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(Article begins on next page)

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Removal of inorganic contaminants from aqueous solutions: evaluation of the remediation efficiency and of the environmental impact of a Zero-Valent Iron substrate

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Abstract

This work presents an evaluation of the remediation efficiency and of the environmental impact of a Zero-Valent Iron commercial substrate used for the removal of heavy metals from groundwater in different conditions. A specific feature of the substrate is the presence of ZVI, organic carbon and sulfate. The authors analyzed its composition and performances by means of batch tests in different boundary conditions. In detail, the efficacy was evaluated for metals (Cu, Cr, Pb and Zn) and for nitrates and sulfates. Neutral and acidic pH values, imputable to dangerous waste landfill leachate or to Acid Mine Drainage were considered. The environmental impact of the substrate was also assessed for the investigated pHs. The product showed a high efficiency in the removal of metals (mainly described by a pseudo-second order kinetic model), with a noticeable variability according to the pH of the polluted phase. Nitrate ions removal was inhibited by sulfates at all the considered pH values. Characterization and batch studies revealed that the substrate was a source of Mn, Cr, Pb, Cu and sulfate ions, besides Fe. This study shows that the employment of an optimized amount of reagent, while achieving good performances, is essential to contain the leaching of undesirable substances into aqueous environment.

Keywords

Inorganic contaminants, heavy metals, remediation, groundwater, zero-valent iron, Acid Mine Drainage

1. Introduction

Metal pollution of groundwater is a deeply researched problem, since heavy metals are toxic for humans, animals, microorganisms and plants. Heavy metals do not undergo degradation processes and their mobility and bioavailability change~~s~~ considerably as a result of their interactions with groundwater physic-chemical features (Doumett et al., 2008; Hashim et al., 2011).

High concentrations of metals may be detected in dangerous waste landfill leachates (Zanetti and Genon, 1999), and within polluting phenomena defined as Acid Mine Drainages (AMDs). AMDs are acidic aqueous solutions containing dissolved metals and sulfates, which derive from the exposure of coal and sulfide minerals, to an aqueous environment in the presence of oxygen and oxidizing bacteria (Gibert et al., 2011; Johnson and Hallberg, 2005; Mohan and Chander, 2006). Pollution by AMDs or landfill leachates may dramatically deplete groundwater quality.

Permeable Reactive Barriers (PRBs) constitute a passive approach for *in situ* remediation of metals and inorganic species: groundwater flows through a permeable substrate and pollutants are removed by the formation of hydroxides, carbonates and sulfides (Blowes et al., 2000) and by their adsorption on the substrate. PRB media conventionally employed in full scale reclamation installations are made of inorganic or organic substrates, or of easily oxidizable non toxic metals, such as Zero-Valent Iron (ZVI) (Agrawal et al., 2002; Cheng and Wu, 2001; Cundy et al., 2008; Furukawa et al., 2002; Rangsivek and Jekel, 2005; Vogan et al., 1999). Recent research activities are focused on ZVI nanoscale particles (Tosco et al., 2014), also studied in bimetallic substrates (Hosseini and Tosco, 2013). ZVI, oxidized by oxygen and dissolved species (i.e. bicarbonates, sulfates) and extensively by water (Noubactep and Schoener, 2009), produces a reduction in the environment and enhances alkalinity (Gillham and O'Hannesin, 1994), as illustrated by the reactions (1)-(5):

$$Fe^0 + 2H_2CO_3 \rightarrow Fe^{2+} + 2HCO_3^- + H_2 \quad (1)$$

$$Fe^0 + 2HCO_3^- \rightarrow Fe^{2+} + 2CO_3^{2-} + H_2 \quad (2)$$

$$Fe^0 + \frac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- \quad (3)$$

$$4Fe^0 + SO_4^{2-} + 9H^+ \rightarrow 4Fe^{2+} + HS^- + 4H_2O \quad (4)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (5)$$

The cleanup of heavy metals by means of ZVI may foresee numerous mechanisms: their reduction by Fe^0 or Fe(II) or H_2, their reversible adsorption on corrosion products, and their co-precipitation and adsorption on iron (oxy)hydroxides (Bartzas et al., 2006; Noubactep and Schoener, 2009; Hashim et al. 2011).

This work focuses on the evaluation of the performances and of the environmental impact a ZVI/Organic Carbon commercial substrate (EHC-M, Adventus) employed for heavy metals remediation in groundwater. The peculiar nature of the reagent is due to the contemporary presence of micrometric ZVI (25-35% w/w), sulfates (25-35% w/w), and organic carbon. Organic carbon and ZVI reciprocally support the biotic and abiotic reduction/oxidation processes (Lindsay et al., 2008; Xin et al., 2008).

The reclamation efficiency of the reagent was evaluated towards heavy metals, in the presence of sulfates and nitrates, and its leaching potential was assessed in aqueous environment. Acidic pH values equal to 1.3 and 5, which are respectively similar to an AMD and a dangerous waste landfill leachate, were considered. Neutral conditions, which are typical of the conventional application of the considered reagent to groundwater remediation, were also tested. An elemental analysis and SEM-EDS was carried out on the substrate before and at the end of the tests, in order to evaluate the formation of corrosion products, and of metallic aggregates and the changes in elemental composition.

2. Materials and Methods

2.1. Instrumentation

The Elemental analysis was carried out by means of a ThermoFisher Scientific Flash 2000 CHNSO analyzer. The Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed by a FEI Quanta Inspect 200LV, equipped with a EDAX Genesis SUTW EDS. Metals Analysis was executed by means of a Perkin Elmer Optima 2000 ICP-OES Spectrometer.

An ion chromatograph ICS3000 (Dionex, Sunnyvale, USA) (sample loop 10 µL , suppressor: ASRS-Ultra (Dionex), column: IonPac AS11-HC; eluent: 30 m*M* NaOH, 1 mL/min flow rate) was employed for the determination of NO_3^- and SO_4^{2-} ions. Spectrophotometric analyses were executed using Nanocolor Test 1-05 (NO_3^-) and Test 1-65 (NH_4^+) from Macherey-Nagel (Düren, Germany) and a 150-20 Model

spectrophotometer (Hitachi). pH and Eh measurements were carried out by an Expandable Ion Analyzer EA920 (Orion Research).

2.2. Reagents

Sulfuric (95-98%), nitric (65%), hydrochloric acids (32%), lead acetate, copper sulfate (99.5%), potassium dichromate (99.5%), zinc sulfate (99.5%) were from Sigma-Aldrich; Sodium hydroxide (50%, Baker) was form Merck. All solutions were prepared with high-purity water (Millipore, Vimodrone, MI, Italy).

2.3. Removal kinetics

Triplicate batch kinetics experiments were carried out at pH values equal to 1.3, 5.0 and 7.0, by stirring 50 g of the substrate with 0.25 L of a 3000 mg/L SO_4^{2-}, 1500 mg/L NO_3^-, 5 mg/L Cr(VI), 5 mg/L Pb^{2+}, 5 mg/L Zn^{2+} and 5 mg/L Cu^{2+} solution at 25 °C. Samples were withdrawn at 10 different contact times (1, 5, 10, 30, 60 min, and 4, 24, 72, 144 and 168 hours), and they were filtered (0.45-µm) before the analyses. A control sample was run in parallel for each contact time.

2.4. Evaluation of solid-liquid (S/L) ratio

A 3000 mg/L SO_4^{2-}, 1500 mg/L NO_3^-, 5 mg/L Cr(VI), 5 mg/L Pb^{2+}, 5 mg/L Zn^{2+} and 5 mg/L Cu^{2+} solution (at pH 5.0) was placed in contact (for 50 h) with different amounts of the reagent to achieve the following S/L ratios: 1:5; 1:25; 1:50; 1:250. All experiments were performed at 25°C. A control sample was run in parallel for each S/L ratio.

3. Results and Discussion

3.1. Substrate characterization

The elemental composition of the substrate was analyzed on the unemployed material and on the residue gathered from the kinetics tests (Fig. 1). The maximum contents of carbon, nitrogen and sulfur (which were higher than in the unaltered substrate) were observed at pH 5. Carbon, nitrogen and sulfur lowest contents were measured after the tests performed at pH 7. Sulfur content of the unemployed material corresponds to

about 21% w/w of sulfates: this value is congruent with the composition declared by the supplier of the substrate.

SEM-EDS analysis allowed the exam of the morphology, grain size and of the elemental composition of the unemployed material (Fig. 2). The presence of a micrometric iron metallic fraction was revealed (Mn, V and Ti were probably components of the ferrous alloy), and calcium and magnesium sulfates, as well as an organic fraction of possible vegetal origin were detected. The SEM-EDS analysis, also performed on the substrate after the kinetics tests, revealed the presence of non crystalline metallic aggregates and of corrosion products (Fig. 3).

3.2. Removal efficiency

Control samples underwent a preliminary analysis, in order to evaluate any pH change and the leaching from the substrate in high purity water (Fig. 4).

After the first 24 hours pH reached values between 5 and 6, independently of the initial pH of the aqueous phase. The concentration values for sulfates, nitrates, iron and manganese analyzed at the end of the tests in the polluted aqueous phases and in control samples are compared in Table 1, together with the maximum concentration values allowed by Italian regulation (DLgs 152/2006) for groundwater. Actually EC directive 2006/118/EC on the protection of groundwater against pollution and deterioration leaves the single EC Countries free to define their own regulations.

In all cases the experimental values largely exceeded the law limits. At the end of tests, sulfate ions release were always above 50 g/L; besides iron concentration was within 300-1400 mg/L according to the pH, and a relevant concentration (6-10 mg/L) of Mn was observed as well. The contents of Fe and Mn, not included in the preparation of the polluted solution, were monitored together with the considered analytes (Cr, Pb, Zn, Cu), because their release from the substrate was previously observed in high purity water (see Fig. 4).

pH and redox potential (Eh) trends caused by the substrate in the polluted aqueous phase are shown in Fig. 5. pH values confirmed the previously observed behaviour (see Fig. 4), and a shift of the system towards reducing conditions, due to the oxidation of Fe^0 to Fe^{2+} (Suponik and Blanco, 2014), may be appreciated. The removal profile for anions and metals are reported for each pH value in Fig. 6 and 7.

The release of Fe and Mn from the substrate was also considered (Fig. 8). The substrate's removal efficiency and residual concentration values are schematized in Table 2.

Results shown in Fig. 6-8 are discussed in the following sections.

3.2.1. Batch tests, pH 1.3

3.2.1.1 pH and Eh

During the monitored period, pH increased to 5.5 (see Fig. 4 and 5a). As observed for different zero-valent iron substrates (Wilkin and McNeil, 2003), the first 24 h were crucial.

The variation of redox conditions are from about 330 mV to -250 mV in the presence of inorganic dissolved species in the aqueous phase (see Fig. 5b). The Eh decrease (i.e. the increase of pH) is in agreement with the oxidizing action of water on metallic iron (eq. 5). Similar Eh trends were obtained for a substrate composed by zero-valent iron mixed with organic carbon (Lindsay et al., 2008). The control sample exhibits Eh changes from about 170 mV to -74 mV indicating a chief role of the dissolved species, and confirming that water is the main oxidizing agent with respect of ZVI (Noubactep and Schoener, 2009). Although the diminishing trend of Eh is in agreement with other studies on ZVI materials, the definition of a final Eh range is less straightforward being dependent upon the kind of pollution.

3.2.1.2. Anions

Laboratory scale experiments showed that ZVI cannot remove sulfate even for long reaction times (removal efficiency: 1- 50%) depending upon pH, type and amount of employed substrate (Bartzas et al., 2006; Fiore and Zanetti, 2009; Wilkin and McNeil, 2003; Yang and Lee, 2005). Sulfate reduction is a microbially mediated process, and usually it is not captured on laboratory-scale tests (Beak and Wilkin, 2009). Both ZVI and organic carbon are proven to support Sulfate Reducing Bacteria (SRBs), enhancing sulfate reduction rates towards an almost complete sulfate remediation of groundwater in the field (Xin et al., 2008). Sulfate removal may also happen by formation of corrosion products (*green rust:* $Fe_6(OH)_{12}SO_4$) or else by direct reduction (Bartzas et al., 2006) (eq. 4).

In this study sulfate concentration gradually increased with time since it is released by the reagent (Fig. 4 and Table 1). However, this issue may be considered not critical, because in field-application of ZVI PRBs sulfates are usually entirely removed from groundwater plumes (Wilkin and McNeil, 2003).

Removal of nitrate ions by ZVI in anoxic phase is pH dependent (Huang and Zhang, 2004) and it is an acid-driven surface-mediated process (Yang and Lee, 2005). A shifting order kinetic model was proposed to describe nitrates reduction by ZVI at different pHs (Rodriguez-Maroto et al., 2009). Several reaction mechanisms were proposed for nitrate removal (Yang and Lee, 2005) and although a real consensus is not achieved, several studies indicate NH_4^+ or else N_2 (Rodriguez-Maroto et al., 2009) as the end products of nitrate reduction. Nitrate reduction by Fe^0 is a spontaneous process under acidic conditions:

$$4Fe^0 + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \qquad (6)$$

In the here presented experiments nitrate was poorly removed (Fig. 6): its concentration decreased rapidly within 24 h (minimum concentration 1300 mg/L), but it increased with time up to the original concentration (the control did not exhibit any release, see Table 1). This behaviour may be explained by the effect of sulfates (continuously released by the substrate), which are able to delay removal kinetics of nitrate ions (Choe et al., 2004; Su and Puls, 2004). Therefore, differently from ZVI materials used at similar pH values (Yang and Lee, 2005), when employed for metal ions removal, the reagent is not efficient in the removal of nitrates.

NH_4^+ concentration was also monitored during the batch experiments. The initial decrease of nitrate ions concentration corresponds to an increase of NH_4^+ concentration. However, differently from what was observed in traditional Fe^0 systems (Rodriguez-Maroto et al., 2009), NH_4^+ concentration was not constant in this research, but it rapidly decreased after the first 10 h. A nitrogen balance evaluated at the maximum NH_4^+ concentration value was not quantitative, due to possible side-reactions (e.g. complexation by Zn and Cu or N_2 formation).

3.2.1.3. Metals

The sulfate ions released by the substrate may react with the organic substance according to the following reaction:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \qquad (7)$$

The formed H_2S contributes to the overall removal of metals according to the following reaction (Me^{2+}: divalent metal ion):

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+ \quad (8)$$

The following qualitative test was performed in order to evaluate if the reaction depicted in eq. 7 (and in turn in eq. 8) could take place in our system. The reagent was put in contact with a 5 mg/L Zn solution, and after 24 h (enough to release SO_4^{2-} -Fig. 4- and to react according to eq. 4), the aqueous phase was filtered and a saturated solution of lead acetate ($Pb(CH_3COO)_2$) was added drop-wise. The addition of a single drop of $Pb(CH_3COO)_2$ immediately induced the formation of a black precipitate (PbS), confirming the presence of H_2S and the occurrence of reaction 8.

The accepted immobilization mechanism for Cr(VI) by ZVI is reduction to Cr(III) and precipitation with oxidized iron minerals and adsorption to iron oxides, according to eq. 9 (Blowes et al., 2000):

$$\begin{aligned} &CrO_{4(aq)}^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr_{(aq)}^{3+} + 4H_2O \\ &(x)Cr_{(aq)}^{3+} + (1-x)Fe_{(aq)}^{3+} + 2H_2O \rightarrow Cr_xFe_{(1-x)}OOH_{(s)} + 3H_{(aq)}^+ \end{aligned} \quad (9)$$

The minimum concentration of total Cr obtained by the authors was 0.4 mg/L (after 2 days, Fig. 7). Nevertheless, Cr concentration increased to 0.7 mg/L, meaning that a mobilization process occurred from its adsorbed fraction. The increase of Cr concentration cannot be ascribed neither to a release by the substrate (maximum Cr concentration in the control: 20 µg/L and constant with time), nor to pH (Magalhaes et al., 2009) since after 50 h it was constant at 5.5. Nevertheless a contribution due to the decreased Eh in the last 24 h of the experiments must not be neglected. In the presence of Pb^{2+} ions, precipitation of $PbCrO_4$ ($K_s=10^{-12.5}$ (Sillen and Martell, 1971)), can also occur. A Cr removal of about 87% was achieved (Table 2).

The removal of Pb as PbS (Adventus, 2006) was faster if compared to Cr(VI): it occurred after 24 h, reaching a minimum concentration of 0.3 mg/L (Fig. 7). Nevertheless, Pb concentration increased up to 1 mg/L after 7 days, providing a final removal percentage of 81% (Table 2). This increase could not be ascribed only by the reagent's release (see control sample), and it might be connected to the reversibility of adsorption.

Several studies observed that low pH and high dissolved organic carbon are limiting factors (Bartzas et al., 2006; Rangsivek and Jekel, 2005) in Zn remediation. As shown in Table 2, Zn was quantitatively removed after 24 h, without any long-term concentration increase. Zn was never observed in control samples.

Copper removal followed a faster kinetic, and after 24 h a minimum concentration of 0.05 mg/L was achieved, providing a 89% removal. Nevertheless Cu concentration increased with the contact time to 0.5 mg/L (see Table 2). Since copper concentration in the controls kept constant (0.02 mg/L) a substrate contribution should be excluded and a reversibility of the adsorption process must be assumed. Reduction for copper (and Cd as well) and plating on iron surface was proposed (Shokes and Moeller, 1999), even if not supported by the batch experiments (Wilkin and McNeil, 2003). Copper cleanup might be better explained by redox processes (Bartzas et al., 2006) (formation of Cu_xS species), whereas $Cu(OH)_2$ precipitation can only occur beyond pH 6.7.

For what concerns the leaching potential of the substrate (see Table 1), Fe concentration in the aqueous phase increased rapidly within the first 24 h and then more gradually with time, both in the control sample and in the polluted solution. Although the same Fe concentration was released in both within the first 48h, the presence of dissolved species accelerated Fe oxidation. According to the experimental data, after 7 days, a dissolution of 33% of total Fe from the reagent occurred and a further release should be expected.

As mentioned, also Mn was gradually released by the substrate, and traces of other metals (V, Ti) were detected by SEM-EDS in the reagent at the end of batch tests (Fig. 3). Mn release was probably promoted by the presence of dissolved species in the aqueous phase (Table 1). Mn release was also observed from Peerless ZVI at acidic pH values (Wilkin and McNeil, 2003). Mn remediation is a well known critical issue (Hallberg and Johnson, 2005), and MnS precipitation ($K_s = 5.6 \cdot 10^{-16}$) is expected only when the concentration of other competing metals is very low (Cheong et al., 1998). In addition since the pH increase was not sufficient to drive hydroxide precipitation, the removal of Mn released was not possible in the tested experimental conditions.

3.2.2. Batch tests, pH 5.0

3.2.2.1. pH and Eh

Despite the initial change, the substrate provided an increase of pH up to 6, as previously observed for more acidic conditions. This behavior was different from that of granular zero-valent iron observed by other authors (Wilkin and McNeil, 2003). Nevertheless it should be remarked that for pH 1.3, as previously shown,

higher increases of pH were observed, as the oxidation of Fe^0 proceeded more rapidly at low pH, according to eq. 3 and 5.

Eh values varied from -90 mV to -180 mV and if compared with the results obtained at pH 1.3, less reducing conditions are achieved, in agreement with a slower Fe^0 dissolution (Suponik and Blanco, 2014). Differently from what previously observed, the control samples exhibited similar Eh variations, meaning that iron oxidation and metal ion removal reactions do not significantly alter the reducing conditions.

3.2.2.2. Anions

Less acidic conditions caused a higher release of sulfate ions from the reagent in the polluted solution if compared with control samples (Table 1 and Fig. 6) and the presence of dissolved substances entails the release of about 30000 mg/l more than in plain water. The minor conversion of SO_4^{2-} into HS^- at less acidic pH values (eq. 4) might explain the higher concentration of sulfate in respect to pH 1.3.

As for nitrate (Table 1 and Fig. 6), the substrate exhibited a higher removal rate, in agreement with the mentioned inhibiting effect of low pH values, but for longer contact times nitrate concentration increased. Also for pH 5, no contribution by the product in the control sample was observed.

3.2.2.3. Metals

Removal efficiency was higher than at pH 1.3, where only Zn was removed quantitatively (Table 2). Differently from what observed at highly acidic pHs, Cr removal was completed within 5 days without mobilization, due to the presence of less acidic conditions during the reaction as shown in Fig. 5. Also for control samples, no release of Cr was observed.

For Pb, a removal efficiency higher than at pH 1.3 was observed, since it was removed within the first 48 h of reaction (Fig. 7).

The good performance of the substrate towards Zn already observed at pH 1.3 were confirmed (Fig. 7).

Copper removal was slower at pH 5.0 than at 1.3 (after 4 h Cu concentration was equal to 2.8 mg/L *vs* 0.6 mg/L), in agreement with what reported by Suponik and Blanco (Suponik and Blanco, 2014). The minimum Cu concentration was obtained after 48 h (*vs* 24 h at pH 1.3). As already observed at more acidic conditions, mobilization of Cu occurred up to 0.5 mg/L (Fig. 7). The substrate released about 0.1 mg/L Cu (Fig. 4).

In agreement to the fact that Fe dissolution is an acid-driven process (eq. 4) (Yang and Lee, 2005), a lower final Fe content was observed (Table 2). Differently from what previously observed, the release of Fe was linear with time and the releasing behavior of controls and of the polluted solutions were different only after 144 h. At the end of the tests, the presence of metal and anionic species in the synthetic solution caused the dissolution of about 180 mg/L additional Fe (Fig. 4 and 8).

Mn release was linear with time both for the substrate in the polluted solution and in the control samples (see Fig. 4 and 8). Their behavior slightly set apart only after 7 days. As shown by Table 1, the release of Mn was not so different at pH 1.3 and 5.0.

3.2.3. Batch tests, pH 7.0

3.2.3.1. pH and redox

A decrease of pH was observed within the first 30-60 min of contact, and then pH increases to 5.6 when equilibrium is reached. A similar behavior was observed for control samples (Fig. 4 and 5).

Eh values varied from 50 mV to -250 mV while for the control Eh varied from 50 mV to –310 mV, indicating that slightly less reducing conditions were achieved in the synthetic solution at neutral pH.

3.2.3.2. Anions

As already observed comparing results at pH 1.3 and 5.0, final sulfate concentration (Table 1) increased since conversion to HS^- according to eq. 4 was limited by pH conditions.

The behavior of the reagent towards nitrates removal did not present significant differences from what observed at pH 5.0: within the first 4 h nitrate concentration was reduced to about 1000 mg/L and further increases to 1700 mg/L (Fig. 6). The control samples showed that no release by the substrate occurred (Table 1).

3.2.3.3. Metals

As regards Cr, its total concentration increased in the first sampling times, due to the corresponding pH decrease that caused a dissolution of precipitated Cr compounds. Nevertheless, Cr was removed

quantitatively even at pH 7 (Table 2), even if the control exhibited a not negligible release (0.2 mg/L after 7 days, see Fig. 4 and 8).

The removal of Cr obtained was significantly higher than that observed by nanoscale ZVI (66% and 46% at pH 5 and 7, respectively) (Li et al., 2012). Lead was removed within the first 2 days of contact, with a slightly lower rate than the one observed at pH 5.0 but with the same efficiency (Table 2). A release of 0.27 mg/L Pb from the reagent was noticed.

The good performance of the substrate against Zn was confirmed also at neutral pH conditions without any release in the control sample.

As previously observed for Cr, also Cu concentration seemed affected by the pH changes introduced by the product. In fact an increase of Cu concentration was followed by a reduction to about 0.5 mg/L (Fig. 7). The control exhibited a quite constant release of Cu (about 0.12-0.16 mg/L) at all the sampling times (Fig. 4).

A linear release of Fe by the substrate was again observed (Fig. 8). Final concentration (about 800 mg/L) was the lowest observed among the pH conditions evaluated, supporting that the oxidation of ZVI proceeds at a lower degree at higher pH values. The presence of the matrix favored the dissolution of additional 500 mg/L Fe (Table 1). A similar behavior was exhibited by Mn. Neutral pH represented the condition of minor impact of the reagent for Mn contamination.

3.2.4. Summarized Remarks

a) independently from the initial pH conditions, ECH-M buffered the pH to about 5-6 within the first 48-72 h of contact;
b) Cr(VI) and Zn are removed quantitatively at pH 5.0 and 7.0. Despite the good performance of the substrate for Pb (about 99%), the final Pb concentration didn't satisfy the Italian regulation for groundwater (DLgs 152/2006);
c) At acidic pH values, Cr(VI) removal was not quantitative (about 87%) and at the considered pHs, the requirements of Italian regulations were not fulfilled even as total Cr.
d) Although removal percentages for Cu were in the range 89-90%, the substrate couldn't quantitatively remove Cu in none of the evaluated pH values. However, the fulfillment of the Italian regulation was achieved;

e) The reagent turned out to be an efficient substrate for Zn removal at any evaluated pH value;

f) The substrate was a source of Fe/SO_4^{2-} and Mn/Cr/Pb/Cu, which were present as impurities in the substrate. Even if the release was lower in the presence of metal ions, Fe, SO_4^{2-}, Mn concentrations did not fulfill the legislative requirements (Table 1).

g) Whichever the pH value, the reagent could not remove NO_3^- ions. The continuous release of sulfate by the substrate caused an inhibiting effect.

3.3. Removal Kinetics

The majority of the results of the studies reported in literature are represented as a pseudo-first order rate mechanism (Rangsivek and Jekel, 2005; Wilkin and McNeil, 2003) and other available kinetic models are rarely used to test and correlate the experimental data.

In order to investigate the removal mechanisms and the potential rate controlling steps, the authors used first order, pseudo-first order (Ho, 2004), pseudo-second order (Ho and McKay, 1999) and Elovich (Cheung et al., 2000; Low, 1960) kinetics models to the experimental data obtained within 0-24 h. Details of the used models can be found elsewhere (Bruzzoniti et al., 2012).

Poor correlation of kinetics data at each pH value was found for the Elovich model, except for Pb at pH 5 (R^2=0.9730). Removal of species was generally better described by a pseudo-second order model (Table 3).

With the exception of nitrate (pH 5.0 and 7.0) and Zn (pH 1.3), a very good consistency of the calculated q_e value (amount adsorbed at equilibrium, expressed as mg g^{-1}) with the experimental data was obtained. The initial sorption value *h* (mg $g^{-1}h^{-1}$) was found to be pH dependent.

For nitrate (pH 1.3), Pb (pH 1.3), Cu (pH 5.0) the kinetics were better described by the pseudo-first order model. Uptake rates for Cu (k_1=0.117 h^{-1}) at initial pH 5.0 were in the same magnitude order if compared with the values obtained for ZVI at the same pH conditions (0.103-0.275 h^{-1} according to the amount of dissolved organic carbon in solution) (Rangsivek and Jekel, 2005) or for Peerless Fe^0 at pH 4.5 (k_1=0.27 h^{-1}) (Wilkin and McNeil, 2003).

As for nitrate, in agreement with what obtained for nanosized iron at pH 3 (Yang and Lee, 2005), experimental data at pH 5.0 and 7.0 were not described either by the pseudo-first order or by the pseudo-

second order models. Agreement with the pseudo-second order model (R^2= 0.9805) was obtained only for pH 1.3.

3.4. Optimization of solid/liquid ratio

Minimizing the mass of reagent required to achieve the desired performance would be of benefit to maximize the cost-effectiveness of this approach with the lowest environmental impact.

Therefore, the removal performance of the substrate as well as its environmental impact were assessed for several S/L ratios (Table 4), considering a 50 h contact time with the aqueous phase.

The best compromise between removal and release was obtained for a 1:50 S/L ratio, where Pb and Zn were quantitatively removed. Cu removal was about 92% and the final concentration (0.41 mg/L) satisfied the Italian regulations for groundwater (1 mg/L). Although Cr(VI) removal was about 99%, the final concentration (0.064 mg/L) didn't satisfy the law limits (50 µg/L as total Cr). The release of Fe, Mn and sulfate ions from the reagent were clearly lower than those at 1/5 and 1/25 S/L ratios, but for none of the species the limits set by Italian regulations (Table 1) were fulfilled. The same consideration holded true for the 1/250 S/L ratio, where, in addition, the removal of metal species couldn't be considered satisfactory (Zn and Cr removal is 62% and 98%, respectively).

4. Conclusions

In this study the environmental impact of a commercial ZVI substrate was evaluated and its reclamation efficiency towards water polluted by metals and inorganic anions was investigated at different pH values. Although the substrate was able to drive the pH to about 6, independently of the initial pH conditions, remediation capabilities are pH dependent.

In agreement with the characterization study, the substrate was a source of Mn, Cr, Pb, Cu and sulfate ions, besides Fe. The leaching of undesirable substances by the substrate into aqueous environment should be controlled by tailoring a proper solid/liquid ratio. Our findings allow to suggest that a solid/liquid ratio equal to 1:50 was a proper compromise between removal efficiency and environmental impact of the studied substrate. Several kinetic models were tested for the fitting of experimental data: in the considered boundary conditions, a pseudo-second order kinetic model was consistent with the majority of the gathered data.

The evaluation of the efficiency of a reagent and of its leaching potential, both driven by groundwater physic-chemical features, also taking into account kinetic aspects, is mandatory for a correct choice for the remediation of a polluted site. The here presented results confirm the well-known advantage of ZVI substrates: they are effective at wide pH ranges (although not able to fulfill in all cases the Italian regulation limits for groundwater), they are not strictly contaminant specific, and a re-mobilization of metals at typical groundwater pH values is not likely to occur. For the above mentioned reasons, ZVI materials may be employed in PRBs or directly injected in the aquifer as nano-sized particles for the remediation of groundwater polluted by metals.

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References

Adventus: 2006, 'Technical note', Immobilization processes for dissolved trace metal using ECH-M, http://www.adventusgroup.com.br/pdfs/EHC-M_mechanisms.pdf

Agrawal, A., Ferguson, W. J., Gardner, B. O., Christ, J. A., Bandstra, J. Z. & Tratnyek, P. G.: 2002, 'Effects of Carbonate Species on the Kinetics of Dechlorination of 1,1,1-Trichloroethane by Zero-Valent Iron', Environ. Sci. Technol. 36, 4326-4333.

Bartzas, G., Komnitsas, K. & Paspaliaris, I.: 2006, 'Laboratory evaluation of Fe0 barriers to treat acidic leachates', Miner. Eng. 19, 505-514.

Beak, D. G. & Wilkin, R. T.: 2009, 'Performance of a zerovalent iron reactive barrier for the treatment of arsenic in groundwater: Part 2. Geochemical modeling and solid phase studies', J. Contam. Hydrol. 106, 15-28.

Blowes, D. W., Ptacek, C. J., Benner, S. G., McRae, C. W. T., Bennett, T. A. & Puls, R. W.: 2000, 'Treatment of inorganic contaminants using permeable reactive barriers', J. Contam. Hydrol. 45, 123-137.

Bruzzoniti, M. C., De, C. R. M., Sarzanini, C., Caldarola, D. & Onida, B.: 2012, 'Novel insights in Al-MCM-41 precursor as adsorbent for regulated haloacetic acids and nitrate from water', Environ. Sci. Pollut. Res. 19, 4176-4183.

Cheng, S. f. & Wu, S. c.: 2001, 'Feasibility of using metals to remediate water containing TCE', Chemosphere 43, 1023-1028.

Cheong, Y.-W., Min, J.-S. & Kwon, K.-S.: 1998, 'Metal removal efficiencies of substrates for treating acid mine drainage of the Dalsung mine, South Korea', J. Geochem. Explor. 64, 147-152.

Cheung, C. W., Porter, J. F. & McKay, G.: 2000, 'Elovich equation and modified second-order equation for sorption of cadmium ions onto bone char', J. Chem. Technol. Biotechnol. 75, 963-970.

Choe, S., Liljestrand, H. M. & Khim, J.: 2004, 'Nitrate reduction by zero-valent iron under different pH regimes', Appl. Geochem. 19, 335-342.

Cundy, A. B., Hopkinson, L. & Whitby, R. L. D.: 2008, 'Use of iron-based technologies in contaminated land and groundwater remediation: A review', Sci. Total Environ. 400, 42-51.

Doumett, S., Lamperi, L., Checchini, L., Azzarello, E., Mugnai, S., Mancuso, S., Petruzzelli, G. & Del Bubba, M.: 2008, 'Heavy metal distribution between contaminated soil and Paulownia tomentosa, in a pilot-scale assisted phytoremediation study: Influence of different complexing agents', Chemosphere 72, 1481-1490.

Fiore, S. & Zanetti, M. C.: 2009, 'Preliminary tests concerning Zero-Valent iron efficiency in inorganic pollutants remediation', Am. J. Environ. Sci. 5, 556-561.

Furukawa, Y., Kim, J.-w., Watkins, J. & Wilkin, R. T.: 2002, 'Formation of Ferrihydrite and Associated Iron Corrosion Products in Permeable Reactive Barriers of Zero-Valent Iron', Environ. Sci. Technol. 36, 5469-5475.

Gibert, O., Roetting, T., Cortina, J. L., de, P. J., Ayora, C., Carrera, J. & Bolzicco, J.: 2011, 'In-situ remediation of acid mine drainage using a permeable reactive barrier in Aznalcollar (Sw Spain)', J. Hazard. Mater. 191, 287-295.

Gillham, R. W. & O'Hannesin, S. F.: 1994, 'Enhanced degradation of halogenated aliphatics by zero-valent iron', Ground Water 32, 958-967.

Hallberg, K. B. & Johnson, D. B.: 2005, 'Biological manganese removal from acid mine drainage in constructed wetlands and prototype bioreactors', Sci. Total Environ. 338, 115-124.

Hashim, M.A., Mukhopadhyay, S., Sahu, J.N., Sengupta, B. : 2011, 'Remediation technologies for heavy metal contaminated groundwater', J. Environ. Manag. 92, 2355-2388.

Ho, Y.-S.: 2004, 'Citation review of Lagergren kinetic rate equation on adsorption reactions', Scientometrics 59, 171-177.

Ho, Y. S. & McKay, G.: 1999, 'Pseudo-second order model for sorption processes', Process Biochem. (Oxford) 34, 451-465.

Huang, Y. H. & Zhang, T. C.: 2004, 'Effects of low pH on nitrate reduction by iron powder', Water Res. 38, 2631-2642.

Johnson, D. B. & Hallberg, K. B.: 2005, 'Acid mine drainage remediation options: a review', Sci. Total Environ. 338, 3-14.

Li, Y., Li, J. & Zhang, Y.: 2012, 'Mechanism insights into enhanced hexavalent chromium removal using nanoscale zerovalent iron supported on pillared bentonite by macroscopic and spectroscopic studies', J. Hazard. Mater. 227-228, 211-218.

Lindsay, M. B. J., Ptacek, C. J., Blowes, D. W. & Gould, W. D.: 2008, 'Zero-valent iron and organic carbon mixtures for remediation of acid mine drainage: Batch experiments', Appl. Geochem. 23, 2214-2225.

Low, M. J. D.: 1960, 'Kinetics of chemisorption of gases on solids', Chem. Rev. (Washington, DC, U. S.) 60, 267-312.

Magalhaes, F., Pereira, M. C., Fabris, J. D., Bottrel, S. E. C., Sansiviero, M. T. C., Amaya, A., Tancredi, N. & Lago, R. M.: 2009, 'Novel highly reactive and regenerable carbon/iron composites prepared from tar and hematite for the reduction of Cr(VI) contaminant', J. Hazard. Mater. 165, 1016-1022.

Mohan, D. & Chander, S.: 2006, 'Removal and recovery of metal ions from acid mine drainage using lignite. A low cost sorbent', J. Hazard. Mater. 137, 1545-1553.

Noubactep, C. & Schoener, A.: 2009, 'Fe0-based alloys for environmental remediation: Thinking outside the box', J. Hazard. Mater. 165, 1210-1214.

Rangsivek, R. & Jekel, M. R.: 2005, 'Removal of dissolved metals by zero-valent iron (ZVI): kinetics, equilibria, processes and implications for stormwater runoff treatment', Water Res. 39, 4153-4163.

Rodriguez-Maroto, J. M., Garcia-Herruzo, F., Garcia-Rubio, A., Gomez-Lahoz, C. & Vereda-Alonso, C.: 2009, 'Kinetics of the chemical reduction of nitrate by zero-valent iron', Chemosphere 74, 804-809.

Shokes, T. E. & Moeller, G.: 1999, 'Removal of Dissolved Heavy Metals from Acid Rock Drainage Using Iron Metal', Environ. Sci. Technol. 33, 282-287.

Sillen, L. G. & Martell, A. E.: 1971, Stability Constants of Metal-Ion Complexes, Supplement No. 1, Pts. 1 and 2: Inorganic Ligands. Organic Including Macromolecule Ligands (Chemical Society, Special Publication No. 25), Chem. Soc., 865 pp. pp.

Su, C. & Puls, R. W.: 2004, 'Nitrate Reduction by Zerovalent Iron: Effects of Formate, Oxalate, Citrate, Chloride, Sulfate, Borate, and Phosphate', Environ. Sci. Technol. 38, 2715-2720.

Suponik, T. & Blanco, M.: 2014, 'Removal of heavy metals from groundwater affected by acid mine drainage', Physicochemical Problems of Mineral Processing 50, 359-372.

Vogan, J. L., Focht, R. M., Clark, D. K. & Graham, S. L.: 1999, 'Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater', J. Hazard. Mater. 68, 97-108.

Wilkin, R. T. & McNeil, M. S.: 2003, 'Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage', Chemosphere 53, 715-725.

Xin, Y., Yong, K., Duujong, L. & Ying, F.: 2008, 'Bioaugmented sulfate reduction using enriched anaerobic microflora in the presence of zero valent iron', Chemosphere 73, 1436-1441.

Yang, G. C. C. & Lee, H.-L.: 2005, 'Chemical reduction of nitrate by nanosized iron: kinetics and pathways', Water Res. 39, 884-894.

Zanetti, M. C. e Genon, G.: 1999, 'Physical properties of industrial wastes: laboratory tests', Resources, Conservation and Recycling 25, 195-213.

Table 1. Evaluation of the environmental impact of the substrate in the polluted aqueous phase (A) and in high purity water (B) according to Italian regulations.

pH	**Sulfate (mg/L)**		**Nitrate (mg/L)**		**Fe (mg/L)**		**Mn (mg/L)**	
	A	B	A	B	A	B	A	B
1.3	61000	51000	1500	-	2000	1300	14	7.6
5.0	83300	55000	1700	-	870	690	13	9.6
7.0	88700	54000	1700	-	800	324	11	5.7
Italian law limits for groundwater (DLgs 152/2006)	250		-		0.20		0.05	

Table 2. Removal of metal species by the substrate at different pH conditions after 168 h and comparison of residual concentrations with Italian law limits

Metal species	pH 1.3	pH 5.0	pH 7.0	Italian law limits for groundwater (DLgs 152/2006)
	% removal [final metal concentration, mg/L]			(mg/L)
Cr(VI)	86.7 [0.7]	100 [<0.005[a]]	100 [<0.005[a]]	0.05[a]
Pb	81 [1]	98.6 [0.065]	99.0 [0.050]	0.01
Zn	100 [<0.005]	100 [<0.005]	100 [<0.005]	3.00
Cu	88.9 [0.5]	88.9 [0.5]	90.4 [0.48]	1.00

[a] as total Cr

Table 3. Removal isotherm constants for the pseudo-first and pseudo-second order kinetics models.

Species		**Pseudo-first order**		**Pseudo-second order**				
		k_1 (h^{-1})	R^2	K_2 (g mg^{-1} h^{-1})	Calculated q_e (mg g^{-1})	Experimental q_e (mg g^{-1})	h[a)] (mg g^{-1} h^{-1})	R^2
Nitrate	**1.3**	0.316	0.9972	0,942	0.833	0,8022	0,654	0,9805
	5.0	-	0.0485	n.c.	0.920	2.172	n.c.	0.9914
	7.0	-	0.0246	n.c.	0.612	2.511	n.c.	0.9948
Cr(VI)	**1.3**	0.0280	0.8099	701	0.0209	0,0226	0,306	0,9998
	5.0	0.0599	0.9972	216	0.0234	0.0250	0,118	0.9990
	7.0	0.0466	0.9896	417	0.0237	0.0250	0,234	0.9997
Pb	**1.3**	0.145	0.9833	31,4	0.0234	0,0233	0,0172	0,9542
	5.0	0.182	0.9905	112	0.0250	0.0249	0,0700	0.9983
	7.0	0.020	0.8740	3706	0.0243	0.0250	2,1880	1.000
Zn	**1.3**	0.340	0.986	n.c.	0.0850	0,0250	n.c.	0,9980
	5.0	0.352	0.9881	135	0.0252	0.0250	0,0857	0.9992
	7.0	-	0.7451	26.8	0.0258	0.0250	0,0178	0.9517
Cu	**1.3**	0.326	0.9866	24,2	0.0262	0,0247	0,0166	0,9927
	5.0	0.117	0.9973	36	0.0230	0.0234	0,0190	0.9731
	7.0	-	0.4549	86.3	0.0207	0.0232	0,0370	0.9890

[a)] initial adsorption rate calculated from $h=k_2q_e^2$.

n.c.= not calculated, since q_e calculated is very different from q_e experimental

Table 4. Performance and environmental impact of the substrate at different S/L ratios

Species	**S/L**				**polluted aqueous phase features**
	1/5	**1/25**	**1/50**	**1/250**	
	(% removal or mgL^{-1} released)				pH 5.0
SO_4^{2-} (mg/L)	43460	13290	11050	5960	300 mg/L
NO_3^- (% removal)	8%	9%	-	15%	1500 mg/L
Cr (% removal)	99.4%	99.1%	98.7%	97.2%	5 mg/L
Pb (% removal)	100%	100%	100%	98.2%	5 mg/L
Zn (% removal)	100%	100%	100%	61.6%	5 mg/L
Cu (% removal)	93.2%	90.2%	91.8%	66.4%	5 mg/L
Fe (mg/L)	212.9	42.0	17.7	2.2	-
Mn (mg/L)	4.5	1.5	1.1	0.5	-

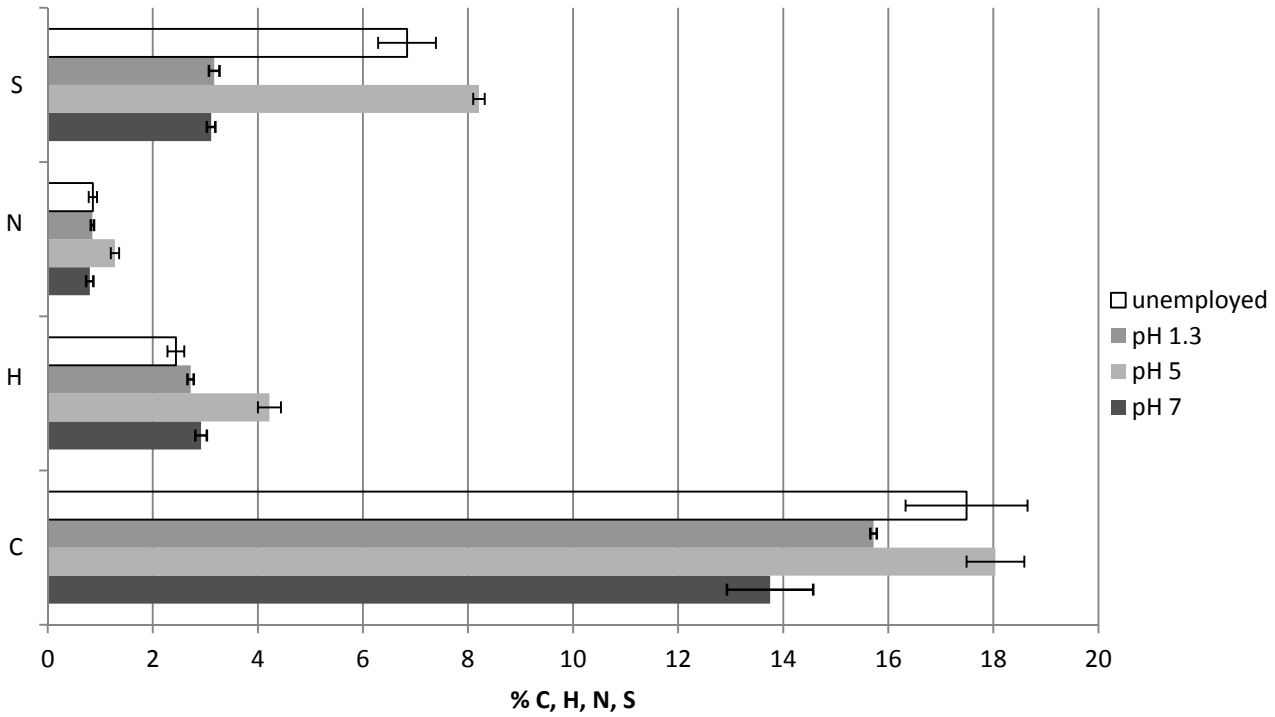
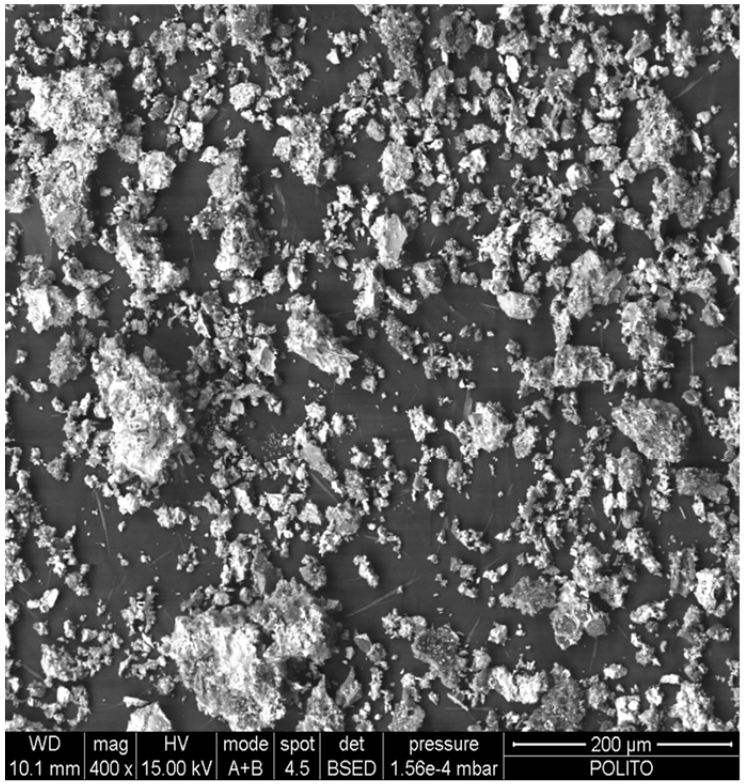
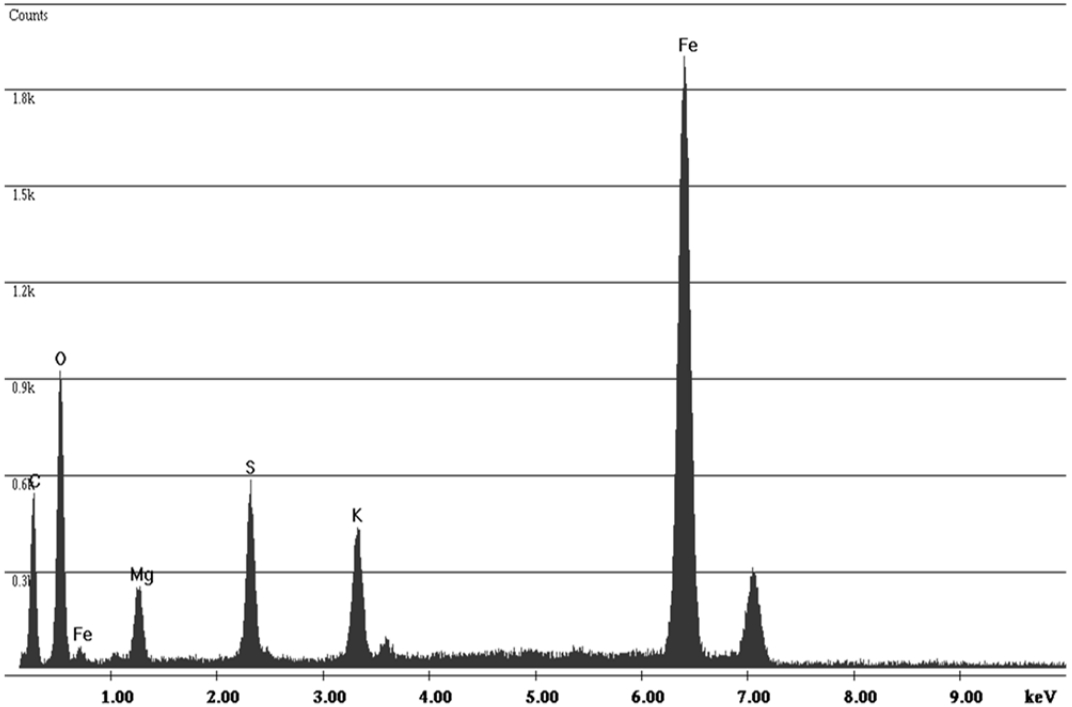


Figure 1. Elemental analysis of the substrate: unemployed and after the batch tests.



(A)



(B)

Figure 2. SEM/EDS analysis of the unemployed substrate: A) morphology, B) qualitative analysis

Figure 3. SEM/EDS images of the substrate after the kinetics tests: A) morphology, B) qualitative analysis on oxidized iron and on metallic and corrosion products (C)

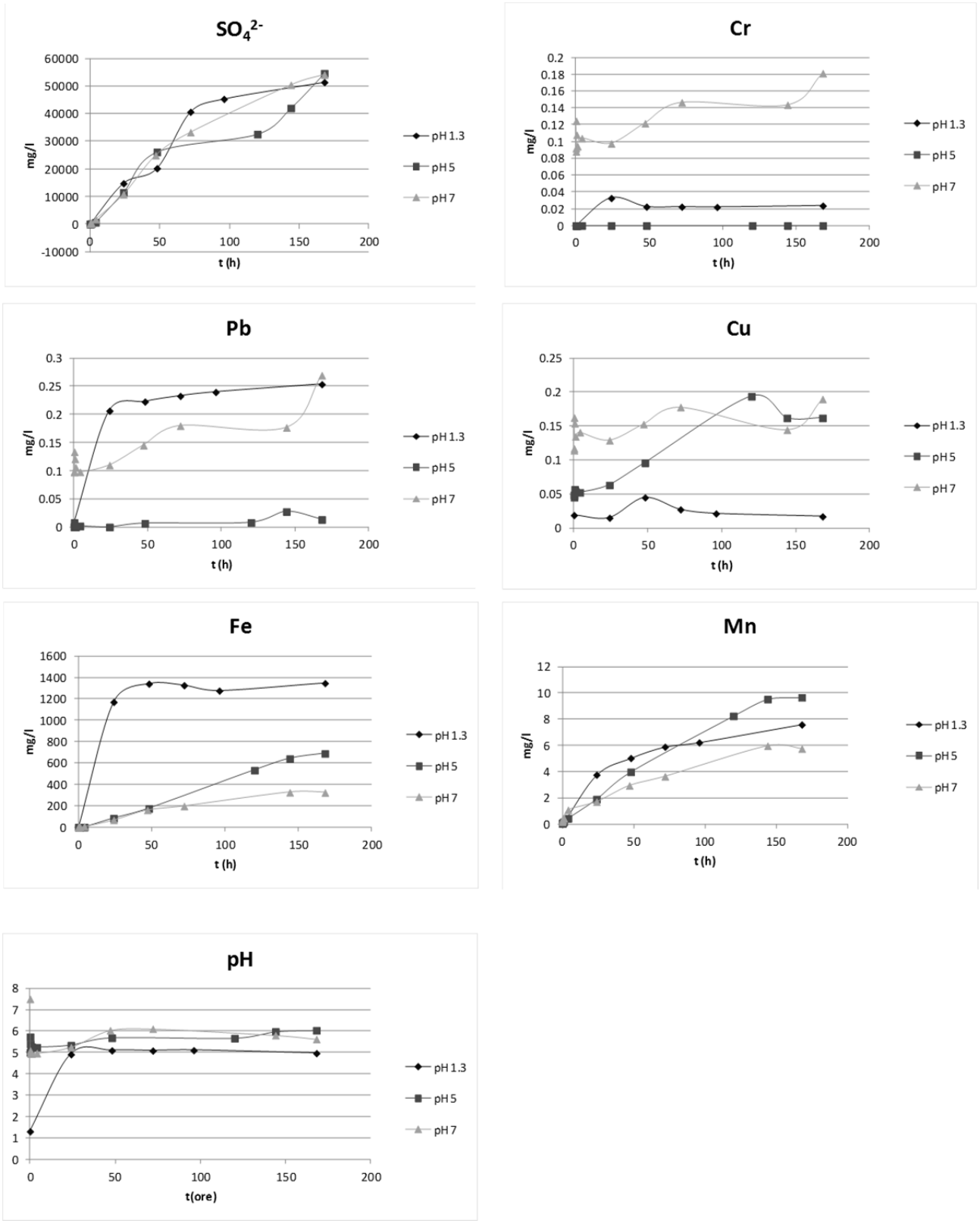


Figure 4. Evaluation of the leaching potential and pH trend of the unemployed substrate (controls) in high purity water

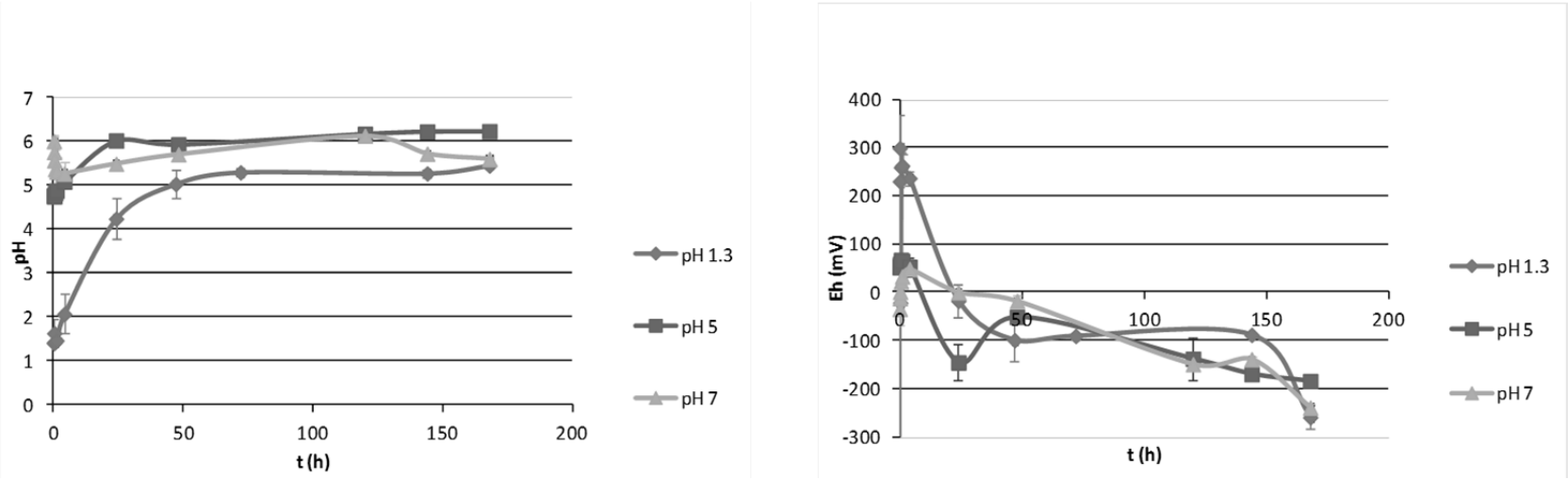


Figure 5. pH (a) and redox potential (b) trends caused by the substrate in the polluted aqueous phase

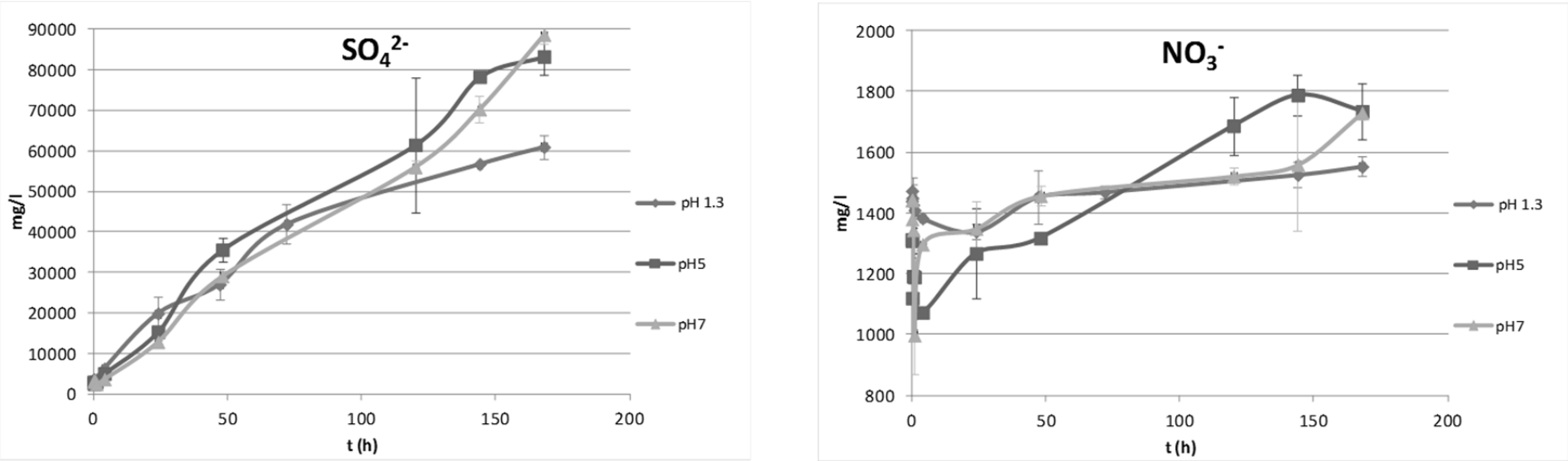


Figure 6. Sulfates and Nitrates trends caused by the susbtrate in the polluted aqueous phase.

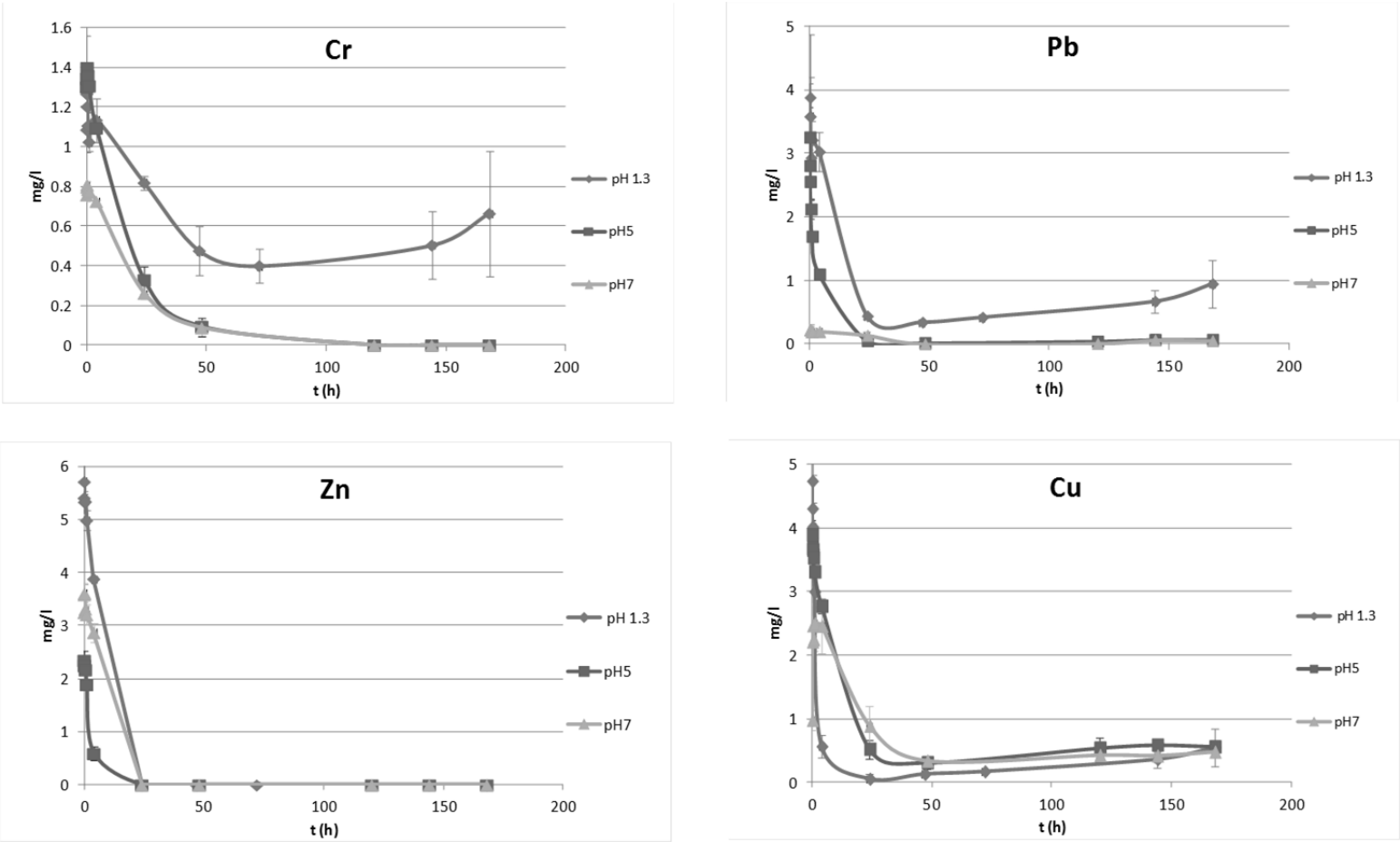


Figure 7. Removal of Cr, Cu, Pb and Zn by the substrate at different pH values of the polluted aqueous phase

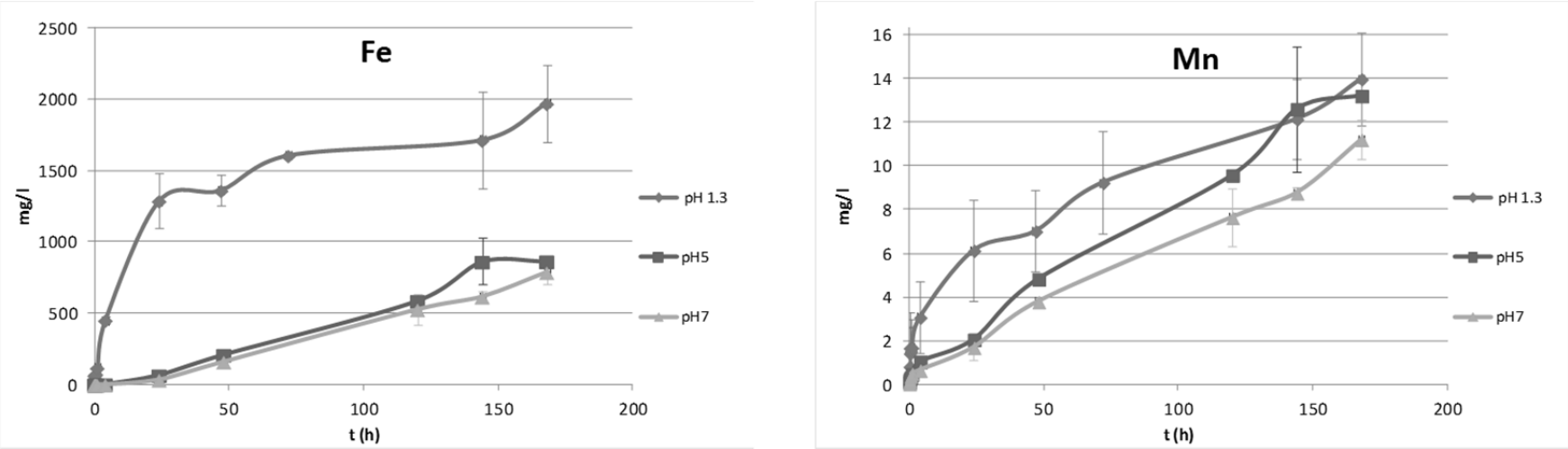


Figure 8. Release of Fe and Mn caused by the substrate in the polluted aqueous phase.