

Article III: Municipal-based mixture for acid mine drainage bioremediation. Metal retention mechanisms

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MUNICIPAL COMPOST-BASED MIXTURE FOR ACID MINE DRAINAGE BIOREMEDIATION: METAL RETENTION MECHANISMS

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Abstract: An upflow packed column was operated to evaluate the potential of a mixture of municipal compost and calcite to promote sulphidogenesis in the remediation of a simulated mine water at high flows ($>0.1 \text{ m d}^{-1}$). Results showed that the pH was neutralised and metals (Fe, Al, Zn, Cu) were significantly removed. Metal removal was attributed to the combined result of precipitation as metal (oxy)hydroxides and carbonates, co-precipitation with these (oxy)hydroxides and sorption onto the compost surface rather than to precipitation as metal sulphides. The two last mechanisms are especially significant for Zn, whose hydroxide is not expected at pH 6-7. Before the saturation of compost sorption sites, 60% of the influent Zn was estimated to have been removed by co-precipitation with Fe- and Al-(oxy)hydroxide and 40% by sorption onto the municipal compost.

Key words: acid mine drainage, sorption, compost, co-precipitation, passive remediation, sulphate-reducing bacteria

1. Introduction

A major environmental concern currently facing active and inactive mining industries throughout the world is the treatment of acid mine drainage (AMD), which results from chemical and biological oxidation of residual sulphide minerals. The seepage of such acidic discharges into the water system constitutes a potential risk to natural ecosystems.

Current technologies in the *in-situ* treatment of AMD are (1) the permeable reactive barriers (PRB), whereby a reactive material is emplaced underground in the path of the contaminated plume (Blowes et al., 2000), and (2) the reducing alkaline promoting systems (RAPS), where the reactive material is deposited in ponds and is infiltrated by contaminated surficial discharge (Hedin et al., 1994). This material must be chemically effective to eliminate contaminants and must maintain a permeability at least equal to that of the surrounding material to ensure preferential flow through the remediating system.

The biological approach to AMD treatment is based on the use of sulphate-reducing bacteria (SRB), which under favourable conditions convert sulphate to sulphide by the oxidation of organic carbon (Dvorak et al., 1992). Bacterially *in-situ* generated sulphide can precipitate dissolved metals, while bicarbonate can increase the alkalinity of the acidic water.

The success of the process depends ultimately on the extent of the sulphate reduction by SRB. Cheap, widely available and highly effective organic substrates are desirable. Natural organic substrates tested to date include a wide range of roughage and organic wastes (Waybrant et al., 1998; Chang et al., 2000; Gibert et al., 2003).

These laboratory studies conclude that available complex organic substrates, commonly accompanied by an alkaline agent, mainly limestone, provide hardly any carbon to promote sulphidogenesis in continuous systems. Despite this lack of bacterial activity, a significant metal removal is achieved, demonstrating that metal retention cannot be attributed to microbial mediated sulphate reduction but to other mechanisms. These mechanisms could be precipitation such as (oxy)hydroxides and carbonates (Dvorak et al., 1992; Lyew and Sheppard, 1997), co-precipitation with these precipitates (Benner et al., 1999; Cravotta and Trahan, 1999; Song et al., 2001) and sorption onto the organic substrate (Machemer and Wildeman, 1992; Song et al., 2001; Gibert et al., 2003). However, the identification of these processes is upon to debate.

The present paper investigates in a laboratory-scale column experiment the feasibility of remediating AMD by using municipal compost in combination with calcite from a chemical point of view. Our study forms part of the investigation on spillage of the toxic waste at the Aznalcóllar Mine (Spain) in April 1998, when a dam holding the tailings was ruptured. The consequent spill of the mine wastes over the River Agrio bed prompted the installation of an organic-based PRB. In contrast to other barriers (Benner et al., 1997; Ludwig et al., 2002), high water flows ($>0.1 \text{ m d}^{-1}$) are encountered in the Agrio aquifer (Carrera et al., 2001). In order to facilitate the interpretation of field data, we performed column experiments to reproduce the behaviour of the PRB at Aznalcóllar.

This study was carried out in three stages: (1) evaluation of a municipal compost-based mixture; (2) identification of the contribution of the co-precipitation of metals with Fe- and Al-(oxy)hydroxides and (3) quantification of the sorption of metals onto the compost surface.

2. Materials and methods

2.1. Column experiment

In the experimental set-up, acidic water was gravity fed into the column (Figure 1). Simple gravity flow through the column was chosen instead of a peristaltic pump to simulate the barrier emplaced in the aquifer. The column was flooded from bottom to top. Effluent was discharged from the end of a tube held at a fixed reference elevation. Flow rate was controlled by maintaining constant the level of the feed water (A) and the outlet (B) using a level sensor connected to a pump. The flow was measured by weighting water samples at the outlet at a given time. Moistured nitrogen was continuously bubbled through the feed reservoir in order to reduce oxygen content. The column consisted of a transparent metacrylate cylinder (length of 50 cm and inner diameter of 5 cm). The body of the column was designed to minimise channelling by embossing relief rings on the inner side of the column wall.

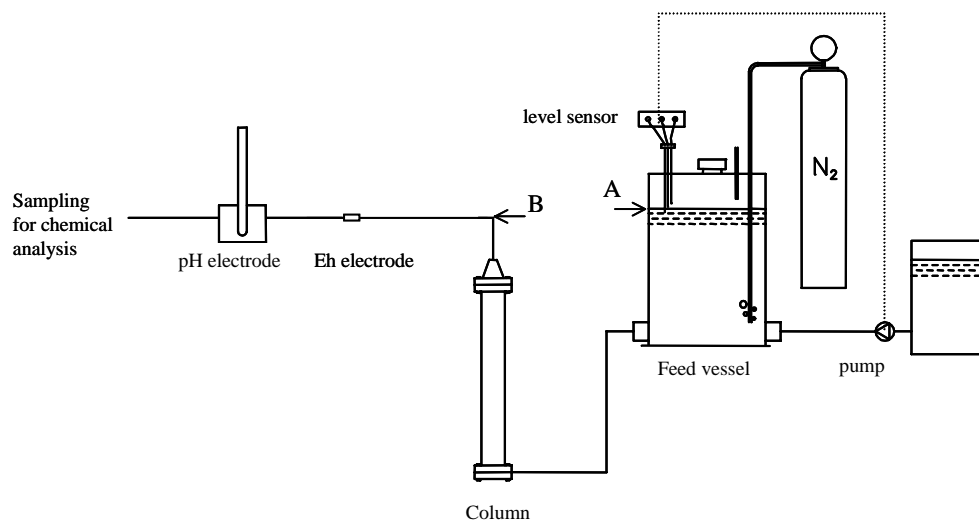


Fig. 1. Schematic of the experimental set-up. Acidic water was gravity fed into the column at a fixed flow by maintaining constant the difference between the level of the feed (A) water and the effluent discharging point (B)

Packing material composition (vol %) was 50% of crushed natural calcite (755 g), 40% of municipal compost (189 g) and 10% of river sediment (378 g). River sediment acted as the SRB source, municipal compost was the provider of the organic carbon necessary to sustain bacterial activity and limestone was used as the pH neutralising agent. The compost consisted of a 2:1 (by volume) mixture of pine bark and composted municipal sewage sludge and was supplied by a biological treatment plant at Manresa, Catalonia (Spain), and limestone came from a quarry (2-4 mm size). These materials were mixed and homogeneously packed in the column, yielding a porosity of 0.5. No inert material was added. The column was covered with an opaque material to simulate light conditions encountered in the aquifer.

Simulated mine water was prepared in the laboratory taking into account the groundwater composition in the Agrio aquifer at Aznalcóllar (SW Spain). Metals and anions were added as sulphates and chlorides, and pH was adjusted to 3.0 by HCl addition. The chemical composition is given in Table 1.

Composition	Concentration (mg dm ⁻³)
SO ₄ ²⁻	1000
Fe(III)	10
Zn(II)	20
Cu(II)	20
Al(III)	10
pH	3.0

Table 1. Composition of the simulated mine-drainage water taking into account the composition of the groundwater in the Agrio aquifer.

The average inflow rate was 0.5 cm³ min⁻¹, which represents a Darcy velocity of 0.73 m d⁻¹ (16 hours residence time). The experiment was run at room temperature (21±2 °C), and lasted approx half a year (158 days), during which the effluent was collected for pH, E_h, metal (Fe, Al, Zn, Cu), SO₄²⁻ and HS⁻ analysis.

All pH measurements were made routinely in a sealed flow-through cell placed at the exit of the column with a HAMILTON combination pH electrode coupled to a CRISON GLP22 pH meter. E_h was measured using a tubular platinum electrode at the exit of the cell paired with an Ag/AgCl-reference electrode. Samples for metal and sulphate analyses were filtered through a 0.22 µm syringe filter and acidified with HCl prior to analysis. Fe, Zn, Cu

were measured by inductively-coupled plasma mass spectroscopy (ICP-MS) (VG Plasma Quad PQ2), whereas Al was analysed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Spectra). Sulphate was measured by liquid ion chromatography (ALLIANCE model Waters 2690) coupled to an electrical conductivity detector (Waters 996). Dissolved HS⁻ was determined with a Ag/AgS electrode. To this end, HS⁻ was trapped to prevent loss through volatilisation as hydrogen sulphide and/or through aerial oxidation. The trapping solution, which acted as a sulphide antioxidant buffer (SAOB), was composed of an alkaline solution containing EDTA as complexing agent and ascorbate as reductant.

On the completion of the experiment, fractions of precipitate were sampled from the inlet of the column and examined by scanning electron microscope (SEM) (JEOL JSM 6400) equipped with an energy dispersive X-ray (EDX) analyser (EDX-LINK-LZ5). Mineral phases were identified by X-Ray Diffractometry (XRD) (BRUKER D5005) with Cu L α radiation.

2.2. Co-precipitation with Fe- and Al- (oxy)hydroxides experiments

As stated above, one suspect mechanism responsible for the removal of metals such as Zn (whose stable solid phases are not expected at pH 6-7) was the co-precipitation with amorphous Fe- and Al- (oxy)hydroxides.

Column experiments were performed to test the Zn and Cu removal by precipitation/co-precipitation in a calcite column system. Three columns (length of 5 cm and internal diameter of 1.4 cm) were filled with 20 g of calcite, each receiving a synthetic water containing (A) Zn, (B) Zn and Fe, and (C) Zn and Al. The concentrations of these metals are given in Table 2. All these solutions were acidified to a pH of 3.0 (by HCl addition) and prepared in a sulphate (1000 mg dm⁻³) and carbonate (60 mg dm⁻³) medium to meet the same conditions as in the previous column experiment. At day 37, an amount (1000 mg dm⁻³) of Ca was added (as CaCl₂) to the inflow to limit the calcite dissolution reaction and achieve the pH value of 6.8. An analogous set of column experiments were conducted with metal solutions containing Cu instead of Zn. In this case, a Ca concentration of 1000 mg dm⁻³ was provided at the start of the experiment.

	Zn system			Cu system		
	Zn(II)	Fe(III)	Al(III)	Cu(II)	Fe(III)	Al(III)
Column A	17	-	-	11	-	-
Column B	18	22	-	16	22	-
Column C	15	-	14	16	-	14

Table 2. Feed water composition in the co-precipitation tests (expressed in mg dm^{-3})

These feed waters were pumped by means of a multi-channel variable-speed Gilson Minipuls peristaltic pump at a flow rate of $0.036 \text{ cm}^3 \text{ min}^{-1}$, which represents a Darcy's velocity of 0.59 m d^{-1} (4 hours average residence time). At the end of the experiments, precipitates were retrieved for SEM-EDX and XRD analyses.

2.3. Sorption onto compost experiments

Experiments were conducted to test the ability of the municipal compost to sorb Zn and Cu on its surface. Batch equilibrium sorption experiments were carried out using standard batch methodology described elsewhere (Vegliò et al., 2002): given volumes (20 cm^3) of prepared aqueous solutions (concentrations ranging from 4 to 300 mg dm^{-3}) were shaken overnight with weighted amounts of dry compost (0.3 g, particle size of 3-5 mm) in glass tubes using a continuous rotary mixer (50 min^{-1}) at room temperature ($21 \pm 2 \text{ }^\circ\text{C}$). Following a 15 h period of agitation, the concentration of the metal ions in the remaining aqueous solution was determined after filtration ($0.22 \text{ }\mu\text{m}$). Experiments were conducted at a fixed pH (6.5 for Zn and 5.5 for Cu, the latter being lower to prevent Cu precipitation as hydroxide), which was checked and adjusted periodically to the desired value. A sulphate (300 mg dm^{-3}) and carbonate (60 mg dm^{-3}) medium was provided for each batch experiment to better simulate real conditions of the passage of AMD through a compost/limestone mixture PRB.

3. Column experiments: results and discussion

3.1. Water chemistry evolution

Figure 2 shows the evolution of chemical parameters of interest. Effluent pH approached neutrality from the beginning of the experiment. Initial removal efficiency of heavy

metals was very high, with measured concentrations in the effluent lower than 0.150 mg dm^{-3} (retention levels >99%). From day 50, Zn showed an exceptional behaviour, with an increase in the effluent Zn concentration to nearly 8 mg dm^{-3} . Al concentration was always below the detection limit (0.010 mg dm^{-3}). Despite the metal removal, sulphate concentration was not found to decrease and hydrogensulphide concentration was always below the detection limits (0.005 mg dm^{-3}). These results, together with the positive E_h values (around 400 mV), suggest that SRB activity was negligible. These difficulties in achieving sulphate reducing conditions by using municipal compost correlates with an earlier study where vegetal compost was employed as a carbon source (Gibert et al., 2003).

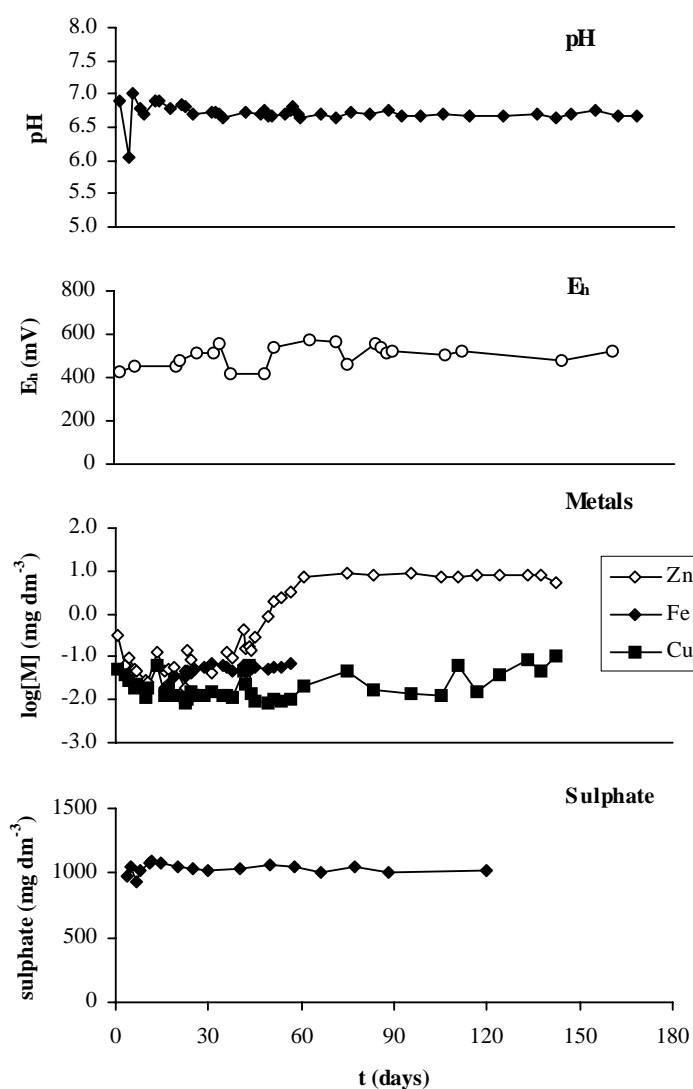


Fig. 2. Evolution of chemical parameters of interest in the effluent over the experiment.

Because Zn exhibited a special behaviour with respect to the other metal ions, attention was focused on this element. Figure 3a shows the species distribution diagram as a function of pH for the system $\text{Zn}^{2+}\text{-CO}_3^{2-}\text{-SO}_4^{2-}\text{-H}_2\text{O}$ for a total Zn concentration of 20 mg dm^{-3} in a sulphate (1000 mg dm^{-3}) and carbonate (60 mg dm^{-3}) medium similar to that encountered in the column. The species distribution diagram for Cu is shown in Figure 3b for comparison.

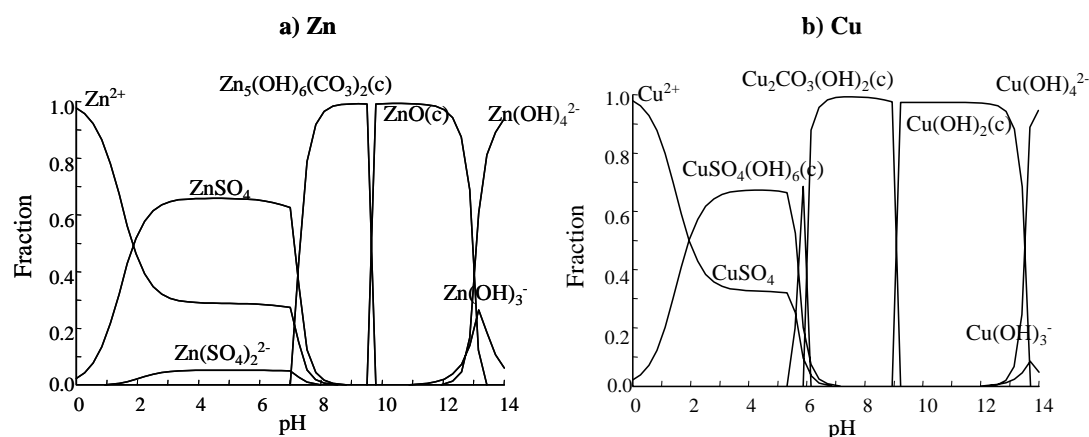


Fig. 3. Species distribution diagram as a function of pH for the system a) $\text{Zn}^{2+}\text{-CO}_3^{2-}\text{-SO}_4^{2-}\text{-H}_2\text{O}$ and b) $\text{Cu}^{2+}\text{-CO}_3^{2-}\text{-SO}_4^{2-}\text{-H}_2\text{O}$. Metal ions concentration: 20 mg dm^{-3} ; sulphate: 1000 mg dm^{-3} ; carbonate: 60 mg dm^{-3} (calculations performed with the Medusa and Hydra codes; Puigdomènech, 2001).

It is worth noting (see Fig 3a) that the solubility of Zn is significantly affected by pH due to the formation of solid phases. At pH 6.8, the value reached in the effluent of the column experiment, almost all the Zn is expected to remain in solution (primarily as dissolved species $\text{Zn}(\text{SO}_4)_{(\text{aq})}$, Zn^{2+} and $\text{Zn}(\text{SO}_4)_2^{2-}$), resulting in the absence of solid phases. This contrasts sharply with the Zn profile obtained in the column (Fig 2). The effluent Zn concentrations are marginal during the first 50 days, after which concentration achieved a final value of approx 8 mg dm^{-3} (which from a total concentration of 20 mg dm^{-3} corresponds to a 60% retention). These findings suggest that certain mechanisms account for the partial depletion of Zn from the contaminated water. These mechanisms could be co-precipitation onto Fe- and Al-(oxy)hydroxides and sorption onto compost.

In contrast to the behaviour of Zn, Cu is expected to significantly precipitate at pH 6.8, primarily as $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (Fig 3b), which correlates with the profile in Figure 2.

3.2. Solid analysis

Pale brown and gelatinous grey precipitates formed near the inlet of the column, suggesting that Fe- and Al-(oxy)hydroxides precipitation occurred. The SEM-EDX analysis revealed the presence of a pervasive cryptocrystalline layer made up of Al-Fe-O. Smaller amounts of Zn and Cu were systematically detected in this solid phase (Fig 4a). Despite the abundance of such coating, XRD did not detect any peak, probably because of its poor crystallinity.

This finding correlates with the results of earlier studies conducted under non reducing conditions (Amos and Younger, 2003; Karathanasis and Thompson, 1995; Gibert et al., 2003). The ability of Fe- and Al- (oxy)hydroxides to act as a secondary sorbent phase and a partner for co-precipitation, which can incorporate heavy metal and metalloids, has been reported by other authors (Machemer and Wildeman, 1992; Cravotta and Trahan, 1999).

At the outlet of the column, spherical shaped framboids constituted by Fe and S averaging 10 μm in diameter were occasionally observed (Fig 4b). These precipitates are assumed to occur locally in reducing pores since measured Eh values in the water phase were too high (Fig 2) for sulphide generation. Metal sulphides have been observed in previous laboratory experiments (Herbert et al., 1998; Gibert et al., 2003) and in field applications in full-scale permeable reactive barriers (Herbert et al., 2000) and artificial wetlands (Karathanasis and Thompson, 1995).

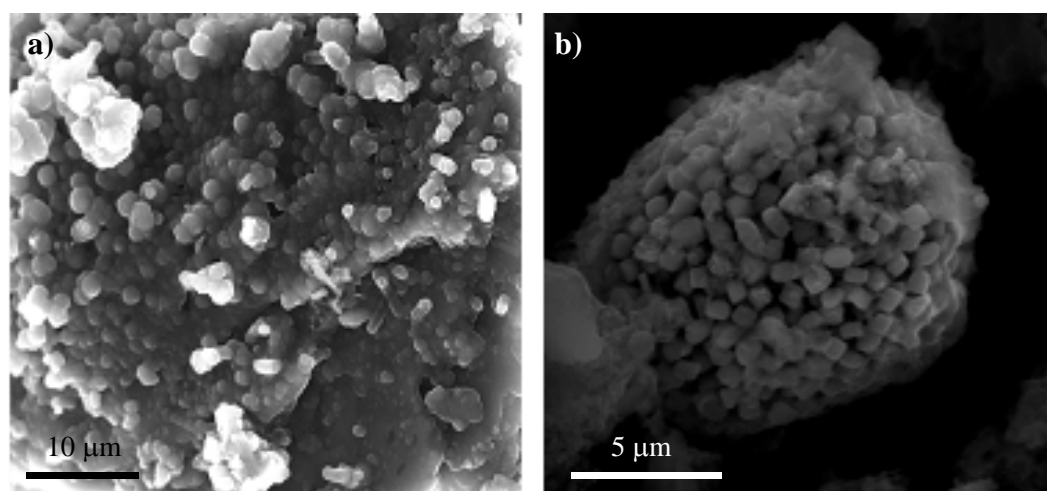


Fig. 4. a) Cryptocrystalline coating layer of spherulics made up of Al-Fe-O containing minor amounts of Cu and Zn; b) Spherical aggregates of Fe and S, observed in samples from the outlet part of the column.

4. Results of experiments on metal retention processes

4.1. Co-precipitation with Fe- and Al- (oxy)hydroxides

Figure 5 compares the evolution of pH, Zn, Cu, Fe and Al concentrations over column A, B and C experiments.

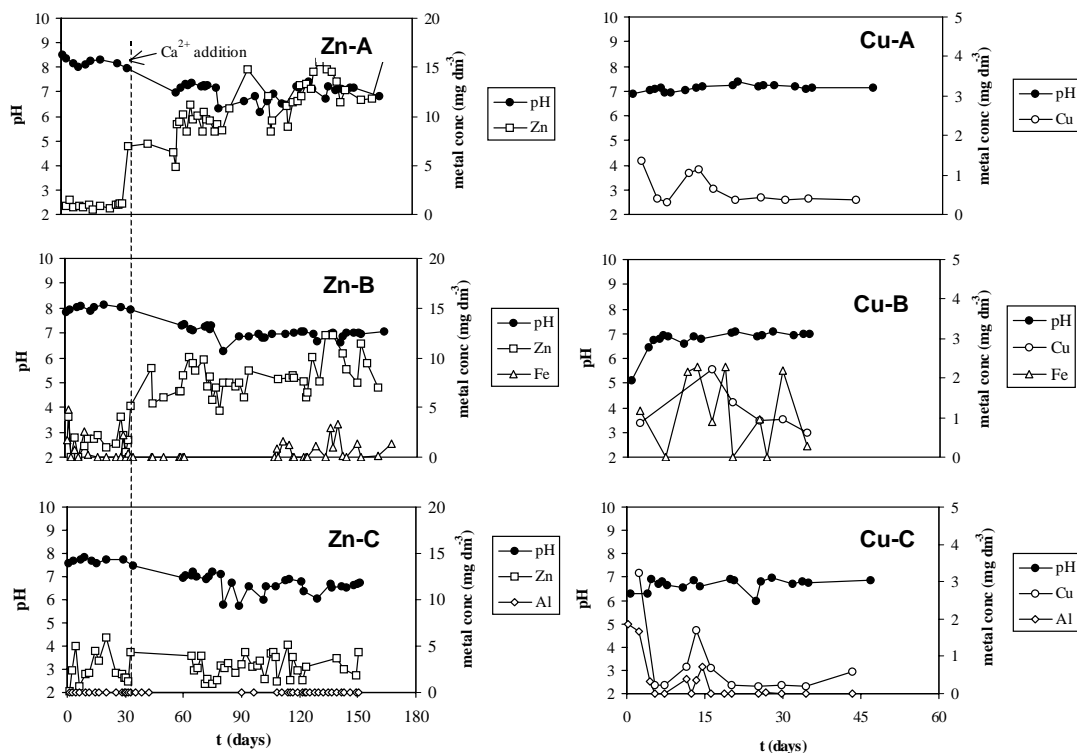


Fig. 5. Effect of Fe and Al on the removal of Zn and Cu by calcite in the co-precipitation tests. Each column containing 20 g of calcite received synthetic water containing (A) Zn/Cu, (B) Zn/Cu and Fe, and (C) Zn/Cu and Al. The concentrations of these metals are given in Table 2.

The presence of Fe and Al affects effluent pH since these metals hydrolyse to form insoluble Fe- and Al-(oxy)hydroxides, thereby decreasing the initial pH to lower values (8.0 and 7.7 for columns Zn-B and Zn-C respectively) with respect to column Zn-A (pH of 8.2). These Fe- and Al-(oxy)hydroxides were visible as orange-yellow and pale grey precipitates near the inlet. In column Zn-A a white precipitate was also formed at the entrance of the column. Hence, and unexpectedly, the presence of Fe and Al led to a slight increase in

dissolved Zn concentration during the initial days because of acidification rather than to a decrease due to co-precipitation in accordance with Figure 3a. At day 37, an amount (1000 mg dm^{-3}) of Ca was added to the inflow to limit the calcite dissolution and achieve the desired pH value of 6.8, closed to the value in Figure 2.

At the adjusted pHs, and again in correlation with Figure 3a, an increase in dissolved Zn concentration was found in column Zn-A, with effluent average concentrations of 14 mg dm^{-3} (85% of the inflow content). The 15% removal of Zn could be attributed to the prevalent pH, which could cause Zn precipitation, or to the sorption onto calcite (Zachara et al., 1991). The Zn precipitation was supported by XRD analysis, which detected hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (Fig 6). Moreover, according to thermodynamic data (Schindler et al., 1969; Hayek and Gleispach, 1965) hydrozincite is expected to be stable under the column pore water conditions (Fig 3a). On the other hand, the sorption contribution was assumed to be very low taking into account earlier works highlighting the surface area as a key factor in the metal sorption. García-Sánchez and Álvarez-Ayuso (2002) studied Zn sorption onto calcite and found that the maximum sorption capacity obtained at a particle size $<0.1 \text{ mm}$ was 185 mg Zn g^{-1} calcite, which diminished to 25 mg Zn g^{-1} calcite (87% reduction) at a particle size of $0.2\text{-}1 \text{ mm}$. The sorption capacity at a particle size of $2\text{-}4 \text{ mm}$ used in our experiments was thus expected to be very low with the result that this mechanism was ruled out.

Effluent Zn concentrations were much lower for columns B (9 mg dm^{-3} , 50%) and C (3.5 mg dm^{-3} , 25%) (Fig 5), suggesting that co-precipitation of Zn with Fe- and Al-(oxy)hydroxides occurred. Based on a mass balance between influent and effluent concentrations, the presence of Fe and Al induced an average decrease in Zn concentration of 50% and 75%, respectively. These Zn removal percentages were higher than the 15% found in the absence of Fe or Al. Zn has thus a greater capacity to co-precipitate with Al than with Fe. SEM-EDX analysis of precipitates from column Zn-B showed a pervasive cryptocrystalline coating layer composed of Fe-O with Zn, suggesting co-precipitation with Fe-(oxy)hydroxide. XRD analysis revealed the presence of calcite, gypsum and zincite (ZnO) and goethite (FeOOH) (Fig 6). According to Figure 3a, ZnO was not expected at pH around 7 and its presence warrants clarification. For column C, SEM-EDX observation showed an omnipresent cryptocrystalline coating made up of Al-O and Zn, also suggesting co-precipitation of Zn with Al-(oxy)hydroxide. XRD analysis of these precipitates did not detect any mineral phase probably because of the poor crystallinity of the precipitates.

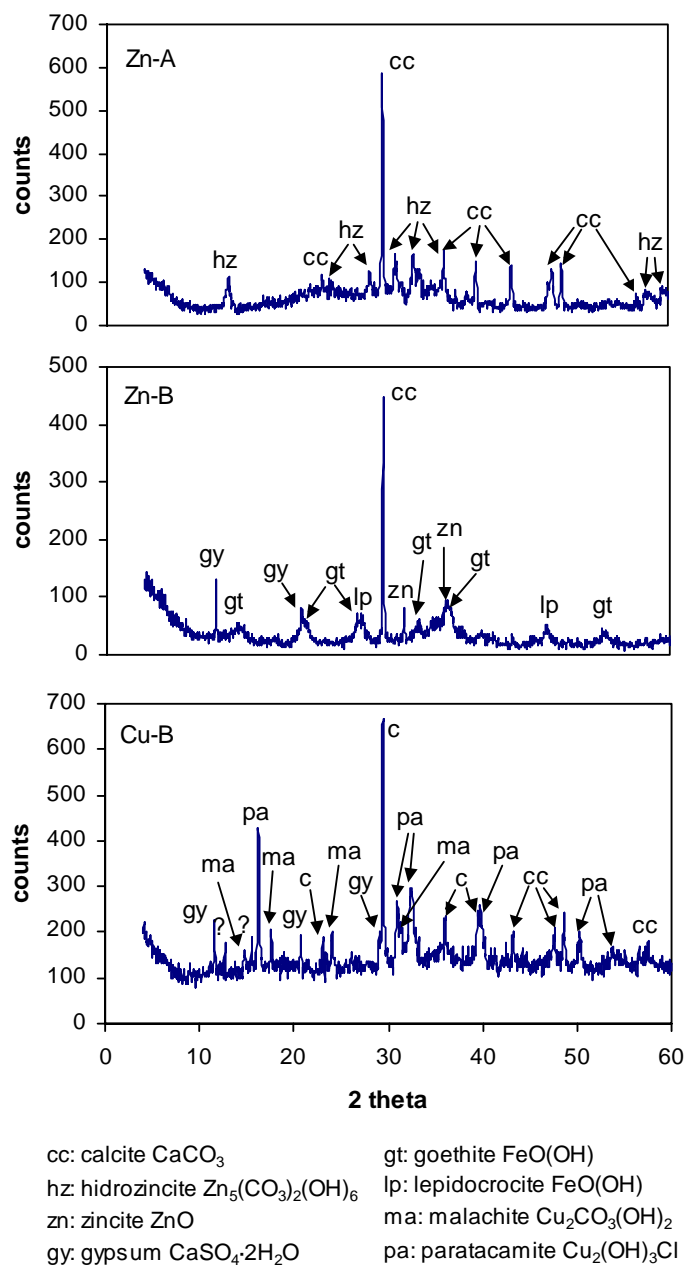


Fig. 6. XRD diffractogrammes of precipitates collected from columns Zn-A, Zn-B and Cu-B after the co-precipitation tests.

For Cu columns, similar patterns were obtained with pH values stabilised at around 6.8. In sharp contrast to Zn columns, Cu concentrations were lower for the three columns, with effluent concentrations below 1.5 mg dm^{-3} (removal levels of $>86\%$), showing that Cu removal is basically governed by its precipitation induced by the increase in pH rather than by the co-precipitation with Fe- and Al- (oxy)hydroxides. The predominant minerals detected by XRD were malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) and paratacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$), besides calcite and gypsum (Fig 6). The high content of Cl in the feed water is due to the addition of this element as heavy metal chlorides, CaCl_2 and HCl . The formation of paratacamite is consistent with chemical equilibrium data, which predict the presence of this mineral within the pH range of 5.5-6.7.

4.2. Sorption onto municipal compost

Sorption onto the municipal compost surface is the second suspect mechanism that could account for the metal removal. This phenomenon has been demonstrated, under non-sulphate-reducing conditions, with a large list of biomasses (Machemer and Wildeman, 1992; Aderhold et al., 1996; Artola et al., 2001, Chen and Peng, 2000).

In Figure 7 equilibrium metal concentrations in the solid phase (Γ in mg g^{-1} dry compost) are plotted versus concentrations in the solution (c_L) at a pH of 6.5 for Zn and 5.5 for Cu (the latter being lower to avoid Cu precipitation by hydrolysis). The amount of metal taken up by compost was determined through a mass balance from liquid-phase measurements. Typical sorption profiles were obtained for both Zn and Cu tests.

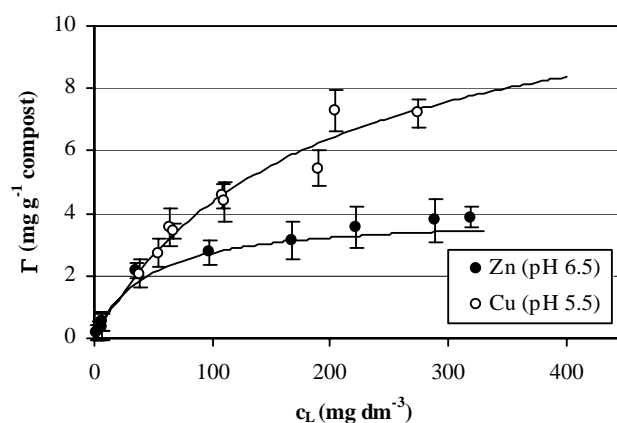


Fig. 7. Constant pH equilibrium uptake isotherms for Zn and Cu onto municipal compost at a pH of 6.5 for Zn and 5.5 for Cu. Curves are based on the Langmuir model with appropriate constant values.

These sorption data of Zn and Cu onto compost can be modelled by a non-competitive Langmuir-type adsorption isotherm:

$$\Gamma = (b c_L \Gamma_{\max}) / (1 + b c_L) \quad (3)$$

where Γ_{\max} is the maximum adsorption capacity of the adsorbent and b is the apparent affinity constant. Experimental Γ and c_L data were used to determine the constants (Γ_{\max} and b) from a linearised form of equation (3) and using least-square regression analysis. The curves in Figure 7 were generated from Langmuir model equations with the obtained constants.

Table 3 gives published values of Γ_{\max} and b concerning the sorption of Zn and Cu onto a broad range of biomasses. As can be seen, Γ_{\max} values for Cu obtained in this study were comparable to those reported for other sorbents, whereas Γ_{\max} values for Zn were lower for our municipal compost.

Figure 7 reveals a sorption preference of compost for Cu over Zn. This finding is consistent with other studies reporting a similar relationship when using *Microcysters* (Pradhan and Rai, 2001), resin (Chandra and Rempel, 1993), apple residue (Maranon and Sastre, 1992) and mushroom compost (Machemer and Wildeman, 1992) as biosorbents.

	Adsorbent	pH	Γ_{\max} (mg g⁻¹)	b (dm³ mg⁻¹)	Reference
Zn	Fungal biomass	5.5	10.9-13.9	0.152-0.505	Zhou, 1999
	Fungal biomass	4	9.2-11.1	0.043-0.064	Puranik and Paknikar, 1999a
	Algal biomass	5	9.0-89.0	0.005-0.100	Leusch et al., 1995
	Algal biomass	6	121.9	0.028	Valdman and Leite, 2000
	Bacterial biomass	6.5	23.6	0.160	Puranik and Paknikar, 1999b
	Bacterial biomass	2-6	9.7-82.6	0.035-0.110	Celaya et al., 2000
	Calcium alginate	5	70.6	0.177	Chen and Peng, 2000
	Lignite	5.1-5.6	22.9	0.070	Chu and Hashim, 2002
	Oil palm ash	3.6	4.7-10.7	0.039-3.222	Allen and Brown, 1995
	Sewage sludge	6	10.9	0.213	Lister and Line, 2001
	Seaweed biomass	4.5	44.5	0.035	Chong and Volesky, 1995
	SRB	5.5-6.8	6.4-37.0	0.041-1.832	Chen et al., 2000
	Compost	6.5	3.9	0.024	This study
Cu	White-rot fungus	5.2	248.1	0.051	Sing and Yu, 1998
	Synthetic resin	5.2	66.1	0.004	Sing and Yu, 1998
	Sewage sludge	6	19.3	0.143	Lister and Line, 2001
	Fungal biomass	4	3.1-23.8	0.038-0.438	Muraleedharan et al., 1995
	Algal biomass	5	69.3-83.9	0.096-0.263	Yu et al., 1999
	SRB	4-6	2.0-9.3	0.127-0.826	Chen et al., 2000
	Calcium alginate beads	2.5-5	6.0-15.0	0.001-0.003	Vegliò et al., 2002
	Seaweed biomass	4.5	62.9	0.064	Chong and Volesky, 1995
	Compost	5.5	12.1	0.005	This study

Table 3. Capacities of evaluated biomasses (Γ_{\max} and b values) in the adsorption of Zn and Cu reported in the literature

4.3. Contribution of mechanisms in Zn removal

Results from the aforementioned co-precipitation and sorption tests can be applied to interpret the profile of Zn concentration in Figure 2. Initially Zn removal can be attributed to the combined effect of co-precipitation with Fe- and Al-(oxy)hydroxides and sorption onto compost, resulting in marginal concentrations in the effluent (below 1 mg dm⁻³). At day 50, the compost sorption sites became saturated, increasing the Zn concentration in the effluent to levels of approx 8 mg dm⁻³. Thereafter, Zn did not continue to sorb onto compost but continued to co-precipitate with fresh Fe- and Al-(oxy)hydroxides. Figure 8 represents the contribution of

each mechanism in the Zn removal along the experiment. On the application of a steady-state mass balance for the first 50 days, approximately 60% of the influent Zn was estimated to have been removed by co-precipitation with Fe- and Al-(oxy)hydroxides, and 40% by sorption onto compost.

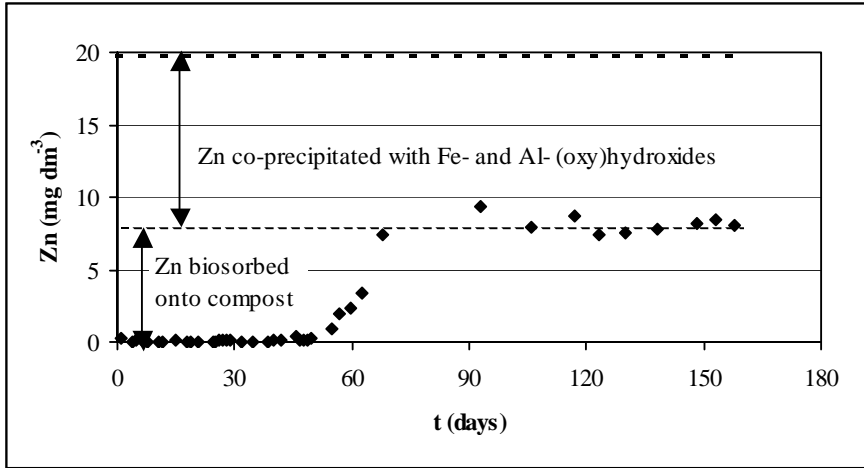


Fig. 8. Contribution of co-precipitation with Fe- and Al- (oxy)hydroxides and sorption onto municipal compost in the Zn removal along the column experiment with calcite and municipal compost.

The expected Zn removal by biosorption during the first 50 days could be calculated (1) from the sorption capacity of the compost (yielding 737 mg Zn, calculated as $m_{\text{compost}} \cdot \Gamma_{\text{mx}}$, where m_{compost} is the mass of compost in the packing material (189 g) and Γ_{mx} is its maximum Zn adsorption capacity (3,9 mg g⁻¹)) and (2) from water analysis (yielding 288 mg Zn, calculated as $\Delta t \cdot q \cdot c_{\text{Zn}}$, where Δt is the time elapsed before saturation of sorption capacity (50 days), q is the average flow rate (0.5 cm³ min⁻¹), and c_{Zn} is the average Zn concentration in the effluent after compost saturation (8 mg dm⁻³)).

As can be seen, there is a difference of 60% between the computations. This imbalance demonstrates that not all the potential sites of compost are used for Zn sorption but for other ions, indicating competition of metals. Despite the fact that metal competition fell outside the scope of this study, it could have played an important role (Aderhold et al., 1996; Pradhan and Rai, 2001; Chong and Volesky, 1995).

5. Conclusions

In the light of our findings, the following conclusions can be drawn:

- Municipal compost was found to be particularly poor at providing nutrients to promote and sustain SRB activity since SO_4^{2-} inflow concentration is not significantly reduced, HS^- is not detected, and E_h is kept above 400 mV throughout the column experiment.
- Acidity neutralisation was achieved from the start of the experiment and it was due to calcite dissolution rather than to bacterial activity.
- The removal of Fe, Al, Zn and Cu concentrations at $\mu\text{g dm}^{-3}$ levels meant a reduction of >99%, with the exception of Zn, whose concentration in the effluent reached a stabilised concentration of 8 mg dm^{-3} (removal of 60%) after 50 days.
- Of the mechanisms governing this removal, three are quantitatively worth noting: precipitation of (oxy)hydroxides and hydrated carbonates related to pH changes, co-precipitation with Al-Fe (oxy)hydroxides, and sorption onto municipal compost. The two last mechanisms are especially important for Zn, whose stable solid phases are not expected at pH 6-7.
- It can be estimated that 60% of the influent Zn was removed by co-precipitation with Fe- and Al-(oxy)hydroxide and 40% by sorption onto compost before saturation of compost sorption sites occurred. Once sorption sites of compost were saturated, co-precipitation appeared to be the only mechanism responsible for the Zn removal.
- Sorption tests with single metal solutions showed a preference of compost for Cu over Zn ions, with Γ_{max} of 3.9 and 12.1 (mg g^{-1} compost) for Zn and Cu, respectively. The results from the column experiments with a multi-metal solution suggest metal competition for sorption sites in the compost.

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