EFFECT OF pH ON SORPTION CHARACTERISTICS OF NANOIRON DURING STABILISATION OF SELECTED RISK ELEMENTS

VLIV pH NA SORPČNÍ CHARAKTERISTIKY NANOŽELEZA PŘI STABILIZACI VYBRANÝCH RIZIKOVÝCH PRVKŮ

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Abstract
The study is focused on the investigation of nano zero-valent iron (nZVI) as a potential sorbent of risk elements in contaminated soils. During our research mainly the influence of pH on the sorption efficiency of the redox-sensitive elements and selected metals, has been studied. The research was divided into (i) the investigation of sorption characteristics of nZVI in model solutions of Cr and (ii) testing of nZVI in contaminated soils using the pH-static system.

Keywords
nano zero-valent iron, chromium, risk elements, pH, sorption

Introduction
The application of nano-sorbents for remediation and immobilisation of trace metals/metalloids in the environment is a fast emerging method. Compared to conventional treatment of contaminated soil (i.e. excavation and dumping or *ex situ* washing) the use of nanoparticles is very efficient and environmentally friendly. This study is focused on the application of nZVI as a sorbent of risk elements in the soil system considering the changes in pH and its influence on metal/metalloid stabilisation. The nano-sorbent reaction is significantly faster than that of particles in milli and micro scale (Mueller et Nowack, 2010; Waychunas et al., 2005). The advantage of nZVI application is high reactivity and large specific surface area of Fe nanoparticles, which are oxidised rapidly in the presence of oxygen or water, resulting in an efficient capture of redox-sensitive elements such as Cr (Li et al., 2006; Zhang, 2003). Chromium can be found in two different valences in the environment, namely Cr(III) and Cr(VI). The most hazardous form is hexavalent Cr. Chromium represents anthropogenic pollutants that come from metallurgical and chemical industry (production of steel, paints, plating, etc.) (Barnhart, 1997). Hexavalent chromium is highly mobile in natural systems, highly toxic to living organisms and has carcinogenic effects to humans (Nickens et al., 2010).

The aim of this study was (i) to determine the sorption characteristics of nZVI for chromium as a function of pH and other factors and assess the sorption efficiency for Cr (III, VI), (ii) to determine the leachability of risk elements (As, Cr, Pb, Zn) from contaminated soil as a function of pH and time and (iii) to assess the efficiency of the chemical stabilisation of contaminated soils using nZVI.

Methodology
All experiments were performed under laboratory conditions. During the first step the nZVI–Cr interaction was investigated in a model solution of Cr(VI) (initial concentration of 120 mg/l), which was prepared by dissolving $K_2Cr_2O_7$ in water. The experiment was conducted as a function of pH and ionic strength of the solution ($NaNO_3$ background electrolyte yielding 0.1, 0.01 and 0.001 M, respectively was used during the sorption). Samples were separated using AG1-X8 ionex in order to determine the particular forms of Cr(III) and Cr(VI). After decantation, residual solid fractions of the nanoiron were dried in a nitrogen atmosphere (to prevent from oxygen), and further subjected to mineralogical analysis by transmission electron microscopy (TEM, JEOL JEM-3010, JEOL, Japan) with an energy dispersive spectrometer (EDS) or using selected area electron diffraction (SAED).

Soil from the area of Příbram-Litavka was tested in the second step; a heavily metal-contaminated soil due to former metallurgical activities (Pb 4200 mg/kg, Zn 4100 mg/kg, As 330 mg/kg, Cr 30 mg/kg).

For purposes of this study, the soil (<2 mm) was firstly mixed with a corresponding amount of nZVI (1 wt.%) incubated for 30 days at 60–70% water holding capacity in order to ensure equilibrium conditions. After this period, the soil was dried and used for leaching experiments as a function of pH and time (CEN/TS 14997, pH-static leaching test), particularly in the range of pH 4–8 at two different time intervals (48 h and 192 h). Control soil sample without the addition of nZVI was tested for comparison. The concentrations of the studied elements in the solution/leachate were determined by optical emission spectrometer with inductively coupled plasma (ICP-OES; Agilent 730, Agilent Technologies, USA).

Results and Discussion

The efficiency of Cr adsorption onto nZVI increased with decreasing pH, which corresponds to the characteristic trend of anionic forms of metals/metalloids (Wu et al., 2009). The investigation of solid residues of nanoiron particles by TEM/EDS and TEM/SAED provided both visualisation of the nanoparticles and determination of their chemical composition as well as studying the nZVI transformations during sorption experiments (Fig. 1). Although detectable concentrations of Cr were low, the analysis showed the presence of Cr in tiny particles and possible transformation of Fe into maghemite (Fe_2O_3).

The highest concentrations of Pb and Zn were released at pH 4 from the soil. The leachability of metals generally decreased with increasing pH and increased with time, while the released amount of As was higher with increasing pH. The leaching trend of Pb showed a typical U-shaped curve for pH-dependent release of metallic cations with increased concentrations at low & high pH. As a result of the application of nZVI, decreased concentrations of Pb and As were observed in leachates at pH 6–8; however, this effect was not observed under acidic conditions. Despite our assumption, the application of nZVI did not result in lower leachability of Zn. Leached concentrations of Cr were around the detection limit.

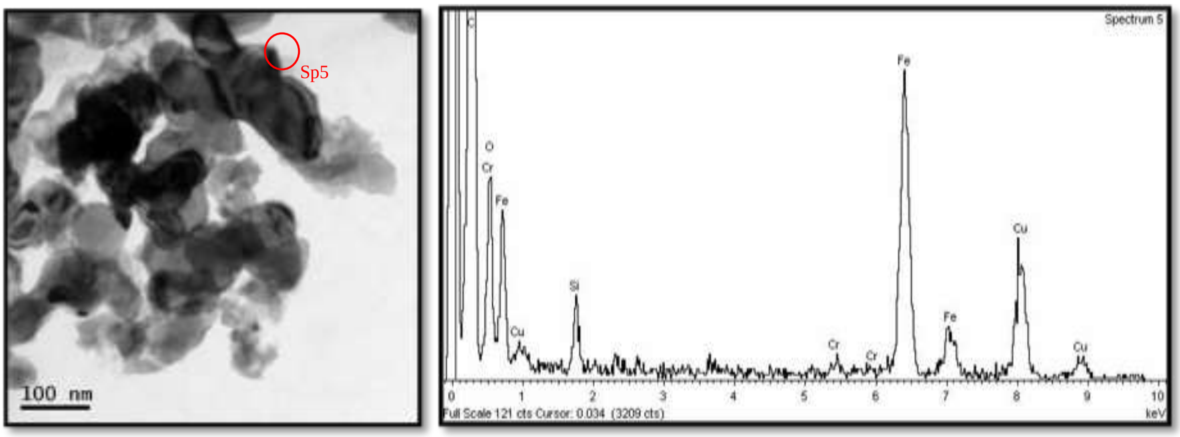

Fig. 1: TEM image of nZVI after sorption experiment (pH 3). Iron nanoparticles and their oxidation products (left); energy dispersive spectrum (EDS) with Fe and adsorbed Cr (right).

Conclusion

This study shows the first results on the interaction of nZVI with Cr(VI) and provides information about the behaviour of risk elements in contaminated soil. pH is a key parameter affecting the sorption processes and the release of elements from the soil. The leachability of metals generally increased with decreasing pH and increasing time, while concentrations of As decreased with decreasing pH. Despite the assumption, the application of nZVI did not show obvious impact on reducing the leachability of metals. The method requires detailed research of the behaviour of nZVI under various environmental conditions.

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