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Long-term performance of enhanced-zero valent iron for drinking water treatment: A lab-scale study

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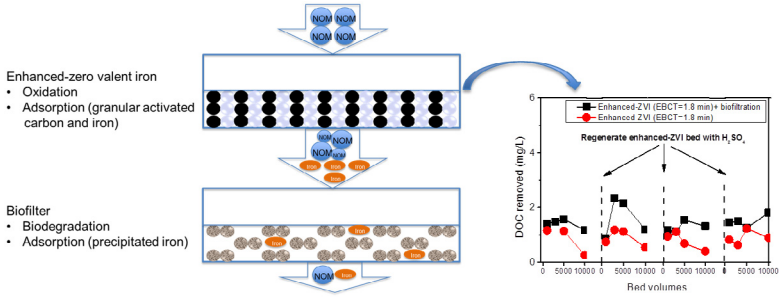
HIGHLIGHTS

- Enhanced-ZVI bed become passivated after 10,000-bed volumes operation.
- The passivated enhanced-ZVI bed could be regenerated with sulfuric acid.
- Enhanced-ZVI could improve the performance of subsequent biofiltration.
- A novel water treatment train incorporating enhanced-ZVI was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Former studies have shown that enhanced-zero valent iron (ZVI) could effectively remove various contaminants. The present study evaluates for the first time the long-term performance of enhanced-ZVI to remove natural organic matter (NOM), an important water quality parameter in drinking water. Lab-scale flow-through experiments showed that averagely 7–14% dissolved organic carbon (DOC) and 6–15% ultraviolet absorbance at 254 nm (UV_{254}) reduction could be achieved by enhanced-ZVI in the first 10,000 bed volumes filtration when a 0.36 or 1.8 mins empty bed contact time (EBCT) was applied. After 10,000-bed volumes, the enhanced-ZVI bed became passivated. However, sulphuric acid was able to regenerate the passivated enhanced-ZVI bed, recover the capacity of enhanced-ZVI in removing NOM, and hence make the best use of the available ZVI. The acidic rinsing solution containing dissolved iron was suitable as a supplemental source of iron for coagulation. In addition, during the long-term experiments, the biofilters following enhanced-ZVI (1.8 min EBCT) removed more NOM than biofilters without any pre-treatment. This could be explained by the formation of biodegradable organic matter (BDOC) during the enhanced-ZVI process and the precipitation of iron in the biofilters. Based on these findings, a novel water treatment train, incorporating enhanced-ZVI with periodical regeneration, biofiltration, and coagulation, was proposed and evaluated.

1. Introduction

Zero valent iron (ZVI) has been used in water treatment process to remove various contaminants, including removing heavy metals [1,2], reducing chlorinated organic and nitrate groundwater pollution [3–6], oxidating organics [7–9], and inactivating pathogens [10,11], with key advantages being its relatively cheap price and easy availability. However, one major drawback of ZVI-based treatment is a low intrinsic reaction rate due to mass transfer limitations imposed by the available surface area, which is aggravated by gradually increasing passivation as iron corrosion products accumulate

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on the ZVI grains over time [12]. To overcome the limitation, Guan et al. [12] proposed several countermeasures. One of them is to add a second material acting as cathode promoting spontaneous galvanic corrosion to accelerate the process (e.g. granular activated carbon (GAC)) [13,14]. When GAC is incorporated as a cathode material into this enhanced-ZVI process, different electrode reactions occur [15]. During the enhanced-ZVI process, the contaminants are removed by iron-based coagulation, GAC adsorption, electrochemical aggregation, Fenton-like oxidation and redox reactions involving nascent hydrogen production [13,14].

Natural organic matter (NOM) is ubiquitous in surface waters. Although there is no legal requirement for target NOM concentration (usually expressed as dissolved organic carbon (DOC) or ultraviolet absorbance at 254 nm (UV_{254})) in drinking water treatment, at least in Australia, the existence of NOM has significant impacts on the performance of water treatment, including increasing coagulant and disinfectant doses, transporting metals and hydrophobic organic chemicals, contributing to colour, taste and odour, fouling membranes and acting as substrate for bacterial growth in distribution systems [16,17]. More importantly, the reactions between free chlorine, the predominant disinfectant applied in much of the world, and NOM produce disinfection by-products (DBPs). Some DBPs have been linked to bladder cancer [18] and reproductive defects [19]. Therefore, minimising the amount of NOM is an important objective for drinking water production. To date, most ZVI-based studies related to NOM mainly focused on the interactions between NOM and the removal of other contaminants, but NOM removal was not the main target [20–22]. Also, in drinking water treatment processes, few studies have been reported on the enhanced-ZVI process, such as the removal of trichloroethylene [23] and arsenic contamination [24], but only our previous study reported upon about how this enhanced process impacted NOM removal during drinking water production from surface waters [25].

Liu, et al. [25] has demonstrated that enhanced-ZVI process was able to remove NOM substantially, and the results showed that within 24 h treatment of enhanced-ZVI (corresponding to only 1.8 min of empty bed contact time (EBCT)), DOC decreased from 11.20 ± 0.21 to 4.33 ± 0.16 mg-C/L, while UV_{254} reduced from 0.341 ± 0.001 to 0.104 ± 0.006 cm^{-1}, corresponding to reduction efficiencies of 61 ± 3% and 70 ± 2%, respectively. But, in that study, the enhanced-ZVI filters were operated in a batch recirculation mode, which does not mimic realistic field conditions. Also, the long-term performance of enhanced-ZVI bed could not be obtained based on those batch experiments. Thus, one of the objectives of the work reported in this study was to investigate the long-term performance of enhanced-ZVI operated in a once flow-through mode that would represent a typical application of this approach in practice. In addition, former studies have shown that enhanced-ZVI could improve the biodegradability of treated water [14,15,25–27], so the synergistic effect between enhanced-ZVI and biodegradation for NOM removal in drinking water treatment in long-term operation was investigated as well. Moreover, although various studies have reported the passivation of ZVI after long-term operation [5,28,29], there is no research about the generation of passivated ZVI. Therefore, the ways to regenerate passivated enhanced-ZVI and how to effectively utilise the regeneration solution were studies as well in this work.

2. Materials and methods

2.1. Raw water

Raw water used in this study was collected from a surface water reservoir, which is the source water for a local drinking water treatment plant (WTP) in Southeast Queensland, Australia. 400 L raw water was collected onsite and concentrated with a lab-scale reverse osmosis system using 2.5″ spiral wound reverse osmosis membrane (RO ESPA2540, Hydranautics, USA) to around 45 L (concentration factor of 8.88) for increased ease of storage in a cold room at 4 °C for future use. Prior to experimentation, the concentrate was reconstituted with deionised water obtained from a Milli-Q Advantage system (Millipore Pty Ltd, USA). Unless stated, the initial DOC and UV_{254} for the raw water used in all experiments were 9.32 ± 0.24 mg/L and 0.243 ± 0.008 cm^{-1}, respectively.

2.2. Enhanced-ZVI materials

ZVI was purchased from Alfa Aesar (Australia) with a size of 1–2 mm and purity of 99.98% (metals basis). GAC (ACTICARB GA1000 N) was obtained from Activated Carbon Technologies Pty Ltd, Australia, and had a size of 1.2–2.4 mm. The rough bulk densities for ZVI and GAC were 7.14 g/cm^3 and 1.43 g/cm^3, respectively. Before use, new GAC was rinsed with Milli-Q water several times to remove impurities, and then dried at 100 °C overnight. After cooling down to room temperature in a drying closet, these GAC particles were stored in sealed bottles for future use.

2.3. Experimental procedures

All experiments were conducted in lab-scale columns with a diameter of 8 mm and a total length of 120 mm. According to previous studies [13,30], enhanced-ZVI achieved the best performance when the volumetric ratio of ZVI to GAC was 1:1. Hence, the same volumes of ZVI and GAC were thoroughly mixed first and then transferred to the column reactors.

2.3.1. The impact of EBCT and flow rate on the performance of enhanced-ZVI and the synergy between enhanced-ZVI and biofiltration

To determine the impact of flow rate on the performance of enhanced-ZVI as well as the synergy between enhanced-ZVI and biofiltration, 10 experimental conditions were used in this study (groups 1–10 in Table 1 and Fig. S1). For biofilters, bioactive anthracite collected from a rapid sand filter in a local WTP was used as media. Following the operational conditions in the WTP, 6 min EBCT was used for the biofilters.

Due to the scale of the experiments, it was impractical to conduct the necessary measurements with water samples collected from a single filtration bed volume. Therefore, at each sampling point, 100-bed volumes of effluent was collected, mixed, and analysed as a single sample. For example, for the sampling point at 1,000-bed volumes, the effluent of each column was continually collected from 900 to 1,000-bed volumes. For the experiments with the enhanced-ZVI and biofiltration columns in series (group 4), the effluent of the biofiltration column was collected first, followed by the enhanced-ZVI column samples, to minimise any impacts of the sampling process on the operation of the down-stream biofiltration column, For example, for the 1,000-bed volumes sample in experimental group 4, the effluent of the biofilter was collected from 900 to 1,000-bed volumes, while the effluent of the corresponding up-stream enhanced-ZVI column was collected from 1,000 to 1,100-bed volumes. As later shown, this 100-bed volumes difference did not have a significant impact on the result and the validity of this procedure was verified by the reproducibility of the duplicated columns.

Feed water was prepared daily and the initial pH was adjusted to 7.0 with 0.5 N H_2SO_4 or 0.5 N NaOH. A ten channel peristaltic pump (Watson Marlow 323, Australia) was used to pump water into the columns and the different flow rates were regulated by using pumping tubings of different sizes.