Immobilization of Arsenic and Manganese in Contaminated Groundwater by Permeable Reactive Barriers Using Zero Valent Iron and Sheep Manure

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A permeable reactive barriers (PRBs) column test was carried out to remove arsenic (As) and manganese (Mn) from groundwater using zero valent iron (ZVI), sheep manure, compost and woodchips as reactive materials. Arsenic was mainly immobilized through sorption and co-precipitation with iron-bearing minerals, and also possibly precipitation as FeAsO₄. The presence of sulfate-reducing bacteria (SRB) in the inoculated column was suggested by decrease of sulfate concentrations and increase of δ⁵³S in the effluent. Arsenic was more effective to immobilize in the inoculated than in the sterilized column due to co-precipitation with sulfides formed by reduction of sulfate in addition sorption and/or co-precipitation with carbonates. The Mn was mainly immobilized through adsorption onto compost and ZVI, and partly by precipitation as carbonates. Manganese was more effectively immobilized in the sterilized than in the inoculated column. The result demonstrates that As is more effective to immobilize using mixture of sheep manure with ZVI than only ZVI as reactive materials in PRBs.


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1. Introduction

Groundwater contamination with As is a threat in water resources that can have severe human health effects such as cancer of skin, lung, bladder, and kidney as well as pigmentation changes, skin thickening, neurological disorder, muscular weakness, loss of appetite, and nausea. In order to minimize risk, World Health Organization (WHO) implemented the guideline for the maximum concentration limits (MCL) of drinking water and industrial drainage of As are 10 µg dm⁻³ and 100 µg dm⁻³, respectively. Arsenic can be released into the environment by anthropogenic activities including nonferrous metal mining and smelting, fossil fuel processing and combustion, wood preserving, pesticide production and application, and disposal and incineration of municipal and industrial wastes. In addition, high As concentrations (>50 µg dm⁻³) in groundwater caused by natural geological condition have been reported in Asian developing countries such as Bangladesh, India, Taiwan and China. In cases of mining activities, there is additional contaminants: for example, there is groundwater contamination impacted by Mn with more than MCL as well as As at Sumbawa Island, Indonesia. It is well known that Mn is difficult to remove at neutral pH, therefore, the Mn contamination is often encountered in active and/or abandoned mine sites and agricultural sites. Intake of Mn in the body leads nervous system problem, lung embolism and bronchitis. Manganese is also regulated by WHO to be less than 0.4 mg dm⁻³ and 10 mg dm⁻³ in drinking water and industrial drainage, respectively. In these contaminated sites, less costy technologies are desired.

Permeable reactive barriers (PRBs) is one of the passive and in-situ groundwater treatment techniques for organic and inorganic contaminants, including chlorinated solvents, petroleum hydrocarbons, selected pesticides, chromium and other heavy metals, nitrate, phosphate and sulfate-rich mine drainage, and have developed for 15 years mostly in North America. When the contaminated plume goes through the barrier, the contaminant species react with barrier materials to reduce the concentration based on sorption, precipitation and decomposition. Chemical and microbiological reactions can be involved in the process of PRBs. It has several advantages to enable the usage of ground surfaces for the other objectives and to save the operation and maintenance cost without facility and electricity. These advantages are more desirable and acceptable as monitoring natural attenuation (MNA) in modern environmental technologies than conventional methods. One direction of development in PRBs researches is to find the cost effective reactive materials. Although zero valent iron (ZVI) is the most commonly used as a reactive material for As in PRBs, less costly materials such as granules blast furnace slag (GBFS) and basic oxygen furnace slag (BOFS) have been investigated as alternatives in laboratorial and full scales of PRBs, resulting in acceptable efficiencies in some cases. According to the USEPA report, the price of ZVI for the PRBs application in USA and Canada varies in a range of $0.33 and $0.77 kg⁻¹ recently.

Other direction of development is focused on underground microbiology in PRBs. It is believed that there are innumerable kinds of species underground, which contribute the groundwater remediation. For the representative example, sulfate-reducing bacteria (SRB) have been utilized in process for the bioremediation of metal contaminated waters particularly from mining activities. SRB assimilates simple organic compounds by utilizing sulfate as an electron acceptor to generate sulfide, S²⁻, and alkalinity. This biogenetically produced sulfide can react with dissolved metals and metalloids to form metal sulfide precipitates since the solubilities of most heavy metal sulfides are generally very low.
2CH₃OH + SO₄²⁻ → 2HCO₃⁻ + H₂S

H₂S + Me²⁺ → MeS↓ + 2H⁺.

(1)

(2)

where Me²⁺ indicates metallic ions.

In addition, some species of SRB are capable of respiring arsenate.²¹ For the present, a large variety of carbon sources, including a wide range of biomass like roughage, woodchips, sawdust, animal manure, has been investigated to accelerate the microbial activity.²² The control of microbial activities can save the cost of metal removal from contaminated groundwater and maintain the lifetime of PRBs.²³ Animal manure has been investigated for acid mine drainage treatment in groundwater,²²⁻²⁸ but there are no specific research in which animal manures were used to remove As in groundwater. In the present work, permeable reactive barrier column using ZVI and sheep manure as reactive materials are investigated on the process for the passive treatment of As and Mn in groundwater simulated mine tailing filtrates at Sumbawa Island, Indonesia, to discuss the mechanism of As and Mn immobilization in the system, and to expect the lifetime of PRBs.

2. Experimental

2.1 Batch tests

First, to understand the reactions of ZVI, sheep manure, compost and woodchips with arsenite and Mn²⁺ prior to column tests, single batch tests were preliminarily conducted. To find the effective sorbent, five grams and one gram of each sterilized material was mixed in a 0.25 dm³ solution containing of 50 mg dm⁻³ of As(III) and 60 mg dm⁻³ of Mn(II), respectively at the initial pH 6.25. Next, to obtain the sorption isotherm of arsenite onto ZVI and Mn²⁺ onto compost, batch tests were conducted using the solution with the required concentrations of As(III) and Mn(II) using K₂AsO₃ and MnSO₄·5H₂O from Wako, at the initial pH 6.25. Five grams of ZVI or 2 grams of compost were added to 0.25 dm³ of the above solution. For both experiments, nitrogen gas was purged for 20 min to remove dissolved oxygen in the solutions. All solutions were shaken at 100 rpm and 25°C until the sorption equilibrium was attained. Supernatant was taken at intervals, filtrated using a 0.2 μm pore sized membrane filter, and kept under anaerobic condition before measurement. The Mn concentrations were determined by atomic adsorption spectrometry (Solar AAS Thermo Elemental). The total As concentrations were determined by HG-AAS (Thermo Elemental HYD-10U and the above AAS), providing 0.1 μg dm⁻³ of the detection limit for As according to JIS K0102.

2.2 Column tests

Simulated groundwater for column tests was prepared using chemical reagents, based on the composition of As-contaminated groundwater found at Sumbawa, Indonesia. The groundwater has been impacted by the geological condition of the area and contains 1.27 mg dm⁻³ As and 16.7 mg dm⁻³ Mn. The As and Mn concentrations were spiked to be mostly 40 times and 4 times respectively of actual groundwater to evaluate the treatability within the restricted periods. The simulated groundwater was prepared as follows (in gram per 1 liter of deionized water): CaCO₃ (0.069), MgCO₃ (0.065), KNO₃ (0.001), MnSO₄·5H₂O (0.263), K₂AsO₃ (0.058) and KH₂AsO₄ (0.048). The pH was adjusted to 6.25 ± 0.25 with 1 mol dm⁻³ HCl and 1 mol dm⁻³ NaOH. The solution was purged with nitrogen gas for 2 h to minimize the content of dissolved oxygen and kept under anaerobic conditions prior to use.

The PRB column tests were performed using two acrylic cylindrical columns with 40 cm in height, 7.5 cm in inner diameter, 13 side ports along the vertical direction, and approximately 1767.86 cm³ in internal volume. The bottom layer (1.5 cm) and top layer (1.5 cm) of the column packing consisted of 100% glass beads (0.6–0.8 mm in diameter) as non reactive material. The middle reactive layer was composed of 5(v/v)% ZVI, 23(v/v)% compost, 22(v/v)% woodchips, 30(v/v)% glass beads, and 20(v/v)% gravels. The ZVI (Connelly-GPM™, Chicago, Illinois, USA) and organic materials are reactive materials here. The present ZVI has the following physical properties: a density of 2.24–2.56 g cm⁻³, diameters of 8–50 mesh, and a specific surface area of 2.4 m² g⁻¹. Three kinds of organic materials were used here, that is sheep manure, compost, and woodchips. Sheep manure was added as a source of sulfate-reducing bacteria (SRB) for the inoculated column.²⁹ It was taken from livestock in Mitsuse, Saga Prefecture a few days before use. The identification of SRB was partly published,³⁰ and the details is under preparation. In order to maintain the permeability of the column, glass beads (average φ 0.5 mm) and gravels (average φ 12 mm) were added as unreactive materials. In the inoculated column, 2(v/v)% of woodchips was replaced by 2(v/v)% sheep manure. Parallely the sterilized column was also prepared as a control to evaluate the microbiological contribution from sheep manure in the inoculated column. All materials were sterilized by autoclaving at 121°C for 20 min, except for sheep manure in the inoculated column. Then, all materials were mixed homogeneously, filled uniformly in the columns, and nitrogen gas with pressure 0.3 MPa was purged for 12 h to generate anaerobic conditions according to the previous PRB works.³¹ The total volume of N₂ gas corresponds to more than 7 L, which is more than 10 times of the total porosity of the column. To activate anaerobic microorganisms, such as SRB, in the inoculated column, 1.5 L of 1000 mg dm⁻³ Na₂SO₄ and 5% Na-lactate were introduced for 72 h. The porosities were gravimetrically determined to be 37.4 and 36.2% in the inoculated and sterilized columns, respectively. The flow rate of influent was initially set at 0.21 cm h⁻¹ from the bottom to the top by peristaltic pumps (EYELA 10413787, Rikakikai Co. Ltd., Japan), resulting in 2.78 days and 2.76 days of residence time, and monitored regularly. All experiments were conducted in an anaerobic glove box (COY, Michigan, USA) purged with a gas mixture containing of 95% N₂ and 5% H₂.

Effluent solutions were regularly collected twice a week, while 36 times of pore volume of influent solutions travels. Pore volume (pv) is defined as the required time to travel for the influent from the bottom to the top of the column and used as a time unit. At pv 36 the side-port samples were taken from each column. The sampling method was
described in details elsewhere. Temperature, pH, redox potential, and alkalinity were measured immediately after sample collection. Temperature and pH were measured using TOA WM-22EP GST-2729C electrodes, the redox potential was determined using TOA RM-20P PST-2739C electrodes and converted to \( \text{Eh vs NHE} \). Alkalinity was determined using a Hach™ digital titrator (Titration Method 2320B; American Public Health Association (APHA), 1992). The determination of As and Mn concentrations are the same with in the batch tests. Sulfur isotopic compositions were measured using a continuous flow-isotope ratio mass spectrometer (IsoPrime™ EA, GV Instruments, UK) and were reported in the conventional \( \delta^{34}\text{S} \) notation relative to Vienna Cañyon Diablo Troilite. The overall reproducibility of the sulfur isotopic analysis was \( \pm 0.2\%e \). Major anions and cations were determined using a Dionex DX-120 ion chromatograph. Other heavy metal concentrations were determined by an inductively coupled plasma optical emission spectrometer VISTA-MPX ICP-OES (Seiko Inst., Japan). Saturation index (SI) for representative minerals was calculated using a geochemical calculation code of MINTEQA2. After taking side ports samples at \( pv 36 \), the column materials were also taken by decomposing the columns under anaerobic condition. Residual materials in a reactive zone were divided into 10 fractions along the water traveling direction as follows: \( 1.5–5.2 \, \text{cm}, 5.2–8.9 \, \text{cm}, 8.9–12.6 \, \text{cm}, 12.6–16.3 \, \text{cm}, 16.3–20 \, \text{cm}, 20–23.7 \, \text{cm}, 23.7–27.4 \, \text{cm}, 27.4–31.1 \, \text{cm}, 31.1–34.5 \, \text{cm} \) and \( 34.8–38.5 \, \text{cm} \) from the bottom of the column. The residual ZVI granules were separated using a magnet covered with a plastic bag from PRB materials in an anaerobic glove box, to provide for X-ray diffraction (XRD; RINT-2100, Rigaku), scanning electron microscopy (SEM, VE-9800, Keyence Co.) and energy dispersed X-ray analysis (EDX, EDAX Genesis, EDAX Japan Co., Ltd.).

3. Results and Discussion

3.1 Batch tests

In the 1st preliminary experiment, \( 51.57 \, \text{mg} \, \text{dm}^{-3} \) As was well immobilized onto 1 gram ZVI grains and reached to the equilibrium concentration of \( 0.53 \, \text{mg} \, \text{dm}^{-3} \) within \( 48 \) h with the final pH 9.35 as shown in Fig. 1(a). Compost, wood chips and sheep manure did not immobilize arsenite at all for around \( 100 \) h. In the 2nd preliminary experiment, the sorption isotherm of arsenite onto ZVI was obtained in Fig. 2(a). Figure 2(a) indicates that the isotherm is fit to the Langmuir type at less than \( 0.0167 \, \text{mmol dm}^{-3} \) of arsenite at the equilibrium, \( C_e \) in \( \text{mmol dm}^{-3} \), according to the following equation:

\[
Q = \frac{30.96C_e}{(C_e + 53.83)}
\]

in which \( Q \) indicates the amount of adsorbed arsenite in \( \text{mmol kg}^{-1} \). As a result, \( Q_{\text{max}} \) is given to be \( \approx 30.96 \, \text{mmol kg}^{-1} \). However, at \( C_e \geq 0.0167 \, \text{mmol dm}^{-3} \), the relation is not fit to eq. (3), giving significantly larger \( Q \) values. This indicates the immobilization mechanism is governed by other principles at \( C_e \geq 0.0167 \), probably co-precipitation of As(V) with Fe(III) on ZVI.

Figure 1(b) shows compost is the most effective sorbent as long as investigated here. The equilibrium pH was 6.14 with compost. The sorption isotherm of Mn\(^{2+} \) onto compost was acquired in Fig. 2(b) which is also fit to Langmuir type:

\[
Q = \frac{238.09C_e}{(C_e + 42)}
\]

The result provides that \( Q_{\text{max}} \) is around \( 238.09 \, \text{mmol kg}^{-1} \).

3.2 Column tests

Time courses of pH, Eh, alkalinity, and temperature during the column experiments are presented in Fig. 3. Initially, pH increased in both columns from 6.25 in the influent to around 7 in the effluent and then decreased after pv 34. It is known the reactions of ZVI with H\(_2\text{O}\) and H\(^+\) produce OH\(^-\) (eq. (5)) and H\(_2\) (eq. (6)). The pH increased until pv 34 according to the reactions, but became stable after pv 34, probably due to changes of the surface on ZVI to less active.

\[
2\text{Fe}^{0} + 2\text{H}_2\text{O} + \text{O}_2 \rightleftharpoons 2\text{Fe}^{2+} + 4\text{OH}^- \quad (5)
\]
\[
\text{Fe}^{0} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2 \quad (6)
\]
The Eh decreased in both columns throughout the experiments, indicating that reduction occurred. Alkalinity in the effluent was higher in the inoculated column than in the sterilized one, but after pv 25, it suddenly dropped to similar values to those of the influent. The large increase of alkalinity in the inoculated column was probably caused by the formation of bicarbonate, which is produced by the respiration of SRB using organic carbon according to eq. (1). Decrease of alkalinity after pv 25 in the inoculated column was probably caused by decline of SRB activity. Temperature varied from 26°C to 20°C, depending on season but it did not change during transportation in the columns.

Time courses of major ions in both columns are shown in Fig. 4. Calcium, magnesium, and potassium concentrations initially showed decrease in the effluent of the inoculated column from in the influent, then after pv 7, they increased to reach a balance with those in the influent until the end of the experiment (Fig. 4(a), (b), (c)). Figure 4(d) shows the Na⁺ concentration was conservative except for high sodium concentrations in the initial effluent of the inoculated column. This is due to the residual sodium lactate for microbial activation prior to loading the influent. The concentration of chloride was relatively conservative during the experiment in both columns (Fig. 4(e)). The sulfate concentration in the effluent of the inoculated column decreased rapidly while there was no decrease in the sterilized one (Fig. 4(f)). The sulfate removal was mainly from the SRB activity and some parts probably sorption onto organic materials. The sulfur
Fig. 4 Changes of major ions, (a) Ca\(^{2+}\), (b) K\(^+\), (c) Mg\(^{2+}\), (d) Na\(^+\), (e) Cl\(^-\), and (f) SO\(_4^{2-}\) in the inoculated and sterilized columns with pv. Symbols are the same as in Fig. 3.

Isotopic ratio of $\delta^{34}$S was determined to be $-4.3\%e$ and $+0.2\%e$ in the influent and effluent at pv 36 of inoculated column indicating that $^{32}$S was predominantly consumed by SRB in the inoculated column.\(^{34}\) On the other hand, $\delta^{34}$S value was determined to be $-3.9\%e$ in the effluent at pv 33 of the sterilized column that mostly same with the influent. The variation of sulfate concentration in the effluents demonstrated the changes in sulfate reducing activity of SRB in the inoculated column. In the effluent of the inoculated column, the minimum of sulfate concentration was 42.97 mg dm\(^{-3}\) at pv 12, showing that maximum sulfate removal rate was calculated to be 0.26 mmol dm\(^{-3}\) d\(^{-1}\) in average based on the residence time. Decrease of sulfate removal after pv 15 and alkalinity in the inoculated column indicates decline of SRB activity due to lack of nutrients.

Figure 5 shows the variation in As, Mn and Fe concentrations as a function of pv. The removal rate of As in the inoculated column was relatively higher than that of the sterilized one (Fig. 5(a)). Initially, the total As concentrations in the effluent of both columns had decreased to under the detection limit of HG-AAS. After pv 15, more than the MCL for As was detected in the effluent of the inoculated column. This was also observed in the sterilized column earlier and more remarkably than the inoculated one. The concentrations of As in the effluent of both columns increased rapidly after pv 25, in which the As concentrations were still lower in the inoculated column than those in the sterilized one. The integral of accumulated As was estimated to be 1296.71 mg in the inoculated column and 1166.21 mg in the sterilized one. Considering 30.96 mmol kg\(^{-1}\) of $Q_{\text{max}}$ obtained in the
batch tests and 220 g of total amounts of ZVI in each column, the maximum amount of As immobilized is calculated to 510.15 grams. However, total of As immobilized in both columns were much higher than the calculated value, indicating that the mechanism of As removal with ZVI is not only sorption but also precipitation and co-precipitation with iron-bearing minerals in column test. It was also confirmed by XRD pattern for the residual ZVI particles in 1.5 cm to 5.2 cm layer fraction as shown in Fig. 6, showing that magnetite (Fe₃O₄), goethite (α-FeOOH), lepidocrocite
(γ-FeOOH) and FeAsO₄ were formed in addition to metallic iron. Only 1st major peak was observed for FeAsO₄, however other peaks were over laid by other minerals. These peaks assigned to FeAsO₄ were observed in all fractions including the sterilized column and the intensity of 1st major peak decreased with the distance from the inlet. These results might be not perfect evidence to show the FeAsO₄ precipitation, however, the precipitation of FeAsO₄ can not be excluded in the case of As removal mechanism. The results of MINTEQA2 calculations supported the interpretation of XRD assignment with the positive SIs for iron-bearing minerals in both columns (Fig. 7(c), (d)). Other iron-bearing minerals such as hematite and ferrihydrite were not detected in XRD pattern probably as a poor crystalline or trace amounts. The results of SEM-EDX shows that As were intensely observed at the cross point on the ZVI surface (Fig. 8(a), (b)), probably caused by co-precipitation and/or sorption.

The difference of As removal efficiencies in both columns was caused by the presence of SRB in the inoculated column. Rittle et al. reported that some of the As was precipitated as a Fe–As–S solid phase by actively sulfidogenic microcosms containing As. Therefore, some of As in the inoculated column might be probably caused by co-precipitation with
the biogenic iron sulfides. In addition, some of As in the inoculated column would be probably immobilized by sorption and/or co-precipitation with CaCO$_3$. SEM images of ZVI granular collected from bottom part of the inoculated in Fig. 8(c), (d) shows high intensity of As, O, C and Ca on the surface of new precipitates. It was also supported with positive SIs of carbonates as shown in Fig. 7(a), (b).

Time courses of Mn$^{2+}$ concentrations in the inoculated and sterilized columns are illustrated in Fig. 5(b). Manganese has been removed in the sterilized column under the MCL until pv 30, but in the inoculated column only until pv 22. With the $Q_{\text{max}}$ value of 238.09 mmol kg$^{-1}$, 2016.62 grams of Mn should be immobilized on the loaded compost in each column. However, the total of Mn accumulated in the sterilized and inoculated columns was calculated to be 1701.08 mg and 1660.57 mg. It suggests that both columns have still more capacities of sorbents for sorption of Mn$^{2+}$. The difference of Mn removal in both columns would be indirectly caused by microbiological metabolism. Organic materials are biodegraded, therefore, the capability of compost to immobilize Mn might have decreased in the inoculated. Other major cations are competitive species to Mn$^{2+}$ sorption onto compost, therefore, Mn immobilization was less effective in the both columns than in the batch tests. Some of Mn were probably also precipitated as rhodocrocite (MnCO$_3$) due to high pH and high alkalinity in the inoculated column until pv 25. This interpretation was supported by positive SIs for MnCO$_3$ in the results of MINTEQA2 in Fig. 7(e). The solubility product is smaller in rhodocrocite than in calcium carbonates, which is likely to precipitate in Fig. 8(c), (d). However, after pv 25 the precipitation of MnCO$_3$ became unlikely with decrease in alkalinity. It is considered that Mn and As removal is indirectly related each other via microbiological reactions. The removal of Mn in the inoculated column shows a highly positive correlation with As ($R^2 = 0.892$), while a low correlation ($R^2 = 0.154$) in the sterilized column as emphasized in Fig. 9. High positive correlation between As and Mn removal in the inoculated column can be explained by production of bicarbonate in biodegradation of organic matters, followed by formation of MnCO$_3$ and co-precipitation of As. On the contrary, in the sterilized one the mechanism of Mn removal largely depends on sorption to compost and ZVI because of less alkalinity. High concentrations of iron were observed in the effluent of the inoculated column until pv 3 probably due to oxidation of ZVI by residual sodium lactate as shown in Fig. 5(c).

The lifetime of PRB is greatly influenced by the contaminant concentrations, PRB materials, thickness, and the groundwater flow rate. According to the hydrogeological description in Sumbawa, Indonesia, the groundwater level is fluctuated between 2.5 meters and 5 meters with 15.77 m year$^{-1}$ of an average flow rate. The maximum concentrations of As and Mn in groundwater were recorded as 1.27 mg dm$^{-3}$ and 16.7 mg dm$^{-3}$ respectively from the monitoring well in a downstream area. Therefore, 2.00 mg of As flows through in each 1 cm$^2$ of cross section...
of the plume every year. The result from column tests can be used to estimate the PRB lifetime in the full scale. If As concentration is reduced to under the MCL for industrial drainage, total of immobilized As in 1 cm$^3$ of PRB materials in the inoculated column is 0.3152 mg-As. Assuming the thickness of PRBs in the full scale is 1 meter and the mixing PRBs materials and their ratio are the same as in the column tests, the accumulated mass of As in each 1 cm$^2$ of inoculated PRB materials is 31.52 mg-As. Therefore, the lifetime of inoculated PRBs in a full scale is estimated to be 15.76 years. On the contrary, it is calculated to only 6.74 years without microbiological contribution. Using the MCL of industrial drainage of Mn as the limiting factor, the lifetime of PRBs can be calculated to be 2.30 years and 3.35 years in the inoculated and sterilized barriers, respectively. Therefore, the lifetime is estimated to be shorter based on Mn than As. However, As is more toxic than Mn, therefore, As should be preferentially considered as a target for PRBs.

Modification of PRB materials and their mixing ratio prolongs the lifetime of PRBs. Sasaki, et al. have demonstrated PRB including 10(v/v)% ZVI (Connelly-GPM) reduced 2 mg dm$^{-3}$ selenate to less than 100 µg dm$^{-3}$ with a linear velocity 0.13 cm h$^{-1}$ of groundwater for 75 years. Therefore, the mixing ratio of ZVI significantly affect to the lifetime of PRBs. Additionally, the supplement of some alkalizing materials like limestone and dolomite as the second layer would help to maintain the acceptable efficiency for the Mn immobilization.

4. Conclusions

The immobilization of As and Mn was investigated using PRB column experiments. Immobilization of As in both columns was mainly caused by sorption and co-precipitation with iron-bearing minerals and also possibly precipitation as FeAsO$_4$. Additionally co-precipitation with biogenic iron sulfides and sorption and/or co-precipitation with carbonates are also likely in the inoculated column, but unlikely in the sterilized one. The use of sheep manure in the inoculated column showed a significant contribution in the efficiency of As immobilization. The decrease of sulfate concentrations and the increase in $\delta^{34}$S in the inoculated column effluent were good evidence that sulfate-reducing bacteria (SRB) worked successfully in the inoculated column. High As concentrations and lack of nutrients in the inoculated column inhibited the SRB activity leading to decrease in sulfate removal.

The mechanism of Mn removal was mainly explained by adsorption onto compost and ZVI, and partly precipitation as carbonates. The microbiological activities of heterogeneous bacteria might contribute negatively to immobilization of Mn in PRBs in a view point of long term.

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