South African sands as a low cost alternative solution for arsenic removal from industrial effluents in permeable reactive barriers: Column tests

C. Trois, A. Cibati *

School of Engineering, University of KwaZulu-Natal, Howard College Campus, Durban 4041, South Africa

HIGHLIGHTS

- Column tests for the treatment of arsenic contaminated industrial effluent.
- Mixes of Berea red sand and ZVIs were selected for arsenic removal.
- Higher amount of Berea red sand in the mixed substrates increased the removal.
- Berea red sand favors arsenic removal by adsorption respect than complexation.
- Berea red sand can be considered a cost-effective and efficient arsenic adsorbent.

ABSTRACT

This study has investigated mixes of South African sands and zero valent iron (ZVI) for the design of low cost permeable reactive barriers (PRB) for Arsenic removal. After preliminary batch tests conducted to select the substrates with the highest Arsenic removal capacities and to identify the best operative conditions, column tests were performed to simulate environmental conditions that occur when a PRB is interested by a contaminated effluent. Column experiments were carried out in two columns of different sizes (small and large columns) using two mixes of Gotthart Maier Metallpulver GmbH ZVI (GmbH ZVI) and Berea red sand (BRS) (75–25% and 50–50% of column volume) and only GmbH ZVI as filling material. In small column tests, higher amounts of BRS reflected in 100% of Arsenic removal both at 8.4 ml min^{-1} and 16.8 ml min^{-1} flow rates. In large column tests, 100% of Arsenic removal was observed for all flow rates investigated. A first-order kinetic model was used to describe the Arsenic adsorption kinetics.

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1. Introduction

Arsenic (As), a carcinogenic metalloid, is widely distributed in a number of complex minerals, mainly as arsenides of copper, nickel and iron, or as Arsenic sulfides or oxides.

Arsenic compounds are mainly used in agriculture and forestry as pesticides, herbicides and silvicides and other human activities including mining and smelting, are major sources of Arsenic contamination in the environment [1]. Prolonged exposure to Arsenic may affect the respiratory system, gastrointestinal apparatus, skin system, and nervous system with acute and chronic toxicity and cancer of various apparatus and birth defects [2].

In 2006 the U.S. Environmental Protection Agency (EPA) [3], established a maximum contaminant level (MCL) for Arsenic in water of 0.01 mg L^{-1}. The evidence of high toxicity of Arsenic,

combined with the widespread presence in the environment as result of human activities, have stimulated research for the development of new treatment technologies for the removal of Arsenic from waters. Several technologies are available for the removal of Arsenic from waters, such as adsorption, membrane filtration, ion exchange, precipitation, reverse osmosis, bioremediation, phytoremediation and permeable reactive barriers [4–9]. To improve the efficiency of the treatment and reduce the operation and maintenance costs, in the last decades, most studies have been focused on the development of passive methods such as permeable reactive barriers for the removal of contaminants from waters [10–13].

PRB is a promising *in situ* remediation passive system consisting of a wall of reactive media that is placed down-gradient of a contaminant plume. As the water flows through the barrier under the natural hydraulic gradient, the reactive medium degrades, trap or adsorb the pollutants [14]. The reactive medium may consist of zero valent iron, limestone, amorphous ferric oxide, zeolite and activated carbon. Most of barrier so far installed are iron based [15].

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* Corresponding author. Tel.: +27 31 260 1639.
E-mail address: cibale1983@gmail.com (A. Cibati).

Despite the knowledge about the capabilities of iron oxides such as ferric iron to co-precipitate Arsenic from water as ferric-arsenate, few studies have been conducted using naturally-occurring iron oxide minerals for Arsenic removal from waters [16–20]. Iron oxide minerals are widespread in nature and are relatively cheaper, which could make the use of these natural minerals a valid and economic alternative for water treatment.

Therefore, in this study, a South African soil (indigenous of the region of Kwazulu-Natal) was investigated as alternative PRB's reactive medium for the removal of Arsenic from water. The soil investigated was Berea Red Sand, a soil widely available in the surrounding area of Durban, mainly consisting of iron oxides.

The objective of this research was focused on the evaluation of the efficiency of a PRB system in relation to a type of ZVI reactive and BRS soils employed.

The overall aims of the research are to determine the relationship between the pollution dynamics occurring between the saturated soil and the reactant into a permeable reactive barrier and to design an appropriate PRB for Arsenic removal from water.

Column tests were performed based on the data obtained by previous preliminary batch experiments; such experiments were aimed to simulate the environmental conditions that more likely occur in a full scale PRB when interested by a contaminated flux.

2. Materials and methods

2.1. Liquid effluent

Arsenic used in this study (As_2O_3) was collected from a production cycle of pesticides. The effluent had a total Arsenic concentration in the range 13–17 mg L^{-1} and a total iron concentration in the range 0.5–1 mg L^{-1}. In this study it was used to determine the Arsenic removal capacity of BRS, Umgeni sand (US), GMP ZVI (Zero valent iron from Connelly GPM Inc., USA) and GmbH ZVI solids substrates in preliminary batch and column tests.

2.2. Local sands

BRS and US belong to one of the strata that contribute to the formation of the Umgeni Valley; this stratum consists of silt, dark grey clay, fine, medium and coarse sands. In this study, US and BRS were used as reactant materials for the treatment of industrial effluents containing Arsenic in preliminary batch experiments, while only BRS was used for column experiments.

2.3. Iron fillings

The Zero Valent Iron used in this study was provided by two different company of ZVI distribution. Gotthart Maier Metallpulver GmbH (Germany) and the other from Connelly-GPM, Inc. (U.S.A.).

The GmbH ZVI consisted of coarse size particles (from 1 to 2 mm) while the Connelly-GPM had a larger spectrum, with particle size from 2.36 to less than 0.075 mm. Both GmbH ZVI and GPM ZVI were used for the preliminary batch trials, while only GmbH ZVI was used in column experiments.

2.4. Solids substrates characterization

The characterization of the solid substrates comprised of:

– Sieve analysis.
– Porosity test.
– Chemical and mineralogical characterization.

2.4.1. Sieve analysis

Sieve analyses were conducted to understand the distribution size of the BRS and US. Sieves with different mash size were arranged in descending order starting from the bottom as follows: 0.063 mm, 0.075 mm, 0.15 mm, 0.3 mm, 0.425 mm, 0.6 mm, 1.18 mm, 2 mm, 4.75 mm, 6.7 mm, 9.5 mm. 500 gr of oven-dried sample (105 °C for 24 h) was placed in the top sieve and agitated for 5 min by a shaker. Then the mass of soil retained on each sieve was weighted in order to get the particle size distribution of the samples investigated.

2.4.2. Porosity test

Porosity (n = Vv/Vtot) tests were conducted to determine the void volume in BRS and US. The volume of the voids (Vv) can be derived by subtraction between the total volume (Vtot) and the volume occupied by the solid particle. The porosity tests were conducted based on DAS [21]. In addition to the porosity (n), void ratio (e), relative density (Dr) and specific gravity values for the solids substrates used were also determined.

2.4.3. Chemical and mineralogical characterization

The chemical compositions of the ZVIs used were received from the manufacturers. The mineralogical characterization of BRS and US was conducted by XRD Rigaku-X-ray diffraction at the University of Cagliari (Italy).

2.5. Preliminary batch tests

Batch experiments were designed to investigate the kinetics and efficiencies of BRS, US, GmbH and GPM ZVI (Table 1) for the Arsenic removal under semi-aerobic and anaerobic conditions (the anaerobic condition was achieved purging nitrogen by Tetratec High Porosity Airstone AS25 for 30 min).

45 g of reactant and 900 ml (S/L ratio 1:20 g/ml) of inorganic arsenic and iron-contaminated solution (13–17 ppm and 0.5–1 ppm respectively) were placed in a 1000 ml Schott Duran

Table 1
Operational conditions of preliminary batch tests.

Condition	Substrate	Solid/liquid ratio (g ml^{-1})	[As] (mg L^{-1})	[Fe] (mg L^{-1})	Duration time (h)
Semi-aerobic	GmbH ZVI	1/20	13–17	0.5–1	72
	GMP ZVI	1/20	13–17	0.5–1	72
	BRS	1/20	13–17	0.5–1	72
	US	1/20	13–17	0.5–1	72
	75% GmbH ZVI − 25% BRS	1/20	13–17	0.5–1	72
	50% GmbH ZVI − 50% BRS	1/20	13–17	0.5–1	72
Anaerobic	GmbH ZVI	1/20	13–17	0.5–1	72
	GMP ZVI	1/20	13–17	0.5–1	72
	BRS	1/20	13–17	0.5–1	72
	US	1/20	13–17	0.5–1	72
	75% GmbH ZVI − 25% BRS	1/20	13–17	0.5–1	72
	50% GmbH ZVI − 50% BRS	1/20	13–17	0.5–1	72