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# Chemodynamics of chromium reduction in soils: Implications to bioavailability

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### HIGHLIGHTS

- Examined the effects of sorption, pH and C sources on Cr(VI) reduction and toxicity.
- The rate of Cr(VI) reduction decreased with an increase in Cr(VI) adsorption and pH.
- The proton dynamics in Cr(VI) reduction was assessed in relation to remediation.
- A novel black carbon showed the highest reduction rate of Cr(VI) in soils.
- Black carbon decreased the bioavailability and phytotoxicity of Cr(VI) in soils.

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### ABSTRACT

Chromium toxicity in soils can be mitigated by reduction of Cr(VI) to Cr(III) which is influenced by the presence of free Cr(VI) species in soil solution, and the supply of protons and electrons. In this study, the effects of Cr(VI) adsorption (i.e. availability of free Cr(VI) species in soil solution), soil pH (i.e. supply of protons) and three electron donor carbon sources [black carbon (BC), chicken manure biochar (CMB) and cow manure (CM)] on the reduction of Cr(VI) to Cr(III) in soils were investigated. The results indicated that the rate of Cr(VI) reduction decreased with an increase in Cr(VI) adsorption and soil pH, which is attributed to decreased supply of free Cr(VI) ions and protons, respectively. Among the three different amendments tested, BC showed the highest rate of Cr(VI) reduction followed by CM and CMB. Furthermore, addition of BC, CM and CMB decreased the bioavailability of Cr(VI) in contaminated soils. The high efficiency of BC on Cr(VI) reduction was due to the electron donor's functional groups such as phenolic, hydroxyl, carbonyl and amides. The study demonstrated that free form of Cr(VI) ions in soil solution and carbon amendments enriched with acidic functional groups favored the reduction of Cr(VI), thereby mitigating its bioavailability and toxicity in contaminated soils.

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## 1. Introduction

There has been a rapid increase in the utilization of chromium (Cr) by many industries including electroplating, chrome tannery processing, wood-pulp preserving, petroleum refining, pigment production and nuclear power plants [1]. For example, USEPA's Toxic Release Inventory listed 1,762 industrial facilities that released a total of 52,600 metric tons of Cr into the environment [2]. In Australia, around 157,290 hectares of land are under vineyard cultivation, and approximately 3,400 metric tons of Cr(VI) is used to treat poles in Australian vineyards [3].

The bioavailability and toxicity of Cr depends mainly on its oxidation state. Chromium is a redox active heavy metal that exists in several oxidation states;  $-2$  to  $+6$ , but only  $+3$  [Cr(III)] and  $+6$  [Cr(VI)] are prevalent in the environment. Chromium(VI) is highly toxic, mutagenic and teratogenic, whereas Cr(III) is an essential dietary nutrient at minute quantities ( $50$ – $200$   $\mu\text{g}/\text{d}$ ) to humans [4]. Chromium(VI) minerals are highly soluble; Cr(VI) oxidized species such as  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  are negatively charged and hence their limited adsorption to soil minerals makes Cr(VI) highly mobile. Whereas, Cr(III) behaves as a hard Lewis acid and complexes with several ligands, retains strongly to soil minerals, relatively insoluble and less available for plant uptake, hence less toxic to biota [5]. The maximum threshold level of Cr(III) in waste and ground waters is  $5$   $\text{mg}/\text{L}$  [6]. For Cr (total), the maximum permissible limit is  $2$   $\text{mg}/\text{L}$  for surface waters, whereas in drinking water, the maximum threshold limit for Cr(VI) is only  $0.05$   $\text{mg}/\text{L}$  [7]. Therefore the need prevails to eliminate Cr(VI) from the water and

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soil and thus eradicate the deleterious impact of Cr(VI) on public health and ecosystem integrity.

The toxicity of Cr(VI) can be eliminated by means of adsorption onto soil particles and/or reduction to Cr(III). One of the most practical approaches in the remediation of Cr(VI) in the environment is the addition of immobilizing materials to decrease the bioavailability of Cr(VI) [8]. However, the mobility, toxicity and bioavailability of Cr depends mainly on its oxidation state, so the best remediation strategy to permanently mitigate Cr contamination is to reduce soluble, mobile and toxic Cr(VI) to insoluble and non-toxic Cr(III) [9].

Chromium(VI) adsorption (i.e. supply of free Cr(VI) ions in soil solution), soil pH (i.e. supply of protons), and organic matter (i.e. supply of electrons) are the primary factors, which influence the Cr redox reactions [10]. When free Cr(VI) ions are present in solution, the reduction occurs readily under acidic conditions in the presence of organic matter such as manures, composts, humic acids and fulvic acids [11,12].

Although the effect of soil pH and organic amendments on the reduction of Cr(VI) has been examined [13], there was no comprehensive research involving the effect of three important rate limiting factors (i.e. supply of free Cr(VI) ions, protons and electrons) on Cr(VI) has been conducted. This study is designed to examine the effects of Cr(VI) adsorption (i.e. availability of free Cr(VI) species in soil solution), soil pH (i.e. supply of protons) and various electron donor carbon sources [black carbon (BC), chicken manure biochar (CMB) and cow manure (CM)] on the reduction of Cr(VI) to Cr(III) in soil. The effect of organic amendments on the bioavailability of Cr(VI) was also examined.

## 2. Materials and methods

In this study, the effect of Cr(VI) adsorption on its reduction was examined by: (i) using a range of soils with different Cr(VI) adsorption capacity and (ii) amending a low Cr(VI) adsorbing soil with increasing levels (0–5%) of high Cr(VI) adsorbing iron(III) oxide (May and Baker Ltd., Dagenham, England). The effect of pH on Cr(VI) reduction was examined by: (i) using five natural soils with different pH values (4.6–8.1) and (ii) amending the neutral soil to different pH values (4.2–9.3) using 0.1 M Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) or 0.1 M Hydrogen chloride (HCl). The role of organic amendments on Cr(VI) reduction was examined using three carbon sources (BC, CM and CMB) in an alkaline soil (pH 8.1).

### 2.1. Soils

Five different soils (0–10 cm depth) were collected from uncontaminated sites in Adelaide Hills, Clare Valley and Kulpara Bay in South Australia; Pittsworth and Redland Bay in Queensland. Adelaide Hills (ADH) soil was classified as Kurosol, Clare Valley (CLV) soil as Sodosol and Kulpara bay (KPB) soil as Chromosol, Pittsworth (PWT) soil as Vertosol and Redland bay (RBB) soil as Ferrosol. The soil samples were characterized for various properties including pH, cation exchange capacity (CEC), total organic matter, and Fe and Al contents [14].

The effect of adsorption on the reduction of Cr(VI) was examined using the five soils that vary in pH and also by treating the alkaline soil (KPB) with increasing levels of Fe(III) oxide ( $\text{Fe}_2\text{O}_3$ ) addition (0, 1, 3 and 5% (w/w)). To examine the effect of pH on Cr(VI) reduction, neutral soil (CLV) sample with a pH buffering capacity of 10.13 mM  $\text{OH}^-$  or  $\text{H}^+$   $\text{kg}^{-1}$   $\text{pH}^{-1}$  was treated with various levels of 0.1 M  $\text{Ca}(\text{OH})_2$  or 0.1 M HCl to achieve a pH range of 4.18–9.25. Calcium hydroxide was used for an accelerated reaction instead of calcium carbonate ( $\text{CaCO}_3$ ), the most commonly used liming

material. These samples were incubated in a greenhouse for 4 weeks and subsequently used for Cr(VI) reduction measurements.

### 2.2. Organic carbon sources and their characterization

Black carbon (BC) was prepared from South Australian common weed plant, *Solanum elaeagnifolium* L. The weed plants were collected, washed with water, dried in air under shade for 1 week and oven dried at 80 °C for 2 days. The plant residue (100 g) was pyrolyzed aerobically in a muffle furnace for 3 h at 300 °C. The charred residues were ground to less than 250  $\mu\text{m}$  size and treated four times with 1 M HCl for 4 h and then four times with 1:1 mixture of 1 M HCl–1 M HF to remove silica and other inorganic materials without damaging the surface property of BC [15]. The protonated BC was washed several times with distilled water to remove Si, residual acids and soluble salts. Black carbon was dried in an oven at 60 °C for 3 days and stored in a glass container. Cow manure (CM), purchased from a local agricultural shop, and chicken manure biochar (CMB) (prepared from poultry litter), obtained from Pacific pyrolysis (NSW, Australia), were dried at 60 °C for 24 h to remove moisture and pyrolyzed at 550 °C and stored in a glass container after cooling to room temperature.

### 2.3. Chromium(VI) adsorption

Adsorption of Cr(VI) in natural soils and  $\text{Fe}_2\text{O}_3$ -amended soils was measured using a batch experiment at known Cr concentrations (0–500 mg/L) using  $\text{K}_2\text{Cr}_2\text{O}_7$  [Cr(VI)] with 0.1 M  $\text{KNO}_3$  as the background electrolyte. The soil samples (3 g each) were mixed with 30 mL of Cr(VI) solution in a centrifuge tube and shaken on an end-over-end shaker at room temperature ( $22 \pm 2$  °C). After 16 h of shaking, suspensions were centrifuged at 1789 g, filtered through a 0.45  $\mu\text{m}$  Millipore filter tips, and Cr(VI) concentration was measured using 1,5-diphenyl-carbazide at an absorbance value of 560 nm against a blank solution at room temperature [16]

The amount of Cr(VI) sorbed by soils was calculated from the Eq. (1)

$$S_{\text{ads}} = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $S_{\text{ads}}$  is the amount of Cr(VI) sorbed (mg/kg),  $C_0$  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 sorption capacity as measured by coefficients ( $K_f$ ) was obtained by fitting the adsorption data to Freundlich isotherm (Eq. (2)).

$$S_{\text{ads}} = K_f C_e^n \quad (2)$$

where  $S_{\text{ads}}$  and  $C_e$  are sorbed (mg/kg) and equilibrium solution (mg/L) concentrations of Cr, respectively;  $K_f$  is sorption coefficient, which is an index of sorption capacity (L/kg) and  $n$  denotes the degree of deviation from the isotherm linearity.

### 2.4. Chromium(VI) reduction

Chromium(VI) reduction was examined by incubating the natural soils,  $\text{Fe}_2\text{O}_3$ -, pH- and organic materials-amended soils with 500 mg/kg of Cr(VI). The treated samples were sampled at various intervals and shaken with 1 M  $\text{KH}_2\text{PO}_4$  at a soil to solution ratio of 1:10 on an end-over-end shaker at room temperature ( $22 \pm 2$  °C) for 1 h, centrifuged at 1789 g and filtered through 0.45  $\mu\text{m}$  filter tips.

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