

Effect of organic and inorganic amendments on sorption of Cr(VI) and Cr(III) in soil

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Abstract

Chromium retention by soil and soil amended with organic and inorganic substances was investigated. Heavy metals are sorbed by a variety of soil phases with hydroxyl groups on their surfaces and edges including the clay minerals, where sorption reactions are often rapid. Clay minerals represented by the SiO–H appear to play an important role in the sorption of Cr(VI) and Cr(III). Soil and amended soil treated with solutions containing Cr(III) adsorbed 1.3 to 9 times more Cr than those treated with Cr(VI). The adsorption of the Cr(VI) and Cr(III) in the soils with organic amendments was in the order: oak > pine > olive oil mill residues > reed > soil. While the adsorption of the Cr(VI) and Cr(III) in the soils with inorganic amendments was in the order: coal > clay > oil shale > soil > zeolite. When the equilibrium concentration of chromate was 85 mg/L, for example, the adsorption capacity for the soil and soil-organic amendments mixtures was 0.063, 0.15, 0.18, and 0.45 mg/g, for soil, reed, oil mill residues, oak and pine, respectively. The adsorption capacity for soil-inorganic amendments mixtures was 0.05, 0.07, 0.09, and 0.17 mg/g, for zeolite, oil shale, clay, and coal, respectively.

Key Words

Chromium sorption; biomass, clay, oil shale, oil mill, zeolite.

Introduction

Soil contaminating chromium is released into the environment through various industrial activities, including electroplating, mining, pulp and paper production, timber treatment and petroleum refining (Yu *et al.* 2004). Chromium exists in soils in two stable oxidation states, Cr(III) and Cr(VI). These two oxidation states of Cr have very different behaviors (Lee *et al.* 2005). Chromium(VI) exists in oxyanion forms, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, under most conditions, and therefore it has high mobility in soils. Even at low concentration, Cr(VI) is considered carcinogenic and mutagenic to humans (Stewart *et al.* 2003). On the other hand, cationic Cr(III) is highly adsorbable by soil particles and is an essential human nutrient (Zayed *et al.* 1998). Since Cr(III) is considered less mobile, less soluble and less toxic than Cr(VI) (Bartlett and Kimble 1976), the existing remediation of Cr(VI)-contaminated sites usually involves the reduction of Cr(VI) into Cr(III) to reduce its mobility and toxicity (Patterson and Fendorf 1997). Adding organic materials to Cr(VI)-contaminated soils to promote Cr(VI) reduction is a commonly used method. In addition to accomplishing the intended remediation, this method is also environmentally friendly, inexpensive, and can reuse agricultural organic residues. Several researches have demonstrated that various organic materials, such as powdered leaves, biosolid composts, farm yard manure and brown seaweed can enhance the Cr(VI) reduction because of the dissolved organic carbon (DOC) and the small organic compounds released from the organic materials (Park *et al.* 2004). The objectives of this work were: to study the influence of organic and inorganic amendments on adsorption of Cr(III) and Cr(VI) when mixed with soil, and to measure, describe, and explain the equilibrium sorption characteristics; and to examine the sorptive capacity of soil amended with organic and inorganic substances as a possible technique for chromium immobilization in the environment and its availability for leaching in soil and plant uptake.

Materials and methods

Soil

The soil used in this study was taken from the 0 to 25-cm layer of a site in the Ajlun agricultural region of northern Jordan. The soil organic carbon (OC) content was determined by the Walkley-Black method. The pH and electrical conductivity were measured in soil suspensions with a soil to water ratio of 1:1 (w/v). The cation exchange capacity was determined by the method outlined by EPA. Particle size distribution was determined by the hydrometer method. Calcium Carbonate (%CaCO₃) was determined by the acid neutralization method. Total free iron oxides were determined using the citrate-bicarbonate-dithionite

extraction procedure for free iron oxides with colorimetric determination of iron by 1, 10 phenanthroline method. The specific surface area was determined by the EGME method. Fourier transform infrared (FTIR) spectroscopy (Jasco Corporation, Japan, range 4400-440 /cm) was used to characterize surface functional groups of soil and amendments.

Amendments

Organic amendments (reed, pine, oak, oil mill) and inorganic amendments (coal, zeolite, oil shale, and clay) were homogeneously mixed with air-dried soils at the rate of 10%.

Chromium(III) and Chromium(VI) Adsorption

Soil and amended soil samples were mixed with the Cr solutions at a soil to solution ratio of 1:5 by shaking on an end-over-end shaker for 16 h at room temperature. The soil suspension was filtered through a 0.45- μ m syringe filter and the solution stored at 4°C for Cr analysis. The concentration of Cr in the soil solutions was measured with an atomic absorption spectrophotometer for total Cr and the colorimetric analysis for Cr(VI) with diphenylcarbazide reagent. From these values the concentration of Cr(III) in the extracts was calculated.

Results

Influence of Soil Properties on Chromium Sorption

The effect of the initial concentration on the Cr(VI) and Cr(III) adsorption was investigated in the range 0.1–100 mg/L. The percent chromium adsorption decreased with increase in initial concentration, but the actual amount of chromium adsorbed per unit mass of the adsorbent increased with the increase in concentration in the test solution (Figure 1). As the chromium concentration in the test solution was increased from 0.1 to 100 mg/L, the amount of Cr(III) adsorbed on soil increased from 0.47 to 565 mg/kg, and the amount of Cr(VI) adsorbed on soil increased from 0.37 to 63 mg/kg. The removal percentage of Cr(III) and Cr(VI) at an initial concentration of 0.1 mg/L was 98% and 68%, respectively; while the removal percentage of Cr(III) and Cr(VI) at an initial concentration of 100 mg/L was dropped to 74% and 13%, respectively.

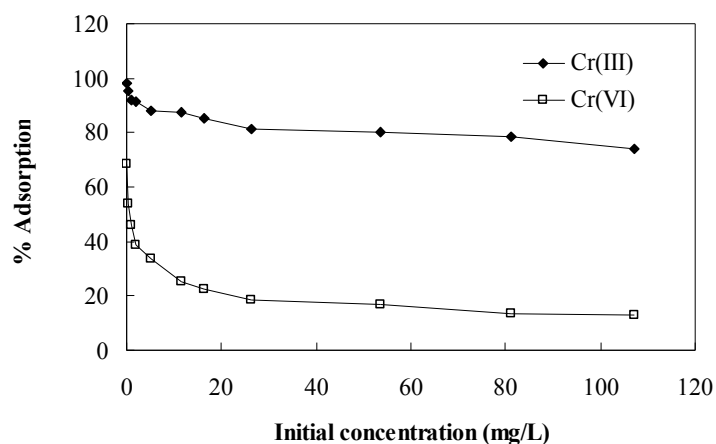


Figure 1. Effect of initial concentration of chromium adsorption by soil.

Soil treated with solutions containing Cr(III) adsorbed 1.3 to 9 times more Cr than those treated with Cr(VI) (Figure 1). This results from a larger cation exchange capacity vs. anion exchange capacity and the propensity for Cr(III) to precipitate on mineral surfaces at pH values above 5.5. The adsorption of both Cr species became more similar on soil because abundant Fe-oxides provided positive surface charges, thereby enhancing Cr(VI) sorption. (Zachara *et al.* 1987). The soil used had high pH creating an environment that favored Cr(III) adsorption. Deprotonation of oxides and organic matter occurs in soils with higher soil pH values, which results in more negatively charged sites that attract cations such as Cr(III). Also, when the soil pH is above 5.5, the Cr(III) most likely precipitates from solution as hydroxides creating a surface coating on a variety of soil mineral surfaces (Bartlett and Kimball 1976). This suggests that larger solid phase concentrations of Cr(III) can often be expected in soils with higher pH and abundant inorganic and organic carbon as shown by Stewart *et al.* (2003).

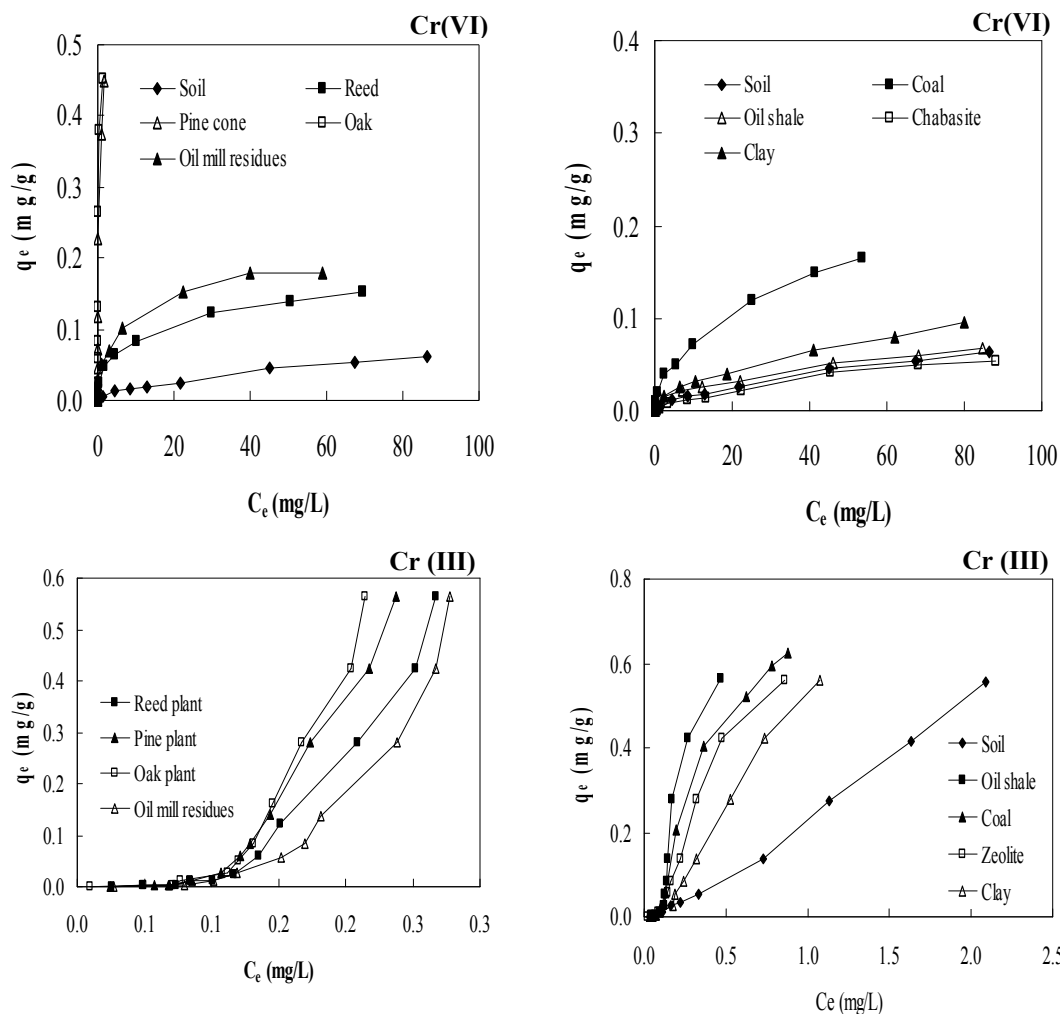


Figure 2. Adsorption isotherms for Cr(VI) and Cr(III) adsorption onto soil amended with organic and inorganic amendments.

Adsorption isotherms of Cr(VI) and Cr(III) onto soil amended soil with organic and inorganic amendments

The isotherms for the Cr(VI) and Cr(III) adsorption onto soil amended with organic and inorganic substances are presented in Figure 2. Clearly, the adsorption of the Cr(VI) and Cr(III) in the soils with organic amendments were in the order: oak > pine > olive oil mill residues > reed > soil. While the adsorption of the Cr(VI) and Cr(III) in the soils with inorganic amendments were as follows: coal > clay > oil shale > soil > zeolite. When the equilibrium concentration of Cr(VI) was 85 mg/L, for example, the adsorption capacity for the soil and soil-organic amendments mixtures was 0.063, 0.15, 0.18, and 0.45 mg/g, for soil, reed, oil mill residues, oak and pine, respectively. The adsorption capacity for soil-inorganic amendments mixtures was 0.05, 0.07, 0.09, and 0.17 mg/g, for zeolite, oil shale, clay, and coal, respectively.

Conclusion

Soil and amended soil treated with solutions containing Cr(III) adsorbed 1.3 to 9 times more Cr than those treated with Cr(VI). The adsorption of the Cr(VI) and Cr(III) in the soils with organic amendments was in the order: oak > pine > olive oil mill residues > reed > soil. While the adsorption of the Cr(VI) and Cr(III) in the soils with inorganic amendments was in the order: coal > clay > oil shale > soil > zeolite.

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