



Article Zerovalent Iron Nanoparticles-Alginate Nanocomposites for Cr(VI) Removal in Water—Influence of Temperature, pH, Dissolved Oxygen, Matrix, and nZVI Surface Composition

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Abstract:** The immobilization of zerovalent iron nanoparticles (nZVI) is a way to facilitate their use in continuous flow systems for the treatment of aqueous pollutants. In this work, two types of nZVI (powdered, NSTAR; and slurry suspended, N25) were immobilized in millimetric alginate beads (AL) by coagulation, forming nanocomposites (NCs). These NCs, N25@AL and NSTAR@AL, were structurally studied and tested for Cr(VI) removal. For both NCs types, SEM analysis showed a uniform distribution of the nanoparticles in micron-scale agglomerates, and XRD analysis revealed the preservation of α -Fe as the main iron phase of the immobilized nanoparticles. Additionally, Raman spectroscopy results evidenced a partial oxidation of the initially present magnetite. For both nZVI types, the Cr(VI) removal efficiency increased with temperature, decreased with pH, and did not show any significant change in anoxic or oxic conditions. On the other hand, N25@AL resulted a faster removal agent than NSTAR@AL; however, both materials had the same maximum removal capacity: 133 mg of Cr(VI) per gram of nZVI at pH 3. Cr(III) formed during the removal of Cr(VI) was retained by the alginate matrix, constituting a clear advantage against the use of free nZVI in suspension at acidic pH.

Keywords: nZVI; alginate; Cr(VI) removal; immobilization; biopolymers

1. Introduction

Iron-based nanoparticles (NPs), as zerovalent iron (nZVI) or iron oxides (nFeOx), have been used for the removal of a wide range of pollutants, including metals and metalloids in water [1–4]. Compared with their bulk counterparts, nanomaterials have a higher density of surface reaction per unit mass, displaying a notably higher reactivity for surface-mediated processes. Thanks to these characteristics, and to their reduced size and mobility in soils, nZVI and nFeOx are often used in the in situ remediation of sites with a high content of contaminants in groundwater [5,6]. In recent years, Adeleye et al. [7] reported that nZVI have been proven to efficiently remove pollutants of great health and environmental concern, such as Cr(VI), with application costs that are comparable with the cost of several traditional water treatment technologies.

nZVI present a core constituted by metallic iron covered by a thin shell of mixed Fe(II)/Fe(III) iron oxides, enriched by Fe(III) at the surface, which mediates the electron transfer from iron in the core. The structure of the shell depends on the synthesis procedure: though the nZVI obtained by borohydride reduction are covered by a smooth amorphous oxide layer, the nZVI produced by thermal reduction with H₂ present different domains of crystalline oxide structures [8]. Some NPs are manufactured in a way to provide a

surface consistent of a thin oxide layer that passivates them, reducing their reactivity, and easing air handling and conservation. For proper use in contaminant removal experiments, an activation procedure needs to be applied to recover their reactivity. This activation promotes the degradation and thinning of the oxide shell, enhancing electron transfer, and leading to an increase in the specific surface area of the NPs. Different processes have been used for activation, among them, ultrasound assisted methods improve the dispersion of nZVI while partially cracking the oxide layer, increasing its reactivity [9].

There are multiple disadvantages of using free NPs in suspension for contaminant removal. Even when the use of free nZVI in suspension leads to remarkable removal efficiencies [10], the experimental conditions necessary to reach them (vigorous and constant stirring) can only be achieved in laboratory conditions, otherwise the aggregation of the NPs takes place. Additionally, the fate of NPs in the environment is not clear, and long-term studies evaluating the degree of leaching of retained metals are scarce [11,12]. Immobilization of nZVI allows for their dispersion, and prevents the action of magnetic, electrostatic, and van der Waals forces during water treatment. Several nZVI-containing nanocomposites (NCs) have been produced using different supporting materials, such as activated carbon [13,14] and biochar [15-17], as well as polymeric matrices, such as cellulose [18], chitosan [19], polyacrylonitrile [20], and alginate (AL) [21,22]. The formation of hybrid nZVI-polymer NCs is a versatile option, as they can be developed in endless geometries and diverse scales, allowing tailoring of the reactive material for different situations by rational modification of the based supporting material. NCs in the shape of beads have high potential for their use in fixed bed reactors, filter columns, and domestic filters [23,24], a major advantage over free nZVI that tend to form poorly dense iron oxides that obstruct the water flow [3].

The entrapment of nZVI in alginate beads has been studied in recent years, and showed to be very efficient for the removal of nitrate, TCE, As(V), and Cr(VI) [21,25,26]. AL is a bioderived nontoxic anionic polysaccharide usually obtained with Na⁺ as counter-ion (NaAL), and has strong gelation and complexing abilities [27]. It can form a thermo irreversible gel by reaction with polyvalent cations, forming a crosslinking bond. When Ca²⁺ is added to a NaAL solution, it displaces part of Na⁺ and H⁺ to form a calcium alginate gel. Its ability to capture metallic ions via ion exchange with the original cross-linking cations can be combined with the redox capacity of nZVI, forming very reactive composites.

Chromium is a major water and soil pollutant coming from several industrial processes (electroplating, wood treatment, leather tanning, and steel manufacturing, among others [28–31]), mostly present as $HCrO_4^-$ and Cr^{3+} . Though Cr^{3+} is considered an essential nutrient, $HCrO_4^-$ is carcinogenic [32]. The World Health Organization established 50 µg L⁻¹ as a recommended maximum concentration of total chromium in drinking water [33], and the US Environmental Protection Agency has determined a maximum level of Cr(VI) of 0.02 µg L⁻¹ [34]. Cr(VI) reduction to Cr(III) by nZVI is a well-known reaction system, and extensive work has been carried out [10,13,16,20,35–37], making it suitable to use as probe for iron-based nanoparticles' or nanocomposites' reactivity, rate of electron transfer, and retention capacity.

Cr(VI) removal by nZVI is mainly based on two phenomena, conversion of Cr(VI) into Cr(III) and retention of Cr(III) on the external structure of the nZVI. In acidic conditions, Cr(VI) is rapidly reduced on the surface of nZVI by electron transfer from Fe(0) (Equation (1)), or by the oxidation of Fe(II) to Fe(III) (Equation (2)). These reactions are thermodynamically driven by the favorable reduction potentials of Cr(VI) to Cr(III) against Fe(0)/Fe(II) ($\Delta E_{298 \text{ K}}^0 = 1.77 \text{ V}$) and Fe(II)/Fe(III) ($\Delta E_{298 \text{ K}}^0 = 0.56 \text{ V}$) couples.

$$2HCrO_4^{-} + 14H^+ + 3Fe^0(s) \rightarrow 2Cr^{3+} + 8H_2O + 3Fe^{2+}$$
(1)

$$HCrO_4^{-} + 7H^+ + 3 \equiv Fe(II) \rightarrow Cr^{3+} + 3 \equiv Fe(III) + 4H_2O$$
(2)

where Fe^{2+} indicates Fe(II) in solution, and \equiv Fe(II) refers to Fe(II) at the NP surface.

The global reaction for Cr(VI) reduction can be described by Equation (3):

$$HCrO_4^{-} + 7H^{+} + Fe^0 \rightarrow Cr^{3+} + 4H_2O + Fe^{3+} (o \equiv Fe(III))$$
 (3)

Once produced, Cr^{3+} can remain in solution, or precipitate in the nZVI surface as amorphous $Cr(OH)_3$ or mixed Fe(III)-Cr(III) hydroxi(oxides) [38].

It is interesting to observe the effect of the immobilization on the nZVI removal capacity of different supporting materials. Several works undertaken with nZVI supported in polyacrylonitrile [20], chitosan [37], carbon nanotubes [39], resin [40], and alginate [26] showed evidence of preservation of the Cr(VI) removal capacity when free and immobilized nZVI are compared. In other works, the reactivity was even increased, such as in the case of the immobilization on graphene [41] and modified polyacrylonitrile [42].

In this work, two commercial nZVI immobilized in AL (nZVI@AL) were studied against Cr(VI) removal by reduction to Cr(III). The reaction system was chosen for environmental reasons, but also because it constitutes a simple, robust, and standardizable strategy to evaluate nZVI reactivity. The analysis was focused on the effects of immobilization on the nZVI oxide layer, and how they impact the reactivity of the iron nanoparticles.

2. Materials and Methods

2.1. Materials

Sodium alginate of medium viscosity (KeltoneTM, KT-9529-21, hereafter KT) and low viscosity (KelcosolTM, KL-5057-31, hereafter KL) were provided by Kelco Company (Atlanta, GA, USA). NANOFER 25 (N25) and NANOFER STAR (NSTAR) nZVI were purchased from Nanoiron s.r.o.; their main physicochemical characteristics can be found in the supplementary material document (SM). N25 is supplied as a nZVI suspension, and it was used without further modification. NSTAR is a powder product, and was used as received and after surface activation, according to the protocol described by Ribas et al. [9]. Briefly, a 200 g L^{-1} NSTAR suspension was prepared by ultrasonication, and left for 24–48 h in deoxygenated water (DW). Cr(VI) and Cr(III) solutions were prepared using $K_2Cr_2O_7$ (Merck) and $Cr(NO_3)_3.9H_2O$ (Riedel-de Haën), respectively. o-phenantroline (Mallinckrodt), H₂SO₄ (Biopack), NaOH (Biopack), hydroquinone (Merck), acetone (Anhedra), 1,5-diphenylcarbazide (Merck), phosphoric acid (Biopack), and CaCl₂.2H₂O (Biopack), were of analytical reagent grade, and used without further purification. In all experiments, MilliQ water was used (resistivity =18 M Ω cm). Standard solutions of 1000 ppm $Fe(NO_3)_3$ and $Ga(NO_3)_3$ were purchased from Chem-Lab NV for analysis of total iron and chromium concentrations ([Fe] and [Cr]).

2.2. Synthesis and Characterization of nZVI@AL Beads

The nZVI were entrapped into alginate beads by a modification of the procedure developed by Bezbaruah et al. [26]. Briefly, 0.24 g of sodium alginate was introduced in 12 mL of deoxygenized water, and stirred under N₂, bubbling until complete dissolution of the solid. The sodium alginate solution was left to stand for 30 min to allow the remaining N_2 bubbles to escape, and then, once the solution was free of bubbles, the iron nanoparticles were added: 0.12 g for NSTAR, or 536 µL of N25. The mixture was manually stirred with a glass rod for 1 min, and then further ultrasonicated to homogenize the suspension. The effect of ultrasonication time and protocol on the nanocomposites was evaluated using 5, 15, or 30 min of continuous sonication; or three intervals of 5 min of sonication, inserting 1 min of manual stirring between intervals. Good dispersion of the nanoparticles directly impacts in the removal efficiency, and the combination of several steps of stirring and ultrasonication led to the most reactive nanocomposites, as can be observed in Figure S1 (SM) where the effect of different ultrasonication protocols is shown. Finally, the suspension of nZVI-alginate was introduced dropwise into a 3.5% (v/v) solution of calcium chloride (7.8 g of CaCl₂.2H₂O in 120 mL of DW) using a 1000 µL pipette. The formed beads were left to harden in the solution for 4 h, and then rinsed and stored in DW. Samples of 2 mL of the remaining solution were collected to determine the amount of Fe released into solution after the synthesis.

Prior to SEM analysis, the nZVI@AL were lyophilized. The beads were studied by a FEI Inspect F50 microscope equipped with SE (secondary electrons), BSE (backscattered electrons), and EDS detectors; and a SUPRA 40 Carl Zeiss NTS microscope with SE detector.

XRD analyses were performed over the beads (previously grinded in an agate mortar) in a Philips PW-3710 X-ray diffractometer, using Cu K α radiation.

Raman spectroscopic measurements were done in a LabRAM HR Raman system (Horiba JobinYvon, Kyoto, Japan), equipped with a confocal microscope, two monochromator gratings, and a charge-coupled device detector (CCD). A 1800 g/mm grating and 100 μ m hole resulted in a 2 cm⁻¹ spectral resolution. The 514.5 nm line of an Ar⁺ laser was used as the excitation source. Measurements were carried out in a backscattering geometry, with an objective magnification of 50x. Acquisition time was 180 s and four accumulations.

2.3. Chromium Removal

Kinetic removal experiments were performed in a batch reactor containing 100 mL of Cr(VI) solution under constant magnetic stirring. Temperature was controlled by water recirculation through the jacket using a Polyscience 9106 Circulator. NCs and Cr(VI) or Cr(III) solutions were added to the reactor, so the Fe:Cr molar ratio (MR) was equal to 55, using a chromium initial concentration of 64 μ M. pH was adjusted to the desired value by dropwise addition of H₂SO₄ 0.5 N or NaOH 0.5 N. The reactor was open to the air in all cases, except when studying the effect of dissolved oxygen, in which case the experiment was carried out under a 0.5 mL min⁻¹ bubbling of 99.9995% N₂.

A series of experiments were performed to evaluate the maximum removal capacity of the nZVI@AL beads. For these experiments, 0.5 g of nZVI@AL beads were placed in sealed glass tubes, and then 10 mL of Cr(VI) solutions of different concentrations (from 8.93×10^{-4} M to 8.93×10^{-3} M) were added in each tube at pH = 3. The concentrations were varied in such a way to cover the range of Fe:Cr MR between 2 and 20.

The samples were left to reach equilibrium overnight, and then [Cr(VI)] was quantified.

2.4. Analytical Methods

In all experiments, 500 μ L samples were periodically withdrawn. The supernatant was used separately to determine Cr(VI), total Cr, and total Fe. Cr(VI) was measured spectrophotometrically using the diphenylcarbazide method at 540 nm [43]. Fe and Cr concentrations were measured employing total reflection X-ray fluorescence (TXRF; S2 PICOFOX (Bruker)), using a solution of [Ga] = 10 μ M as internal standard. The experimental error was calculated as the standard deviation of experimental replicates, and it was never higher than 10%.

3. Results

3.1. SEM-EDS, XRD, Raman Analysis

The synthesized beads were of millimetric size (between 1–3 mm). The dehydrated structure of the beads, as seen in Figure 1a–d, revealed the inherent porosity of the AL spheres giving rise to a complex micro- to nano-channeled structure. As shown in Figure 1, despite the mild lyophilization procedure, the size of the beads decreased due to the elimination of water, particularly in the case of nZVI-loaded beads.

In all nZVI@AL NCs, the iron nanoparticles were found distributed throughout the structure of the alginate beads, forming micro-aggregates of variable size and shape, surrounded by the polymer matrix. For instance, as seen in Figure 1g, several chrysalid-like structures were spotted. Detailed imaging information can be consulted in Figures S2 and S3, where secondary electrons and EDS mapping show that the bright spots in the SE-SEM images in Figure 1 correspond to nZVI clusters.



Figure 1. SEM images of AL beads, NSTAR@AL, and N25@AL beads in $100 \times$, $6000 \times$, $10,000 \times$, and $100,000 \times$, from left to right. The images of $100 \times$ and $6000 \times$ were taken with FEI Inspect F50 instrument, whereas the images with $10,000 \times$ and $100,000 \times$ were collected using a SUPRA 40 Carl Zeiss NTS microscope. In all cases, KL was used as source of AL.

When comparing the SEM images of N25@AL with NSTAR@AL, two differences were exposed: (1) N25 clusters were smaller and more uniformly distributed than NSTAR clusters; (2) NSTAR nanoparticles boundaries were well delimited in the clusters, even when the NPs were stuck to each other, whereas N25 nanoparticles boundaries in the clusters were blurred and the NPs seemed wrapped together.

Figure 2a shows the XRD patterns obtained for bare AL beads and both synthesized nZVI@AL nanocomposites.

As expected, AL presents a broad peak at low angle, typical of amorphous carbonaceous polymers. In the NCs beads, it can be clearly observed the preeminence of the α -Fe phase by the presence of four diffraction peaks at 44.674° (110), 65.023° (200), 82.335° (211), and 98.949° (220). Despite the similarities in both nZVI@AL patterns, N25 clearly displays two groups of peaks (around 46° and 62°) that can be ascribed to either maghemite and/or magnetite [10], or even lepidocrocite, as evidence of partial oxidation of the nZVI after the 4 h aqueous synthesis of the NCs.

The Raman spectra of N25@AL (Figure 2b) clearly shows the preeminence of lepidocrocite in the outer oxide layer of the immobilized nanoparticles, as can be seen from the clear coincidence of peak patterns between sample and reference. The magnetite peak expected for N25@AL in the Raman spectra is probably hidden by the large and intense lepidocrocite peak centered around 650 cm⁻¹.

In the case of NSTAR@AL, the main iron oxide phase detected was magnetite, and a small peak found at ~250 cm⁻¹ also suggests the presence of a minor proportion of lepidocrocite. Maghemite was not found.

Evidence of oxidation was also confirmed by analysis of the Fe released into the solution after the synthesis process. In agreement with XRD and Raman analysis, NCs with NSTAR were less affected by the synthesis process. As can be observed in Figure S4, only

(b) (a) α-Fe (110) Lepidocrocite N25@AL α-Fe (211) Maghemite α-Fe (200) α-Fe (22 Magnetite Ē NSTAR@AL Rel. NSTAR@AL N25@AL 10 20 30 40 50 60 70 80 90 100 100 300 400 200 500 600 700 800 900 1000 2θ (°) v (cm⁻¹)

1.4% of the original Fe content in the NSTAR@AL synthesis batch was delivered into the solution, compared to 8.6% in the case of N25@AL.

Figure 2. (a) XRD pattern for pure AL beads, and NSTAR@AL and N25@AL nanocomposites. (b) Raman spectra of samples NSTAR@AL and N25@AL. The Raman spectra of maghemite, lepidocrocite, and magnetite are also included for reference. KL alginate was used.

3.2. Cr(VI) Removal

the experiments reported in this work.

3.2.1. Effect of pH, Dissolved Oxygen, Temperature, and Alginate Viscosity

Solution pH demonstrated to have a pronounced effect on Cr(VI) removal. After 15 min of reaction, 100% removal of Cr(VI) was achieved at pH 3, whereas only 57% and 37% Cr(VI) removal was obtained at pH 5 and 7, respectively, as can be observed in Figure 3a: the removal efficiency and removal rate decrease as the initial pH increases. The reduction of Cr(VI) to Cr(III) by nZVI is a pH-dependent reaction, as shown in Equations (1)–(3); thus, the more acidic the initial pH, the more effective the Cr(VI) removal. After 15 min of reaction, the removal regime seems to change for experiments at pH 5 and 7. As demonstrated in a previous work, in the case of free-in-suspension nZVI, at pH > 3, the precipitation of Fe(III)–Cr(III) oxyhydroxides on the surface is promoted, covering the iron nanoparticles with a highly passivating layer that can stop or delay the reaction after the first 10 min [10].

As shown in Figure 3b, normalized Cr(VI) profiles vs. time were identical in the presence and in the absence of dissolved oxygen, indicating that the O₂ presence in solution does not affect the removal of Cr(VI) in these conditions. Both reactions, reduction of Cr(VI) and reduction of O₂ by Fe(0), are thermodynamically feasible ($E_{HCrO_4^-/Cr^{3+}}^0 = 1.36$ V and $E_{O_2/H_2O}^0 = 1.23$ V), and, usually, they are competing reactions. The fact that dissolved oxygen did not interfere in Cr(VI) removal could be ascribed to its slower reaction kinetics with nZVI, but also to a Fe:Cr MR high enough for both reactions to occur with no mutual interference. Either way, in the experimental conditions studied here, dissolved oxygen had no impact on Cr(VI) removal; accordingly, it was not necessary to use N₂ in the rest of

The Cr(VI) removal is thermally enhanced by increasing the experiment temperature. All experimental conditions tested (Figure 3c) resulted in the complete removal of Cr(VI), but higher reaction temperature reduced the time for complete removal: 5, 8, and 10 min for 40 °C, 25 °C, and 10 °C, respectively. The strong influence of this factor on the removal efficiency of Cr(VI) led us to maintain strict control of the experiment temperature, which, for the rest of the experiments, was set at 25 °C.

Finally, Figure 3d shows the results of Cr(VI) removal using NCs with the same nanoparticle type (NSTAR), but different base polymer. The difference in the kinetics



between NSTAR@KT and NSTAR@KL was negligible. The same effect was observed when using N25 (Figure S5, Supplementary Materials).

Figure 3. Effect of (a) initial pH (N25@KT), (b) dissolved oxygen (NSTAR@KT), (c) temperature (N25@KT), and (d) alginate viscosity for the Cr(VI) removal by nZVI@AL. $[Cr(VI)]_0 = 64 \mu M$, nZVI@AL = 1 g, MR (Fe:Cr) = 55.

3.2.2. N25 vs. NSTAR

N25@AL and NSTAR@AL beads reached complete Cr(VI) removal after 24 h using a Fe:Cr MR of 7 (Figure S6 of the Supplementary Materials). However, when comparing the results obtained with NSTAR@AL with those ones corresponding to N25@AL, the kinetics of Cr(VI) removal was different. Figure 4 shows the results obtained for free and AL immobilized NSTAR and N25, and for bare KT beads in 60 min experiments.

N25@AL showed faster kinetics than NSTAR@AL. N25@AL beads led to complete Cr(VI) removal after just 8 min, whereas NSTAR@AL needed 30 min to reach the same result. This behavior is consistent with the much faster kinetics observed for free N25 compared with free NSTAR in suspension.

AL beads were not capable of removing Cr(VI) under the selected experimental conditions, as the [Cr(VI)] was not reduced after 60 min of contact. However, it is evident that either the immobilization process or the base polymer matrix affected N25 and NSTAR reactivity in different ways. Free N25 in suspension removed 100% of Cr(VI) in the first 2 min of contact, whereas N25@AL reached the same result in 8 min. Therefore, N25 immobilization slowed down Cr(VI) removal. On the other hand, after 60 min, free NSTAR in suspension removed around 20% of Cr(VI)₀, whereas, in only 30 min, NSTAR@AL beads completely removed Cr(VI) from the solution. The insert in Figure 4 shows the results from



a series of Cr(VI) removal experiments with NSTAR free-in-suspension and immobilized in AL; with and without activation.

Figure 4. Normalized Cr(VI) removal over time with NSTAR and N25 free and supported in AL, and with bare AL beads. Insert: Normalized Cr(VI) removal over time with free activated NSTAR (NSTARact), inactivated NSTAR, and immobilized activated NSTAR (NSTARact), [Cr(VI)]₀ = 64 μ M, nZVI@AL = 1 g, MR (Fe:Cr) = 5, pH 3, T = 25 °C, AL = KT.

Activation of NSTAR in suspension was crucial for enhanced reactivity: though activated free NSTAR completely removed Cr(VI) after 2 min of reaction, inactivated free NSTAR only removed 70% of Cr(VI) after 60 min. However, the immobilization of inactivated NSTAR showed an increase in its removal efficiency, as NSTAR@AL eliminated Cr(VI) from the solution in 30 min. On the contrary, the immobilization of activated NSTAR decreased the removal capacity of the NPs.

3.2.3. Chromium Removal and Speciation Using NSTAR@AL

Results of the experiments aimed at evaluating the performance of the NSTAR@AL NCs on Cr(VI) removal are displayed in Figure 5. After 40 min of reaction time with 1 g of NSTAR@AL, 97% of Cr(VI) was removed, and complete removal was attained at 60 min of contact with the NCs. Nevertheless, complete removal of chromium was not achieved, as 54.7% of the total chromium remained in solution as Cr(III).

The removal performance of Cr(III) with bare AL beads was evaluated, and the results are depicted in the insert of Figure 5. After 50 min of treatment, around of 23% of the Cr(III) initially present in the solution was removed by the adsorption of AL beads. Therefore, it is possible to calculate that NSTAR are responsible for the retention of c.a. 32% of Cr(III) generated by the reduction of Cr(VI), as in the Cr(III) removal experiment, we used the same Cr initial concentration as in the rest of this work.

Experiments performed with the simultaneous addition of NSTAR@AL and AL spheres showed a slower Cr(VI) removal when compared with the experiments where only NSTAR@AL NCs were present (Figure 5). However, the Cr(VI) removal capacity was preserved, reaching complete Cr(VI) removal at 60 min. On the other hand, Cr(III) release into solution was significantly lower, resulting in a total chromium removal of 63.5%.



Figure 5. Normalized time-resolved Cr(VI), Cr(III), and Cr curves for chromium removal experiments with 1 g of NSTAR@AL (black) and 1 g of NSTAR@AL + 1 g of AL (green). Insert: Removal of Cr(III) with 1 g of AL beads. $[Cr]_0 = 64 \mu M$, pH = 3, T = 25 °C.

4. Discussion

4.1. Impact of Immobilization on nZVI Physicochemical Identity

XRD results showed that α -Fe is the main component of both nZVI types, preserving their main chemical identity. However, N25 and NSTAR nanoparticles suffered oxidation during the immobilization process, as can be deduced by the appearance of lepidocrocite (γ -FeO(OH)) in the Raman spectra, and the partial dissolution of Fe. The first step of immobilization, the suspension of the nZVI in sodium alginate, is carried out in anaerobic conditions, where, as thoroughly studied by Filip et al. [44], α -Fe can be oxidized to form Fe(OH)₂, as shown in Equation (4) (k = $1.14 \times 10^{-3} h^{-1}$; $t_{1/2}$ = 608 h). As reported by the authors, in contact with O₂, Fe(OH)₂ can be readily oxidized to a more stable oxide phase, such as magnetite (Equation (5)). During the second step of immobilization, magnetite can be subsequently transformed into lepidocrocite (Equation (6)) in neutral media, given the continuous oxygenation of the CaCl₂ solution [45]. Afterwards, lepidocrocite can also be transformed into magnetite by reaction with Fe(II) in a reaction promoted by alkaline media (Equation (7)) [46].

$$Fe(0) + 2H_2O \rightarrow Fe(OH)_2 + H_2 \tag{4}$$

$$Fe(OH)_2 + O_2 \rightarrow Fe_3O_4 + H_2 \tag{5}$$

$$4Fe_3O_4 + O_2 + 6H_2O \rightarrow 12\gamma - Fe - OOH$$
(6)

$$\gamma - \mathrm{Fe} - \mathrm{OOH} + \mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}_3\mathrm{O}_4 + 2\mathrm{H}^+ \tag{7}$$

In consequence, both nanoparticles underwent oxidation, and the delivery of dissolved iron species to the surrounding water occurred. Even when both types of nanoparticles present an initial magnetite layer (see Table S1) that prevents the iron in the core from fast conversion upon reaction with water or dissolved oxygen, defects in this protecting layer can expose Fe to the solution. Then, reactions (4)–(7) take place, thickening the oxide shell at the expense of the α -Fe consumption during the immobilization process [47]. As demonstrated by Kašlík et al. [48], nZVI reactivity is determined by the extent and chemical composition of the external oxide layer, but also the by the concentration of defects alongside its structure, i.e., the nanoparticles will be more reactive as the Fe in the core is more accessible.

Free N25 have a thinner and more cracked external oxide layer than NSTAR that poorly covers iron in the core from reaction with water, dissolved oxygen, or water pollutants [9]. The latter explains its better dispersion in the AL beads in comparison with NSTAR, and the former justifies a larger oxidation extent that led to formation of large lepidocrocite crystals in the outside layer, and to the dissolution of a higher proportion of Fe species (Figure S4). Nevertheless, in both cases, α -Fe remained as the main iron phase of both types of immobilized nanoparticles, as undeniably demonstrated by the XRD patterns in Figure 2a.

4.2. Role of the Polymer Matrix in Cr(VI) Removal

Alginate hydrogels formed with precursors of different viscosities did not make a differential impact in neither the Cr(VI) removal capacity nor in the removal rate with NSTAR@AL and N25@AL beads. In Figure 6, the time of complete removal is plotted against the temperature of the process for NSTAR and N25 immobilized in KT and KS.



Figure 6. Time for 100% removal of Cr(VI) with different types of material at different temperatures. $[Cr(VI)]_0 = 64 \ \mu\text{M}$, NSTAR@AL= 1 g, Fe:Cr MR = 55 and pH = 3.

These experimental reprocessed results from Figure 3c and Figure S5 clearly depict the negligible effect of the alginate viscosity in the removal performance compared with the impact of different types of immobilized nanoparticles. In addition, alginate was not able to remove Cr(VI) due to electrostatic repulsion between $-COO^-$ groups of the polymer and $HCrO_4^-$, the main Cr(VI) species in water at $pH \ge 3$ [49]. Though Lei et al. [50] proposed that the functional groups constituting alginate as -C-H, -C-COOH, and -C-OH are able to transform Cr(VI) in Cr(III) in aqueous media, this reactivity was not evidenced in our experiments, but its influence in longer time span experiments must not be discarded.

Together, these two experimental observations build the image of a polymeric matrix that acts simply as a chemically inert host retaining nZVI. However, chemical interaction with Cr(VI) is not the only way to intervene in the removal process. Free-in-suspension nanoparticles achieved complete Cr(VI) removal faster than their immobilized counterparts. Two factors seem to explain this finding: Cr(VI) species intra-bead diffusion, and alginate interaction with iron cations. The accessibility of nZVI aggregates can be physically obstructed by the intricated inner channeled structure of the alginate beads, which interposes

a tortuous pathway to Cr(VI) in its way towards the nanoparticles surface. In parallel, Fe(III) and Fe(II) in the surface of nZVI can interact with the polymer oxygenated functional groups, especially with carboxylates, as they do as free cations in the structure of Fe(II) or Fe(III) alginate hydrogels [51,52]. Therefore, the immobilized nZVI are expected to be partially covered by alginate chains anchored to their surface through Fe(II) and/or Fe(III). Both phenomena have also been exposed in Cr(VI) removal experiments using polyacrylonitrile immobilized NSTAR [20].

4.3. nZVI Physicochemical Identity and Cr(VI) Removal

Free N25 nanoparticles in suspension removed 100% of Cr(VI) in 2 min, whereas only 20% of Cr(VI) was removed by inactivated NSTAR after 60 min (Figure 4). Though, as shown in Section 3.2.2, when activated, free NSTAR showed an identical Cr(VI) removal curve than the one of free N25. After the activation process, the flaking off of the NSTAR thick and compact magnetite layer [53], and the dissolution of anionic iron hydroxo-species in the nZVI shell [54] made the NPs core more accessible. However, it has been reported that even after activation, NSTAR reacts slower than N25 [48,55]. Thus, the similar Cr(VI) time-resolved removal curves from free N25 and activated NSTAR depicted in Figure 4 could be explained by the large Fe:Cr MR used in our experiments.

The different reactivity of each type of nZVI was evidenced after immobilization: N25@AL reach faster complete Cr(VI) removal than NSTAR@AL and NSTARact@AL. In fact, NSTARact@AL did not reach complete removal of Cr(VI) after 60 min, and, surprisingly, showed a worse performance than NSTAR@AL. Increased exposure of α -Fe, and higher surface concentration of Fe(III) species are opposite consequences of the immobilization process: the first entails higher reactivity; and the latter results in higher concentration of firmly anchored alginate chains to the surface, which hinders the Cr(VI) removal process. The mild oxidation of non-activated NSTAR during the immobilization process seems to result in a beneficial trade-off between these two factors.

Further evidence of a mild activation process achieved by NSTAR is suggested by results in Figure 6, where the temperature effect is more pronounced for NSTAR@AL than for N25@AL. NSTAR partially activated after immobilization had the polymer softly attached to the surface of nZVI. Therefore, the increase in Cr(VI) mobility with temperature was reflected in a pronounced boost of removal rate, going from 60 min to 20 min to achieve complete withdrawing of Cr(VI) from the solution at 10 °C and 40 °C, respectively.

Despite AL delaying the nZVI surface accessibility for Cr(VI), immobilized nZVI responded in a similar manner than free nZVI in suspension: (1) the removal efficiency was improved at lower pH; (2) dissolved oxygen had no effect in the removal process; and (3) higher temperature led to faster C(VI) removal [36,56,57]. The first two experimental facts were approached in Section 3.2.1.

To the best of our knowledge, only three works evaluate the batch Cr(VI) removal efficiency of nZVI immobilized in AL, and the main experimental data is resumed in Table 1.

The nZVI@AL beads prepared by Ravikumar et al. [58] had a 16-times lower removal capacity of Cr(VI) than the ones reported by us, using a similar immobilization strategy: they immobilized nZVI after their synthesis through NaBH₄ reduction. The authors demonstrated the presence of Fe(0) in their nZVI@AL NCs based on the XRD pattern from chemically synthesized nanoparticles. However, their immobilization protocol involved drying the nZVI@AL beads at 100 °C, a very aggressive condition for non-air-stabilized nZVI, which could explain the lower reactivity with respect to the maximum removal capacity reported in this work.

On the other hand, the data summarized in Table 1 reveals that greater removal capacity was achieved in the works where reduction with NaBH₄ was performed over the alginate beads, even when previously synthesized nZVI were immobilized. In this regard, direct reaction of NaBH₄ with Cr(VI) (Equation (5); $\Delta E_{298K}^0 = 2.3$ V) could take place inside alginate spheres, as they can effectively store sodium borohydride [59]. Furthermore, in both works in Table 1 where NaBH₄-treated alginate beads were used for the removal of

Cr(VI), there is a lack of solid proof of the presence of metallic Fe in the final material. As discussed in Section 4.1, during water-mediated immobilization processes, even air stable nZVI tend to suffer fast oxidation of iron in the core that can be transformed into magnetite, which can also reduce Cr(VI), but at lower rate and extent [60].

$$8HCrO_{4}^{-}+26H^{+}+3BH_{4}^{-} \rightarrow 8Cr^{3+}+23H_{2}O+3H_{2}BO_{3}^{-}$$
(8)

Table 1. Removal capacity of various materials based on nZVI@AL for the removal of Cr(VI).

Reference	Material	pН	Removal Capacity (mg Cr(VI) g nZVI ⁻¹)	Contact Time (h)	Immobilization Procedure
Huang et al. [49]	nFe@AL	3	142.41	50	Infiltration of Fe(III) ions in alginate beads, followed by reduction with NaBH ₄ .
Ravikumar et al. [58]	nFe@AL	7	8.108	67.5	Immobilization of nZVI previously synthesized by reduction of Fe(II) with NaBH ₄ . Filtrated and dryed at 100 °C.
Lv et al. [56]	nFe/F3O4@PVA/AL	5	666*	24	Immobilization of synthesized nZVI by reduction with NaBH ₄ , combined with Fe ₃ O ₄ nanoparticles, followed by stabilization of 12 h in Na ₂ SO ₄ . Re-reduction with NaBH ₄ after immobilization.
This work	nFe@AL	3	133	24	Immobilization of commercial nZVI in AL. 4 h of hardening

Note: The value was calculated per mass of $(Fe^0 + Fe_3O_4)$.

4.4. Retention of Cr(III)

It is well documented that at a pH higher than 4, Cr(III) is efficiently retained in the surface of nZVI as a passivating oxi(hydroxide) layer of Cr(III) with Fe(III) [61]. The coprecipitation of Cr(III) is a competitive process for the dissolution of the external iron oxide layer. At pH values lower than 4, a depressed chromium retention, and an enhanced iron oxide dissolution continuously peels off the nanoparticles' protective shell, promoting the consumption of iron from the core, instead of shielding it behind a passivating layer [10]. Moreover, Fe(II) released from the nZVI surface offers an additional reduction pathway for Cr(VI). In other words, the pH condition that offers the higher Cr(VI) removal capacity leads to a high concentration of dissolved Cr(III). In this aspect, alginate brings an additional advantage as base polymer for supporting nZVI and its use in Cr(VI) removal: Cr(III) is partially entrapped after the Cr(VI) removal process at pH 3, in good agreement with results obtained by other authors [56,58,62]. On one hand, Cr^{3+} is a hard cation that can displace Ca^{2+} in the beads, and bind to the polymer through hydroxylic and carboxylic groups of alginate [63]. On the other hand, this strong interaction with the polymer and the intricate internal structure of the beads might also interfere with the delivery of Cr(III), favoring its co-precipitation over the nZVI surface. Figure 7 schematizes the overall removal mechanism of Cr(VI) with nZVI@AL.



Figure 7. Schematic representation of Cr(VI) removal by nZVI@AL. (a) Cr(VI) penetration into the beads, and reaction with nZVI. (b) Cr(III) fate and distribution after reaction.

5. Conclusions

A robust and reproducible protocol was achieved for nZVI immobilization on AL beads. The prepared materials were useful for fast and efficient Cr(VI) removal, showing that Cr(VI) can be completely eliminated in 10 to 30 min, depending on the immobilized nZVI at pH 3, which constitutes the best option, as has been largely demonstrated. The entrapped nZVI showed lower reactivity in suspension due to surface complexation of

Fe(III) and Fe(II) ions, but also due to the intricate inner structure of the beads, which slows down the Cr(VI) diffusion towards the surface of the occluded NPs. As counterpart, the polymer also obstructs the delivery of Cr(III) into the solution, resulting in a higher removal of Cr in comparison with free nZVI in suspension at the same initial pH.

We also probed that the chosen immobilization process modified the physicochemical properties of nZVI, along with their Cr(VI) removal performance. Given the inherent reactivity of nZVI towards water and/or dissolved oxygen, it is key to have a clearly characterized material, in part to be able to make a correct comparison with other works in the literature, and also to promote the correct development of hybrid materials, such as those presented here. In this sense, it is worth highlighting that the confirmation of the presence or absence of zerovalent iron is imperative when it comes to explaining the mechanisms and physicochemical changes of the system under study without falling into excessive speculation.

Finally, though the spent material final destiny has not been addressed in this work, this issue represents an open question in the scientific community. However, immobilization of nZVI, particularly in a biodegradable hydrogel supporting host such as alginate, is a well oriented strategy towards minimalizing the environmental impact of such a removal agent after its remediation use.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/w14030484/s1, Figure S1. Relative Cr(VI) removal for different sonication protocols; Figure S2. Secondary electrons and backscattered electrons SEM image for N25@AL and NSTAR@AL; Figure S3. EDS Mapping of NSTAR@AL bead; Figure S4. Percentual iron delivered into the solution CaCl₂ solution after nZVI immobilization; Figure S5. Effect of (d) alginate viscosity in Cr(VI) removal by N25@AL; Figure S6. Maximum removal capacity of N25@AL and NSTAR@AL. Table S1. Main characteristics of NSTAR and N25 nanoparticles informed by the provider, Nanoiron s.r.o.

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