2.72	Allophane, Imogolite
Umi–C	6.8	3	22	tr.	3.1	4	2.71	Vermiculite
Umi–F	6.8	4	36	tr.	5.5	11	3.99	Vermiculite

tr.; trace

was added and shaken on a reciprocal shaker for 1 h. The tube was centrifuged and clear supernatant solution was collected for analyses of pH and Cr concentration. The Cr concentration was determined by an atomic absorption spectrophotometer equipped with polarized Zeeman background correction system. Similar extraction experiments were repeated with HCl solutions with concentrations of 0.0001, 0.005, 0.02, 0.04, 0.05, 0.1, 0.2, 0.5 and 1 mol L^{-1}.

RESULTS AND DISCUSSION

Of the nine soil samples the Choyo–B and Goshi–A samples are Andisols derived from volcanic ash. The major clay minerals of these samples are allophane and imogolite. Their contents in these soils are approximately equal. However the Goshi soil exhibits higher effective cation exchange capacity (ECEC) probably due to its higher humus content. The major clay minerals in other soils are layer silicates. The ECEC of these soils depends on both the type of layer silicate and clay content. The smectitic Chikugo–A sample shows much higher ECEC than the kaolinitic Sasaguri2–B sample. Fairly high organic matter content is the characteristics for Sasaguri1–A and Yoshiki–A samples. The Choyo–B, Sasagur2–B and Goshi–A samples showed fairly high ferrihydrite content.

The pH and contents of the total Cr and Cr(VI) of the prepared soil samples are listed in Table 2. The total Cr content of the samples ranged from 859 to 1140 mg kg^{-1} and the content of Cr(VI) was much less than the total content, indicating that the hexavalent Cr was partly reduced to trivalent Cr. The reduction of Cr(VI) was conspicuous in the Sasaguri1–A and Yoshiki–A samples that contained large amounts of organic matter. Approximately 20% of the total Cr remained as Cr(VI) in the Goshi sample whose organic matter content was comparable to that of the Sasaguri1–A and Yoshiki–A samples. This may be due to the stabilization of chromate as surface complexes on allophane. More than half of the total Cr remained in the sandy Umi–F and Umi–C samples.

Table 2. Total and hexavalent chromium contents and pH of artificially contaminated samples.

Sample name	pH	Total Cr	Cr(VI)
		mg kg^{-1}	
Sasaguri1–A	5.9	941	6
Sasaguri2–B	4.9	976	214
Yoshiki–A	6.2	859	19
Yoshiki–B	6.3	1002	144
Chikugo–A	6.2	1077	209
Goshi–A	6.2	1140	186
Choyo–B	6.1	1060	206
Umi–C	6.9	992	512
Umi–F	6.6	1062	647

A typical reduction reaction of dichromate ion is

$$4Cr_2O_7^{2-} + C_6H_{12}O_6 + 32H^+ = 8Cr^{3+} + 6CO_2 + 22H_2O \quad (1)$$

in which 8 moles of proton are consumed in the reduction of 1 mole of dichromate ion. The rise in soil pH during sample preparation (Tables 1 and 2) is probably due to this reaction.

The amount of extracted Cr was plotted against the concentration of HCl in Fig. 1–a. The extracted amount of Cr was also plotted against solution pH in Fig. 1–b. The extracted amount of Cr, in general, only gradually increased as the concentration of the added HCl increased above 0.1 mol L^{-1}. Below this critical concentration, the increased concentration of the HCl solution had little effect on the extraction efficiency. Fig. 2 shows the relationship between the concentration of added HCl and the solution pH, i. e., the acid buffer curves of the soil samples. The buffer curves show that the solution pH was effectively dropped from above 6 to below 2 as the concentration of the added acid increased from 0.0005 to 0.1 mol L^{-1}. Nevertheless, there was no improvement in extraction efficiency in this acid concentration range. This is more clearly seen from the plots in Fig. 1–b, which shows that the extracted amount of Cr was almost constant in a pH range from above 6 to around 2 for all the soils.

Figs. 1 and 2 also show that the extracted amount of Cr greatly differed from one sample to another. The Cr extractions from the Umi–C and –F soils were higher than those of other soils in the entire concentration range. On the other hand, the Yoshiki–A and Sasaguri1–A samples exhibited the lowest extraction. The amount of Cr extracted from the Choyo and Goshi

samples was as low as that for the Sasaguri1–A and Yoshiki–A samples at low HCl concentration but it increased with increasing HCl concentration and approximately 50% of the total Cr was extracted in 1 mol L^{-1} HCl. The extraction patterns for the Sasaguri2–B, Yoshiki–B and Chikugo–A samples were similar in that about 200 mg kg^{-1} of Cr was extracted in 0.1 mmol L^{-1} HCl and the extraction increased up to 400–500 kg^{-1} as the HCl concentration increased.

The comparison of Table 2 and Fig. 1 suggests that the order of extraction efficiency roughly paralleled the order of the Cr(VI) content. The extracted amount of Cr in 0.1 mmol L^{-1} HCl was plotted against the Cr(VI) content in Fig. 3. This plot clearly shows that there is a 1:1 relationship between the extracted amount of Cr in 0.1 mmol L^{-1} HCl and the Cr(VI) content for soil samples other than Goshi–A and Choyo–B, suggesting that Cr(VI) was almost quantitatively extracted in the dilute HCl at around pH 6. The big deviations from 1:1 relationship for the Goshi–A and Choyo–B samples are probably due to the adsorption of chromate by allophane in these soil samples.

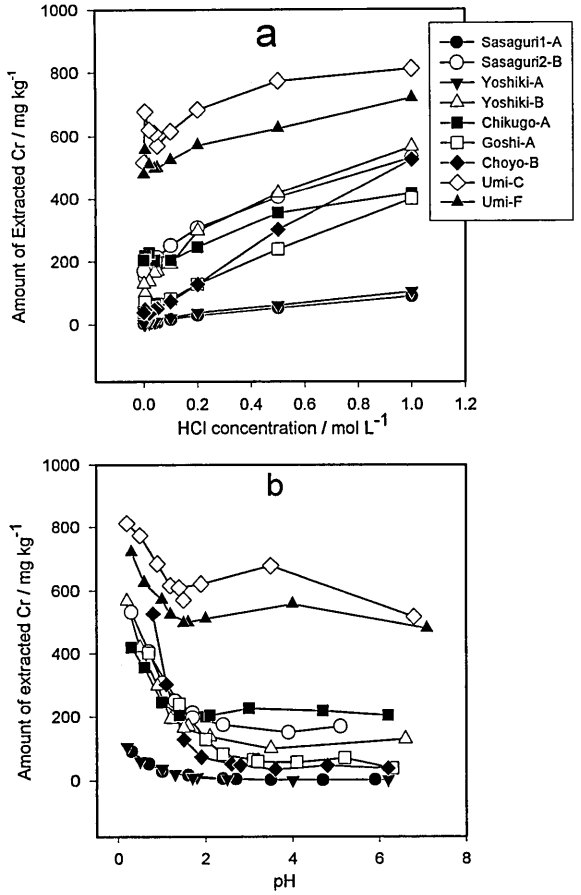

Fig. 1. Extracted amount of Cr as plotted against HCl concentrarion (a) and solution pH (b).

According to previous adsorption studies (Zachara *et al.*, 1989; Dzombak and Morel, 1990), chromate adsorption by soils and iron oxide minerals increases as pH decreases below 8. Under a fixed chromate load, the adsorption starts to increase at around pH 8 and reaches plateau at slightly below pH 7. Since the solution pH of the present soil samples were in a range from 6.5 to 7 when the 0.1 mmol L^{-1} HCl was added and equilibrated, all the chromate should have been adsorbed. The unexpected near complete extraction of chromate may be partly due to the competition with silicic acid (Garman *et al.*, 2004). It is naïve to generalize the present results but Fig. 3 strongly suggest that the adsorption of chromate is not significant in non–allophanic soils.

The adsorption studies also show that the adsorption of chromium ion (Cr(III)) decreases as solution pH deceases. Compilation by Dzombak (1990) shows that Cr(III) adsorption via surface complexation starts to decrease at pH of about 5 and becomes negligible below pH 3. In the present experiment, however, the Cr extraction was nearly constant in the pH range from 6 to 2 (Fig. 1–b). This seemingly contradictory result may be explained by taking other adsorption mechanisms into consideration. One is the complexation by humic substances. Although there is no data on the complexation of Cr(III) by humic substance but similarity of Cr(III) to aluminum ion suggests that it forms stable complexes with humic substance. Another one is the adsorption via cation exchange reaction. Fig. 4 shows the relationship between the percentage of Cr extracted in 1 mol L^{-1} HCl and ECEC, in which fairly high negative correlation is noticeable. This trend supports the view that the retention via cation exchange is a cause of the unexpectedly

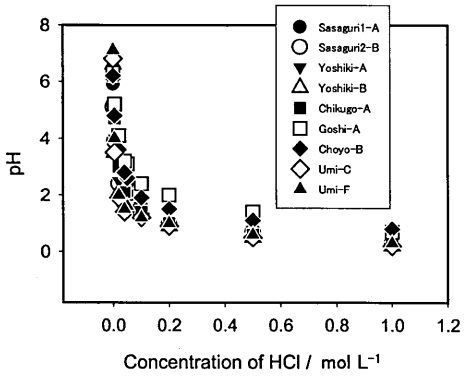

Fig. 2. Equilibrium pH as plotted against concentration of added HCl.

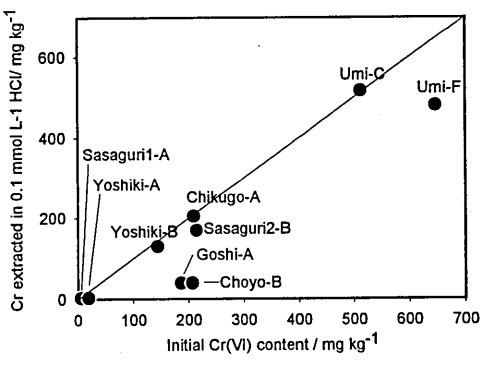

Fig. 3. Relationship between initial Cr(VI) content and amount of Cr extracted in 0.1 mmol L^{-1} HCl.

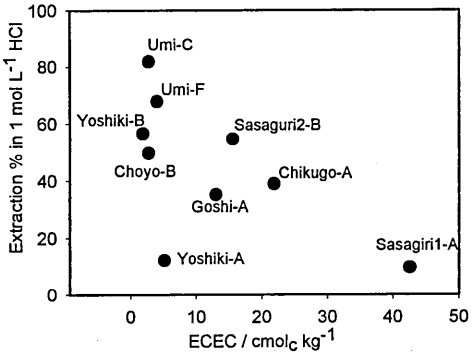

Fig. 4. Relationship between ECEC and Cr extraction percentage in 1 mol L^{-1} HCl.

low extraction. The plot point for the Yoshiki–A sample markedly deviates from the trend, suggesting that the complexation by humic substance also contributed the low extraction efficiency.

Table 2 shows that at least a part of the spiked Cr(VI) was reduced to Cr(III) during air–drying and storage in soils having pHs around 6. Since the reduction reaction is favored by acidification as expected from the stoichiometry of the reaction (Eq. (1)), the reduction reaction must have advanced further during extraction at pHs$<$4. This is favorable for detoxification of Cr because Cr(III) is much less toxic than Cr(VI). As already discussed the washing with HCl can effectively remove Cr(VI) at least from non–allophanic soils. The washing with acid is, therefore, effective method for at least detoxification of Cr in soils if not for decontamination of Cr.

One concern is that Cr(III) is oxidized to Cr(VI) in some soils (Chung and Sa, 2001; Cooper, 2002; Kim and Dixon, 2002; Stepniewska *et al.*, 2004). Mn oxide minerals were identified as oxidant of Cr(III) in soils and Cr(III) oxidation potential increases as the content of Mn oxides increases (Kim and Dixon, 2002). The Cr(III) oxidation by Mn oxides in soils are favored by low organic matter content and high pH (Cung and Sa, 2001). Thus, necessary conditions for suppressing Cr(III) oxidation do not accord with those for minimizing solubility of cationic heavy metals such as Pb^{2+} and Cd^{2+}. For cationic heavy metals, soil pH should be maintained at 7 or above by liming to reduce the solubility of remaining heavy metals. For Mn–rich soils that are contaminated with both Pb and Cr, washing with acid and subsequent liming may not be enough for reducing risk.

CONCLUSIONS

The soil washing with dilute acid could effectively remove Cr(V) from non–allophanic soils. It was, however, not effective for extracting Cr(III). Retention of Cr(III) on cation exchange sites and formation of stable complexes with soil organic matter are the possible causes for the low Cr(III) extraction efficiency. The acid–washing would successfully remove cationic heavy metals and Cr(VI) from multiply contaminated soils leaving most part of Cr(III). Since Cr(III) is gradually oxidized to give Cr(VI) in Mn–rich soils at high pH, the application of soil washing with acid and subsequent alkalinization for stabilization to such soils should be avoided.

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