Original Article

Synthesis and characterization of zero-valent iron nanoparticles supported on SBA-15

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This paper aims to synthesize zero-valent iron nanoparticles (nZVI) supported on SBA-15 nanosilica. The nanosilica generate in the system by polymer reaction with hydrochloric acid under controlled temperature. After, the iron nanomaterial was obtained by sodium borohydride reduction as described in this work. Afterward the synthesis of the nanoparticles contained iron supported on silica SBA-15, the material was characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, zeta potential and X-ray fluorescence spectroscopy. The results indicated that nanomaterial obtained was in nanometric scale, by TEM results, and showing characteristic peaks at EDS results, with 11.9% iron and 14.0% silicon content, respectively, and containing 73.0% and 27.0% of their respective oxides by X-ray fluorescence spectroscopy. The isoelectric potential of the sample was around 2.0, close to the value reported for silica, due to the higher percentage of silica in the sample when compared to iron. The obtained material can be used, for some cases, as an possible alternative, to the Fenton reaction for the degradation of xenobiotic compounds or other applications in the groundwater and wastewater treatments.

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1. Introduction

Over the years various xenobiotic substances resistant to biodegradation have been synthesized by man for applications in various sectors such as the agriculture, oil, petrochemical and textile segments, among others. However after their use, these substances, being refractory to biological degradation, are discarded in nature and have the potential to promote several environmental impacts and compromise the quality of water supply systems [1,2].

The nanotechnology is the engineering and art of manipulating matter at the nanoscale between 1 and 100 nm [3,4].

The use of iron nanoparticles, compared the micrometric particles is because to greater efficiency in reduction reactions, high reactivity, due to the high surface area, mobility and filtration efficiency when used in technologies for remediing a certain environment. The particles being in nanosize remain in suspension for a long period of time, thereby facilitating the various known applications such as water treatment and wastewater [5].

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Zero-valent iron ions (ZVI), hematite and magnetite, among others, may be used in the Fenton reaction [6–12] or in the wastewater treatment from explosive manufacturing [13], as an possible alternative to this reaction mentioned. When iron in its zero-valent form, Fe0 is used the Fenton reaction may occur via a homogeneous reaction after dissolution to Fe2+ or on the particle surface. Iron nanoparticles are another source of iron for this homogeneous reaction, during the oxidation of elemental iron. The advantages of using iron nanoparticles compared to micrometer particles include their higher efficiency in the degradation reactions, high reactivity due to high surface area, high mobility and high filtration efficiency. Being nanosized, they also remain in suspension longer, thereby facilitating their various known applications [8,9,14,15].

Iron nanoparticles can also be used supported on other materials, such as silica, carbon, resins or nylon membranes. Silica is more advantageous when compared to other materials, since it agglomerates ZVI nanoparticles, better than other materials [16–18]. This increased agglomeration drastically reduces reactivity and particle mobility during "in situ" treatments. Since silica is inert biocompatible, non-toxic, and shows good chemical and thermal stability, the stabilized iron nanoparticles tend to disperse on the silica surface [16–19].

The use of highly organized nanostructured SBA-15 silica is well known, with applications in several areas, such as catalysis, drug delivery [19] and as a support to immobilize well-dispersed ZVI nanoparticles [20,21]. This type of silica is able to interact with atoms, ions and molecules, not only the surface, but also inside its approximately 10 nm diameter nanochannels.

So, this paper aims to synthesize and characterize ZVI nanoparticles supported on SBA-15 nanosilica. This synthesized material can be used in other studies involving advanced oxidation processes reactions, which may promote the degradation of xenobiotic compounds or in other applications for groundwater treatment.

2. Methods

2.1. Materials

Iron III nitrate nonahydrate (Fe(NO3)3·9H2O), sodium borohydride (NaBH4) and hexane, used for the synthesis of iron nanoparticles, were all PA grade (VETEC, Rio de Janeiro, Brazil). The co-triblock Polymer reagent (Pluronic P123, 5800, (C2H2O−C2H4O)n) and Tetraethyl orthosilicate (TEOS) were used for the SBA-15 silica synthesis (Sigma–Aldrich, St. Louis, USA).

2.2. Sample preparation

2.2.1. SBA-15 silica synthesis

Different methods are reported in the literature for the synthesis of SBA-15 silica [19,21,22]. The procedure adopted herein is an adaptation of some reported methodologies [21,22]. In the present study, 2.0 g of P123 were added to a mixture of 15 mL of water and 60 mL of an aqueous 2.0 mol L−1 HCl solution and stirred for 2 h at 308 K. If the mixture was completely solubilized before the 2-h period, waiting was not necessary. Subsequently, 4.25 g of TEOS were added to the solution under moderate stirring (150 rpm for 10 min). A few minutes (5–10 min, nearly) after the addition of TEOS to the system the formation of a white-colored precipitate was observed, which should remain in the system during the mentioned time-frame. After stirring, the mixture was maintained at 308 K for 20 h in a fume-hood to dry the acid present in the solution, and then maintained at 373 K for 24 h.

The solids were then washed with deionized water and collected by filtration at room temperature to remove excess unreacted material. The washing was carried out several times, until no more foaming was observed in the permeate. The sample was then dried in a laboratory oven at 373 K for 24 h and calcined at 823 K for 5 h.

2.2.2. Iron deposition on the silica

One gram of silica nanoparticles obtained by the above method was solubilized in 30 mL of hexane with rapid stirring (500 rpm) for 30 min. A small amount of iron III nitrate 2.0 mol L−1 solution was then added dropwise to the system. The volume of the ferric nitrate solution is three times the mass of silica used in the system. After mixing, the hexane was drained from the system and stored for the other stages of the process. The solid phase was then dried on a hot plate inside a fume-hood at 318 K.

2.2.3. Reduction of the iron-deposited silica

One gram of silica permeated with iron was solubilized with 30 mL of hexane. To facilitate solubilization a HCl solution at pH 2.0 was used. The reduction reaction with sodium borohydride is reported in the literature [3,10,14,23–26]. An 8.0 mol L−1 sodium borohydride solution prepared in a 50% alcohol solution was added dropwise to the system under strong stirring, and a vacuum of ~500 mmHg. The boron/iron ration used was 4:1. The system heats up during the reaction, due to a spontaneous exothermic reaction, however cooling is not necessary. The system remained under stirring and vacuum until all the gaseous byproducts were removed by the vacuum. The final pH of the system was around 9.0. The sample was then washed several times with PA alcohol, until the solution remained clear with no more gas formation. The zero-valent iron nanoparticles supported on the SBA-15 silica were then stored in vials containing pure alcohol in a desiccator.

2.3. Characterization

2.3.1. X-ray diffraction

This assay allows for the characterization of the crystalline structure of the material. By using a set of information from the crystallographic planes of known materials it is possible to identify the chemical composition of unknown materials. The X-ray diffraction experiments were performed on a Rigaku Miniflex II apparatus at 30 kV and 15 mA, ranging from 5 to 90°, with a variation of 0.5°. The characterization of individual peaks was performed by the Materials Date Jade 5 (5.0.37) XRD Pattern Processing software package.

2.3.2. Transmission electron microscopy (TEM)

The microscopy images were obtained on a FEI Morgagni 268 electron microscope operated at 80 kV. 0.047 mm copper grids were used (#300 and 63 μm) for supporting the material. The
grids were prepared using a dilute 0.3% solution of form-var in 1,2-dichloroethane, and the samples then received a graphite layer in the vacuum recipient. A small amount of the sample was then diluted in PA alcohol until almost full transparency. Two or three drops, at most, of this diluted sample were then placed on the grid, subjected to vacuum until complete alcohol evaporation, and then examined under the microscope.

2.3.3. Scanning electron microscopy (SEM)
A JEOL 6460 LV scanning electron microscope coupled to a Noran System Six EDS operated at low vacuum under 20 kV was used. A small amount of non-metallized sample was placed in the vessel and introduced into the microscope.

2.3.4. X-ray fluorescence spectrometry (XRF)
This test was carried out on Primini Rigaku fluorescent X-ray spectrometer and the dry sample was analyzed by the ZSX software package.

2.3.5. Zeta potential (ζ)
This assay was conducted on a +3.0 Zetameter by the electrophoretic mobility/velocity technique, with an indifferent NaCl electrolyte solution (0.01 mol L⁻¹). The pH adjustment was conducted with NaOH and HCl, ranging between 0.01 and 0.1 mol L⁻¹. The concentration of the iron sample with silica was of 50 mg L⁻¹.

3. Results and discussions
The characterization by X-ray diffraction results are displayed in Fig. 1, in which the bottom figure (a) corresponds to the ZVI diffractogram, in which the characteristic peak of highest intensity occurs at 44.75°. The middle line (b), associated with pure SBA-15 silica, is a constant line since this is an amorphous substance. Finally, the top line (c) displays the graph for

Fig. 1 – Diffractogram (a) zero-valent iron, (b) SBA-15 and (c) Fe–Si.

Fig. 2 – Micrographs of the ZVI nanoparticles (a), SBA-15 (b), ZVI supported on SBA-15 (c) and (d).
zero-valent iron supported on silica. A larger phase is associated with Fe₅Si and a smaller phase is associated with the zero-valent iron.

The images obtained by transmission electron microscopy reveal that most of the ZVI particles have diameters of less than 100 nm, as displayed in Fig. 2(a). Fig. 2(b) displays the SBA-15 silica structure with no iron particles. Fig. 2(c) and (d) displays the spherical nZVI supported on the SBA-15 silica. As observed in latter two figures, the supported amount of iron is associated with the volume of the solution added to the system during reduction with sodium borohydride.

The photomicrograph of the SBA-15 silica is displayed Fig. 3(a). A cluster of the structures is observed due to the 2000× resolution. The photomicrograph of the SBA-15 silica with nZVI is displayed in Fig. 3(b) at a 5000× resolution. The agglomerated iron particles are noticeably much smaller compared to the SBA-15 silica.

Fig. 4(a) and (b) illustrates the EDS of the SBA-15 silica and ZVI supported on the SBA-15 silica, respectively. Peaks belonging to carbon are displayed in both figures, due to the presence of the tape used to secure the sample in the container, that contains carbon. The peaks found during the scan for sodium (Fig. 4b) are due to the sodium borohydride used during the iron reduction process. However, these peaks are quite minor compared to other peaks, for example, silicon and iron. These elements, also displayed in Fig. 4(b), represent a percentage by sample weight of 11.86% silicon and 14.01% iron, respectively.

The non-destructive X-ray fluorescence assay indicated 26.96% Fe₂O₃ and 73.04% SiO₂ in the sample, as predicted and confirmed by other characterization tests.

The surface of the hydrated sample may favor increased charges. The pH value at which there is a charge neutrality of the liquid surface of the sample is the isoelectric point (IEP), a function of pH. Fig. 5 displays this behavior at different pH values. The IEP obtained for the ZVI nanoparticles was close to a pH value of 2.0. This value is close to the IEP of silica, as described in the literature [27,28], while the IEP for ZVI nanoparticles reported in the literature [3,21] is around 8.3. This corroborates the greater presence of silica in the sample, as verified by the X-ray fluorescence results.

The Eh-pH diagram is displayed in Fig. 6, obtained at 298 K and at a ratio of 4:1 (B: Fe) and 0.15 mol L⁻¹ of silica. At pH 2.0 the silica is present in its anionic form, while the metal is in ferric ion form. Iron is attracted to the silica and remains in solution, subsequently undergoing reduction with
borohydride within the silica pores, thus generating the ZVI nanoparticles.

4. Conclusions

The permeation of the SBA-15 silica with a ferric nitrate solution and reduction with sodium borohydride allowed for the synthesis of the zero-valent iron nanoparticles supported on SBA-15, confirmed by XRD, TEM, SEM, EDS and XRF analyses. The samples were found to oxidize easily, requiring handling and preparation in an alcoholic solution. A nitrogen stream, however, was not necessary. The characterization techniques confirmed the presence of silicon and iron nanoparticles in the sample, in weight percentage of 11.86% and 14.01% for the EDS, respectively, and 73.04% and 26.96% for their respective oxides. The IEP of the sample was close to 2.0, due to the silica present in higher amounts as confirmed by the quantitative results, attracting the iron into its pores. Therefore, the first layer of the sample is predominantly filled by the silica. At this IEP value, the iron is present as ferric ions, being electrostatically attracted to the silica and subsequently reduced to pH 2.0 to ZVI nanoparticles. Over time the nanoparticles tend to agglomerate, especially in water due to existing charges, thus forming oxides and hydroxides in the micrometer range.

It is suggested that ZVI nanoparticles can be used to support, for example, on SBA-15, can be a good alternative for application in Fenton-type reactions, since the iron oxidation tends to occur in the silica itself, can thus minimizing the formation of undesired sludge as a result of the classical Fenton reaction.

Conflicts of interest

The authors declare no conflicts of interest.

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