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ORIGINAL PAPER

# In situ removal of arsenic from groundwater by using permeable reactive barriers of organic matter/limestone/zero-valent iron mixtures

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**Abstract** In this study, two mixtures of municipal compost, limestone and, optionally, zero-valent iron were assessed in two column experiments on acid mine treatment. The effluent solution was systematically analysed throughout the experiment and precipitates from both columns were withdrawn for scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffractometry analysis and, from the column containing zero-valent iron, solid digestion and sequential extraction analysis. The results showed that waters were cleaned of arsenic, metals and acidity, but chemical and morphological analysis suggested that metal removal was not due predominantly to biogenic sulphide generation but to pH increase, i.e. metal (oxy)hydroxide and carbonate precipitation. Retained arsenic and metal removal were clearly

associated to co-precipitation with and/or sorption on iron and aluminum (oxy)hydroxides. An improvement on the arsenic removal efficiency was achieved when the filling mixture contained zero-valent iron. Values of arsenic concentrations were then always below 10 µg/L.

**Keywords** Acid mine drainage · In situ remediation · Permeable reactive barrier · Organic matter · Zero-valent iron · Arsenic removal

## Introduction

Groundwater contamination by acid mine drainage (AMD) occurs at numerous current and former mining sites worldwide as a result of the percolation of oxidised leachates generated from the oxidation of residual sulphur ores. These leachates, referred to as acid mine drainage, are characterised by high acidity and high concentrations of arsenic (As), heavy metals (Fe, Zn, Cu, Cd etc.) and sulphate (Waybrant et al. 1998). The incorporation and spread of such pollutants into the groundwater system can result in a potential hazardous impact on the subsurface ecosystems, with the result that treatment is necessary to meet legislation standards (Younger et al. 2002).

Among the constituents of AMD, As is acknowledged to be a serious pollutant to the aquatic ecosystems because of its persistence, toxicity and

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bioaccumulation. Arsenate (As(V)) and arsenite (As(III)) are the primary forms of As in the natural environment, their distribution being strongly dependent on the pH and Eh (Lien and Wilkin 2005; Triszcz et al. 2009). The toxicological effects associated with As in drinking water have been well documented, and include skin and lung cancers, diabetes and neurological dysfunctions (Beak and Wilkin 2009; Brammer and Ravenscroft 2009). Because of its acute toxicity, the World Health Organization, the European Commission and the U.S. Environmental Protection Agency have all set up a maximum threshold of 10 µg/L As for drinking water regulations (Tyrovola and Nikolaidis 2009; Zouboulis and Katsoyiannis 2005).

The management of AMD-contaminated groundwater has been achieved most often by conventional pump-and-treat systems, whereby groundwater is pumped to the land surface prior to ex-situ treatment and further redispersion (Burghardt et al. 2007). However, since these methods have proved to be expensive and often ineffective at achieving the proposed level of cleanup, attention has been paid to more cost-effective in situ treatments for contaminated groundwater. Among these, permeable reactive barriers (PRB) have gained considerable interest (Ludwig et al. 2009; Wilkin et al. 2009). A PRB consists of excavating a trench into the aquifer and refilling it with an appropriate reactive material able to remove and/or retain the pollutants from contaminated groundwater by various in situ transformations as groundwater flows through the PRB (Blowes et al. 2000). The selection of appropriate filling reactive materials is a critical step on the performance of a PRB (Gibert et al. 2004). PRB materials investigated for AMD-contaminated groundwater comprise a sulphate-reducing bacteria (SRB) source and an organic substrate to promote and maintain SRB activity. This biological approach for the treatment of AMD seeks to biologically reduce sulphate to sulphide by the oxidation of the organic substrate so that the bacterially in situ generated sulphide can then precipitate dissolved As besides metals such as Fe, Zn and Cu as solid-phase sulphides (Gibert et al. 2004; Ludwig et al. 2009). Additional proposed materials for PRBs for AMD are limestone (to neutralise pH and facilitate bacterial activity) (Hammack et al. 1994) and silica sand or gravel (to enhance permeability for hydrodynamic purposes) (Waybrant et al. 1998).

Zero-valent iron (ZVI), which is extensively used to treat organic contaminants, has been proved to also contribute to the removal of As and heavy metal. Fe<sup>0</sup> corrosion produces ions Fe<sup>2+</sup>, Fe<sup>3+</sup> (their speciation depending on redox conditions) and OH<sup>-</sup>, which, in turn, precipitate as Fe(OH)<sub>2</sub>, a variety of Fe(II/III) (oxy)(hydro)oxides and Fe(OH)<sub>3</sub>. These precipitation reactions can promote both the coprecipitation of As with iron and the sorption of As onto iron-corroded surfaces, contributing to the removal of As from the solution (Su and Puls 2003; Ludwig et al. 2009; Triszcz et al. 2009). The mechanisms of this As removal by ZVI are acknowledged to be rather complex and they clearly need to be better understood to properly design control and remediation measures for As removal. To date, a considerable body of laboratory-scale research has focused on ZVI and its potential for the treatment of As from water (Lien and Wilkin 2005; Su and Puls 2003), and only a few experiences of full-scale PRB for As-contaminated groundwater are reported (Ludwig et al. 2009; Wilkin et al. 2009).

The main objective of this work was to evaluate in column experiments the effect of ZVI in a biologically mediated treatment of a synthetic AMD with an emphasis on As removal. ZVI was added as a component in combination with calcite, creek sediment as the source of SRB and a natural organic substrate (municipal compost) to promote sulphate-reduction activity.

## Materials and methods

### Experiments description

Two different mixtures where municipal compost was accompanied by a source of SRB, limestone and, optionally, ZVI were assessed in laboratory column experiments to treat synthetic mine-drainage water with high contents of sulphate, metals and As. The compositions of the reactive mixtures and the synthetic AMD are given in Tables 1 and 2, respectively.

The source of SRB consisted of sediment collected from the anoxic zone of a local creek. The presence of SRB was anticipated by a strong H<sub>2</sub>S odour. The municipal compost was added as the organic carbon source to promote and sustain the SRB activity. It was provided by Aplicaciones de la Biomasa S.A.

**Table 1** Composition of column reactive mixtures (in vol %)

	Column 1 (without ZVI)	Column 2 (with ZVI)
Limestone	50	55
Municipal compost	45	30
Creek sediment	5	10
Zero-valent iron (ZVI)	–	5

**Table 2** Simulated mine-drainage water composition with pH = 3.0

	(mmol L <sup>-1</sup> )
As (V)	0.03
Fe(II)	0.18
Al (III)	0.37
Zn (II)	0.31
Cu (II)	0.32
Cd (II)	0.02
SO <sub>4</sub> <sup>2-</sup>	10

from Sevilla (Spain). Limestone (2–4 mm size) was used as a pH-neutralising agent. ZVI was added in Column 2 to assess its effect on As removal by the biological system. The ZVI used for our experiments was supplied by Connelly-GPM (USA) (2–4 mm). Both mixtures in Columns 1 and 2 had an estimated porosity of 0.5, which was determined gravimetrically from the amount of water that was used to filled the solid.

The chemical composition of the synthetic mine-drainage water used for our experiments was based on the analysis of contaminated groundwater of the Agrio aquifer (Aznalcóllar, Spain). Metals were added to the dissolution as sulphates and anions (SO<sub>4</sub><sup>2-</sup> and HAsO<sub>4</sub><sup>-</sup>) as sodium salts and after pH was adjusted using HCl or NaOH. Arsenic and metal speciation was obtained by speciation computations with the software codes Hydra and Medusa (developed by I. Puigdomènech from KTH, Stockholm, Sweden, and available at <http://w1.156.telia.com/~u15651596/>), which solve the mass balance equations of the different species present in the system in terms of equilibria and stoichiometric formation constants. Arsenic was found to be as As(V).

The column experiments were conducted using vertical glass columns (20 cm height and 2.5 cm internal diameter), where the reactive mixtures were packed. The synthetic AMD was kept in a closed reservoir with low oxygen by bubbling N<sub>2</sub> and

pumped in an up-flow mode using a peristaltic pump at a flow rate of 4.5 cm<sup>3</sup>/h. Both experiments were carried out at room temperature (23 ± 1°C). The experiment lasted for more than 2 months.

### Analytical techniques

The effluent from both columns was sampled and analysed to determine the pH, As, heavy metal and sulphate concentrations. All pH measurements were made routinely in a sealed flow-through cell placed at the exit of the column with a pH electrode. As, Zn, Fe, Cu and Cd were measured by inductively coupled plasma mass spectroscopy (ICP-MS), whereas Al was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Sulphate was measured by liquid ion chromatography (Alliance model Waters 2690) coupled to an electrical conductivity detector. At the end of the experiments, fractions of precipitate from both columns were retrieved to be visualised using scanning electron microscopy (SEM) and analysed by energy-dispersive X-ray spectroscopy (EDS) (JEOL 6450, EDX-LINKLZ5) and X-ray diffraction (XRD) (Siemens D-500). Precipitates from Column 2 were subjected also to digestion for total analysis and to sequential extraction following established protocols (Davidson et al. 1998).

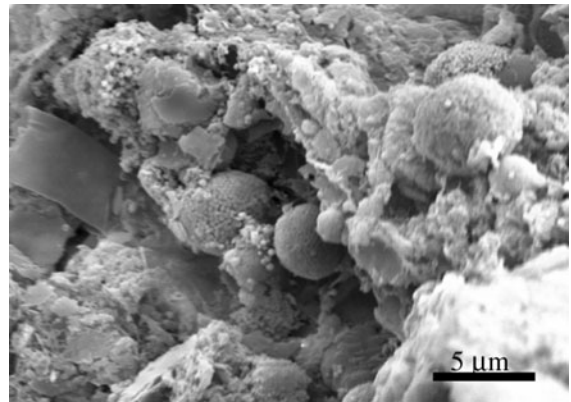
### Results

Figure 1 shows the evolution of (a) pH and (b) As for both Columns 1 (with ZVI) and 2 (without ZVI), respectively. With regards to pH, both columns raised the pH from 3 to about circumneutral values due to calcite neutralisation. During the first 2 months of the experiment, the pH in Column 2 was higher than in Column 1, possibly due to the corrosion of ZVI, which reacts under anaerobic conditions, consuming acidity and producing H<sub>2</sub> (Herbert et al. 2000), according to the reaction shown below (Eq. 1). The pH in Column 2 decreased gradually and, after 2 months, it achieved similar pH values to those obtained for Column 1 in the absence of ZVI. This pH decrease can be attributed to the precipitation of (oxy)hydroxides, which possibly formed a film on the ZVI surface coating the reaction sites and, thus, reducing the reactivity of the ZVI (Roh et al. 2000;

Herbert et al. 2000). After iron passivation, the pH was controlled by limestone dissolution in both columns.

Columns efficiency on As removal was very high in both columns since the beginning of the experiment, as shown in Fig. 1b. Column 2 containing ZVI provided levels of As below the WHO threshold of  $10 \mu\text{g/L}$  ( $1.3 \times 10^{-4} \text{ mmol}$ ) throughout the experiment (i.e. 99.5% removal efficiency). For Column 1, however, an erratic trend with variable As values (up to  $190 \mu\text{g/L}$ ) was observed during the first 2 months of the experiment. Thereafter, As concentrations were maintained between 10 and  $20 \mu\text{g/L}$ , very close to the threshold level defined by the WHO. The columns performance on metals removal (Zn, Cu, Cd, Al and Fe) (not shown in this work) was also very effective for both columns (>99%). Nevertheless, despite this significant metal retention, the net sulphate consumption was not detectable, suggesting that As and metal removal was due to processes other than sulphide precipitation.

Brown and pale grey precipitates (iron and aluminium (oxy)hydroxides) formed in the inlet port of both columns from the beginning of the experiment. SEM examination of these precipitates showed a pervasive layer coating the surface of the column material (Fig. 2). This layer was made up of Al, Fe and O (in accordance with aluminium and iron (oxi)hydroxide precipitation predicted from thermodynamic equilibrium calculations) with minor amounts of Zn, Cu and As. These metals were distributed homogeneously throughout the layer according to EDS mapping. No recognisable crystals could be identified by XRD owing to their small amount and poor crystallinity. Occasional iron-sulphide framboids could be detected near the outlet of Column 2, suggesting that sulphate-reducing activity could locally be achieved in the presence of ZVI. Also in Column 2, and in line with the latter finding, octahedral crystals of metallic Cu



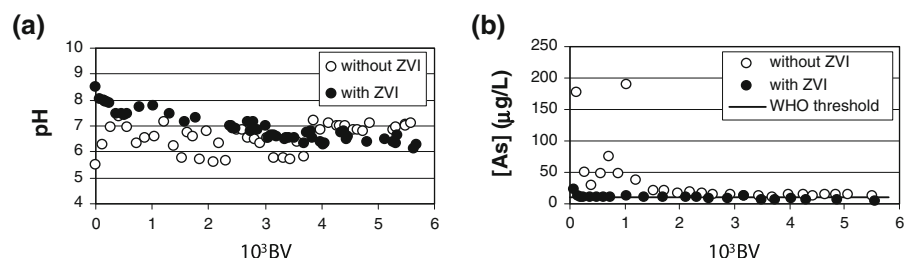
**Fig. 2** Aggregates of spherulites made up of Fe, Al and O with minor amounts of Zn, Cu and As observed in samples from Column 2. Spherical-shaped aggregates of Fe, S and minor amounts of Zn were also observed, together with the pervasive layer of spherulites

were observed, corroborating that strong reducing conditions could be locally achieved in the presence of ZVI.

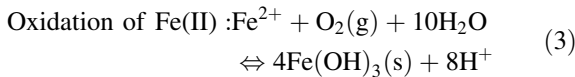
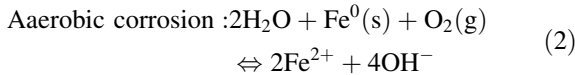
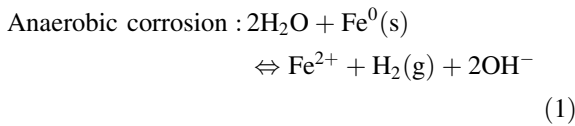
Mechanisms whereby As removal took place in Columns 1 and 2 might be more related to the pH increase rather than to biogenic sulphide precipitation, as no net sulphate reduction was observed. It has been reported that amorphous iron (oxy)hydroxide precipitates can act as a strong secondary sorption phase for As and metals. This statement is consistent with the sequential extraction results from the loaded material, which found that As and metals were mainly associated (>90%) with carbonate and iron (oxi)hydroxide fractions.

ZVI has been proposed, in fact, as a new sorption medium for removing both arsenate ( $\text{AsO}_4^{3-}$ ) and arsenite ( $\text{AsO}_3^{3-}$ ) from polluted waters (Su and Puls 2003; Wilkin et al. 2009). These studies have shown that ZVI may potentially be used in PRB technologies to remove As from groundwater via surface complexation or precipitation. Specific mechanisms

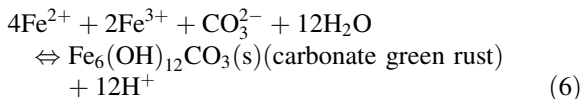
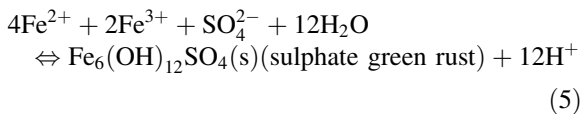
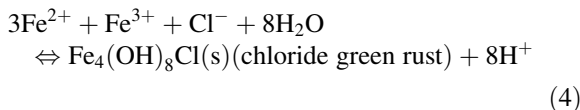
**Fig. 1** Evolution of **a** pH and **b** As for both Columns 1 and 2 with and without ZVI, respectively



of As removal by ZVI are, nowadays, under evaluation (Tyrovola and Nikolaidis 2009; Ludwig et al. 2009). Both aerobic and anaerobic corrosion can occur to ZVI ( $\text{Fe}^0$ ):



Common anions in the aqueous solution can influence the effectiveness of  $\text{Fe}^0$  barriers for As remediation through the formation of the following new mineral phases and competitive surface adsorption/coprecipitation by these phases (Su and Puls 2003):



These studies report that iron corrosion products (oxides and green rusts) are most likely the solid phases that host the sorbed As. The mechanisms whereby As(V) and As(III) is fixed by ZVI have been identified with the help of X-ray absorption spectroscopy to comprise the formation of inner-sphere bidentate complexes with the  $\text{Fe}^0$  corrosion products and synthetic iron oxides (goethite, lepidocrocite, maghemite, magnetite and hematite).

It can be concluded that municipal compost assessed under our experimental conditions was too poor a carbon source to support continuous SRB activity. However, the efficiency of the organic matter/limestone/ZVI mixtures for As and heavy metal removal was high and, with regards to As, measured concentrations in the treated water were below the WHO threshold of 10  $\mu\text{g/L}$ .

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