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Sorption studies of Zn(II) and Cu(II) onto vegetal compost used on reactive mixtures for in situ treatment of acid mine drainage

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Abstract

The efficiency of the sulphate reducing bacteria-based in situ treatment of acid mine drainage is often limited by the low degradability of the current carbon sources, typically complex plant-derived materials. In such non-sulphate-reducing conditions, field and laboratory experiences have shown that mechanisms other than sulphide precipitation should be considered in the metal removal, i.e. metal (oxy)hydroxides precipitation, co-precipitation with these precipitates, and sorption onto the organic matter.

The focus of the present paper was to present some laboratory data highlighting the Zn and Cu sorption on vegetal compost and to develop a general and simple model for the prediction of their distribution in organic-based passive remediation systems. The model considers two kinds of sorption sites ($\succ SO_2H_2$) and the existence of monodentate and bidentate metal-binding reactions, and it assumes that only free M^{2+} species can sorb onto the compost surface. The acid–base properties of the compost were studied by means of potentiometric titrations in order to identify the nature of the involved surface functional groups and their density. The distribution coefficient (K_D) for both Zn and Cu were determined from batch experiments as a function of pH and metal concentration. The model yielded the predominant surface complexes at the experimental conditions, being $\succ SO_2Zn$ for Zn and $\succ SO_2HCu^+$ and $(\succ SO_2H)_2Cu$ for Cu, with $\log K_M$ values of -2.10, 3.36 and 4.65, respectively. The results presented in this study have demonstrated that the proposed model provides a good description of the sorption process of Zn and Cu onto the vegetal compost used in these experiments.

Keywords: Metal sorption; Zn(II) and Cu(II); Acid mine drainage; Natural organic compost; Passive remediation; Surface complexation

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1. Introduction

The increasing awareness and concern about the environment has motivated in the recent years extensive research into developing new efficient technologies for the acid mine drainage (AMD) remediation. AMD is characterised by high contents of acidity, heavy metals

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and sulphates, and its potentially damaging impact when it incorporates into the groundwater system has been reported (Younger et al., 2002).

The recent biological approach in the in situ passive remediation of groundwater contaminated by AMD is based on the use of sulphate-reducing bacteria (SRB), which are able to reduce sulphate by the oxidation of an organic source, thereby the biogenic sulphide can precipitate most of dissolved heavy metals. However, there are many circumstances that limit the enhancement of the activity of the SRB (Scherer et al., 2000; Gibert et al., 2002), particularly the low degradability of the current carbon sources (typically complex plant-derived materials) used in such treatments. In these non-sulphate-reducing conditions, field and laboratory experiences have shown that mechanisms other than sulphide precipitation should be considered in the metal removal, i.e. metal (oxy)hydroxides precipitation, co-precipitation with these precipitates (McGregor et al., 1998), and sorption onto the organic matter (Machemer and Wildeman, 1992). Sorption of heavy metals onto a broad range of low-cost and waste organic materials has successfully been applied to the treatment of industrial effluents and natural waters (Lister and Line, 2001).

This study follows from a previous investigation where vegetal compost was evaluated as a carbon source for SRB in the treatment of AMD. Results revealed that vegetal compost was a poor source of food and energy for bacterial development and different mechanisms other than SRB activity were responsible for metal removal (Gibert et al., 2003). Precipitation and co-precipitation mechanisms were discussed, and sorption was anticipated from preliminary tests (Gibert et al., 2005).

The focus of the present paper was to present some laboratory data highlighting the Zn and Cu sorption on vegetal compost, and to develop a general and simple model for the prediction of their distribution in organic-based passive treatments for AMD. In a first step the acid–base properties of the compost will be studied in order to identify the nature of the involved acidic surface functional groups and their density. Then, the distribution coefficient (K_D) for both Zn and Cu will be determined from batch experiments as a function of pH, metal concentration and binding group concentration. The data will be treated numerically to determine the predominant surface complexes at the experimental conditions and their corresponding thermodynamic complexation constants (K_M).

2. Materials and methods

2.1. Materials

The raw material was provided by a conventional biological treatment plant in Manresa, Catalonia (Spain). It is the resulting product from the aerobic composting of a mixture of forest woods (basically pine and evergreen oak barks) and sludge at a ratio (in vol%) of 9:1. The compost was sieved and the fraction of 4–8 mm, formed mainly by the gross vegetal particles of the compost, was used in this study as the organic substrate with potential sorptive capacity of Zn and Cu.

Subsamples of compost were digested with $HClO_4$ (Merck, analytical reagent grade). Subsequent analysis of the extractable fraction, after filtration (0.22 μm), by atomic absorption spectrophotometry (AAS) (Varian Spectra-AA 640) showed negligible concentrations of Zn and Cu in the compost ($<0.1\,\mathrm{mg\,g^{-1}}$).

An elemental chemical analysis of subsamples of the same fraction of the compost determined the contents (in wt%) of C (27.2), N (1.3), H (3.4), S (0.5), P (0.9) (Gibert et al., 2004).

2.2. Acid–base characterisation of the vegetal compost

Dissolved transition metals can sorb at the interface by exchanging of H^+ at the acidic functional groups (Boily and Fein, 2000; Čežíková et al., 2001). Prior to the metal interaction studies, the acid–base properties of the vegetal compost (i.e. the concentration of the total acidic functional groups and their acidity constants) were determined by means of a potentiometric titration. A potentiometric titration consists essentially of the determination of the pH value at which protonation/deprotonation of the acidic functional groups in the solid surface takes place.

Compost was subjected to both acid and basic titrations using an automatic burette system (Micro TT Crison) and a combined glass electrode (Crison 52-02) coupled to a pHmeter (Crison GLP22). In both cases, titrations were conducted following the methodology described elsewhere. A dried sample of ground compost (1.2 g) was suspended in a reaction vessel containing 20 $\mathrm{cm^3}$ of 0.1 $\mathrm{mol\,dm^{-3}}$ $NaClO_4$ (Merck a.r. grade) used as an inert electrolyte to ensure a constant ionic strength. The solution was stirred using a Teflon©-coated magnetic stirring bar, while a small nitrogen overpressure was applied in the vessel. A standardised titrant (0.1 $\mathrm{mol\,dm^{-3}}$ HCl or 0.1 $\mathrm{mol\,dm^{-3}}$ NaOH, both containing 0.1 $\mathrm{mol\,dm^{-3}}$ $NaClO_4$) was added to the vessel and the solution pH was monitored. After each addition, at least 10 min passed to obtain a stable electrode potential. Acid and base titrations of the background electrolyte solution (0.1 $\mathrm{mol\,dm^{-3}}$ $NaClO_4$) were also conducted as control titrations.

The acid–base characterisation was complemented by Fourier-transform infrared (FTIR) (Perkin-Elmer 1600) analysis of compost samples equilibrated with acid ($pH = 1$), neutral ($pH = 6$) and basic ($pH = 13$) aqueous solutions. This analysis was carried out by diluting the compost samples in pressed KBr disks.