Cr-removal Efficiency as Affected by the Cr-bonding Fractionation in Soil Treated with Trivalent and Hexavalent Chromium

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Abstract: Under natural environmental conditions, chromium is often present in trivalent Cr(III) or hexavalent Cr(VI) states. Cr(III) and Cr(VI) have different mobility and toxicity. Furthermore, trivalent chromium is present in cationic state, e.g. $CrCl_3$ and $Cr(NO_3)_3$, and hexavalent chromium as oxyanions, e.g. $K_2Cr_2O_7$ and K_2CrO_4. This study was to compare the adsorption and distribution of Cr(III) and Cr(VI) in contaminated soils and the influence of citric acid and pH on soil washing efficiency. $CrCl_3$ and $K_2Cr_2O_7$ were the selected as the representative cationic (Cr^{+3}) and anionic ($Cr_2O_7^{-2}$) species for study. Two synthetic Cr-contaminated soils were prepared by immersing the soil column in the Cr solutions and the Cr bonding fractions in soils was studied. Furthermore, citric acid solutions with various pH values were used to wash the contaminated soils. The washing efficiency of various chromium bonding fractions as affected by pH and washing time was studied. The results showed that there was no significant difference in the distribution of Cr bonding fraction between the cationic Cr^{+3} and anionic $Cr_2O_7^{-2}$ treated soils. For Cr^{+3} and $Cr_2O_7^{-2}$ contaminated soils, the Fe-Mn oxide bonding fraction was the most dominant, followed by the organic bonding fraction. For the $CrCl_3$ contaminated soils, when the washing time was adequate (48 h), citric acid with lower pH had the highest Cr removal efficiency. For the $K_2Cr_2O_7$ contaminated soil, the citric acid with pH 6 had the best removal efficiency.

Keywords: Cr(III); Cr(VI); bonding fraction; soil washing.

1. Introduction

Chromium is a major soil contaminant. According to Taiwan EPA, there are more than 100 locations identified as Cr contamination-control sites. Chromium has been used widely in various industrial processes, including textile dying, metallurgy, steel refining, electroplating, leather tannery, and wood preserving [1-3]. Under natural environmental conditions, chromium often is present in either the trivalent Cr(III) or the hexavalent Cr(VI) states [1, 2, 4]. Cr(VI) is present in oxyanionic form e.g. chromate (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$). Cr(III) is usually

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present in cationic state, e.g. $CrCl_3$ and $Cr(NO_3)_3$ [2, 4]. Cr(VI) is extremely toxic to human and may cause dermatitis or trigger cancer and mutation [1-5]. On the other hand, Cr(III) is known to be an essential trace nutrient that promotes many enzymatic reactions in human body such as regulating glucose, lipid and protein metabolism [3, 5]. Cr(VI) has greater mobility and leachability than Cr(III). The mobility of Cr(VI) increases as soil pH increases; the trend is inversed for other cationic metals [4, 6]. Cr(VI) can be reduced to Cr(III) by Fe^{+2}, S^{-2} and soil organic matters under anaerobic conditions [2, 7]. Cr(III) seldom occurs in the environment as a free ion; rather Cr(III) and water form an octahedral hydrate $[Cr(H_2O)_6^{+3}]$, which hydrolyzes to form hydroxyl complexes [2,8]. Under alkaline to slightly acidic conditions, Cr(III) is much less mobile and precipitates readily as $Cr(OH)_3$ or $Fe_xCr_{1-x}(OH)_3$ [2, 7]. Cr(III) is the dominant form of chromium at pH < 4, and forms complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{-2}, and soluble organic ligands [7]. Cr(III) is gradually oxidized to Cr(Vl) in Mn(VI)-rich soils at alkaline pH [2, 6]. Laborda et al. (2007) [8] reported that Cr(VI) accounted for 6% of the total chromium in the compost, and no significant amount of Cr(VI) was mobilized in the pH 4~10 range. When Cr(III) is bound to humic acid, its solubility and mobility decrease as pH increases due to increase in the solubility of humic acid.

According to Taiwan Environmental Protection Agency, soil washing was the most frequently practiced technique in remediating soil contaminated by heavy metals in Taiwan. Soil washing presents several advantages such as: (1) rapid revitalization of the site, (2) considerable reduction of the volume of contaminated soil during further treatment, (3) the permanent removal of metals with possibility of metal recovery by extracting from the washing effluents and (4) possible

return of the treated soil to the site [9]. For soil washing, acid solution often was used to leach the metals from contaminated soils. Strong mineral acid such as hydrochloric (HCl), sulfuric (H_2SO_4), nitric (HNO_3), phosphoric (H_3PO_4) or weak organic acid such as acetic acid and citric acid were commonly used [9]. The mechanisms contributed to the extraction of metals from soil using acid solution include: (1) desorption of cationic metals via ion exchange, (2) dissolution of metal compounds, and (3) dissolution of soil mineral components (e.g., Fe-Mn oxides) which may contain metal contaminants [9]. A number of studies indicate that the acid washing method is not reliable for remediating the chromium-contaminated soil primarily because the treatment efficiency of various forms of chromium is uncertain. The removal efficiency of an acid solution strongly depends on the metal type, the soil geochemistry, metals associated with soil fraction and the reagent concentration [9-11]. Isoyama and Wada (2006) [6] reported that HCl leaching was efficient for chromate (CrO_4^{-2}) removal from non-allophanic soils but it was inefficient for the removal of Cr(III), particularly from soils having high cation exchange capacity and organic matter content due to complexation by humic substance and adsorption via cation exchange reactions. Neale et al. (1997) [12] asserted that the difficulty in removing Cr using acid reagents may be attributed to the presence of Cr in the insoluble Cr(III) oxidation state in the soils. Furthermore, the adsorption of oxyanionic Cr(VI) species is enhanced at low pH. Kuo et al. (2006) [10] showed that acid leaching with 0.1M HCl contributed to a significant dissolution of Fe and Al oxides and phyllosilicates. At pH < 2.2, the dissolution process, instead of ion exchange, becomes the major mechanism for metal extraction. Jean et al. (2007) [13] proposed that citric acid was the most effective

leaching agent for Cr mobilization; the effectiveness could be attributed to the ability to solubilize the mineral matrix and by competing with anionic Cr(VI) for surface sites. Citric acid is an nontoxic organic weak tricarboxylic acid with acidity constants of 3.15, 4.77 and 6.40 for pKa_1, pKa_2 and pKa_3, respectively. Over a wide pH range, citric acid is a ligand that can form complexes with heavy metals. Complex reactions often outcompete with acid dissolution as mechanism for the extract of metals from soil. Citric acid is commonly known as a chelating rather than acid agent. Kantar et al. [14, 15] demonstrated that citric acid was highly effective in removing uranium from contaminated soils. Neale et al. (1997) [12] showed that citric acid was an effective extracting agent for removing Cr from soils compared to strong mineral acids such as HCl [16]. According to Logue et al. (2004) [17], the metal mobility in the presence of citrate was substantially enhanced by three major processes: (1) complexation with metal, (2) physical surface alteration, and (3) chemical surface alteration. Kantar and Honeyman (2006) [14] reported that complexing ligands such as citrate may compete for the surface adsorption sites with metals and decrease the extent of metal adsorption via the formation of non- or weakly adsorbing species. The extraction by citric acid exhibits a short period of about 10 h of rapid initial leaching followed by a slower, extended leaching process of about 15-80 h [14]. The initially rapid step may be attributed to a reaction-rate-controlled extraction of metals from the soil surfaces; the slower reaction step may be caused by various processes, including interparticle diffusion, diffusion into large aggregates, or structural rearrangement of surface species [18]. Kantar and Honeyman (2006) [14] reported that the maximum effect of citrate on metal iron leaching was observed at pH between 5 and 8 due to complexation reactions between metal ions and citrate. However, Francis et al. (1999) [19] reported that uranium removal by citric acid from the Fernald soils with high removal efficiency was associated with low pH values.

This study investigated the bonding of cationic Cr(III) and anionic Cr(VI) species with soil matrix. Soil washing test was conducted with citric acid at different pH values to assess the removal efficiency and the mechanism of Cr removal. Results will be valuable to the design of soil remediation strategy.

2. Materials and methods

Cationic Cr(III) was prepared with $CrCl_3$ (Acros Organics) and anionic Cr(VI) was prepared with $K_2Cr_2O_7$ (Acros Organics). Soil samples used in this research were collected from the top 15-cm layer of a farmland in Dali, Taichung city, Taiwan. After air drying, screening by a 2-mm sieve, the soil texture, pH, cation exchange capacity (CEC), soil organic matter (SOM) and soil heavy metal content were analyzed [20]. Soil texture analysis was conducted by wet sieving and sedimentation, following the steps: 50 g soil were placed in a 500 mL flask, 100 mL of 50 mg L^{-1} sodium hexametaphosphate and 250 mL of deionized water were added, the solution was mixed well by shaking and set asides overnight, then the soil solution was poured into 270-mesh (0.053 mm) sieve to separate the sand, the filtrate was transferred to 1000-mL cylinder. Sedimentation test was conducted at 25 ℃ to separate the silt and clay particles according to the Stokes law. The soil CEC was determined by the sodium acetate method [20]. Air dried soil (4g) was subjected to desorption exchange reaction using sodium acetate followed by ammonium acetate treatment to extract the sodium ion. Na content was determined by atomic absorption spectrophotometer (AA) and the soil CEC was calculated. The soil

organic matter content was determined by $K_2Cr_2O_7$ titration [20]. $K_2Cr_2O_7$ and concentrated sulfuric acid were added to 0.5 g of soil. The mixture was titrated with $FeSO_4$ solution to determine the $K_2Cr_2O_7$ consumption and calculate the soil organic matter content.

Column leaching test was carried out to determine the adsorption of cationic Cr(III) and anionic Cr(VI) in soil. The acrylic column, 70 cm long and 5 cm in diameter was filled with a 5-cm layer of glass beads (0.5 cm diameter) and quartz sand at the bottom followed by 15 cm of test soil (about 400 g), in the midle section and 4 cm of glass beads at the top. $CrCl_3$ and $K_2Cr_2O_7$ (Acros Organics) solutions were prepared at a concentration of about 1000 mg L^{-1} as Cr respectively. Peristaltic motor (MasterFlex, model 7518-00) was used to inject $CrCl_3$ or $K_2Cr_2O_7$ solution to the top of the column, allowing the solution to soak the soil fully. The drain valve at the bottom of the column was closed first and then the peristaltic motor was turned off when the liquid height rose to 6 cm above the soil top. After 24 h of soaking, the drain valve was opened to discharge the solution, then a peristaltic motor was restarted to fill the column with Cr-containing solution. The soaking and draining step were repeated for five times. Finally, the soil column was flushed with the leaching solution, 3 times of the soil weight, then the soil was removed from the column and placed in a crucible to dry. The soil was then crushed and mixed well in a mortar for the Cr(III) and Cr(VI) adsorption test. To determine the total Cr and its various fractions in the soil, aqua regia digestion method and Tessier sequential extraction procedure were used for Cr extraction, and the Cr content in each fraction was determined by using flame atomic absorption spectrometry (Perkin Elmer, AAnalyst 400). For aqua regia digestion, 3 g of soil were introduced to 21 mL of concentrated hydrochloric acid and 7 mL of concentrated nitric acid. The mixture was shaken and mixed well, set asides for 22 h, and then heated to boiling for about 2 h. The Cr-bond species were analyzed by the sequential extraction method of Tessier et al. (1979) [21] for exchangeable, carbonate, Fe-Mn oxides and organic bonding fractions; the residual fraction was done by the aqua regia digestion method [22-24].

Batch washing of Cr contaminated soil using citric acid followed the procedures: i) prepare 0.1 M of citric acid solution with pH adjusted to 2, 4, 6, 8, using NaOH; ii) place 40 g of soil sample in 250 mL of plastic bottle (10 cm deep and 6.5 cm in inner diameter); iii) add 200 mL of washing solution at the solid to liquid ratio of 1:5; iv) mount bottles on shaker and shake at 200 rpm under room temperature; v) take partial soil samples at 2, 12, 24, 48 and 72 h, rinse with deionized-distilled water 3 times the weight of the test soil sample, then dry and grind the soil samples with a mortar and mix well; vi) determine the total Cr and bonding Cr contents according to the methods described above.

3. Results and discussion

Bonding Fractions of $K_2Cr_2O_7$ and $CrCl_3$ in Soil. Table 1 shows the major properties of soil studied. The soil texture was sandy loam with an average organic matter contain of 5.7 %. Figure 1 shows the speciation of Cr(III) and Cr(VI). Over the five cycles of Cr uptake experiment, the mean Cr content was 534.0 and 2416.8 mg kg^{-1} of soil samples contaminated by $K_2Cr_2O_7$ and $CrCl_3$, respectively. According to past studies, Cr(VI) mobility was higher than that of Cr(III) [2, 4, 7]. In this study, the Cr content of the $CrCl_3$-contaminated soil was four times higher than that contaminated by $K_2Cr_2O_7$, indicating that Cr(III) had higher accumulation in soil than Cr(VI).

Table 1. The basic properties of study soil

organic matter (%)	CEC (cmol/kg)	pH	weight (%)			soil classification
			sand	silt	clay	
5.7±0.4	14.0±2.0	6.79	69.4	27.0	3.58	sandy loam

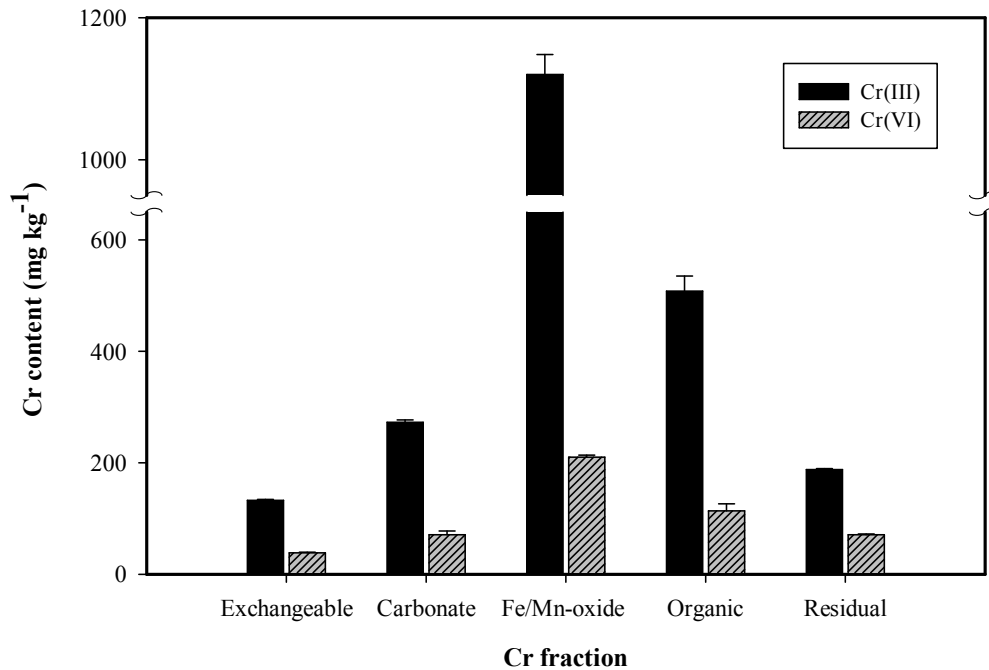**Figure 1.** The Cr fractionation distribution of $CrCl_3$ and $K_2Cr_2O_7$-contaminted soil

Chromium was present in soil mainly in the Fe-Mn oxide fraction, at 41.9 and 50.4 % of total Cr, respectively, for soil contaminated by $K_2Cr_2O_7$ and $CrCl_3$. The second most common fraction was the organic bonding fraction, accounting for 22.7 and 22.9 %, respectively, in soils contaminated by $K_2Cr_2O_7$ and $CrCl_3$. Kolelli (2004) [25] analyzed 12 Turkish agriculture soils and found that the majority of Cr was present in the residual fraction at about 90%.

Other studies by Weng (2005) [26] and Fu (2006) [27] showed that the iron and manganese oxide-bound chromium was the predominating chromium species in the contaminated soils. Kuo et al. (2006) [10] reported that Cr easily bound with Fe-Mn oxides in soils with the formation of mixed α-(Fe,Cr)OOH (goethite structure) [10, 28,

29]. Banks et al. (2006) [2] reported that Cr(III) under alkaline to slightly acidic conditions was present as $Cr(OH)_3$ or $Fe_xCr_{1-x}(OH)_3$ in soils leading to immobility of Cr in the subsurface. Evanko and Dzombak (1997) [7] reported that chromate and dichromate also were adsorb on the soil surfaces, specifically iron and aluminum oxides. The pH values of the $K_2Cr_2O_7$ and $CrCl_3$ leaching solutions were 4.94 and 3.64, respectively; the pH of the $K_2Cr_2O_7$ solution was higher than that of the $CrCl_3$ solution. Increasing the pH of the $K_2Cr_2O_7$ solution will increase the mobility of Cr(VI) [7]. When pH < 5, the Cr(III) mobility was decreased by clay adsorption or oxide minerals bonding [7], lead to more stable Cr(III). Cr(VI) may react with soil organic matter and be reduced to Cr(III). This study

adopted the method proposed by James et al. (1995) [30] to analyze the content of Cr(VI) in $K_2Cr_2O_7$-contaminated soil (use 0.28 M Na_2CO_3 and 0.5 M NaOH solutions to extract 60 mins at 90~95 ℃, and use AA to determine the Cr concentration). The results showed that the total Cr consisted of about 65~70 % of Cr(VI). Isoyama and Wada (2006) [6] treated soils with $K_2Cr_2O_7$ and reported that the Cr(VI) content of high organic matter soils was about 20 %, whereas in sandy soil samples, the Cr(VI) content was above 60% of the total Cr. In this study, although part of the Cr(VI) might have been reduced to Cr(III), the majority of Cr(VI) contaminated soil was in the Cr(VI) form.

According results of x^2 test on the Cr content in soils contaminated with $K_2Cr_2O_7$ and $CrCl_3$, there was no significant difference in fractional distribution of Cr(VI) and Cr(III) in soils of this study. Since there was no difference in the fraction distribution of Cr(III) and Cr(VI) in soils, it appeared that it was insufficient in determining the source of contaminants using the distribution of Cr fractions in environmental forensics. As shown by previous researchers [2, 7], both hexavalent chromium and trivalent chromium were bound easily with Fe-Mn oxides. In soils contaminated by $K_2Cr_2O_7$ and $CrCl_3$, the fraction bound to Fe-Mn oxides were 41.9 and 50.4 %, followed by the organic-bond fractions of 22.7 and 22.9 %, respectively; whereas the total percentage of the Fe-Mn oxides and organic-bond fractions were more than 60 %.

Influence of pH on the washing efficiency of Cr(III) and Cr(VI) with citric acid solution.

The influence of pH on the washing efficiency of soil Cr(III) and Cr(VI) using citric acid is shown in Figure 2 and 3. Washing experiments were conducted in batch mode and NaOH and HCl were used to adjust the pH of the citric acid solution

(0.1 M) to 2, 4, 6 and 8, respectively. As shown in Figure 2, the $CrCl_3$-contaminated soil, after 2 hr of washing, the Cr removal percent at pH 2 was the lowest, about 42.5 %; the Cr removal efficiency at other pH values, namely 4, 6, 8, were indistinguishable in the range of 55 ~ 60 %. At pH 2, the washing efficiency increased significantly with washing time; the extent of Cr washing at 48 h exceeded those of all other pH conditions. The washing efficiency at pH 4, 6, and 8 were high during the first two hours but increased slowly later. At pH 4 and over 48~72 h washing time, there was an increase in Cr washing of 1.4 %. Whereas there was less than 0.5 % increase by other solutions. Results indicated that washing had reached equilibrium at washing time of 48 h. The final trend after 48 h was that the citric acid solutions had higher washing efficiency at lower pH values. The removal efficiency at pH 2 was the highest at about 72 %; at pH 8 was the worst at about 60 %.

Figure 3 shows the Cr removal in the soil contaminated by $K_2Cr_2O_7$. At the washing time of 2 h, the Cr removal was around 62 %, greater than that of the $CrCl_3$-contaminated soil. The washing efficiency at pH 6 was the highest at all washing times with pH 8 being the lowest. Between 48 and 72 h, the removal percent increased significantly compared to the $CrCl_3$-contaminated soil with large variation at pH 2. At 72 h, the removing efficiency at pH 6 was the highest at about 86 % followed by at pH 4 at a removal of about 83 %. At pH 8 the removal was the lowest at about 74 %. In Figure 2, for Cr(III)-contaminated soil, the washing efficiency was higher at lower pH; whereas the optimal washing efficiency occurred at pH 6 for Cr(VI) removal. In the pH range of 2 to 6, the Cr washing efficiency increased with pH. The result was consistent with the trend of the soil adsorption of Cr(III) and Cr(VI) that the Cr(III) solubility increased as pH decreased; whereas the Cr(VI) solubility increased with

pH [7]. At pH 8, Cr(VI) washing efficiency was the lowest. Kantar and Honeyman (2006) [14] demonstrated that the maximum effect of citrate on metal leaching was at pH between 5 and 8 due to complexation reactions between the metal ions and citrate. Cr(VI) did not exhibit the highest washing efficiency at pH 8 due in part to unfavorable complex formation with citrate ions.

Figure 2 shows that poor washing efficiency occurred at pH 2 when wash time less than 12 h. The removal efficiency at pH 2 exceeded other washing solutions when washing time over 48 h. Reports showed that the metal extraction by citric acid exhibited a short initial leaching period of about 10 h which was attributed to reaction-rate-controlled of metal from the soil surfaces. The rapid extraction step was followed by a slower extended leaching process of 15~80 h, most likely caused by various diffusion processes [14, 18]. Kuo et

al. (2006) [10] speculated that when acid leaching at pH < 2.2, the dissolution process might replace the ion exchange reaction in metal extraction. Washing Cr(III) from soil using citric acid solution at pH 2 was accomplished by dissolution. The dissolution is controlled by diffusion process and as a result Cr(III) leaching efficiency at pH 2 lagged in the first 12 h. Jean et al. (2007) [13] reported that citric acid was the most effective for Cr(VI) mobilization due to its ability to render the mineral matrix soluble and the competition for the surface sites with Cr(VI). As shown in Figure 3, during the final 48~72 h, the Cr(VI) washing efficiency at pH 2 exceeded that at pH 4. The poor removal efficiency at pH 2 in the first 12 h may be due to the diffusion-control of dissolution as suggested by Kuo et al. (2006) [10] and Jean et al. (2007) [13]. Consequently, a longer time was needed to achieve high percent Cr removal.
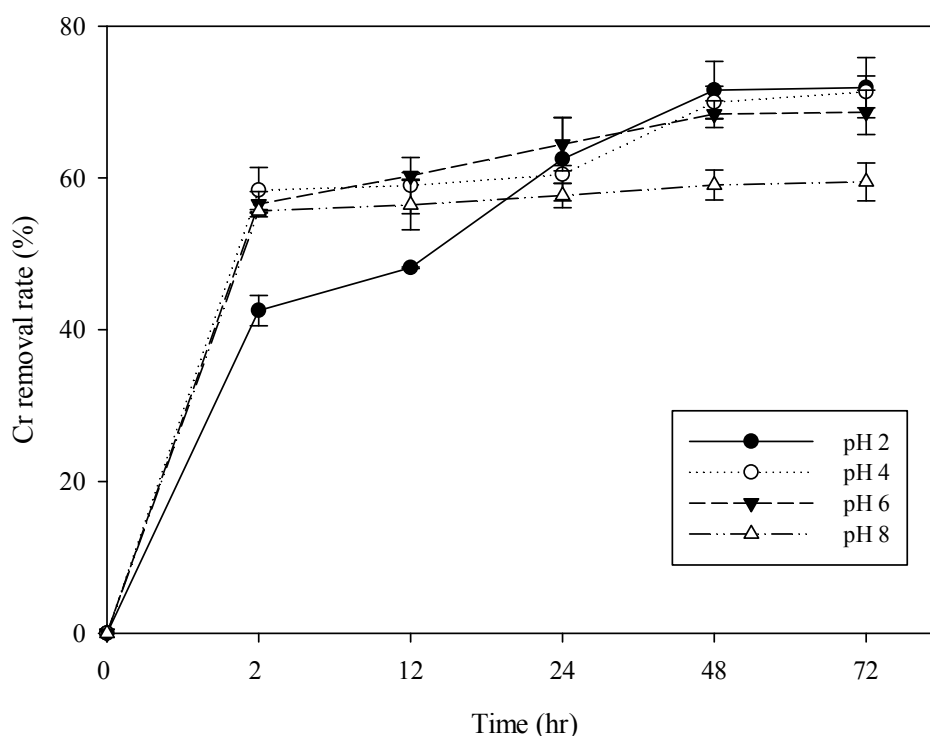

Figure 2. Batch washing of 0.1 M citric acid solution on CrCl$_3$-contaminated soil by different pH values and washing time. Error bars represent the standard deviation with n = 3

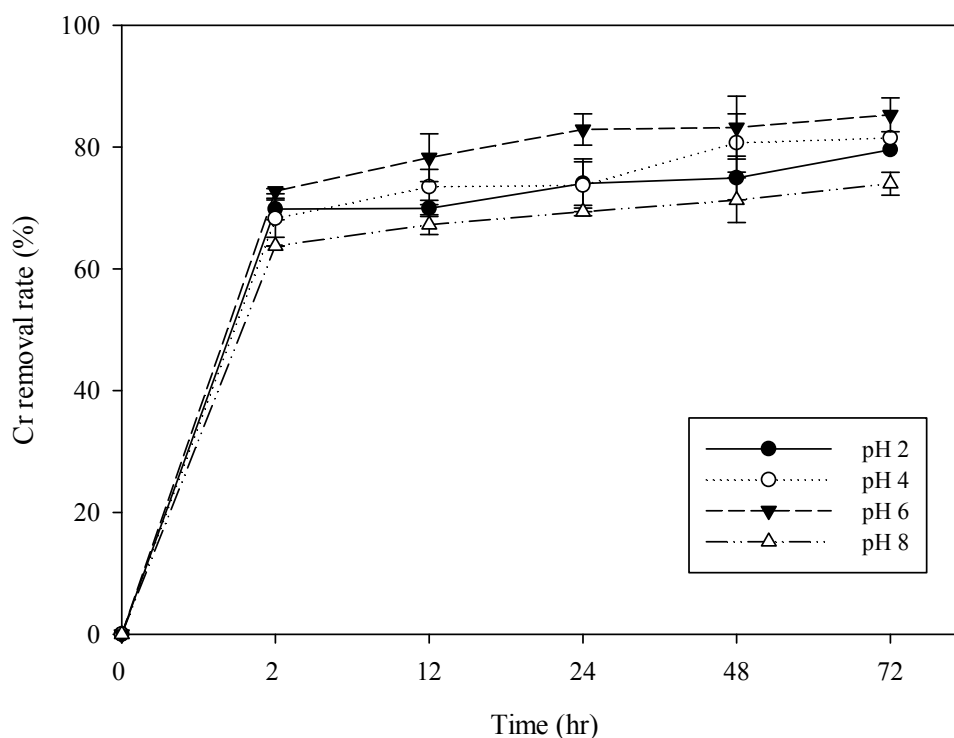Shu Fen Cheng, Chin Yuan Huang, Yao Tin Tu, and Jia Rong Chen

Figure 3. Batch washing of 0.1 M citric acid solution on $K_2Cr_2O_7$-contaminated soil by different pH values and washing time. Error bars represent the standard deviation with n = 3

Figure 4(a) and 4(b) show the distribution of Cr in the $CrCl_3$-contaminated soil at washing time of 2 and 72 h, respectively. At washing time of 2 and 72 h, the washing efficiency was slightly poor at pH 2 for both the exchangeable and the carbonate bonding fractions. The removal of the exchangeable fraction at pH 2 was about 65 % in 2 h; with an average removal percent of 86 % by other pH washing solutions. For the carbonate fraction, the removal was about 75 % at pH 2 and about 92 % at other pH values. The removal of the Fe-Mn oxide, the organic and the residual fractions at 2 h was no statistical difference. The average removal percent of the Fe-Mn oxide, the organic and the residual fractions were about 50, 15 and 70 %, respectively. At 72 h, the removal efficiency increased for all fractions, especially significant for the Fe-Mn oxide, and the organic bonding fractions. The removal percent at pH 2 of the Fe-Mn oxide

and the organic fractions were increased to 69 and 61 %, respectively. The Fe-Mn oxide fraction had higher removal efficiency at lower pH. The removal efficiency for the organic fraction was poor at pH 8 and the washing efficiency at the other 3 pH values were close. The residual fraction had a slightly large degree of removal at pH 2 and 6 with little difference of 31.5 and 43.0 mg kg^{-1}, respectively.

Figure 4(c) and 4(d) show the distribution of Cr in the $K_2Cr_2O_7$-contaminated soil at washing time of 2 and 72 h. At 2 h, the exchangeable fraction had the lowest removal efficiency at pH 8 of about 79 % and was greater than 90 % at other pH values. At 72 h, all washing solutions could remove the exchangeable fraction completely. For the carbonate fraction, all washing solutions achieved 100 % removal efficiency in 2 h. The Fe-Mn oxide fraction had the lowest removal efficiency at pH 8.

The removal percent at 72 h did not increase as compared with that at 2 h with an average of about 75 %. For three other washing solutions, the removal efficiency were close to each other with a mean removal of about 80 % at 2 h and about 85 % at 72 h. The washing efficiency of the organic fraction at various pH values was insignificantly varying in 2 h with a mean removal of about 70 %. At 72 h, the removal efficiency increased significantly at pH 2 and pH 6 with an average removal of about 83 %. The washing efficiency of two other washing solutions remained unchanged at about 70 %. The removal efficiency of the residual fraction at 2 h was slightly higher than at pH 2, about 27 %. The removal of Cr by three other washing solutions was below 20 %. At 72 h, the removal efficiency increased most significantly at pH 6, as high as 58 %, whereas the removal efficiency was less than 40 % at other pH values. Although the removal of the residual fraction of the $K_2Cr_2O_7$-contaminated soil by various washing solutions was lower than that of the $CrCl_3$-contaminated soil, the residual Cr concentration was 29.8 and 44.4 mg kg^{-1} at pH 6 and 2, respectively. For the $CrCl_3$-contaminated soil, the residual fraction concentrations were 31.5 and 43.0 mg kg^{-1} respectively at pH 2 and 6 at 72 h. The residual concentration of both Cr-contaminated soils close to each other after washing, averaging around 37 mg kg^{-1}, which indicated that the residual Cr should be incorporated in the soil matrix and hence could not be easily removed by washing.

For $CrCl_3$-contaminated soil, the citric acid solution at pH 2 had the highest removal efficiency yet required longer reaction time. As shown in Figure 4, extending the reaction time improved the removal efficiency of the Fe-Mn oxide and the organic fractions. Trivalent chromium

washing efficiency was dependent upon the Fe-Mn oxide fraction, which was about 50 % of the total Cr. The removal efficiency of the Fe-Mn oxide fraction was significantly higher at pH 2 than other pH values. The chromium washing efficiency of the $CrCl_3$-contaminated soil was affected by the Fe-Mn oxide fraction. The removal of the Fe-Mn oxide fraction at pH 2 was achieved by dissolution, which was controlled by diffusion processes and thus required a longer time. For the $K_2Cr_2O_7$ treated soil, the Fe-Mn oxide fraction had the highest removal percentage, but differed very little in the pH range between 2 and 6. The removal efficiency of the Fe-Mn oxide fraction from the $K_2Cr_2O_7$–treated soil was governed by two mechanisms. The Fe-Mn oxide dissolution according to which the lower the pH the higher is the efficiency of removal and the $Cr_2O_7^{-2}$ absorption according to which the higher the pH the higher is the degree of desorption. Under these two mechanisms, the washing efficiency of the Fe-Mn oxide bound hexavalent chromium differed indistinctively with the washing solutions of pH in the range of 2 to 6. In Figure 3, the removal efficiency of the hexavalent chromium at pH 2 was increased at 72 h. In Figure 4(d), the removal efficiency of the Fe-Mn oxide and the organic fractions at pH 2 improved significantly at 72 h. Therefore, it can be predicted that as the washing time was extended, the washing efficiency of the pH 2 citric acid solution was expected to be greater than that of pH 4. Although the desorption efficiency of hexavalent chromium in soil increased with pH, low pH acidic solutions still had high washing efficiency of hexavalent chromium. Since the primary removal mechanism was dissolution, longer reaction time was needed.
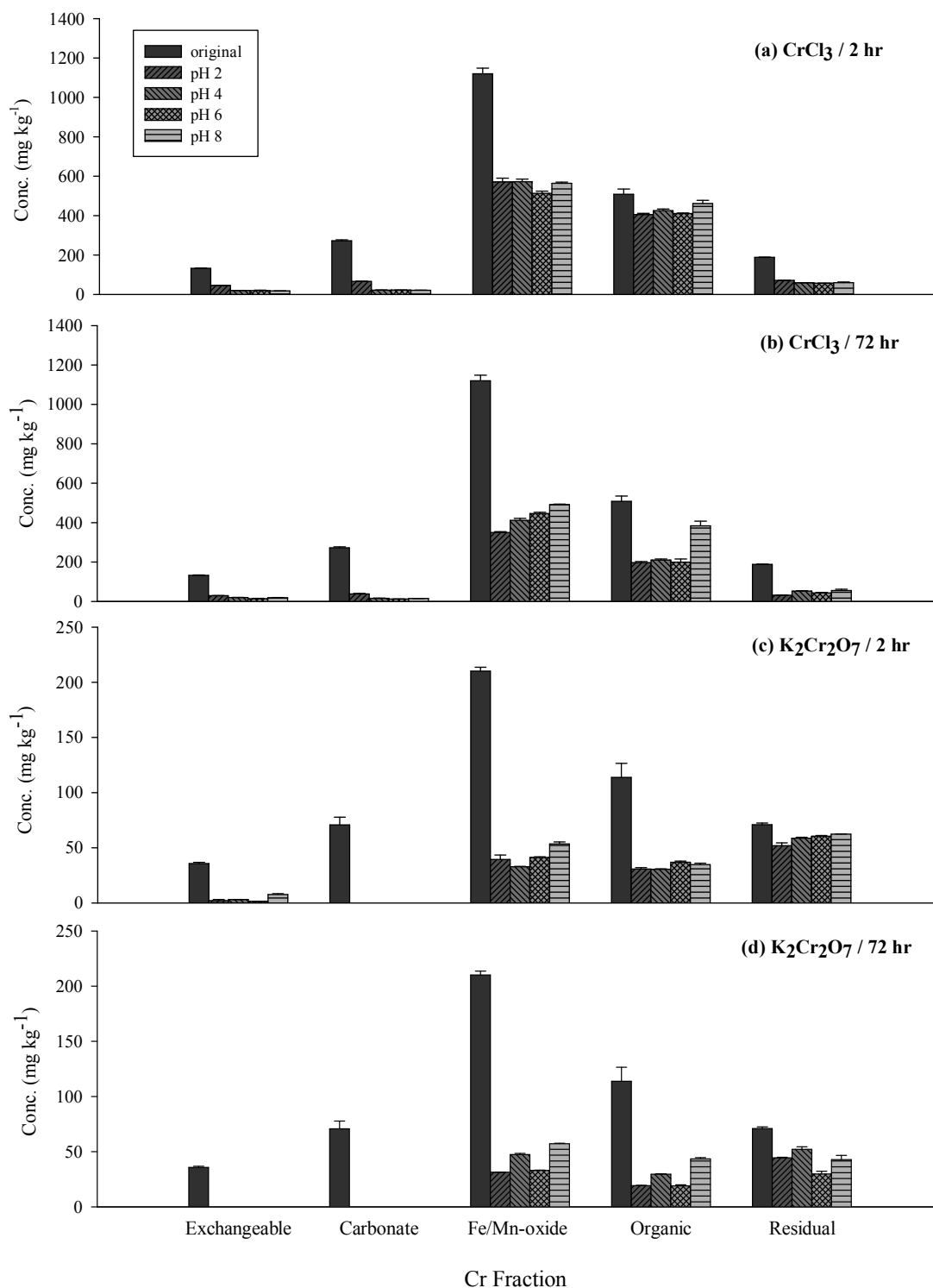
Figure 4. Citric acid solution (0.1 M) removing various fractions of Cr in CrCl₃ and K₂Cr₂O₇-contaminated soil, by different pH values and Cr fractions. (a) and (b) present the residual contents of various forms of CrCl₃ in soil after washing 2 h and 72 h, respectively; (c) and (d) present the residual contents of K₂Cr₂O₇ in soil after washing 2 h and 72 h, respectively. Error bars represent the standard deviation with n = 3

4. Conclusions

In $CrCl_3$- and $K_2Cr_2O_7$- contaminated soils, there was no difference in the distribution of the form of Cr fraction. The Fe-Mn oxide fraction was the most dominant followed by the organic bonding fraction. Therefore, it can be concluded that there will be no sufficient difference in determining the contamination source using Cr bonding fractions in environmental forensics. In terms of pH influence on the washing efficiency of citric acid, some differences occurred between the $CrCl_3$-and the $K_2Cr_2O_7$-contaminated soils. For the $CrCl_3$-contaminated soil, the lower the pH the higher was the removal efficiency. The washing mechanism of the citric acid solution at pH 2 was dissolution, thus longer washing time was required to achieve the washing efficiency. For the $K_2Cr_2O_7$-contaminated soil, the washing solution at pH 6 had the best removal efficiency because the desorption of hexavalent chromium increased with the pH. Although a lower pH of the washing solution inhibited the hexavalent chromium desorption, it was capable of dissolving oxide minerals and organic matters at low pH and aided in extracting hexavalent chromium. Especially in the case of high percentage of Fe-Mn oxide bonding fraction, citric acid at low pH had the same good washing efficiency for hexavalent and trivalent chromium due to the main mechanism of dissolution. Citric acid at low pH required longer reaction time. Washing time longer than 48 h was often required to achieve a higher efficiency.

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