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Nanoscale Zero Valent Iron for Environmental Cadmium Metal Treatment

Keyla T. Soto-Hidalgo and Carlos R. Cabrera

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Abstract

In the course of developing methods to treat heavy metal contaminants in wastewater, nanoscale zerovalent iron (nZVI) has been found to be an alternative approach. This nanoparticle has been used to remove metals such as Cr^{6+} , Cu^{2+} , Pb^{2+} , Ba^{2+} , As^{3+} , As^{5+} , and Co^{2+} from aqueous solutions. Iron nanoparticles are useful for decontamination purposes due to their smaller size, surface area-to-weight ratio, and capacity to remove groundwater contaminants. The large specific surface area of the iron nanoparticles further fosters enhanced reactivity for the transformation of environmental pollutants. Because of their smaller size, nanoscale-based iron materials are much more reactive than conventional iron powders, and they can be suspended in slurry and pumped straight to the contaminated site. The ZVI is often applied for the remediation of wastewater or groundwater with several kinds of reducible contaminants, which are near its surface reduction potential. This chapter seeks to present the efficiency of zerovalent iron nanoparticles (nZVI) to remedy the cadmium ion pollution in water as well as the use of the remediation product in photoelectrochemical devices.

Keywords: nanoscale zero valent iron, heavy metals, environmental remediation, photoelectrochemical solar cells

1. Introduction

Environmental pollution is one of the most important problems in the world and is the focus of a wide array of studies in the scientific community [1]. The development of advanced technology and rapid industrialization are the most predominant factors that increase environmental pollution [2]. One of the major hazards to human health from environmental contamination is heavy metals due to their tendency to bioaccumulate in plants and animals that are part of the human food chain [3]. Numerous anthropogenic activities such as mining,

landfills, electroplating, metal processing, textile, petroleum refining, pesticides, battery and paint manufacturing, and printing and photographic industries release these metals into the environment. Heavy metals can persist for a long time in the environment [4].

Many metals that do not play any physiological role such as lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg) have adverse effects on human health because they have been cataloged as risk factors for the development of cancer, respiratory conditions, neurodegenerative disorders, and arthritis [5]. Lead is the most common of these toxic materials, and all Pb species are generally toxic (see **Table 1**). Volcanic activity and geochemical weathering are the greatest natural sources; man-made sources include lead-based paints, gasoline additives, food-can soldering, and battery making [6]. The movement of Pb from absorbing root hairs, is apparently impeded by several biochemical and/or physical processes involving Pb binding, inactivation, and/or precipitation [7]. Lead has accumulated in different terrestrial and aquatic ecosystems, and has been shown to accumulate in plants from several sources, including soil; however, the reports on accumulation of Pb within plants are variable [8, 9].

Arsenic is highly toxic to human health (see **Table 1**) [8, 10]. All species of As (III) and As (V) are toxic. Inorganic and most toxic forms of arsenic (arsenate and arsenite) are found in soil, crops, and water, particularly in groundwater from deep wells, often used as drinking water. These compounds are also found in environmental tobacco smoke and arsenic-treated wood, used in most outdoor wooden structures in the United States. High levels of arsenic are present in agricultural fertilizer that is used for soil treatment; as a consequence, any vegetables and fruits, if grown in this soil, will contain high levels of arsenic.

Cadmium ions, commonly found in soil and water systems, affect vital organs such as liver and kidneys (see **Table 1**) [8, 11]. This metal is considered one of the most toxic environmental substances due to its ubiquity, toxicity, and long half-life. All species of Cd are toxic. Exposure to cadmium occurs through inhalation (particularly in active cigarette smokers), groundwater consumption, industrial exposure, and contaminated food. It causes a wide variety of toxic effects when taken up by plants such as the inhibition of several plant physiological processes like oxidative reactions and nitrogen metabolism [12, 13]. Currently, there are many traditional chemical methods to remove these heavy metals from contaminated sites such as alkaline precipitation,

Pollutants	Major sources	Effect on human health	Permissible level (mg/l)
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis, poisoning	0.02
Cadmium	Welding, electroplating, pesticide, fertilizer, Cd, and Ni batteries, and nuclear fission plant	Renal dysfunction, lung disease, lung cancer, bone defects, increased blood pressure, kidney damage, bronchitis, gastrointestinal disorder, bone marrow, and cancer	0.06
Lead	Paint, pesticide, smoking, automobile, emission, mining, and burning of coal	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, damage to the nervous system, liver, and kidney	0.1

Table 1. Major sources of As, Cd, and Pb and their effect on human health [8].

ion exchange columns, electrochemical removal, filtration, and membrane technologies [8], but these methods are expensive and use many equipments to efficiently remove the contaminants. On the other hand, following the principles of Green Chemistry is necessary to use alternative products that prevent waste after remediation process, use less hazardous chemical synthesis, and minimize energy requirements of all chemical processes and environmental and economic impacts.

2. Iron nanomaterials for remediation process

Iron nanoparticles are a new generation of materials for environmental remediation. Various metallic ions, including Pb^{2+} , Cr^{6+} , Ni^{2+} , As^{3+} , As^{5+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , and Ba^{2+} have been fixated from water using this new technology [14]. In situ remediation strategies are useful to reduce the mobile fraction of metals and metalloids in the soil that could reach the groundwater or be taken up by soil organisms. As such, several strategies have been used to promote the immobilization of metals in soil [15]. In the course of developing suitable options to remove heavy metal contaminants from wastewater, nanoscale zero valent iron (nZVI) particles have been found to be an alternative approach to reduce the concentration of several kinds of contaminants, mainly targeting chlorinated organic contaminants, inorganic anions, metals, and metalloids [15–19]. Although the benefits of this strategy are evident, governments and environmental agencies must evaluate any associated environmental risks because currently available ecotoxicology data are not enough [20].

Previous column experiments have showed the effectiveness of nZVI for the in situ immobilization of heavy metals, which reduces their potential leachability, as a strategy to prevent their transport into deeper soil layers, rivers, and groundwater [21]. Iron nanoparticles are particularly attractive for environmental remediation because these are much more reactive than iron powders and they can be suspended in slurry and moved to the polluted site [22, 23]. Recently, the synthesis and utilization of iron-based nanomaterials with novel properties and functions have been widely studied, both for their nanosize and for their magnetic characteristics [14]. In the environment, iron oxides are present naturally, but can also be chemically produced in nanoparticles of the order of 100 nm or less, which provide them with specific and better affinity for ions metals adsorption. For this reason, these nanoparticles are being used for in situ experiments [15, 16]. In environmental engineering, the application of nZVI is commonly used for the removal of metal/metalloids from polluted waters and soils, or their stabilization [17]. For example, during the remediation of contaminated soils, nZVI has become a widespread amendment for in situ applications, since it can form a permeable barrier in the soil in order to prevent the dissemination of contaminants by the soil pore water, thus achieving their immobilization [18, 24].

Efficient nZVI remediation of groundwater contaminants has been shown in multiple studies; however, regarding nZVI-induced soil toxicity, limited data have been reported, providing preliminary results about the effects of nZVI on soil biota and some plant species [19]. Most of the reported studies have been conducted either under no real conditions or only considering

short-term exposure. Therefore, the impact of nZVI treatment on soil properties and functionality remains unclear. On the other hand, very few investigations of nZVI materials present a detailed study of the products formed in the remediation process for reusability of these nZVI after treatment [25–27]. An alternative use of the remediation product of nZVI could be for photoelectrochemical solar cells (PSC) applications.

In the nZVI reaction, metallic iron is oxidized in the presence of water, which can remove other metal ions from aqueous media by chemical absorption. In this process, iron oxides such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) are produced [27]. Hematite has been studied for catalytic applications because of the presence of active photochemical properties [28]. Even so, the application of hematite in PSC is a challenge for the scientist community because this species is highly active in UV range but not absorbed in the visible range. The aim is to employ $\alpha\text{-Fe}_2\text{O}_3$ in commercial solar-based devices using high temperature synthesis methods for doping structures and an alternative method to produce dye-sensitized solar cells [28–31].

3. Nanoscale zero valent iron (nZVI) for cadmium decontamination process

Of all the metallic contaminants, cadmium draws special attention because of its high affinity and water solubility [32]. Cadmium species have been detected in aquatic ecosystems and found to bioaccumulate in organisms in nanomolar to micromolar concentrations [33]. Efficient nZVI remediations of groundwater contaminants have been shown in multiple studies [33–37]. However, in the literature, there is a lack of comparable studies for different nZVI materials and deployment strategies [38].

Various adsorption and kinetic models to describe metal adsorption on nZVI and Cd-nZVI surfaces using SEM/EDX and XPS measurements have been studied [26, 38] but, to our knowledge, the interactions between surface Fe^0 and other heavy metals in particular Cd^{2+} and subsequent cadmium retention in nZVI particles have not been the subject of detailed study.

Results from our study provide important information of the products formed during the remediation process of cadmium. Studies of redox and adsorption processes after treatment of nZVI have been evaluated [39]. However, it is necessary to understand in detail what occurs in the cadmium adsorption process at the nanoparticle surface. The reduction potential of Cd is larger than standard reduction potential (E°) of nZVI (-0.40 V , 25°C , -0.447 V), respectively [26]. Our data suggest that Cd^{2+} ions are sequestered on nZVI by adsorption process [27].

Results of the Cd concentration reduction on nZVI sample were analyzed using an inductively coupled plasma (ICP). The maximum cadmium adsorption percentage relative to the initial Cd^{2+} concentration of 6 ppm was 93%. This percentage was obtained after a period of 5 h, which indicates that longer interaction times between cadmium ions and nZVI promoted larger cadmium concentration reduction.

These results show that nZVI is an alternative to decrease high Cd concentration in contaminated sites. However, there are no sufficient data about the possible formation of toxic product

after treatment with nZVI. For this reason, a structural analysis of used nZVI was deemed imperative to gain an understanding of the interactions between the nZVI and cadmium. This new knowledge may serve to optimize the remediation process and to provide alternative uses for the remediation product. The formations of unexpected nanofibers and cadmium ferrite structures have been reported. This remediation product or environmental waste has been suggested as a photocatalyst material that has great potential application for light harvesting [40]. These results could be useful because we can prevent the waste formation after chemical process, and reuse the products of remediation processes for other energy applications. This will decrease the amount of new hazardous substances produced after water decontamination processes.

A structural model of Cd-nZVI fibers is illustrated in **Figure 1**. This conceptual model of Fe⁰ nanofibers was presented considering the results of X-ray diffraction patterns, X-photoelectron spectroscopy results, X-ray absorption spectroscopy, and high-resolution transmission electron microscopy (HRTEM) images. **Figure 1** shows the (A) Fe⁰ nanoparticles, (B) the Fe⁰-H₂O, where we observe Fe₂O₃ and FeOOH surrounding small quantities of Fe⁰, and (C) Fe⁰-Cd where we observe CdFe₂O₄, FeOOH, Fe₂O₃, and Fe⁰. For the formation of the structure presented in **Figure 1C**, cadmium ions act as the limiting reagent, where the onset of the reaction of Cd, Fe⁰, Fe₂O₃, and FeOOH allowing the possible formation of cadmium ferrite.

The oxyhydroxide iron (FeOOH) has a crystal structure containing tunnel-shaped cavities that run parallel to the c-axis. These sites are bound by double rows of fused octahedral, in which cadmium ions probably reside [41]. In **Figure 2a**, HRTEM images of nZVI exhibit spherical shapes and well-aligned aggregates with a diameter range between 25 and 70 nm.

These clusters of nanoparticles are caused by magnetic dipole-dipole interactions of the individual particles [42]. After nZVI Cd²⁺ exposure, shown in **Figure 2b**, nanofibers are organized [43]. These nanofibers were possibly produced by the diffusion of absorbed Cd²⁺ ions through the core-shell structure [36]. In iron oxide, an electron transfer reactions between Cd²⁺ ions and the Fe⁰ might probably occur in the core (**Figure 2**).

The fiber formation as a product of nZVI in the presence of cadmium ions is possibly due to the rearrangement of the nanomaterial structure as a consequence of the adsorption process. The interactions of Cd²⁺ and Fe³⁺, particularly, possibly promote the formation of CdFe₂O₄.

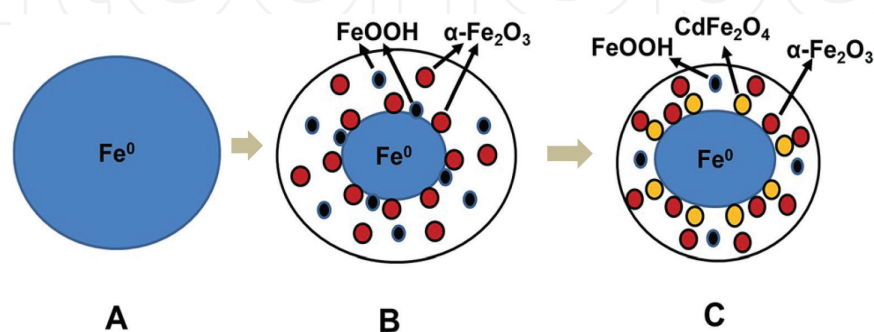


Figure 1. Conceptual model of cadmium adsorption process on nZVI nanostructures with cadmium-iron oxides on the surface [43].

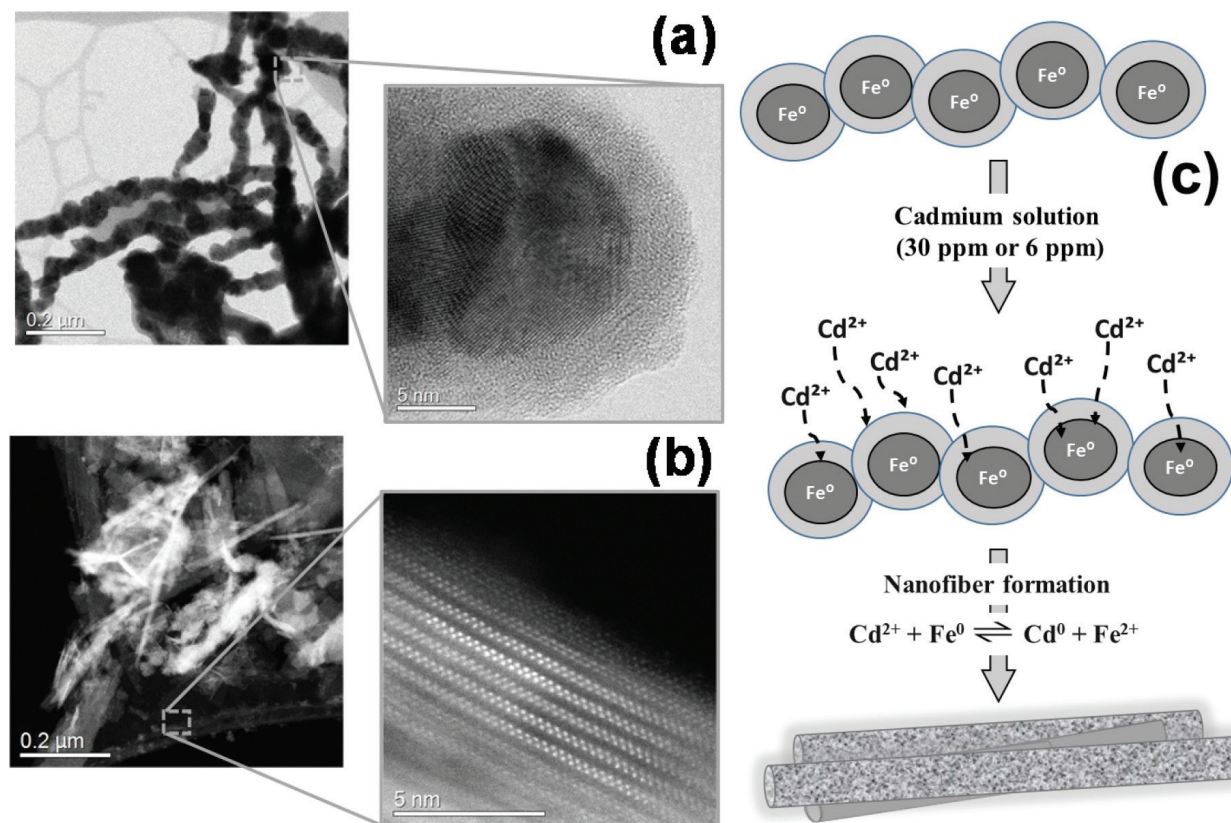


Figure 2. HRTEM images of (a) nZVI particles synthesized and (b) iron nanofibers formed during the cadmium ion remediation process. (c) Conceptual model representing the Cd^{2+} atoms interaction in Fe^0 core of nZVI [43].

which is in accordance with what is reported in the literature; these results show fiber formation analogous to previous studies with CdFe_2O_4 particles synthesized by a coprecipitation method [41]. These studies in HRTEM presented the aggregation of fine particles of CdFe_2O_4 having two kinds of shapes, fibrous and granular. The unintended formation of CdFe_2O_4 nanofibers as a remediation product presents an opportunity to reuse the remediation products for applications pertaining to light harvesting.

4. Applications of nZVI in photoelectrochemical solar cell devices

Photoelectrochemical solar cells use light to carry out a chemical reaction, converting light to chemical energy or power [44–46]. A photoelectrochemical cell is a photocurrent-generating device that has a semiconductor in contact with an electrolyte. It consists of a photoactive semiconductor working electrode (either n-type or p-type) and counter electrode made of either metal (e.g., Pt or C) or semiconductor. These electrodes are immersed in the electrolyte containing redox species with its standard potential being within the semiconductor bandgap potential region. In a metal-electrolyte junction, the potential drop occurs entirely on the solution site, whereas in a semiconductor-electrolyte junction, the potential drop occurs on the semiconductor site as well as the solution site [47].

The charge on the semiconductor side is distributed in the interior of the semiconductor, creating a space charge region. If the junction of the semiconductor-electrolyte is illuminated with a light having energy greater than the semiconductor bandgap, photogenerated electron-hole pairs are separated in the space charge region [48, 49]. The photogenerated minority carriers arrive at the interface of the semiconductor-electrolyte where a redox reaction will occur.

Photoelectrochemical cells, such as those produced by Brian O'Regan and Michael Grätzel, have been of interest to scientist because of their low manufacturing cost [44]. Photoelectrochemical devices require exhaustive optimization of their quantum conversion efficiency, which is affected by the electron transfer processes.

In the nanoscale iron reaction with water, metallic iron is oxidized to $\alpha\text{-Fe}_2\text{O}_3$ [27]. Using $\alpha\text{-Fe}_2\text{O}_3$ as an alternative of TiO_2 has been evaluated to produce dye-sensitized solar cells [31]. Methods such as doping with other metals and changing the structural arrangement of the system have been employed to overcome challenges regarding electron transfer processes [28]. The incorporation of Cd ions on the surface of the oxidized nZVI may produce surface structure changes. It has been found that oxide structures such as Fe_xO_y and the formation of CdFe_2O_4 may be present at the surface of the nanoparticles [43]. As described in recent reports, this surface process may occur without using high-temperature processes, a common surface reaction described in the literature [29, 30]. Moreover, photovoltaic and photoelectrochemical processes have been studied with CdFe_2O_4 . However, few reports have shown the use of heavy metal doped ferrite particles as semiconductors in photovoltaic and photoelectrochemical devices [30, 50–52]. Recently, the use of Cd^{2+} ions exposed nZVI as semiconductors in PSCs has been reported. Brian O'Regan and Michael Grätzel reported similar systems in the 1990s, which caught the attention of the scientific community due to their low cost of fabrication [53].

Photoelectrochemical devices are challenging due to the optimization of their quantum conversion efficiency, which is affected by the electron transfer processes in the system. In our study, nZVI was exposed to different Cd^{2+} concentrations (1–30 ppm), similar to values found in contaminated areas of Puerto Rico. The novelty of these results was to analyze the material produced after the Cd decontamination processes in water using nZVI as a photoactive substance. The product formed exhibited capable photoactive behavior for photoelectrochemical solar cell applications.

In **Figure 3**, incident to photocurrent efficiency (IPCE) normalized signals of two PSCs are observed, each one with different material in the photoanode [54]. The samples prepared using the nZVI do not display significant signals (lowest curve). Particles treated with 30 ppm Cd^{2+} solution, however, exhibit a relative broadband from approximately 300–450 nm (black curve). This region is similar to the absorption results obtained in the UV/Vis analysis. Such a high photovoltage can be explained by an improvement in the electron transfer dynamics of the material in the PSC at higher cadmium concentrations due to structural changes as previously suggested in the literature [30]. As one of the principle of Green Chemistry, these results provide a new alternative to reuse nanomaterials used in decontamination processes and generate modified iron oxide photocatalyst without using high temperature. These data have a significant value for future applications in photoactive materials synthesis.

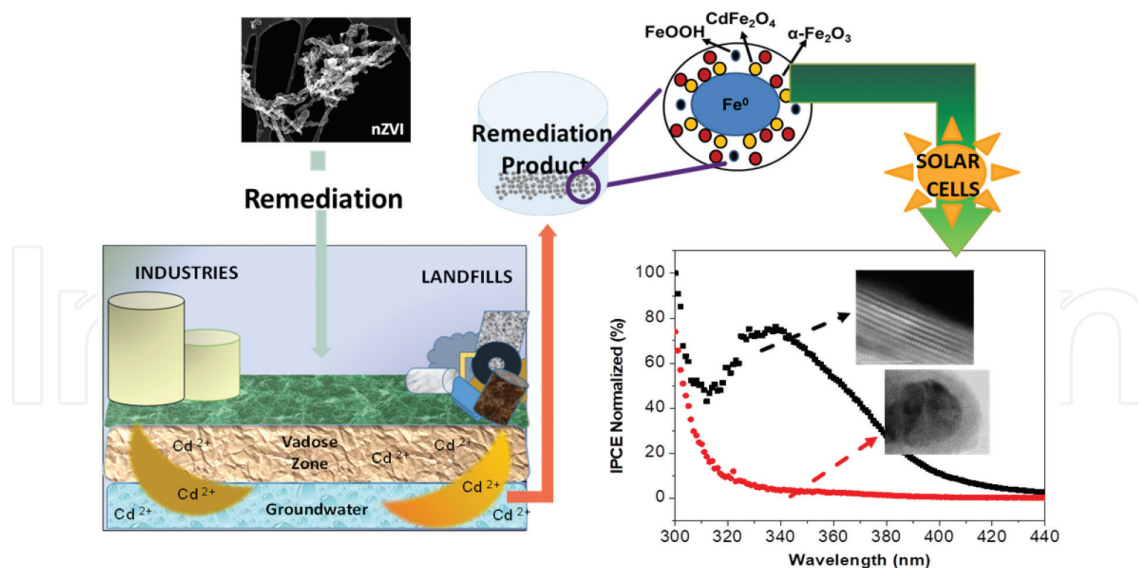


Figure 3. Graphical representation of cadmium water remediation to photoelectrochemical solar cells using nanoscale zero valent iron [54].

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Author details

Keyla T. Soto-Hidalgo^{1*} and Carlos R. Cabrera²

*Address all correspondence to: keyla.soto@upr.edu

1 NSF-CREST Center for Innovation, Research and Education in Environmental Nanotechnology (CIRE2N), University High School, University of Puerto Rico, San Juan, Puerto Rico

2 Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico

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