

Remediation of toxic metal contaminated sediment using three types of nZVI supported materials

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Abstract. For in situ remediation of river sediment the most extensively applied nanoparticle is nano zero valent iron (nZVI). It is due to nZVI properties and effectiveness in the removal of toxic metals as well as low-cost regarding its production. The application of in situ treatment in laboratory conditions with kaolinite, bentonite and carboxymethyl cellulose supported nZVI was demonstrated. Small-scale laboratory studies have shown that the percentage of removed metal (Ni, Zn and Pb) ranged up to 80% depending on the material used for supporting nZVI. A microwave-assisted sequential extraction procedure was employed to assess toxic metal potential mobility and risk to the aquatic environment. In order to evaluate the extraction potential of toxic metals and the effectiveness of the treatment applied, single-step leaching tests were performed (TCLP, DIN and SPLP). In situ treatment in the laboratory proved to be very effective, providing the choice of optimal doses of three different material used for supporting nZVI towards the concentration of toxic metals in the sediment. Generally, nZVI can be an effective and versatile tool for remediation of sediment polluted with toxic metals.

Keywords: supported nZVI, toxic metal, in situ remediation, sediment

1. Introduction

Various remediation technologies have been developed for the removal of pollutants including toxic heavy metals, dyes, pesticides, fertilizers, organic acids, halogenated and phenolic compounds, among others. More recently, nanotechnology-based techniques have opened up new methods for the removal of environmental pollutants. The rapid rise of nanotechnologies derives from different physico-chemical, optical and magnetic properties of materials at the nanoscale. As the exciting field of nanotechnology develops, the broader environmental impacts of nanotechnology will also need to be considered. It is well known that one of the most used metal nanoparticles for environmental remediation are zero valent iron (ZVI) nanoparticle. nZVI are electro donor

molecules that can participate in the degradation of chlorinated compounds and the reduction of heavy metals through redox reactions (Trujillo-Reyes *et al.*, 2014).

However, it is necessary to pay attention to the complexities concerning the application of nanomaterials in natural conditions. For example, nanomaterials may react with a variety of natural ingredients that are found in soil and groundwater and thus reduce the capacity that is available for reaction with the target contaminant. Another problem that hinders the implementation of nanomaterials is poor mobility under the surface. Because of the strong forces between the nanoparticles, especially magnetic, nZVI tends to agglomerated in particles of a micron size, which have the limited mobility in the porous media. To overcome this problem, various polymers and coatings, are used to stabilize nZVI particles, with varying degrees of success (He, F., Zhao, D., 2007). For this reason, in this study nZVI was stabilized with kaolinite, bentonite and carboxymethyl cellulose.

The need for sediment analysis stems from the fact that the sediment shows strongly pronounced binding tendency and thus represents a reservoir of toxic and persistent compounds predominantly of anthropogenic origin. Sorption of heavy metals as persistent, bioaccumulative and toxic substances in sediment creates a potential environmental risk at both the local and global levels. Selection of appropriate methods for sediment remediation depends on the specific characteristics of the given sediment, metal concentrations in the individual fractions, the concentration and the type of pollutant to be removed, as well as the end use of the contaminated sediments (Nemati *et al.*, 2011). Development of an innovative remediation technology, therefore, is crucial in achieving the proper cleaning of contaminated sites. The use of nanomaterials in remediation of sites contaminated with toxic metals has received considerable attention mostly because of the ability to quickly transform pollutants in controlled laboratory experiments.

This study aims to synthesize nZVI supported with two type of clay (bentonite and kaolinite) and carboxymethyl cellulose for the stabilisation of nickel, lead and zinc in sediment. The main objectives of this study are assessing the characteristics of untreated and treated sediment and evaluating its environmental risk and evaluation of the

effectiveness of stabilization treatment by assessing the leaching potential and environmental impact based on the different leaching procedures.

2. Materials and methods

2.1. Synthesis and characterization of nanomaterials

Kaolinite (K), bentonite (B) and carboxymethyl cellulose (CMC) samples containing nanometer sized zero valent iron particles were prepared using a conventional liquid-phase method by the reduction of ferric iron by borohydride in the presence of selected material (Tomasevic *et al.*, 2014).

The weight ratio of bentonite to nZVI was 1:1, and the same ratio was used in kaolinite-supported nZVI and carboxymethyl cellulose-supported nZVI as well. The concentration of iron in 1 L of solution was 14.000 ppm.

Kaolinite composition was (wt %) SiO₂ (45.9 %), Al₂O₃ (37.2 %), Fe₂O₃ (3.34 %), MgO (1.40 %), CaO (0.25 %), K₂O (0.14 %), Na₂O (0.10 %), ignition loss (13.3); bentonite composition was SiO₂ (58.9), Al₂O₃ (22.7), Fe₂O₃ (4.83), MgO (1.40), CaO (1.85), K₂O(0.24), Na₂O (0.12), ignition loss (10.6).

Transmission electron microscope (TEM; Philips CM 10) and scanning electron microscope (SEM; Hithchi S-4700 Type II) images were recorded to determine the morphologies, size and particles distribution of the K-nZVI, B-nZVI and CMC-nZVI. For scanning electron microscopy (SEM) images, powdered samples were first affixed onto adhesive tapes supported on metallic discs and then covered with a thin, electric conductive gold film. Images were recorded at different magnifications at an operating voltage of 30 kV. For the determination of the inner and outer diameters investigated stabilized nZVI it was used transmission electron microscopy (TEM, Philips CM 10). A suspension of nanomaterials has been prepared in methanol and one drop of a methanol solution was added to a copper grid. After drying, the samples were analyzed.

2.2. Methods of analysis of sediment general parameters

The dry organic matter was determined by drying 5-10 g of sample at 105°C to constant weight, and then undergo the ignition at 550°C to determine the weight loss on ignition in accordance with the so-called procedure Netherlands NEN Normalization Institute (NNI): NEN 5754: 1994th.

Pseudo-total metal content in the sediment samples was determined according to the method microwave digestion EPA 3051 (Milestone, star E) and then the samples were analyzed by flame AAS technique (Perkin Elmer 700™ AAnalyst) for the total content

of the metals Ni, Pb and Zn in accordance with the procedure of EPA 7000B. The results of sediment metal pseudo-total concentrations presented in the study are discussed in reference to the corresponding Serbian

standards (Ministry of Natural Resources, Mining and Spatial Planning the Official, Gazette 35/2011).

2.3. Preparation of mixtures of sediment and nZVI stabilized with kaolinite, bentonite and carboxymethyl cellulose

Simulation of in-situ conditions was carried out so that the small vessels with 750g of contaminated sediment were injected with nanomaterial. The mixture was prepared by adding 0.4, 0.8 and 1.2% nZVI stabilized with kaolinite in relation to the total weight of the sediment. After injection of nanomaterials, sediment was mixed so that there was a complete distribution of nanomaterials in sediment. Samples were taken at given time intervals: every 7 days during four weeks, and analyzed for metal content on AAS. The samples were then dried at 105°C, pulverized and subjected to the leaching test in order to determine the character of the obtained material.

2.4. Microwave assisted sequential extraction procedure (MWSE)

MWSE was performed for treated and untreated sediment samples as described by Jamali *et al.* (2009), using identical operating conditions applied in each individual Community Bureau of Reference (BCR) fraction and validated by the CRM BCR 701.

2.5. Leaching tests

Three leaching methods were used to evaluate the leaching potential of Ni, Pb and Zn in untreated and treated sediment samples as follows. Toxicity Characteristic Leaching Procedure-TCLP specially designed to mimic the acidic conditions of the sanitary landfill and to identify waste that has the potential to contaminate ground water (USEPA method 1311, 2002b). German standard test- DIN 3841-4S4 is used as a standard leaching test in determining the general characteristics of granular waste materials and sludge. Synthetic Precipitation Leaching Procedures – SPLP test (US EPA Method 1312, 2003) with a single extraction has been developed as an alternative to the TCLP test for situations where the waste is disposed outside of municipal landfill. Metal concentrations were determined by atomic absorption spectrometry AAS (Perkin Elmer AAnalyst™700) using standard procedures.

3. Results and discussion

3.1. Characterization of K-nZVI, B-nZVI and CMC-nZVI

nZVI particles, synthesized by a liquid phase reduction method, rapidly developed the shell around the core due to reaction with air or water, but they may vary in size and in the particle surface, crystallization degree, thickness and oxidized shell composition (Nurmi *et al.*, 2005). nZVI is subject to aggregate and form a chain-like structure, which

further results in a decrease in the reactivity of nZVI. Coating the nZVI reduces aggregation and increase mechanical strength. Clays, as low-cost and efficient adsorbents, have great potential as an ideal support material for nZVI, due to large specific surface area and developed mesoporous and microporous structure. Kaolinite and bentonite were selected in order to represent the two extremes of physicochemical clay behaviour based on their surface area and CEC. The CEC (meq 100 g⁻¹) was 19.1 for kaolinite and 70.4 for bentonite, while the respective surface areas (m² g⁻¹) were 9.84 and 24.01, so it can be concluded that bentonite has almost triple the BET specific surface area of kaolin. The multi-point BET specific surface areas of synthesized nanomaterials are significantly higher than those of the appropriate clays, for K-nZVI it is 14 m² g⁻¹ and for bentonite it is 40 m² g⁻¹. This suggests that the presence of zero-valent nanoparticles significantly increases the surface area, which is critical in high performance catalysts as the surface area of a porous material is one of the most useful microstructural parameters for defining its properties. Polymers such as CMC provide steric stabilization that exhibit a larger repulsion force than electrostatic repulsion, hence they can help to stabilize Fe⁰ nanoparticles and superparamagnetic ferrofluid via carboxylate binding. CMC-stabilized nZVI exhibited relatively better dispersity and reactivity over many other stabilized forms. CMC is a commercial, environmentally friendly material that has high water solubility and biocompatibility. It is thereby predictable to witness a booming prospect of CMC-nZVI owing to its superior physicochemical properties (Zhou *et al.* 2014). nZVI particles supported on kaolinite and bentonite were clearly discrete and well dispersed in the clay carriers, without aggregation. The obtained particles are close to spherical with grain size ranging from 20 to 100 nm in diameter. These results proved that all used clays prevented the nZVI particles from aggregating together. However it can be seen that there is a difference between average nanoparticle sizes depending on the clay used. Nanoparticle size decreased in series of 80 nm > 30 nm when kaolin and bentonite were used for supporting nZVI, indicating that there is a clear link between the dispersion of synthesized nano zero-valent iron particles and the BET specific surface area and porosity of materials used for support. Regarding CMC-stabilized Fe⁰ nanoparticles, they also appear to be clearly discrete and well-dispersed, close to spherical in shape, and their sizes range from 20 to 250 nm in diameter (Fig. 1c).

SEM images (Fig. 1a, b) when using clays, indicated that there were many nodular protrusions over the surface. These nodules were the in-situ prepared Fe⁰ particles. They were spherical in shape, and were distributed throughout the surface of the clays without noticeable aggregation. In addition, the presence of CMC minimized agglomeration of the resulting iron particles and thus maintained the high surface area and potential reactivity of the particles.

3.2. Features of sediment

The percentage of solids in the sediment, which was used for testing the application of kaolinite, bentonite and carboxymethyl cellulose stabilized nZVI as immobilization agents varied in the range from 9.1 to 12%. Sediment was taken from the most ecologically endangered sections of Nadela watercourse. Sediment was characterized on the basis of the pseudo-total metal content, where the concentration of chromium was 420.2 mg/kg, nickel 471.4 mg/kg, copper 394.1 mg/kg, zinc 882.0 mg/kg, arsenic 41.25 mg/kg and concentration of lead was 394.1 mg/kg. As such, it represents an extreme risk to the environment and it belongs to the fourth and last quality class according to the Regulation on limit values for pollutants in surface groundwater and sediments, and the deadlines for their achievement (Official Gazette of RS, no. 50/12). Organic matter content ranged approximately from 5.8 to 16.3%. A sequential extraction procedure was utilized to divide the metals into four fractions: exchangeable and carbonate bound, iron and manganese oxides bound, organic matter bound and residual metal. The distribution of analyzed metals in different phases extracted by the MWSE procedure as described by Jamali *et al.* (2009) is shown in Figure 2.

The relative availability obeys the following order: EX > CB > OX > OM > RS.

Figure 2 shows the changes in the fractions of the four Ni, Pb and Zn species in the untreated and treated soils. The primary Ni species for the untreated sediment were split among EX (19.2%), RE (42.0%), OX (20.5%) and RS (18.3%). As it can be seen from the figure 2 following the addition of immobilization agents Ni is dominantly in the residual phase (over 50%), which makes it practically unavailable for aquatic systems. Nevertheless, percentage of added immobilisation

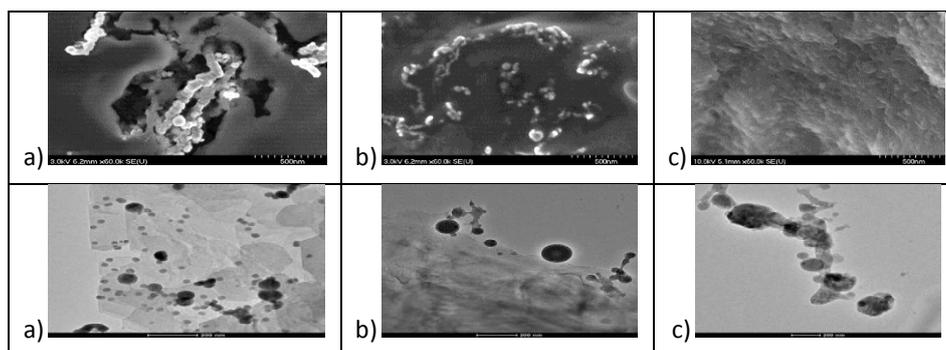


Figure 1. a) TEM and SEM of K-nZVI, b) TEM and SEM of B-nZVI, c) TEM and SEM of CMC-nZVI

3.3. Microwave assisted sequential extraction procedure (MWSE)

material did not significantly influence the alteration of the Ni species. Regarding lead, from the figure 2 it can be seen that the high percentage of lead is in residual phase in non-treated sediment sample, though 27.2% of Pb is in the Fe-Mn phase. The Fe-Mn oxides fraction includes the soluble metal oxides/hydroxides under slightly acidic pH as well as the metal associated with reducible amorphous Fe-Mn oxyhydroxides. After the remediation treatment of sediment a significant proportion of Pb was also bound to organic matter (21.4%-61.55% depending on percentage of nanomaterial used). Oxidizing conditions lead to enhanced mineralization of organic matter, where there is a release of metals from these fractions. This distinctive alteration in Pb speciation, especially the substantial increase in OX fraction, accounted for the reduced leachability and bioaccessibility of Pb in the previous study (Liu and Zhao, 2007).

Judging from the results of sequential extraction (Fig. 2) significant proportion of Zn (46%) in untreated sediment sample is present in the first fraction. Metals in exchangeable fraction can be exchanged and are in equilibrium with the ionic content in water. This fraction is sensitive to pH variations. Overall, the conversion of more easily available Zn (EX) to the less available OX and RS species was evident, and thus was held responsible for the enhanced stability of Zn following the nanoparticle treatment.

Although speciation of Ni, Pb and Zn in the sediment were different, we applied the same remediation. The main objective of every remediation procedure dealing with several contaminants is to carry out the treatment with the same agents, and thus achieve economic and environmental benefits.

3.3. The treatment of the contaminated sediments using K-nZVI, B-nZVI and CMC-nZVI in-situ in the laboratory

The ability of K-nZVI, B-nZVI and CMC-nZVI to remove metal ions from the sediment are presented in Figure 3 and it shows a significant change in the percentage removal of

metals (Ni, Pb and Zn). If we observe the percentage of the metals removed as a criterion of the treatment efficiency, then the in situ laboratory sediment treatment with the nZVI stabilized with kaolinite, bentonite and carboxymethyl cellulose as immobilization agent, proved to be very effective in the case of all metals. Assessing treatment efficacy from the stand point of removed metals, from the figure 3 we can notice that the best removal for all three examined metal was CMC-nZVI treated sediment.

The use of zero valent iron (Fe^0) in the in-situ remediation technique is currently undergoing evaluation. The basic mechanism for removal, originally suggested, involves the reduction of metal contaminants, then their subsequent precipitation of insoluble forms. Oxidation and co-precipitation by iron oxides are the other possible reaction mechanisms depending upon the prevailing geochemical conditions such as pH, Eh and initial concentration and speciation of contaminant metals. While reacting with nZVI, Pb^{2+} precipitates as $Pb(OH)_2$ and oxidizes as $\alpha-PbO_2$ (Lien *et al.*, 2007). Zn may also be removed by precipitation on the oxidized nZVI surface as $Zn(OH)_2$.

TCLP test, SPLP test as well as German Standard DIN 38414-4 leaching test, were performed on mixtures after in-situ process after 4 weeks, and the results are shown in Table 2. All mixtures met the criteria regulated by the TCLP procedure in terms of the leached concentration. SPLP is frequently used to assess the risk to groundwater posed by contaminated soils and in the risk assessment process for determining beneficial uses of solid wastes. SPLP test results show that the concentrations of Zn after treatment with all applied immobilisation agents, do not exceed the limit value for third class of water (Official Gazette of RS, 67/2011 and 48/2012).

In some cases even below the limit values for the class II, with good water ecological status. As for Pb all samples were below the limit concentration of metal in the surface water level prescribed for the third class of water, except the treatment where it was used the smallest amount of nanometrial.

From the stand point of the Regulations on categories, testing and classification of waste (The Official Gazette 56/2010) all metals in all mixtures can be classified as non-hazardous waste.

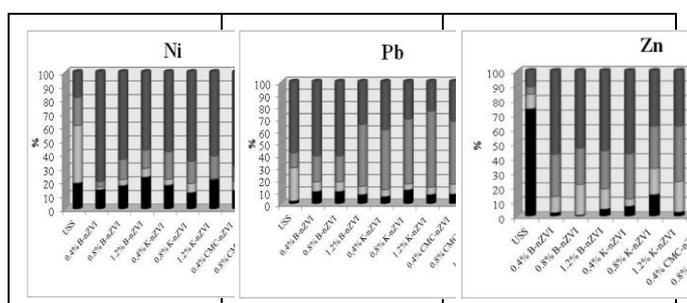


Figure 2. Distribution of analyzed metals in sequential extraction fraction of in situ treated sediment sample

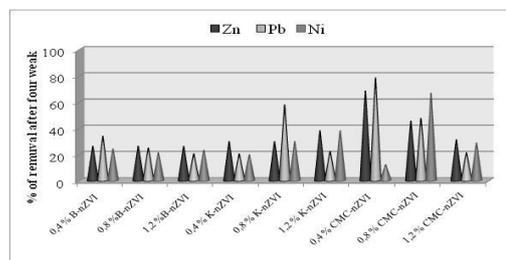


Figure 3. Percentage of metals removal (Ni, Pb, Zn) from the mixture of sediment and K-nZVI (%), B-nZVI (%) and CMC-nZVI (%)

Table 1. Leached concentrations of toxic metals after TCLP, SPLP and DIN test of in situ treated sediment sample and their comparison with relevant standards

Test/metal			A	Sample								
				K-nZVI			B-nZVI			CMC-nZVI		
				0,4%	0,8%	1,2%	0,4%	0,8%	1,2%	0,4%	0,8%	1,2%
TCLP	mg/l	Ni	20	1,62	1,67	1,40	2,38	2,11	4,61	1,02	1,59	2,57
		Zn	250	0,21	0,24	0,15	0,20	0,19	0,36	0,02	0,01	0,01
		Pb	5	0,49	0,45	0,46	0,40	0,49	0,72	0,61	0,63	0,29
SPLP	mg/l	Ni	-	0,32	0,58	0,69	0,47	0,05	0,80	0,02	0,07	0,01
		Zn	2	0,09	0,08	0,15	0,11	0,07	0,07	0,41	0,18	0,01
		Pb	0,05	0,11	0,02	0,08	0,16	0,07	0,08	0,01	0,01	0,01
DIN	mg/kg	Ni	0,4	8,52	16,1	86,4	28,1	30,1	40,3	38,9	33,5	29,2
		Zn	4	21,9	21,2	23,6	15,0	24,8	17,8	21,3	26,9	37,0
		Pb	0,05	7,71	2,43	4,35	1,13	0,01	20,6	4,7	11,0	17,7

A: TCLP – Limit values for metals according to TCLP procedure [USEPA method 1311, 2002b]; SPLP – Emission limit values for waste water from surface waste disposal [Official Gazette of RS, 67/2011 and 48/2012]; DIN – Maximum allowed concentration of accepting waste as inert [The Official Gazette 56/2010]

4. Conclusions

This work extends nanotechnology into stabilization of toxic metals in contaminated sediments. To reduce the leachability of toxic metals in sediment, nZVI supported with kaolinite, bentonite and carboxy metal cellulose were synthesized. Surface coating with two types of clay and polymer prevented the nZVI particles aggregation and enhanced their mobility in soil media. Characterization of sediments contaminated with toxic metals, based on the pseudo-total content of lead, nickel and zinc, showed that the sediment can be considered toxic. Based on the above findings, the in-situ treatment in the laboratory proved to be very effective, providing the choice of optimal doses of nanomaterials towards the concentration of toxic metals in the sediment. TCLP, SPLP and DIN 3841-4 S4 tests applied to determine the potential leaching of metals, showed that in all stabilized mixtures, leaching of metals is very limited. Lastly, this study indicated that K-nZVI, b-nZVI and CMC-nZVI might be used for the in-situ remediation of Ni, Pb and Zn contaminated sediment.

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