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

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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.

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Keywords: Biofiltration; enhanced-zero valent iron; long-term; natural organic matter; drinking water treatment.

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 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].

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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.

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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 GA1000N) 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.

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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 Figure 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.

Table 1 Operational conditions for different experimental groups

Group number	Flow rate (mL/min)	Enhanced-ZVI column		Biofilter	
		Bed depth (cm)	EBCT (min)	Bed depth (cm)	EBCT (min)
1	1.39	1	0.36	n/a	n/a
2	1.39	1	0.36	16.6	6
3	0.28	1	1.8	n/a	n/a
4	0.28	1	1.8	3.3	6
5	0.28	1	1.8	n/a	n/a
6	1.39	5	1.8	n/a	n/a
7	1.39	5	1.8	n/a	n/a
8	0.28	5	9	n/a	n/a
9	0.28	5	9	n/a	n/a
10	0.28	n/a	n/a	3.3	6
11	0.28	1	1.8	3.3	6
12	0.28	1	1.8	3.3	6

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 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 (groups 2 and 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 downstream biofiltration column, For example, for the 1,000-bed volumes sample in experimental group 2, the effluent of the biofilter was collected from 900 to 1,000-bed volumes,

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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.

2.3.2 Regeneration of passivated enhanced-ZVI bed

After 30,000-bed volumes filtration, the enhanced-ZVI columns from the experimental groups 3, 4, and 5 were regenerated with 12 mL (per column) of 1 M HCl, 1 M HNO_3, or 0.5 M H_2SO_4, respectively. The results in Figure S3 showed that H_2SO_4 regeneration was most effective in restoring the NOM removal capacity, and thus was selected for subsequent experiments. A previous study reported that oxalic acid was effective in dissolving iron oxide through complexation [31]. To compare this alternative with the H_2SO_4 regeneration, two separate experimental groups were used (groups 11 and 12 in Table 1) for the long-term regeneration experiments. The passivated enhanced-ZVI bed was regenerated with either acid after each 10,000-bed volumes filtration stage. Totally, 40,000-bed volumes filtration and three regeneration steps were conducted for these two groups. For each regeneration, 12 mL freshly prepared 0.5 M H_2SO_4 (group 11) or oxalic acid (group 12) was circulated through the enhanced-ZVI bed at a flow rate of 0.28 mL/min for 100-bed volumes, during which the valve between enhanced-ZVI column and the biofilter was closed to prevent the potentially harmful effects of acid on the biofiltration biomass. After regeneration, the 'waste acid' was collected and normal feed water was pumped through the enhanced-ZVI bed at a flow rate of 1.4 mL/min to flush out the residual acids. When the effluent pH increased to 7.0 (after about 2 h flushing), the biofiltration unit was re-connected and the experimental setup was operated under the standard conditions described in Table 1.

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2.4 Analytical methods

2.4.1 DOC, UV_{254} and Specific UV absorption ($SUVA_{254}$)

Before analysis, all samples were filtered with 1.2 µm glassfibre filter (Cole-Palmer, USA), which reproducibly removes particulates but passes dissolved and colloidal NOM into the filtrate [32]. Although this is strictly speaking not directly equivalent to dissolved organic carbon only, for the sake of convenience the acronym DOC will be used throughout the study here forth. DOC was measured with a TOC-L total organic carbon analyser (Shimadzu, Japan) with a TNM-L total nitrogen analyser unit (Shimadzu, Japan)and ASI-L autosampler (Shimadzu, Japan). Since ferric ions can interfere with ultraviolet absorbance, hydroxylamine was used to eliminate the effect of ferric [33]. 5 mL filtered sample was mixed with 5 mL Milli-Q water and 1 mL buffered hydroxylamine solution (0.3 g hydroxylamine hydrochloride, 1.8 g sodium acetate trihydrate, and 2.1 mL glacial acetic acid with water to a final volume of 10 mL), and after 24 h, UV_{254} was measured in a quartz cuvette with a Varian Cary 50 Bio UV-Visible spectrophotometer. The reported absorbance values were corrected for the procedural dilution factor. $SUVA_{254}$ was calculated by multiplying UV_{254} by 100 and then dividing by the DOC (mg-C/L) to obtain units of L/mg-C·m.

2.4.2 Iron speciation

The sum of dissolved and colloid iron in water samples was measured according to the method of ISO 6332. Firstly, the following solutions were mixed: 4 mL filtered sample (1.2 µm glassfibre filter) + 4 mL Milli-Q water + 2 mL 1,10-phenantroline solution (1 g/L) + 2 mL pH buffer solution solution (75 g ammoniumacetate and 175 mL acetic acid were diluted to 250 mL). After 1 min, the absorbance of the mixture at 510 nm (Varian Cary 50 Bio UV-Visible spectrophotometer, Australia) was recorded for the calculation of ferrous concentration, and then 1-2 spatula tips of ascorbic acid were added into the mixture (to reduce ferric to ferrous ions), which was stored in a dark place. Finally, after 24 h, the absorbance of the mixture at 510 nm was recorded again to calculate the total

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iron concentration, and the difference between the total iron and the initial ferrous concentration is considered to be the initial ferric concentration of the sample.

The total iron in the regenerated H_2SO_4 or oxalic acid solution was measured with inductively coupled plasma optical emission spectrometry (ICP-OES, 7300DV, PerkinElmer).

2.4.3 Size exclusion chromatography

Size exclusion chromatography (SEC) was performed with a Shimadzu Prominence high performance liquid chromatography system with UV–Vis photodiode array detector (SPD-M20A) and organic carbon detector (OCD, Sievers 900 portable TOC analyser-Turbo, GE, USA). The chromatographic column TSK HW 50S (250 mm × 20 mm, 3000 theoretical plates, Tosoh, Japan) was supplied by DOCLabor Huber and run at 35°C. The mobile phase used was 25mM phosphate buffer solution (1.5 g/L $Na_2HPO_4 \cdot 2H_2O$, Sigma Aldrich, Australia; 2.9 g/L $NaH_2PO_4 \cdot 2H_2O$, Ajax Finechem, Australia) with a flow rate of 1.0 mL/min. Before use, the mobile phase was filtered with 0.45 μm nylon filters (PM Separations, Australia). The sample injection volume was 1000 μL, and the total analysis time was 100 min. For the OCD detector, 15% ammonium persulfate solution (APF 90150-01, GE, USA) was used as oxidiser with a flow rate of 4.0 μL/min, and 6 M phosphoric acid solution (APF 90310-01, GE, USA) was used to acidify the samples with a flow rate of 3.0 μL/min. The interpretation of the peaks followed the method described by Huber, et al. [34].

2.4.4 Calculation of DOC and UV_{254} removal efficiencies

The absolute DOC or UV_{254} values at all sampling points for both raw water and the effluent of a certain column were plotted with line-symbol charts, and the area under the curve was calculated using software Origin Pro.8.5. The removal efficiency was calculated by the following equation.

$$Removal\ efficieny = \frac{Area_{raw\ water} - Area_{treated\ water}}{Area_{raw\ water}} \times 100\% \quad \text{(Eq.1)}$$

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Since DOC or UV_{254} removal rate changed during the long-term operation of enhanced-ZVI columns (as shown in the following sections), the calculated removal efficiency was actually the average value during a certain period of filtration.

3. Results and discussion

3.1 The impact of EBCT and flow rate on the performance of enhanced-ZVI

As shown in Figure 1, both EBCT and flow rate affect the performance of enhanced-ZVI. Using a 1 cm enhanced-ZVI bed and 1.8 min EBCT, 3.36±0.36 mg/L DOC and 0.086±0.033 cm^{-1} UV_{254} could be removed after 100-bed volumes filtration (although the enhanced-ZVI bed in groups 3, 4 , and 5 were similar and operated under the same conditions, an unexpectedly high standard deviation was observed for the triplicated samples, which could not be properly explained by available information), while only 1.44±0.03 mg/L DOC and 0.025±0.007 cm^{-1} UV_{254} were removed with a shorter EBCT (0.36 min). Over the duration of the experiments, the performance difference was diminishing, although the enhanced-ZVI columns with 1.8 min EBCT always had better performance, especially for UV_{254} reduction. After 10,000-bed volumes filtration, the difference between the enhanced-ZVI columns with different EBCTs became insignificant, with only about 0.5 mg/L DOC and 0.010 cm^{-1} UV_{254} being removed, indicating the passivation of the enhanced-ZVI bed. For the 5 cm enhanced-ZVI beds, a similar trend was observed. After 100-bed volumes filtration, 4.25±0.18 mg/L DOC and 0.109±0.013 cm^{-1} UV_{254} were removed by enhanced-ZVI columns with EBCT of 1.8 min, while 5.52±0.57 mg/L DOC and 0.160±0.014 cm^{-1} UV_{254} reductions were achieved with a longer EBCT (9 min). The improved performance of the 9 min EBCT column extended until after 5,000-bed volumes filtration, beyond which no data was collected. In general, for the same enhanced-ZVI column length, the longer EBCT achieved a better performance (even when compared at the same total bed volumes, ie treated water volumes), which indicates that the contact and reaction time of the NOM in the electrolysis process and GAC adsorption is an important parameter for the removal performance [13, 14]. Furthermore, for

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columns with the same EBCT (1.8 min), the longer the enhanced-ZVI bed the better the removal performance. This might be due to the higher flow rate applied in the longer column to achieve the target EBCT, increasing the shear rate inside the packed columns and hence reducing the liquid boundary layer around the particles, which results in a higher reaction rate of the NOM with the GAC and/or ZVI particles [35]. Overall, when 0.36 or 1.8 min EBCT was applied, 7-14% DOC and 6-15% UV_{254} reduction could be achieved by enhanced-ZVI after 10,000 bed volumes filtration (Table S1 and Table S2).

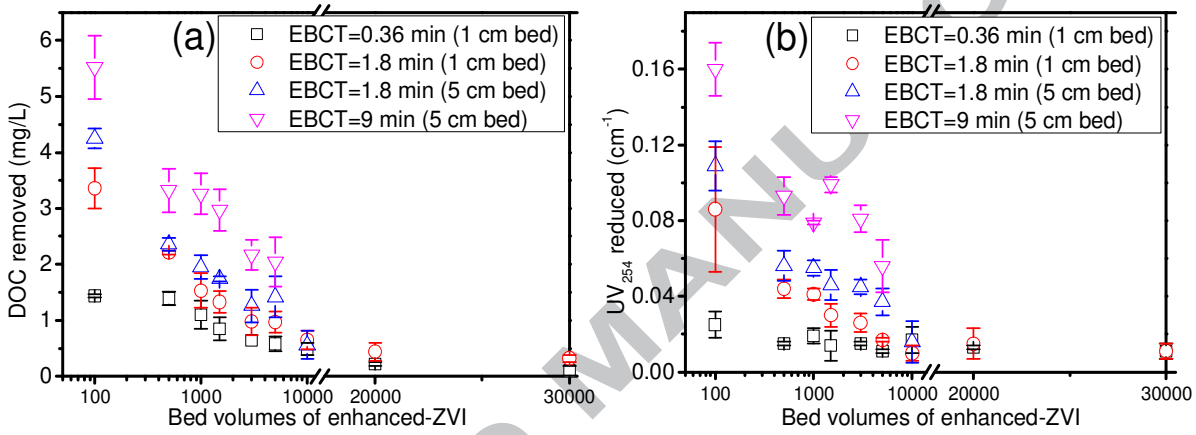

Figure 1 The removal of (a) DOC and (b) UV_{254} for enhanced-ZVI with different EBCTs (for EBCT=0.36 min (1 cm bed) the error bars represent the mean deviation of groups 1 and 2; for EBCT=1.8 min (1 cm bed) the error bars represent the mean deviation of groups 3, 4 and 5; for EBCT=1.8 min (5 cm bed) the error bars represent the mean deviation of groups 6 and 7; for EBCT=9 min (5 cm bed) the error bars represent the mean deviation of groups 8 and 9).

In the previous batch experiments of Liu, et al. [25], 61% DOC and 70% UV_{254} were removed when 400 mL water was treated with a 1 cm enhanced-ZVI bed for 24 h, which corresponded to 800-bed volumes filtration of an enhanced-ZVI column with 1.8 min EBCT. However, in this study, even for the column with 5 cm enhanced-ZVI bed and 1.8 min EBCT, only 29% DOC and 29% UV_{254} were removed over the first 1,000-bed volumes filtration (Table S1 and Table S2). Considering the significantly different operational modes, this discrepancy could be due to the following reasons. Firstly, in the previous batch experiments, a much higher flow rate was used (about 40 mL/min), which could promote the mass transfer and increase the reaction/adsorption rate of organic matter with the GAC or ZVI surface, while 0.28 or 1.39 mL/min flow rate was applied in this study.

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Secondly, in the previous study coagulation was found to play an important role in NOM removal [25]. Coagulation would only happen once a certain amount of negatively charged compounds were neutralized by the ferric or ferrous cations generated in the process [17, 36]. Thus, the relatively slower iron dissolution in this study (as shown in Figure 3) might not have been generating enough cations to trigger an effective coagulation and hence render coagulation insignificant under the flow-through operation mode. In addition, the longer contact time between NOM and ferric in feed water bottle under recirculation mode might promote coagulation as well.

3.2 The improvement of biofiltration by enhanced-ZVI

In order to determine the synergistic effect between enhanced-ZVI and biodegradation, a biofilter was added after the enhanced-ZVI columns for experimental group 4. As shown in Figure 2, when the EBCT of the enhanced-ZVI was 1.8 min, the subsequent biofiltration process consistently removed more DOC and UV_{254} than the biofiltration alone over the whole 30,000-bed volumes filtration period (p=0.039 for DOC removal and p=0.047 for UV_{254} removal).

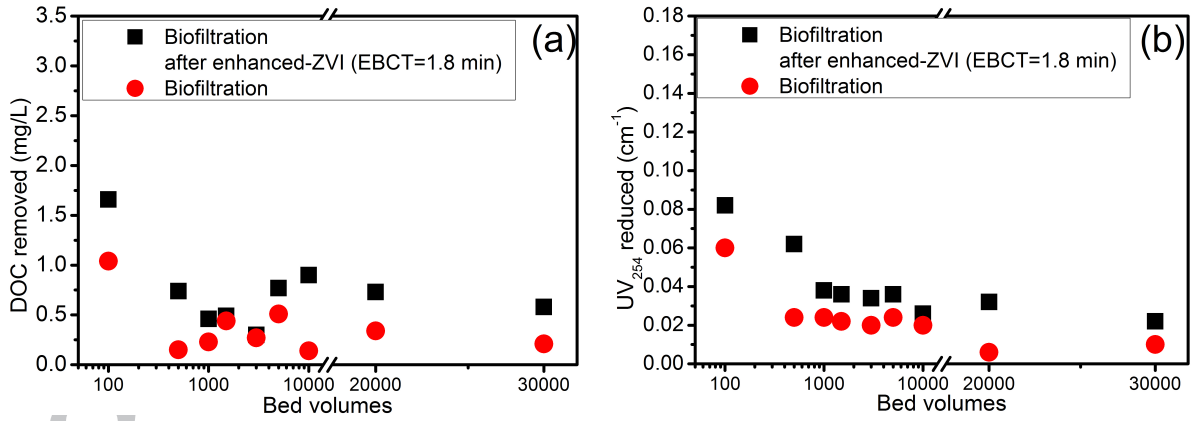

Figure 2 The removal of DOC and UV_{254} for combined biofiltration (after enhanced-ZVI) and biofiltration alone (for (a) and (b), the data was from groups 4 and 10).

Former studies have shown that oxidants produced during the enhanced-ZVI process could improve the biodegradability of organic matter to some extent, hence being beneficial for the subsequent bio-treatment [25-27]. As shown in the SEC-UV-OCD (Figure S4), after the treatment with 1.8 min EBCT enhanced-ZVI, new peaks appeared in the low molecular weight acids and low molecular

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weight neutrals fractions, indicating that a certain extent of oxidation occurred [37]. Smaller and more oxidised molecules are more amenable to biodegradation due to their easier transportation across the cell membranes and higher susceptibility to degradation by metabolic enzymes [38]. Thus, the better performance of the biofiltration following the 1.8 min EBCT enhanced-ZVI could be ascribed to the formation of more biodegradable compounds in the advanced oxidation reactions taking place during the enhanced-ZVI process.

Moreover, Figure 3 shows that when the effluent of the enhanced-ZVI column passes through the biofilter, the concentration of dissolved plus colloidal ferric ions decreases, implying the precipitation of ferric in the biofilter. With the aging of the precipitated iron, the initially formed amorphous ferric hydroxide may be changing to crystalline ferric oxide [39], both of which are reported to have NOM adsorption capacity [17, 40]. Similarly, the results from a control experiment (Figure S5) confirmed that in this study adsorption by the precipitated ferric likely contributed to the improved NOM removal of the biofilters.

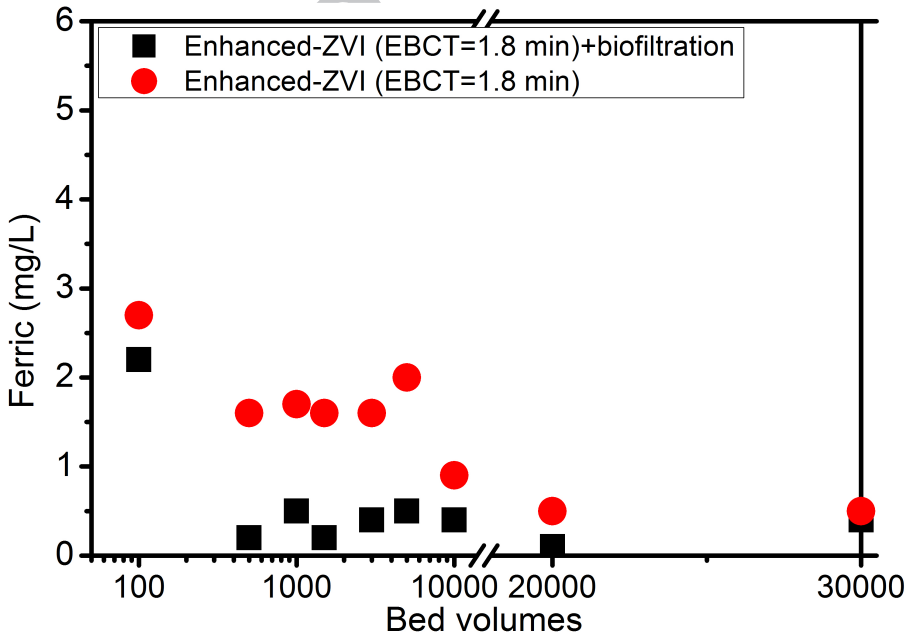

Figure 3 The change of ferric concentration after enhanced-ZVI and enhanced-ZVI+biofiltration (the data was from group 4)).

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3.3 Regeneration of passivated enhanced-ZVI bed

As mentioned above, after 10,000-bed volumes filtration, the enhanced-ZVI bed became passivated, and as a result, only limited DOC and UV_{254} removal was achieved at that point. Precipitation of iron oxidation products may also have resulted in the partial blocking of the filter bed and reduced contact of the liquid with the enhanced-ZVI bed particles [41]. Therefore, in order to restore the performance of the enhanced-ZVI column and reduce the bed clogging, regeneration of the enhanced-ZVI bed is necessary. As shown in Figure 4 and Figure S6, regeneration with 0.5 M H_2SO_4 solution after 10,000-bed volumes filtration could increase the removal performance of the enhanced-ZVI bed from 0.5 mg/L DOC and 0.02 cm^{-1} UV_{254} to 1.0 mg/L and 0.05 cm^{-1}, respectively. Former studies have shown that precipitation of iron oxidation products onto ZVI surface is the main reason for ZVI passivation [42, 43]. The dissolution of iron oxidation products in acids follows three principle reactions: protonation, reduction, and complexation producing ferric cations, ferrous cations and ferric or ferrous complexes, respectively [44]. Based on the experimental results in this study, it is not possible to determine which reactions are the dominant ones when H_2SO_4 was used to regenerate the passivated enhanced-ZVI bed, although it can be hypothesized that protonation should be the main mechanism. Complexation is likely to play a less important role as the oxalic acid, a stronger complexing agent forming chelate complexes with iron ions overall showed worse performance compared to sulfuric acid in the regeneration. Furthermore, the sulphur atom in sulphate is already fully oxidized (+VI), hence it is illogical to assume the reduction of ferrous and ferric iron in the regeneration step.

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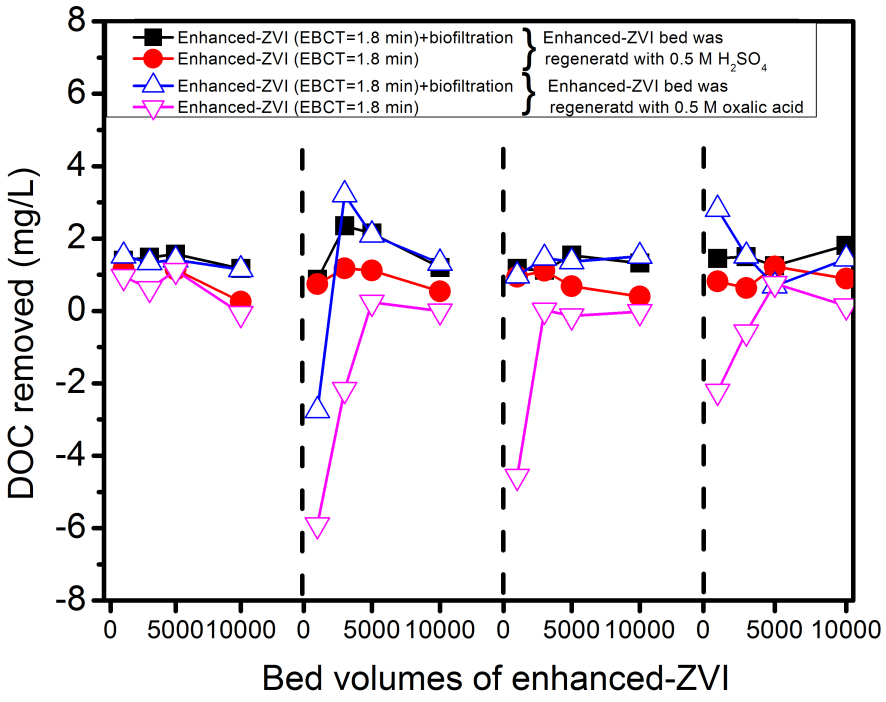

Figure 4 The long-term performance of enhanced-ZVI and enhanced-ZVI+biofiltration in removing DOC after regenerating enhanced-ZVI beds with 0.5 M H_2SO_4 or 0.5 M oxalic acid (0.5 M H_2SO_4 was used to regenerate enhanced-ZVI bed for group 11; for (b) 0.5 M oxalic acid was used to regenerate enhanced-ZVI bed for group 12; dashed lines indicate the regeneration of the enhanced-ZVI bed).

The regeneration benefits also the combined enhanced-ZVI+biofiltration process. Figure 2(a) shows that from 10,000 to 30,000-bed volumes, the DOC removal without regeneration decreases from 1.37 to 0.96 mg/L gradually. However, after regular regeneration of the enhanced-ZVI bed with 0.5 M H_2SO_4 solution (Figure 4), even at 40,000-bed volumes, about 1.5 mg/L DOC removal is still maintained. As discussed above, since adsorption by precipitated ferric contributed to the overall NOM removal in the biofilters, the continual precipitation of ferric into the biofilters after enhanced-ZVI regeneration (as shown in Figure S7) could provide additional adsorption sites for NOM, and therefore, extend the good performance of the biofilters as well.

When oxalic acid was used to regenerate the passivated enhanced-ZVI bed, no DOC removal could be observed in the enhanced-ZVI column for the first 3,000-bed volumes filtration following the

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regeneration, during which the DOC concentration of the effluent was even higher than that of the raw water, most likely due to the release of adsorbed or complexed oxalic acid from the enhanced-ZVI bed. However, the released DOC could be removed by the subsequent biofiltration, leading to the similar overall DOC removal to that achieved when H_2SO_4 was used for regeneration.

Although both acids could be used to regenerate the passivated enhanced-ZVI bed, for practical applications the use of H_2SO_4 would appear to be a better option. Firstly, when using oxalic acid, there is a potential risk that the released organic matter from the enhanced-ZVI bed could pass on to the subsequent treatment processes, and may increase the formation of disinfection by-products. Secondly, the price of oxalic acid is much higher than that of H_2SO_4 (www.alibaba.com).

3.4. Potential benefits and application

Although enhanced-ZVI has been reported to alleviate the passivation of ZVI grains through faster dissolution [12], some passivation still happened as discussed above after a certain operation period. However, acid could effectively remove the passivation layer, hence regenerate the enhanced-ZVI bed and recover the removal capacity of enhanced-ZVI for NOM. From this point-of-view, enhanced-ZVI with periodic regeneration could be an effective way to fully utilise ZVI. For practical application of this technology to drinking water treatment process, an additional coagulation step may still be needed to guarantee adequate removal of contaminants. Also, the potentially existed iron in the effluent of the biofilter could be further removed in the coagulation step, which would reduce the impact of iron on water quality. The dissolved iron in the acidic regeneration liquid could potentially be used as a supplementary coagulant as ferric salts may be commonly used as coagulants in drinking water treatment processes [17]. Therefore, a water treatment train incorporating the enhanced-ZVI process could be envisaged as shown in Figure 5.

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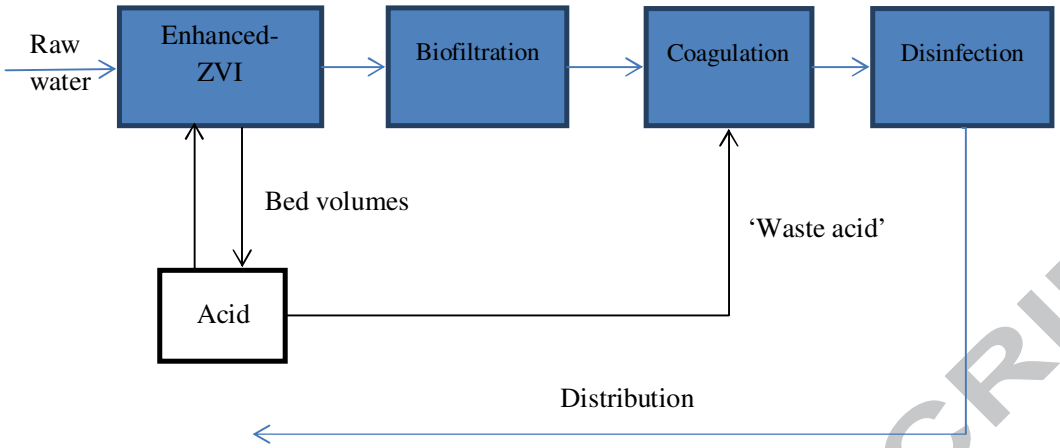

Figure 5 A proposed drinking water treatment train incorporating enhanced-ZVI.

To evaluate the performance of the enhanced-ZVI+biofiltration process in treating different source waters, as well as to test the feasibility of the proposed treatment train in Figure 5, a preliminary test with a low NOM content raw water (DOC and UV_{254} of 4.47±0.16 mg/L and 0.123±0.007 cm^{-1}) was conducted. As shown in Figure 6, the enhanced-ZVI+biofiltration process also removes NOM effectively for this relatively clean source water, with average DOC and UV_{254} removal efficiencies of 22% and 37% over 10,000-bed volumes filtration (Tables S1 and S2).

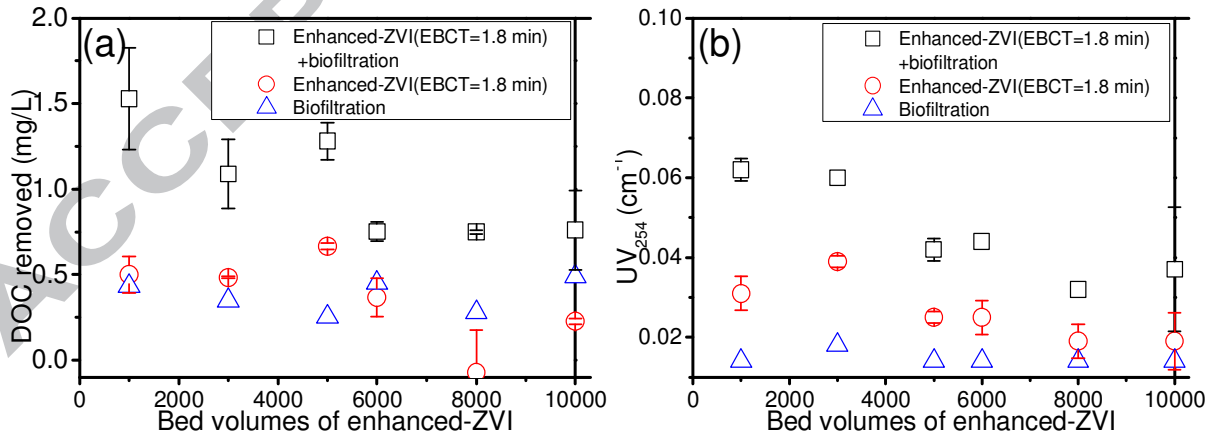

Figure 6 The performance of enhanced-ZVI and enhanced-ZVI+biofiltration in removing (a) DOC and (b) UV_{254} for source water with low organic matter content (error bars represent the mean deviation of duplicate experiments).

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In addition, compared with direct coagulation, the proposed water treatment train saves 60% coagulant dose by using 'waste acid' as a supplementary coagulant without compromising DOC removal, and at the same time, better UV_{254} removal could be achieved than with coagulation alone (Figure 7). Accordingly, more $SUVA_{254}$ reduction occurred (3.02±0.12 versus 2.47±0.15 L/mg-C·m). $SUVA_{254}$ is used to indicate the aromatic content of NOM and activated aromatic structures (aromatic sites substituted with oxygen- and nitrogen-containing functional groups, i.e., phenolics and aromatic amines), which are the primary sites of attack by chlorine or other oxidants [45, 46]. Therefore, NOM with high $SUVA_{254}$ is more likely to form disinfection by-products (DBPs) [47, 48]. For water utilities mainly concerned with the reduction of DBPs, the enhanced-ZVI based treatment train may have valuable advantages over the traditional coagulation process alone.

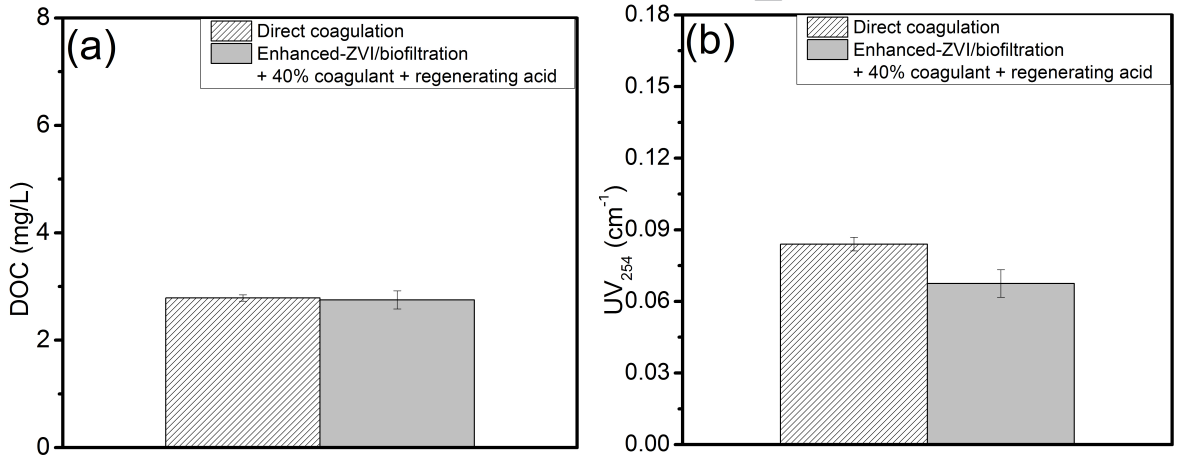

Figure 7 The comparison between direct coagulation and proposed water treatment process in removing (a) DOC and (b) UV_{254} (error bars represent the mean deviation of duplicate experiments).

In terms of practical application, the enhanced-ZVI reactors could be constructed into several parallel filters, each of them at a different ZVI-aging state to make sure enough water could still be produced during the regeneration of each filter. Importantly though, a detailed cost-benefit analysis should be conducted to determine if the new treatment train has clear overall economic advantages over the traditional coagulation process. As shown in Table S7, for the low NOM source water used in this study, the consumption of consumables (coagulant and lime) during the enhanced-ZVI

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related process was lower than that used in the traditional coagulation process (saving \$11/1000 m^3 drinking water treated), hence providing some lower operating costs. Also, the acid dose needed for regeneration was just based on an empirical assumption (see Text S2). An optimised acid dose might further reduce the total cost of the enhanced-ZVI process. Moreover, the adsorption of micropollutants by GAC [49] and the removal of pathogens [10] and subsequent saving in disinfectants may also add credits to the enhanced-ZVI incorporated treatment train. However, these benefits would need to be further investigated first, as this was outside of the scope of this present study.

4. Conclusion

Enhanced-ZVI is effective in removing NOM during drinking water treatment. Extending the EBCT and/or the filtration bed length could improve the overall performance of this process. In addition, compared with direct biofiltration, the combination of a 1.8 min EBCT enhanced-ZVI bed prior to a biofiltration process achieved better performance, likely due to the formation of biodegradable organic compounds during the enhanced-ZVI process and the precipitation of iron in the biofilter. However, after about 10,000-bed volumes filtration the enhanced-ZVI bed became passivated under all conditions used in this study. To regenerate the passivated enhanced-ZVI bed , fully utilised the available ZVI, and recover the NOM removal capacity, periodic regeneration of the enhanced-ZVI bed with H_2SO_4 is a good option, based on which a novel water treatment train was proposed and preliminary experimental results indicated that this new treatment process achieved better NOM and SUVA reduction than the traditional coagulation process alone.

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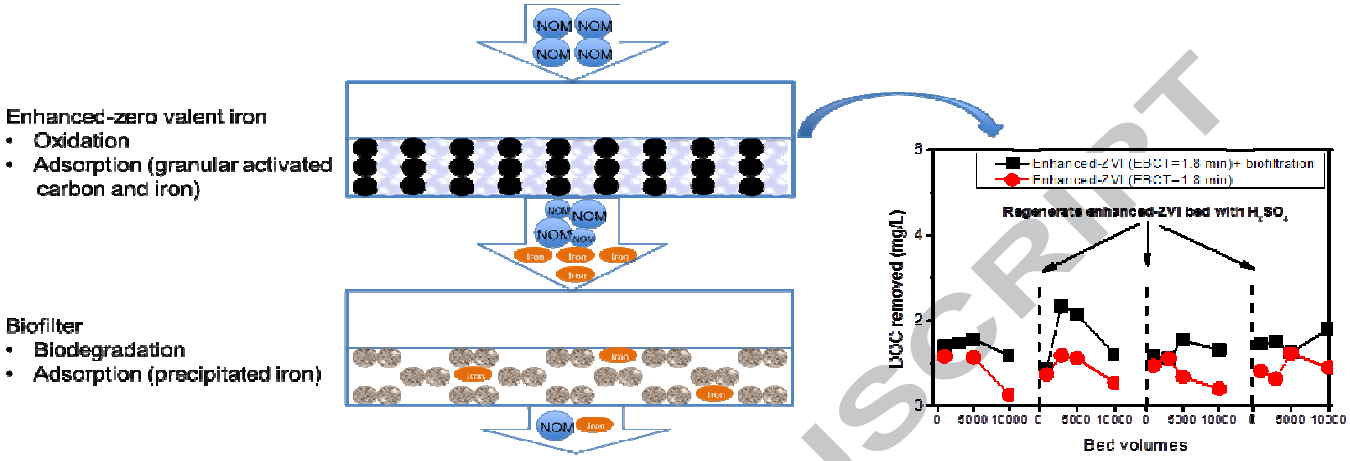
Graphical abstract



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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

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