



# Characterization of the uptake of aqueous Ni<sup>2+</sup> ions on nanoparticles of zero-valent iron (nZVI)

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## ABSTRACT

This study investigates the fixation of aqueous Ni<sup>2+</sup> ions by nanoparticles of zero-valent iron (nZVI) prepared using the borohydride reduction method. The uptake of Ni<sup>2+</sup> was tested under various experimental conditions like initial concentration, time, pH, and repetitive application of nZVI. Part of the experiments was devoted to comparing the extent of uptake of Ni<sup>2+</sup> ions with those of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, and Sr<sup>2+</sup> ions, which belong to a wide range of standard reduction potentials. Particle size analysis of nZVI in aqueous solution indicated that the material suffered extensive aggregation, much above the extent of aggregation known for dry nZVI. Nevertheless, nZVI showed fast uptake kinetics and very high uptake capacity. The overall results demonstrated the high fixation capability of nZVI towards the studied transition metal ions in aqueous solution. The same conclusion is, however, not valid for the removal of Sr<sup>2+</sup> ions.

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## 1. Introduction

Zero-valent iron nanotechnology is an emerging environmental technology that is suggested to convey cost effective solutions for *in situ* and *ex situ* remediation [1]. By virtue of their high surface/volume ratios, nanoparticles of zero-valent iron (nZVI) possess enormous amount of energy that brings about a high sequestration capacity and provide a kinetic advantage in the uptake process [2]. Although the application of iron nanoparticles suffers from some still unresolved uncertainties, the material is being accepted as a versatile tool for the remediation of different organic and inorganic environmental pollutants [3]. The topic of metal ion retention by nZVI is an expanding area that has been handled by various research groups during the last decade. The effectiveness of nZVI for the removal of Co<sup>2+</sup> and Cu<sup>2+</sup> ions from aqueous solutions has been recently reported by our group [4–6]. The applicability of nZVI and nZVI-based materials for the fixation of different metal cations (like As, Cu, Co, Pb, Cd, etc.) and some anions (like chromate and nitrate) has been documented in literature in a number of previous works [e.g. 7–13]. This area continues to extend in the direction of enhancing the properties of nZVI and gaining better understanding for the mechanism of interaction.

Heavy metals are among the priority pollutants as they are not biodegradable, and consequently can accumulate in the environment causing potential short term and long term hazards [14]. Nickel, is a heavy metal that is used in manufacturing alloys, stainless steel, and in plating. The discharge of this element into the aqueous environment will bring about detrimental effects on the biosphere. The retention of Ni<sup>2+</sup> ions on nZVI was reported in a previous study that investigated the topic from a mechanistic view point [15]. To our knowledge, no detailed study on the effect of various experimental parameters on the extent of Ni<sup>2+</sup> uptake by nZVI is available in literature.

This work aimed at investigating the mechanism of uptake of Ni<sup>2+</sup> on nZVI, studying the extent of uptake as a function of concentration, time, pH, and repetitive application of nZVI. Desorption tests were also performed to test the stability of uptake. Another part of the experiments was devoted to comparing the extent of uptake of Ni<sup>2+</sup> ions with those of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, and Sr<sup>2+</sup> ions, which belong to a wide range of standard reduction potentials. The relevant experiments aimed at investigating possible correlation between the extent of uptake and the standard reduction potentials for the studied cations. The aqueous concentration of Ni and the other elements was determined using Flame Atomic Absorption Spectrometry (FAAS). The synthesized nZVI material was characterized using Zeta meter, BET-N<sub>2</sub>, scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX), high resolution-transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

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## 2. Experimental

### 2.1. Preparation of nZVI

The synthesis of nZVI was performed using the method of liquid-phase reduction utilizing  $\text{NaBH}_4$  (Aldrich 4511-2) as the reducing agent. The applied procedure was reported in detail in our earlier works [e.g. 4]. In brief, a 17.8 g sample of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (Sigma-Aldrich 22029-9) was dissolved in 50.0 mL solution of absolute ethanol (Riedel-de Haën 32221) and distilled water (4:1 v/v). An 8.47 g  $\text{NaBH}_4$  was separately dissolved in 220 mL of distilled water.  $\text{NaBH}_4$  solution was then added to a  $\text{Fe}^{2+}$  solution drop wise while providing well-stirring to the reaction mixture. After the addition of all the  $\text{NaBH}_4$  solution, the mixture was mixed for extra 20 min period. The iron powder was then separated from the solution by vacuum filtration, and the filtrate was washed at least three times with 99% absolute ethanol. The powder was dried in the oven at 75 °C overnight under atmospheric oxygen.

### 2.2. Characterization techniques

The solid samples were characterized using XPS, XRD, HR-TEM and SEM/EDX. In the XPS analysis, the samples were analyzed under high vacuum ( $<1 \times 10^{-7}$  mbar) in a Thermo Fisher Scientific Escapose X-ray photoelectron spectrometer equipped with a dual anode. The anode X-rays consisted of Al- $K_{\alpha}$  radiation at 400 W (15 kV). The analysis of the data was realized using Pisces (Dayta Systems, UK) software. The XRD analysis was performed using a Philips X'Pert Pro instrument in which the source consisted of Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). SEM/EDX analysis was carried out using a Philips XL-30 S FEG type instrument. The nZVI samples were sprinkled onto adhesive carbon tapes supported on metallic disks, and their images and elemental contents were recorded at different magnifications. HR-TEM analysis was done using a Tecnai F20. The instrument was operated at 200 kV acceleration voltages. Prior to analysis, the nZVI sample was dispersed in ethanol using an ultrasonic bath. Subsequently, a drop of the dispersion was applied to a holey carbon TEM support grid and excess solution was blotted off by a filter paper.

The particle size analysis of nZVI was performed using a Malvern Mastersizer 2000 instrument. For this purpose, 2.5 g of nZVI was dispersed in 25 mL of Millipore water (18.2 M $\Omega$ ) and the mixture was introduced to the instrument in small portions. Additional water was added to the suspension whenever required to increase the signal intensity, while subjecting the mixtures to ultrasonic shaking.

The surface area of the nZVI samples was determined by the BET- $\text{N}_2$  method using a Micromeritics Gemini 5 instrument. The iso-electric-point (IEP) of nZVI was determined using a Zeta-Meter 3.0 instrument. The zeta potential was measured for a series of suspensions in the pH range 6.0–12.0, at a concentration of 0.1 g/L.

### 2.3. Uptake experiments

Throughout these experiments, the aqueous  $\text{Ni}^{2+}$  solutions were prepared by dissolving appropriate amounts of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Carlo Erba 464645) in high purity water (Millipore, 18.2  $\Omega$ ). All the experiments were carried out at ambient temperature and pressure using 50.0 mL falcon tubes. The contents of the tubes were mixed on an orbital shaker operating at 350 rpm, and were subsequently centrifuged at 6000 rpm at the end of the uptake experiments. The supernatant solutions were filtered and transferred into clean falcon tubes and acidified with concentrated nitric acid (1% v/v), and were then analyzed using a Thermo Elemental SOLAAR M6 Series atomic absorption spectrometer with air-acetylene flame.

The experiments were performed in duplicate sets and the values presented in this work stand for the arithmetic averages of the obtained data.

In the kinetic experiments, 0.025 g of nZVI samples was added into separate 10.0 mL portions of 100.0 mg/L  $\text{Ni}^{2+}$  solutions, and the mixtures were shaken for 10 min, 30 min, 1 h, 4 h, 8 h, and 24 h contact times.

The effect of the initial  $\text{Ni}^{2+}$  concentration on the extent of uptake was investigated at 10.0, 25.0, 50.0, 75.0, 100.0, 200.0, 300.0, 400.0, and 500.0 mg/L concentrations. The experiments were performed by adding 0.025 g, 0.050 g, or 0.10 g of nZVI sample into 10.0 mL portions of  $\text{Ni}^{2+}$  solutions. The mixtures were shaken on the orbital shaker for 4 h prior to centrifugation. The supernatant solutions were then filtered and transferred into clean tubes until AAS analysis.

The experiments investigating the pH effect were conducted after adjusting the initial pH's of the mixtures to 4.0, 6.0, 8.0, or 10.0 using 0.01 M, 0.1 M, or 1.0 M of  $\text{HNO}_3$  and NaOH solutions. In each experiment 10.0 mL portions of  $\text{Ni}^{2+}$  solutions were contacted with 0.025 g nZVI for periods of 4 h. The pH of the solutions was also measured at the end of shaking process.

Part of the experiments was performed to assess the reusability of nZVI materials in successive uptake trials. In each experiment 0.025 g nZVI sample was added into 10.0 mL aliquot of 10.0 mg/L or 100.0 mg/L  $\text{Ni}^{2+}$  solutions. After shaking periods of 30 min, the mixtures were centrifuged; the supernatant solutions were transferred into new tubes and acidified. Then fresh 10.0 mL aliquots of  $\text{Ni}^{2+}$  solution were added onto the residual nZVI samples and the mixtures were shaken again for 30 min. These trials were repeated for seven times.

In the desorption tests, 10.0 mL portions of high purity water were added onto the Ni-loaded nZVI samples and were shaken for 24 h. The supernatant solutions were then analyzed for possibly released Ni ions.

A series of experiments was performed to compare the extent of uptake of  $\text{Ni}^{2+}$  with those of  $\text{Cd}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$  ions. The solutions of these cations were prepared from  $\text{CdCl}_2$  (Fluka 20899),  $\text{Cu}(\text{NO}_3)_2 \cdot 5/2\text{H}_2\text{O}$  (Riedel-de Haën 31288),  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  (Merck 393065), and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fluka 96482). The experiments were studied at the initial cation concentrations of 10.0, 25.0, 50.0, 75.0, 100.0, 200.0, 300.0, 400.0, and 500.0 mg/L. In each experiment, 0.025 g nZVI dose was contacted with 10.0 mL portions of metal solutions.

## 3. Results and discussion

### 3.1. Characterization of nZVI

XRD analysis of freshly synthesized nZVI showed that nZVI is dominated by  $\text{Fe}^0$  characterized by its main reflection at 44.9°. Weak signals of iron oxides (hematite,  $\text{Fe}_2\text{O}_3$  and magnetite,  $\text{Fe}_3\text{O}_4$ ) were detected in the nZVI samples after several weeks of storage under ambient conditions. The obtained results are in parallel with the ones we reported earlier for nZVI [4,5]. The presence of Fe and O in the nanoparticles surface is evident in the XPS spectrum given in Fig. 1, which indicates also the presence of some boron (must be originating from  $\text{NaBH}_4$  used during synthesis). The incorporation of B in the outer shell of Fe nanoparticles was reported earlier to take place in the form of oxidized B (borate) and some reduced B (boride) [16]. This inclusion was suggested as an auxiliary factor in the particle resistance against oxidation by atmospheric attack [17]. The primary reason for the slow oxidation is due to the oxide shell which is reported to be insoluble over the neutral pH conditions [18].

The structure of nZVI was also analyzed using HR-TEM. Typical images of fresh and aged nZVI samples are shown in Fig. 2. The nZVI particles demonstrated the characteristic chain-like structure, with the size of individual particles ranging within 10–60 nm (Fig. 2a). The chain-like morphology leads to decreasing the reactivity of the nanoparticles in terms of the available surface area, but at the same time provides the advantage of easier sorbent-solution phase separation at the end of uptake operation. The well known core-shell

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