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Evaluation of the Efficiency of Nanoscale Zero-Valent Iron (nZVI) to Stabilize Heavy Metals in a Calcareous Soil

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With best regards,
Prof. Giancarlo Renella, Conference chair of the 11th ICOBTE

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# Evaluation of the efficiency of nanoscale zero-valent iron (nZVI) to stabilize heavy metals in a calcareous soil

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## Abstract

The effect of iron compounds including micrometric zero-valent iron (ZVI), nanoscale zero-valent iron (nZVI), micrometric iron oxide (IOx) and nanoscale iron oxides (nIOx) and incubation times in changing the availability of heavy metals was evaluated in a calcareous soil contaminated with Cd, Zn, Pb, and Ni. Results showed that DTPA extractable heavy metals significantly decreased in soil treated with ZVI, compared to untreated soil. The mean decrease of Ni, Cd, Zn and Pb was 28%, 32%, 37% and 28% for ZVI and 12%, 0%, 25% and 21% for nZVI, respectively. In contrast, presence of nano and micro iron oxides caused significant increase of DTPA extractable heavy metals in soil except for Ni. Moreover, Ni-DTPA decreased significantly with time whereas it was constant for the other examined elements. In this study, the observed decrease of heavy metals by ZVI was higher than other treatments whereas the stabilization efficiency of nZVI was not significant in the soil.

## Introduction

New discoveries in nanoscience and technology give researchers the opportunity to make nanotechnology applicable to agricultural and environmental science. Soil and water, as the most important components of environment, are widely treated for heavy metal pollution due to ever-increasing demand for food and energy and uncontrolled agricultural and industrial activities. The pollution caused by heavy metals affects the health of people worldwide.

Iron (in zero-valent and oxide forms) is used to remove numerous organic and inorganic contaminants in environment through oxidation-reduction reactions or adsorption and precipitation mechanisms. According to Zhang and Li (2007), nanoscale zero-valent iron (nZVI) has a core-shell structure. The core mainly consists of zero-valent iron which has the reducing power for reactions with environmental contaminants. The shell which is formed from the oxidation of zero-valent iron is mainly iron oxides/hydroxides. Therefore, it provides sites for chemical complexation of metals. Recent studies show that nZVI is more efficient in reducing wide ranges of heavy metals availability in groundwater compared to traditional remediation tools (Zhang and Li, 2006; Ponder et al., 2000). This is due to the multiple mechanisms of ZVI to remove heavy metals, high reactivity and specific surface area of nanoparticles. However, there are few reports on the remediation of heavy metals contaminated soils using nZVI in the literature (Liu and Zhao, 2007; Xu and Zhao, 2007; Zhao and Liu, 2007). Therefore, this experiment was performed to evaluate: i) the effect of iron amendments in nano and micro scale on Ni, Cd, Zn and Pb availability in a calcareous soil, and ii) the effect of different incubation time on the heavy metal availability in a calcareous soil in the presence and absence of iron amendments.

## Materials and Methods

A calcareous soil sample was chosen because calcareous soils are common in Iran. The soil sample was air-dried and sieved to remove the coarse fraction (>2.0 mm) then used for experimentation. The main soil characteristics are given in Table 1. The soil was contaminated with 300, 5,800 and 500 mg kg$^{-1}$ of Ni, Cd, Zn and Pb, respectively (as an aqueous solution of nitrate salts) and was kept at room temperature near field capacity soil moisture conditions for two weeks for equilibration. After being air-dried and homogenized, the soil samples in a randomized complete design with two replications were amended with 0 and 2% iron compounds including micrometric zero-valent iron (ZVI), nanoscale zero-valent iron (nZVI), micrometric iron oxide (IOx) and nanoscale iron oxide (nIOx). After 1, 2 and 4 weeks of the experiment, DTPA-extractable heavy metals in soil (Lindsay and Norvell, 1978) were determined using atomic absorption spectrometry (Shimadzu AA-670). Statistical analysis of data including the Duncan's multiple range test ($p \leq 0.05$) was performed using MSTAT-C software.

*Table 1* Some physico-chemical characteristics of the study soil.

| Parameter | Value | |
|---|---|---|
| Texture | Sandy Loam | |
| pH $_w$ (1:2) | 7.52 | |
| EC$_w$(1:2) dS.m$^{-1}$ | 2.32 | |
| Organic Mater (%) | 0.53 | |
| CaCO$_3$ (%) | 14.80 | |
| Ni (mg.kg$^{-1}$) | 0.40* | 47.80** |
| Cd (mg.kg$^{-1}$) | 0.06* | 1.00** |
| Zn (mg.kg$^{-1}$) | 0.90* | 46.07** |
| Pb (mg.kg$^{-1}$) | n.d$^1$* | 8.60** |

$^1$Not determined; *DTPA-extractable; **Total concentration.

## Results and Discussion

The results showed that DTPA extractable heavy metals significantly decreased in soil treated with ZVI, compared to untreated soil. However, such a behavior was not observed for Cd in nZVI treated soil. The significant decrease in DTPA-Ni and DTPA-Pb was probably due to both sorption and reduction mechanisms with ZVI. Low efficiency of iron oxide compared to ZVI in Ni immobilization may be related to the fact that iron oxides have no reducing capacity for metal ions, thus it seems that the removal mechanism is just surface adsorption. Moreover, it is expected that Zn and Cd were immobilized on ZVI surface by sorption and complex formation (Zhang and Li, 2007). In contrast, the presence of iron oxides caused significant increase in DTPA extractable heavy metals in soil except for Ni. However, there were no significant differences between iron oxide treatments (in both micro and nano scales). Since the iron oxides obtained from acid washed steel processing containing hydrochloric acid, they may induce local decrease in soil pH leading to an increase in heavy metals availability. Table 2 shows mean efficiency of the iron amendments for decrease DTPA extractable heavy metals in the soil during the whole incubation time.

*Table 2* Mean efficiency of iron amendments applied to decrease DTPA extractable heavy metals in the soil.

| Amendment | Ni (%) | Cd (%) | Zn (%) | Pb (%) |
|---|---|---|---|---|
| ZVI | -28 | -32 | -38 | -28 |
| nZVI | -12 | 0 | -25 | -21 |
| IOx | 0 | +43 | +82 | +10 |
| nIOx | -12 | +43 | +82 | +10 |

(-): Decrease; (+): Increase

Effect of different incubation times on DTPA extractable heavy metal was not significant except for Ni. DTPA-Ni appeared to decrease with time in soil with and without iron amendments whereas the DTPA extractable Cd, Zn and Pb in all treatments was constant during incubation time. Although it is well documented in the literature that the calcareous nature of the soil plays a key role in the heavy metals immobilization, our results did not support such a finding. It appears that the decrease in Cd, Zn and Pb availability was probably due to the presence of ZVI amendments and therefore the role of soil carbonate fraction was not significant or was masked by ZVI in the current research.

Unexpectedly, in this study, the observed capacity for heavy metal decrease by ZVI was higher than nZVI. It seems that nZVI have limited lifetime in the soil media. As Tratnyek and Jahnson (2006) described, high reactivity of nZVI originates from its small size preparing nZVI to be involved in non-target reactions. This may explain lower metal decrease efficiency of nZVI in comparison to ZVI.

## Conclusions

The results found in the current investigation have some implications for the application of nZVI as a promising tool in the amelioration of contaminated soils. The best immobilization efficiency was achieved by ZVI whereas the efficiency of nZVI was not significant in the soil. Moreover, Ni-DTPA decreased significantly with time whereas it was constant for the other elements examined. Compared to the reducing effect of ZVI both in micro and nano scale, application of iron oxides significantly increased availability of heavy metals except for Ni. This behavior may be related to the acidic properties of the iron oxides which caused local decrease in the soil pH leading to an increase in heavy metal solubility.

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