Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.0704

69 (2017) 302–307
March

Enhancement of stability and reactivity of nanosized zero-valent iron with polyhydroxybutyrate

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Received 22 June 2016; Accepted 25 August 2016

ABSTRACT

Polyhydroxybutyrate (PHB) is a bacterial storage polyester, which is produced directly in the activated sludge process. In the present study, PHB was tested as a scaffold material for stabilization of nanosized zero-valent iron (nZVI). The morphology of the resulting composite was assessed using transmission electron microscopy (TEM) and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) analysis. In addition, the surface chemistry and particle stabilities of nZVI and nZVI/PHB were determined with zeta potential analysis and disc centrifuge measurements, respectively. Moreover, the sedimentation rate of bare nZVI was tested and compared with that for nZVI/PHB. Batch experiments further confirmed that nZVI/PHB particles are not only more stable but also more reactive toward perchloroethene (PCE) and Cr(VI) in comparison with the bare nZVI. These results suggest that PHB can be developed as an inexpensive and environmentally friendly material for the stabilization of nZVI particles.

Keywords: PHB; nZVI; Stabilization; VOC; Remediation; Cr(VI)

1. Introduction

Polyhydroxybutyrate (PHB) is a polymer of hydroxybutyric acid (Fig. 1) that belongs to the polyhydroxyalkanoate family, known for its good biodegradability, biocompatibility and also being bioderived from renewable resources by bacterial synthesis [1]. In addition, it serves as an intracellular storage material for carbon and energy and is built up as granules within the cytoplasm of the microbes [2].

In recent years, production of PHB from waste activated sludge or from food waste has gained great interest, and large amounts of this polymer can be cost-effectively produced [3].

Therefore, there is a need to create methods allowing for its introduction to the market. One possible route can be its use for the stabilization of nanometals and enhancement of the biodegradation process.

During the last 20 years, nanoscale zero-valent iron (nZVI) has gained attention due to its ability to bring about

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Presented at the EDS conference on Desalination for the Environment: Clean Water and Energy, Rome, Italy, 22–26 May 2016.

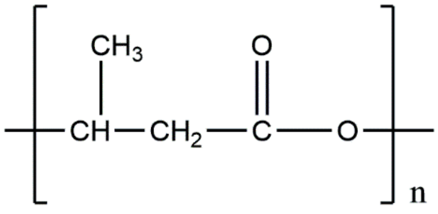

Fig. 1. PHB structural formula.

rapid decontamination of chlorinated compounds [4] and heavy metals [5]. The major problems associated with nZVI remediation technology of contaminated water and soil are in its limited stability against aggregation, restricted mobility in subsurface environments and short lifetimes under subsurface conditions [6].

To maintain the stability and reactivity of nZVI, many researchers have focused either on the optimal synthesis conditions of nZVI or on its surface alteration. Countless approaches like the inclusion of polymer stabilization (e.g., carboxymethylcellulose modification) [7] or iron oxide double shell surface stabilization [8] can be adopted to improve the dispersion of nZVI and efficiently support their stability and reactivity. Such stabilizations are accomplished by improvement of the steric or electrostatic repulsions [6] among the particles in order to inhibit nZVI aggregation. Simultaneously, the degradation efficacy of contaminants by surface modified nZVI can significantly increase, in comparison with that achieved by conventional nZVI [6].

In this study, a detailed investigation evaluating changes in the particle stability of nZVI due to PHB stabilization was carried out. Nanoparticle characterization as well as reactivity tests toward PCE and Cr(VI) were performed. To the best of our knowledge, this is the first assessment showing stabilization of nZVI with PHB.

2. Materials and methods

2.1. Reagents and solutions

PHB was purchased from Biomer (Krailling, Germany); nanoscale ZVI (Nanofer Star, Fe^0 stabilized with a thin iron oxide shell) was provided by NANO IRON, s.r.o. (Czech Republic); and chloroform (≥99%) was obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Analytical

Thermal stability and composition of the PHB and nZVI/PHB were determined using Mettler Toledo apparatus: TGA/SDTA851e. The experimental atmosphere was nitrogen at a flow rate of 20 ml/min. The sample was heated from 30°C to 700°C.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR–FTIR) spectra were obtained on a spectrophotometer (NICOLET IZ10, Thermo Scientific, USA). The spectrometer was equipped with a single reflection angle 45° horizontal ATR accessory. The spectra was obtained with a resolution of 4 cm^{-1} at 4,000–400 cm^{-1} using a germanium ATR crystal.

The composition and morphology of PHB, nZVI and nZVI/PHB were studied using a scanning electron microscope (SEM) with a beam current between 12 and 40 nA and acceleration voltage from 0.02 to 30 kV and with a complete detection system comprising in-lens energy and angle selective backscatter detector (EsB); four-quadrant solid-state backscattered detector (AsB) and conventional secondary electron detector (Everhart-Thornley, ZEISS, Ultra/Plus, Germany). The energy dispersive X-ray analysis (EDXA) analysis was conducted to determine the presence of various elements in PHB and nZVI/PHB nanoparticles.

For high-resolution transmission electron microscopy (HRTEM) observation, both samples were prepared on the standard Cu TEM grids covered with carbon thin foil. Drops of PHB or nZVI/PHB were dispersed in ca. 1 ml of isopropanol in ultrasound (10 min). In both cases, a drop of solution was gently spread on the upper surface of the carbon covered Cu TEM grid.

The zeta (ζ) potential values of PHB and nZVI/PHB nanoparticles were determined in freshly prepared suspension by Zetasizer ZS (Malvern Instruments Ltd, UK). Measurements were performed (10 runs each) with autocorrelation functions of 10 sec. Each result was the average of triplicate measurements.

Stabilities of nZVI and nZVI/PHB were assessed by the size distribution analysis in aqueous media and the batch sedimentation test. The centrifugal particle sedimentation (CPS) technique (CPS Disc Centrifuge, DC24000UHR, CPS Instruments Inc., USA) was used for particle size distribution analysis. Measurements were made at a disc rotation speed of 4,000 rpm, and the particle sedimentation was carried out in a 8%–24% (w/w) sucrose density gradient. Prior to each sample measurement, the instrument was calibrated using a PVC nanosphere standard (483 nm). The refractive index for measurements was chosen to be 2.87 [5].

As for sedimentation experiments, 2 ml suspensions of 50 g/L nZVI and nZVI/PHB were inserted into two vials. Subsequently, at selected time points, photographs were taken and used for comparing stability.

To determine the reaction kinetics of Cr(VI) and perchloroethene (PCE) removal, nZVI and nZVI/PHB at dosages of 1 g/L (for the Cr(VI) tests) and 5 g/L (for the PCE tests) were added to airtight 50-ml reactors containing water spiked with potassium chromate [Cr(VI)] – (initial concentration = 10 mg/L) and groundwater taken from the Pisecna site (PCE initial concentration = 18.5 mg/L). At selected time intervals, samples were taken out, filtered and analyzed.

PCE was qualitatively searched for in full scan mode of a GC/ion trap MS instrument (Varian Saturn 3800).

The Cr(VI) concentration in the solution was estimated by the colorimetric method specified in Method 7196A of US environmental protection agency (USEPA) (1,5-diphenylcarbazide procedure) [9].

2.3. Preparation method

nZVI STAR was activated before use. This involved preparation of a 20% solution of nZVI STAR (w/w) and blending it at a speed of 15,000 rpm, before and after a 48-h storage period at room temperature. A 0.5 g/L of PHB was then dissolved in chloroform and 200 ml of the resulting solution mixed with 50 ml of nZVI containing 250 mg of Fe^0. The mixture obtained was sonicated for 15 min and evaporated using a rotary evaporator. Subsequently, the resulting solution was freeze-dried and used for further analysis. Before the experiments, the nZVI/PHB composite was again blended at 15,000 rpm.

3. Results and discussion

3.1. Thermogravimetric (TGA) and Fourier transform infrared spectroscopy (FTIR) analysis

The TGA plots of PHB and the nZVI/PHB composite can be observed in Fig. 2(a).

TGA analysis was performed in an inert nitrogen atmosphere. From the TGA curves generated, it is evident that the nZVI stabilized with PHB decomposed in two major weight-loss steps as compared with PHB, which decayed in a single step. The initial decomposition step for nZVI/PHB occurred at 200°C. In the case of PHB, the weight loss was observed at 246°C due to decomposition of PHB, and no further weight loss took place. Thermogravimetric analysis estimated an nZVI content of approximately 60% for the nZVI/PHB composite. To identify the functional groups that participate in the nZVI/PHB chemistry, FTIR characterization was carried out (Fig. 2(b)). In the PHB sample, there can be observed a strong C=O band at around **AQ4** 1,725 cm^{-1}. The reduced intensity of this peak in nZVI/PHB sample (compared with the peak for PHB) can indicate that the negatively charged carbonyl groups could bind to positive sites on the surface of the nZVI as suggested by Comba and Sethi [10].

3.2. SEM/EDX and TEM analysis

Morphologies of PHB, nZVI and nZVI/PHB were evaluated using TEM and SEM, and their corresponding elemental analysis is being conducted with energy-dispersive X-ray spectroscopy (EDX) (Fig. 3). Lyophilized PHB with granular structures (Figs. 3(a) and (d)) could easily interact with nZVI to form an nZVI/PHB composite. Particles of nZVI were found inside the network of the PHB scaffold (SEM and EDX in Fig. 3(c) and TEM in Fig. 3(f)) similar to natural nZVI (Figs. 3(b) and (e)).

3.3. Zeta potential analysis

The surface potential charges of PHB, nZVI and nZVI/PHB particles were determined using the ζ-potential values, which, for PHB, nZVI and nZVI/PHB particles, were found to be –38.4 ± 1.0 mV, +0.74 ± 0.4 mV and –17.7 ± 0.5 mV at pH 7.0, respectively. The magnitude of the surface potential, in general, determines the level of electrostatic repulsion between the particles and the tendency of particles to interact with the rocky environment. The ζ-potential of nZVI particles was neutral at pH 7. PHB, possibly due to the non-bonding electrons of the oxygen atom belonging to the carbonyl group, has a much lower ζ-potential. This is a useful advantage in groundwater remediation processes [6].

3.4. Stability tests

Stability of nZVI suspensions was further tested by sedimentation experiments and CPS measurements. Fig. 4 shows sedimentation of bare nZVI and nZVI/PHB composite at the selected time points.

Without PHB, nZVI at the high concentration of 50 g/L settled in a few minutes. However, nZVI stabilized with PHB had not sedimented significantly throughout the experimental period (120 min). Samples with bare nZVI showed a clear upper liquid layer because most of the nZVI had become aggregated and settled. PHB stabilization resulted in the enhancement of nZVI stability. This is consistent with the change of the particle size distribution over time, as shown in Fig. 5. Our results are in agreement with reported literature concerning nZVI stabilization using guar gum [11].

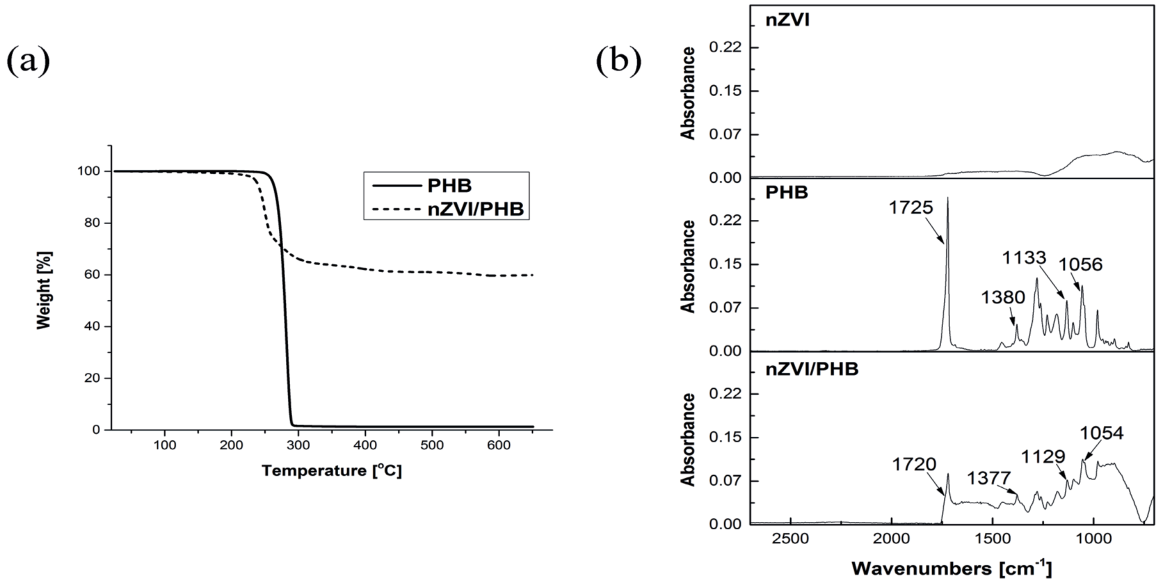

Fig. 2. (a) TGA curves of PHB and nZVI/PHB composite and (b) FTIR spectra of nZVI, PHB and nZVI/PHB composite.

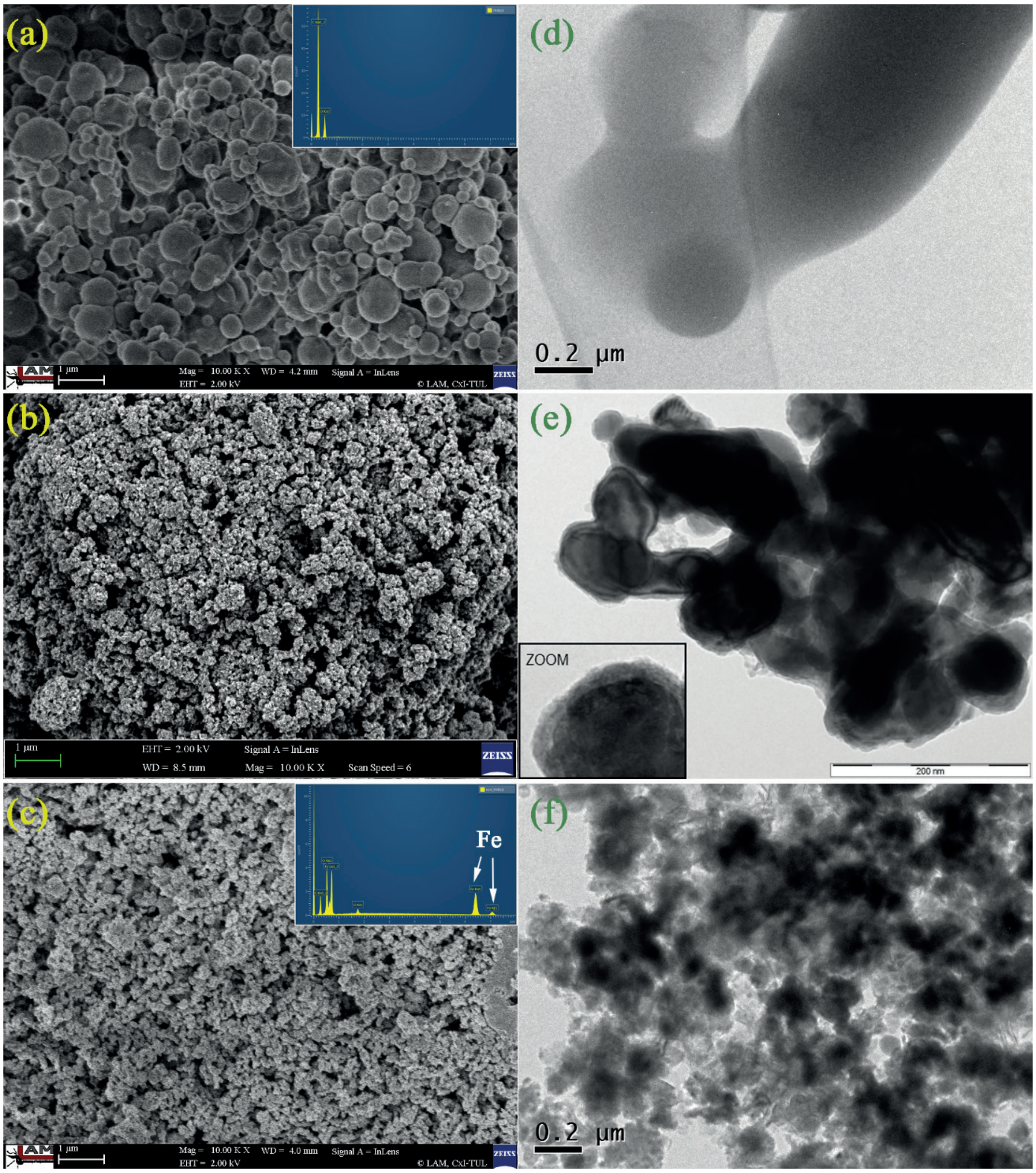

Fig. 3. SEM pictures of: (a) PHB, (b) bare nZVI and (c) nZVI/PHB and EDX analysis (insets) showing the presence of nZVI; and TEM pictures of (d) PHB, (e) bare nZVI and (f) nZVI/PHB (Fig. 3(e) was taken from reference [8]).

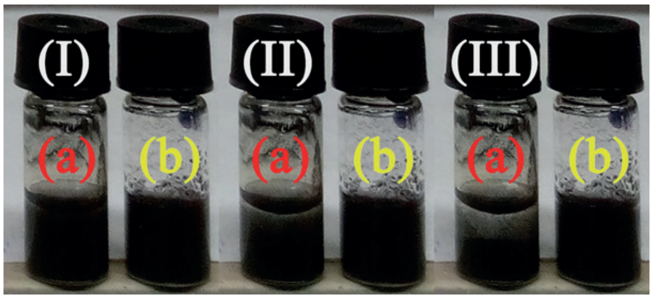

Fig. 4. Qualitative determination of sedimentation rates of: (a) bare nZVI and (b) nZVI/PHB composite at the selected time points of (I) 5 min, (II) 10 min and (III) 120 min ($nZVI_C$ = 50 g/L, $nZVI/PHB_C$ = 50 g/L).

3.5. Reactivity tests

Bare nZVI and nZVI/PHB were tested for their reactivity toward contaminated water samples containing PCE (Pisecna site, Czech Republic) and artificially prepared Cr(VI) solution. Removal of PCE and Cr(VI) with the use of nZVI and nZVI/PHB can be observed in Fig. 6.

Both reactors with stabilized nZVI had shown significant degradation efficacy of Cr(VI) and better degradation of PCE in comparison with the same dosage of bare nZVI. The probable reason is that in addition to enhancing nZVI stability, faster contaminant reduction can be achieved owing to a less agglomerated and more negatively charged nZVI/PHB [12]. Positive effects of stabilization on the nZVI's reactivity were observed also in a study conducted by Xiong et al. [13], in which starch and CMC stabilizers improved degradation of perchlorate by 1.8 and 5.5 fold, over uncoated nZVI, respectively. In another study, it was also found that CMC90K, CMC250K, and CMC700K all outperformed uncoated nZVI and all other polyelectrolyte treatments both in terms of nanoparticle size and reactivity, with CMC250K proving best [14]. Furthermore, one of the possible advantages of coupling PHB with nZVI can be the enhancement of biodegradation in long term, in situ studies because PHB is used as a source of organic carbon for bioremediation [15]. The higher negative charge of nZVI/PHB will also enhance nanoparticle mobility in the subsurface. It is clear that further work has to be done in order to determine the exact degradation mechanism of the nZVI/PHB composite.

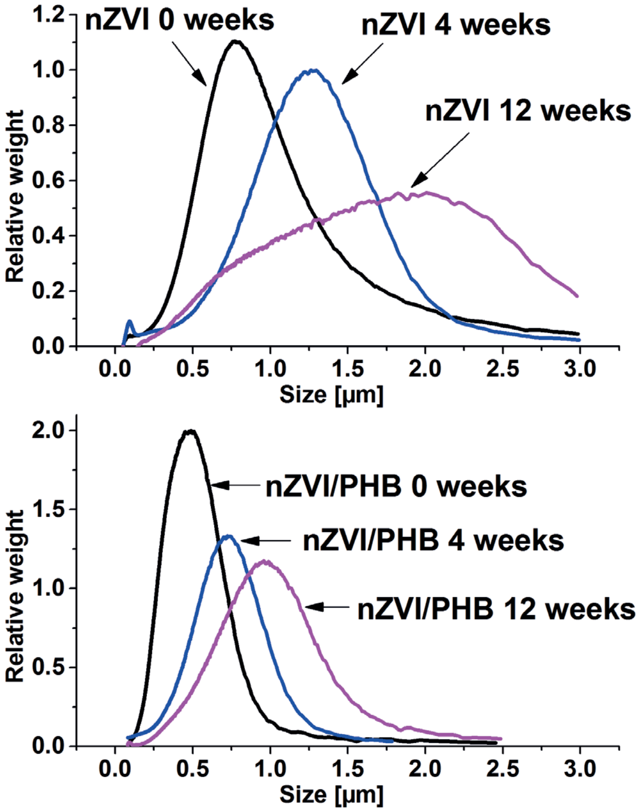

Fig. 5. Change of the particle size distribution over time determined for bare nZVI and nZVI/PHB composite.

4. Conclusions

We have demonstrated that PHB can serve as an effective stabilizing agent for nanosized zero-valent iron, and the following conclusions can be drawn:

- Based on sedimentation tests and measurements of the particle size distribution over time, nZVI/PHB shows better stability in comparison with the bare nZVI particles.
- PHB has improved the reactivity of nZVI in the batch test experiments on water contaminated with PCE and on artificially prepared Cr(VI) solutions.
- Low solubility of PHB in water makes production of nZVI/PHB inefficient, emphasizing the necessity of further studies in order to overcome this drawback.

Acknowledgments

The research presented in this article was supported by the Italian project – development and characterization of reactive materials for groundwater remediation Grandi Progetti Ateneo 2015, University of Rome "La Sapienza"; and the Ministry of Education, Youth and Sports in the framework of the projects KONTAKT II (LH14067), the National Programme for Sustainability I (LO1201), Research Infrastructure NanoEnviCz (LM2015073) and the OPR&DI project "Institute for Nanomaterials, Advanced Technologies and Innovation", CZ.1.05/2.1.00/01.0005.

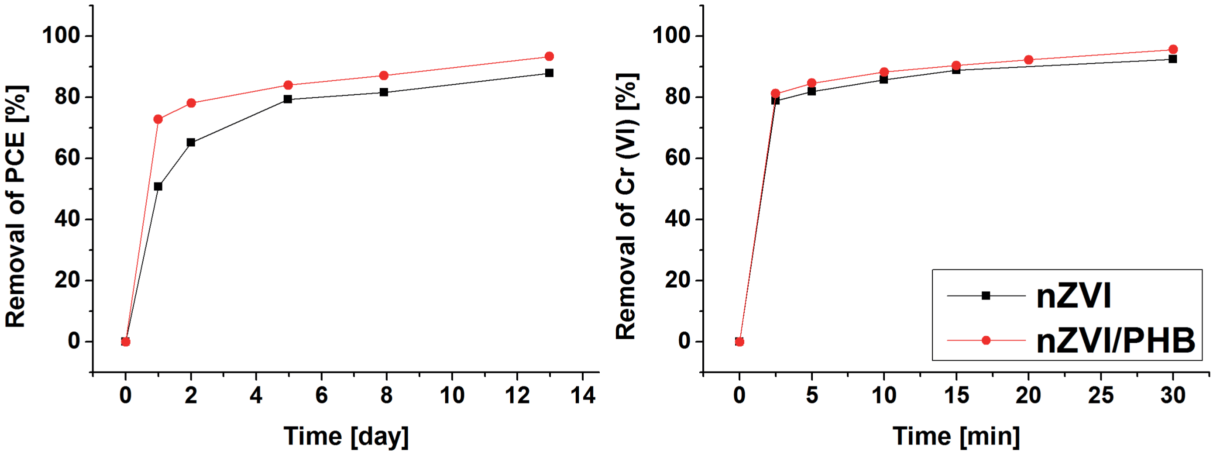

Fig. 6. Removal of PCE from groundwater from Pisecna site and of Cr(VI) in artificially prepared solution, with nZVI and nZVI/PHB (pH = 6.5, temperature = 23°C, PCE_C = 18.5 mg/L, $Cr(VI)_C$ = 10 mg/L).

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