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Review

The use of zero-valent iron for groundwater remediation and wastewater treatment: A review



Fenglian Fu^{a,*}, Dionysios D. Dionysiou^b, Hong Liu^c

- ^a School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, PR China
- ^b Environmental Engineering and Science Program, University of Cincinnati, Cincinnati, OH 45221-0012, USA
- ^c Chongging Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongging 401122, PR China

HIGHLIGHTS

- The recent advances in ZVI are reviewed.
- A review of contaminants removed by ZVI from groundwater and wastewater is made.
- Excellent removal efficiencies of contaminants by ZVI are reported.
- Reaction mechanisms of ZVI with contaminants are discussed.
- The review suggests research needs for future work.

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GRAPHICAL ABSTRACT



ABSTRACT

Recent industrial and urban activities have led to elevated concentrations of a wide range of contaminants in groundwater and wastewater, which affect the health of millions of people worldwide. In recent years, the use of zero-valent iron (ZVI) for the treatment of toxic contaminants in groundwater and wastewater has received wide attention and encouraging treatment efficiencies have been documented. This paper gives an overview of the recent advances of ZVI and progress obtained during the groundwater remediation and wastewater treatment utilizing ZVI (including nanoscale zero-valent iron (nZVI)) for the removal of: (a) chlorinated organic compounds, (b) nitroaromatic compounds, (c) arsenic, (d) heavy metals, (e) nitrate, (f) dyes, and (g) phenol. Reaction mechanisms and removal efficiencies were studied and evaluated. It was found that ZVI materials with wide availability have appreciable removal efficiency for several types of contaminants. Concerning ZVI for future research, some suggestions are proposed and conclusions have been drawn.

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^{*} Corresponding author. Tel.: +86 20 39322296; fax: +86 20 39322547. E-mail address: fufenglian2006@163.com (F. Fu).

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Nomenclature

WHO World Health Organization

ZVI Zero-valent ironDO Dissolved oxygen

COCs Chlorinated organic compounds
NACs Nitroaromatic compounds

TCE Trichloroethylene NB Nitrobenzene

nZVI Nanoscale zero-valent iron
PRBs Permeable reactive barriers
COD Chemical oxygen demand
EPA Environmental Protection Agency

GAC Granular activated carbon

AACs Aromatic amine compounds
TNT 2,4,6-trinitrotoluene

HA Humic acid

MWCNTs Multiwalled carbon nanotubes

1. Introduction

1.1. The current water pollution

Environmental pollution in certain areas of the world is becoming more and more severe. Water is one of the basic necessities required for sustaining life. With the process of industrialization and urbanization, global water utilization has doubled every 15 years. According to the data of the World Health Organization (WHO), the scarcity of water resources has created challenges for over 40% of the world population, i.e., more than 2 billion people have no access to enough or clean water. Meanwhile, industrial and urban activities have led to increasing concentrations of a wide range of pollutants in groundwater and wastewater, affecting the health of millions of people worldwide. So groundwater remediation and wastewater treatment are of critical importance.

1.2. Zero-valent iron

Iron is the fourth most abundant element in the earth's crust. Over the last decade, a great deal of research has been focused on the removal of contaminants by zero-valent iron (ZVI) because ZVI is non-toxic, abundant, cheap, easy to produce, and its reduction process requires little maintenance. ZVI is a reactive metal with standard redox potential ($E^0 = -0.44 \, \text{V}$). It is thus an effective reductant when reacting with oxidized contaminants such as Cr(VI). The removal mechanism of contaminants by ZVI concerns the directional transfer of electrons from ZVI to the contaminants which

transforms the latter into non-toxic or less toxic species. On the other hand, ZVI can degrade and oxidize a series of organic compounds in the presence of dissolved oxygen (DO) since ZVI transfers two electrons to O_2 to produce H_2O_2 (Eq. (1)). The produced H_2O_2 can be reduced to water by another two-electron transfer from ZVI (Eq. (2)). Moreover, the combination of H_2O_2 and Fe^{2+} (known as Fenton reaction) can produce hydroxyl radicals (*OH) which possess strong oxidizing capability towards a variety of organic compounds (Eq. (3)).

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2$$
 (1)

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O$$
 (2)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$
 (3)

ZVI has been successfully applied for the remediation/treatment of groundwater and wastewater contaminated with chlorinated organic compounds (COCs) [1–4], nitroaromatic compounds (NACs) [5,6], arsenic [7–9], heavy metals [10–12], nitrate [13–15], dyes [16,17] and phenol [18,19]. There is an increasing interest on the use of ZVI for the removal of contaminants from groundwater and wastewater, and this is reflected in the increasing number of journal articles published recently. The articles on ZVI published in the last decade comprise approximately 90% of all publications according to ISI Web of Knowledge data base. It is also notable that the major contaminants treated by ZVI during the last 10 years include trichloroethylene (TCE), nitrate, arsenic, Cr(VI), phenol, and nitrobenzene (NB).

In this paper, the recent advances of ZVI and the use of ZVI in the remediation/treatment of hazardous contaminants from groundwater and wastewater are reviewed. The review focuses on experimental procedures, efficiency, and reaction mechanism in the investigation of a range of applications of ZVI, including those performed with COCs, NACs, arsenic, heavy metals, nitrate, dyes and phenol. The review also suggests research needs for future work.

2. Recent advances in ZVI

2.1. Nanoscale zero-valent iron (nZVI)

In the last 10 years, the adaptation of nZVI to remove many kinds of contaminants has received increasing attention due to its higher surface area and higher reactivity than ZVI. The published papers on nZVI comprise 15.8% of the total ZVI.

As is known, nZVI has a strong tendency to become oxidized. Greenlee et al. [20] investigated the oxidation kinetics for stabilized nZVI and iron-nickel nanoparticles with a quartz crystal microbalance and found nZVI oxidized primarily to the iron oxide-hydroxide

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