

ALKALINE HYDROTHERMAL STABILIZATION OF Cr(VI) IN A SANDY SOIL

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Keywords: Chromium speciation; soil remediation; XRPD; μ -XRF

Introduction

Chromium (Cr) pollution of soil is a serious environmental problem, especially in industrialized areas. Risks for human and environmental health are strictly connected to Cr oxidation state, which is usually trivalent or hexavalent in soil. While Cr(III) is stable, scarcely mobile and weakly toxic, Cr(VI) is highly soluble, mobile and carcinogenic. Among the different remediation strategies, stabilization/solidification (S/S) is used as rapid and cost-effective technique for heavy metal polluted soils. It consists of the addition of appropriate materials to the polluted soil, mostly under alkaline conditions, in order to chemically and/or physically transform the contaminant in a stable and less toxic form. Waste materials like coal fly ash or other cheap sources of Si and Al can be used to stabilize heavy metals in soil (Terzano et al., 2005).

This study aims at evaluating a new S/S process for the reduction of Cr(VI) to Cr(III) in polluted soils and the incorporation of Cr(III) in newly formed minerals by using a reactive mixture of glass and aluminum (recovered from solid municipal wastes) and an alkaline hydrothermal treatment.

Methods

A sandy agricultural soil was spiked with 1500 mg kg⁻¹ Cr(VI). After 3 months of soil aging, Cr(VI) concentration naturally decreased to 580 mg kg⁻¹. An appropriate glass and aluminum mixture (MIX), prepared on the basis of outcomes reported in Terzano et al. (2015), was added as fine powder to the soil at ratios of 1/10 and 1/20 (w/w). Soil samples, including a sample without MIX, were added with KOH and deionized water (1:2 w/v) to reach a concentration of 5M KOH, and stored at 90°C in closed HDPE bottles. Soil aliquots were taken at different time intervals between 1 day and 3 months, and analyzed for Cr(VI) concentration (methods US EPA 3060A and 7196A) and Cr mobility (BCR sequential extractions). In order to study the mechanisms of Cr stabilization, soil samples were also examined for their structure (high resolution micro X-ray computed tomography - μ CT), mineralogical composition (X-ray powder diffraction - XRPD; Rietveld analysis), and elemental distribution (micro X-ray fluorescence - μ -XRF).

Results

Alkaline hydrothermal treatment halved Cr(VI) concentration in the control soil (without MIX) after 24h, and reduced it to 11 mg kg⁻¹ (-98%) after 3 months. Concomitantly, Cr mobility decreased and, after 3 months, 80% total Cr was scarcely available and/or bound to more recalcitrant soil fractions. When the hydrothermal treatment was applied to the soil added with MIX, Cr(VI) reduction occurred much faster and, after only 1 month, Cr(VI) concentration decreased to 11 mg kg⁻¹ independently of the MIX/soil ratio used. Moreover, Cr mobility was considerably reduced after 7 days, when 90% Cr was almost unavailable.

In most of the samples, XRPD analysis revealed the formation of a zeolite (edingtonite) and a strong decrease of quartz and illite. Micro-XRF analysis showed a strong modification of the soil structure during the hydrothermal treatment (Fig. 1), with a complete redistribution of Cr towards the formation of large

aggregates containing Cr along with Si, K, Al, Fe and Mn. Further microanalyses with electron microscopy and μ CT are in course to elucidate the mechanism of Cr inclusion into these soil aggregates.

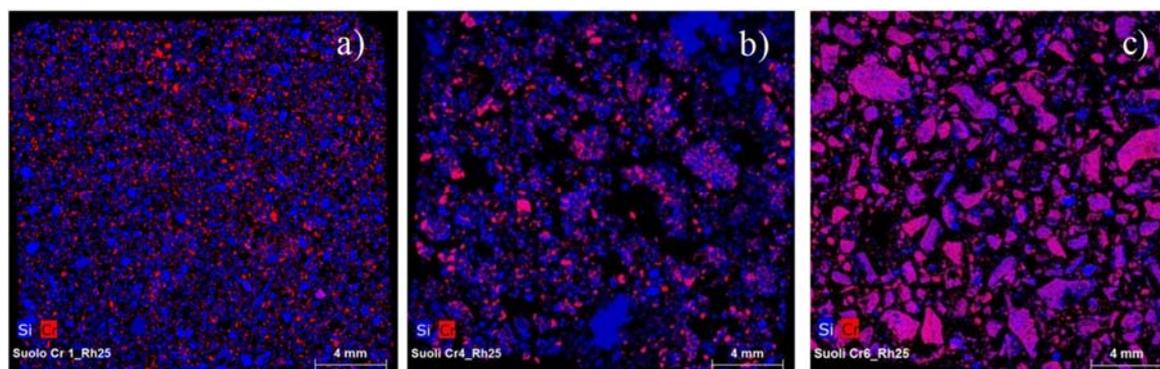


Figure 1. Maps obtained from μ -XRF analysis showing the distribution of Cr and Si in the control soil before (a) and after 1 month (b) and 3 months (c) of alkaline hydrothermal treatment.

Conclusion

Alkaline hydrothermal treatment is very efficient for the reclamation of a Cr(VI)-polluted sandy soil. The soil addition with a mixture of recycled glass and aluminum accelerates this remediation process. X-ray microanalyses are extremely useful to study the mechanisms of Cr stabilization in soil.

References

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