Comparative sorption of chromium species as influenced by pH, surface charge and organic matter content in contaminated soils

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ARTICLE INFO

ABSTRACT

Excessive use of chromium (Cr) in several industrial applications has a significant impact on soil biota. Chromium when present in soil and water occurs in two forms [Cr(III) and Cr(VI)] which exhibit contrasting characteristics and therefore retention of these two species is of prime importance to arrest Cr contamination in the environment. In this study, the effect of lime, elemental sulfur (to change pH), Fe(III) oxide (for surface charge) and cow manure (organic matter content) was tested on the retention capacity of Cr(III) and Cr(VI) in contaminated soils. The results showed that the addition of lime increased Cr(III) retention while elemental sulfur (S^o), Fe(III) oxide and cow manure increased Cr(VI) retention. The effect of S^o on Cr(VI) sorption is mediated through a decrease in soil pH, which facilitated an increased retention of Cr(VI) as measured by Freundlich sorption coefficient from 0.079 (in pristine soil, pH 7.15) to 21.06 L/kg (in S^o amended soil, pH 4.08). Also, Fe(III) oxide addition at 5% has favoured for an increase in the retention of Cr(VI) (K_f = 91.15 L/kg). Cow manure promoted Cr(VI) reduction, possibly due to the presence of functional groups that are present along with dissolved organic carbon and also by increased microbial activity. It is concluded that the mitigation of Cr toxicity is brought about by the addition of amendments which manipulate the properties of soil to increase retention of Cr(III) and Cr(VI).

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1. Introduction

Industrial intensification has increased the utilization and release of heavy metals into the environment. Some of the industries such as tannery, electroplating, paints, cooling towers and timber treatment discharge effluents that contain chromium (Cr). The Cr level in the effluents should be decreased in order to maintain ecosystem integrity. Enhancing the sorption of Cr in soil is an effective strategy to decrease their mobility and availability, thereby arresting further contamination in soil and water.

The behaviour of Cr in soil depends on the physicochemical properties including pH, organic matter, cation exchange capacity (CEC) and oxidation state of Cr (Banks et al., 2006). The retention of Cr in soils is important to decrease ground water and soil contamination, which is mainly controlled by sorption, precipitation, redox and nucleation reactions (Bradl, 2004). An increase in soil pH increases the retention of Cr(III) in soils. Whereas positive charge from iron oxides and organic matter in the soil and soil colloids increases Cr(VI) retention (Jardine et al., 2013; Stewart et al., 2003). There are several methods to mitigate

Cr toxicity in soil and aquatic systems including chemo and biosorption, and reduction of toxic Cr(VI) to less toxic Cr(III) species using various organic (plant biomass, seaweed, black carbon) and inorganic amendments (lime, elemental sulfur (S^o)) (Bolan et al., 2003b; Choppala et al., 2015; Hsu et al., 2009; Sahinkaya et al., 2012).

Several researchers have reported the utilization of amendments such as agricultural by-products, activated carbon, and minerals for the retention of Cr in waste water (Leyva-Ramos et al., 1995; Samantaroy et al., 1997). However, there is no comprehensive research on the comparative retention of Cr(III) and Cr(VI) as influenced by soil pH, surface charge and organic matter content using amendments such as Fe(III) oxide, cow manure, S^o and lime in soils. Iron(III) oxide carries both positive and negative charge in soil based on pH and point of zero net charge (PZNC) and therefore can be used to retain both anions and cations in soils (Ranst, 1998).

The presence of positive charge of soil also influences Cr(VI) sorption in soils, whereas for Cr(III) sorption, high pH, CEC, clay and native organic matter have significant positive effects. Cow manure adds significant amounts of organic matter into the soil and encourages microbial population. In addition, organic matter in cow manure comprises several functional groups, capable of donating electrons to reduce and retain Cr in soils. Addition of lime increases the pH by releasing hydroxyl ions

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and also increases surface negative charge in soil; and incorporation of S^o decreases soil pH by releasing H^+ ions, thereby increasing the retention of Cr(III) and Cr(VI), respectively (Bolan et al., 2003b; Cui et al., 2004; Haynes and Naidu, 1998). The objectives of this study was to investigate the behaviour of Cr(III) and Cr(VI) as influenced by the changes in soil pH, surface charge and organic matter content and to gain insights into their retention and reduction processes.

2. Materials and methods

2.1. Soils, amendments and their characterisation

A neutral soil (CLV) was collected from Clare valley, South Australia. The soil was mixed thoroughly, air dried, sieved through 2 mm steel screen prior to the storage in plastic containers until further analysis. Lime, S^o and Fe(III) oxide were selected as inorganic soil amendments and cow manure was selected as an organic soil amendment. Lime, S^o and cow manure were purchased from a local agricultural store and manure was dried, ground and sieved through 2 mm steel screen. Iron(III) oxide (analytical grade) was purchased from Chem-supply, South Australia. To change the pH of the soils, lime and S^o were mixed at various levels (1, 2 and 3 units) based on the buffering capacity of the soil (10.13 mmol/kg) and incubated at field capacity for a month. The soils were mixed with Fe(III) oxide and cow manure at an application rate of 5% (w/w basis) and incubated for a month at field capacity.

The pH, CEC and organic carbon (OC) content of soils were analysed using the methods described in Rayment and Higginson (1992). A factor of 1.72 was used to convert organic carbon to organic matter. The buffering capacity of soil was estimated by titrating soil with increasing volumes of 0.2 M hydrochloric acid (HCl) and sodium hydroxide (NaOH) (Aitken and Moody, 1994). The solutions were added to 20 g soil at different volumes from 2 to 6 mL, appropriate amount of Milli-Q (MQ) water was added to make total volume of solution to 8 mL and soil suspension sample was shaken in an end-over-end shaker for 25 min at 24 °C. The soils were further mixed with 42 mL MQ water to equilibrate for further 5 min and pH was recorded. Titration curves were plotted using the pH of soil suspension and acid/base input; buffering capacity was deduced from drawing a tangent to the curve of best fit in the graph and results were expressed in mM OH^- or H^+/kg soil/pH.

To measure the surface charge, 2 g of (<0.5 mm) air-dried soil was mixed with 40 mL of 1 M NaCl solution in a weighed centrifuge tube, centrifuged (20 min, 1789g), for 30 min, and soil was retained for four further washings with 0.1 M NaCl. The soil was then shaken with 0.02 M NaCl solution for 5 min to reduce the concentration of entrained solution. The tubes were weighed and the adsorbed Na^+ and Cl^- ions were extracted by shaking for 20 min with 20 mL of 1 M NH_4NO_3 solution. The concentration of Cl^- was estimated using ion chromatography (IC, ICS-2000, Dionex, California, USA) and Na was measured by inductively coupled plasma - mass spectroscopy (ICP-MS, Agilent, 7500ce, Washington, USA).

2.2. Sorption experiments

Batch sorption experiment was conducted to measure the extent of sorption at various concentrations of Cr(III) and Cr(VI) by the amended soil samples. Experiments were conducted in triplicates at 24 °C with a background electrolyte of 0.1 M KNO_3. Chromium(III) and Cr(VI) solutions were prepared in 0.1 M KNO_3 using chromium sulfate and potassium dichromate, respectively. Sorption of Cr was measured at various concentrations in the range of 0–500 mg/L. Soil samples were mixed with Cr solutions at a soil: solution ratio of 1:10 by shaking on an end-over-end shaker for 16 h. The resulting samples were centrifuged at 1789g for 20 min and filtered through 0.45 μm filters.

The concentration of total Cr was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 5300V, PerkinElmer, Massachusetts, USA) and Cr(VI) species was measured

by an UV–Visible spectrophotometer at 540 nm using 1, 5-diphenyl carbazide as a colour developing reagent. Chromium(III) was calculated by subtracting Cr(VI) from total Cr. The amount of adsorbed Cr was calculated from the difference between the added amount that remained in the solution after equilibration of 16 h. The amount of Cr(III) and Cr(VI) sorbed by soils was calculated using Eq. (1)

$$S = \frac{(C_o - C_e)V}{W} \tag{1}$$

where S is the amount sorbed (mg/kg), C_o is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solution volume (L), and W is the weight of the air-dried soil sample (kg). The Cr(III) sorbed was calculated from the difference between Cr (total) and Cr(VI) levels that were adsorbed from the soil solution onto the soil colloid particles. After sorption, Cr(VI) incubated soils were extracted with 1 M KH_2PO_4. There was negligible difference between Cr(VI) added and Cr(VI) remained in solution at equilibrium after sorption + KH_2PO_4 extractable Cr(VI), which confirms the insignificant reduction of Cr(VI) in the tested soils.

2.3. Sorption isotherms

The most commonly used isotherms, Langmuir (Eq. (2)) and Freundlich (Eq. (3)) were fitted to experimental isotherm data for the soil.

$$S = \frac{bX_mCe}{(1 + bCe)} \tag{2}$$

$$S = K_f Ce^n \tag{3}$$

where S is the quantity of solute adsorbed (mg/kg), C_e is solute concentration at equilibrium, b is the binding constant that reflects the relative rates of sorption at equilibrium, X_m is the maximum sorption capacity of the soil (mg/kg), K_f is the sorption coefficient (L/kg), and n is the sorption intensity (dimensionless).

2.4. Statistical analysis

All parameters including pH, CEC, OM, surface charge and Cr(VI) reduction were calculated from triplicates of each treatment. Microsoft Excel software was used for data evaluation and standard deviations of the replicates. The impact of amendments on the retention of Cr(VI) and Cr(III) was examined by correlation analysis (Version 18.0.0; SPSS, Inc., Chicago, IL)). Grapher™ software 9.0 (Golden Software, Version 9, USA) was used to draw the sorption isotherms.

3. Results and discussion

3.1. Characteristics of soil and amendments

The physico-chemical properties of soil are listed in Table 1. The soil pH was 7.15, CEC was 6.93 cmol/kg and clay content was 38.6%. The pH buffering capacity of soil was 10.1 mM OH − or H^+/kg soil pH. The pH of

Table 1
The effect of amendments on soil properties.

Amendment	Level (%) (w/w)	pH	CEC (cmol/kg)	OM (%)
Control		7.15	6.92	2.58
Lime	0.037	8.23	7.46	2.74
	0.074	9.12	7.91	2.83
Elemental sulfur	0.16	6.23	6.33	2.51
	0.32	5.12	5.98	2.34
	0.48	4.08	5.41	2.02
Fe(III) oxide	5.0	7.68	5.87	2.54
Cow manure	5.0	5.36	7.53	5.84

neutral soil (7.15) was altered to 8.23 and 9.12 using lime; to 6.24, 5.13 and 4.38 using S^o. When S^o is added to soils, it is oxidised to sulphuric acid and further dissociates into H^+ ions and SO_4^{2-} ions (Eq (4)). The addition of lime neutralises H^+ ions, precipitates Al^{3+} ions into non-toxic forms, and Ca^{2+} and Mg^{2+} from the lime increases percentage base saturation, thereby raising the pH (Bolan and Hedley, 2003) (Eq. (5)).

$$2S^O + 2H_2O + 3O_2 \rightarrow 2SO_4^{2-} + 4H^+ \tag{4}$$

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^{-} + OH^{-} \tag{5}$$

3.2. Sorption of chromium in soils

The results revealed that sorption of Cr in control soil (CLV) as measured by Freundlich sorption coefficients (K_f) for Cr(III) and Cr(VI) was 1259.8 and 0.079 L/kg, respectively, suggesting that Cr(III) sorption is far higher than Cr(VI) (Table 2). Sorption of Cr was highly influenced by the addition of organic and inorganic amendments (Bolan and Duraisamy, 2003; Chiu et al., 2009). The sorption of Cr(III) was higher in soils that were incubated with lime and Fe(III) oxide. The addition of Fe(III) oxide, also increased the retention of Cr(VI) in soils. The addition of cow manure increased the sorption of Cr(VI), K_f increased from 0.079 (control) to 91.15 L/kg after 5% addition of cow manure and also promoted the reduction of Cr(VI), followed by immobilization of Cr(III). In the presence of lime and Fe(III) oxide, there was no change in the oxidation state of added Cr. In contrast, when Cr(VI) was added to soil that was mixed with cow manure, after equilibration, the soil solution comprised both Cr(VI) and Cr(III), suggesting that Cr(VI) was reduced to Cr(III) and subsequently adsorbed.

In relation to isotherms, Freundlich equation fitted better than the Langmuir equation as indicated by higher correlation coefficient values, which is applicable for non-specific sorption on heterogeneous soil surface (Table 2). The better fit of Freundlich isotherm for sorption of Cr(VI) and Cr(III) species was also supported by other studies (Dubey and Gopal, 2007; Lazaridis and Asouhidou, 2003; Li et al., 2007).

3.3. Effect of lime on sorption of Cr in soil

The addition of lime greatly increased the sorption of Cr(III) in the soils (Fig. 1a). As the pH of soil amended with lime increased from 7.15 to 8.23 and 9.12, the K_f values for Cr(III) in these soils were 4017.9 and 5390.1 L/kg, respectively (Table 2). In contrast, the K_f values of Cr(VI) was not significantly influenced by lime addition, which changed from 0.079 L/kg (control) to 0.11 and 0.09 L/kg for the soils with pHs 8.23 and 9.12, respectively (Table 2). Retention of Cr species is unlikely to change the toxicity, however reduces the risk in the environment (Fendorf, 1995).

Soil solution pH is one of the major factors determining the surface properties of soils (Barrow, 1986; Sposito, 1984). Several reasons contribute to the pH-induced immobilization of metals in soil. An increase in pH in variable charge soils leads to the formation of negative charge on hydroxyl-Fe and Al surfaces that arise from the deprotonation potential determining $M\text{-}OH_2^{0.5}$ and $M\text{-}OH^{0.5-}$ groups (Bolan et al., 2003a; Naidu et al., 1994). Hence the activity of hydroxyl ions increases and favours the specific sorption of Cr(III) and Cr(III) hydroxyl species ($Cr(OH)_2^+$) have greater affinity for retention on soil colloids and Cr(III) mostly precipitates as $Cr(OH)_3$ in alkaline soils (Bartlett, 1991; Bradl, 2004). Once the sorption sites are saturated by retaining Cr(III) ions, polymerization of $Cr(OH)_3$ occurs and finally precipitates on the surface of soil colloids (McBride, 1994).

The sorption of Cr(VI) species ($K_f = 0.079$) by the CLV soil was low compared to Cr(III) sorption ($K_f = 1259.8$). The difference in the sorption of Cr species may be attributed to the difference in amount of negative (28.4 cmol/kg) and positive (4.81 cmol/kg) charges in the soil (Choppala et al., 2013). In contrast to Cr(III) sorption, the addition of lime decreased the Cr(VI) sorption in soils (Fig. 1b). Chromium(VI) sorption is favoured when the soil surface contains positive charge through surface complexation and addition of lime increases net negative charge in soils (Bolan et al., 2003a; Bradl, 2004). An increase in soil pH decreases the sorption of Cr(VI) due to decrease in positive charge on soil surfaces (Bolan and Thiagarajan, 2001). The increased pH resulting from liming also diminishes the reduction of Cr(VI) to Cr(III) as the availability and activity of H^+ decreases in alkaline soils, since Cr(VI) reduction is dependent on the activity of H^+ ions (Chrysochoou et al., 2010).

3.4. Effect of elemental sulfur on the retention of Cr in soils

The addition of S^o decreased the pH of soils, thereby slightly decreasing the sorption of Cr(III) (Fig. 2a). However, it resulted in a significant increase in Cr(VI) sorption (Fig. 2b). The incubation of soils with S^o decreased the pH of soil from 7.15 to 6.23, 5.12 and 4.08 at 1, 2 and 3 units, respectively. The sorption coefficients of Cr(III) were 1259.8, 1043.5, 1012.1 and 956.1 L/kg in soils with pH values of 7.15, 6.23, 5.12 and 4.08, respectively (Table 2).

Dissolved Cr(III) concentration in soil solution is dominated by the ionic forms in acidic conditions such as hydroxyl species; $Cr(OH)_2^+$, $Cr_2(OH)_4^+$ and $Cr_3(OH)_6^+$ (Kotaś and Stasicka, 2000). However, in alkaline condition, Cr(III) species undergo either ion-exchange reactions with soil surface or precipitates as $Cr(OH)_3$. The solubility of Cr(III) hydroxides is low and the sorption of Cr(III) is stronger than Cr(VI) sorption on clay minerals. However in acidic soils, H^+ ions replace the cations from the surface of soils, hence the sorption of Cr(III) reduced with a decrease in soil pH.

Elemental sulfur addition increased the sorption of Cr(VI) in soils (Fig. 2b). Freundlich coefficients of soils were 9.84, 16.13 and 21.05 L/

Table 2
Sorption coefficients of Cr(III) and Cr(VI) in soils with different amendments.

| | Freundlich isotherm | | | | | | Langmuir isotherm | | | | | |
| | Cr(III) | | | Cr(VI) | | | Cr(III) | | | Cr(VI) | | |
	K_f (L/kg)	n	R^2	K_f	n	R^2	X_m (mg/kg)	b	R^2	X_m	b	R^2
CLV (control)	1259.8 ± 4.4	0.13 ± 0.03	0.980	0.079 ± 0.024	0.094 ± 0.015	0.855	3815	0.0005	0.745	123	0.0161	0.788
CLV + lime												
pH: 8.23	4017.9 ± 7.6	0.11 ± 0.01	0.954	0.11 ± 0.01	1.07 ± 0.05	0.897	8206	0.0003	0.814	83	0.0241	0.761
pH: 9.12	5390.1 ± 6.013	0.13 ± 0.011	0.961	0.09 ± 0.003	0.90 ± 0.024	0.913	8842	0.0002	0.708	65	0.0306	0.816
CLV + S^o												
pH: 6.23	1012.1 ± 6.814	0.14 ± 0.034	0.988	9.84 ± 0.042	0.44 ± 0.031	0.976	3732	0.0053	0.842	155	0.0128	0.814
pH: 5.12	956.1 ± 4.485	0.15 ± 0.006	0.976	16.13 ± 0.178	0.48 ± 0.057	0.937	3708	0.0054	0.863	318	0.0062	0.855
pH: 4.08	1460.9 ± 3.941	0.15 ± 0.013	0.903	21.06 ± 0.124	0.54 ± 0.043	0.958	3635	0.0053	0.747	580	0.0034	0.782
CLV + Fe oxide												
5% (w/w)	1185.4 ± 5.841	0.13 ± 0.01	0.924	91.15 ± 0.275	0.32 ± 0.008	0.816	4506	0.0004	0.722	824	0.0024	0.674
CLV + cow manure (5%) (w/w)	1284.1 ± 2.274	0.20 ± 0.04	0.913	4.46 ± 0.048	1.01 ± 0.042	0.934	3725	0.0004	0.835	305	0.0057	0.713
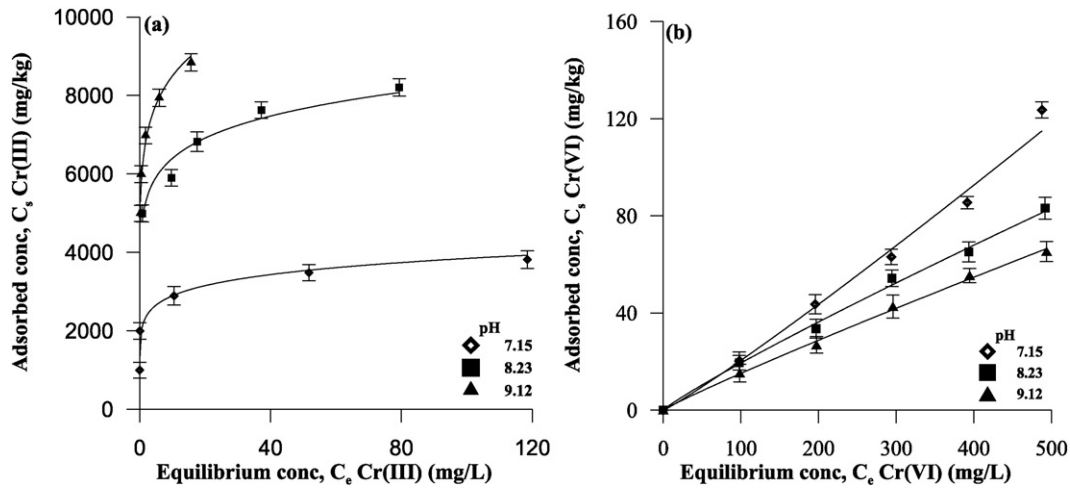
Fig. 1. Effect of lime addition on the sorption of Cr(III) (a) and Cr(VI) (b) in neutral soil.

kg in soils that have pH values of 6.24, 5.13 and 4.38, respectively (Table 2). It is estimated that each Cr(VI) ion can react and occupy 3–4 hydroxyl ions of surface sites (Benjamin and Bloom, 1981). There are different mechanisms that could explain the sorption of Cr(VI) in low pH soils. In acidic soils, mineral dissolution increases and Cr(VI) will be retained or reduced by Fe(II) bearing minerals (Qafoku et al., 2010). The increased Cr(VI) adsorption in acidic to slightly alkaline conditions can be described as surface complexation reaction between Cr(VI) species and surface hydroxyl sites (Eary and Rai, 1991). High soil pH and low iron oxides decreases Cr(VI) sorption in soils. Jiang et al. (2008) noticed the decreased sorption of chromate with an increase in system pH of three soils tested. The increase in soil pH can cause rise in negative charge and consequently repels the Cr(VI) ions from surface of soils. Ajouyed et al. (2010) found that Cr(VI) has high sorption affinity in acidic medium. Similarly, low Cr(VI) sorption was noticed in chromate ore processing residue soils, because of their high pH (Matern and Mansfeldt, 2016).

3.5. Effect of iron oxide on the retention of Cr in soils

The addition of Fe(III) oxide influenced the sorption of both Cr(III) and Cr(VI) (Fig. 3). The sorption coefficient (K_f) for Cr(VI) increased from 0.079 (control soil) to 91.15 L/kg after incubation of soil with 5% Fe(III) oxide for a month. In contrast, the sorption of Cr(III) decreased from 1259.85 (control soil) to 1185.42 L/kg in soil that was incubated with 5% Fe(III) oxide (Table 2).

Chromium(VI) participates in surface complexation reaction with hydroxyl species of iron oxides (Fendorf, 1995). Chromium(VI) sorption has often been shown to increase with increasing Fe content, which may be attributed to high positive charge (Zachara et al., 1989). Iron(III) oxide addition provides positive charge to the soil, thereby influencing Cr retention. Since Fe(III) oxide carries high PZNC, it can effectively adsorb oxyanions such as Cr(VI) in the pH range of 2–7 (Zachara et al., 1987). Chromium(VI) forms inner sphere surface complexation with positively charged Fe(III) oxide in soils. Similarly, Khaodhiar et al.
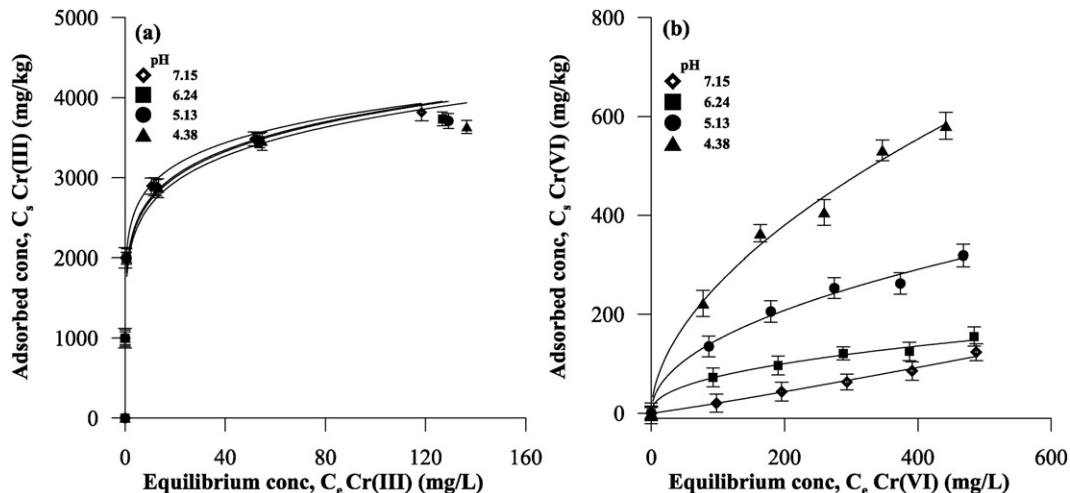

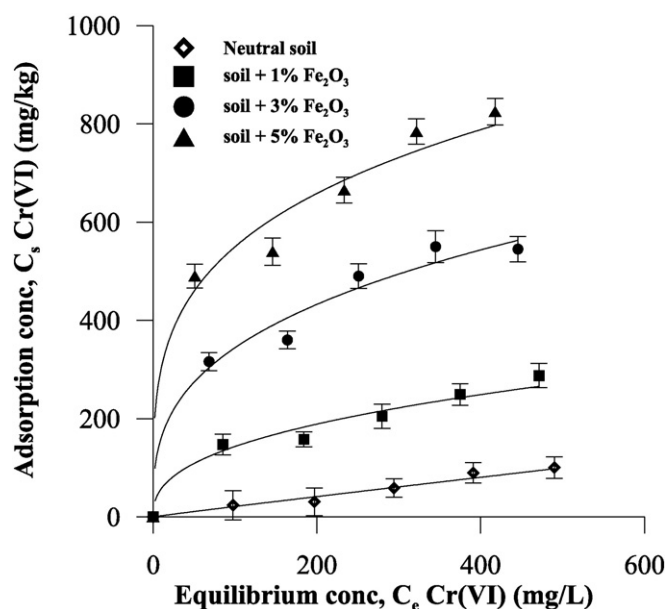Fig. 2. Influence of addition of elemental sulfur on sorption of Cr(III) (a), and Cr(VI) in soil (b).

Fig. 3. Effect of addition of Fe(III) oxide on sorption of Cr(VI) in neutral soil.

(2000) observed an increase in Cr(VI) and arsenate [As(V)] sorption by soil in the presence of Fe(III) oxide.

In general, cations participate in isomorphic substitution with Fe on clay or retained by oxy-hydroxides surfaces. However, the increase in positive charge of soils with the addition of Fe(III) oxide may be attributed to the decrease in Cr(III) sorption due to the repulsion between similar charge of Fe(III) oxide and cationic Cr(III). Removal of Fe(III) oxide using dithionate method increased the sorption of cationic heavy metals such as cadmium, copper, zinc and lead (Elliott et al., 1986).

3.6. Effect of cow manure on the sorption of Cr in soils

In the presence of cow manure, sorption of Cr(III) and Cr(VI) increased from 1259.8 to 1284.1 L/kg and from 0.079 to 4.46 L/kg, respectively (Table 2). Increased sorption of Cr(III) in cow manure amended soil is attributed to the increase in CEC. However, the increased sorption of Cr(VI) results from two main mechanisms; sorption and reduction. In the presence of cow manure, the reduction process dominates, resulting in the reduction of Cr(VI) to Cr(III) (El-Shafey, 2005). Organic amendments stimulate microbial population after incorporation in the soils, and biotic reduction of Cr(VI) is higher in soils than chemically mediated reduction (Banks et al., 2006).

The supply of carbon and protons are considered to be the major factors in enhancing the reduction of Cr(VI) (Losi et al., 1994). In soils, dissolved organic carbon (DOC) is identified as one of the potential drivers of Cr(VI) reduction (Jardine et al., 1999). Organic amendments can also increase the retention of Cr(VI) in soils. The protonated active functional groups in biosorbents will retain Cr(VI) at low pH. Also, at lower pH levels, Cr(VI) reduces to Cr(III) (Liu et al., 2006).

4. Conclusions

The sorption of Cr(VI) and Cr(III) in soils can be increased by the addition of organic and inorganic amendments. The two important soil parameters, pH and surface charge are vital in determining the sorption of Cr species. While addition of lime increased the Cr(III) sorption, there was a slight decrease in Cr(VI) sorption. This was attributed to the increased pH of soils, where Cr(III) precipitates or adsorbs to hydroxyl ions. An increase in soil pH decreases positive charge, hence decreasing the sorption of Cr(VI). Elemental sulfur decreased the soil pH, hence

showed opposite effect of lime on Cr(VI) and Cr(III) species. The increased sorption of Cr(VI) was due to the increase in protonated surface sites, where Cr(VI) participates in surface complexation or specific sorption. Sorption of Cr(VI) increased with the addition of Fe(III) oxide in soils; however Cr(III) sorption decreased. Addition of cow manure increased both Cr(VI) and Cr(III) sorption. Furthermore, Cr(VI) was reduced to Cr(III), which may be due to increased microbial activity and the DOC of cow manure. Finally, soil amendments; lime and S^o can be used for the increased retention of Cr(III) and Cr(VI), respectively through surface charge manipulation. Further research on surface characteristics may be needed to investigate the mechanisms controlling the retention of Cr species as influenced by amendments in contaminated soils.

Acknowledgements

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