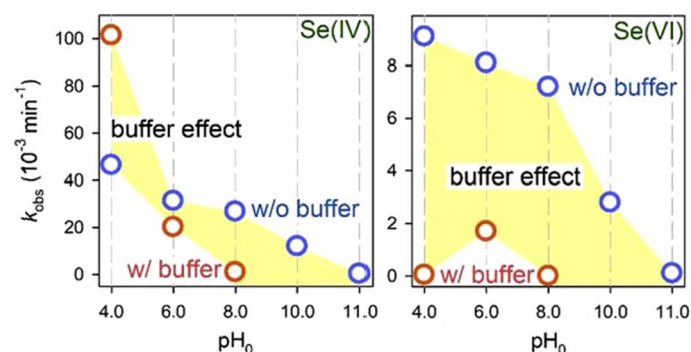# Unexpected effect of buffer solution on removal of selenite and selenate by zerovalent iron

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GRAPHICAL ABSTRACT

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ABSTRACT

Many studies used buffers to control pH during the reaction of ZVI, but the effect of buffer solutions received little attention. In this study, the effect of buffers on selenite (Se(IV)) and selenate (Se(VI)) removal by ZVI was systematically investigated. It was found that the addition of buffers can hinder the corrosion of ZVI, and then affect Se removal. Although the removal of Se(IV) by ZVI at initial pH (pH_0) 4.0 was accelerated due to the presence of buffer, less Se(IV) was removed in buffered systems than that in unbuffered systems at $pH_0 \geq 6.0$. Buffers also dramatically inhibited Se(VI) sequestration at pH_0 4.0–10.0. These effects were caused by the buffers instead of their influence on pH variation during the reaction, evidenced by the experiments that decoupled pH effect from overall buffer influences. The zeta potentials of the suspension in buffered systems were more negative than those in the unbuffered systems, implying the adsorption of buffer onto the ZVI surface. Accordingly, the effect of buffers observed in this study was mainly caused by its adsorption on ZVI surface, which may interfere the corrosion of ZVI as well as the adsorption of Se(IV)/Se(VI) on the surface of corroded ZVI, the first step of Se(IV)/Se(VI) sequestration by ZVI. These results suggest that it requires careful evaluation for the suitability of buffers in some reactions to study the kinetics and mechanisms.

1. Introduction

Zerovalent iron (ZVI) is one of the most frequently used materials in water treatment and groundwater remediation [1–3]. It is a strong reducing and cost-effective agent with environmentally benign nature, which has led to great interests in ZVI related research. One of the most frequently examined factors investigated in contaminants removal by ZVI is pH, and many studies revealed that the kinetics of contaminants removal by ZVI is a function of pH. In many studies, pH was controlled with buffer or pH controllers [4], while some studies did not control pH

during the reaction [5]. The most frequently used buffers in ZVI systems are HAc/NaAc and a group of Good's buffers [6], including 2-(*N*-morpholino)ethanesulfonic acid (MES), *N*-(2-hydroxyethyl)piperazine-*N′*-2-ethanesulfonic acid (HEPES), etc. In most of the studies, the effects of buffer on their reaction systems were not considered. Although some researchers have noticed that buffers may affect the performance of contaminants removal by ZVI, there are some contradictory results in the literature.

Several researchers reported that buffers have no significant effect on reactions of ZVI. Matheson and Tratnyek [7] used a bunch of buffers in their study, including MES, HEPES, tris(hydroxymethyl)aminomethane (Tris), 2-(*N*-cyclohexylamino)ethanesulfonic acid (CHES), and 3-(*N*-morpholino)propanesulfonic acid (MOPS). They showed that unbuffered systems gave dehalogenation rates consistent with buffered systems at similar pH values. Moreover, individual buffers did not cause different influence on carbon tetrachloride dehalogenation. Liu and Lowry [8] also found that the addition of 50 mM HEPES buffer did not affect the hydrogen evolution rate at pH 8.9, indicating that the buffer effect was very small. Nonetheless, some other studies have documented either positive or negative effects of buffers on ZVI performance. Xiong et al. reported that the application of a 0.05 M HEPES buffer increased the nitrate removal rate constants (k_{obs}) by 15 times compared to that without pH control [9]. Cheng et al. [10] compared the removal of nitrate by ZVI in the unbuffered system at initial pH (pH$_0$) 5.0 and that in buffered systems at pH$_0$ 5.0, 6.0, and 7.0 controlled with 0.05 M HAc/NaAc, 0.1 M MES, and 0.1 M HEPES, respectively. Although pH of all the three buffered systems rapidly increased to 8.8 within 20 min, nitrate reduction to ammonia in buffered systems was markedly faster than that in unbuffered one. The authors concluded that the delayed pH increased in the presence of buffer resulted in the delayed surface passivation and improved nitrate reaction. Zhang and Huang [11] also found the improving effect of selected Good's pH buffers on nitrate reduction by ZVI by reacting with ZVI to release ferrous ion (Fe(II)). A buffer was reported to be necessary for PCE reduction by ZVI because the buffer could maintain lower pH [12]. Lipczynska-Kochany et al. [13] also reported that HEPES promoted the reduction of carbon tetrachloride by ZVI, which may result from its buffering properties (pH 6.5) and from the iron-induced reduction of the sulphonic acid group to produce the S^{2-} ion, a strong reducing agent. However, the negative effect of buffers on contaminants removal by ZVI had also been observed. Liu et al. [14] reported that the rate constant of TCE dechlorination by ZVI decreased from 5.4×10^{-3} to $0.64–1.2 \times 10^{-3}$ L h^{-1} m^{-2} due to the presence of 50 mM HEPES buffer, although the final pH value (9.5) of the unbuffered system was higher than that of the buffered system (6.9–7.4). In summary, the effect of buffer is often ignored and the involved mechanisms are far from clear.

Se pollution is a worldwide problem and mainly originates from agricultural practices, manufacture processes, coal combustion and mining processes [15]. Se was found to be present in elevated concentrations in acid mine drainage which varied from 1 to 7000 μg L^{-1} [16]. The oxidized forms of Se, selenite (Se(IV)) and selenate (Se(VI)), are soluble, mobile and potentially toxic. Comparing to other methods for Se(IV) and Se(VI) removal, such as adsorption and electrochemical reduction, reductive removal of Se(IV) and Se(VI) by ZVI has been proved to be more effective [17,18]. Thus, Se(IV) and Se(VI) were selected as the probe contaminants to investigate the influence of several typical buffers (namely HAc/NaAc, MES, and HEPES) on contaminant removal by ZVI at different pH and the possible mechanisms involved were identified.

2. Materials and methods

2.1. Chemicals

All chemicals employed in this study were of analytical grade and

used as received. Sodium selenite (Na$_2$SeO$_3$, Se(IV)) and sodium selenate (Na$_2$SeO$_4$, Se(VI)) were supplied by the Xiya Reagent Company. Sodium chloride (NaCl), sodium hydroxide (NaOH), and HEPES were purchased from Qiangshun Chemical Reagent Company, Sinopharm Chemical Reagent Company, and Chinasun Specialty Products Company (China), respectively. Hydrochloric acid (HCl), acetic acid, sodium acetate and MES were obtained from Sinopharm Chemical Reagent Company (China). ZVI used in this study was bought from Aldrich Chemical Company (China) and it was the same as that in our previous study [19]. ZVI was not pretreated before added to the working solutions. Its specific surface area was 0.01 m^2/g, determined by BET method (Micrometrics ASAP 2020). Some other properties are shown in Fig. S1 (in Supplementary Materials).

2.2. Experimental procedures

Se(IV) and Se(VI) stock solutions were prepared by dissolving Na$_2$SeO$_3$ and Na$_2$SeO$_4$ in ultrapure Milli-Q water, respectively. The working solutions were freshly prepared by diluting the Se(IV) and Se(VI) stock solutions. The concentration of Se(IV) or Se(VI) in working solutions was 10 mg/L. NaCl of 0.01 M was added in all the experiments as a background electrolyte. For the experiments with buffer, 0.1 M HAc/NaAc, MES, and HEPES were employed to control the pH$_0$ at pH 4.0–5.0, 6.0, and 7.0, respectively. In the experiments without buffer, pH$_0$ of the working solutions was adjusted using dilute HCl and/or NaOH. The batch experiments were initiated by dosing 0.5 g ZVI into a 0.50 L working solution. All experiments were carried out in open air, and the solution was stirred at 300 rpm by a mechanical stirrer (D2004W, Shanghai Sile Instrument Co., Ltd), at 25 °C controlled by a water bath.

For the batch experiments differentiating the pH effect from the influence of buffers, several assays were designed. One was to determine the kinetics of Se(VI) sequestration by ZVI at pH$_0$ 4.0 or 6.0 and during the reaction, pH was maintained at pH 4.0 ± 0.2 or 6.0 ± 0.2 by adding 0.1 M and 0.01 M HCl when pH was elevating. The kinetic data were calibrated based on the volume of HCl solution added to the reactor. The other case was to examine the influence of buffers (0.05 M HEPES, 0.01 M HEPES, and 0.1 M HAc/NaAc) on Se(VI) or Se(IV) removal at pH$_0$ 8.0, where the change of pH was minor even there was no buffer. It should be noted that HEPES has buffering ability at pH 8.0 while HAc/NaAc has no buffering capacity at all. All experiments were carried out in duplicates for a given condition, and all points in the figures are averaged and error bars represent the standard deviation.

2.3. Analytical methods

Samples of the batch tests were collected at given time intervals using a 10-mL syringe and filtered immediately through a 0.22-μm membrane filter, then acidified for analysis. The concentrations of total soluble Se and Fe were determined with ICP-AES (Agilent, 720ES). The variation of pH in the system with time was monitored with a pH probe. The Fe(II) concentration was determined with the 1,10-phenanthroline colorimetric method using an UV/visible spectrophotometer (TU-1901, Purkinje General Instrument) at 510 nm [20].

After specific tests, the precipitates were collected on membrane filters (0.22 μm) and washed with deionized water, freeze-dried under vacuum, and then put into zipper bags before solid phase characterization. The Se *K*-edge and Fe *K*-edge X-Ray Absorption Fine Structure (XAFS) spectra of the samples were recorded at room temperature using a 4 channel Silicon Drift Detector (SDD) Bruker 5040 at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. Fe *K*-edge XAFS spectra were recorded in transmission mode while Se *K*-edge XAFS spectra were recorded in fluorescence mode. The samples were sealed using Kapton tape film and placed into aluminum sample holders when analyzing at beamline. Negligible changes in the lineshape and peak position of Fe and Se *K*-edge X-ray absorption near edge