South African sands as an alternative to zero valent iron for arsenic removal from an industrial effluent: Batch experiments

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ABSTRACT

This work aimed to verify the potentials of two sands as a valid alternative of zero valent iron (ZVI) for the removal of arsenic from an industrial effluent. Batch experiments were conducted using Umgeni sand (US), Berea Red Sand (BRS), two types of zero valent iron (GmbH ZVI, and Connelly-GPM ZVI) and a mixture of BRS and GmbH ZVI. The experiments were carried out to study the removal kinetics of arsenic under semi-aerobic and anaerobic conditions and in the presence of sulfate, nitrate and phosphate anions. The GMP ZVI showed the best performance in terms of arsenic removal (100% of removal after 7 h). BRS showed 61.75% of arsenic removal by itself and 86.32% of removal in combination with GmbH ZVI. The presence of oxygen increased the Arsenic removal efficiency for all substrates investigated. Sulfate and nitrate anions increased the removal efficiency while phosphate affected the arsenic removal efficiency.

Introduction

Arsenic is a metalloid with particular physical–chemical properties. In nature, it is widely distributed in a number of complex minerals, mainly as arsenides of copper, nickel, and iron, or as arsenic sulfides or oxides. In water, arsenic is usually found in the form of arsenate or arsenite. Arsenic compounds are mainly used in agriculture and forestry as pesticides, herbicides, and silvicides [1,2]. The presence of arsenic compounds in groundwater, and eventually in drinking water, is a serious environmental problem. In oxidizing conditions, arsenate (As(V)), is the predominant arsenic form, while in reducing conditions, arsenite (As(III)), is the predominant one [3,4]. Due to its higher mobility in the environment, arsenite is considered more toxic than arsenate [2]. Long-term exposure in high levels of arsenic may cause skin changes, damage to major body organs and some types of cancer. Inorganic arsenic compounds are more toxic than organic arsenic compounds. Problems reported for the inorganic arsenic involve the respiratory system, gastrointestinal apparatus, skin system, and nervous system with acute and chronic toxicity and cancer of various apparatus [5]. A recent study, Tien-Hui et al., [6] demonstrated that inorganic arsenic significantly decreased cell viability and induced apoptosis in neuronal cells and also increased oxidative stress damage. WHO (World Health Organization) [7],

established the drinking water limits of arsenic for human consumption to $10\,\mu g\,LP^{-1}$. This strict threshold forces municipalities that have problems with elevated arsenic concentrations, to apply efficient remediation techniques for the removal of arsenic.

Several techniques have been proposed to treat waters, soils and wastes contaminated by arsenic. Among them, the most common are solidification/stabilization, vitrification, soil-washing extraction, coagulation-precipitation using iron and aluminum substances, membrane filtration, reverse osmosis, ion exchange, phytoremediation, bioremediation, permeable reactive barriers and adsorption [8–14].

Various adsorption materials have been used for the removal of arsenic from contaminated waters/wastewater, such as activated carbon, fly ash, ferric hydroxide, activated alumina, iron oxide coated sand, biomass adsorbent, resins, gels, silica and zero valent iron [15–19].

Studies [18,19] showed high arsenic removal capacity by ZVI and it has been concluded that could be used for remediation of contaminated industrial effluents and groundwater.

A valid alternative to ZVI for arsenic removal is represented by natural iron-based minerals that by means of iron oxides such as ferric iron, lead to a co-precipitation of arsenic from water as ferric-arsenate [20,21]. In fact, iron oxide minerals being widespread in nature could lead to new efficient and cheaper technologies for arsenic removal from water.

The overall aim of this work was to evaluate the efficiency and suitability of two South African sands (named Umgeni Sand (US) and Berea Red Sand (BRS) indigenous of the Durban area), to

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Nomenclature

50% GmbH ZVI–50% BRS	Mixed substrate (ZVI and BRS (w/w))
75% GmbH ZVI–25% BRS	Mixed substrate (ZVI and BRS (w/w))
As	Arsenic
BRS	Berea Red Sand (South African soil)
DO	Dissolved oxygen
GmbH ZVI	Zero valent iron from Gotthart Majer Metallpulver (Germany)
GPM ZVI	Zero valent iron from Connelly GPM inc (USA)
TDS	Total dissolved solids
US	Umgeni sand (South African soil)
WHO	World Health Organization
ZVI	Zero valent iron

remove arsenic from an industrial effluent in alternative to ZVI. The experiments, including kinetics studies, were conducted in batch trials under semi-aerobic and anaerobic conditions and in presence of different anions (sulfates, nitrates and phosphates).

Materials and methods

Preparation and characterization of liquid effluent

Arsenic used in this study was collected from a production cycle of pesticides. The chemical collected contained arsenic trioxide (As_2O_3). In this study it was used to determine the arsenic removal capacity of BRS, US, GmbH ZVI and GMP ZVI solids substrates in semi-aerobic and anaerobic environmental conditions, by batch trials.

Preparation and characterization of sorbents

Berea Red Sand (BRS) and Umgeni sand (US) are sands easily available and widespread in the region of KwaZulu-Natal. BRS and US belong to one of the strata that contribute to the formation of the Umgeni Valley; this stratum consists of silt, dark gray clay, fine, medium and coarse sands.

In this study BRS and US were used as reactants materials for the treatment of an industrial effluent containing arsenic in batch trials.

The Zero valent irons used in this study came from two different company of ZVI distribution. Gotthart Maier Metallpulver GmbH (Germany) and the other one 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.

The characterization of the solid substrates comprised of:

- Sieve analysis
- Porosity test
- Chemical and mineralogical characterization by XRD and FT-IR analysis.

Sieve analysis was conducted on BRS and US. The sieving analysis was conducted following the standardized method [22] as follows: 500 gr of sample were oven-dried at 105 °C for 24 h. Sieves with different mesh sizes 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. The oven-dried sample 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 determine the particle size distribution of the samples investigated.

Porosity ($n = V_v/V_{tot}$) analysis was conducted in order to determine the void volume in the BRS and US samples. The volume of the voids (V_v) can be derived by subtraction between the total volume (V_{tot}) and the volume occupied by the solid particle. The porosity tests were conducted based on Rees [23].

As well as the porosity (n), also void ratio (e), relative density (Dr) and specific gravity (Gs) values for the solids substrates used were determined.

The chemical composition of the ZVI used, was 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).

FT-IR analysis was conducted by PerkinElmer Spectrum RX1 FT-IR spectrometer at the University of Durban (South Africa) to establish the nature and possible presence of organic materials. In order to complete this study and gather a sense of the amount of organic fractions present in the substrates, ignition tests were carried out according to standard methods [24].

Batch tests

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

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 glass bottle for 3 days at room temperature and agitated by LABCOM shaker at 250 rpm.

20 ml of arsenic/iron contaminated solution was collected by syringe, filtered by Whatman filter 0.45 μm, acidified by HNO_3 and stored at 4 °C. A total amount of 18 samples were collected during the 3 days of experimentation at different intervals of time (each 30 min for the first 2 h, each 60 min until 7 h and then up to longer intervals of time). Eh and pH were measured by a Thermo electron corporation ORION 2 Star pH Benchtop and by ORION Model 410A. The DO (dissolved oxygen) was measured using Hiltech Micro Systems DO/OUR Meter UCT.

Mixtures of solid substrates were also carried out to determine the arsenic removal efficiency as shown below:

- 75% of GPM ZVI–25% BRS (w/w)
- 75% of GmbH ZVI–25% BRS (w/w)
- 50% of GPM ZVI–50% BRS (w/w)
- 50% of GmbH ZVI–50% BRS (w/w)

Batch experiments were also conducted (only for GmbH ZVI) to investigate the effect of anions such as sulfates, nitrates and phosphates at different concentrations, on the arsenic removal capacity. The salts used were:

- Saarchem Potassium Sulfate–K_2SO_4 at 300, 600, 1200 mg/l;
- Saarchem Sodium Nitrate–$NaNO_3$ at 10, 30, 50, 400, 800, 1200 mg/l;
- Saarchem di-Sodium Hydrogen Phosphate dodecahydrate–$Na_2HPO_4 \cdot 12H_2O$ at 100, 400, 1200 mg/l.

After 1 h of contact, 20 ml of sample was collected, filtered, acidified and stored at 4 °C for the ICP-OES analysis of iron and