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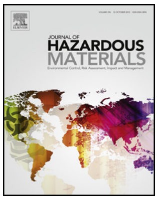

# *In-situ* arsenic remediation by aquifer iron coating: Field trial in the Datong basin, China

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## HIGHLIGHTS

- An *in-situ* As removal technology based on Fe-coating has been first confirmed in the field.
- The impact factors including water chemistry and redox conditions on *in-situ* Fe coating for As removal were discussed.
- This technology has promising for the field application to treat natural high As groundwater.

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## ABSTRACT

An aquifer Fe-coating technology was evaluated for *in-situ* As remediation. The groundwater in the aimed aquifer has low dissolved Fe(II) concentration and high As(III) concentration, which has a low affinity toward Fe-oxides/hydroxides. To overcome these challenges, dissolved Fe(II) (5.0 mM) and NaClO (2.6 mM) were injected into the studied aquifer to promote the formation of Fe oxides/hydroxides and to oxidize As(III) into As(V), thus removing aqueous As *via* adsorption and/or co-precipitation. During field experiment, As concentration in groundwater from the pumping well significantly decreased. Fe and As speciation calculations indicate that incorporation of negatively charged As(V) into goethite was the probable mechanism for As removal. Both chemical sequential extraction results and spectroscopic data also support that alternating injection of Fe(II) and NaClO can achieve aquifer Fe coating and immobilize As *via* adsorption onto Fe oxides/hydroxides. Geochemical modelling further confirms that although competition for sorption sites between As and other dissolved species is expected in the natural groundwater system, high surface area of the Fe oxides/hydroxides can provide sufficient sites for As retention. The ability to effectively decrease As concentration of *in-situ* aquifer Fe-coating technology indicates that this approach should have extensive applicability to similar high As groundwater occurred worldwide.

## 1. Introduction

Arsenic (As)-contaminated groundwater has been documented in many parts of the world, especially in India, Bangladesh, Vietnam, Cambodia and China [1–4]. In these areas, As contamination in groundwater poses a great risk to human health, especially in the rural areas where local residents are reliant on As-contaminated groundwater as drinking water source. Modified or novel treatment technologies are urgently needed in those areas for As removal from contaminated groundwater to meet drinking water standard (10 μg/L).

Various *ex-situ* treatment technologies have been developed and applied for As removal [5–10]. Many of them, however, have shortcomings such as high cost, requirement of As-rich waste disposal, technological complexity or certain limitations when applied to rural areas. *In-situ* treatment of As-contaminated groundwater is another type of technology that is more promising for supplying safe drinking water in the rural areas [11,12]. Iron (Fe)-based materials such as Fe(III) oxides/hydroxides have been widely proposed for As removal from groundwater [13–15]. One recently developed *in-situ* treatment technology is to coat Fe oxides/hydroxides onto the aquifer sediments *via* directly delivering Fe salts and associated oxidants into aquifers to achieve As immobilization. In the presence of oxidants, Fe(II) salts can be converted into goethite (FeOOH) or ferrihydrite [$Fe(OH)_3$] within the aquifers under alkaline pH conditions [16,17]. Apart from As retention, the precipitation of Fe oxides/hydroxides onto sediment

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surfaces can prevent further As release from sediments into the groundwater through water-sediment interaction. The As retention mechanism of this approach is mainly based on adsorption and co-precipitation reactions between As and Fe oxides/hydroxides [18]. However, these processes could be impacted by a variety of factors such as groundwater oxidation–reduction potential and the presence of hydrochemical species. For examples, As removal by Fe(III) oxides/hydroxides suffers a challenge under reducing conditions that usually prevail in high As groundwater systems. This because that Fe(III) oxides/hydroxides may reductively dissolve into aqueous Fe(II) with the simultaneous release of As. The study conducted by Roberts et al. [18] indicated that Fe(III) oxides/hydroxides could sustain for more than one year under oxidizing to moderately reducing conditions. Therefore, it is feasible apply Fe(III) oxides/hydroxides to immobilize As in groundwater under oxidizing to moderately reducing conditions. In addition, natural groundwater is a complex multi-components system. It is likely that the occurrence of high concentration of phosphate and bicarbonate, which are usually the dominant anions in groundwater, can result in the desorption of As from Fe(III) oxides/hydroxides [19,20]. Therefore, to overcome these problems encountered in natural groundwater aquifers, it requires not only to promote the formation of Fe(III) oxides/hydroxides, but also to transfer As(III) into As(V) to improve As adsorption onto Fe(III) oxides/hydroxides. Our previous study has confirm that Fe(III) oxides/hydroxides coating onto quartz sands has achieved As removal from groundwater [21]. However, for the implications of this method in natural aquifers, some concerns remains to be clearly answered. For instance, Fe coating approach through alternating injection Fe(II) salt and oxidants need to be tested within natural groundwater systems under oxidizing to moderately reducing conditions. Moreover, the effects of concurrent competitive sorption and co-precipitation of bicarbonate, phosphate and sulfate toward As(III) and As(V) during the formation of Fe(III) precipitates also need to be explored.

In this study, therefore, we present a field trial that combines hydrochemical monitoring and modelling to: (1) confirm the feasibility of aquifer Fe coating approach under a moderately reducing to oxidizing natural groundwater conditions; (2) discuss main factors affecting the removal capacity of Fe coating for As during field trial; (3) investigate the potential of the *in-situ* treatment of natural As-contaminated groundwater by aquifer Fe coating technology.

## 2. Materials and methods

### 2.1. Site description

The Daying Village of Shanyin County was selected for our field trial because this site is known to have high As concentration in groundwater. The Daying Village is located in the central part of the Datong basin (DY site, Fig. 1B). There is a gentle hydraulic gradient and groundwater moves roughly from SW toward the NE within the experimental plot. High As groundwater mainly occurs in the shallow aquifers with depths less than 50 m at this study site. The shallow aquifer is comprised of three relatively independent semi-confined aquifers in the depths of approximate 19 m, 26 m and 38 m below the land surface, respectively (Fig. 1C). Clay and silty clay interlayers function as the aquitards to prevent the infiltration of atmospheric oxygen and maintain an anoxic environment in the underlying aquifers. Sediment materials of the three aquifers are fine to medium sands or sandy silts with gray, dark/black gray or black color that are mainly made of quartz, feldspar, carbonates, illite and chlorite. Because of different hydrological and geochemical conditions, distinct redox conditions exist in those aquifers and groundwater As concentrations spatially vary significantly.

### 2.2. Field operation

The study site has high As (234 μg/L) and $HS^-$ (30 μg/L) concentrations but low $SO_4{}^{2-}$ (26 mg/L) and $NO_3{}^-$ (below the detection limit) concentrations, as well as low oxidation–reduction potential (ORP) (−170 mV). A total of five 40 m-depth wells (one pumping well and four injection wells) were installed for *in-situ* aquifer Fe coating experiment. The pumping well was located at the centre of the square area and the injection wells were at the each corner (Fig. S1). The distance from each injection well to the pumping well was set as 5 m. All wells were constructed with 2.0-inch (for injection wells) or 10.0-inch (for pumping well) tube and had a depth of 40 m with the 1.5 m length of perforated tubes.

In this study, $FeSO_4$ and NaClO were used as iron salt and oxidant, respectively, to implement *in-situ* aquifer Fe coating. An alternating injection method was adopted to deliver $FeSO_4$ and NaClO solutions into the aimed aquifer. Once NaClO oxidized aqueous Fe(II), coating layers of Fe oxides/hydroxides were expected to form on the surfaces of aquifer sediments. A schematic figure illustrating subsurface *in-situ* aquifer iron coating is shown in Fig. S2. To avoid clogging by the large amount of precipitates near the injection wells, deionized water was used to flush the tubes between the injection of $FeSO_4$ and NaClO solutions, which ensured the uniform diffusion of $FeSO_4$ and NaClO throughout the aquifer and the formation of homogeneous Fe oxides/hydroxides coatings on sediment surfaces. The procedure was briefly described as follows: (1) 20 L $FeSO_4$ solution (5.0 mM) was pumped into the aimed aquifer at a rate of 4–5 L/min; (2) 20 L deionized water was then pumped at the same rate; (3) idling for 2 h; (4) 20 L NaClO solution (2.6 mM) was pumped into the aimed aquifer at a rate of 4–5 L/min; (5) 20 L deionized water was pumped once again at the same rate; (6) idling for 2 h. The procedures (step 1–6) were repeated until groundwater Fe concentration in the pumping well did not change significantly.

During field trial, hydrochemical parameters in the pumping well (including pH, ORP and T) were measured on site using portable meters (Yellow Springs Instruments, 600XLM). The concentration of $HCO_3{}^-$ was immediately measured titrimetrically after sampling. The total Fe concentration in groundwater was measured using the Ferrozine method and by a spectrophotometer (HACH, DR2800) on-site. Samples for analysis of As, other trace elements and major cations were collected into 50 mL pre-cleaned HDPE bottles and acidified to pH < 2 using ultra-pure $HNO_3$ immediately after collection and filtration (<0.45 μm). Samples for analysis of anions were collected in pre-cleaned 50 mL HDPE bottles without acidification after filtration. On-site groundwater As species (As(III) and As(V)) separation was conducted using a silica-based strong anion-exchange cartridge (Missisauga, ON) following Le et al. [22]. The collected samples for As species determination were acidified using ultra-pure HCl and stored in 10 mL cleaned HDPE bottles.

Before and after Fe coating, undisturbed aquifer sediment samples were collected from the aimed aquifer at the depth of 36.5 m to 38 m. The core samples were capped immediately with PVC pipe and wax-sealed after recovery in the field and stored in the dark.

### 2.3. Laboratory analysis

The total As and Fe contents in aquifer sediments collected before and after Fe coating test were determined by inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer ELAN DRC-e) after digestion using the mixture of HCl and $HNO_3$. Chemical sequential extraction was performed to differentiate adsorbed As (ion exchangeable phases), As in poorly-crystalline Fe phase and