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Nano-scale Zero Valent Iron (nZVI) Treatment of Marine Sediments Slightly Polluted by Heavy Metals

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Zero valent iron (ZVI) is an electron donor that is used to reduce or indirectly oxidize several contaminants in soil and groundwater (e.g. halogenated species). The development of stable nano-scale ZVI (nZVI) products has gained a growing interest in environmental remediation with numerous applications all over the world. Several studies addressed both treatment efficiency and ecotoxicological effects of nano-based products for site remediation. However only a few information related to nZVI use for the treatment of marine sediments slightly polluted by heavy metals are available. The present study was aimed at evaluating the effectiveness of nZVI treatment for the decontamination of marine sediments polluted by heavy metals, using the commercial product Nanofer 25s. Two kinds of experiments labelled as (i) sediment at low dosage (2, 3 and 4 g nZVI per kg of SS) and (ii) sediment at high dosage (5, 10 and 20 g nZVI for every kg SS) were performed on sieved sediment with a size < 5 mm. The optimal amount of nZVI to be potentially used for sediment reclamation was identified. According to results, nZVI is more suitable to be used for specific elements removal rather than to be applied for a generalised contamination, meaning that a mix of techniques can be suggested for whole sediment remediation.

1. Introduction

Sediment tends to accumulate inorganic contaminants representing one of the main sinks and sources of pollution (Gomes *et al.*, 2013). As a result, remediation of contaminated sediments has raised a great deal of scientific and public concern around the world, representing a significant actual challenge both under a technical and technological point of view (Lofrano *et al.*, 2017).

Sediment management strategies may involve non removal options as monitored natural recovery (De Gisi *et al.*, 2017), in-situ capping, and removal options, such as dredging with containment, and dredging with sediment treatment (Lofrano *et al.*, 2017). In situ remedial alternatives generally involve the only capping or the combination of capping and adsorption (Erto *et al.*, 2009, 2015). Ex situ remedial alternatives typically require a number of component technologies to remove, transport, pre-treat, treat, and/or dispose sediments and treatment residues.

Recently nanotechnology has emerged as an efficient, cost effective, environment friendly and promising technology for soil remediation (Lofrano *et al.* 2017; Adamaki *et al.* 2016; Wang *et al.* 2016). Zero valent iron (ZVI) is an electron donor that is used to reduce or indirectly oxidize several contaminants in soil and groundwater. The development of stable nano-scale ZVI (nZVI) products gained a growing interest in environmental remediation with numerous applications all over the world. It is among the most abundant metals of the earth and hence the adsorbents prepared from this metal could be very cost effective. Additionally, iron metals are non-toxic in their elemental form and hence they are environmentally friendly, and no special account should be taken for their application in the soil contaminated site (Rabbani *et al.*, 2016). Zero-valent iron nanoparticles are strong reducing agent and very good adsorbents for various pollutants (Cundy *et al.*, 2008). They are widely used to remove heavy metal from soil and groundwater such as mercury

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(Hg), nickel (Ni), cadmium (Cd), lead (Pb) and chrome (Cr) from contaminated soil. The key mechanisms involved in heavy metal removal by nZVI are adsorption and reduction. Heavy metals are converted to less toxic species, immobilized or become less available in soil (Cundy *et al.*, 2008; Li *et al.*, 2006).
The reaction mechanism occurring between metal contaminant and zero-valent iron depends on the standard redox potential (E^0) of the heavy metal. Heavy metals such as Cd and zinc (Zn) which have more negative E^0 value than ZVI nanoparticles or similar E^0 value to ZVI nanoparticles are being adsorbed on iron shell. On the other hand, heavy metals with much more positive E^0 value than ZVI nanoparticles are reduced and precipitated in soil. Heavy metals (Pb, Ni) with slightly positive E^0 value than ZVI nanoparticles (Cr, As, Cu) are reduced and also adsorbed on ZVI nanoparticles (Sun et *al.*, 2017).
Laboratory investigations showed how nZVI is capable of degrading chlorinated organic compounds, being particularly effective in removing heavy metals and radioactive nuclides (Cecchin *et al.*, 2017). Several studies addressed both treatment efficiency and ecotoxicological effects of nano-based products for site remediation. However only a few information related to nZVI use for the treatment of marine sediments slightly polluted by heavy metals are available.
The present study was aimed at evaluating the effectiveness of nZVI treatment for the decontamination of marine sediments polluted by heavy metals, using the commercial product Nanofer 25s (NANOIRON s.r.o., Czech Republic). Two kinds of experiments labelled (i) sediment at low dosage (2, 3 and 4 g nZVI per kg of SS) and (ii) sediment at high dosage (5, 10 and 20 g nZVI of for every kg SS) were performed in order to determine the optimal amount of nZVI to be potentially used for sediment reclamation.

2. Materials and methods

2.1 nZVI slurry

nZVI particles (Nanofer 25S) were produced from nanosized ferrihydrite from the NANOIRON Company (Czech Republic, EU). Nanofer 25S consisting of nZVI coated to polyacrylic acid (PAA) was provided in aqueous suspension at pH = 11 (Table 1).

Table 1: Main characteristics of the Nanofer 25S in accordance to the EC No. 1907/2008.

Slurry composition	
Component	Weight (%)
Fe	14 – 18
Fe_3O_4	2 – 6
C	0 – 1
H_2O	77
Surfactant	3
Chemical-physical characteristics	
Physical aspect	Liquid
Colour	Black
Grain size	d50 < 50 nm
Specific surface area	> 25 m^2/g
Density	1.15 – 1.25 g/cm^3 (at 20°C)
Surface charge	Zero (0)
Odour	Odourless
pH	11 - 12
Stability and reactivity	
Reactivity	A limited volume of hydrogen (< 1l/kg/h) is generated in contact with water
Chemical stability	The product is stable under the specified storage conditions
Possibility of hazardous reactions	No possibility
Conditions to avoid	Avoid contact with the air, high temperatures, flames or ignition sparks
Incompatible materials	Oxidizing agents and acids
Toxicological information (Acute toxicity of the components)	
LD50 for ingestion (rats)	30,000 mg/kg
LD50 for dermal contact (rats or rabbits)	Not tested
Ecological information (Acute toxicity of the product)	
LC50 (96 hours, fishes)	12.4 g/l
EC50 (48 hours, *daphnia magna*)	55.2 g/l
IC50 (72 hours, algaes)	4.5 g/l

The mean primary diameter of all the particles (as stated by the producer) was 50 nm; the total iron content was about 80 - 90 wt. %, and the Brenauer–Emmett–Teller (BET) specific surface area was 20–25 $m^2\ g^{-1}$.

Due to the narrow size distribution of nanoparticles and sophisticated stabilization process, the product exhibits a high reactivity with a large scale of pollutants and very low degree of agglomeration, which implies excellent migration and sedimentation properties. The nZVI dosing range was performed by comparing the concentration of pollutants present in sediment and those reported in literature.

2.2 Marine sediments

Sediments samples were collected from the Gulf of Taranto in Southern Italy. The initial moisture content of sediments was 45.9%. The loss in weight, measured by the ignition method at 600°C, was 8.7%. The organic matter and volatile materials lead to the smaller density and the loss in weight for marine sediments.
Finally, the particle size analysis showed a content of silt and sand of 31.8% and 68.2%, respectively (on a dry mass basis, determined by wet sieving and hydrometer tests).

2.3 Experimental plan

Experimental activities were conducted on sieved sediment with a size < 5 mm.
Each sediment sample was treated following the subsequent three steps: (i) Sediment dry weight measurement and extraction of fine fraction; (ii) Addition of Nanofer 25s; (iii) Determination of heavy metal concentrations
In the first step sediment samples were dried for 24 h into a muffle, then pulverized and homogenized in a porcelain mortar; finally, they were sieved (5 mm). The fine fraction was weighed and mixed with distilled water (DW) to hydrate the sample according to the 2:1 proportion, 200 ml DW per 100 g dry matter (SS).
In the second step the nZVI was added under a continuous flux of N_2, to avoid its premature oxidation, and mixed with Rotax for 24 h at 12 rpm, at room temperature. Treatments with nZVI included 2, 3 and 4 g per kg of SS in the case of low dosages and 5, 10 and 20 g per kg of SS in the case of high dosages. The dosages were chosen on the base of previous tests with the goal of optimize the chemical reaction, so reaching the maximum pollutant reduction with the minimal reagent consumption.
The third step involved the determination of heavy metal concentrations in the supernatants. Each supernatant was collected and then filtered at 0.45 μm by means of a vacuum system; measurements of pH and conductibility were also performed; finally, 10 ml aliquots of each filtered samples were collected and 200 μl of HNO_3 were added for the analyses ICP-OES. The concentrations of the main elements were determined by Inductively Coupled Plasma Optical - Emission Spectrometr (ICP-OES) (Thermo Scientific, iCAP 7000 series). The concentrations of aluminum (Al), arsenic (As), boron (B), barium (Ba), cobalt (Co), copper (Cu) and nickel (Ni) were also obtained by ICP-OES measurement.
The detection limit of the main elements was 1 μg/l. By-products into the water solution were not investigated.

2.4 Identification of the optimal nZVI dosage

Optimal dosage identification was based on the comparison of the percentage of the individual contaminant removal by varying the nZVI dosage both in the case of low and high dosages. The optimal dosage was the one that maximizes the percentage removal of all contaminants in accordance to the methodology in De Feo *et al.* (2013).

3. Results

3.1 Sediment characterization

The sediment characterization included the determination of the moisture, organic matter and ashes contents as well as the grain size analysis. The sediment was characterized by a moisture content of 45.8% (Table 2). The amount of organic substance, equal to 8.74%, was probably related to different discharges from domestic, agricultural, aquaculture and industrial activities.

Table 2: Moisture content, organic matter and ash content in the sediment.

Parameter	Unit	Test 1	Test 2	Average value	Coefficient of variation (CV)
Moisture content	%	45.82	45.91	45.87	0.10
Organic matter content	%	9.10	8.38	8.74	4.10
Ash content	%	44.62	45.21	44.92	0.66

The ash content, equal to 44.92%, was particularly high suggesting a non-negligible amount of inorganic material in the sediment. The grain size analysis highlighted a high sand content (68.18%) as well as the absence of gravel.

3.2 Efficacy of nZVI treatment

Experimental nZVI provided element-related removal rates from 0% (B) up to 100% (Co) (see Figure 1).

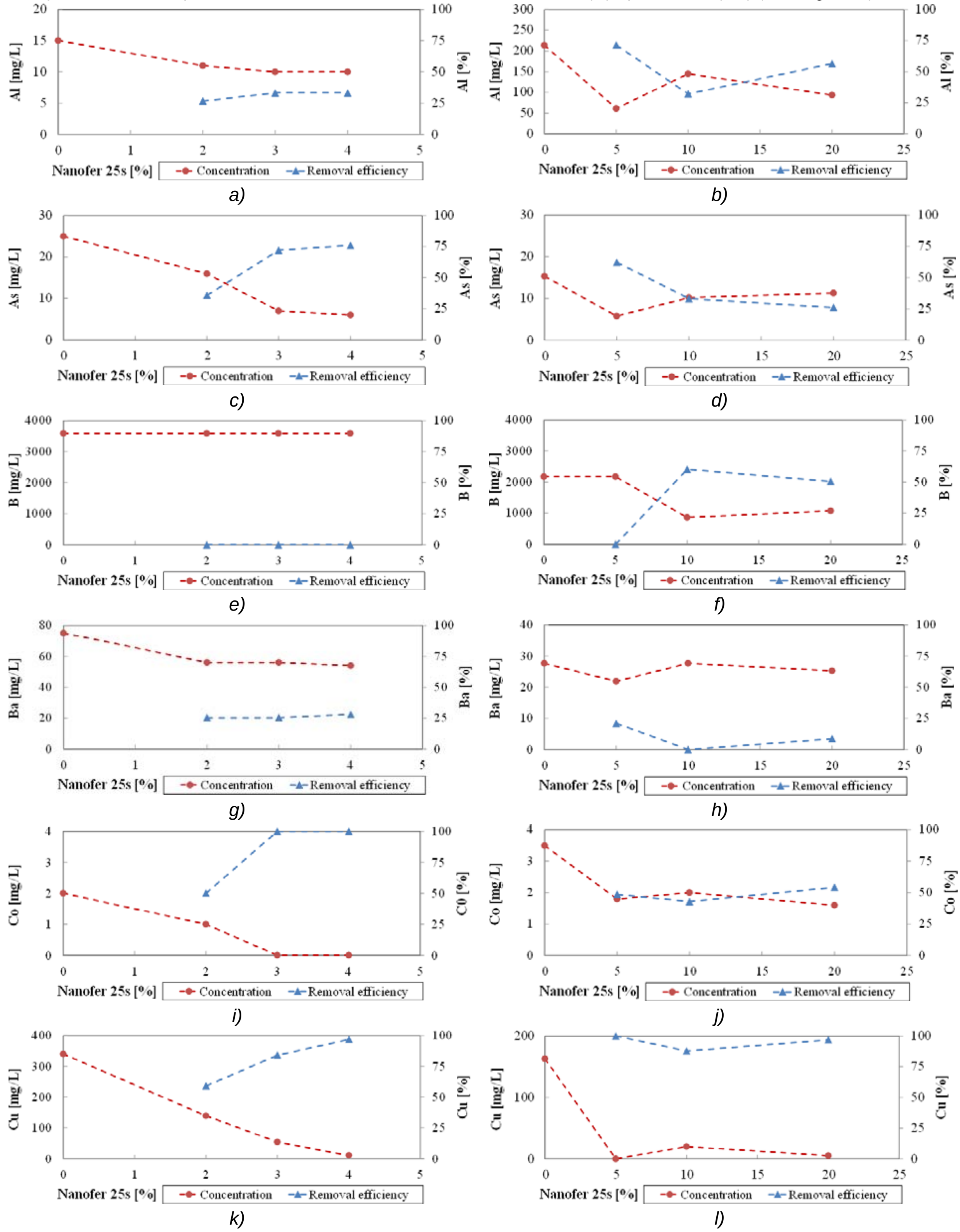
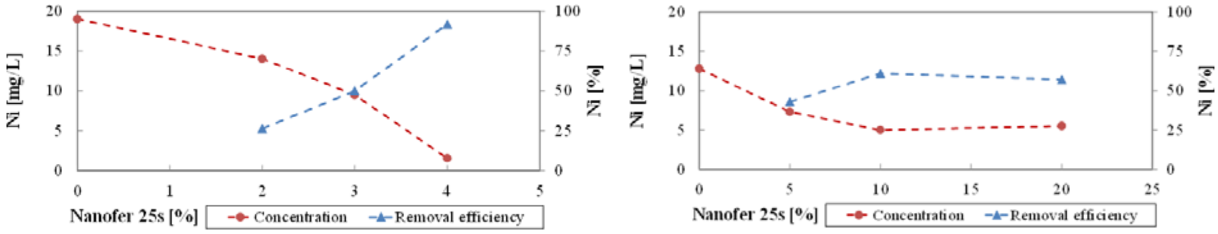


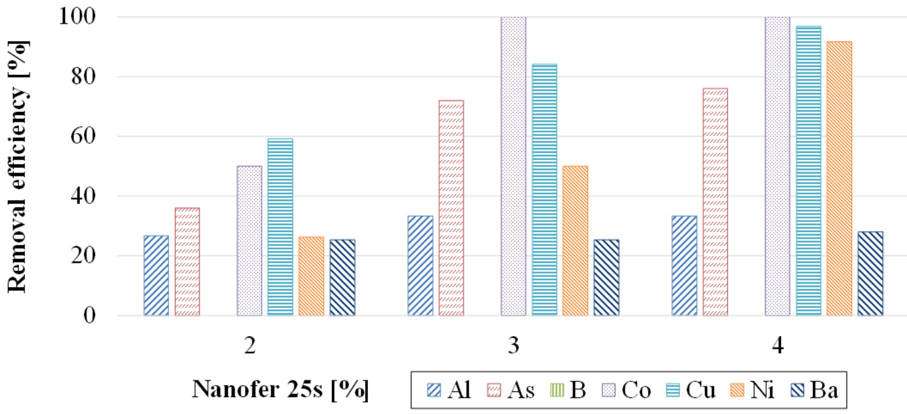
Figure 1: Results of the experimentation having used low (2, 3 and 4%) and high (5, 10, 20%) dosage of Nanofer 25s: (a, b) Al; (c, d) As; (e, f) B; (g, h) Ba; (i, j) Co; (k, l) Cu and (m, n) Ni. (continue)



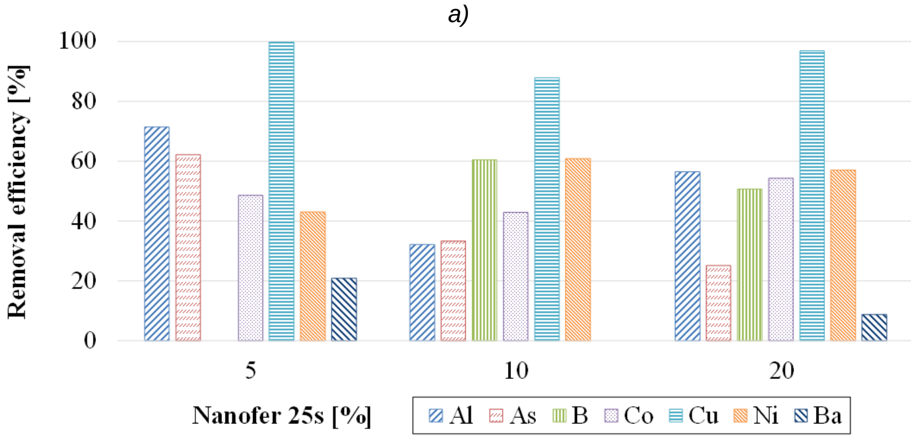
m) n)

Figure 1: Results of the experimentation having used low (2, 3 and 4%) and high (5, 10, 20%) dosage of Nanofer 25s: (a, b) Al; (c, d) As; (e, f) B; (g, h) Ba; (i, j) Co; (k, l) Cu and (m, n) Ni.

At low dosages, the maximum removal was: 100%, at 3 g of nZVI for Co; 33.3%, 76%, 96.8% and 0% at 4 g of nZVI, respectively for Al, As, Cu and B. At high dosages, the maximum removal was: 71.4%, 100% and 62%, at 5 g of nZVI, respectively for Al, Cu and As; 60.4%, at 10 g of nZVI for B; 54.3%, at 20 g of nZVI for Co. The value for Pb was in line with Kim *et al.* (2013) that obtained a removal of more than 96% with reference to 100 mL of solution containing 100 mg Pb(II)/L within 140 min of mixing with 0.1 g Z–nZVI.
According to results, nZVI was more suitable to be used for specific elements removal rather than to be applied for a generalised contamination, meaning that a mix of techniques can be suggested for whole sediment remediation.



a)



b)

Figure 2: Comparative analysis of the obtained results having used low (2, 3 and 4%) and high (5, 10, 20%) dosage of Nanofer 25s.

The need to have good performance in most of the heavy metals in the contaminated sediment led to a comparative analysis of the obtained results. The obtained results showed a dosage of 4% and 5% concentration as the best solution in the case of low and high dosages, respectively.

4. Conclusions

The present study was aimed at evaluating the effectiveness of nZVI treatment for the decontamination of marine sediments polluted by heavy metals, using the commercial product Nanofer 25s. Experimental activities were conducted on sieved sediment with a size < 5 mm and the treatments with nZVI included 2, 3 and 4 g of product per kg of SS in the case of low dosage and 5, 10 and 20 g for kg SS in the case of high dosage. The optimal amount of nZVI to be potentially used for sediment reclamation was selected (4% and 5% in the case of low and high dosages, respectively). According to results, nZVI was more suitable to be used for specific elements removal rather than to be applied for a generalised contamination, meaning that a mix of techniques can be suggested for whole sediment remediation.

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