

## Remediation of groundwater contaminated with hexavalent chromium using a mixture of Zero-Valent Iron and Pyrite

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### Abstract

Permeable Reactive Barriers (PRBs) with Zero Valent Iron (ZVI) have been used to remediate groundwater contaminated with metals such hexavalent chromium Cr(VI). Cr(VI) is of particular environmental concern due to its toxicity and mobility and is challenging to remove from industrial wastewater. It is a strong oxidizing agent that is carcinogenic and mutagenic, and diffuses quickly through soil and aquatic environments. It does not form insoluble compounds in aqueous solutions, so separation by precipitation is not feasible. While Cr(VI) oxyanions are very mobile and toxic in the environment, trivalent Cr(III) cations are not. Like many metal cations, Cr(III) forms insoluble precipitates. Thus, reducing Cr(VI) to Cr(III) makes its removal from effluent easier and also reduces its toxicity and mobility. At high pH values iron precipitations are expected to occur which lead to changes in ZVI surface, therefore the reactivity and hydraulic performance of ZVI decrease over time. ZVI reactivity was prolonged by adding pyrite (FeS<sub>2</sub>) to ZVI for scavenging oxygen in feed water as well as neutralizing the effects of OH<sup>-</sup>. An increase in Cr(VI) removal was found in ZVI preceded by FeS<sub>2</sub>.

**Keywords:** Permeable reactive barriers; Polluted groundwater; Hexavalent chromium; Zero valent iron; Pyrite.

### Introduction:

The use of subsurface Permeable Reactive Barriers (PRBs) for groundwater remediation is emerging as an effective alternative to pump-and-treat technologies (Thiruvengkatachari *et al.* 2008). The key advantages of PRBs are lack of aboveground structures, low maintenance and operation costs, and the potential for years of operation with little intervention. The most common PRBs are those containing granular Zero Valent Iron (ZVI) and have typically been used to treat groundwater contaminated with hexavalent chromium Cr(VI) (Fenglian *et al.*, 2014; Daoud *et al.*, 2015). It has been shown that the Fe(0) surface is the site of reaction (Kenneke & Mccutcheon, 2003).

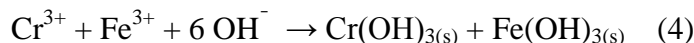
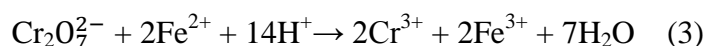
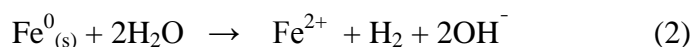
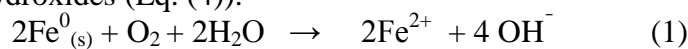
Chromium generally exists in water with two stable oxidation states: hexavalent Cr(VI) and trivalent Cr(III) (Weng *et al.*, 2007). Although Cr(VI) is reported to have toxic effect on humans, and it is considered to be genotoxic and carcinogenic in nature (Cheuhan & Sankararamakrishnan, 2011), Cr(III) is less toxic and can be readily precipitated out of solution in the form of Cr(OH)<sub>3</sub> (Singh *et al.*, 2011; Daoud *et al.*, 2016).

The most probable Cr(VI) species in aqueous solution are Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, and HCrO<sub>4</sub><sup>-</sup>, the relative distribution of which depends on solution pH, on Cr(VI) concentration and on redox potential (Barrera-Díaz *et al.*, 2003). However, none of these Cr(VI) species form insoluble precipitates making separation through a direct precipitation method unfeasible (Lugo-Lugo *et al.* 2010). On the other hand,

the trivalent state of Cr does form insoluble species. Thus, to form a chromium solid phase easily separated from the aqueous media, it is necessary to change the oxidation state.

Passive in-situ reactive barriers have proven to be viable and cost-effective systems for remediation of Cr-contaminated groundwater at some sites. In PRBs containing granular ZVI, it has been found that removal rate of Cr(VI) by ZVI decreases over time and the (PRB) layer becomes almost inefficient especially under alkaline or mild acid conditions ( $\text{pH} > 4.5$ ). One explanation for this decrease may be attributed to a change in Fe(0) surface. The passivation of Fe(0) surface leads to a decrease in electron transfer and Fe(0) reactivity (Bonin *et al.*, 2000).

In ZVI treatment systems, the removal mechanism for Cr(VI), the more soluble and toxic form of Cr, is believed to involve reduction of Cr(VI) to Cr(III), where the corrosion process induced by water or dissolved oxygen in the influent groundwater reacting with the Fe(0) material leading to the formation of  $\text{Fe}^{2+}$ , hydrogen gas and  $\text{OH}^-$  (Eqs.(1) and (2)) (Daoud *et al.*, 2015). The release of  $\text{OH}^-$  causes an increase in pH value within reactive media. The electron transfer takes place coupled with the oxidation of Fe(0) to Fe(II), then to Fe(III) (Eqs. (2) and (3)) and the subsequent precipitation of sparingly soluble Fe(III)-Cr(III) hydroxides (Eq. (4)).



Magnetite and green rusts (iron(II)-iron(III) hydroxides) have been detected on the surface of Fe(0) particles, resulting in a slower rate of charge transfer relative to Fe(0) (Bonin *et al.* 2000). From an engineering perspective, the formation of precipitates can decrease PRB hydraulic conductivity and result in the failure to meet treatment objectives.

To solve these problems, some materials have been added to ZVI such pyrite ( $\text{FeS}_2$ ) which has been used to scavenge oxygen in column feed water and neutralize the effects of  $\text{OH}^-$ . Also,  $\text{FeS}_2$  had a significant impact on pH whether placed at the head of the column or dispersed throughout the Fe(0) layer (Cippollone, 1998). It was also reported that in laboratory studies using groundwater, flow diminished to a negligible level in a column containing 100% Fe(0) due to the reaction of Fe(0) with dissolved oxygen and the formation of ferric hydroxide precipitates, but the flow through a column containing Fe(0) amended with 10%  $\text{FeS}_2$  was almost unaffected after 90 days of operation (Mackenzie, 1999). The effect of sulfur compounds on the degradation of carbon tetrachloride was studied elsewhere, concluding that the addition of  $\text{FeS}_2$  to Fe(0) should accelerate treatment (Kenneke & Mccutcheon, 2003). nZVI was supported on MgO grains to facilitate the treatments for remediation of chromium-contaminated waters (Siciliano, 2016). Also, sodium alginate (SA) was used to modify nZVI to generate dispersed SA-nZVI. SA-nZVI particles found the presence of SA enhanced mobility of nZVI and effectively prevented sedimentation and aggregation (Zihan *et al.*, 2019). An adsorbent of Fe- $\text{FeS}_2$  mixture for effective arsenic removal was successfully prepared by mechanical ball milling (Min *et al.*, 2017).

In this research, bench top laboratory studies with micro ZVI have been carried out to evaluate treatment effectiveness and reaction processes for treating Cr(VI) and to predict the longevity of ZVI systems used for groundwater cleanup and changes of ZVI efficiency over time. The aim of this research is to prolong micro ZVI reactivity and control the hydraulic performance by using a PRB composed of 10% ZVI /sand and 10%  $\text{FeS}_2$ /sand. So, iron and chromium precipitation is minimized which leads to an increase in efficiency and lifespan of ZVI.

#### Materials and Methods:

**Materials and characterization:**

Distilled water was used in all preparations. Potassium dichromate ( $K_2Cr_2O_7$ ) and de-ionized [DI] water were used to prepare synthetic chromium. The solution pH was adjusted to the desired value by adding  $H_2SO_4$  or NaOH.

Uncontaminated sand with non-uniform size (mean diameter  $d_{50} = 0.65 \pm 0.2$  mm) was used as porous medium. The sand was characterized for bulk density ( $r_b = 1.703$  g/cm<sup>3</sup>), particle density ( $r_s = 2.62$  g/cm<sup>3</sup>), average porosity ( $n = 0.35$ ), and average saturated hydraulic conductivity ( $K = 0.52$  cm/s). The micro ZVI particles and all chemical reagents were obtained from Merck Company (Germany).

The simulated groundwater polluted with Cr(VI) was prepared from a stock solution using deionized water. Solution pH values were 3, 4.5, 6.5 and 7.5 with different values of initial Cr(VI) concentrations. For each condition, two pilots were used in which the PRB layer was composed of uncontaminated sieved sand on 50 – 100 mesh (0.3 – 0.15 mm) and the reactive media. One pilot with PRB layer which had only 20% micro ZVI in sand, and the second one had 10% micro ZVI and 10%  $FeS_2$  in sand which  $FeS_2$  was crushed and sieved to 50 – 100 mesh. All media used in the PRB layer were of approximately the same size (50 – 100 mesh).

**Methods:****Preparation of chromium solution:**

A stock solution of 1.0 g/L was prepared by dissolving 2.8298 g of potassium dichromate ( $K_2Cr_2O_7$ ) in 1.0 L of double-distilled water, which was further diluted for the preparation of test solutions. Several solutions at different initial concentrations of potassium dichromate were prepared. The required pH was adjusted by drop addition of 0.4M  $H_2SO_4$ , depending on sample acidity.

**Preparation of uncontaminated sand:**

Sand was soaked in water for 24 h to dissolve the lumps, washed on the No 200 sieve until the wash water was clear, and then dried by Coleparmer's laboratory oven at 105° C for 24 h. The used sand was poorly graded.

**Preparation of reactive media:**

Micro ZVI may not be suitable for use in PRBs because the small particle size may result in low permeability. To eliminate this shortcoming, several methods are used to enhance the permeability of reactive micro scale materials (Hosseini *et al.*, 2011). Given the reactive barrier existed in sand and micro ZVI, more than 65% of the particles were finer than 10  $\mu m$  with an average diameter of 60  $\mu m$ . The sand used had an average diameter between 0.15 and 0.6 mm.

**Apparatus and Instrumentation:**

The pH values of solutions were measured by Hanna pH meter using a combined glass electrode.

The metal ions Cr(VI) were determined by UV-vis spectrophotometer (HACH DR 4000).

Samples were examined with a scanning electron microscopy (SEM)XL 30 ESEM with EDAX: Resolution: up to 2A<sup>o</sup>; Acc. voltage: 30 kV; Magnification: up to 2,50,000x (Make: Philips, Netherlands). The analysis of samples was performed by X-ray diffraction, which XRD patterns were obtained using an ARL EQUINOX 3000 powder X-ray diffractometer with Cu  $\alpha_1$  radiation ( $\lambda = 1.54$  A<sup>o</sup>)

**Analytical procedure:**

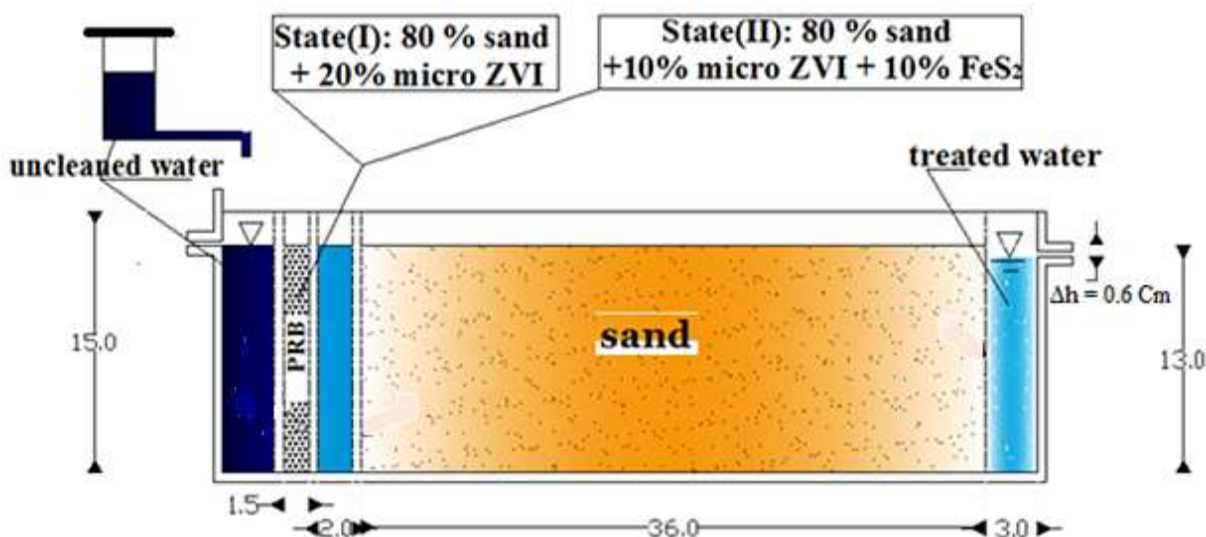
The analysis of Cr(VI) was carried out using spectrophotometer (HACH DR 4000; program: number 1560) according to the 1.5-Diphenylcarbohydrazide method using a single dry powder formulation called ChromaVer 3 chromium reagent for Cr(VI). Samples taken were analyzed with a method having a method detection limit (MDL) of 0.006 mg/L. The maximum concentration of Cr(VI) that can be measured and reported with 99-percent confidence is 0.7 mg/L.

**Experimental set-up:**

The studies of continuous adsorption reduction of Cr(VI) by micro ZVI were conducted in a pilot bench-scaled laboratory setup as shown in Figure 1, schematically. Uncontaminated sand was used as a

porous medium. The length of the porous medium after PRB position was 36 cm. There are several compartments separated by movable and perforated walls, one of them before the position of PRB and the other after it for monitoring pH and Cr(VI) concentration in these reservoirs during the experimental periods. The thickness of the reactive barrier was 1.5 cm.

The laboratory pilot was made of Plexiglas. A main reservoir was provided to supply influent water with certain Cr(VI) concentration into the sand/reductant mixture. One reservoir in up-stream and another in down-stream of sand/reductant mixture were considered to create a steady-state condition of flow through sand. The down-stream reservoir and sand are separated by polyethylene plastic mesh with openings size (0.2 x 0.2) mm. A certain pore velocity through sand was made with regulation of water level in these reservoirs through the hole in entrance reservoir and other hole in the outlet reservoir which the vertical between them 0.6 cm as shown in Figure 1.



**Figure 1. Schematic laboratory set-up showing a reservoir for uncleaned water (solid dark blue), PRB mixture of sand and reactive medium (black dots), two reservoirs before and after a sand column used to maintain flow rate (solid light blue), and sand. Double-walled dashed lines designate perforated walls and a single dashed line after the sand column indicates a plastic mesh. Measurements are given in cm.**

#### Experimental procedure:

The simulated groundwater contaminated with Cr(VI) was prepared from a stock solution using deionized water. This water is supplied to the entrance compartment, and then collected at an compartment after PRB at appropriate interval where it is analyzed for Cr(VI) concentration and pH. The temperature during the operation was  $25 \pm 5^\circ\text{C}$ .

Removal efficiency of Cr(VI) was calculated as:

$$\text{Cr(VI)} = [(C_0 - C)/C_0] \times 100 \quad (5)$$

Where  $C_0$  and  $C$  are the initial and final concentrations of Cr(VI), respectively.

Flow was periodically measured by collecting the effluent from the pilot in a graduated cylinder as shown in Figure 1. The coefficient of permeability  $k$ , was calculated according to Darcy's law:

$$k = QL/Ath \quad (6)$$

Where  $Q$  is quantity of solution discharged at time  $t$ ,  $L$  is distance between exit and entry chambers (42.5 cm),  $A$  is cross sectional area of porous medium (5 cm), and  $h$  is height difference between entry and exit chambers.

#### Results and discussion:

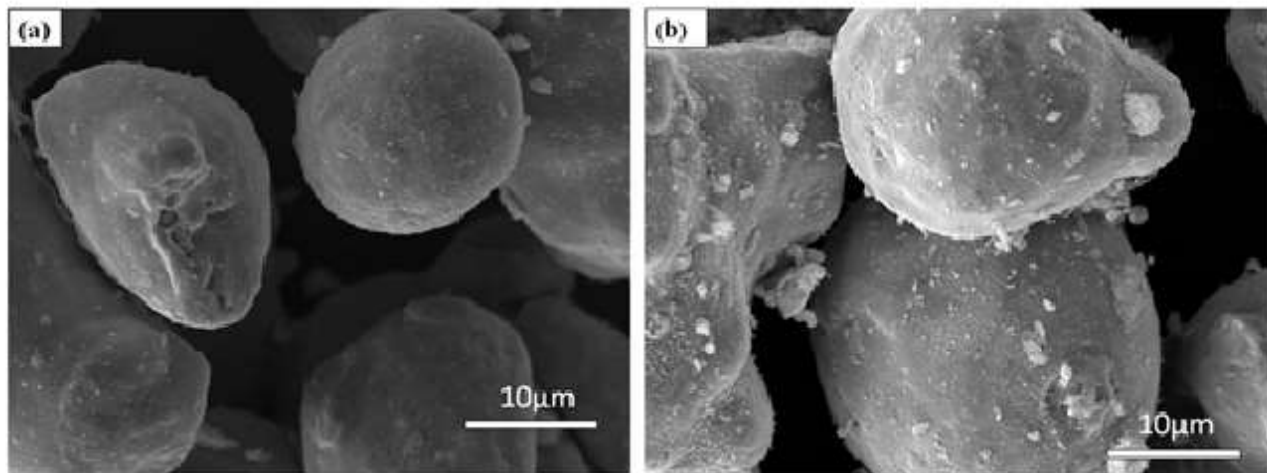
In the control runs, no addition of micro ZVI and no removal of Cr(VI) were found over the time period of typical experiments, i.e. only micro ZVI removes Cr(VI) from contaminated water.



### SEM and XRD observation

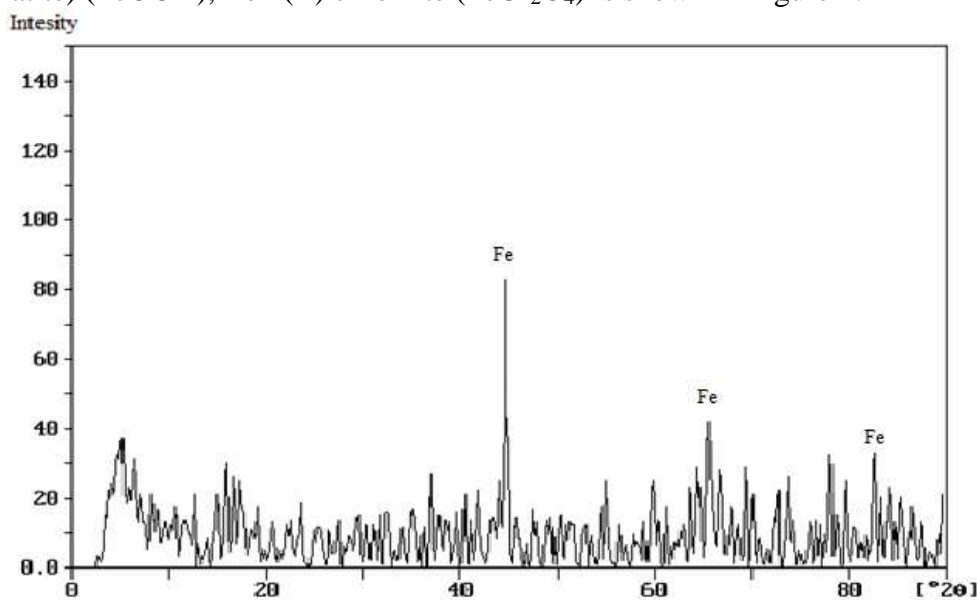
The surface morphology of two representative micro ZVI particles before and after use as a PRB is shown in Figure 2. SEM images show that the fresh micro ZVI particles are generally spherical in shape with the majority in the size range of 10-50  $\mu\text{m}$  (Figure 2(a)). A close-up image reveals that the particles are presumably connected due to magnetic dipole interactions and chemical aggregation.

SEM images of the ZVI samples after being used as a PRB in an experiment (with starting pH 7.5 and Cr concentration of 17.5 mg/L) exhibit acicular aggregation, cryptocrystallinity of particles and less regular surface covering (Figure 2(b)). It is worth mentioning that the used materials in (Figure 2(a)) and (Figure 2(b)) are from the same sample which is used in the test, but the size of particles is different.

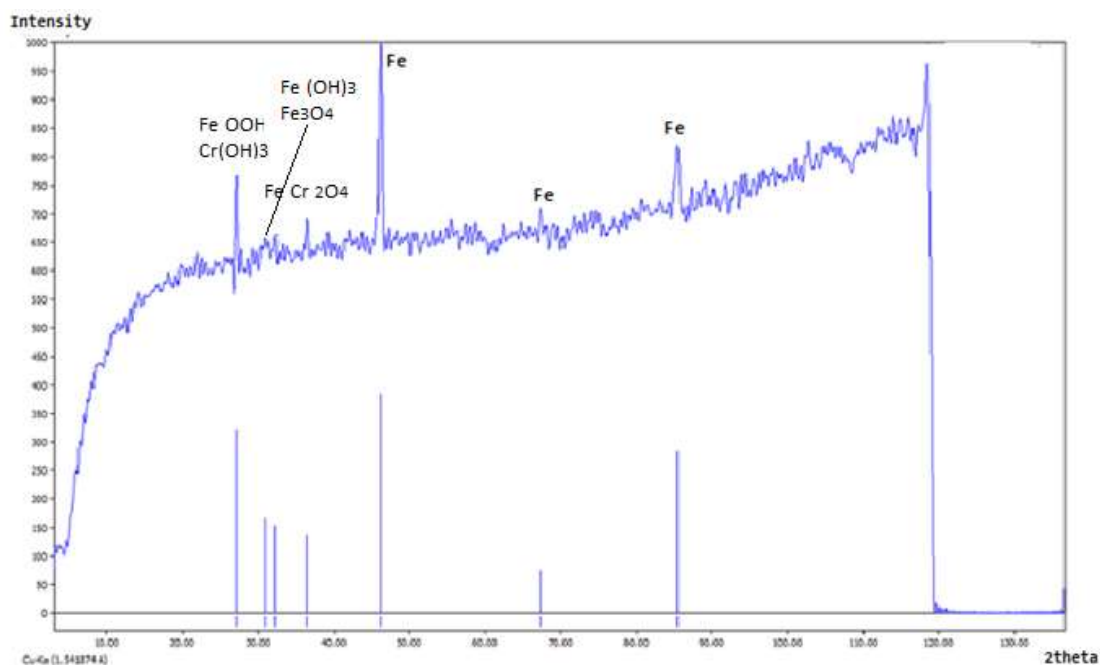


**Figure 2. The surface morphology of two samples of micro ZVI particles: (a) before and (b) after use as a permeable reactive barrier.**

Furthermore, the X-ray diffraction data of samples from the micro ZVI particles before use in the PRB layer is shown in Figure 3, while that used in PRB with all major peak positions and relative intensities for iron oxides and chromium and ferric hydroxide like magnetite ( $\text{Fe}_3\text{O}_4$ ), lepidocrocite (hydrohematite) ( $\text{FeOOH}$ ), iron (II) chromite ( $\text{FeCr}_2\text{O}_4$ ) is shown in Figure 4.



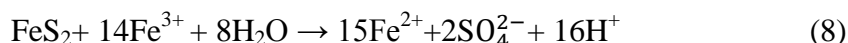
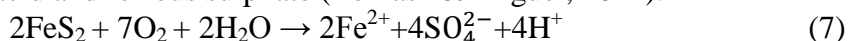
**Figure 3. X-ray diffraction of samples from the micro ZVI particles before use in the PRB layer.**



**Figure 4. X-ray diffraction of samples from the PRB layer after treatment of contaminated water, shown with the indexing peaks of selected phases.**

The pH value observed in laboratory after PRB ranged between 6 – 7.5. Under these conditions iron salts are insoluble and precipitate as ferric oxyhydroxides (ferrihydrite), amakinite ( $\text{Fe}(\text{OH})_2$ ) or magnetite  $\text{Fe}_3\text{O}_4$ . The corrosion processes and subsequent precipitation of minerals may lead to cementation and decreasing permeability of reactive material (Phillips *et al.*, 2000). A decrease in the reactivity of the iron media may also occur due to formation of surface coating. The formation of  $\text{H}_2$  gas bubbles can reduce the porosity of reactive material, resulting in decreasing hydraulic permeability (Zhang *et al.*, 2005).

It is reasonable to assume that on the basis of Eqs. 6 and 3, if oxygen and  $\text{OH}^-$  concentrations could be decreased prior to contacting with  $\text{Fe}(0)$  zone, the detrimental effects of precipitate formation might be minimized. So, pyrite ( $\text{FeS}_2$ ) was used to scavenge oxygen in reactive media as well as to neutralize the effects of  $\text{OH}^-$  according to (Eqs. (7) and (8)) and pyrite reaction with water and oxygen produces a solution of sulphuric acid and ferrous sulphate (Tomasz & Miguel, 2014):



$\text{FeS}_2$  had a significant impact on pH when dispersed throughout the  $\text{Fe}(0)$  and appeared to improve the rate of  $\text{Cr}(\text{VI})$  degradation. Flow diminished to a negligible level in a test containing 20% ZVI/sand and to almost zero level at high initial concentration (Figure 5) due to  $\text{Fe}(0)$  reaction with dissolved oxygen and formation of chromium and ferric hydroxide precipitates, while the flow through the set-up containing  $\text{Fe}(0)$  amended with  $\text{FeS}_2$  in PRB layer was almost higher than these experiments in which only micro ZVI was used. The effect of sulfur compounds on the degradation  $\text{Cr}(\text{VI})$  was also studied, concluding that the addition of  $\text{FeS}_2$  to  $\text{Fe}(0)$  prevents ZVI degradation. Figure 6 compared several laboratory-tests for removal of  $\text{Cr}(\text{VI})$  from contaminated water, and the results provided evidence that secondary iron bearing mineral products may enhance the capacity of zero valent iron systems to remediate  $\text{Cr}$  in groundwater, either through redox reactions at the mineral-water interface or by the release of  $\text{Fe}(\text{II})$ .

It is worth mentioning that the iron sulfide material is cheaper than micro ZVI, also the mixture of the micro ZVI and  $\text{FeS}_2$  with the most efficient, this means that the more reduction of  $\text{Cr(VI)}$  in PRB(ZVI +  $\text{FeS}_2$ ) the lower costs.

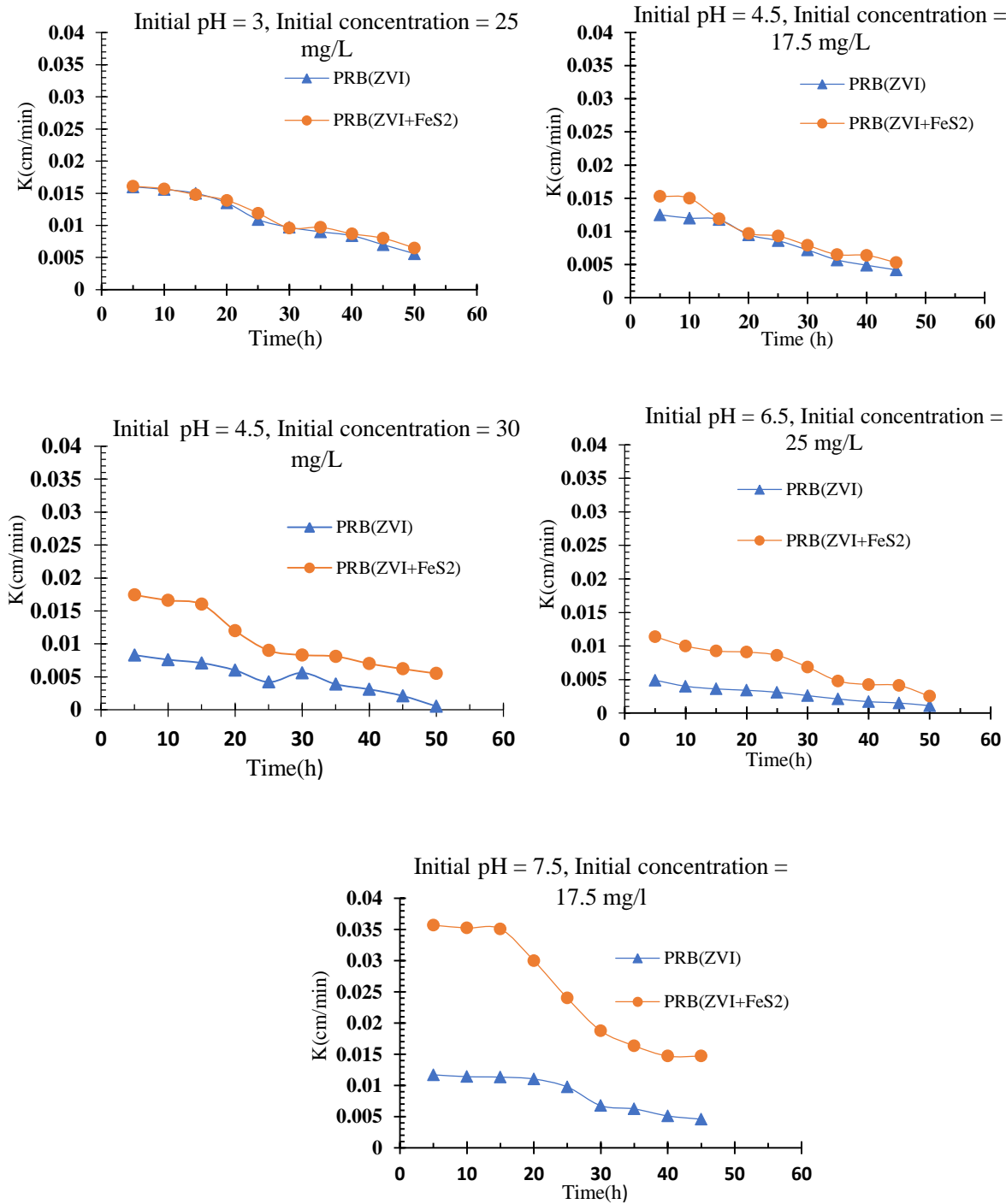


Figure 5. Variations of permeability over time of reactive media in PRB in two states: (1) PRB (sand+20%ZVI), (2) PRB (sand + 10% ZVI + 10%  $\text{FeS}_2$ ).

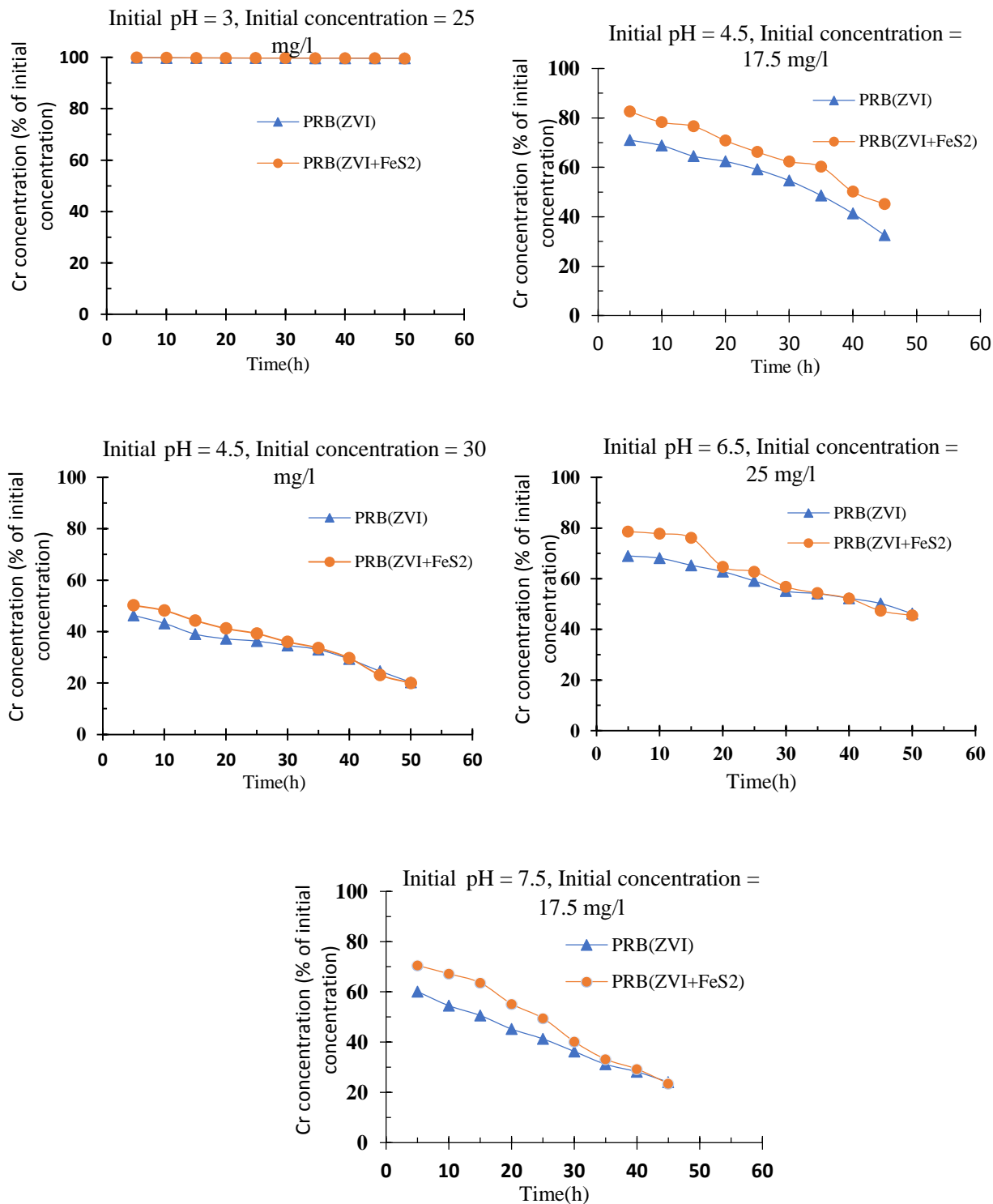


Figure 6. Variations of the percentage of Cr(VI) removal by PRB over time in two states: (1) PRB(sand+20%ZVI), (2) PRB (sand + 10% ZVI + 10% FeS<sub>2</sub>).

#### Conclusion:

The chromate is reduced to the nontoxic and insoluble chromic ion Cr(III) by micro ZVI which presumably forms an insoluble mixed chromium/ferric hydroxide phase via corrosion of the element



Fe. Formation of hydroxides results in changes in Fe(0) surface and affects electron transfer significantly, so the reactivity and hydraulic reactivity of the media is diminished over time.

A comparison between the efficiency / conductivity of a PRB composed of 10% ZVI /sand + 10% FeS<sub>2</sub>/sand and another PRB of 20% micro ZVI/sand was made. It was concluded that the addition of FeS<sub>2</sub> to micro ZVI accelerated the treatment and increased Cr(VI) reduction in PRB(ZVI+FeS<sub>2</sub>) due to minimization of iron/chromium precipitation, and thus the flow through the setup of this state was increased. Therefore, Fe(0) amended with FeS<sub>2</sub> in PRB was the most efficient media for Cr(VI) reduction at lower costs.

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## معالجة المياه الجوفية الملوثة بالكروم السداسي التكافؤ Cr(VI) باستخدام الحديد الصفري (ZVI) بإضافة سولفيد الحديد (FeS<sub>2</sub>)

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### الملخص

تم استخدام الحواجز الفعالة النفوذة (PRBs) التي تستخدم الحديد الصفري (ZVI) كمادة جاذبة لمعالجة المياه الجوفية الملوثة بالمعادن الثقيلة، مثل: الكروم السداسي التكافؤ Cr(VI). وحيث أنه تُعتبر Cr(VI) مادة خطيرة نتيجة السمية الشديدة لهذه المادة، وقابليتها للحركة، وصعوبة نزعها من المياه الملوثة بها، وبما أنها مادة مؤكسدة ومسببة للسرطان وسريعة الانتشار بسرعة في التربة والأوساط المائية، علاوةً على أن عدم تواجدتها بشكل مركبات غير قابلة للانحلال، يجعل فصلها بطريقة الترسيب أمر غير ممكن. وفي الوقت الذي تُعتبر فيه شوارد Cr(VI) مادة مؤكسدة وشديدة الحركة والسمية فإن الكروم الثلاثي التكافؤ Cr(III) على عكس ذلك. لذلك فإن تبديل Cr(VI) إلى Cr(III) يسهل عملية إزالة الكروم، كما يخفض من درجة سميته في المياه. وحيث أنه عند قيم pH العالية يُتوقع ترسيب الكروم وهيدروكسيد الحديد على سطوح حبيبات ZVI مسبباً تغييراً في سطح حبيباته، الأمر الذي يؤدي إلى تخفيض فعالية الحديد الصفري وكذلك نقصان نفاذيته مع مرور الزمن. في هذه الدراسة تم تحسين فعالية ZVI بإضافة سولفيد الحديد (البيريت) (FeS<sub>2</sub>) الذي يقوم باستهلاك الأوكسجين وتوليد شوارد H<sup>+</sup> الأمر الذي يقلل من رسوب هيدروكسيدات الحديد والكروم، وبالتالي إطالة العمر المفيد للحاجز المانع الفعال المحتوي على الحديد الصفري (ZVI) PRB والتقليل من حجم تناقص النفاذية مع مرور الزمن.

**الكلمات المفتاحية:** الحواجز الفعالة النفوذة، المياه الجوفية الملوثة، الكروم السداسي التكافؤ، الحديد الصفري، البيريت.