

Evaluation of calcium polysulfide as a reducing agent for the restoration of a Cr(VI)-contaminated aquifer

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Abstract

This work aims at investigating the efficiency of applying calcium polysulfide (CPS) as a reducing agent for the decontamination of a heavily Cr(VI)-contaminated aquifer. Series of batch experiments were carried out in order to evaluate the reductive behavior of CPS towards the aqueous and solid phase. CPS was added in several stoichiometric excesses (2.0X, 2.6X, 4.6X and 6.5X) with respect to the Cr(VI) concentration measured in the contaminated groundwater. The effect of time on Cr(VI) reduction by CPS was tested performing short term batch experiments. In addition, the effect of CPS on other groundwater constituents, e.g. nitrates, and potential mobilization of soil elements, sensitive to redox changes (Mn, As, Co, etc.), were also evaluated. The experimental results showed that CPS can be effectively used for the remediation of the Cr(VI) contaminated aquifer without affecting significantly the soil properties.

Keywords: calcium polysulfide, groundwater, hexavalent chromium, reduction

1. Introduction

Chromium is a heavy metal and a very common contaminant of soils and groundwater. In the geoenvironment chromium exists mainly in two oxidation states, as hexavalent (Cr(VI)) and trivalent (Cr(III)) chromium. In Cr(VI)-contaminated sites many remedial approaches have been used. The most common approach is the use of inorganic or organic electron donors aiming at Cr(VI) reduction and thus its immobilization as insoluble chromium hydroxide (Chrysochoou et al., 2010). Many reducing agents have been used in several sites such as ferrous sulfate, nano-zero valent iron (n-ZVI), sodium hydrogen sulfite/thiosulfate and organic materials (Chrysochoou and Ting, 2011). As an alternative reducing agent calcium polysulfide (CPS) has been extensively used in water treatment systems in the USA and has been approved for in-situ decontamination at several sites (Graham et al., 2006). This study investigates the efficiency of applying CPS as a reducing agent for the treatment of Cr(VI)-contaminated aquifers. More specifically the aim of the present study was to investigate the reductive behavior of CPS and the effect

of time on Cr(VI) reduction by conducting series of batch tests. In addition, the effect of CPS on other groundwater contaminants and soil elements were evaluated.

2. Materials

2.1. Materials

Groundwater and soil samples were collected from a heavily Cr(VI)-contaminated site at Inofyta, Greece. Soil was air dried, homogenized and sieved at -2.0 mm. The CPS was synthesized at the laboratory by mixing 100 g of Ca(OH)₂ with 300 mL deionized water under agitation and simultaneous heating for obtaining a homogenous suspension. Then 200g of sulphur and 700 mL of deionized water were added in the suspension of Ca(OH)₂. The suspension was boiled for 45 minutes and a brownish solution was formed. The final suspension was cooled to room temperature and the supernatant solution was separated by filtration. The S content of the solution was analyzed by the methylene blue method (8131 method of HACH).

2.2. Batch experiments

Batch experiments were carried out using 20 mL polyethylene bottles, filled with soil and groundwater keeping constant the solid to liquid ratio equal to 1/4 (5 g soil, 14.5 mL groundwater and 5.5 mL of CPS solution) at all experimental series. CPS was added at the suspensions at a stoichiometric ratio calculated based on the Cr(VI) concentration used in the batch tests. The concentration was equal to 1 mg/L (0.019 mmol/L Cr(VI)). The calculations were based on the reaction of Cr(VI) reduction (Eq. 1.)



According to this reaction (Eq. 1) the required molar ratio of sulfides (S²⁻) for Cr(VI) reduction is equal to 3/2 mole/mole. Consequently for the complete reduction of Cr(VI) in the aqueous solution the required amount of S²⁻ is 0.0288 mmol/L. Different stoichiometric ratios were used in all the experimental series, applying CPS excess of 2.0X, 2.6X, 4.6X and 6.5X times the stoichiometrically required amount of S²⁻. For each stoichiometric excess,

two batch series were conducted. The first series of tests aimed at investigating possible consumption of CPS by groundwater contaminants. The mixture contained contaminated groundwater and CPS. The second series of batch experiments included the simultaneous addition of CPS, groundwater and soil.

Another series of batch tests were performed in order to determine the effect of CPS a) on potential mobilization of other metals contained in soil and b) on other heavy metals detected in groundwater. Cr(VI) was analyzed by the diphenyl-carbazide method (USEPA 7196a). Aqueous solutions were analyzed for Mn, Ni, Co and As, by ICP-MS.

3. Results

In the first series of experiments the effect of CPS on Cr(VI) removal from groundwater was investigated. As it can be observed from Figure 1 only in the case of using CPS in excess of 4.6 and 6.5 times, the Cr(VI) concentration decreased below the existing regulation limit of 50 µg/L. For all tested excesses Cr(VI) reduction was completed in 24 h. These results indicate that CPS acts as reductant not only for Cr(VI), but also for other groundwater components as well. Otherwise Cr(VI) concentration should be zeroed due to the S²⁻ excess. Another contaminant possibly reduced by S²⁻ is nitrates. In order to verify the possible reduction of nitrates their concentration over time was determined using 6.5X excess of CPS. A significant decrease at nitrates concentration was observed during the first two days with concentration decreasing from 42 to 35 mg/L. After the second day nitrates concentration remained constant about 35 mg/L.

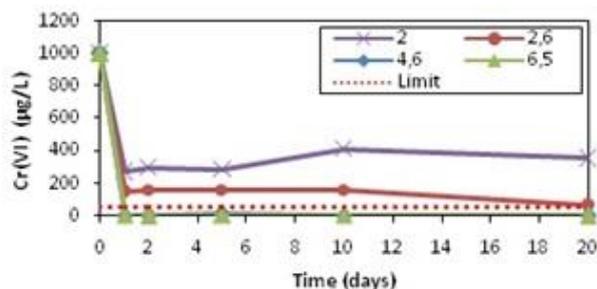


Figure 1. Cr(VI) concentration as a function of time in the presence of different S²⁻ excesses added in contaminated groundwater.

In the second series of experiments CPS was added in a suspension containing both groundwater and soil. Figure 2 presents the results of Cr(VI) concentration versus time for the four cases of excesses tested. As it is observed only in the case of using the 6.5X excess Cr(VI) concentration decreased below the legislation limit of 50 µg/L. The decrease was very fast since occurred in 24 h. The effect of other soil constituents on CPS consumption was observed in the case of using the 4.6X excess. When

the 4.6X excess was used only with groundwater, Cr(VI) concentration decreased below the legislation limit, while the addition of soil caused final Cr(VI) concentration higher than 50 µg/L.

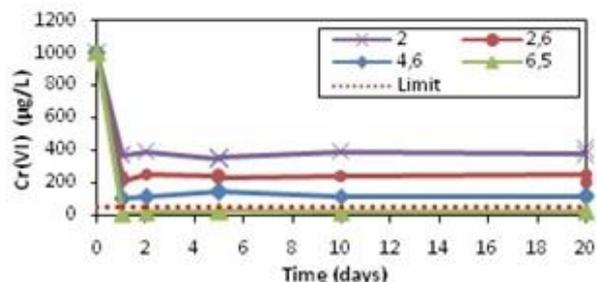


Figure 2. Cr(VI) concentration as a function of time in the presence of different S²⁻ excesses added in suspensions of soil and groundwater.

In order to determine the possible effect of CPS to other heavy metals encountered in groundwater or in the soil material of the aquifer, a series of other tests were also conducted. For evaluating the effect of alkaline conditions (pH 9.5) that CPS creates a suspension containing soil and 0.01 M NaOH was used. No mobilization of the tested heavy metals was observed. Secondly, the effect of CPS on mobilization of soil elements was investigated by mixing the soil with CPS 6.5X and deionized water for 5 and 20 days. At 5 days CPS caused the mobilization of Mn up to 43.51 µg/L., but the mobilized Mn precipitated again after 20 days. No mobilization was observed for the other metals. Nickel is another heavy metal often determined in concentrations exceeding the regulatory limit of 20 µg/L, in groundwater of the tested area. Using an aqueous solution of 1,300 mg/L Ni and applying CPS 6.5X, 50% removal was achieved. In the case of adding soil in the Ni solution almost complete removal of Ni from the aqueous phase was observed, indicating the occurrence of adsorption phenomena. Finally, the ability of CPS to remove both Ni and Cr was tested. The results showed that CPS efficiently removed both Ni and Cr(VI), but due to high levels of the two elements a higher amount of CPS should be applied in order to decrease both concentrations below the regulatory limit.

References

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