

Extended Abstract

Removal of As(III) from Water Using “Green” Synthesized Zero Valent Iron in the Presence of Competing Phosphate Ions [†]

Đurđa Kerkez, Anita Leovac Maćerak *, Milena Bečelić-Tomin, Dragana Tomašević Pilipović, Jovana Jokić, Nataša Slijepčević and Božo Dalmacija

Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Serbia; djurdja.kerkez@dh.uns.ac.rs (D.K.); milena.becelic-tomin@dh.uns.ac.rs (M.B.-T.); dragana.tomasevic@dh.uns.ac.rs (D.T.P.); jovana.jokic@dh.uns.ac.rs (J.J.); natasa.slijepcevic@dh.uns.ac.rs (N.S.); bozo.dalmacija@dh.uns.ac.rs (B.D.)

* Correspondence: anita.leovac@dh.uns.ac.rs; Tel.: +381-21-485-2734

† Presented at Environment, Green Technology and Engineering International Conference (EGTEIC 2018), Caceres, Spain, 18–20 June 2018.

Published: 17 October 2018

Abstract: Nanoscale zero valent iron (nZVI) has been widely investigated for treatment of environmental contaminants. Various technologies are currently available to remove As(III) and phosphate from aqueous environment, but among them, adsorption is most common because its simplicity, treatment stability and cost effectiveness. This study is focused on the removal efficiency of As(III) in the presence of competing phosphate ions by nZVI synthesized using polyphenols from oak and mulberry leaf extracts producing OAK-nZVI and M-nZVI, respectively. The highest removal efficiency of As(III) was obtained for M-nZVI (up to 91% at all nZVI doses). 87% removal was obtained for OAK-nZVI. The same conclusion could be retrieved in the case of PO₄³⁻ removal (the highest removal, up to 78% at all nZVI doses for M-nZVI). Concerning OAK-nZVI, removal efficiencies increased with increasing nZVI doses (21–76% for doses 2–16 mL). Adsorption of As(III) in the presence of competing PO₄³⁻ ions on M-nZVI, decreased from 91% to 79%. On OAK-nZVI material, significant changes could not be observed. One can conclude that the presence of PO₄³⁻ ions in arsenic aqueous solutions would reduce effectiveness of the M-nZVI for As(III) remediation. This conclusion was supported by the fact that M-nZVI particles had a greater antioxidative capacity in comparison to OAK-nZVI which directly influenced nanoparticles synthesis and stability.

Keywords: nanoscale zero valent iron (nZVI); arsenic; phosphate; oak leaves; mulberry leaves

1. Introduction

Natural sources of arsenic are dissolution and degradation of arsenic minerals. Anthropogenic activities, such as mining, fossil fuels burning, smelting of metal ores, and use of wood preservatives, pesticides and arsenic additives to livestock feed may also release arsenic directly to the environment. [1]. Arsenic is stable in several oxidation states, of which the arsenite, As(III), and arsenate, As(V), are the most common forms in natural waters. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one. Adsorption is a common practice for arsenic removal from water matrix due to technological and cost advantages. Because of their high affinity for arsenite As(III) and arsenate As(V), elemental iron and iron (hydr)oxides are widely applied as the adsorbents for arsenic removal [2].

Phosphorus is introduced to natural waters by several exogenous sources such as fertilizers, industry, household detergents, and weathering rock [3]. Different phosphorus removal processes have been used to mitigate phosphorus discharge to the environment including biological and chemical treatments. Among the well-known processes adsorption is an effective, simple and rapid process that can effectively be used for the removal of phosphate [4]. There is a significant interest for development of ecological and sustainable methods for nanomaterial synthesis. Therefore, the development of nonhazardous, bio-based, low-cost, simple, and eco-friendly synthesized methods for nZVI is needed. Synthesis of such materials using ecological and biocompatible agents can reduce the toxicity of materials and bioproducts. Techniques that use naturally occurring reagents, such as vitamins, sugars, plant extracts, biodegradable polymers and microorganisms, can be considered in development of nanotechnology. In addition to the listed reagents, plant materials are most suitable for the “biosynthesis” of nanoparticles [5]. For the synthesis of the nanoparticles different parts of plants, such as leaf, root, seeds and stems can be used. It is believed that key active agents for such synthesis are polyphenols present in plants. The “green” synthesis of the nanoparticle has an advantage over others methods due to its simplicity, low cost and usually result in more stable materials.

In this work, the green synthesis of nZVI using extracts of oak and mulberry leaves is used to treat the mixture of As(III) and phosphate ions, as the nZVI represents the promising alternative for its removal due to involvement of both adsorption and redox mechanism.

2. Materials and Methods

Nano-zero valent iron is synthesized using oak and mulberry leaves extract as a reducing agent according to Machado et al., 2013 [6]. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectrometry (EDS) was used to determine the surface and spatial structure of the nanomaterial. The toxicity test for bacteria *Vibrio fischeri* was done according to ISO 11348-1: 2008 Water quality – Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminiscent bacteria test) [7].

Removal efficiency experiments were obtained by adding different nZVI doses in the range of 2–16 mL to aqueous solutions with initial As(III) and PO_4^{3-} concentrations of 40 $\mu\text{g/L}$ and 5 mg/L , respectively. Experiments were performed for As(III) and PO_4^{3-} separately and then in a mixture. The reaction time was 1 h. Sample bottles were placed on shaker at 180 rpm. After the shaking solutions were centrifuged for 12 min at 4000 rpm and then filtered through 0.22 μm filter. Residual phosphate concentrations were determined according to SRPS EN ISO 6878:2008 method [8]. Residual concentrations of As(III) were determined by inductively coupled plasma with mass spectrometry (ICP-MS, Agilent Technologies 7700 Series).

3. Results and Discussion

SEM images of synthesized OAK-nZVI and ML-nZVI are presented in Figure 1. The spherical structure of both nZVI particles can be observed. Also there is no significant aggregation of produced nanoparticles which indicate on nanomaterial stability.

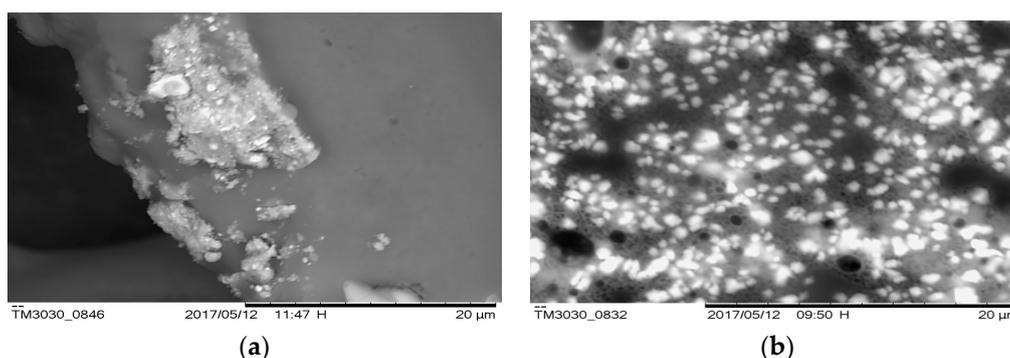


Figure 1. SEM images of (a) OAK-nZVI and (b) ML-nZVI.

EDS mapping revealed the present elements on the surface of the nanomaterials. The presence of Fe as an intense peak indicated on Fe nanoparticle formation. Intensive chlorine peak originates from iron salt used for nanomaterial synthesis (Figure 2). Also, there are potassium, calcium, carbon and oxygen elements originating from plant extract and confirming biomolecule coverage on the nanoparticle surface.

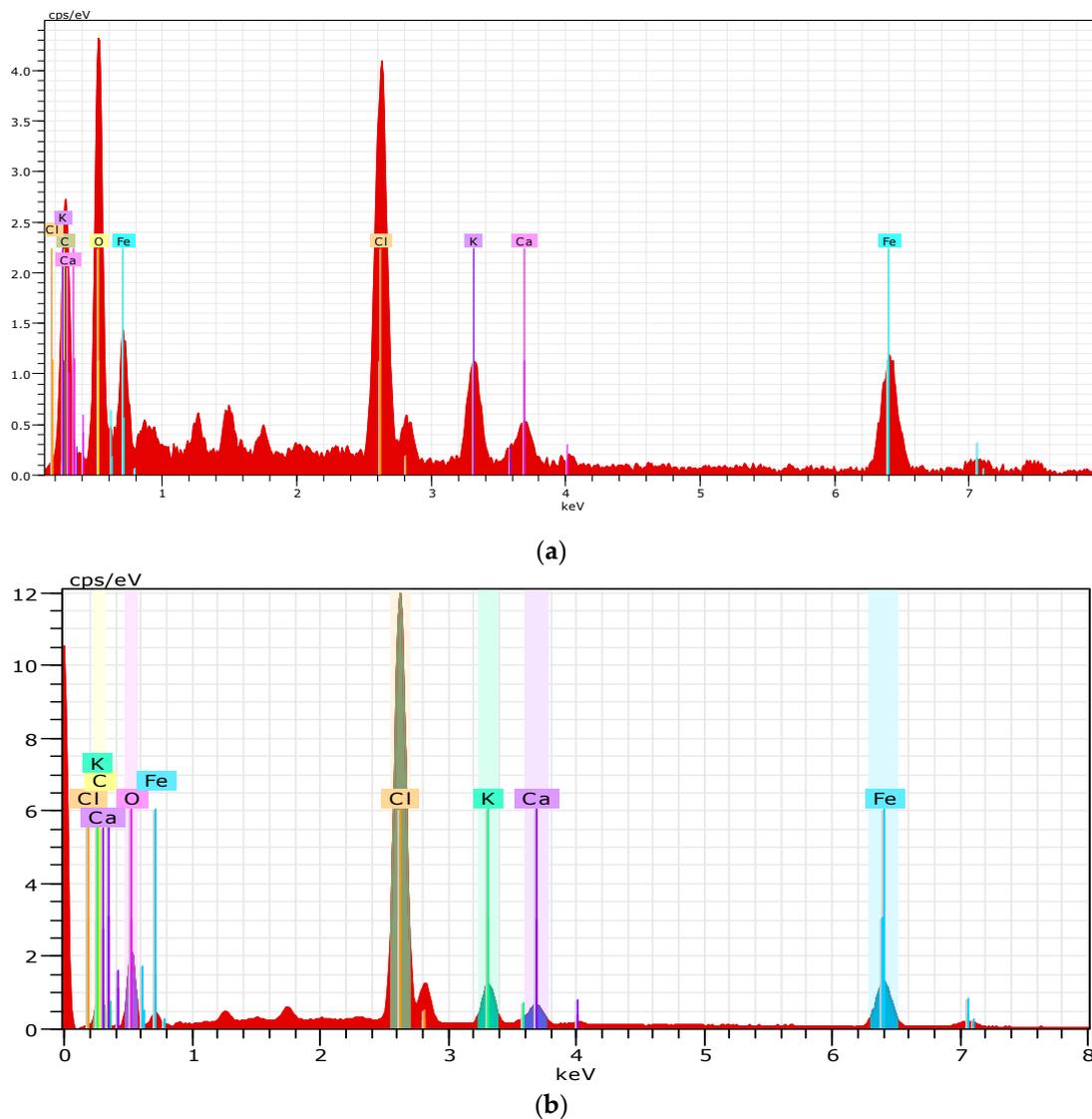


Figure 2. EDS atomic mapping of (a) OAK-nZVI and (b) ML-nZVI.

Toxicity test on bacteria indicated inhibition of 32.61% for OAK-nZVI. This percent of inhibition falls within the range below 50%, which makes this nanomaterial practically non-toxic. The toxicity test of the nZVI sample synthesized by mulberry leaf extract showed that this kind of nZVI nanoparticles was at the boundary between the moderately toxic and non-toxic matrix, as the inhibition of *Vibrio fischeri* bacteria activity is 50.0%. Toxicity test generally indicate that these nanomaterials are safe for environmental application.

As(III) removal efficiencies when using OAK-nZVI ranged from 81 to 87%. The highest removal efficiency for As(III) was obtained in case of M-nZVI usage (91%). Also, for M-nZVI the nanomaterial dosage did not have significant influence. Similar conclusion could be retrieved for PO_4^{3-} as OAK-nZVI dose increase resulted in removal efficiency increase ranging from 21–76%. Removal of As(III) when in a mixture with PO_4^{3-} did not significantly decrease in case of OAK-nZVI (Table 1).

Table 1. As(III) (40 µg/L) removal efficiencies when in a mixture with PO₄³⁻ using OAK-nZVI and M-nZVI.

Sample (nZVI Dosage)	OAK-nZVI		M-nZVI	
	C (µg/L)	Removal (%)	C (µg/L)	Removal (%)
2 mL	18.2	52.4	10.3	73.2
4 mL	6.92	81.9	10.0	73.8
8 mL	6.34	83.4	9.84	74.3
10 mL	6.34	83.4	9.43	75.4
12 mL	6.33	83.5	8.34	78.2
16 mL	6.30	83.6	7.82	79.6

The difference is noticeable only in the case of the smallest amount of nanomaterial used. Adsorption of As(III) in the presence of competing ions on M-nZVI, decreased from 91% to 79% (Table 1). One can conclude that the presence of PO₄³⁻ ions in arsenic aqueous solutions would reduce effectiveness of the M-nZVI for As(III) remediation. The effect indicates on the competition between arsenic species and phosphate for the same adsorption sites that exist on the surface of nanomaterial. Similar conclusions were brought by Zhu et al., 2009 [2] where presence of phosphate caused significant decrease in As(III) and As(V) kinetic when using zero valent iron and nano zero valent iron on activated carbon. It is considered that phosphate maybe adsorbed onto inner-sphere complex with the hydroxyl groups of the materials, forming stronger bonds than arsenic. Removal efficiencies of PO₄³⁻ in the presence of As(III) did not significantly differ from the sole presence of phosphate ion and OAK-nZVI (Table 2). On the other hand, when using M-nZVI, removal efficiency for PO₄³⁻ reduced significantly, as in the case of As(III) (Table 2).

Table 2. PO₄³⁻ (5.06 mg/L) removal efficiencies when in a mixture with As(III) using OAK-nZVI and M-nZVI.

Sample (nZVI Dosage)	OAK-nZVI		M-nZVI	
	C (µg/L)	Removal (%)	C (µg/L)	Removal (%)
2 mL	3.96	21.8	2.67	47.2
4 mL	3.77	25.5	2.63	48.1
8 mL	3.36	33.5	2.50	50.6
10 mL	3.06	39.6	2.38	52.9
12 mL	1.60	68.3	2.29	54.6
16 mL	1.06	79.1	2.04	59.8

4. Conclusions

Oak and mulberry leaves extract were successful in OAK-nZVI and M-nZVI synthesis. Synthesized nano zero valent iron was well dispersed and stable due to polyphenols and other biomolecules present in the leaves extracts. Both nanomaterials proved to be efficient for removal of phosphate and As(III) separately as well as in the mixture. Removal of arsenic in the presence of the competing ions decreased as well as PO₄³⁻. This effect is more pronounced in the case of M-nZVI.

Author Contributions: Đ.K. and A.L.M. designed the experiment. M.B.-T. and D.T.P. helped with the data analysis. J.J. performed the experiments. N.S. participated in nanomaterial synthesis and characterization. B.D. contributed reagents and materials.

Acknowledgments: The authors acknowledge the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia within the Project III43005.

Conflicts of Interest: The authors declare no conflict of interest

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