Use of two different approaches to the synthesis of nano zero valent iron for sediment remediation

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Abstract

Heavy metals are one of the main pollutants of river sediments. Stabilization technology proved to be an effective method for solving this problem. Stabilization covers a wide range of remediation techniques that are used to transform waste into forms that will be less problematic for the environment. Stabilization of Great Backi Canal sediment was carried out using nanomaterials, namely nano zero valent iron. Two different approaches for the synthesis of nanomaterials were used, conventional and so-called "green" method. For conventional borohydride method, nZVI was stabilized with native clay as porous material which proved to be very effective because of its specific surface area. For green method oak leaves extract was used, which contains polyphenols and has increased antioxidant capacity representing promising agents for the nZVI synthesis. Assessment of the treatment efficiency was performed using semi-dynamic leaching test ANS 16.1. These results showed that metals were successfully immobilized in the sediment.

Keywords: heavy metals, nZVI, sediment, stabilization

1. Introduction

Sediment that represents an essential component of a dynamic ecosystem often becomes contaminated with heavy metals from different effluents discharging into rivers, lakes and etc. Great Backi Canal represents such an environment, as it is also called a “black point”, by the amount of contamination of organic or inorganic origin. Sorption of heavy metals, as well as persistent, bioaccumulative and toxic substances in the sediment, creates potential environmental risks at both the local and global levels. (Tomasevic, 2013) A remediation technique called stabilization showed as efficient solution for the removal of metals from the river sediment, which involves the addition of a binder to immobilize heavy metals. Iron nanoparticles (nZVI) proved as an effective material/binder for immobilization. Two different approaches for the synthesis of nZVI were used, conventional and so-called "green" method. nZVI particles are of small size, but they have large specific surface area and great reactivity of surface sites. Conventional production of nano zero-valent iron includes the chemical reaction of $NaBH_4$, as a reducing agent, with iron salts (Sun *et al*., 2006). However, by this method synthesized nZVI nanoparticles tend to either react with surrounding media or agglomerate into a chain-like structures, (Sun *et al*., 2007) resulting in significant loss of reactivity of surface area. Iron particles stability upon agglomeration can be enhanced by imparting electrostatic repulsion, using organic surfactants, different stabilizers or through the use of capping agents (Sun *et al*., 2007). A wide variety of stabilizers, like different porous material, have been proposed to modify nZVI particle surface characteristics (He and Zhao, 2005; Wang *et al*., 2014), which will prevent particle aggregation. More recently, kaolin-supported nZVI (Chen *et al*., 2012), bentonite-supported nZVI (Chen *et al*., 2011) and native clay-supported nZVI (Kerkez *et al*., 2014) have been used to reduce the extent of nZVI aggregation. These indications suggest that implementing stabilized nZVI particles may represent an effective method for remediation of contaminated river sediment. Nowdays so-called green method or green synthesis of iron nanoparticles has been developed recently as an alternative to this traditional method. This method don’t use sodium borohydrate, which is known for its toxicity, corrosiveness and flammability (Hoag *et al*., 2009). This green method involves the fast reaction of aqueous extract of tea, tree or bush leaves, which contains polyphenols, with iron salts. (Hoag *et al*., 2009, Machado *et al*., 2013). Polyphenols in oak leaves extract can reduce metals, act as both reducing and capping agents, thanks to high antioxidant capacity (Machado *et al*., 2013) that protects the iron nanoparticles from oxidation and also imparts steric stabilization against agglomeration/aggregation (Hoag *et al*., 2009). Polyphenols also contain molecules carrying alcoholic functional groups, which can be used for reduction as well as for stabilization of nano zero-valent iron (Nadagouda and Varma, 2008; Nadagouda *et al*., 2010) Proposed mechanism of synthesis of Fe^{2+} with polyphenols and other polyol compounds, can be also applied for the synthesis with Fe^{3+}, which is given by Smuleac *et al* (2011), and shown through this general reaction:

$$nFe^{2+} + 2Ar-(OH)_n \rightarrow nFe^0 + 2nAr = O + 2nH^+$$

Where Ar is the phenyl group and n is the number of hydroxyl groups oxidized by Fe^{2+}. This new green synthetic method is very simple to approach, environmental friendly, which can produce very stable quantities of nano zero-valent iron (Hoag *et al*., 2009).

Material which was created as waste after stabilization treatment technique can be used at the end of a particular purpose, or we can disposal it on the landfills. Over the time, the composition of landfill waste is changed, and a large part of this material is not easily biodegradable. Leaching is the time longest emission from landfills used to dispose of such waste material. In order to estimate the time required for the treatment of leaching, now different methods of small tests are applied upon a large-scale field test. It is, therefore, reasonable to assume that as the assay conditions are closer to field conditions, the results will be closer to the actual values for future emissions at the landfill. In order to design the leaching tests that are reliable for long-term predictions, the knowledge of the factors affecting the leaching is the most important. The basic division of leaching tests are on the extraction and dynamic. Dynamic tests include continuous or occasional renewal of extracting agent in order to maintain a large difference in concentration between the solid and liquid phases. They provide information regarding the kinetic immobilization of contaminants and of complex mechanisms in connection with the leaching.

The aim of this research was to stabilize and immobilize heavy metals, in this case copper and nickel, from river sediment of Great Backi Canal by two different approaches of sythesize nZVI particles. The tretament efficiency of this remediation technique was performed by semi-dynamic leaching test ANS 16.1 (ANS, 1986).

2. Materials and methods

2.1. Preparation of clay supported nZVI particles

The chemical composition of native clay from Kanjiza (Vojvodina, Serbia) was (wt%): SiO_2 (55.7%), Al_2O_3 (14.9%), Fe_2O_3 (5.78%), MgO (2.86%), CaO (5.90%), K_2O (0.830%), TiO_2 (0.800%) and loss of ignition 14.03%.

NC-nZVI was prepared using a conventional liquid-phase method by the reduction of ferric iron by borohydride, in presence of native clay. Weight ration of native clay and nZVI was 1:1. From the beginning to the end of process N_2 gas was applied through the solution to prevent oxidization. The prepared NC-nZVI was refrigerated at 4ºC.

2.2. Preparation of green zero-valent iron nanoparticles

Oak leaves were collected from Quercus pea trees, growing in the forest near the Danube river, at Novi Sad, Vojvodina, Serbia. The leaves were milled using a kitchen chopper, then sieved using a 2 mm sieve and pre-dried at 50ºC in an oven for 48 h. The amount of 3.7 g of the oak leaves was measured and carried to a 300 mL Erlenmeyer flask, to which 100 mL of water was added. Then the flask was put in a shaker bath at 80ºC for 20 min. The extraction procedure was given according to Machado *et al*. (2013). Extract of oak leaves was mixed with 0.1 M Fe (III) solution ($FeCl_3 \cdot 6H_2O$, Centrohem Serbia) in a volume ratio of 3:1. The presence of intense black colored precipitate was indication of the Fe nanoparticles.

2.3. Characterization of OL-nZVI and NC-nZVI

Transmission electron microscopy (TEM; Philis CM 10) and scanning electron microscope (SEM) analyses (SEM; Hithchi S-4700 Type II) images were recorded to determine the morphology, size and nZVI particles distribution.

2.4. Sediment collection and preparation

Sediment samples were collected from the Great Backi Canal river basin (Vojvodina, Serbia). Pseudo-total trace metal contents were assessed on sample triplicate after nitric acid digestion employing US EPA standard method (USEPA Method 3051a 2007), and mean values were used. The relative standard deviations (%RSD) obtained (n = 3) were below 10 %. Metal contents were determined by AAS (Perkin Elmer AAnalystTM 700) according to the standard procedure (USEPA Method 7010 2007). According to the Serbian system, the class limits are defined for ‘‘standard sediment’’, with 10 % organic matter and 25 % clay. Metal concentrations of the sediment were first corrected to standard sediment based on correction formulas and then classified according to the Serbian national evaluation scheme. Finally, the overall sediment quality was established using the ‘‘worst class’’ sediment parameters. According to Serbian regulation standards, the sediment is polluted with Cu (class 4), and Ni (class 3). In the third and fourth classes, sediments are of unacceptable quality and urgently require dredging, disposal in special storage reservoirs and, if possible, sediment cleanup measures. Samples were designated by the capital letter (OL-nZVI: oak nano zero-valent iron, NC-nZVI: native clay nano zero-valent iron) followed by a number indicating the percent weight of the given attribute. The content of nanomaterial was expressed as percentage of the total solids weight. During the leaching test, 4 types

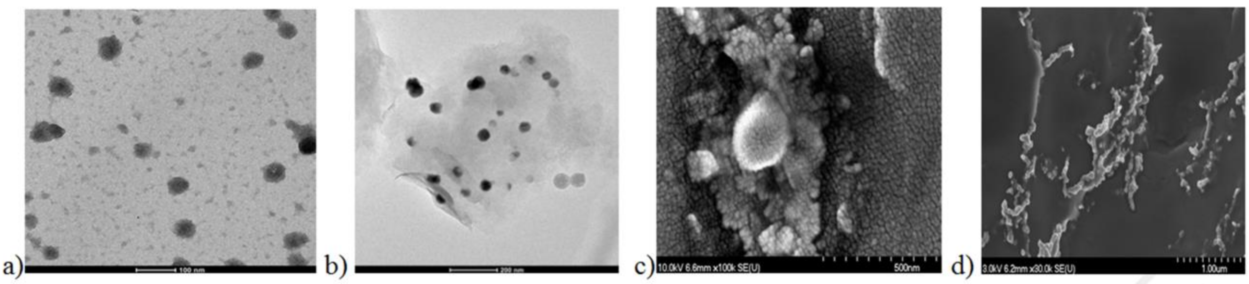

Figure 1. TEM and SEM images of OL-nZVI and NC-nZVI: a) TEM image of OL-nZVI, b) TEM image of NC-nZVI, c) SEM image of OL-nZVI, d) SEM image of NC-nZVI (Kerkez et al., 2014; Poguberovic et al.,2016)

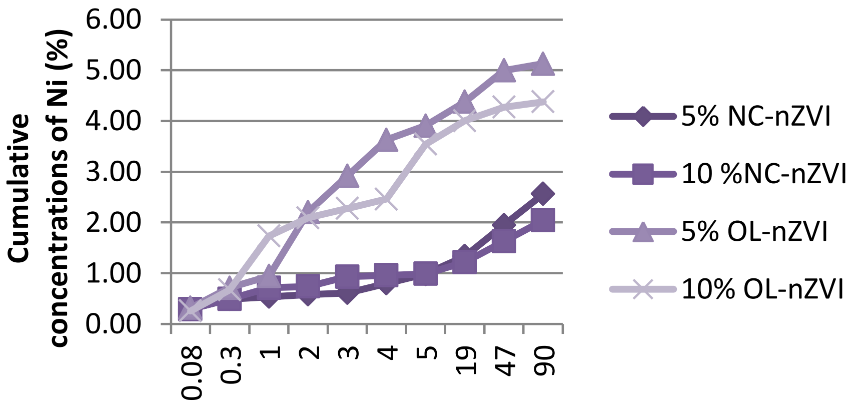

Figure 3. Cumulative leaching concentrations of Ni (%)

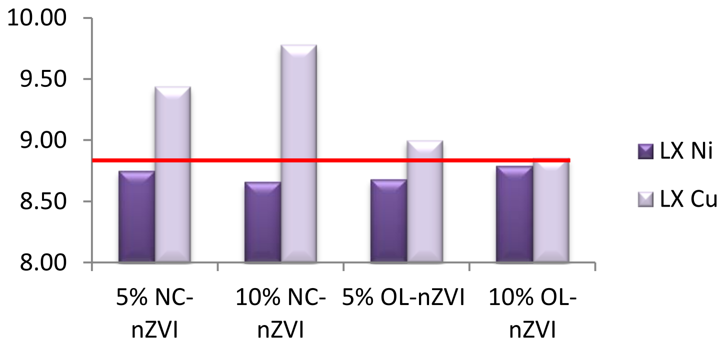

Figure 4. Mean leachability index (LX) **References**

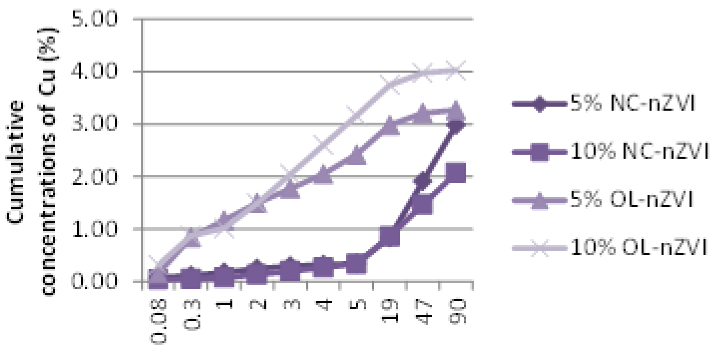

Figure 2. Cumulative leaching concentrations of Cu (%)

of specimens were tested: 5% OL-nZVI, 10% OL-nZVI,

5% NC-nZVI, and 10% NC-nZVI. Samples were prepared in the form of monolithic cubes [(3 ± 0.1) 9 (3 ± 0.1) 9 (3 ± 0.1) cm] by compaction at an optimum water content, defined as the water content at which the maximum dry density is achieved for a given compactive effort. The compaction was performed according to ASTM D1557-00 procedure, and after 28 days subjected to semi-dynamic test ANS 16.1 (ANS 16.1, 1986).

2.5. ANS 16.1 test

The long-term leaching behavior of Cu, Ni, from treated sediment samples was evaluated using ANS method 16.1 (1986). From applying this test we get a cumulative fraction of metals leached 90 days. A mathematical diffusion model based on Fick's second law is used to evaluate the leaching rate as a function of time, and the leachability index which currently is used by Environment Canada (1991), presents an average of the negative logarithm of the effective diffusivity terms. According to ANS 16.1 test (1986), the liquid/solid ratio was 10/1 (l kg^{-1}) and collected leachate from defined time intervals were filtered through a 0.45-μm-pore-size membrane filter, and subjected to AAS for concentrations of Cu and Ni.

3. Results and discussion

3.1. Characterization of produced nanomaterials

The TEM images presented in Fig. 1 confirm the formation of nano zero-valent iron particles. Native clay-supported nZVI particles were clearly distinct and well dispersed in the clay carriers, without aggregation. The obtained particles are close to spherical, with grain size of 50 nm in diameter (Fig. 1b). SEM images (Fig. 1d) of NC-nZVI showed many nodular protrusions over the surface. They were spherical in shape, and were distributed throughout the surface of the native clay without noticeable agglomeration (Kerkez *et al*., 2014). TEM images of OL-nZVI (Fig. 1a) show that particles are spherical and non-agglomerated, with size within 10-30 nm (Poguberović *et al*., 2016). SEM images also show spherical shape of nanoparticles, with no significant agglomeration, because polyphenols from oak leaves act as both dispersive and capping agents (Fig. 1c).

3.2. Pseudo-total metal concentrations of untreated sediment sample

Pseudo-total concentrations of Cu was 440.04 ± 15 mg kg-1 and Ni 111.02 ± 7 mg kg-1. Mineral fraction of <2 μm was 15.08% of sediment dry weight, and the fraction of 2-63 μm ranged from 6.80 to 47.43 % sediment dry weight (ISO 11277:2009). The content of organic matter in the sediment sample was 11.9 % (NEN 5754:1994). Average initial moisture content of sediment samples was 72.5 %, so they were dried at 105ºC to constant mass and then mixed with OL and NC-nZVI in different weight percentage.

3.3. ANS 16.1 test

Cumulative percentages of leached metals (Cu (Fig. 2) and Ni (Fig. 3)) from the mixtures with sediment and nZVI synthesized using the oak leaf extract (OL-nZVI) and using native clay for supported nZVI (NC-nZVI) are presented as a function of leaching time. Cumulative percent of leach metals after 90 days in deionized water ranged for samples with OL-nZVI:

• from 0.26% to 4.02% for copper,

• from 0.26% to 5.13% for nickel,

and for samples with NC-nZVI:

• from 0.04% to 2.99% for copper

• from 0.29% to 2.56% for nickel.

So far as the percentage of leach metals is observed as the criterion of the treatment efficiency, then treatment with nZVI synthesized using the extract of oak leaves and supported nZVI proved effective in the case of copper and nickel because leaching percentage did not exceed 6%. If the cumulative value compares with the national legislation ("Off. Gazette of RS", no. 56/2010), it can be concluded that all mixtures with OL-nZVI and NC-nZVI in terms of the concentration of Cu and Ni may be considered as non-hazardous waste, because leaching concentrations satisfy the values laid down in national legislation. ANS 16.1 leaching model benefits Fick diffusion theory and provides a diffusion rate that can enable the evaluation of effectiveness from stabilization treatment (ANS, 1986; Dermatas and Meng, 2003; Dermatas *et al*., 2004; Moon *et al*., 2004; Moon and Dermatas, 2007) based on the determination of diffusion coefficients (De) and leaching index (LX). According Nathwani and Phillips (1980), the diffusion coefficients of the metals of the mixture generally range from values for highly mobile metals, about E-05 cm^2 s^{-1} to E-15 cm^2 s^{-1} (practically immobilized metals in the stabilized compositions).

Mean values of diffusion coefficients (De) generally ranged:

• from 2.59E-09 cm^2 s^{-1} to 6.50E-09 cm^2 s^{-1} in the mixtures with OL-nZVI

• from 1.95E-09 cm^2 s^{-1} to 3.74E-09 cm^2 s^{-1} in the mixtures with NC-nZVI.

Thanks to shown values of diffusion coefficients, we can concluded that copper and nickel are partly mobile in all mixtures of sediment and nanomaterials. According to the Canadian Agency for Environmental Protection (Environment Canada, 1991) LX values can be taken as a criterion for the use and disposal of the treated waste. If efficacy of the treatment is observed in terms of the value of LX, the treatment can be considered to be partially successful because in all mixtures of OL-nZVI and NC-nZVI, LX values for Ni were between 8 and 9, therefore, these mixtures can be safely disposed of an landfill. (Fig. 4). For copper, LX values for mixtures with NC-nZVI were higher than 9, and can be considered for "controlled utilization", while for OL-nZVI this LX values were below 8, and can be safely disposed of an landfill. As the worst value defines the criteria for the use of waste, these mixtures can be safely disposed off in isolated or sanitary landfills. The external (hydro) oxide layer of Fe nanoparticle can act as an effective adsorbent for various contaminants including metals. The specific removal mechanisms involved in treatment of heavy metal contamination with nZVI depend on the standard redox potential (E^0) of the metal contaminant. Metals with a more positive E^0 of Fe^0 (for example, Cu) are preferentially removed by reduction and precipitation (Li and Zhang, 2007). Metals with a little more positive E^0 than Fe^0, (for example, Ni) can be removed as both by reduction and adsorption. Oxidation and co-precipitation of iron oxide are other possible mechanisms. They depend on the prevailing geochemical conditions, such as pH value, initial concentration and speciation of metals. Passivation of nZVI as well as difference of pH values can reduce or decrease this removal of heavy metals from sediment, thus the oxidation of nZVI. So we can conclude that polyphenols in oak leaf prevent oxidation of nZVI particles and increase the immobilization of metals in sediment, as well as reactivity of OL-nZVI. Clay also play an important role in the environment because they are natural "sponge " of pollutants, binding their anions or cations by ion exchange or adsorption. There is a chemical change and substitution with other cations when crystal of clay are suspended in water. In addition, ions may also be adsorbed on the clay crystal edges and be exchanged with the other ions in the water/soil (Patel *et al*., 2007) This clay mineral used for supported nZVI particles behaved like a chelating agent for heavy metals and also nZVI particles. Therefore, this two nanomaterials have shown similar results and can be efficiently used for a treatment of heavy metals with a small amount value added in sediment. However, this is very significant for using a new green method which can be applied for sediment remediation, avoiding the use of toxic chemicals, such as $NaBH_4$. Plants are such renewable resources, which are considered wastes or do not have any added value, so we can use them for very useful and economical purposes.

4. Conclusion

This research reaches nanotechnology into stabilization of heavy metals in contaminated river sediments. To reduce the leachability of copper and nickel in sediment nZVI supported with native clay, and synthesized from oak leaf extract were used as stabilization agents. Surface coating of native clay and polyphenols from oak leaves prevented the nZVI particles from agglomerating or oxidizes, enhancing their mobility and reactivity in soil media. These applied nanomaterials have proved to be effective in immobilization of copper and nickel in river sediment. Further research should be focused on the toxicity of this nanomaterials and also more detailed about their bioavailability, then determining the fraction of metals with different liabilities and etc. Data showed that for the sediment quality assessment a variety of standard methods must be used, in order to safely assess the risk to the environment.

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