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Preparation of air stable nanoscale zero valent iron functionalized by ethylene glycol without inert condition



Claudio Adrian Ruiz-Torres^a, René Fernando Araujo-Martínez^a, Gabriel Alejandro Martínez-Castañón^a, J. Elpidio Morales-Sánchez^a, Jesús María Guajardo-Pacheco^a, Jesús González-Hernández^b, Tae-Jin Lee^c, Hyun-Sang Shin^c, Yuhoon Hwang^c,^{*}, Facundo Ruiz^{a,*}

^a Facultad de Ciencias, Universidad Autónoma de San Luis Potosí (UASLP), Avenida Manuel Nava 6, Zona Universitaria, C.P. 78290 San Luis Potosí, SLP, Mexico
 ^b Centro de Ingeniería y Desarrollo Industrial (CIDESI), Av. Playa Pie de la Cuesta No. 702, Desarrollo San Pablo, C.P. 76125 Santiago de Querétaro, Qro, Mexico
 ^c Department of Environmental Engineering, Seoul National University of Science and Technology, 232 Gongreung-ro, Nowon-gu, Seoul 01811, Republic of Korea

GRAPHICAL ABSTRACT



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ABSTRACT

The use of nanoscale zero-valent iron has been widely studied in recent years for potential application in environmental engineering, due to its affinity for a large number of contaminants, which may be in aqueous or solid phase, and for its abundance, which makes it an attractive tool for environmental remediation. However, there exist some variables in the production of nZVI that complicate the generation of the material, such as the complex methodologies of synthesis and the cost of inert conditions like nitrogen or argon atmosphere, which have the purpose of preventing the oxidation and reducing the instability of the material under ambient conditions. As a simple and economical synthesis methodology, this work presents an optimized method to synthesize functionalized nanoscale zero-valent iron (nZVI) using ethylene glycol (EG) without need for inert conditions. The coordination of iron ions during the nZVI-EG synthesis and the functionalization mechanism of the nanoparticles were identified by UV–Vis absorption spectroscopy and Fourier transform infrared spectroscopy (FTIR). Functionalized nZVI showed increased dispersibility due to the effects of steric repulsion between the grafted polymers. Ethylene glycol functionalized nZVI showed stability against oxidation during dry atmospheric condition, while significant oxidation was observed in the case of unfunctionalized nZVI. This result

* Corresponding authors. E-mail addresses: yhhwang@seoultech.ac.kr (Y. Hwang), facundo@fciencias.uaslp.mx (F. Ruiz).

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Received 28 August 2017; Received in revised form 31 October 2017; Accepted 8 November 2017 Available online 11 November 2017 1385-8947/ © 2017 Elsevier B.V. All rights reserved. was also correlated with actual capacity for contaminant reduction. Therefore, the possibility was verified of using ethylene glycol in an effective surface modification method to prepare air stable nZVI for environmental remediation.

1. Introduction

Environmental nanotechnology provides novel tools for remediation based on the synthesis and application of advanced materials that can be functionalized; the process of functionalization optimizes material environmental application, allowing material to act as a contaminant immobilizer in the environment or promoting contaminant degradation [1,2]. A good example is the use of zero-valent iron nanoparticles (nZVI). Because of their high surface area and standard redox potential ($E_0 = -0.44$ V), these materials allow a high rate of reactivity with contaminants via electron transfer during the oxidation of Fe⁰ to Fe²⁺ and eventually Fe³⁺; this makes these materials efficient reducing and oxidizing agents [3,4] and provides them with specific affinity for toxic contaminants in aqueous systems [5]. Examples include chlorinated organic solvents, organochlorine pesticides, organic dyes [6–8], and metal ions such as Pb (II), Cu (II), Ni (II), and Cr (VI) [9–13].

Nevertheless, in the application of nZVI to environmental nanotechnology, the stability plays an important role due to high material tendency to react in response to large surface area; such materials are usually unstable when exposed to the air. Moreover, in the synthesis and handling of nZVI, this material is widely known to form an iron oxide thin layer around the particle called the core-shell; this layer is established by interaction of the metal core with oxygen present in the surrounding environmental, creating a passivation of the surface, which can take different crystalline structures such as Wüstite (FeO), magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), or Goethite (α -FeOOH) [14–17]. The main function of this layer is to prevent the additional particle oxidation [18].

However, most authors report that, in order to prevent oxidation as much as possible, the synthesis and application of nZVI must make use of nitrogen or argon atmosphere during the manipulation of the material. On the other hand, the implication of inert conditions in the synthesis process is a highly cost method, which hinders the development and application of this material in real cases. In relation to this highly relevant fact of nZVI production, it is extremely important to find new ways to stabilize and protect nZVI in the presence of air, where they are highly sensitive to oxygen. For this reason, nanomaterial surface modification has been a widely studied area and has great interest because it can provide tools to modify the interactions that materials may have with the surrounding environment [19]. Changes of stability, compatibility, and reactivity are some examples of modifications in materials via a coated surface; such modifications then lead to an increase in potential applications.

Coating techniques can generally be divided into two large groups: first, coating of nanomaterials by use of inorganic materials such as precious metals (Ag, Au, Pt, Pd) [20-23] and silica [24]; second, the coating of nanomaterials by use of organic shields such as surfactants or polymers [25,26]. Researchers have emphasized the latter group in recent years, and advances in polymer nanotechnology have led to new and different methodologies to stabilize nanomaterials as protective agents [27,28]; these agents have been applied in the development of systems of organic-inorganic composites. Using nanoparticle functionalization to optimize material proprieties, it is possible to dramatically increase the applicability of nanomaterials, because polymers grafted on particles surface form a protective layer that imparts different properties to the material; as well, it has been reported that the presence of layers of different varieties of polymers, like coated agents, makes it possible to control the size and agglomeration of nanoparticles by varying the concentration, the geometry, and the terminal groups of

the polymers [29]; this is due to the effects of electrostatic repulsion or steric repulsion between the polymers grafted onto each particle. The main interest in the functionalization of nanomaterials based on iron and iron oxide is the stabilization and protection of nanoparticles from excessive oxidation under ambient conditions, which would greatly reduce material reactivity and applicability [30,31].

In general, because there exists a certain affinity of the functional groups contained in polymer molecules with inorganic surfaces, modification of the surface of nanomaterials by use of organic compounds can occur through chemical and electrostatic interactions among the molecules of the polymer and the nanomaterials; therefore, functionalization can be performed by various mechanisms such as physical adsorption, mono-, bi-, or tri-dentate coordination, bridging chemisorption, or chelating chemisorption [32,33]. In view of this, a higher affinity of certain binder groups to specific inorganic surfaces has been reported, an example of which is the use of oleic acid, which has been reported to have a high affinity for magnetic nanoparticles composed of iron and iron oxide; several reports show that functionalization occurs by interaction between O-atoms of the carboxylate and hydroxyl groups and Fe-atoms present in the nanoparticles surface, generating bi-dentate coordination of the particles [33–37]. The higher affinity presented by these types of terminal groups towards the particles compared to that toward different binding groups such as thiol or amine groups can be explained by the high affinity of oxygen for iron and the greater electronegativity of oxygen atoms in contrast to that of others atoms used in the functionalization of materials, increasing the probability of the interaction between the O-atom contained in the ligand group and the surface of the material for their bonding.

However, in metal nanoparticle functionalization, the affinity and solubility of the binding molecule are important aspects, such that the insolubility of oleic acid in aqueous systems produces a lower density of grafted organic molecules on the surfaces of the particles [38]. In relation to this, in some cases, the functionalization of materials is restricted to post-synthesis methods, which have reported a lower density of functionalization relative to the one-step functionalization methods [38,39]. Influenced by this, a greater solubility of the coated agent will have a better effect on the functionalization of the material.

On the other hand, due to the magnetic interaction between ZVI particles there exists a high aggregation rate between these nanomaterials, which implies a reduction in the surface area and in the reactivity of the particles [40,41]. In view of this, and of the fact described above, for a greater interaction with the surface of nanomaterial, it is necessary to functionalize with –OH ligand groups due to the high polarity and hydrophilic nature of this type of binder molecule, as well as to achieve less aggregation via reduction of the interfacial energy between the solvent and the particles and an increase of the dispersibility of the material [19,42,43]; these facts highlight the need to use these types of ligand molecules in contrast to various agents with functional groups such as –COOH, –NH₂, and –SH [38,44].

In relation to this, there have been numerous studies that have described successful mono-dentate functionalization of iron and iron oxide nanomaterials using polyethylene glycol (PEG), which contains a hydroxyl (–OH) ligand groups where, in the same way, free electron pairs of the O-atoms can interact with the surface of the nanoparticles for generation of coordinated covalent bonds, leaving grafted polymer chains [45–47]. However, a limitation in the use of dense polymers with a high degree of polymerization such as PEG, are the effects of steric repulsion due to volume exclusion to which the polymeric brushes are subjected, limiting the insertion of other chains at the surface of the particles, reducing the uniformity of the protective layer and

increasing the exposure area of the catalyst to eventual oxidation [48,49]. Therefore, the use of a short chain polymer such as ethylene glycol provides the chemical and morphological characteristics necessary for the proper functionalization of nZVI and for its protection from corrosion.

In this work, ethylene glycol (EG) was used as a coating agent to provide air stability to synthesized zero-valent iron nanoparticles during synthesis and drying. The functionalization led to better applicability of the material due to the modification of its surface, increasing nanoparticle dispersibility in aqueous media. To corroborate the advantages involved in the functionalization of the material, nZVIs were obtained in the presence and absence of the coating agent; simple (S-nZVI) and stabilized (nZVI-EG) nanoparticles were obtained. The nanomaterials were synthesized and functionalized at room temperature without inert atmosphere of nitrogen or argon. The nZVI functionalization mechanism was analyzed by ultraviolet–visible (UV–Vis) absorption spectroscopy and Fourier transform infrared spectroscopy (FTIR). In addition, the dispersibility of the nanomaterials with and without functionalization was tested by sedimentation test.

Moreover, the air stability of the nZVI-EG and S-nZVI samples and the efficiency of the functionalization as anticorrosive protection were evaluated by the drying of the materials under anaerobic conditions (nZVI-EG₁ and S-nZVI₁) and aerobic conditions (nZVI-EG₂ and SnZVI₂). The oxidation degree of the different samples was characterized structurally in terms of crystallinity, morphology, and elemental composition. The modification of the reactivity due to the corroding of the materials was analyzed by the quantification of reactive iron and the reduction of nitrates.

2. Materials and methods

2.1. Synthesis and functionalization of nZVI

In this work, employing a strong reducing agent such as sodium borohydride, zero-valent iron material synthesis was carried out by aqueous chemical reduction method of a ferric salt. In contrast to most synthesis methods that have been reported [2,15,34-37], nZVI were synthesized in a beaker at regular atmospheric conditions, demonstrating a low-cost methodology for nanoscale zero-valent iron production. First, 50 ml of 0.05 M FeCl₃ was dissolved in deionized water and stirred at 800 rpm for 5 min. Later, 0.4 ml of EG was added under stirring for another 10 min. Finally, 0.05 M NaBH₄ was added to the vessel. The obtained product is a black precipitate, which corresponds to zero-valent iron nanoparticles. Subsequently, the product was washed three times with ethanol to remove the unreacted ions present in solution. S-nZVIs were synthesized under similar conditions without EG addition during the synthesis. The nZVI-EG₁ and S-nZVI₁ samples were dried in anaerobic conditions in an anaerobic chamber for 24 h (N₂:H₂ 95:5). Moreover, in order to compare the air stability and iron core consumption of the two different samples with and without functionalization to atmospheric and inert dried conditions, and to compare their oxidation rate and reactivity to nitrate reduction, samples nZVI-EG2 and S-nZVI2 were dried under aerobic conditions in an open container for 24 h.

2.2. Physical characterization methods

The coordination of iron ions during nZVI-EG synthesis and the functionalization mechanism of the nanoparticles were identified by UV–Vis absorption spectroscopy and Fourier transform infrared spectroscopy (FTIR) characterization techniques. UV–Vis absorption spectroscopy was performed using an S2000-UV–Vis spectrometer from OceanOptics Inc.; Fourier transform infrared spectroscopy (FTIR) was performed using a Shimadzu IRAffinity-1.

Morphological analysis was conducted using a transmission electron microscope (TEM). TEM images at 100 kV were obtained using a JEOL-



Fig. 1. A) UV–Vis aqueous absorption spectra of FeCl₃, $[Fe(EG)_4(H_2O)_2]^{3+}$ and spectra of nZVI functionalized with EG. B) FTIR spectrum of EG and nZVI-EG.

1230; HR-TEM microphotographs were captured on a JEM-2200FS field emission transmission electron microscope at an acceleration voltage of 200 kV. An Energy Dispersive Spectrometer scanning line (EDS) was used to detect the elemental distributions of Fe and O; this was performed by TEM equipment (JEM-2200FS).

Structural changes of nZVI during dry step were characterized by X-ray diffraction patterns. XRD patterns were recorded with a GBC-Difftech MMA diffractometer with filtered CuK α ($\lambda = 1.54$ A) radiation. To corroborate the presence of iron zero-valent (α -Fe) and iron oxide (FexOy), and to perform phase quantification and crystallite size estimation, X-ray data refinement was achieved by subjecting the XRD data to Rietveld refinement [50] using the program MAUD .

Dispersibility of nZVI particles was determined by sedimentation analysis using a UV–Vis spectrophotometer (Cary 50, Agilent Technologies Inc., USA). The dispersions were shaken but not sonicated prior to the experiment. Then, the samples were transferred into a 1-cm plastic cuvette and capped to prevent further oxidation during the sedimentation test. The absorbance of the diluted samples was monitored as a function of time, according to the optical absorbance at 508 nm, to obtain the sedimentation curve. The sedimentation curves were interpreted using the following equation [32].

 $I_t = I_0 e^{-t/\tau}$

where I_t is the absorbance of the solution at time t, I_0 is the initial absorbance, and τ is the characteristic time.



Fig. 2. Schematic illustration showing Fe³⁺ coordination process and functionalization of nZVI by EG.

2.3. Reactivity measurements

2.3.1. Reactive iron contents

Following the methodology reported by Ref. [40], the reactive iron content among prepared nZVI samples was determined by quantification of hydrogen gas (H₂), which is produced during the acid digestion of the sample according to the following reaction, where only the Fe (0) present in the sample will produce H₂. A solution of concentrated hydrochloric acid (37%) with a concentration of 1.5 g/l of nZVI was put in a 22 ml vial. The vial was purged and capped to allow the reaction to proceed for 24 h. The quantification of H₂ was performed using a gastight syringe to remove 0.5 ml of the headspace in the closed vial; the sample was analyzed by gas chromatography. Later, the total iron concentration in solution was measured by atomic absorption spectrometry (AAnalyst 200, PerkinElmer, USA) and then compared with the H₂ value obtained from the calculation of the Fe (0) content of the sample.

$$2Fe^{0} + 6H^{+} \rightarrow 2Fe^{3+} + 3H_{2}$$

2.3.2. Nitrate reduction capacity

The reducing reactivity of the nZVI samples was determined by the reduction of nitrates to ammonia. The experiments were carried out in a 50 ml bottle. 25 mg of nZVI was added to the bottle, along with 23 ml of deionized water; the pH of the solution was adjusted to 5 by adding 1 ml of 250 mM acetic acid buffer solution; the vial was purged with nitrogen and sealed. Then, 1 ml of the nitrate stock solution (625 mg NO₃-N/L) was injected. The final concentrations in the solution are 12.5 mg NO₃-N/L and 1000 mg Fe/L. The bottle was stirred for 1 min for the dispersion of the material and placed in a shaker at 150 ppm. Samples were taken out periodically and filtered through a 0.45 µm membrane; the ammonia content was immediately analyzed. Ammonia analysis was conducted based on the procedure described in previous research [51].

 $4Fe^{0} + NO_{3}^{-} + 10H^{+} \rightarrow 4Fe^{2+} + NH_{4}^{+} + 3H_{2}O$

3. Results and discussion

3.1. nZVI functionalization by ethylene glycol

3.1.1. Functionalization mechanism

In order to identify the mechanisms involved in the functionalization, the sample was characterized by ultraviolet–visible (UV–Vis) absorption spectroscopy and FTIR spectroscopy. In Fig. 1A, the absorption spectrum of the FeCl₃ solution shows a band at 300 nm, which corresponds to the presence of Fe³⁺ ions. Subsequently, when the stabilizing agent is added to the solution, a modification of the absorption band is observed and an absorption peak appears at 245 nm, which can be directly attributed to the interaction of Fe^{3+} with EG, forming a relative stable complex $[Fe(EG)_4(H_2O)_2]^{3+}$ [47,52].

The coordination of the metal ions is possible through the electrostatic attraction occurring between the positively charged iron cations and the negative charges of the free electron pairs of the ligand molecule (-OH), which function as negative charge points. Generating octahedral coordination in which the presence of the four hydroxyl ligands contained in the EG molecule and two H₂O ligands are involved, and in which the presence of these latter is due to the solvation spheres surrounding Fe³⁺, an octahedron is produced as a coordinating structure around the cation $[Fe(EG)_4(H_2O)_2]^{3+}$. The modification of the absorption band can be explained by crystalline field theory, in which it is indicated that the approximation of the lone electron pairs of the ligand molecule to the iron ion d-orbitals will produce d-orbital depletion in two sets with different properties and energies, separated by an energy gap, (Δ_{oct}), called a crystal-field splitting parameter. Therefore, the modification of this parameter and the energies associated with the d-orbitals of the metal ion will directly alter the optical properties, such as the color and the absorption and reflection spectra of the metal complex [53–55].

Finally, the addition of the reducing agent NaBH₄ initiates the nucleation process of nZVI. In the absorption spectrum belonging to nZVI-EG, the absorption peak at 244 nm, associated with the metal complex, is preserved, which implies mono-dentate coordination of the surface of the nanoparticles by the -OH ligand, which likewise modifies the optical properties of the material [53].

Fig. 1B shows the results of FTIR analysis, which was performed with the purpose of comparing the infrared spectra of neat EG and EG stabilized nZVI; this was done to characterize the changes in the chemical bonds that occur due to the functionalization of nZVI. The EG spectrum presents a band at 3137.6 cm⁻¹ (O–H groups stretch band), a band at 2783.1 cm⁻¹ (C–H stretch deformation), a band at 1608.2 cm⁻¹ (OH groups flexural vibration of the water molecules absorbed in the sample), a band at 1405.2 cm⁻¹ (flexural strain of C–H group), a band at 1157.5 cm⁻¹ (C–O stretching vibrational mode) and a band at 1275.6 and 960.5 cm⁻¹ (extension of O–H and C–O–H).

In the FTIR spectrum of nZVI-EG, the characteristic bands of EG found at 3137.6, 1405.2, 1152.2 and 960.5 cm⁻¹ are displaced to 3146.7, 1401.4, 1127.4 and 984.3 cm⁻¹. However, for the case of the deformation by stretching of groups O–H and C–O–H at 984.3 cm⁻¹, there is a noticeable decrease in the intensity of the band. It is widely known that the changes in the intensity of the vibrational frequencies associated with the ligand groups involved in the coordination suggest their direct association as a metal-ligand linker due to the generation of



(c) nZVI nZVI nZVI nZVI nZVI

Fig. 3. A–B) TEM photomicrography of nZVI-EG and S-nZVI and their corresponding histograms. C) Schematic model of ZVI nanochains.

coordinated covalent bonds, which explains the suppression in the intensity of the deformation by stretching of the ligand molecule, indicating its attenuation, this is due to the interaction of the O atoms in the ligand group with the Fe atoms through coordinated covalent bonds [47,56]. Again, the phenomena involved can be described by crystalline field theory, in which the interaction of a ligand with a metal is due to the lodging of lone pairs electrons of ligand atoms in the d orbitals of the iron atoms present on the nanoparticle surface, generating monodentade coordination and functionalization and forming a protective layer by the addition of EG brushes [36]. In view of this information, the air stability of nZVI-EG can be said to be directly related to the



Fig. 4. Sedimentation curves of nZVI and nZVI-EG.



Fig. 5. Powder X-ray diffraction (XRD) patterns of nZVI and functionalized nZVI dried in anaerobic and aerobic conditions.

Table 1

Rietveld refinement of a sample zero-valent iron nanochain with and without EG.

Sample	$\alpha\text{-}Fe\%$ in weight	Fe ₃ O ₄ % in weight	
nZVI-EG ₁	98.87	1.13	
S-nZVI ₁	78.28	21.72	
nZVI-EG ₂	85.17	14.83	
S-nZVI ₂	44.98	55.02	

coordination of the Fe atoms by the occupation of their empty d-orbitals by lone pairs electrons, generating stabilization and reducing or delaying its interaction with oxygen present in the environment, decreasing the rate of oxidation [57]. Finally, the spectrum associated with sample S-nZVI presents two main peaks at 3137.6 and 1663.8 cm⁻¹; these peaks are related to the extension and flexible motions of the O–H bonds of the H₂O molecules, which represent the absorption of water molecules on the surface of the nanoparticles.

Based on the results obtained by UV–Vis and FTIR analysis, the functionalization mechanism can be concluded to be as below. First, the iron ions coordinated through the addition of EG molecules after that, NaBH₄ was added to the solution and Fe (III) ions were reduced to Fe⁰, starting the nucleation process and particle formation according to the following possible reaction.



19

Fig. 6. A-B) TEM photomicrography of nZVI-EG2 and S-nZVI2.

 $Fe_{(aq)}^{3+} + EG_{(aq)} \rightarrow [Fe(EG)_4(H_2O)_2]_{(aq)}^{3+}$

$$4[Fe(EG)_4(H_2O)_2]^{3+} + 3BH_4^+ + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2$$

The particle surface coordination by grafted polymers of the functionalizing agent generates a surrounding layer that modifies the interactions of the material with the medium and gives stability against the presence of oxygen under atmospheric conditions (Fig. 2). Furthermore, because of the high solubility of the polymer in different solvents such as water and organic polar and nonpolar solvents, an increase in the dispersibility of the material can be predicted because of the EG coating process. In response, there is a generation of an inert hydrophilic surface with less adhesion due to the terminal OH groups, which do not adhere to the surface of the functionalized target, modifying the interaction of this material with the medium [19,43].

3.1.2. Structural characterization

TEM images of the materials with and without functionalization display particles with quasi-spherical morphology, with well-aligned aggregates forming zero-valent iron nanochains. The individual particles of nZVI-EG and S-nZVI show average diameters of 54.88 and 76.72 nm with coefficients of variation (CV) of 27.84 and 31.43%, in the size range of 16.96-100.20 nm and 24.50-165.35 nm respectively (Fig. 3A-B). It was possible to obtain smaller average diameter and narrower size distribution by surface modification with EG. This is due to the coordination of Fe^{3+} ions during the synthesis as well as the functionalization of the particles surface by the grafted polymer brushes. The arrangement of zero valent iron nanoparticles in chain structures is mainly caused by the magnetic dipole-dipole interactions of the particles, which generate spherical nanoparticle addition, and an arrangement of the particles in a magnetic cluster with chain morphology [58] (Fig. 3A-B). Fig. 3C provides a conceptual model of the nZVI interactions that form the ZVI nanochains.

The use of EG during the synthesis has no great effect on the size control during the synthesis, because, in the process of nucleation of the material, the primary particles, with sizes that are very small with respect to the final sizes, usually have interaction energies or barriers of very low energy and higher kinetic energy values; on the other hand, the dipole-dipole magnetic attraction properties of these particles promote attraction between them, and the absence of high repulsion values leads to a greater facility to agglomerate and grow to a certain size, where they present greater stability. As the diameter of the particles increases the energy barrier also increases; the kinetic energy is decreased and, in addition, due to the presence of electric charges on the particle surface, which make up the nZVI hydrodynamic radius, it is possible avert complete contact and avoid the agglomeration and growth of particles to mean sizes of > 54.88-76.72 nm; this size control adds to the magnetic effect, generating an attractive-repulsive force and an arrangement of the particles in a magnetic cluster [41,59,60].

3.2. Increased dispersibility by nZVI functionalization

The stability of the materials was analyzed by sedimentation analysis in order to evaluate the increase in dispersibility of the nanoparticles in solution due to the modification of their surface by the presence of grafted polymers. The sedimentation curves were further analyzed using the one-phase decay equation, as described in our previous study [40].

$\mathbf{I}_t = \mathbf{I}_0 e^{-t/\tau}$

In Fig. 4 it is possible to observe a high sedimentation rate for SnZVI, associated with the rapid aggregation of the particles. S-nZVI has an absorbance of 0.045 at its plateau, which means that more than 95% of nZVI will settle down during the sedimentation experiment. On the other hand, 73% of nZVI would settle down in the case of surface functionalized nZVI-EG. Moreover, the characteristic times τ for S-nZVI and nZVI-EG are calculated at 14.7 and 35.8 min, respectively, which means that nZVI-EG is much more stable than S-nZVI.

The slow sedimentation rate can be explained by the increase in the stability of the material in response to the functionalization of the particles and the reduction in the rate of aggregation of these particles due to effects of steric repulsion between the grafted polymers. The increase in dispersibility is due to the polymeric brush, which is only attached at one end to the surface of the particle, has another OH terminal group that is not bound to the surface of another particle, is free to interact with the surrounding medium. This OH group is highly soluble in polar solutions, promoting the dispersibility of the particles, which are covered with a polymer layer of this composition; this layer may be assumed to also increase the interactivity with contaminants to be removed or reduced [19,43,60].



Fig. 7. A-D) HR-TEM photomicrography of nZVI samples (A: nZVI-EG₁, B: nZVI-EG₂, C: S-nZVI₁, D: S-nZVI₂). E-H) Energy dispersive spectrometer scanning line (EDS) of nanoparticles with and without functionalization, dried in aerobic and anaerobic conditions (E: nZVI-EG₁, F: nZVI-EG₂, G: S-nZVI₁).

3.3. Air stability of functionalized nZVI

The samples $nZVI-EG_1$ and $S-nZVI_1$ dried under anaerobic conditions and the samples $nZVI-EG_2$ and $S-nZVI_2$ dried under aerobic conditions were analyzed by XRD, HR-TEM, EDS, reactive iron content analysis, and nitrate reduction in order to demonstrate the consumption of the reactive metallic iron core and the oxygen increase present in the core-shell composed of iron oxide due to oxidation of the material in response to the absence of an EG protective layer and the loss of the reducing capacity of the nanoparticles.

3.3.1. Structural characterization - XRD

Using the Rietveld method, the XRD information was refined: the amount of zero-valent iron and the oxidation species were quantified in the samples. The X-ray spectrum of nZVI-EG₁, and its Rietveld refinement, show characteristic peaks of cubic phase α -Fe located at 44.8° and 65.8°; these are indexed as the (1 1 0) and (2 0 0) planes (JCPDS Card No. 79-0417). For the case of sample S-nZVI₁, zero-valent iron (α -Fe) and iron oxide (Fe_xO_y) crystalline phases are present in the XRD, which similarly shows peaks belonging to the crystallographic phase α -Fe indexed in the planes. However, the peaks at 35.9 and 62.9° correspond to the crystallographic cubic phase magnetite (Fe₃O₄), indexed in planes (3 1 1) and (4 1 1) (JCPDS 06-0696), coinciding with the presence of magnetite and giving evidence of the layered structure of nZVI, which consists of a body-centered cubic (bcc) α -Fe metal core encapsulated by a thin oxide shell [28,29] (Fig. 5).

For the samples dried in aerobic conditions, the XRD result corresponding to nZVI-EG₂ shows an α -Fe peak with an intensity similar to that of the samples described above. The spectrum for S- $nZVI_2$ shows a remarkable difference with respect to the other samples: it shows a

decrease in the intensity of the peak corresponding to α -Fe and an increase in the intensity of the diffracted peaks; this decrease is associated with the presence of magnetite located at 30.3 and 35.8° in planes (200) and (311) (JCPDS 06-0696). The presence of magnetite is due to the corrosion of the reactive iron core and its transformation to the Fe₃O₄ phase (Fig. 5). In the same way as in the quantification of the crystalline phases, we see an interesting decrease in α -Fe and an increase in magnetite (Table 1).

In contrast to the materials dried under anaerobic conditions, the remarkable difference in the oxidation rate of the simple samples dried under aerobic conditions is the result of the material directly reacting with O₂ molecules existing in the environment during the drying process; this process, in the absence of protection, would tend to oxidize the Fe⁰ core until its total consumption. In addition, in the FTIR analysis, the S-nZVI samples showed absorption of water molecules on the surface of the particles; these water molecules will tend to dissolve the iron oxide contained in the core shell to a certain extent, depassivating the surface and re-exposing the nucleus for its eventual oxidation and forming a higher amount of magnetite [18]. For the case of S–nZVI₁, the water molecules absorbed were rapidly extracted from the material by pumps that function to remove water contained in the system, preventing possible corrosion of the sample. In contrast, for the functionalized samples, the protective layer almost entirely inhibits the interaction of O₂ molecules on the surface of the particles, preserving the majority of the metal core during the drying process in aerobic conditions.

3.3.2. Morphological characterization - TEM and EDS

Similarly, TEM images of the samples dried under aerobic conditions were obtained to evaluate sample morphology. The sample nZVI-



Fig. 7. (continued)

Table 2Composition of EDS points in Fig. 3D, wt%.

Element	Fe (%)			O (%)		
Spectrum	1	2	3	1	2	3
nZVI-EG ₁ nZVI-EG ₂ S-nZVI ₁ S-nZVI ₂	81.12 62.4 81.34 27.26	95.97 87.15 83.15 68.8	63.89 79.9 62.06 30.69	18.88 37.6 18.66 72.74	4.03 12.85 16.85 31.2	36.11 20.1 37.94 69.31

 EG_2 presents a behavior similar to that described in the previous section, in which the sample was dried in anaerobic conditions, indicating that, due to the efficiency of the functionalization, this sample is not significantly affected by corrosion effects (Fig. 6A).

In the case of S-nZVI₂, a conservation of the nanochains is observed, which may explain the consumption of the metallic nucleus and the increase of iron oxides while an identical morphology of particles is maintained. Moreover, in the upper part of the image, some needle-like structures can be seen; these are characteristic of a more advanced iron oxidation process (Fig. 6B). Nevertheless, in the XRD information, no peaks other than that of magnetite are shown, which may be interpreted as representing an amount of a type of iron oxide other than Fe₃O₄, one that is insufficient to be detected by X-ray diffraction.

Fig. 7 present HR-TEM images of the different samples, showing changes due to drying in anaerobic and aerobic conditions. The nanoparticles are composed of dense metal cores surrounded by thin coreshells; the magnetite exhibits markedly less contrast than does the zerovalent iron dense core. The cases of $nZVI-EG_1$ and $nZVI-EG_2$ showed similar behavior in the core-shell, with average thickness values of 4.48 and 4.94 nm, respectively, indicating a non-significant increase in

thickness due to oxidation of the reactive iron upon exposure to atmospheric conditions (Fig. 7A–B).

On the other hand, the thickness of the core-shell of S-nZVI₂ significantly increased compared to that of S-nZVI₁. S-nZVI₁ shows a thickness of core-shell of 6.35 nm (Fig. 7C). The S-nZVI₂ sample showed a higher corrosion of particles and a higher consumption of the iron core, leading to an eventual increase in the core-shell thickness. Fig. 7D shows the remarkable increase in the thickness of the iron oxide layer, in contrast to those of the other samples; the layer presents a value of 11.89 nm (Fig. 7D). This result demonstrates the instability of nZVI, in the absence of functionalization, against environmental conditions [18,61].

Energy Dispersive Spectroscopy scanning line (EDS) was used to analyze iron nanoparticle structure composition along nanoscale ZVI chain in the samples subjected to drying under aerobic and anaerobic conditions; this was an attempt to demonstrate the predominance of the α -Fe core, which is surrounded by a thin iron oxide core-shell even for nZVI-EG dried in aerobic conditions; for non-functionalized nZVI, EDS results also show the consumption of the metallic nucleus due to oxidation and the increase of the oxygen present in the core-shell in response to the absence of a protective layer. The spectrum of the dispersed energy scanning line is obtained at three selected points in the area of interest on the sample, forming a Y-modulated signal; this is a rough indication of the number of, and the amounts of, elements present with respect to the spatial location along the line. We plotted a concentration profile to analyze the Fe and O diffusion in the nZVI core and determined the interface between these two materials.

EDS analysis for nZVI-EG dried under anaerobic conditions shows at the center of the particles the Fe spectrum, with a high intensity and a predominance (95.97%) in the sample that correspond to an iron metal core of the particles; moreover, it is possible to observe quite less of a



Fig. 8. A) Reactive iron content of nZVI samples. B) Nitrate reduction by nZVI samples. C) Dissolved iron concentration during nitrate reduction. (Conditions: 12.5 mg NO₃-N/L and 1000 mg Fe/L, pH 5, T = 24 \pm 1 °C).

proportion and spectrum intensity of corresponding oxygen (4.03%). Nevertheless, the iron content and spectrum intensity drop as the edges of the particle (81.12 and 63.89%) are approached; this is in contrast to the increment of the amount of oxygen at the edges (18.88 and 36.11%) due to the presence of the iron oxide core-shell surrounding the α -Fe core and forming an nZVI structure (Fig. 7E). The EDS spectra corresponding to samples S-nZVI₁ (Fig. 7G) and nZVI-EG₂ (Fig. 7F) show modulation of the Fe and O signals, very similar to the first spectrum described. Thus, like the information provided by XRD, TEM, and HR-TEM, the behavior and degree of oxidation of these two materials show no noticeable differences.

For the last case of S-nZVI₂, the most notable differences are the change in the uniformity of the signal corresponding to Fe and the increase in the intensity of the spectrum of O. Having values of Fe in the

center of the particle (68.80%), showing an interesting decrease in the proportion of the metal core and a predominance of the content of O with respect to Fe in the whole particle analyzed, values of Fe–O of 27.26–72.74% and 30.69–69.3% were reached at the edges of the structure (Fig. 7H). Table 2 shows the elemental distributions of Fe and O in the samples.

In view of the information described above, including the preservation of the Fe⁰ nucleus shown in XRD and the slight increase in the core-shell for sample nZVI-EG₂, analyzed using HR-TEM and EDS, it can be inferred that the air stability of the nanoparticles depends on the presence of the polymer layer, EG, and the iron oxide core-shell; for the last of these it has been reported that controlled passivation of the material surface along with slow contact with air can provide anticorrosive protection of the ZVI core [18], whereby the a in the reactivity of the nucleus by particle functionalization induces controlled oxidation and core-shell formation in a uniform manner. However, changes in the conditions of the protective layers would induce reactivity of the zerovalent iron, leading to its oxidation. This can occur by dissolving of the core-shell iron oxides in the aqueous phase, promoting particle depassivation and re-exposing the Fe⁰ nucleus for oxidation, thereby restoring the oxidation-reducing capacity of the nanocatalyst [18,62,63].

3.3.3. Effect of oxidation on nZVI reactivity

The amount of reactive iron remaining after drying under anaerobic and aerobic conditions indicates the degree of oxidation of the sample and its stability. Analyses of this parameter for nanoparticles dried in the anaerobic chamber show values of preservation of Fe(0) of 84.6 and 78.9% for the nZVI-EG₁ and S-nZVI₁ samples, respectively, with the loss of a little more than 15% of the reactive nucleus being due to oxidization during the synthesis; the synthesis is carried out in oxic water in an open container and in the absence of inert gas. The small difference of Fe(0) between the two materials shows the better stability of the particles owing to the functionalization process.

For the samples dried under aerobic conditions, there is a marked contrast between the obtained values of reactive iron. The values of nZVI-EG₂ of 80.2% and S-nZVI₂ of 20.7% demonstrate the instability of simple nanoiron against oxidation during drying (Fig. 8A). Furthermore, despite the conditions described above, a high percentage of Fe (0) was obtained in the functionalized samples (nZVI-EG₂), with the loss of 4.4% of reactive iron between both samples demonstrating the efficiency and protection of the composite layer by the polymers in the aerobic environment. In fact, the calculated percentages of Fe(0) strongly agree with the quantification of α -Fe crystalline phase in the XRD analysis, corroborating the zero-valent iron identity.

Similar results were obtained in the nitrate reduction test. Ammonia, the main reaction product, was monitored through the reaction period, as shown in Fig. 8B [64].

 $4Fe^{0} + NO_{3}^{-} + 10H^{+} \rightarrow 4Fe^{2+} + NH_{4}^{+} + 3H_{2}O \quad \Delta G^{\circ} = -997.71 \text{ kJ}$

The nZVI sample, prepared in anaerobic conditions, showed a more than 78% nitrate reduction in one hour for both cases, while showing that only 7.1% of nitrate could be reduced to ammonia in S-nZVI₂, which is dried in aerobic conditions without functionalization. On the other hand, an almost identical performance, 74% of nitrate reduction in 1 h, was obtained using nZVI-EG₂, which is dried in aerobic condition with functionalization. Dissolved iron content values during nitrate reduction are presented in Fig. 8C. S-nZVI₂ produced the lowest amount of soluble iron, indicating its low reactive iron content and nitrate reduction capacity. This result is in very close agreement with the reactive iron content analysis, and clearly indicates the effectiveness of nZVI functionalization by EG at preventing oxidation during the preparation of nZVI without inert conditions. Furthermore, the reaction kinetics was not hindered by the addition of the organic functionalization agent, EG; this also verifies the possibility of using EG in effective surface modification method for nZVI.

4. Conclusions

In this study, the effectiveness of ethylene glycol as part of a surface modification method for the synthesis of air-stable nZVI without inert conditions was investigated. First, ethylene glycol generates the iron ions coordination, which were further reduced to Fe⁰; then, the functionalization provided stability against the presence of oxygen, as well as high dispersibility in water. It was possible to obtain smaller and narrower size distribution by surface functionalization; this process provided better colloidal stability, which was confirmed by a slower sedimentation curve. The ethylene glycol functionalized nZVI also exhibited a protection effect against oxidation in atmospheric conditions. Even though the nZVI preparation was performed without inert condition, due to the efficiency of the functionalization, the sample was not significantly affected, in terms of its morphology as monitored by TEM/ EDS or its structure as monitored by XRD, by corrosion. The protection effect of ethylene glycol was also revealed in sample contaminant reduction capacity. It was possible to obtain a high percentage of reactive iron and effective nitrate reduction, which demonstrate the effectiveness of nZVI functionalization by EG at preventing oxidation during the preparation of nZVI without inert atmosphere. Moreover, the reaction kinetics was not hindered by the addition of the organic functionalization agent EG, which also verifies the possibility of using EG in an effective surface modification method for nZVI.

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