Activation process of air stable nanoscale zero-valent iron particles

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HIGHLIGHTS

- The activation process consists of submerging the particles in water for 36 h.
- The activation process is simple without stirring and consumption of Fe(0).
- The activated air-stable nZVIs improve reactivity against Cr(VI).
- The improvement in reactivity is due mainly to degradation of the oxide shell.
- The method can be used before injection to enhance the effectiveness of remediation.

GRAPHICAL ABSTRACT
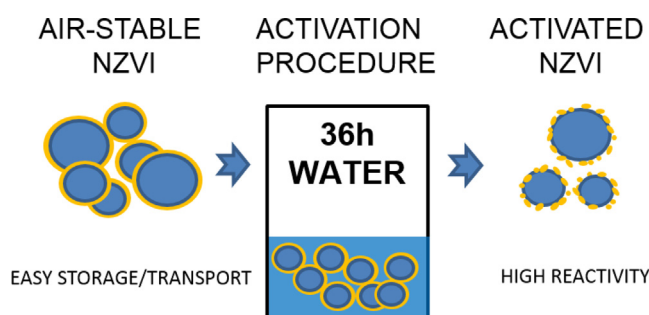
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ABSTRACT

Nanoscale Zero Valent Iron (nZVI) represents a promising material for subsurface water remediation technology. However, dry, bare nZVI particles are highly reactive, being pyrophoric when they are in contact with air. The current trends of nZVI manufacturing lead to the surface passivation of dry nZVI particles with a thin oxide layer, which entails a decrease in their reactivity. In this work an activation procedure to recover the reactivity of air-stable nZVI particles is presented. The method consists of exposing nZVI to water for 36 h just before the reaction with the pollutants. To assess the increase in nZVI reactivity based on the activation procedure, three types of nZVI particles with different oxide shell thicknesses have been tested for Cr(VI) removal. The two types of air-stable nZVI particles with an oxide shell thickness of around 3.4 and 6.5 nm increased their reactivity by a factor of 4.7 and 3.4 after activation, respectively. However, the pyrophoric nZVI particles displayed no significant improvement in reactivity. The improvement in reactivity is related mainly to the degradation of the oxide shell, which enhances electron transfer and leads secondarily to an increase in the specific surface area of the nZVI after the activation process. In order to validate the activation process, additional tests with selected chlorinated compounds demonstrated an increase in the degradation rate by activated nZVI particles.

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1. Introduction

Nanoscale Zero Valent Iron (nZVI) particles have been extensively studied and used to degrade a wide range of contaminants, such as: chlorinated organic and nitroaromatic compounds [1].

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Besides organic (halogenated) compounds, nZVI can reduce and/or immobilize harmful metals and metalloids [2,3] and other ions: PO_4^{3-} NO_3^-, NO_2^- [4]. Depending on the nature of the contaminant, there are many proposed mechanisms and pathways of iron action: reduction, adsorption, reduction and adsorption, adsorption and precipitation or oxidation [5,6]. It seems clear that the chemical energy is mandatorily supplied by iron corrosion [7]:

$$2Fe_{(s)}^0 + 2H_2O_{(l)} \rightarrow 2Fe^{2+} + H_{2(g)} + 2OH_{(aq)}^- \quad E^0 = -0.39 \text{ V} \quad (1)$$
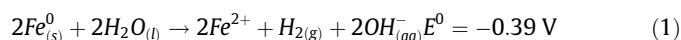
One of the most important features of nZVI is its high specific surface area, boosting its reactivity by several orders of magnitude compared to micrometric ZVI, which results in faster degradation rates of pollutants [8]. It is geometrically demonstrable that particles with a *d* of 0.5 mm and 50 nm have a specific surface area of 1.5 and 15,250 $m^2 \cdot kg^{-1}$, respectively [9]. The increased reactivity of nanosized ZVI presents new challenges at different levels, among which are the possible environmental toxicology and pyrophoricity [10]. With regard to the second point, dry, bare nZVI particles undergo a fast but not explosive exothermic reaction when exposed to the free air-atmosphere [11]. This behaviour entails a handling, safety and logistic problem. Many different approaches have been adopted to desensitize nZVI [12]. The two most common commercial methods are faced with important drawbacks: (I) Transport in a water-slurry form could partially solve safety problems but implies an increase in shipping costs and a loss of reactivity caused by aging [13], (II) Surface passivation of iron powder by the formation of an oxide shell allows storage in air and lower transportation costs but also significantly decreases the reactivity of the product.

Surface passivation is typically performed by leaving the free atmosphere become slowly and progressively in contact with pristine particles. As a result of this process, a superficial and compact oxide layer is generated giving long-term air stability of nZVI [11,14]. The thickness of the oxide shell ranges from 1 to 25 nm depending on the oxidation conditions, and this thickness is nearly independent of the diameter of the nanoparticles [15]. The nature of this oxide shell is being extensively studied since it hinders the electron flow from the metallic iron [16]. As a result, it has been reported that the increase in shell thickness negatively affects the reactivity of nZVI [17,18]. It is therefore important to develop an "activation" method able to restore the reactivity of the particles immediately before its use. Because the formation of the oxide shell is the main parameter responsible for the loss in reactivity [16–18], the activation process should be capable of partial or total removal of the oxide shell in an easy way and in a short period of time.

Up to now, the majority of activation processes of nZVI particles described in literature are more focused on prevention of particle agglomeration or increase in their mobility than on removal of the oxide shell. The use of surfactants or polyelectrolyte polymers to promote colloidal stability is related to the first point [7]. The use of porous materials that support the nZVI particles is also based in the first point, but differing results are reported. In some cases, a decrease of reaction rates have been described due to an increase of the mass transfer resistance [19–21] whereas different studies with mesoporous silica and silica-carbon have shown an increase of Cr(VI) removal related to a large surface area and some protection against oxidation of nZVI particles [22,23]. Another process that has been investigated is the use of ultrasound. On the one hand, the use of ultrasound improve the dispersion of nZVI and consequently there is an increase of reactivity [24]. In addition, it has also been pointed out that if nZVI are coupled with ultrasound the Cr(VI) removal efficiency increases significantly [19]. This improvement, apart from the known increase of dispersion, is related to a partial breaking of oxide layer and the increase of reac-

tive sites for Cr(VI) removal. However, it seems difficult to implement this method in subsurface water remediation processes.

Alternatively, the known reactivity of iron with water could be used as an activation process. On the one hand it has been clearly demonstrated that long-term water exposure decreases the reactivity of nZVI against a wide range of pollutants due to the growing of the oxide/hydroxide shell [11,13,18,25–29], which leads to a passivation of the particles and it is commonly known as water aging [30]. However, there are certain disparities about the effect on the reactivity at short immersion times. An increase in reactivity after 1–2 days of water immersion has been reported for carbon tetrachloride, trichloroethane and 1,1,1,2-tetrachloroethane [18,28,31], but other studies have shown little changes on reactivity during the first days of aging [13,32]. In the cases in which an increase of reactivity was detected, different mechanisms were proposed to explain reactivity recovery: (I) The dissolution of the anionic hydroxo species from a spontaneously-formed oxide/hydroxide shell, such as $Fe(OH)_y^{2-y}$ and $Fe(OH)_x^{3-x}$ known to be soluble and unstable in alkaline media [11]. This process is supported by evidence of the formation of new iron oxide particles in the vicinity of the nZVI particles [11,27,28]. (II) The volumetric expansion of the nZVI core and the intermediate oxides formed during corrosion, which leads the oxide layers to flake off and expose metallic iron to the contaminants [18,31]. The expansion of the corrosion products is being studied due to expected clogging problems in the aquifer matrix during nZVI treatment [33]. In general, theoretical calculations for the different iron oxides formed in nZVI reactions show that the volume of oxides is 2–4 times greater than the volume of iron, which demonstrates a pronounced change in shell volume [34,35].

Because of this lack of definition, the aim of this work is to introduce an activation process to recover the reactivity of air stable nZVI and to describe the main mechanisms of this activation. Three types of nZVI particles, differing in the oxide shell thickness, were selected and subjected to an activation process based on their aging in water in the form of a dense nZVI slurry over a short period of time. The particles were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD) before and after the activation process. In addition, the specific surface area (SSA), the particle size distribution and the Fe(0) content were determined. The reduction of hexavalent chromium has been chosen as a simple method of evaluating changes in nZVI reactivity after the activation process since the reduction of Cr(VI) to trivalent chromium is a common mitigation approach in contaminated waters where nZVI is widely studied as a remedial method in this case. Additional tests for degradation of chlorinated compounds have been included to demonstrate the ability of the nZVI activation process to be applicable also for efficient removal of organic pollutants.

2. Materials and methods

2.1. Iron nanoparticles and suspensions

Iron nanoparticles with a different thickness of shielding oxide layer and Fe(0) to Fe-oxide ratio (labelled here as 25P, STAR 197 and STAR 400) were prepared according to a previously published procedure [18,36]. These nZVI particles were obtained by the thermal reduction of Fe oxides by H_2 at high temperature. Samples STAR 197 and STAR 400 were surface-stabilized by protective oxide layers of different thicknesses. In contrast, 25P had no tailored surface modification. For this reason, 25P nZVI particles remain pyrophoric whereas both types of STAR nanoparticles are air stable.