



Aging study on carboxymethyl cellulose-coated zero-valent iron nanoparticles in water: Chemical transformation and structural evolution



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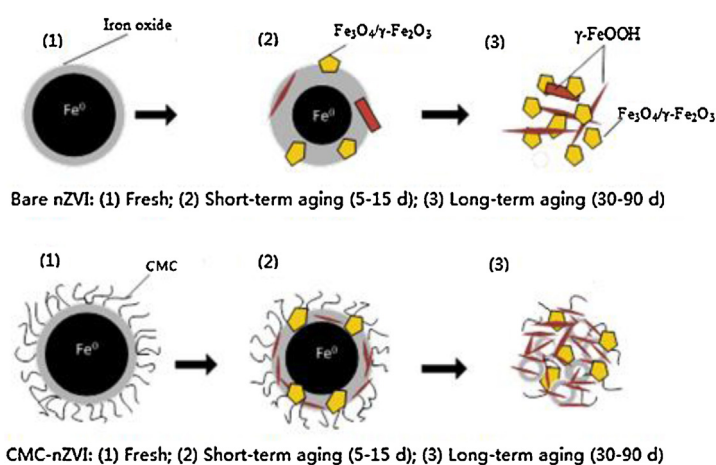
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HIGHLIGHTS

- The chemical transformation and structural evolution of CMC-nZVI were investigated.
- CMC could slow down the aging rate of nZVI and alter the species transformation.
- Fe_3O_4 and/or $\gamma\text{-Fe}_2\text{O}_3$ are the dominant corrosion products of bare nZVI after aging.
- $\gamma\text{-FeOOH}$ is the primary corrosion product of CMC-nZVI after aging.

GRAPHICAL ABSTRACT



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ABSTRACT

To assess the long-term fate and the associated risks of nanoscale zero-valent iron (nZVI) used in the water remediation, it is essential to understand the chemical transformations during aging of nZVI in water. This study investigated the compositional and structural evolution of bare nZVI and carboxymethyl cellulose (CMC) coated nZVI in static water over a period of 90 days. Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy were used to characterize the corrosion products of nZVI and CMC-nZVI. Results show that both the structures and the compositions of the corrosion products change with the process of aging, but the coating of CMC could slow down the aging rate of nZVI (as indicated by the slower drop in Fe⁰ intensity in XRD pattern). For the bare nZVI, magnetite (Fe_3O_4) and/or maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are the dominant corrosion products after 90 days of aging. However, for the CMC-nZVI, the core-shell spheres collapse to acicular-shaped structures after aging with crystalline lepidocrocite ($\gamma\text{-FeOOH}$) as the primary end product. Moreover,

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more lepidocrocite present in the corrosion products of CMC-nZVI with higher loading of CMC, which reveals that the CMC coating could influence the transformation of iron oxides.

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1. Introduction

Iron nanoparticle technology has been considered to be one of the first generation of nanoscale environmental technologies [1]. Substantial researches have demonstrated nanoscale zero-valent iron (nZVI) have large specific surface area and high surface reactivity relevant its core-shell structure with a zero-valent iron core surrounded by an iron oxide/hydroxide layer [2,3]. This material has been used to degrade a wide range of organic and inorganic soil and water contaminants [4–10].

nZVI particles naturally oxidize upon reaction with water and oxygen resulting in a significant decrease in reactivity [11]. The formation of different mineral phases on the particle surface, which may occur within the desired functional lifetime of nZVI particles, affects the reactivity, hydrodynamics, and mobility of nZVI in the environment [12]. Therefore, it is important to understand the transformation of nZVI particles during long-term water exposure.

Previous studies showed that fresh nZVI consists of a Fe⁰ core surrounded by an oxide shell with a near-perfect spherical shape [2]. The structure, shape, and composition of nZVI change with time upon exposure to water. Long-term aging leads to the formation of lepidocrocite and magnetite/maghemite [11,13–15]. Different morphologies and compositions have been observed when iron nanoparticles are oxidized, ranging from iron/iron oxide core-shell structures [16] to iron/iron oxide core-void-shell structures, iron oxide solid spheres, or even iron-based hollow structures [17,18]. It has reported that the structure and composition of aged nZVI varied considerably, depending on the iron types (e.g., Fe^{H₂}, produced by the hydrogen reduction of ferric oxides and Fe^{BH}, prepared using a borohydride reduction method), solution composition, solution pH, DO, temperature, and so on [19–21].

Phenrat et al. [22] has shown that bare (unmodified) nZVI particles can aggregate very rapidly because of attractive magnetic forces. To increase the stability and mobility of nZVI for engineering application, various modification approaches have been attempted, such as bimetallic system [23], carboxymethyl cellulose (CMC) [24–27], guar gum [28], polyacrylic acid [27,29,30] and surfactant [31,32] modification. Until now, the corrosion of bare nZVI during longtime water exposure has been widely reported [11,15,20]; however, the structural characteristics and evolution process of the engineered modified nZVI particles with surface coatings have not been systematically investigated. This information would be of great importance for the understanding of the long-term fate of surface-modified nZVI in the water environment and the risk assessment for the use of the engineered nZVI particles in subsurface remediation.

The overall objective of this study is to investigate the structural and compositional evolution of nZVI modified with carboxymethyl cellulose (CMC) in static aquatic media over a period of 90 days. CMC is a polyelectrolyte and carries carboxylate groups in addition to hydroxyl groups. Previous studies have shown that CMC strongly interact with nZVI particles and stabilize the nanoparticles effectively [24]. Morphological and mineralogical characteristics of bare nZVI and nZVI modified with CMC in various stages of aging are studied by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD) and Raman spectroscopy.

2. Experimental methods

2.1. Materials and chemicals

Carboxymethyl cellulose (CMC, MW = 90,000) were purchased from Jingkang new material technology co. (Changsha). nZVI particles (Nanofer 25, produced from nanosized ferrihydrite) in aqueous dispersion form were graciously supplied by the NANOIRON[®] Company (Czech Republic, EU). All reagents for experiments were of reagent grade and used without further purification. All solutions and dilutions were prepared in ultrapure water (Barnstead D11911).

2.2. Preparation of iron nanoparticles

A stock suspension of Nanofer 25 of 200 g L⁻¹ (referred to as nZVI in this study) was prepared. Suspensions of nZVI (500 mg L⁻¹) were prepared by dilution with stock suspension in N₂-purged water under neutral conditions (pH ~ 7). The solution pH was measured by a pH meter (INESA, PHS-3C). The pure CMC solutions were prepared and homogenized overnight using magnetic stirrers to ensure complete hydration and dissolution [33]. The CMC-coated nZVI (CMC-nZVI) was synthesized by dispersing nZVI particles in aqueous CMC to result in suspensions, comprising iron nanoparticles (500 mg L⁻¹) and CMC of various concentrations (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6 wt%) individually. The particle suspensions were then ultrasonicated for 30 min to complete the formation of CMC-nZVI.

2.3. Sedimentation and aging experiments

A sedimentation assessment of the CMC-nZVI suspensions was then performed to determine the stabilizer concentration for the efficient stabilization. Digital photographs of the vials containing CMC-nZVI suspensions were taken up to 60 min to qualitatively assess the rate of sedimentation and nanoparticle stability by observing the turbidity of the suspension (Fig. S1 in the supporting information (SI)). The bare and CMC-nZVI nanoparticles showed different sedimentation behavior. The iron nanoparticles rapidly settled within 60 min. CMC-nZVI deposited less when the concentration of CMC increased from 0.2 wt% to 1.6 wt%. The sedimentation kinetics of CMC-nZVI with different CMC loadings (0.4, 0.8, 1.2, 1.6 wt%) was further determined quantitatively by monitoring the optical absorbance at 508 nm by UV-vis spectrophotometry (UV-2550, SHIMADZU, Japan) in a drive-time mode for 1 h. CMC-nZVI coated with 0.4 wt% (less efficient stabilization) and 1.2 wt% (efficient stabilization) were employed in the subsequent aging experiments to examine the effect of CMC concentration on nZVI corrosion. The solid samples were filtered and collected after 0, 5, 15, 30, 60, and 90 days of aging. The experiments were carried out in static water (40 mL) in an open vial (50 mL), which represents the static aquatic media exposed to the air. All measurements were made at 25 °C in duplicate.

2.4. Characterization of fresh and aged iron nanoparticles

The collected solid samples of bare nZVI and CMC-nZVI at various aging states were freeze-dried before further analyses by FTIR,

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