nZVI particles production for the remediation of soil and water polluted by inorganic Lead

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Abstract

The present study deals with experiments of Pb removal by nano-Zero Valent Iron (nZVI) in aqueous solution and in soil. Synthetic Pb aqueous solutions were treated by nZVI, at a fixed Pb concentration of 100 mg L^{-1}, varying nanoparticles initial concentration in the range between 27 and 270 mg nZVI L^{-1}. A kinetic study was carried out: Pb adsorption followed a first order kinetic, and half life times between 11 and 26.66 min were determined. Soil samples were first characterized, and Pb speciation and concentration by sequential extractions was determined. Adsorption tests were then carried out at three selected amounts of nZVI, to allow Pb stabilization in the soil matrix. To evaluate the treatment efficiency, sequential extractions were also performed on the treated samples.

Keywords: nZVI, soil-remediation, groundwater-pollution, adsorption.

1. Introduction

The removal of heavy metals, such as mercury, lead, chromium and arsenic, from natural water has become a technical challenge due to very low concentrations permitted by current regulations: the U.S. EPA action level for Pb(II), for instance, is 0.015 mg L^{-1} (Nordberg *et al*., 2014). In the last century, the continuous disposal of wastewaters in the natural water bodies and the uncontrolled pollution of several areas around the earth surface, caused a significant environmental pollution (Forstner and Wittmann, 2012). In particular, the main anthropogenic pathway through which Lead enters aquatic and terrestrial environments is corrosion of household plumbing, effluents from lead smelters, battery manufacturers, mining and many other industries (Deshommes *et al*., 2010). Among the several technologies developed for the remediation of wastewaters and groundwaters from heavy metals (such as precipitation, ultra-filtration, electrode-deposition, reverse osmosis etc.) adsorption is shown to be economically favorable and technically easy (Fu and Wang, 2011). The removal of a heavy metals using magnetic materials has proved to be more selective and efficient due to its remarkable physical properties (Ge *et al*., 2012). Zero-Valent Iron nanoparticles (nZVI) represents a cost-effective solution to the most demanding environmental remediation problems (Vilardi and Di Palma, 2016). This valuable nanomaterial is characterized by large specific surface area and high chemical reactivity which grants remarkable sorption/reduction capacity towards several inorganic and organic pollutants (Grieger *et al*., 2010). In particular, nZVI has been proved to be very efficient for the adsorption of heavy metals. As regards Lead (Pb) pollution, the soprtion capacity of nZVI towards this heavy metal has already been demonstrated, but the sorption mechanism has not been deeply investigated yet (Liu *et al*., 2009). Xi and co-authors for example, reported that after the reaction with Pb(II) the morphology of nZVI surface changed and the chain-like morphology was replaced with flakes/aggregates (Xi *et al*., 2010). The authors stated that the production of elemental Pb and Pb oxides, through redox reactions with nZVI, produced this modification. Considering heavy metal pollution in soil, it is well known that high concentrations of heavy metals in soils may cause long-term risks to ecosystems and humans (Alloway, 1995). Soils receive significant amounts of heavy metals such as Cd, Cu, Pb, and Zn from traffic, smelting activities, dust deposition from fossil fuel combustion, industrial activities and waste disposal (Wuana and Okieimen, 2011). In order to remediate contaminated soils, a wide array of techniques have been proposed (Farrell *et al*., 2010). The remediation techniques of heavy metals in soils include physical remediation, chemical remediation, phytoremediation, and agro-ecological engineering techniques (Akpor and Muchie, 2010). Physical remediation technologies based on the excavation, removal, washing, and landfilling of metal contaminated soils are highly effective at lowering risk, but are very expensive to implement. Although phytoremediation, has received major attention due to its simple application and low-cost, the down-side of this technology is the very low efficiency. Among these technologies, the stabilization of heavy metals by inorganic materials has already been investigated and in particular the use of nZVI for the stabilization of Pb in soil has already proved high efficacy (Wang *et al*., 2014). In this work both polluted soil and water were treated with nZVI, prepared by means of a spinning disk reactor (SDR). The kinetic study was also reported.

2. Materials and Methods

2.1 Materials

The analytical grade chemical reagents used in the experiments ($FeSO_4 \cdot 7H_2O$, Pb^{2+} in stock solution, $MgCl_2$,

CH$_3$COONa, CH$_3$COOH, NH$_2$OH*HCl, H$_2$O$_2$, HClO$_4$, HCl, HNO$_3$, CMC-Na and NaBH$_4$) were purchased from Sigma-Aldrich (Milan, Italy) and were used without further purification.

2.2 Synthesis and experimental procedure

nZVI-particles were synthesized by reduction of iron sulfate heptahydrate (0.04 M) with sodium borohydride (0.08 M). Carboxy-methyl cellulose was used as a dispersing agent in the ratio CMC/Fe^{2+}=0.005 (mol/mol) according to previous studies (He *et al*., 2007). All solutions were prepared in deionized water (DI). Nanoparticles synthesis was carried out by means as reported in previous work (Di Palma *et al*., 2015). A solution of 1 g nZVI L^{-1} was produced. No buffer system was used during the preparation or during the experiments. The stabilization experiments were carried out on several soil samples collected at an industrial site in Northern Italy (plating and steel industries). In brief the experimental procedure consisted of preparing nZVI-soil slurries, by using three different concentration of nZVI (70, 140 and 280 mg nZVI L^{-1}), added on to 20 g of soil, to obtain a Fe(0)/Pb(II) molar excess equal to x5, x10 and x20 respect to the stoichiometric ratio according to the following equation:

$$Fe(0) + Pb(II) \rightarrow Fe(II) + Pb(0) \qquad (1)$$
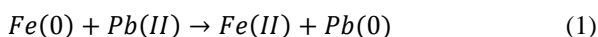
The Liquid/Solid ratio was fixed to 10, as already optimized in previous studies (Gueye *et al*., 2016). At selected times (1, 15 and 30 days) a slurry sample was withdrawn and sequential extractions to evaluate Pb speciation were performed (Gil-Diaz *et al*., 2014), as well as pH measurement. According to Tessier *et al*., (1979), the exchangeable fraction is represented by the water soluble fraction (WSF) and Carbonated associated fraction (CAF), the reducible fraction is represented by the Oxide (iron and manganese) associated fraction (OAF), whereas the oxidizable one is represented by the Organic bounded fraction (OBF) and the residue (bounded to minerals and no-extractable) is represented by the Residual fraction (RF). The organic content was measured using a Shimadzu Total Organic Carbon Analyzer instrument. Soil pH was determined by dissolution in a 0.01 M CaCl$_2$ solution, according to Italian standards (The Ministry of Agricultural, Food and Forestry Policies, 1992). The kinetic batch studies involved five sets of 100 mg L^{-1} Pb^{2+} solutions at pH=5. The tests were carried out at selected nanoparticles amount (27, 54, 81, 135, 270 mg nZVI L^{-1}, corresponding to a Fe(0)/Pb(II) molar excess equal to x1, x2, x3, x5, x10 with respect to the stoichiometric ratio). The flasks were mixed mechanically with a stirring plate at 100 rpm for 1440 min. The concentration of Pb^{2+} in the supernatant solution, after separation by means of a centrifuge (10000 rpm, 10 min), was determined at 1, 10, 20, 30, 45, 60 and 1440 min, using a Agilent AA DUO 240 Fs instrument (Flame Atomic Absorption Spectrometry, FAAS). Each test was carried out in triplicate: the mean value and the standard deviation are reported.

3. Results and Discussion

3.1 Soil characteristics

In Table 1 the characteristics of soil are reported, as well as Pb speciation in soil.

Table 1. Characteristics of soil sample.

| Parameter	Value	Limit for civil reuse (mg/kg)	Limit for industrial reuse (mg/kg)
pH	6±0.1	-	-
TOC (g kg^{-1})	13.4±0.13	-	-
WSF (mg Pb kg^{-1})	144.34±2.4	-	-
CAF (mg Pb kg^{-1})	121.21±1.9	-	-
OAF (mg Pb kg^{-1})	55.57±0.8	-	-
OBF (mg Pb kg^{-1})	109.2±1.3	-	-
RF (mg Pb kg^{-1})	89.32±1.7	-	-
Total (mg Pb kg^{-1})	519.64±8.2	100	1000

Both total Pb concentration (519.64 mg Pb kg^{-1}) and TOC (Total Organic Carbon, 14.4 g kg^{-1}) were significantly high. In particular, the TOC revealed the presence of natural organic matter, such as humic and fulvic acids, which are able to create a complex with heavy metals like Pb. This could explain the remarkable amount of Pb bounded to organic matter in the OBF (> 100 mg Pb kg^{-1}). Regarding the other fractions, Pb amount in the exchangeable fractions (WSF and CAF) was very high compared to the amount found in other studies (Wang *et al*, 2014). This could be attributed to the low soil pH: slight acidic conditions may in fact favour metal solubilization from the soil matrix (Tills and Alloway, 1983).
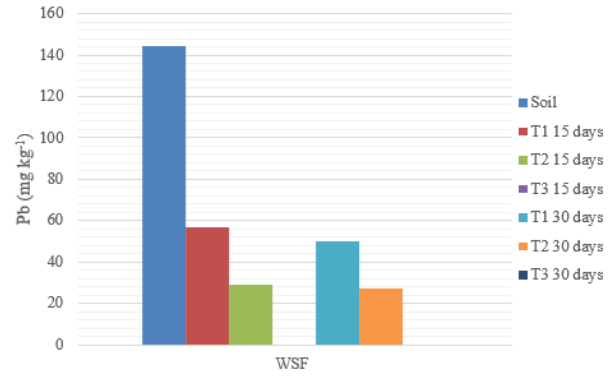
3.2 Stabilization experiments

The effects of nZVI application on Pb availability in the soil was investigated comparing its distribution in the different soil fractions obtained by the sequential extraction procedure. Figure 1-5 show the amount of Pb retained in each untreated soil fraction, compared with that measured for the nZVI-treated soil (after 1 day of treatment). In the graphs T1, T2 and T3 represent the soil samples loaded by 70, 140 and 280 mg nZVI L^{-1}, respectively.
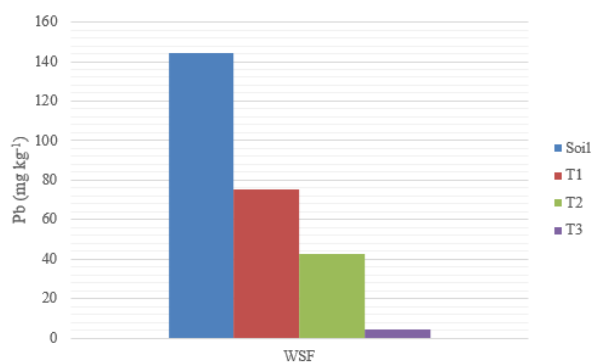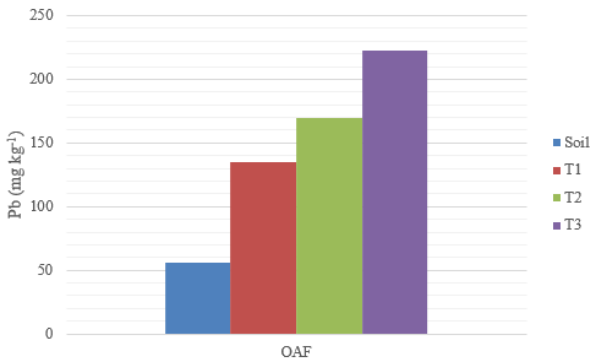

Figure 1. Comparison of stabilization results on WSF (1 day).
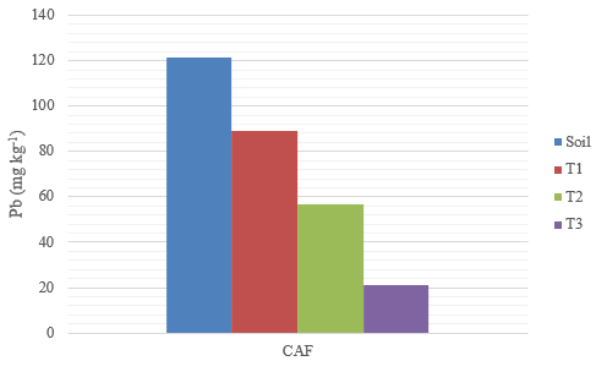
Figure 2. Comparison of stabilization results on CAF (1 day).

Figure 3. Comparison of stabilization results on OAF (1 day).

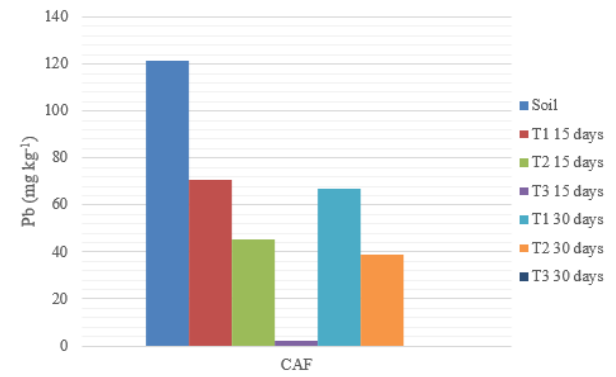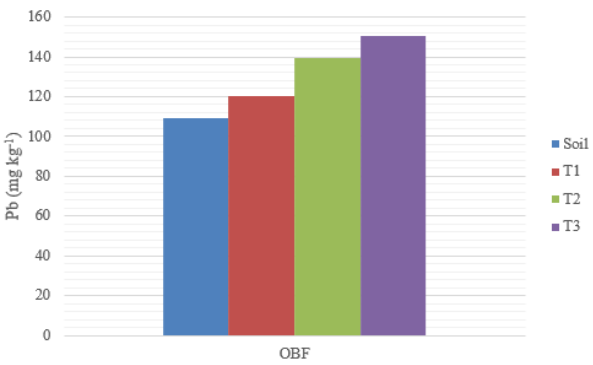**Figure 4.** Comparison of stabilization results on OBF (1 day).

Figure 5. Comparison of stabilization results on RF (1 day).

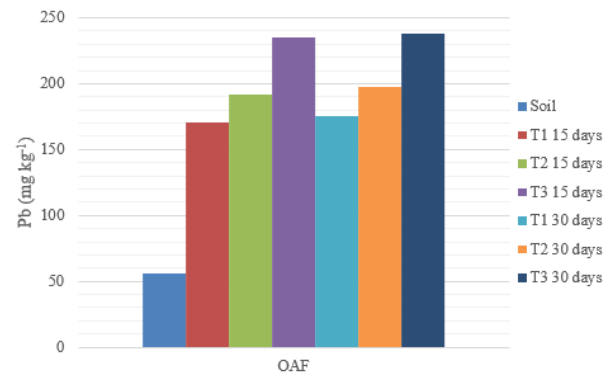**Figure 6.** Comparison of stabilization results on WSF (15 and 30 day).

Figure 7. Comparison of stabilization results on WSF (15 and 30 day).

Figure 8. Comparison of stabilization results on WSF (15 and 30 day).

Figure 9. Comparison of stabilization results on WSF (15 and 30 day).

Figure 10. Comparison of stabilization results on WSF (15 and 30 day).
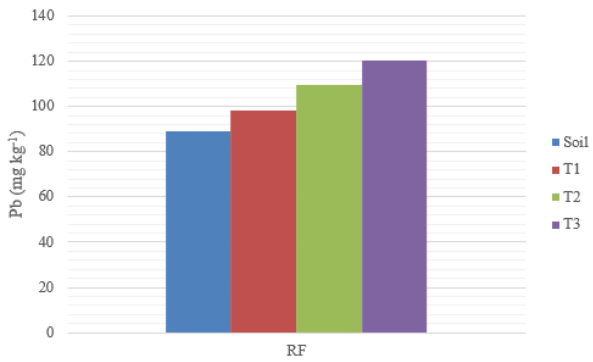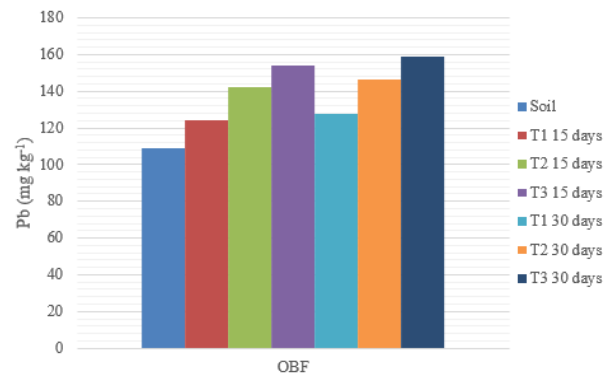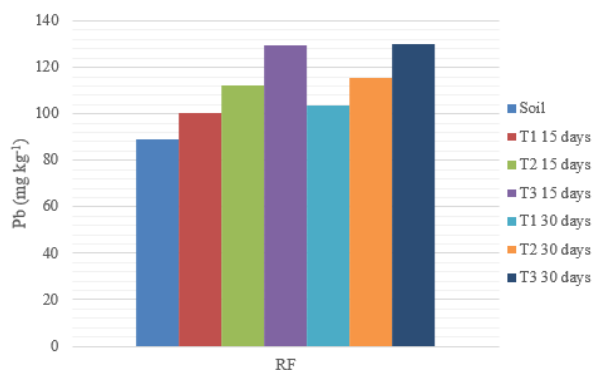
An increase in Pb immobilization was always detected; the amount of Pb associated with the more easily available fractions (WSF and CAF) generally decreased, whereas Pb amount associated with the less available fractions (OAF, OBF and RF) increased. In particular, the WSF decreased by 47.8, 70.5 and 97%, in T1, T2 and T3, respectively, and the CAF underwent a similar decrease. As a consequence, OAF increased by 1-3 fold, depending on the nZVI amount, whilst RF increased by more than 100% in T3; indeed, the OBF also increased. Such behaviour could be due to Pb(II) complexation by CMC, which was negatively charged and, therefore, it was able to attract and bind metal cations. In order to evaluate the time-stability of the treatment, two further sequential extraction were carried out after 15 and 30 days , and the results are shown in Figure 6-10. The stabilization reactions always proceeded after the first day of treatment; in fact, as regards the exchangeable fraction, a further reduction was observed (WSF reached 27 mg Pb kg^{-1} for T2 and 0 mg Pb kg^{-1} for T3, whereas CAF was reduced of another 50% for T1 and reached 0 mg Pb kg^{-1} for T3) and the remaining fractions increased. Another remarkable result was that the difference among the data obtained after 15 and 30 days, were negligible, for all the treatments. This indicated that prolonging the treatment did not determine a further soil stabilization. Similar results were reported in previous studies, dealing with As (Zhang *et al*., 2010) and Pb/Zn stabilization (Gil-Diaz *et al*., 2014).

3.3 Removal of Pb in aqueous solution

Figure 11 shows the results obtained in the tests performed on synthetic wastewater at an initial Pb =100 mg L^{-1}.
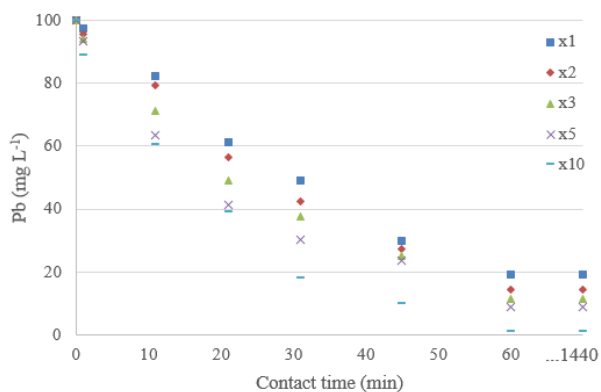
Figure 11. Comparison of Pb removal varying the initial nZVI amount.

As expected, the Pb removal efficiency increased with Fe(0)/Pb(II) molar ratio. In particular, for the stoichiometric amount a removal efficiency of about 80% was obtained after 60 min of treatment, whereas an almost total removal (about 99%) was obtained for Fe(0)/Pb(II) = 10. The experimental data were then fitted by a first order kinetic model. Data were linearized according to the following equation:

$$\ln\left(\frac{Pb}{Pb_0}\right) = -kt \qquad (2)$$

where Pb_0 is the initial Pb concentration (mg L^{-1}), k (min^{-1}) is the kinetic constant and t (min) is the contact time. In Table 2 the obtained kinetic parameters are reported. R^2 is the linear correlation factor, whereas $t_{1/2}$ (min) is the half-time, obtained by the following equation:

$$t_{1/2} = \ln(2)/k \qquad (3)$$

Table 2. Kinetic parameters

Fe(0)/Pb(II)	R^2	k (min^{-1})	$t_{1/2}$ (min)
x1	0.99	0.026	26.66
x2	0.99	0.030	23.11
x3	0.99	0.034	20.39
x5	0.98	0.038	18.24
x10	0.94	0.063	11.01

The R^2 (always larger than 0.9) values validate the fitting goodness. As regards the k and $t_{1/2}$ values, they were in agreement with the theoretical expectations: k values were in fact proportional to the amount of nZVI used, whereas the $t_{1/2}$ was found to be inversely proportional to such parameter.

4. Conclusions

This study reports on the effectiveness of ZVI nanoparticles in the stabilization of Pb in soil and in the removal of Pb(II) in synthetic wastewaters. Regarding the stabilization of Pb in soil matrix, the obtained results demonstrated Pb immobilization by nZVI. A significant decrease of Pb exchangeable fractions (WSF and CAF), determined by sequential extractions, was generally obtained when a large excess of nanoparticles was used with respect to the stoichiometric amount. A complete stabilization was achieved by adding a nZVI amount equal to 20-fold the stoichiometric amount Fe(0)/Pb. The process resulted stable over time (the sequential extractions were carried out also 30 days after the treatment). As regards the Pb removal efficiency from wastewater, more than 80% of Pb was removed in tests performed at stoichiometric ratio between Pb and nZVI, while an almost total removal using a molar ratio Fe(0)/Pb(II) equal to 10 times the stoichiometric value was observed.

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