



Soil and Sediment Contamination: An International Journal

ISSN: 1532-0383 (Print) 1549-7887 (Online) Journal homepage: <http://www.tandfonline.com/loi/bssc20>

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To cite this article: Zeynep Gökem Doğaroğlu & Cetin Kantar (2016): Reductive Immobilization of Chromium in Soils Containing Heterogeneous Fe-Bearing Minerals, Soil and Sediment Contamination: An International Journal, DOI: [10.1080/15320383.2016.1217827](https://doi.org/10.1080/15320383.2016.1217827)

To link to this article: <http://dx.doi.org/10.1080/15320383.2016.1217827>



Accepted author version posted online: 02 Aug 2016.
Published online: 02 Aug 2016.



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**SUBMITTED TO: SOIL AND SEDIMENT CONTAMINATION: AN INTERNATIONAL
JOURNAL**

**Reductive Immobilization of Chromium in Soils Containing Heterogeneous Fe-Bearing
Minerals**

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ABSTRACT

Cr(VI) immobilization in systems containing Fe-bearing soil minerals was studied in batch and column systems. Batch experiments showed that water chemistry such as solution pH and Cr(VI) concentration had a pronounced impact on Cr(VI) removal by Fe-bearing soil minerals. Acidic conditions were observed to be more favorable for enhanced Cr(VI) removal. The dependence of Cr(VI) removal on Cr(VI) concentration indicated that there were limited number of surface sites on Fe-bearing minerals responsible for Cr(VI) removal. A complexing agent, citrate, significantly enhanced both Cr(VI) removal and total Fe-dissolution from the mineral surfaces

relative to non-citrate containing systems, and the iron dissolved from the mineral surfaces was in Fe(III) oxidation form, implying that Cr(VI) removal occurred mainly on mineral surfaces, and the surface Fe(II) sites played an active role in Cr(VI) reduction. The results from column experiments showed that the accumulation of surface precipitates resulted in clogging of pore spaces, thereby creating preferential flow paths within the column. However, the addition of citrate significantly prevented the accumulation of surface precipitates due to the formation of highly soluble Fe-citrate complexes. SEM images revealed that the precipitates accumulated in the column had sponge-like shapes. The EDS analysis provided further evidence that the surface precipitates formed also contained Cr species as well as Fe. Overall it is clear that Fe-bearing minerals may serve as an effective reducing agent for in-situ reductive immobilization of hexavalent chromium in subsurface systems.

KEYWORDS

Fe minerals; immobilization; reduction; chromium; transport

Introduction

Chromium can be found in groundwater and soils at high concentrations because of its wide use in various industrial processes including metal plating, wood processing, leather tanning, metal corrosion inhibition, and pigment production. In subsurface systems, chromium is observed to be in two different oxidation states with different behaviors in toxicity, solubility and transport (Buerge and Hug 1998; Kantar et al. 2008). Hexavalent chromium(Cr(VI)) is much more toxic, soluble and mobile compared to the trivalent Cr species (Cr(III)). Traditionally, the wastewater and subsurface systems contaminated with Cr(VI) can be treated by reducing Cr(VI) to Cr(III) using a reducing agent such as ferrous iron (e.g., Sedlak and Chan 1997). Cr(III) has very low solubility, and precipitates as $\text{Cr}(\text{OH})_3$ and/or has a strong tendency to sorb onto mineral surfaces under slightly acidic to alkaline pH conditions (Palmer and Puls 1994).

Fe(II)-bearing minerals present in subsurface systems serve sources of inorganic reductants for redox sensitive inorganic and organic contaminants such as Cr(VI) and U(VI) (Eary and Rai 1988; Blowes et al. 1997; Buerge and Hug 1998; Loyaux-Lawniczak et al. 2001; Elsner et al. 2004; Chon et al. 2006; Xu and Zhao 2007; Kantar et al. 2015a, b). The most common Fe-bearing minerals in subsurface systems include pyrite, ilmenite, hematite, mackinawite, goethite, biotite and magnetite (Eary and Rai, 1989; Schlautman and Han, 2001). The reaction rate of Cr(VI) reduction with solution and surface-bound Fe(II) species is very fast with half-lives ranging from minutes to hours (Sedlak and Chan 1997; Blowes et al. 1997; Buerge and Hug 1998). However, the reduction of Cr(VI) to Cr(III) by surface bound-Fe(II) is highly dependent on chemical conditions (e.g., pH) (Kantar et al. 2015a). This pH-dependence of

Cr(VI) reduction by Fe(II) has been explained by the high reactivity of surface and solution phase Fe(II) species (Buerge and Hug 1998). Under slightly acidic to alkaline conditions, the Fe(III) species precipitate on mineral surface, and may lead to surface passivation (Patterson et al. 1997; Blowes et al. 1997). The solution pH also greatly affects the mineral isoelectric point with surface charge shifting from positive to negative with increasing solution pH (Sposito 1989).

Studies by several researchers have shown the effectiveness of solution and surface-bound Fe(II) in Cr(VI) reduction under both laboratory and field conditions (Blowes et al. 1997; Loyaux-Lawniczak et al. 2001; Kantar et al. 2015a). Eary and Rai (1989) reported that Cr(VI) reduction by Fe(II)-bound minerals such as biotite was significantly correlated with the amount of Fe(II) release from the mineral surface, indicating that the reaction mainly took place in solution rather than at the mineral-water interface. Blowes et al. (1997) reported that Cr(VI) reduction by Fe-bearing minerals was highly dependent on the type of Fe-mineral used. A study by Kantar et al. (2015a) showed that pyrite was very effective in reducing Cr(VI), and the reaction occurred on the pyrite surface.

Recent laboratory and field studies have demonstrated that both solution and surface-bound-Fe can also stimulate Cr(VI) reduction by low molecular weight organic acids and natural organic matter by acting as a catalyst (Deng and Stone 1996; Yang et al. 2008; Kantar et al. 2015b). In addition, natural organic acids may have a significant impact on Cr(VI) reduction by modifying surface properties of Fe-bearing minerals and by complexing with both Fe(II) and

Fe(III). A study by Kantar et al. (2015b), for instance, showed that organic acids such as oxalate significantly accelerated Cr(VI) reduction by pyrite under acidic conditions.

Subsurface systems are very complex, and may contain multiple different mineral phases. Despite the fact that the studies, primarily performed with pure mineral phases, show the capability of Fe-bearing minerals to reduce Cr(VI) (Blowes et al. 1997), to date, Cr(VI) fate and transport in heterogeneous natural soil systems containing Fe-bearing minerals has not been well documented in the literature (Davis and Olsen 1995). The primary objective of our study was to provide an improved understanding of Cr(VI) reduction and immobilization in natural soil systems containing Fe-bearing minerals. To accomplish our objective, a series of batch and column experiments were performed under variable chemical conditions (e.g., pH) and the reaction mechanisms involved were evaluated. Here, a complexing agent, citrate was also used to increase the solubility of surface oxidation products, and thus minimize surface passivation. Low molecular weight organic acids such as citrate and oxalate are ubiquitous in the environment since they are continuously produced by microorganisms (Sposito 1989).

Materials and methods

Soil samples

Natural Fe-containing minerals were collected from Kastamonu, Turkey. The Fe particles were first sieved, and the samples with less than $< 75 \mu\text{m}$ (< 200 mesh) were directly used in the experiments. The elemental composition as determined using the X-ray fluorescence spectrophotometer (XRF) analysis included Al (1 %), Si (6 %), S (40 %), K (0.1 %), Ca (0.05), Fe (52 %) and Co (1 %). The XRD analysis indicated a large percentage of iron sulfides (e.g.,

pyrite) with low clay, quartz and other minor minerals in the soil (data not shown). Single point BET-N₂ gas adsorption analysis indicated a surface area of 1.22 m² g⁻¹ for Fe-containing minerals used in the experiments. Based on an average site density (n_s) of 2.33 sites/nm² (Davis and Kent 1990), the specific site concentration (SOH_T) of Fe-containing minerals was estimated to be 4.73 μmol g⁻¹ using the following equation:

$$\text{SOH}_T = \frac{S_A n_s 10^{18}}{N_A} \quad (1)$$

where S_A is the BET-surface area (m² g⁻¹), and N_A is the Avogadro constant. For 10 g L⁻¹ Fe-containing minerals, the site concentration was determined to be 47.3 μM.

Chemicals

Water for all experiments was obtained from Millipore Ultraviolet (UV) water system. All chemicals used were reagent grade or better. Stock solutions of Cr(VI) were prepared using potassium dichromate (K₂Cr₂O₇) (Merck Co., Germany). Citric acid was supplied from Merck. The pH measurements were made with Orion 3-Star pH meter, and the electrodes were calibrated with pH buffer solutions (pH 4.01, 7.00 and 10.01).

Batch experiments

Batch experiments were performed to investigate the effects of initial Cr(VI) concentration on Cr(VI) removal by Fe-bearing soil samples. The experiments used 100 mL glass Erlenmeyer flasks. In all batch experiments, the ionic strength was adjusted with NaCl (I=0.01 M NaCl). The batch experiments were performed at a desired pH value with initial Cr(VI) concentration ranging from 52 to 104 mg L⁻¹. The Cr(VI) concentration used lies within the range observed in

Cr contaminated sites (Loyaux-Lawniczak et al. 2001; Fruchter 2002; Lai and Lo 2008). The amount of Fe(II)-bearing minerals used in the experiments was 10 g L^{-1} . In experiments involving citric acid, the citric acid concentration ranged from 0 to 10^{-2} M . The samples were placed on a shaker table for 48 h in the dark at room temperature, samples were taken periodically, and then the solids were separated by centrifugation. The Cr(VI) and Fe (II) concentrations in solution were determined with the diphenylcarbazide and phenanthroline colorimetric method (PG Instruments T90+ UV-Visible Spectrophotometer) at 540 and 508 nm wavelength, respectively (APHA 1995). The total Cr and Fe were analyzed using Atomic Absorption Spectrophotometer (Perkin Elmer, AAnalyst 700). All batch experiments were performed in duplicates.

Column experiments

Laboratory column experiments used a glass column with 2.2 cm (I.D) and 7.2 cm in length. Column was filled with 50 g of the Fe(II)-bearing minerals, and wrapped with aluminum foil to keep out light. The flow was applied from the column bottom at a constant flow rate of 0.1 mL min^{-1} . All solutions were prepared in 0.01 M NaCl as the background electrolyte, and contained 0.514 mM sodium bicarbonate (NaHCO_3) to minimize equilibration times and pH drift. The pH of the input solutions was adjusted to pH 8 by adding small aliquots of 0.1 M NaOH or HCl if necessary. The effluent samples were collected with Retriever 500 (Teledyn ISCO) fraction collector at 70 min. time intervals. The samples collected were analyzed for their Fe(II), Cr(VI) and total Cr and Fe contents. After the completion of experiments, the column materials were also extruded and examined with scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) to determine surface morphology and elemental composition.

Results and discussion

Batch experiments

The results of batch experiments indicate that the rate of Cr removal from solution varied significantly as a function of solution pH and Cr(VI) concentration (Figure 1). The Cr(VI) removal was much higher at lower pH and Cr(VI) concentrations. This pH-dependent Cr(VI) removal by Fe-bearing soil minerals indicated that proton was consumed during Cr(VI) removal. This pH-dependence of Cr(VI) removal by pure Fe-containing minerals has also been reported by other researchers (Sedlak and Chan 1997; Lai and Lo 2008; Lin and Huang 2008; Kantar et al. 2015a, b; Kantar and Bulbul 2016). Under acidic conditions, Cr(VI) exists as HCrO_4^- and interacts more strongly with the surfaces of Fe-containing minerals since the mineral surfaces become positively charged with decreasing solution pH. However, the efficiency of Fe-containing minerals for Cr(VI) removal decreases with increasing solution pH due to strong electrostatic repulsion between negatively charged mineral surfaces and CrO_4^{2-} under alkaline pH conditions (Lin and Huang 2008; Kantar et al. 2015a). In addition, the accumulation of surface oxidation products under alkaline conditions may also lead to surface passivation (Blowes et al. 1997; Patterson et al. 1997; Lin and Huang 2008; Kantar et al. 2015a, b). For instance, Patterson et al. (1997) observed that Cr(VI) reduction took place at the surface of iron sulfide, and the accumulation of solid-phase species (e.g., $\text{Cr}_{0.75}\text{Fe}_{0.25}(\text{OH})_3$) on mineral surfaces led to a significant reduction in Cr(VI) removal especially under alkaline pH values.

As shown in Figure 1, the Cr(VI) removal also showed a strong dependence on Cr(VI) concentration. The low Cr(VI) removal at high Cr(VI) concentrations may be explained through limited number of surface sites present on mineral surfaces. Note that the Cr(VI) concentration

used in the experiments exceeded the surface site concentration, indicating that the experiments were performed under site limited conditions. In all cases studied, the amount of Cr(VI) removed was more than the surface site concentration. This suggests that the sorption of Cr(VI) on to Fe-containing minerals was not significant, and another mechanism such as Cr(VI) reduction was mainly responsible for Cr(VI) removal from solution.

The rate of Cr(VI) removal was also observed to vary with the presence or absence of citrate at pH 3 (Figure 2). The addition of citrate significantly enhanced the Cr(VI) removal relative to non-citrate containing system. A similar effect of citrate on Cr(VI) removal by Fe-containing soil minerals was also observed at different pH values (Figure 3). According to several researcher, the enhanced Cr(VI) removal in the presence of complexing agents is caused by the removal of surface oxidation products which may cause surface passivation (e.g., Kantar 2016). Figure 4 shows the effects of citrate on Fe dissolution from Fe-containing soil minerals. As can be seen, the addition of citrate significantly increased total Fe-dissolution from the mineral surfaces relative to non-citrate containing systems due to the formation of highly soluble Fe-citrate complexes, and in all cases studied, a significant portion of Fe dissolved was in Fe(III) oxidation state with very little Fe(II) in solution. This indicates that Fe(II) associated with minerals such as pyrite was oxidized to Fe(III) while reducing Cr(VI) to Cr(III).

It is known that both Fe and Cr can strongly complex with citrate, and the formation of Fe- and Cr-citrate complexes may increase the solubility of both Fe and Cr (Buerge and Hug 1997; Zhou et al. 2008; Kantar and Bulbul 2016; Kantar 2016). For instance, in experiments involving Cr(VI) removal with pyrite, Kantar et al. (2015b) found that organic ligands such as

oxalate significantly improved Cr(VI) removal efficiency especially under acidic to slightly alkaline pH conditions. Similarly, Yang et al. (2008) found that citric acid catalyzed Cr(VI) reduction by a red soil rich in Fe-oxides. Their results suggest that the citrate-promoted Fe(II) dissolution was responsible for enhanced Cr(VI) reduction in solution. Similarly, Deng and Stone (1996) low molecular weight organic acids with various functional groups stimulated surface-phase Cr(VI) reduction by Fe-containing oxides e.g., goethite.

Column experiments

Figure 5 shows the Cr(VI) breakthrough curves in the absence and presence of citrate at pH 8. The addition of citrate significantly enhanced Cr(VI) retardation relative to non-citrate-containing systems. In the absence of citrate, the C/C_0 for Cr(VI) reached a maximum value of 0.3 at about 8 pore volumes, and decreased gradually to 0.2 at 9.7 pore volumes. While the value of C/C_0 remained constant between 9.7 and 12.9 pore volumes, it decreased sharply at higher pore volumes. The decrease observed in C/C_0 at 9.7 pore volumes may be explained through sorption of Cr(VI) onto oxidized Fe surfaces. However, at pore volumes > 12.7 , the oxidation products such as Fe-oxides accumulated, and clogged the pore spaces within the column, which led to a significant decrease in flow rate. A similar decrease in C/C_0 was also observed at 15 pore volumes in the presence of citrate. This indicates that although citrate enhanced the solubility of surface oxidation products, a significant portion of reaction products was still able to accumulate within the column. Figure 6 shows photographs taken of column materials after the completion of experiments both in the absence and presence of citrate. Note that the photograph taken from column material in the absence of citrate depicts what is clearly the isolated aggregates and

clusters of iron crystals, which seemed to clog the pore spaces, and thus create preferential flow paths within the column material (Figure 6A).

According to several researchers, the precipitate that forms during Cr(VI) reduction by Fe-bearing minerals contains Cr-/Fe hydroxides and/or mixed Cr(III)-Fe(III) (oxy)hydroxides (Patterson et al. 1997; Blowes et al. 1997; Loyaux-Lawniczak et al. 2001). For instance, Patterson et al. (1997) reported a surface precipitate with a reaction stoichiometry of $\text{Cr}_{0.25}\text{Fe}_{0.75}(\text{OH})_3$ in systems containing FeS as the Fe-bearing mineral. Similarly, in a spectroscopic study, Loyaux-Lawniczak et al. (2000) found that the Cr(III)-containing solid phase formed was ferrihydrite. In columns with citrate, on the other hand, the column material did not exhibit any accumulation of reaction products (Figure 6B). The effluent Fe concentrations in the absence or presence of citrate are presented in Figure 7. In systems with no citrate, the effluent total Fe concentration increased gradually with increasing pore volumes. The mass balance analysis performed suggested that nearly 100 % of total Fe in the effluent was in Fe(III) form, and was mainly associated with colloidal Fe-oxides.

In system containing citrate, on the other hand, the effluent Fe concentration increased sharply, and reached a maximum value of 160 mg L^{-1} at about 1.5 pore volumes. At pore volumes higher than 1.5, the effluent Fe concentration decreased down to 20 mg L^{-1} , and remained at this level throughout the experiment. The effluent samples mainly contained dissolved Fe(III) species with very little colloidal Fe. As seen in Figure 7, the amount of Fe dissolved was much higher in the presence of citrate most probably due to the formation of highly soluble Fe(III)-citrate complexes (Smith and Martell 2004; Kantar et al. 2015b; Kantar

2016). Scanning electron micrograph (SEM) of column materials is presented in Figure 8. Note that while the column materials exhibited the accumulation of sponge-like precipitates on column materials in the absence of citrate (Figure 8A), the surface precipitates were observed to be washed out in systems containing citrate (Figure 8B), confirming the results obtained in Figures 6 and 7. The analysis of the column materials with Energy-Dispersive Spectroscopy (EDS) suggested that while the surface precipitates contained peaks related to Cr species, no Cr peaks were detected on the surface of column material in the presence of citrate.

Conclusions

Laboratory batch and column experiments were performed to investigate Cr(VI) immobilization in systems containing Fe-containing soil minerals. Batch results indicated significant dependence of Cr(VI) removal by Fe-bearing soil minerals on solution pH and Cr(VI) concentration. Cr(VI) removal was much higher under acidic conditions (e.g., pH 3) indicating that proton was required for enhanced Cr(VI) removal. While the amount of Fe dissolved was low in the absence of citrate, the addition of citrate significantly enhanced both Cr(VI) removal and total Fe-dissolution from the mineral surfaces relative to non-citrate containing systems, and in all cases studied, a significant portion of Fe dissolved was in Fe(III) oxidation state with very little Fe(II) in solution. This implies that Cr(VI) removal mainly took place at the mineral surfaces, and citrate removed surface oxidation products which caused surface passivation due to the formation of highly soluble Fe(III)-citrate complexes. Column experiments show that the accumulation of surface oxidation products clogged the pore spaces, and thus created preferential flow paths within the column material. However, in systems with citrate, no significant accumulation of surface precipitates occurred within the column due to enhanced dissolution of

Fe-oxides and/or (oxy) hydroxides. SEM images revealed the accumulation of sponge-like precipitates on mineral surface in the absence of citrate. EDS analysis provided further evidence that, in addition to Fe, the surface precipitates also contained Cr species.

Acknowledgement

The authors wish to thank Mersin University Scientific Research Fund (BAP) for financial support (Project No: BAP-FBE ÇMB (ZGG) 2010-2 YL).

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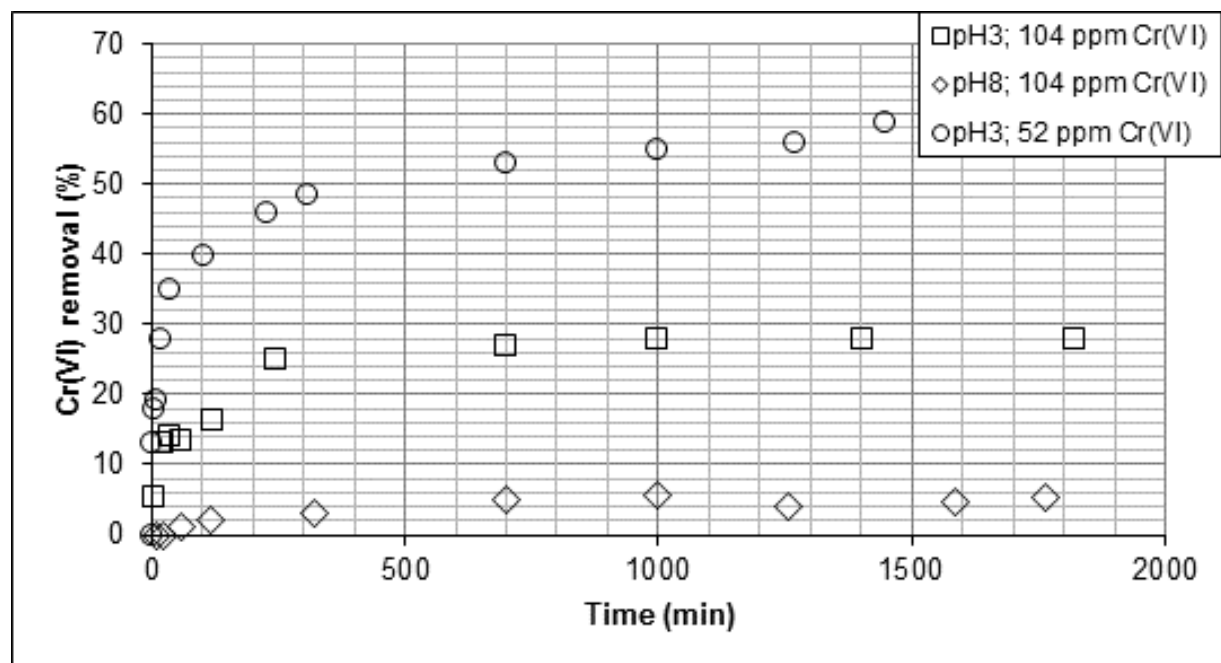


Figure 1. The effect of pH and Cr(VI) concentration on Cr(VI) removal by Fe-containing soil (10 g L^{-1}).

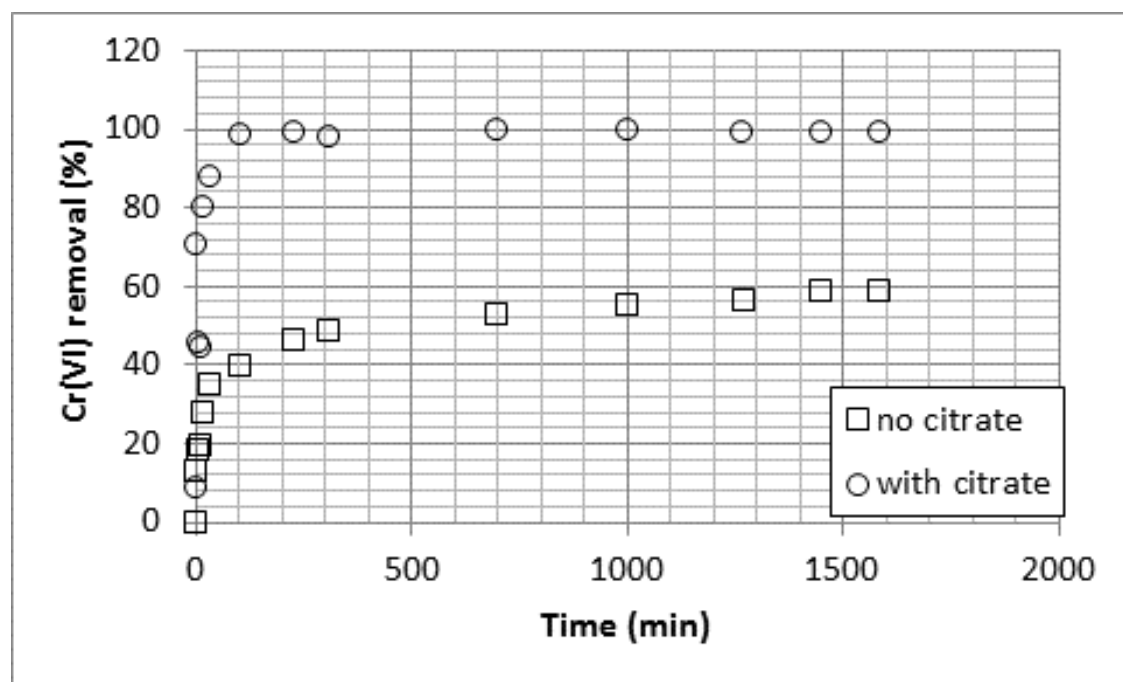


Figure 2. The effect of citrate (10^{-2} M) on Cr(VI) removal by Fe-containing soil (10 g L^{-1}) at pH 3. Cr(VI) = 52 mg L^{-1} .

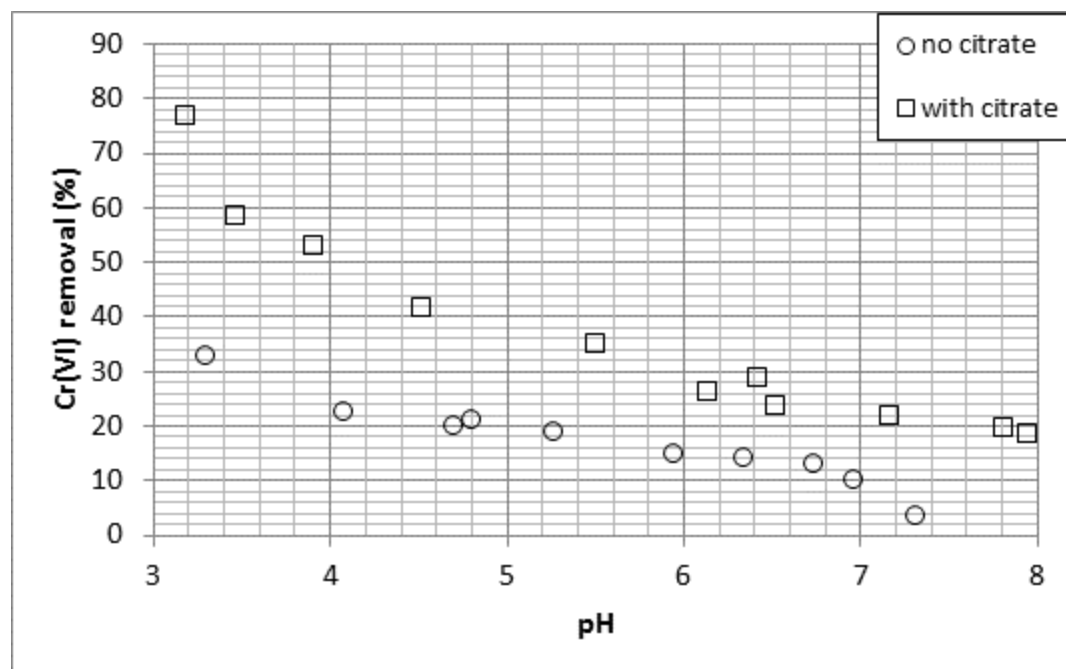


Figure 3. The effect of solution pH on Cr(VI) removal by Fe-containing soil minerals (10 g L^{-1}) in the absence or presence of 10^{-2} M citrate. The total reaction time was 24 h. $\text{Cr(VI)} = 104 \text{ mg L}^{-1}$.

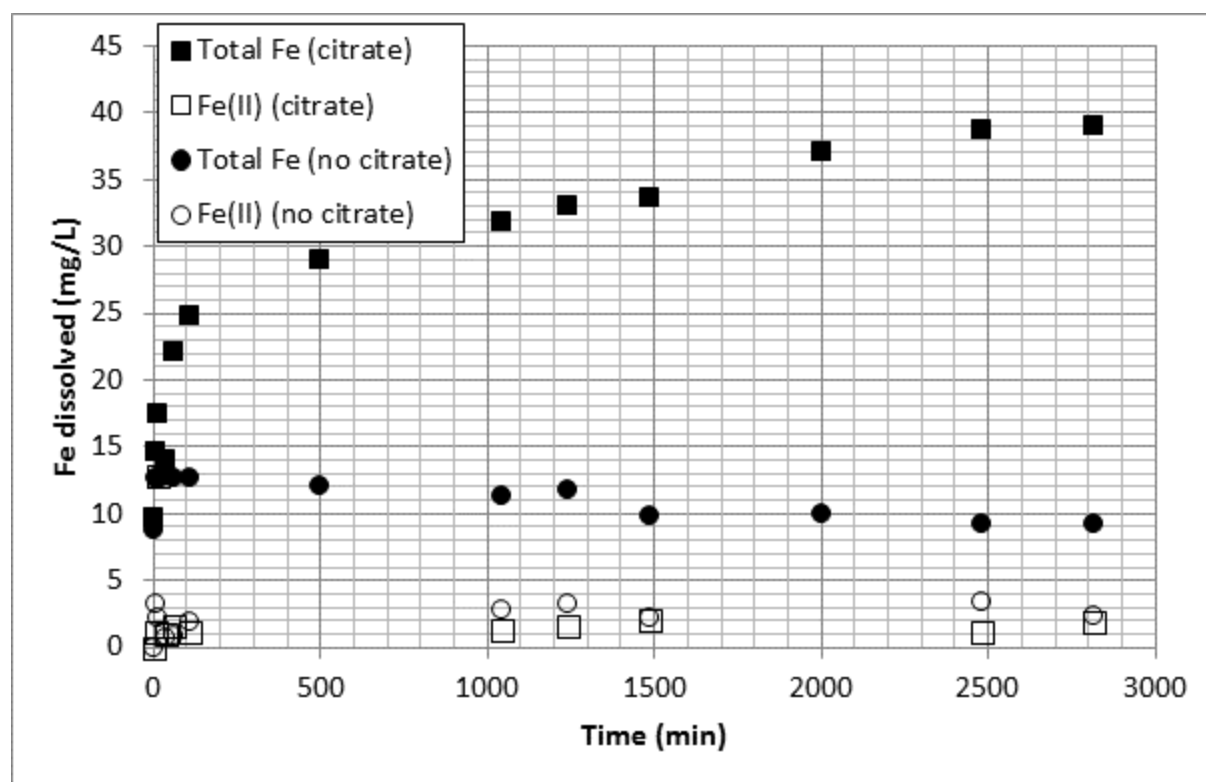


Figure 4. Fe dissolution from Fe-containing soil (10 g L^{-1}) in the absence or presence of citrate (10^{-2} M) at pH 3. $\text{Cr(VI)} = 52 \text{ mg L}^{-1}$.

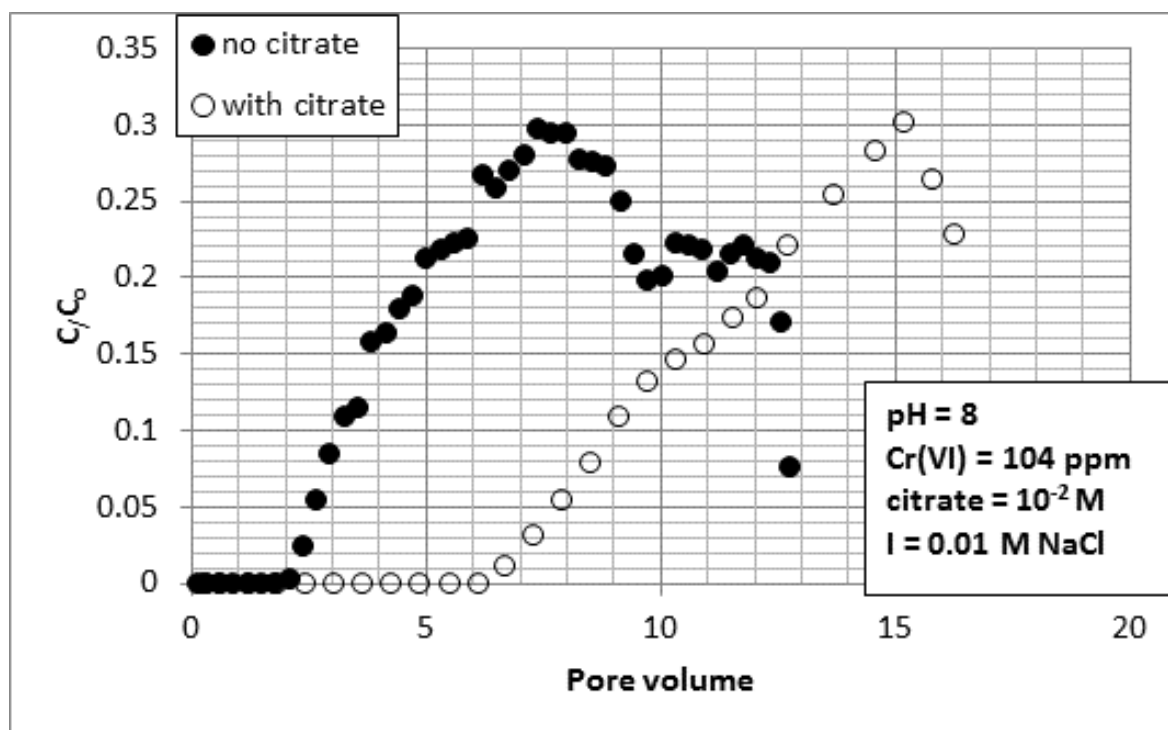


Figure 5. Cr(VI) transport through columns packed with Fe-containing soil in the absence or presence of citrate (10^{-2} M) at pH 8.

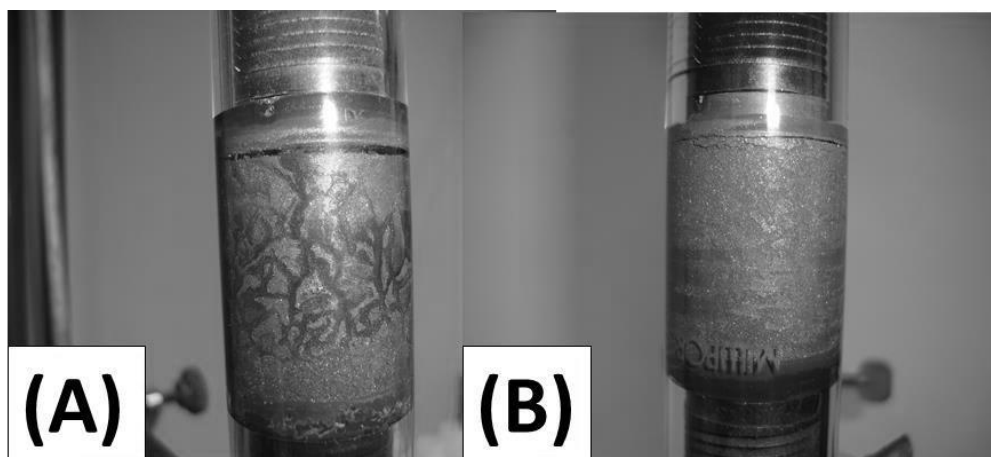


Figure 6. Photographs of column materials in the absence (A) or presence of 10^{-2} M citrate (B).

The photographs were taken after the completion of experiments reported in Figure 5.

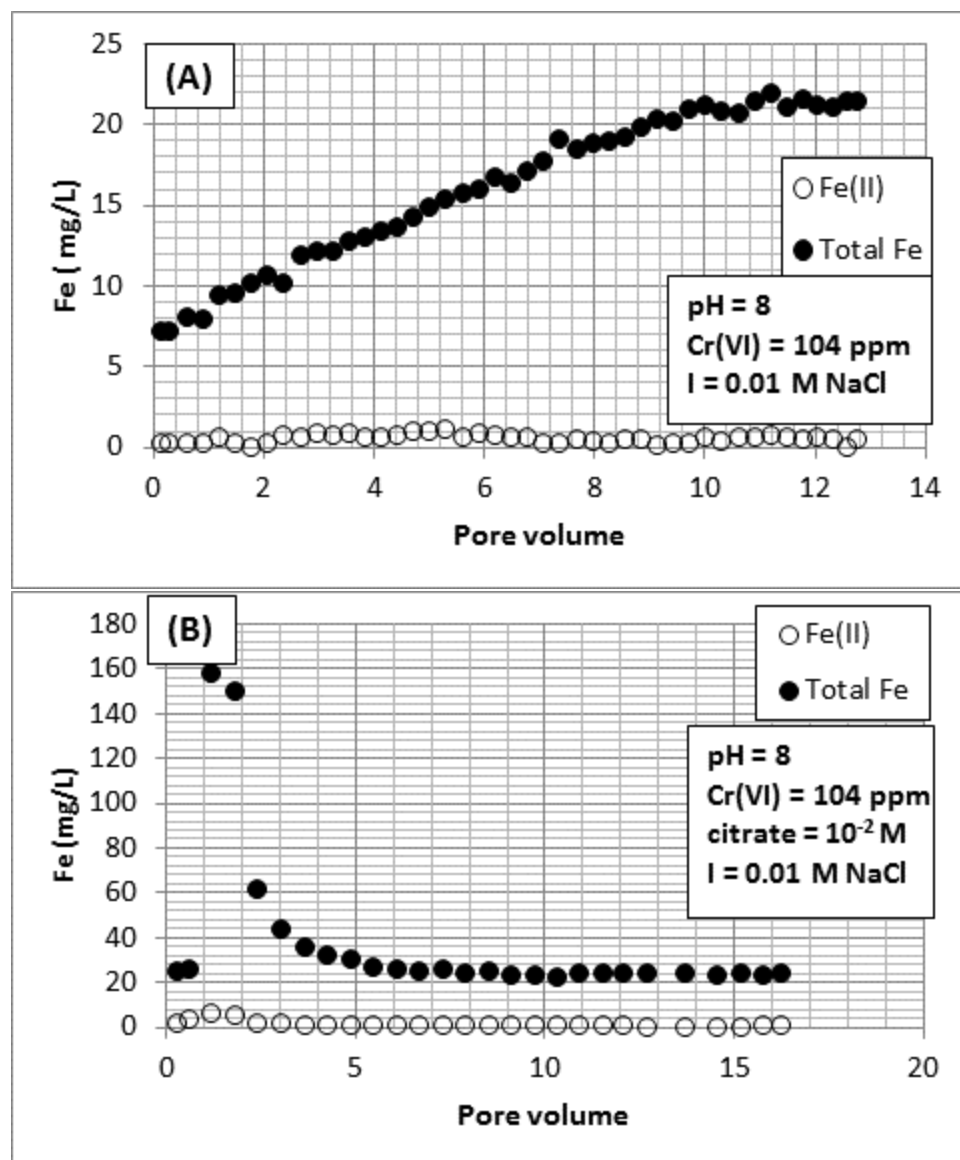


Figure 7. The effluent Fe concentration for column experiments conducted at pH 8 in the absence (A) or presence of 10^{-2} M citrate (B). The Cr(VI) breakthrough curves are reported in Figure 5.

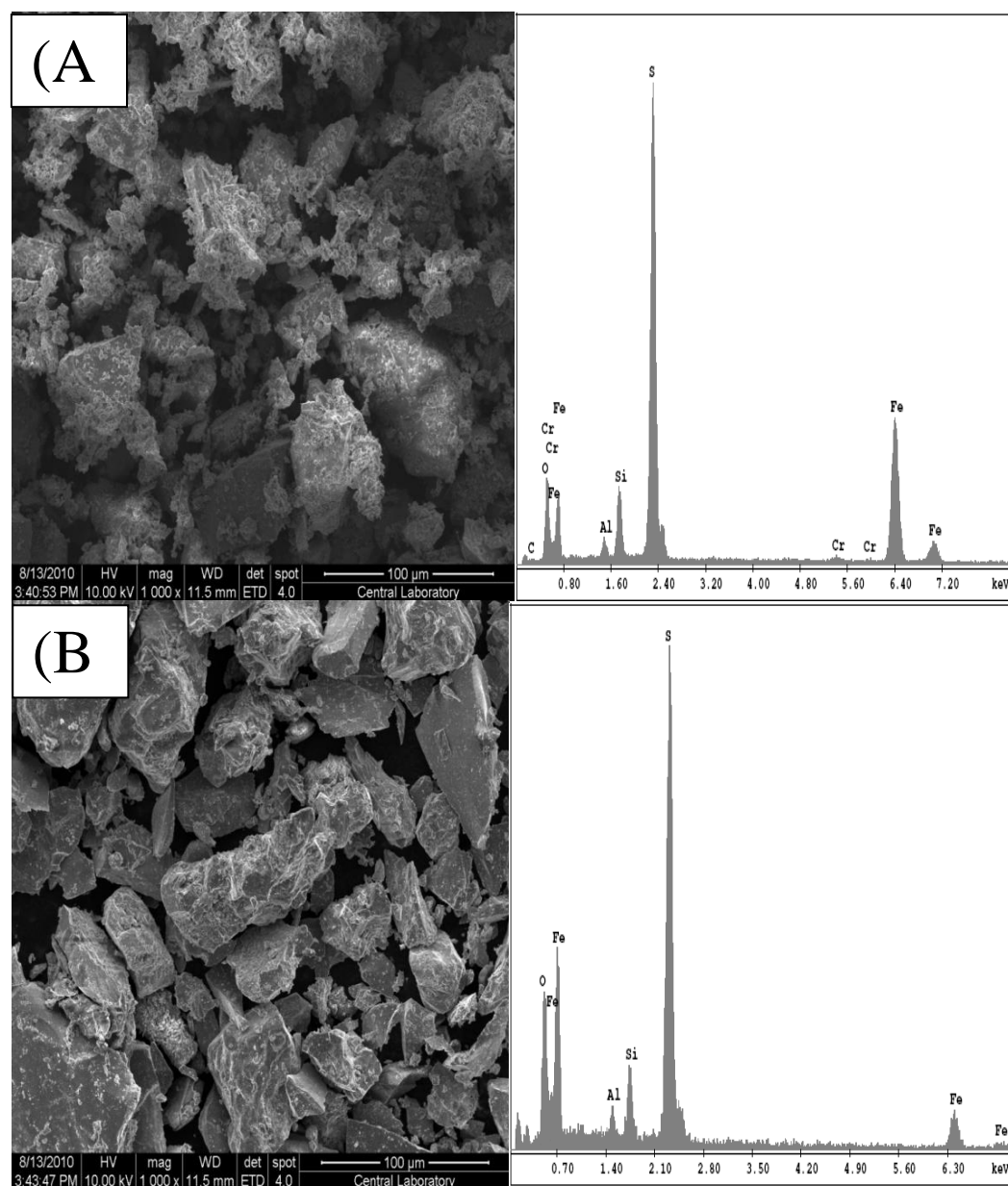


Figure 8. SEM-EDS images of the column materials collected after completion of experiments in the: A) absence of citrate and B) presence of 10^{-2} M citrate.