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In situ stabilization of chromium(VI) in polluted soils using organic ligands: The role of galacturonic, glucuronic and alginic acids

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ABSTRACT

Laboratory batch sorption and column experiments were performed to investigate the role of organic ligands such as galacturonic, glucuronic and alginic acids (main constituents of bacterial exopolymeric substances (EPS)) on Cr(VI) uptake and transport in heterogeneous subsurface media. Our batch sorption experiments demonstrate the addition of galacturonic, glucuronic and alginic acids to soils enhances Cr(VI) uptake by soil at pH values <7.7 depending on the concentration of the ligand and pH used. The enhanced Cr(VI) uptake at pH values <7.7 may be explained through either the catalytic reduction of Cr(VI) to Cr(III) by the surface-bound organic matter/Fe oxides and/or the dissolved metal ions (e.g., Fe(III)) from the soil. On the other hand, organic ligands have no or little effect on Cr(VI) uptake under highly alkaline pH conditions since the catalytic Cr(VI) reduction decreases with increasing pH. Similarly, the results from column experiments show that, depending on the concentration of organic ligands, the Cr(VI) breakthrough curves were significantly retarded relative to the organic acid-free systems at pH 7.6. A significant portion of Cr(VI) initially added to the feed solution was not readily recoverable in the effluent, indicating Cr(VI) reduction in columns, most probably catalyzed by surface-bound metal-oxides (e.g., Fe oxides) or dissolved metal ions such as Fe(II; III). The overall results suggest that EPS constituents such as glucuronic, galacturonic and alginic acids may play a significant role on Cr(VI) stabilization in subsurface systems under acidic to slightly alkaline pH conditions.

1. Introduction

Chromium is a widely used, toxic industrial pollutant that may occur in the environment at elevated concentrations [1–4]. For example, chromium contamination has been found at concentration levels up to 14 600 mg/kg in groundwater and 25 900 mg/kg in soil at some sites in the US [2]. Some serpentine soils also contain natural chromium up to 46 000 ppm [5]. The most important property of chromium with respect to its environmental behavior is its oxidation state since solubility, complexation and sorption behavior differ from one oxidation state to another. Chromium can exist in oxidation states ranging from Cr(II) to Cr(VI), although Cr(III) and Cr(VI) are the most dominant oxidation states in natural systems. While chromium typically occurs in the hexavalent form [Cr(VI)] under standard environmental (oxidizing) conditions, Cr(VI) can be reduced to Cr(III) in reducing environments. Cr(VI) is toxic to organisms, but Cr(III) is an essential element in humans [6]. The major Cr(VI) species include chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) which are thermodynamically stable over a large pH range in the environment [7].

The sorption and transport behavior of chromium highly depend on several chemical conditions including oxidation state, pH and presence of other inorganic and organic materials. Batch sorption studies, primarily performed with pure mineral phases, suggest that although Cr(III) is highly reactive, and may strongly sorb to the mineral phases [12], Cr(VI) exhibits weak to medium binding affinity for metal oxides such as Fe- and Al-oxides [8–10] depending on the environmental conditions (e.g., pH, organic matter content). Relatively, little information is available on Cr sorption and mobility in heterogeneous mineral systems [11,12]. A number of studies demonstrate that organic ligands, clay, dissolved metal ions and Fe(II; III) bearing minerals may act as a catalyzer in the reduction of Cr(VI) to less soluble Cr(III) [7,11,13–20]. Organic ligands may also compete against metal ions for surface sites on mineral surfaces [21–23], thereby reducing the extent of metal ion sorption to mineral surfaces.

Recently, organic ligands capable of reducing Cr(VI) have emerged as a reasonable means of enhancing or reducing Cr mobility and as a key factor to be addressed for assessing the long-term environmental stewardship of sites contaminated with chromium [11,24–27]. Several researchers have, for example, identified the potential role of microbial exudates in Cr oxide solubilization as a key question to be addressed for the development of remediation strategies and accurate assessments of environmental

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risks [27–29]. Exopolymeric substances (EPS) are produced by microbes for a variety of purposes in response to environmental stresses. Quantity and composition of EPS have been shown to vary depending upon bacterial strain and metal exposure in several studies (e.g., Refs. [28–31]). For example, in a study with the hydrogen-producing photosynthetic bacteria strain *Rhodopseudomonas acidophila*, Sheng et al. [31] found that toxic substances such as Cr(VI) and Cd(II) stimulated the production of microbial EPS.

In this study, batch sorption and column experiments were performed to elicit a better understanding of the effects of EPS constituents such as galacturonic, glucuronic and alginic acids on Cr(VI) transport and stabilization in heterogeneous subsurface soils. EPS is composed of carbohydrates, protein and DNA [29,32]. Many EPSs, derived from microbial origin, contain uronic acids such as galacturonic and glucuronic acid moieties in their structure (e.g., Refs. [33,34]). Hung et al. [32] found that the EPS isolated from *P. fluorescens* Biovar II contained acidic groups mainly composed of carboxylic acid. They also determined that up to 70% of total carbohydrates were uronic acids, with COO^- functional groups. Davies [35] reported that the extracellular alginate plays a significant role on biofilm formation. Alginic acids are a family of hydrophilic, colloidal polysaccharides commonly present in soil environments due to production by N_2-fixing bacteria of the genus *Azotobacter* [36]. Alginic acid is an unbranched, binary copolymer composed of varying proportions of β-D mannuronic acid and α-L-guluronic acid linked through the 1- and 4-positions.

2. Materials and methods

2.1. Soil samples

Soil samples were collected from unpolluted agricultural fields located in Mersin, a Mediterranean coastal city of Turkey. The samples were taken from a depth of 0 to 30 cm. The samples were transported to the laboratory in plastic bags. All samples, mixed and homogenized in the laboratory, were air-dried at room temperature, and passed through a 2-mm sieve. Samples were then stored at room temperature in plastic bags until required.

The dry mass of the soil samples was determined by oven drying them for 24 h at 105 °C. The pH was measured in deionized water (soil–solution ratio 1:2 by mass). After 1 h of contact time, the pH of the slurry was measured using a pH meter [37]. The carbonate content was determined by a volumetric calcimeter method as described by Allison and Moodie [38]. Soil particle size analysis was carried out using a hydrometric method [39]. The USDA particle size classes (clay: $<2\ \mu m$, silt: $2–50\ \mu m$ and sand: $50–2000\ \mu m$) were followed when assigning textural classes. Organic matter was measured using the Walkey-Black procedure [40]. Electrical conductivity (EC) was measured in 1:2 soil to water, and the total salt content was calculated from EC values [41]. The elemental analysis of soils was done with X-ray fluorescence spectrophotometer (XRF Rigaku Rix 2000).

2.2. Solution preparation

Unless stated otherwise, all chemicals used in the experiments were reagent grade or better. Water for all experiments was supplied from Millipore (Simplicity 185) UV water system. All labware was first cleaned by scrubbing with detergent, followed by sequential base (1% NaOH) and acid baths (5–10% HCl), after which glassware was rinsed with UV water and allowed to dry. The pH measurements were made with WTW Sentix 41 pH electrode calibrated with pH buffer solutions (pH 4.000, 7.000 and 10.000).

Stock solutions of Cr(VI) were prepared from potassium dichromate (Merck Co., Germany). Similarly, a 10^{-3} M stock solution of Cr(III) was prepared by dissolving reagent grade chromium(III)-nitrate-nonahydrate (Merck Co., Germany) in UV water. A 100 mg of alginic acid purchased as alginic acid sodium monohydrate (Aldrich) was dissolved in 50 mL UV water, and its pH was adjusted to ∼pH 5–6 with sodium hydroxide. The concentration of alginic acid used in the experiments was 142 mg/L. 10^{-2} M stock solutions of D(+)-glucuronic acid sodium salt monohydrate ($C_6H_9NaO_7 \cdot H_2O$) (Merck Co., Germany) and D(+) galacturonic acid ($C_6H_{10}O_7 \cdot H_2O$) (Fluka) were also prepared in UV water, and used in the experiments. All stock solutions were stored in amber glass bottles in the dark at 4 °C.

2.3. Batch sorption experiments

Batch sorption experiments were performed using 50 mL polycarbonate Oakridge centrifuge tubes at a desired soil/solution ratio, total organic ligand and Cr concentration. The tube lids were loosely covered to allow for gas exchange; hence all sorption experiments were open to the environment to facilitate equilibration with atmospheric pressure. In all of the batch experiments, sufficient NaCl was added to the tubes to obtain desired ionic strength ($I = 0.01$ M NaCl). In the batch sorption experiments at pH values greater than 7.0, increasing volumes of $NaHCO_3$ were added to the tubes to facilitate solution equilibration with atmospheric CO_2.

After pre-equilibration with the background solution for 24 h, aliquots of Cr and/or organic ligand were added to obtain the final desired total Cr(VI) and ligand concentration. The pH of the samples was adjusted with HCl or NaOH, and sufficient UV water was added to bring all the samples to the desired volume (20 mL). The samples were then placed on a shaker table in the dark, and allowed to come to equilibrium for 50 h. Kinetic experiments (data not shown) suggest that a reaction time of 50 h was adequate to approximate equilibrium since greater 95% of the sorption occurred within this reaction time. After equilibration, the sample pH was checked, and the solids were separated by centrifugation. The dissolved Cr(VI) concentration in solution was determined with the diphenylcarbazide colorimetric method at 540 nm wavelength [42]. The total chromium content of samples was determined with ICP-MS (Agilent 7500ce) with a detection limit of 4.62×10^{-10} M.

2.4. Column experiments

Column leaching experiments were conducted to investigate the transport of Cr(VI) in soil columns. The movement of Cr(VI) in the soil column was accomplished by leaching the surface-applied Cr through a glass column packed with the soil to a bulk density of $1.1\ g/cm^3$. The column was 2.2 cm in diameter, and the length of soil packed bed was 7 cm. Column packing entailed filling the column with a suspension of 30 g of the soil in 50 mL UV water. Care was taken to purge excess water immediately after filling the columns using a plunger. The columns were wrapped in foil to keep out light. All column experiments were conducted at 24 ± 2 °C and a flow rate of 0.15 ± 0.04 mL/min (corresponding to average linear pore velocity of 0.066 cm/min). The flow was applied in the downward direction. All solutions were prepared in 0.01 M NaCl, and contained sodium bicarbonate ($NaHCO_3$) to minimize equilibration times and pH drift. Prior to performing Cr(VI) displacement experiments, the column was continuously flushed with about 6 pore volumes of 0.01 M NaCl to precondition the column. After pre-equilibration, 25 mL of solution containing 10^{-5} M Cr(VI) or a combination of 10^{-5} M Cr(VI) and an organic ligand at a desired concentration was spiked instantaneously onto the upper layer of the column. Following the injection of Cr or Cr/ligand solution, the soil column was then continuously leached with 0.01 M NaCl until

Table 1
Experimental conditions for column experiments

Experiment	pH	$NaHCO_3$ (mM)	Glucuronic acid (μM)	Cr(VI), % recovered
1	7.9	0.392	0	100
2	7.6	0.202	0	72.72
3	7.6	0.202	100	60
4	7.6	0.202	500	33

complete breakthrough was approached. Effluent samples were collected in 6 mL aliquots after elution through the column using an ISCO Instruments Retriever II Fraction Collector with security valve. Samples collected were analyzed for the total Cr and Cr(VI) concentration in the same manner as the batch sorption experiments. The pore volume and porosity were estimated to be 15.86 mL and 0.59, respectively, using methods described by Kantar and Honeyman [23]. Table 1 shows experimental conditions for the column displacement experiments.

3. Results and discussion

3.1. Soil characterization

Selected physical and chemical properties of soils used in the study are presented in Table 2. The soils were moderately calcareous (5.02%), and slightly alkaline (pH 7.57). The texture class of the soils was sandy loam (SL) with a high sand and silt content according to USDA classifications. The total soluble salt content was 0.031%. As shown in Table 2, the elemental analysis of soil fractions indicates presence of very high concentrations of Fe- and Al-oxides, which are commonly found in natural soils and sediments as reactive, high surface area, secondary mineral coatings. The Fe- and Al-oxides are known to exhibit a great sorption affinity for Cr(VI) [22]. Despite this high Fe contents as observed in XRF analysis, no Fe oxide peaks were detected in XRD analysis of soils (data not shown), indicating that most of the iron in soil may be in the amorphous form. The XRD analyses also suggest that the major clay mineral in soil was montmorillonite.

3.2. Cr(VI) sorption as a function of solid/solution ratio and Cr(VI) concentration

Experiments were performed to study the effects of pH, soil/solution ratio and Cr(VI) concentration on Cr(VI) sorption (Fig. 1). These experiments were open to the atmosphere, and carried out by preparing samples at pH values ranging from 3 to 8.2. As shown in Fig. 1, Cr(VI) exhibits a typical "ligand-like" behavior, with the sorption reaching a maximum in the acidic pH range, and decreasing rapidly towards more alkaline conditions, as consistent with the changes observed in the sorptive properties of the solid phase and the solution speciation of Cr(VI) under both acidic and basic conditions. The decrease in Cr(VI) sorption at high pHs may be partly attributed to the electrostatic repulsion between deprotonated surface groups and CrO_4^{2-} ion in solution. In acidic conditions, the relatively high sorption of Cr(VI) onto soil surface may be explained through the strong interaction of Cr(VI) with Fe- and Al-oxides in soil [8–10].

Table 2
Selected physical and chemical properties of soils used in the experiments

Depth (cm)	0–30	SiO_2 (%)	35.24
pH (l:2)	7.57	$A1_2O_3$ (%)	20.36
Organic matter (%)	3.17	Fe_2O_3 (%)	14.12
$CaCO_3$ (%)	5.02	TiO_2 (%)	1.15
Particle size distribution		CaO (%)	3.6
Sand (%)	62.91	MgO(%)	1.12
Silt (%)	20.54	Na_2O (%)	0.21
Clay (%)	16.55	K_2O (%)	1.3
Salinity (%)	0.031		

An increase in soil/solution ratio from 25 to 100 g/L moves the sorption edge to higher pH values since the number of surface sites increases with increasing soil/solution ratio. Similarly, the Cr(VI) sorption increases with decreasing Cr(VI) concentration (Fig. 1).

3.3. Cr(VI) sorption to soils in the presence of organic ligands

Experiments were performed to determine the effects of increasing organic ligand concentration on Cr(VI) sorption to soil surfaces as a function of pH. These experiments were conducted for a pH range of 3–8.1, 100 g/L soil, either 10^{-6} M or 10^{-5} M $Cr(VI)_T$ and the ligand concentrations ranging from 0 to 10^{-3} M. As shown in Fig. 2, the addition of galacturonic acid enhances Cr(VI) sorption under acidic to slightly alkaline pH range ($pH < 7.7$) relative to the galacturonic acid-free system. Fig. 3 shows that glucuronic and alginic acids also affect the Cr(VI) sorption to soils in a similar fashion with galacturonic acid. However, these results contradict the observations from other studies that suggest that organic ligands compete with Cr(VI) for surface sites, and lead to a decline in Cr(VI) sorption depending on the chemical conditions (e.g., ligand activity, pH) [43]. For example, in a field study with citrate, Johnson et al. [26] found that anion exchange of citrate with chromate resulted in a release of surface-bound Cr into solution.

The increase observed in Cr(VI) sorption in the presence of organic ligands under acidic to slightly alkaline pH conditions ($pH < 7.7$) may be explained through a number of mechanisms including: (1) the direct reduction of Cr(VI) to Cr(III) with organic ligands in solution (e.g., Refs. [14,17]) and (2) catalytic Cr(VI) reduction by surface-bound natural organic matter (NOM), surface minerals (e.g., clays, Fe oxides, TiO_2) [11,16] or dissolved metals (e.g., Fe(II; III) [15,19,20,44]. NOM can reduce Cr(VI) to Cr(III) in solution (e.g., Refs. [7,14,15,17,24] since it contains certain functional groups (e.g., carboxyl (COOH)) that represent a significant reservoir of electron donors for the reduction of Cr(VI) to Cr(III). For example, galacturonic and glucuronic acids are uronic acids with a single carboxylic group in their structure. Note that the pK_a values for the dissociation of carboxylic groups of galacturonic and glucuronic acids are less than 4 [45,46], indicating that both galacturonic acid and glucuronic acid are mostly deprotonated under the experimental conditions studied (e.g., $pH > 4$). Similarly, alginic acid is mainly composed of uronic acid COOH functional groups with a first pK_a value of <3 [47,48]. Carboxylic groups are known to play a

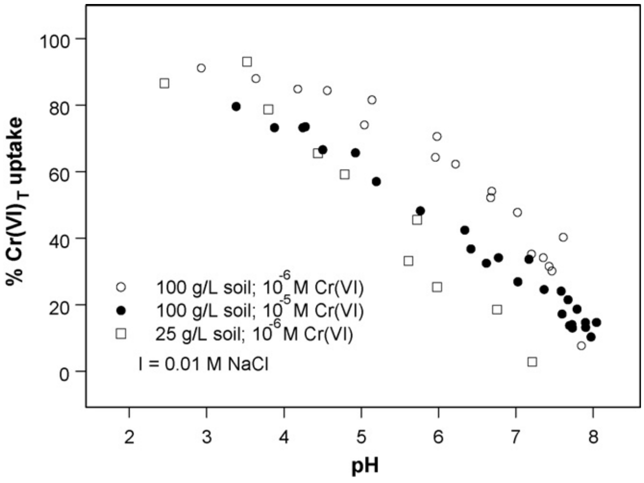

Fig. 1. Cr(VI) uptake by soil surface in 0.01 M NaCl as a function of pH at different soil/solution ratios and $Cr(VI)_T$ concentration.

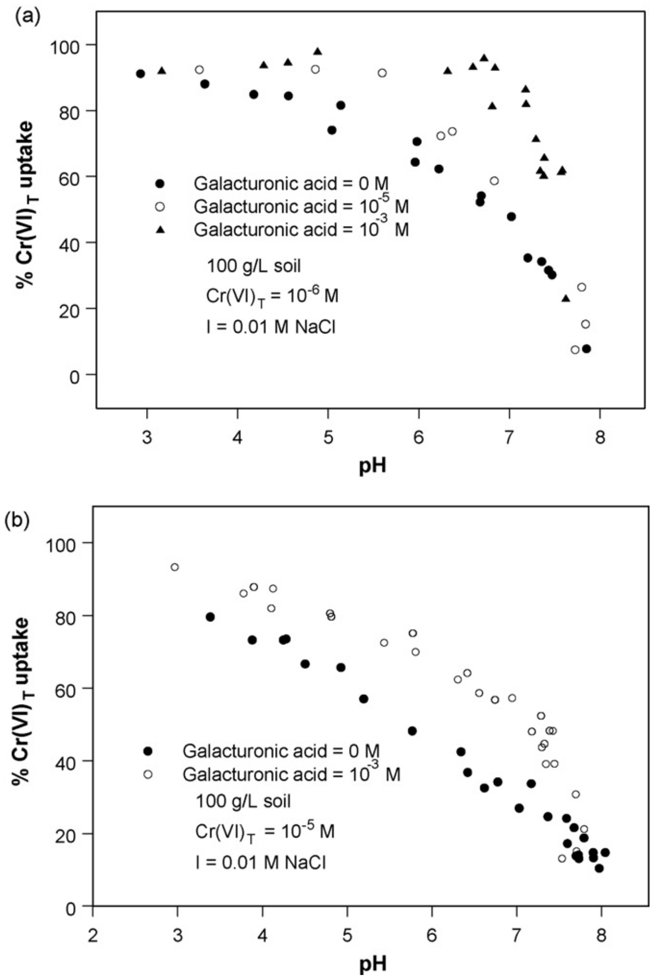

Fig. 2. Cr(VI) uptake by 100 g/L soil in 0.01 M NaCl in the presence of galacturonic acid at: (a) Cr(VI)$_T$ = 10^{-6} M and (b) Cr(VI)$_T$ = 10^{-5} M.

significant role in metal ion complexation and oxidation/reduction reactions [16,48]. However, the direct Cr(VI) reduction with organic ligands in solution is a slow process that may take weeks to months [11,17]. Our results also confirm (data not shown) that the organic ligands used in this study (e.g., galacturonic, glucuronic and alginic acids) could not effectively reduce Cr(VI) in solution within a total experimental time of 50 h in systems containing no soil under both acidic and alkaline conditions.

A number of researchers have found that clays, dissolved and surface-bound metals (e.g., Fe(II; III), Fe-bearing minerals and surface-bound organic matter may catalyze Cr(VI) reduction [11,16,19,25]. The diphenyl carbazide method and ICP-MS analyses of samples from sorption experiments suggest that most of total chromium (>90%) in solution was in the hexavalent form, Cr(VI), indicating that surface-bound organic matter/Fe oxides or dissolved metal ions such as Fe may be responsible for the enhanced Cr(VI) uptake by soil under acidic to slightly alkaline pH conditions. The term “uptake” will be used in the text to describe the sorption of both Cr(VI) and reduced Cr(VI) [e.g., Cr(III)] in the presence of organic ligands hereafter. Under highly alkaline pH conditions (e.g., pH > 7.7), however, the addition of organic ligands has no effect on Cr(VI) uptake by soil (Figs. 2 and 3) since the catalytic Cr(VI) reduction by organic ligands and surface-bound minerals decreases with increasing solution pH [11,14,15,17,24,25]. Gu and Chen [17], for example, found that while the Cr(VI) reduction by organic ligands occurs very fast under acidic conditions, the reaction rates decrease with increasing pH. Branca et al. [49] observed that the reduction of Cr(VI) to Cr(III) by D-galacturonic acid proceeds rather quickly in strongly acidic solutions, it is very slow in moderately acidic to neutral pH conditions. Similarly, Deng et al. [16] found that clays such as smectite and illite catalyzed Cr(VI) reduction by organic ligands, and the catalytic affect decreased as pH increased.

Fig. 4 shows a comparison of iron dissolution from soils in the absence and presence of 10^{-3} M galacturonic acid as a function of pH. The total Fe content of samples was determined through analysis of Fe^{56} isotope in solution with ICP-MS. In both systems, the extent of iron dissolution is highly pH-dependent, and it decreases slightly with increasing pH, and then sharply increases towards more alkaline conditions (pH > 7.7) under the influence of hydroxyl ions. While the addition of galacturonic acid to soils hinders Fe dissolution relative to galacturonic acid-free systems at pHs < 7.7, galacturonic acid has little or no effect on Fe dissolution (Fig. 4) under highly alkaline conditions (e.g., pH > 7.7). It is interesting to note that the enhanced Cr(VI) uptake in the presence of galacturonic acid also occurs at pH values <7.7, indicating that the Fe oxides and Fe dissolution from the soil may also have a role on Cr(VI) uptake. We conducted a separate experiment to determine the influence of dissolved Fe(II; III) ions on Cr(VI) reduction in the presence of organic ligands such as glucuronic and galacturonic acids. The results (data not shown) indicate that, in systems with no soil, Cr(VI) was significantly reduced by both glucuronic and galacturonic acids in the presence of dissolved Fe(III) ions in solution within minutes, and that the catalytic Cr(VI) reduction decreased

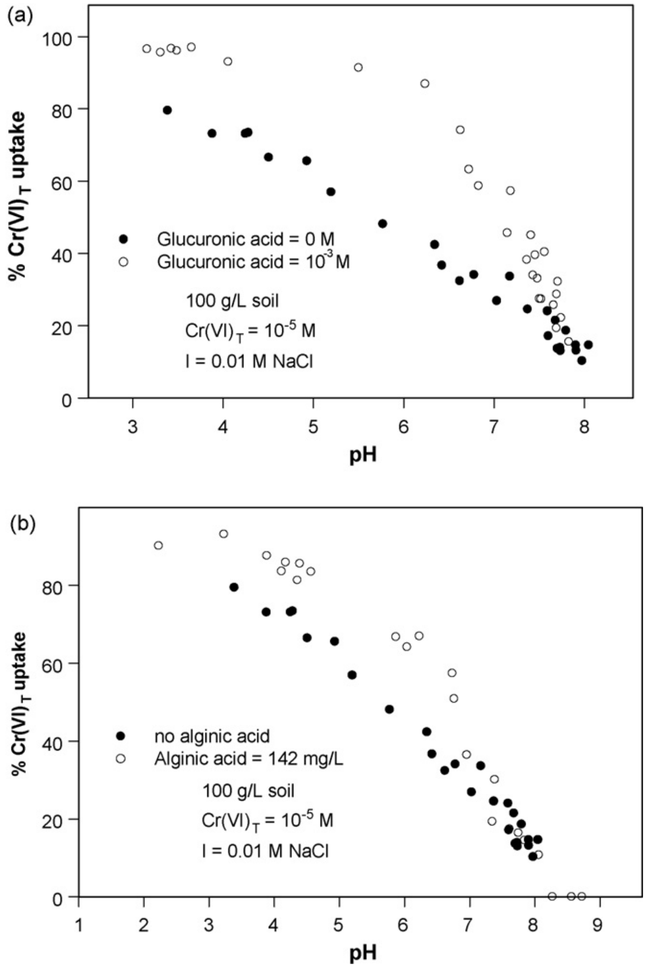

Fig. 3. Cr(VI) uptake by 100 g/L soil in 0.01 M NaCl in the presence of: (a) glucuronic acid and (b) alginic acid. Alginic acid concentration was 142 mg/L.

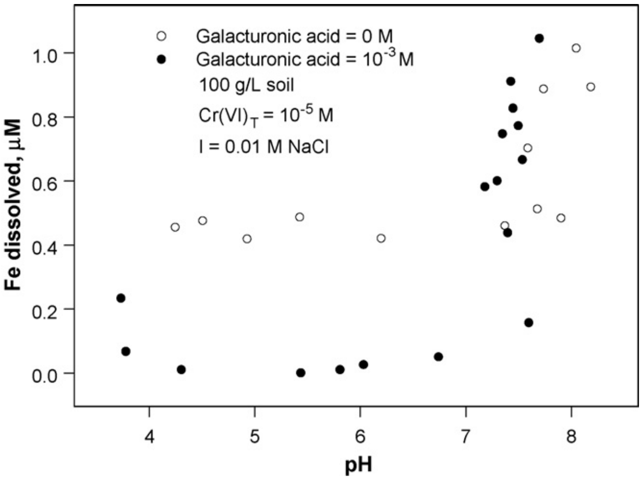

Fig. 4. Fe dissolution as a function of pH in the absence and presence of galacturonic acid. The experiments contain 10^{-5} M Cr(VI), and for data points at pH greater than 7, increasing amounts of $NaHCO_3$ were added to the tubes to facilitate solution equilibration with atmospheric CO_2.

with increasing solution pH. According to Wittbrodt and Palmer [15], Fe may enhance the reduction of Cr(VI) by being alternatively reduced by the natural organic ligands and then oxidized by Cr(VI) as part of a redox cycle.

3.4. Cr(VI) migration

Column experiments were performed to study the effect of organic ligands on Cr(VI) leaching and migration under advective conditions similar to those that might be observed in the field. Experimental conditions are summarized in Table 1. Fig. 5 shows breakthrough curves for Cr(VI) at pHs 7.6 and 7.9 in the presence and absence of glucuronic acid. The breakthrough curves are asymmetrical with a sharp rising front and a long trailing edge. As suggested by Kantar and Honeyman [23], the long tailing may generally be caused by reaction kinetics as well as non-linear sorption/desorption (e.g., Freundlich isotherm-like behavior). The Cr(VI) retardation highly depends on both pH and the concentration of glucuronic acid in solution. The Cr(VI) breakthrough curves at pH 7.6 are more retarded than those at pH 7.9, as consistent with the observation from batch sorption experiments. The results of the mass balance analysis of the breakthrough curves (Table 1) indicate that a portion of Cr(VI) bound to the porous media is not readily recoverable with background electrolyte solution containing 0.202 mM $NaHCO_3$, although the effluent Cr(VI) concentration approaches nearly zero at pH 7.6. However, nearly 100% of Cr(VI) was recovered in the effluent in 4 pore volumes at pH 7.9. The total Cr(VI) recoveries are presented in Table 1. The observed low recovery at pH 7.6 with the electrolyte solution containing $NaHCO_3$ is likely due to the strong binding of Cr(VI) with high energy surface sites [50]. Kantar and Honeyman [23] suggest that, in natural sediments with non-uniform distributions of mineral phases, high energy surface sites (e.g., secondary coatings) play a more significant role in metal sorption in columns than in batch systems.

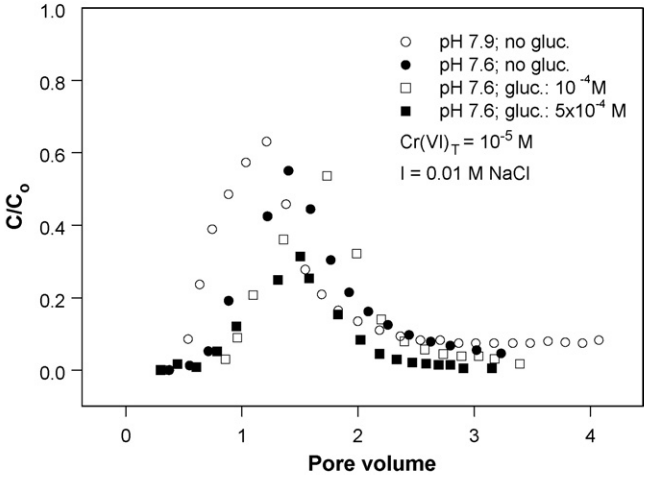

Fig. 5. Cr(VI) breakthrough curves in the presence and absence of glucuronic (gluc) acid.

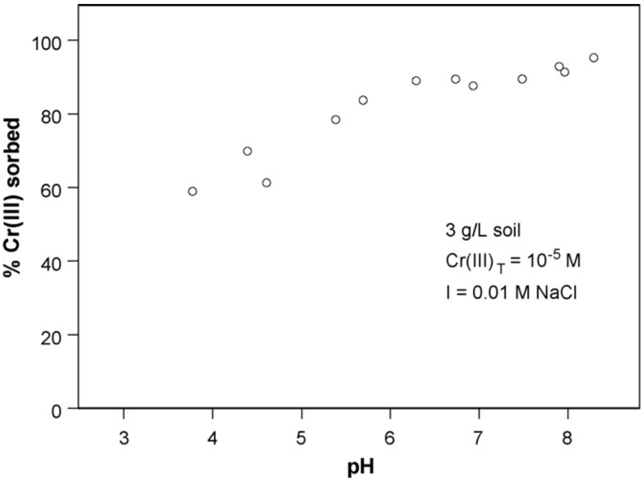

Fig. 6. Cr(III) sorption to soil as a function of pH.

Fig. 5 also shows that the presence of glucuronic acid in the feed solution significantly affected Cr(VI) uptake and migration. The addition of increasing glucuronic acid concentration to the feed solution resulted in an increase in the retardation of Cr(VI) in columns. The results of the mass balance analysis of the breakthrough curves suggest that the amount of Cr(VI) recovered in the effluent decreased sharply with increasing glucuronic acid concentration (Table 1). In a column study with soils previously treated with NOM, for example, Jardine et al. [11] found that the breakthrough of Cr(VI) on the NOM amended soil was significantly more delayed relative to the Cr(VI) breakthrough curves with the untreated soil. In their spectroscopic analysis of soils amended with NOM using XANES spectroscopy, Jardine et al. [11] also determined that both Cr(VI) and Cr(III) resided on the surface, and significantly less Cr(VI) was present in the NOM-amended soils versus the untreated soils, implying that surface-bound NOM more effectively reduces Cr(VI) to Cr(III). The analyses of effluent solution for the total Cr content suggest that nearly all of chromium was in the hexavalent form [Cr(VI)]. This is not surprising since Cr(III) which forms as a result of Cr(VI) reduction strongly sorbs to the soil under the experimental conditions of column experiments (e.g., pH 7.6). Fig. 6 presents the sorption envelope for Cr(III). Note that nearly 100% of Cr(III) is associated with the soil surface under neutral to alkaline conditions, explaining why Cr(III) was not detected in the effluent at pH 7.6 in the column experiments.

One pore volume in columns was transported in approximately 106 min (Table 1). This time is not sufficient for direct Cr(VI) reduction with organic ligands since such reactions are relatively slow, and may take days to complete [16], as was observed in our batch systems. However, Cr(VI) reduction with surface-bound organic matter, surface Fe oxides and/or dissolved Fe(II; III) ions is very fast, and occurs within seconds to minutes [11,15,16]. This suggests that a similar mechanism, involving surface-bound Fe oxides or dissolved Fe(II; III) ions, is probably responsible for the low Cr(VI) recoveries in the presence of organic ligands.

4. Conclusion

In situ remediation of soils contaminated with Cr(VI) is usually accomplished through microbial reduction of Cr(VI) to Cr(III) by soil microorganisms. Cr(VI) is a toxic substance that may stimulate the production of EPS by some soil microorganisms. This study has demonstrated that EPS constituents such as galacturonic, glucuronic and alginic acids play an important role on Cr(VI) uptake and stabilization in heterogeneous subsurface soils. The Cr(VI) uptake by soil surfaces is highly enhanced in the presence of organic matter under acidic to slightly alkaline pH range depending on the concentration of organic ligand and pH. The enhanced Cr(VI) uptake under such conditions is probably caused by either the catalytic reduction of Cr(VI) to Cr(III) by the surface-bound organic ligands/Fe-oxides and/or the dissolved metal ions [e.g., Fe(III)] from the soil. On the other hand, organic ligands have no or little effect on Cr(VI) uptake by soils under highly alkaline pH conditions since the catalytic Cr(VI) reduction decreases with increasing pH.

Column experiments show that the Cr(VI) breakthrough curves were asymmetrical with a sharp rising front and a long trailing edge, indicating a non-linear and/or kinetically controlled sorption process. Depending on the concentration of organic ligand used, the Cr(VI) breakthrough curves were significantly retarded relative to the organic acid-free systems at pH 7.6. The results of mass balance analysis suggest that a significant portion of Cr(VI) initially added to the feed solution did not exit the column; and the extent of Cr(VI) recovery highly depended on Cr(VI)/organic ligand ratio.

Acknowledgements

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