Origin of Cr in alluvial sediments and ultramafic rocks in Sultanate of Oman. Magnetic fractionation and sunlight effect

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Abstract

The present study attempts to identify the sources of Cr(VI) in a coastal alluvial fan soil and soil from a chromite mine. In addition investigates the effect of photochemically oxidized organic matter in the Cr(VI) mobilization in soil. The alluvial bulk soil samples contain several evidence of weathered products of the ophiolite nappe like serpentine and amphiboles. For better characterization we separated different soil fractions with magnetic separation. The results showed that magnetic fraction exhibits high amount of serpentine. The XRF-analysis showed Mg and Cr to be enriched on average by 2.5 and 6 times, respectively. The produced fractions were mixed with glucose to simulate organic carbon and then leached with KH_2PO_4/Na_2HPO_4 for the exchangeable Cr in all fractions before and after the exposure of the samples in the sun for several days. The results showed that soils from chromite mine were influenced by oxidation of organic matter with 20-30% reduction in Cr(VI) release, while alluvial fun soils showed very high capacity to immobilize Cr(VI) without any effect from organic matter oxidation.

Keywords: Geogenic chromium, serpentine, ophiolite, oxidation.

1. Introduction

Chromium, is considered a significant environmental pressure in soils and groundwater since the Word War II. Its industrial use in engines' parts as stainless hard steel alloy has created plumes of contamination in localities around the word (Jacobs and Testa 2005). The last 20 years there is increasing concern on the geogenic origin of Cr(VI) in soils and groundwater (Morrison et al. 2010, Moraetis et al. 2012 and references therein). Aluminosilicates such as serpentine, chlorite and amphiboles could be a source of Cr(III) which potentially is converted to Cr(VI) though oxidation by Mn(IV) (Kazakis et al. 2015). On the other hand, the presence of Fe-oxides and organic matter in soils can immobilize Cr(VI) (Kožuh et al. 2000).

The Sultanate of Oman has the most extensive outcrop of an ophiolite sequence in the world (Rajendran et al. 2012). The presence of serpentine and amphibole are very common in most of the alluvial aquifers and soils. In addition, there are chromite mines scattered in areas of harzburgite outcrops (Rajendran et al. 2012). Further more

recent studies have indicated aquifers where Cr(VI) is either higher or close to the drinking water standard (50 μm/l WHO) (Al-Riyami, 2017). The present study objective is to characterize the possible sources of Cr(VI) in soils and to identify the effect of organic matter oxidation in Oman soils.

2. Methodology

2.1. Sample characterization and magnetic separation

We have analysed 4 soil samples (W12, W10, Barka-2, Barka-5) from Barka coastal area in Oman and one soil (NS8) from the bottom of a chromite mine in Nakhal area. The samples were analysed with Niton™ XL3t (TermoFischer) for bulk chemical composition with X-ray Fluorescence (XRF). Mineralogical analysis was performed with an Aurora M90 instrument from BRUKER Company.

2.2. Sample characterization and magnetic separation

The magnetic separation was performed with an electrical magnet in two different voltages 5V and 20V in wet sample. Two samples were selected for further processing (W12 and NS8). The selected samples were leached with different extraction solutions such as water and phosphate $(KH_2PO_4/Na_2HPO_4.2H_2O)$ (Kožuh et al. 2000). The same phosphate extraction solution was applied also to the same samples after the addition of glucose and Cr(VI) (potassium dichromate) by 100 and by 300 mg/l. The glucose was added in the soil in a percentage of 3%. The mixture of glucose and Cr(VI) were preserved in the sunlight (OUT sample) and in dark (IN sample) in cycles of dryness and wetness for 10 days.
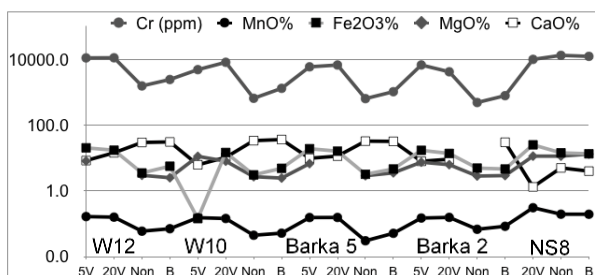
3. Results

3.1. Sample characterization, magnetic separation and total Cr content

The magnetic separation showed in average 88% was not magnetic material, 8% was collected with 20V and 3% was collected with 5V. The mineralogical analysis showed that serpentine (lizardite) was mainly accumulated in the magnetic fraction of the samples along with other minerals such as quartz, calcite and magnetite. The non-magnetic fraction of the samples was comprised of dolomite, calcite, quartz, mica, olivine, pyroxene. The XRF results showed a strong correlation between Fe, Mn,

Mg and Cr content in the magnetic fraction (Figure 1). The average content of Cr in the magnetic fraction (except NS8) of 5V and 20V, in the non-magnetic and the bulk samples was 7090, 7970, 827, 1384 mg/kg, respectively.

3.2. Cr(VI) extraction in bulk soil, magnetic and non-magnetic fraction.

The extraction of Cr(VI) with distilled water and phosphate in sample W12 and NS8 for fractions 20V, bulk (B) and non-magnetic are shown in Figure 2. The extraction with phosphate in both samples without the loading of Cr showed that the non-magnetic fraction of the soils released most of the Cr(VI).The results for the IN and OUT in the soil W12 has high capacity in immobilizing Cr(VI) and showed no statistically sound difference between the samples in dark (IN) and sunlight (OUT). The sample NS8 released most of the Cr(VI) in the IN and OUT samples. The incubation between IN and OUT conditions showed statistically sound difference (T-test) in the magnetic (NS8-20V) and the bulk (NS8-B) samples with the OUT sample to release 21 to 28% less Cr(VI). Finally, the 300 mg/kg loading with Cr(VI) showed similar results as those presented in Figure 2.

Figure 1. XRF analysis results for the 5 samples. 5V and 20V are the magnetic fractions. Non is the non-magnetic and B is the bulk sample (ppm:mg/kg)
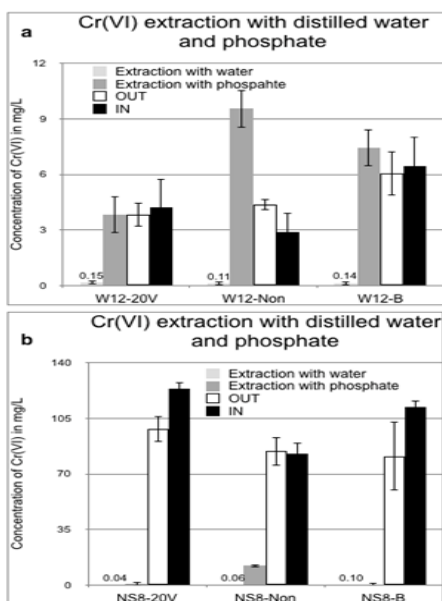
Figure 2. Extraction with distilled water and phosphate solution for samples W12 and NS8 in the magnetic (20V), non-magnetic (Non) and the bulk (B) fractions.

4. Discussion

The presented results show that the magnetic separation accumulates high amount of Cr which is related with serpentine. The amount of precipitated Fe around serpentine grains was possibly influencing the magnetism of serpentine. In that point, we agree also with other researchers correlating the high Cr content in soils with the serpentine presence in soils (Morrison et al. 2010, Moraetis et al. 2012). However, the extraction of Cr(VI) (without Cr loading) showed the highest release of Cr(VI) in the non-magnetic fractions (W12-Non, NS8-Non). This showed that large amount of exchangeable Cr(VI) could be related also to other minerals in the non-magnetic fraction (e.g. calcite) contrary to the high accumulation of Cr in the serpentine surface (Kazakis et al. 2015).

The IN and OUT treatment in W12 showed that the organic matter oxidation under sunlight had no effect in Cr(VI). The IN and OUT treatment in NS8 showed statistically sound evidence of sunlight influence in the Cr(VI) release. We suggest that the photochemically catalysed reaction of organic matter oxidation (Hug et al. 1997) in Oman has a pronounced effect on Cr(VI) immobilization only in areas of ophiolite rocks. In alluvial fan soils, other reactions than oxidation are regulating the high capacity of Cr(VI) immobilization.

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