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Ca(OH)$_2$ coated nanoscale zero-valent iron as a persulfate activator for the degradation of sulfamethazine in aqueous solution

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Abstract

In this work, a novel composite, Ca(OH)$_2$ coated nanoscale zero-valent iron (denoted as nZVI-Ca(OH)$_2$), was synthesized and used as an activator of persulfate for the degradation of sulfamethazine (SMT). The effects of sonication time during composite synthesis, pH, nZVI-Ca(OH)$_2$ dosage and typical groundwater components were investigated by batch experiments. Sonication time during the synthesis of the composite could affect the thickness of Ca(OH)$_2$ shell, however, it exerted no obvious
effect on SMT removal by nZVI-Ca(OH)$_2$ activated persulfate. The initial pH also had
insignificant effect on SMT removal in nZVI-Ca(OH)$_2$/persulfate system. There was
an optimum dosage of nZVI-Ca(OH)$_2$ composites for the activation of persulfate, and
the SMT removal efficiency decreased at both higher and lower dosage. The efficient
performance of nZVI-Ca(OH)$_2$ in synthetic groundwater was observed over a wide
pH range (3-9). However, with the presence of high concentration of HCO$_3^-$ or SO$_4^{2-}$,
SMT removal was inhibited greatly due to the quenching of radicals by HCO$_3^-$ or
SO$_4^{2-}$ and the buffering effect of HCO$_3^-$. In addition, the longevity of nZVI-Ca(OH)$_2$
was also investigated. Even after 30 days of aging in the air, Fe$^0$ could still be
detected in nZVI-Ca(OH)$_2$. Despite some loss of Fe$^0$, the composites kept high
reactivity for activation of persulfate for SMT removal, which might be attributed to
the excellent activation ability of amorphous iron oxides. To sum up, the Ca(OH)$_2$-
shell can protect the inner iron core and consequently prolong the lifetime of nZVI.

Keywords
Calcium hydroxide; Surface coating; Nanoscale zero-valent iron; Persulfate;
Sulfamethazine

Introduction

In recent decades, nanoscale zero-valent iron (nZVI) has been widely applied in
water treatment and soil/groundwater remediation processes [1]. Due to its high
reactivity, nZVI has been applied to remove various environmental contaminants, such as chlorinated organic compounds and heavy metals [2-4]. Apart from directly using nZVI to reduce pollutant, nZVI can also perform heterogeneous catalysis in advanced oxidation system which is more effective for the treatment of refractory organic pollutants [5, 6]. Recently, nZVI has been reported to be an efficient activator of persulfate for the treatment of various organic contaminants [7-9].

Since nZVI particles have large specific surface area and high reactivity [10], Fe⁰ can easily release Fe²⁺ in the presence of dissolved oxygen and persulfate (Eq. 1-2). And then those ferrous ions activate S₂O₈²⁻ to produce sulfate radicals and hydroxyl radicals which can react with various environmental pollutants (Eq. 3 and 4). Furthermore, Fe³⁺ generated from these reactions reacts with Fe⁰ sequentially to give a sustained supply of Fe²⁺ (Eq. 5) [11].

\[
\begin{align*}
2Fe^0 + O_2 + 2H_2O & \rightarrow 2Fe^{2+} + 4OH^- \\
Fe^0 + S_2O_8^{2-} & \rightarrow Fe^{2+} + 2SO_4^{2-} \\
S_2O_8^{2-} + Fe^{2+} & \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{2-} \\
SO_4^{2-} + H_2O & \rightarrow \cdot OH + SO_4^{2-} + H^+ \\
2Fe^{3+} + Fe^0 & \rightarrow 3Fe^{2+}
\end{align*}
\]

However, strong magnetic attraction and van der waals force between nZVI nanoparticles cause them to aggregate into larger size particles [12-18]. The increased size of these cluster result in a sharp decrease in surface area and poor dispersion of nZVI in aqueous solution [13,14]. Thus, to overcome the aggregation of nZVI,
researchers have attempted different stabilization methods for its effective environmental application [12,19,20]. Some supporting materials (e.g., clay, zeolite and biochar) and surface stabilizers (e.g., surfactant, synthetic or natural macromolecule or polyelectrolyte) were chosen to stabilize nZVI [12]. However, the issues concerning the effective release of reactive iron from the supporting material and the reactivity loss after surface modification by surface stabilizer adsorption were reported [15,21,22]. Besides the above supporters and organic stabilizers, one kind of releasable inorganic shell (Ca(OH)$_2$) on nZVI surface was developed [23]. It was reported that the Ca(OH)$_2$ coating layer can effectively enhance the stability and mobility of nZVI. Depending on the solubility of Ca(OH)$_2$, the Ca(OH)$_2$ coating on nZVI surface was supposed as a releasable shell during application for onsite remediation, thus, it would not result in a reactivity loss of nZVI.

Given that one drawback in nZVI+persulfate system is that the activation reactions usually proceed rapidly, resulting in self-quenching of radicals [24], it was presumed that the moderately soluble Ca(OH)$_2$ layer might control the persulfate activation rate by nZVI. Up to date, no studies have applied the Ca(OH)$_2$ coated nZVI (nZVI-Ca(OH)$_2$) for persulfate activation. In this study, nZVI-Ca(OH)$_2$ composites were synthesized for the activation of persulfate. Sulfamethazine (SMT) was chosen as a model contaminant, not only because it is one of frequently detected pharmaceutical compounds in aqueous environment, but the mechanism of SMT degradation by sulfate radicals has been well established in many studies [25,26]. The
effects of critical factors such as coating thickness, initial pH, nZVI-Ca(OH)$_2$ dosage and typical groundwater components were examined. Furthermore, aging experiments were carried out to study the transformation of nZVI-Ca(OH)$_2$ in air and its reactivity evolution with aging time.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade and used as received without further purification. Sulfamethazine (SMT, ≥99\%, w/w) was obtained from Sigma Chemical Company (Beijing, China). HCl, NaOH, CaCl$_2$, FeCl$_3$ • 6H$_2$O, NaCl, NaHCO$_3$, NaSO$_4$, NaBH$_4$, Na$_2$S$_2$O$_8$, ethanol and n-butanol were all purchased from Damao Chemical Reagent Factory (Tianjin, China). Synthetic groundwater was prepared according to our previous work [27], containing Na$^+$ (230 mg/L), Ca$^{2+}$ (32 mg/L), HCO$_3^-$ (183 mg/L), SO$_4^{2-}$ (96 mg/L) and Cl$^-$ (234 mg/L).

2.2. Preparation of Ca(OH)$_2$ coated nZVI composites

nZVI was prepared following the liquid phase reduction method as described in our previous study [15, 28]. In brief, with N$_2$ purging, 100 mL NaBH$_4$ solution (0.2 M) was added dropwise into 100 mL of a 0.05 M FeCl$_3$ solution with strong mechanical stirring. After that, the suspension was stirred for another 30 min. Then the synthesized nZVI particles were separated by a magnet, and washed three times.
with ethanol. After vacuum dried at 60°C for 8 h, the nZVI particles were collected and stored in sealing bags at 4°C in order to avoid oxidization before further modification.

A surface precipitation method was employed to prepare Ca(OH)$_2$ coated nZVI composites [23]. Firstly, CaCl$_2$ (0.025 M) and NaOH (0.05 M) solutions were prepared with ethanol. Then, 600 mg nZVI particles were added into 200 mL NaOH solution. After mixing in a sonication bath for 5 min, the CaCl$_2$ solution was quickly introduced into the nZVI suspension. After that, the mixture was placed in a sonication bath at 60 °C during the coating process. Then the Ca(OH)$_2$ coated nZVI particles were magnetically separated from Ca(OH)$_2$ particles. These separated particles were thoroughly washed with ethanol and vacuum dried. The synthesized nZVI- Ca(OH)$_2$ particles were stored at 4°C before use.

2.3. Batch experiments

2.3.1. SMT-removal experiments

The SMT removal experiments were conducted in 250 mL glass bottles in the dark. In a typical run, 250 mL SMT (0.1 mM) and 100 mL persulfate solutions were introduced in 650 mL water to achieve a SMT concentration of 0.025 mM and persulfate concentration of 1 mM. The reason for the use of higher concentration of SMT (~ 6.9 mg/L) than the realistic concentration (~μg/L) in natural waters was to facilitate the detection of SMT loss and examine the removal capacity of the oxidation
process. After adjusting the solution pH, the mixture was transferred to bottles (with 200 mL for each). Finally, nZVI-Ca(OH)$_2$ particles (10 mg) were added into the bottles, and immediately transferred to a vapour bathing constant temperature vibrator at 20.0 ± 0.2 °C for reaction up to 1 h. At predetermined time intervals, 1 mL of samples were extracted from the suspension and filtered through 0.22-μm membranes, and immediately quenched with 20 μL n-butanol (controlled experiments of SMT removal quenched with n-butanol are shown in Fig. S1). During the reaction period, the pH was monitored by using a pH meter (INESA, PHS-3C).

The concentration of SMT was measured using an Agilent 1200 high performance liquid chromatography (HPLC) with a C18 reversed-phase column (4.6 mm×150 mm). The mobile phase was acetonitrile and ultrapure water (35:65, v/v) with a flow rate of 1.0 mL/min. The temperature of column was 25 °C, and the sample injection volume was 20 μL. UV detection at a wavelength of 266 nm was used to quantify SMT [25]. The SMT removal efficiency (η, 100%) was calculated with the following equation:

\[
\eta = \frac{C_0 - C_r}{C_0} \times 100\%
\]

where $C_0$ (mg/L) is the initial concentration of SMT, $C_r$ (mg/L) is the residue SMT concentration.

Unless stated otherwise, all experiments in this study were performed in triplicate. The reported data took the mean values of each experimental value, and the error bars were presented as well.
2.3.2. Aging experiments

Aging of nZVI-Ca(OH)$_2$ particles was carried out in the air at room temperature. At certain intervals (5 d, 10 d, 20 d and 30 d), 100 mg of aged samples were collected, characterized and applied for the successive SMT removal experiments under the same condition as described above.

2.4. Characterization and analysis

The morphological images of nZVI-Ca(OH)$_2$ particles were recorded with a scanning electron microscope (SEM, JSM-6700). Energy dispersive X-ray spectroscopy (EDS) was coupled with SEM to examine the element on the particle surface. The mass ratio of Ca(OH)$_2$ in the composite of nZVI-Ca(OH)$_2$ was measured by analyzing the Fe and Ca concentration in acid-digestion solution of nZVI-Ca(OH)$_2$ with Atomic Absorption Spectrophotometer (AAS, PEAA700). The crystalline phases were identified with an X-ray diffractometer (XRD, Philips Electronic Instruments).

3. Results and discussions

3.1. Characterization of nZVI-Ca(OH)$_2$ composites

The SEM image of nZVI-Ca(OH)$_2$ composite is presented in Fig. 1a. nZVI-Ca(OH)$_2$ particles are in the size range of nanoscale with shape of sphere. These particles existed in the form of chain-like aggregates. It is noticeable that these nanoparticles were covered by a thin coating layer of several nanometer thickness,
which might be the Ca(OH)$_2$ shell. Further EDS elemental analysis of nZVI-Ca(OH)$_2$
shows a strong Fe peak and a weak Ca peak, indicating the existence of Ca on the
surface of composite (Fig. 1b).

The chemical components of nZVI-Ca(OH)$_2$ were characterized by the XRD
(Fig. 1c). As observed, there is a strong peak at 44.5° which should be assigned to Fe
(0) [29, 30], while no obvious peaks of Ca(OH)$_2$ were found. Similar phenomena
were also reported in other studies [23, 31], in which XRD was used to characterize
surface coated nZVI with Ca(OH)$_2$ and Al(OH)$_3$, and it was found that neither
Ca(OH)$_2$ nor Al(OH)$_3$ was observed. This might be due to their low concentrations or
low degree of crystallinity.

In order to figure out the Ca(OH)$_2$ content coated on nZVI, AAS was used to
determine the ratio of Fe and Ca after acid digestion of the nZVI-Ca(OH)$_2$
composites. Fig. 1d shows the content of Ca(OH)$_2$ coated on the nZVI particles under
different sonication time. It is clear that the sonication time did significantly affect the
coating thickness. The amount of Ca(OH)$_2$ was 1.31% of the total weight after 0.5 h
coating, which rose to 10.19% after 4 h coating. To verify the effect of Ca(OH)$_2$
coating on the mobility of nZVI particles, a simplified sand column test was carried
out and the results show that the Ca(OH)$_2$ coating did improve the transport of nZVI
particles in porous media (Fig. S2). This is consistent with the finding in literature
[23]. However, no obvious difference was observed for the nZVI-Ca(OH)$_2$ with
different amount of Ca(OH)$_2$ (data not shown). In view of the effect of sonication time
on coating thickness, it may influence the reactivity of the composite, which will be discussed in the following part. Overall, the results from SEM, EDS, XRD, AAS analysis and mobility test, collectively, suggested the successful synthesis of nZVI-Ca(OH)$_2$ composite.

3.2. Removal of SMT in nZVI-Ca(OH)$_2$/persulfate system

3.2.1. Effect of sonication time

As mentioned above, the sonication time during synthesis can affect the percentage of Ca(OH)$_2$ on nZVI-Ca(OH)$_2$ particle surface. It could possibly be a critical factor in SMT removal by nZVI-Ca(OH)$_2$ activated persulfate. Thus, effect of sonication time on SMT removal was investigated (Fig. 2). As observed, both removal efficiency and reaction rates of SMT were almost overlapped at different conditions. With the sonication time varied from 0.5 h to 4 h, SMT removal efficiency could reach about 100% after 1 h reaction time. Even though the sonication time affected the Ca(OH)$_2$ coating thickness on nZVI surface, it seems had little influence on SMT removal in persulfate system. Since 0.5 h sonication time was long enough to give an excellent performance in SMT removal for nZVI-Ca(OH)$_2$, it was selected for the preparation of nZVI-Ca(OH)$_2$ in the following study.

3.2.2. Effect of initial pH

SMT removal experiments were carried out at four different initial pH values, i.e. 3, 5, 7 and 9. As shown in Fig. 3a, the final removal efficiency as well as the removal
kinetics were much similar at initial pH from 3 to 9. In order to probe into the underlying mechanism, the changes of pH during reaction were monitored (Fig. 3b). Obviously, no matter at what initial pH value, the solution pH dropped dramatically (within 10 min) to around 3.5 and finally maintained in a very narrow pH range of 3.0 to 3.2. This should be the reason for the similar SMT removal under various pH conditions. The sharp pH change may be due to the release of H\(^+\) from the reaction of Fe\(^{3+}\) precipitation (Eq. 7) \cite{11}, the reaction between SO\(_4\)\(^2-\) and H\(_2\)O (Eq. 4) or the reaction of Fe\(^0\) with persulfate (Eq. 8) \cite{32}. Although the dissolution of the outside Ca(OH)\(_2\) layer would consume protons and then cause a rise in solution pH (Eq. 9), the mass ratio of Ca(OH)\(_2\) is extremely low (1.31%), the influence of Ca(OH)\(_2\) layer on solution pH should be negligible.

\[
Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \quad (7)
\]

\[
Fe^0 + S_2O_8^{2-} + 2H_2O \rightarrow Fe^{2+} + 2 \cdot OH + 2SO_4^{2-} + 2H^+ \quad (8)
\]

\[
Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \quad (9)
\]

3.2.3. Effect of nZVI-Ca(OH)\(_2\) dosage

The effect of nZVI-Ca(OH)\(_2\) dosage on SMT removal was investigated over a range of 10–200 mg/L and the results are illustrated in Fig. 4a. The removal efficiency was 90.31%, 100%, 93.14% and 77.03% with the composite dosage of 10, 50, 100 and 200 mg/L, respectively. With the increasing nZVI-Ca(OH)\(_2\) dosage from 10 to 50 mg/L, SMT removal efficiency was improved. This should be due to the generation of
more amounts of radicals with the existence of more iron ions in the solution. When the dose was further increased up to 200 mg/L, the removal efficiency dropped significantly to 77.03%. To find out the difference among the reaction systems with varying nZVI-Ca(OH)\(_2\) dosage, the pH changes with time in different systems were measured (Fig. 4b). The pH changes in systems of 10 and 50 mg/L showed a similar trend, i.e., a drastic drop in the first 5 min followed by a gradual slowdown. While the systems of 100 and 200 mg/L displayed a very different way with pH increase after the sharp decrease in the first 5 min. As discussed earlier, this sharp pH decrease was mainly attributed to the release of H\(^+\) during the reactions. While for the system of 100 and 200 mg/L, the following pH rise may be due to the dissolution of excessive nZVI-Ca(OH)\(_2\) (Eq. 9 and Eq. 10). The rapid consumption of H\(^+\) and release of OH\(^-\) could lead to an increase in solution pH.

\[
Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{10}
\]

With the increase of nZVI-Ca(OH)\(_2\) dosage from 50 mg/L to 200 mg/L, the dissolution of excessive catalyst would cause a rise of solution pH as well as a break out of ferrous ions. These ferrous ions could possibly have a scavenging effect on radicals (Eq. 11), and thus lowering the removal efficiency of SMT [33]. Moreover, the existence of dissolved iron could be just temporarily, under such pH condition, they could easily tend to get hydrolysis [34]. According to Eq. 3, 11 and 12, the lack of Fe\(^{2+}/Fe^{3+}\) would inhibit the formation of sulfate radicals, and then further resulted in a relative low removal efficiency of SMT [35].
\[ \text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \quad (11) \]

\[ \text{Fe}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{2+} + \text{S}_2\text{O}_8^- \quad (12) \]

### 3.2.4. Effect of typical groundwater components

In natural groundwater, there are many kinds of components that may have some effects on the contaminant removal process. In this study, experiments were carried out in synthetic groundwater under different pH conditions. As demonstrated in Fig. 5a, SMT was removed efficiently at all pH values. However, the reaction rate at pH 9 was much slower than that at other pH values. Specifically, the removal efficiency of SMT at pH 9 was just approximately 15.19% after reaction for 5 min, while around 48.92%, 57.18% and 52.62% were obtained at pH 3, pH 5 and pH 7, respectively. The evolution of pH at different initial pH values was monitored (Fig. 5b). Different from the rapid pH drop in pure water condition, much less changes of pH were observed during the reaction in synthetic groundwater. This should be result from the good buffer capacity of HCO$_3^-$. Under alkaline condition, nZVI-Ca(OH)$_2$ could hardly be dissolved and also it would be favorable for the precipitation of Fe$^{2+}$/Fe$^{3+}$, thus, there would be less free iron ions existed in the system, resulting in the less activation of persulfate [36]. Pang et al. [36] reported that ultrasound irradiation could contribute to acceleration of ZVI corrosion and removal of passive films, resulting in high efficiency in peroxymonosulfate activation. Thus, the precipitation of Fe$^{2+}$/Fe$^{3+}$ could possibly be one reason for the slower removal rate of SMT at pH 9. Besides, bicarbonate can be a scavenger of sulfate radicals (Eq. 13). Although other radicals...
(i.e. CO$_{\cdot}$) are generated from the scavenging reaction, they are quite unreactive compared to S$O_{\cdot}$ toward most organic substrates in aqueous condition [37].

$$SO^{-}_{\cdot} + HCO_{\cdot} \rightarrow H^{\cdot} + S$O_{\cdot}^{2-} + CO_{\cdot}^{-}$$  \hspace{1cm} (13)

In addition, previous studies reported that S$O_{\cdot}^{2-}$ could also exhibit negative effect on the radical-based reactions [38]. S$O_{\cdot}^{2-}$ ions can form bonding with Fe$^{2+}$ and Fe$^{3+}$, producing complexes of FeS$O_{4}$ and Fe$_{2}$S$O_{4}$.$_{3}$. These complex reactions reduced the concentration of free iron ions in the solution for activation of persulfate, thus inhibiting the removal of SMT.

To further identify the role of each individual component, SMT removal in the presence of single ions (i.e., HCO$_{3-}$, S$O_{\cdot}^{2-}$, Cl$^{-}$ and Ca$^{2+}$) was examined respectively with different concentration. As shown in Fig. 6a, all these ions with a lower concentration (1 mmol/L) could barely affect the nZVI-Ca(OH)$_{2}$ performance on SMT removal. Only in the case of HCO$_{3-}$, a slower removal rate was observed. However, after 60 min reaction time, the removal efficiency reached 100% in all reaction systems. When increasing the concentration to 10 mmol/L, the groundwater components showed very different impacts on the removal performance (Fig. 6b). Ca$^{2+}$ and Cl$^{-}$ had insignificant impact on SMT removal, while the presence of HCO$_{3-}$ or S$O_{\cdot}^{2-}$ substantially decreased the SMT removal. The results verified the previous assumption that the drop of SMT removal efficiency in synthetic groundwater was mainly due to the effect of HCO$_{3-}$ and S$O_{\cdot}^{2-}$.

To sum up, the effect of these typical groundwater components at low
concentration were negligible, and even at higher concentration Cl\(^{-}\) and Ca\(^{2+}\) had little
effect on SMT removal. While HCO\(_3^{-}\) or SO\(_4^{2-}\) with higher concentration could inhibit
the degradation efficiency of SMT and the inhibiting effect of HCO\(_3^{-}\) was more
pronounced than the other ions at the same concentration.

3.2.5 Effect of particle aging

To further verify whether the Ca(OH)\(_2\) coating could alleviate the surface
passivation of nZVI caused by corrosion, the nZVI-Ca(OH)\(_2\) particles were aged in
the open air for different time. Then, the removal of SMT by the aged nZVI-Ca(OH)\(_2\)
activated PS were tested for comparison (Fig. 7a). The results show that, after aging
up to 30 days, nZVI-Ca(OH)\(_2\) still kept a high capacity of PS activation for the SMT
degradation.

The reactivity of nZVI-Ca(OH)\(_2\) was associated with its surface composition,
XRD analysis was then conducted to identify the composition evolution and
crystalline change of nZVI-Ca(OH)\(_2\) with aging time. Fig. 7b shows the XRD patterns
of fresh and different aged nZVI-Ca(OH)\(_2\). It is noticeable that the peak of Fe\(^0\) at
44.5\(^{\circ}\) became weaker with aging time. But the Fe\(^0\) peak can still be detected even
after 30 days of aging, indicating the existence of Fe\(^0\) on the surface of particles after
30 days. Our previous study on Fe/Ni bimetal nanoparticles aging process reported
that the Fe\(^0\) peak disappeared in just 5 days [29]. In comparison, it was clear that
coating nZVI with Ca(OH)\(_2\) did prolong its lifetime due to the protection of Ca(OH)\(_2\)
outer shell. For the aged samples, peaks assigned to iron oxide were not detected, which is quite different from the reported XRD patterns of aged nZVI. Typical aging products of nZVI in oxic condition are goethite, maghemite, magnetite and lepidocrocite [39]. Whilst, there were no iron oxides detected in the aging samples of nZVI-Ca(OH)$_2$, which manifests that the corrosion of nZVI in nZVI-Ca(OH)$_2$ was not significant and iron oxides were not existing in crystalline phrase. Even though there were some loss of Fe$^0$ with aging, SMT removal efficiency was barely influenced. This could possibly be attributed to the good persulfate activation capacity of amorphous iron oxides [40]. Since both Fe$^0$ and iron oxides can activate persulfate, fresh and aged nZVI-Ca(OH)$_2$ samples showed similar performance in the process of SMT degradation.

4. Conclusion

In this study, a thin Ca(OH)$_2$ shell was successfully coated on the surface of nZVI particles. The thickness of Ca(OH)$_2$ is related to sonication time during synthesis, the longer sonication time the more Ca(OH)$_2$ coated. Then, nZVI-Ca(OH)$_2$ composites were utilized as an activator of persulfate to remove SMT. The effects of sonication time, pH, nZVI-Ca(OH)$_2$ dosage and typical groundwater components were investigated. The following conclusions were made:

- The sonication time and initial pH had little effect on SMT removal by nZVI-Ca(OH)$_2$/persulfate system, while nZVI-Ca(OH)$_2$ dosage affected the
removal efficiency of SMT greatly. There was an optimum dosage of nZVI-Ca(OH)$_{2}$, at higher or lower dosage, the SMT removal was decreased.

- nZVI-Ca(OH)$_{2}$ showed different performance in synthetic groundwater and pure water over the pH range of 3-9. The effect of typical groundwater components (Ca$^{2+}$, Cl$^{-}$, HCO$_{3}^{-}$ and SO$_{4}^{2-}$) were examined respectively and it was found that the groundwater ions at low concentration showed negligible influence on SMT removal, but HCO$_{3}^{-}$ and SO$_{4}^{2-}$ at high concentration could inhibit the SMT removal in a large degree.

- Effect of aging time on the reactivity of nZVI-Ca(OH)$_{2}$ was investigated, and it was found that the particles kept its reactivity even after 30 days of aging. This suggests that coating nZVI with Ca(OH)$_{2}$ did prolong the lifetime of nZVI.

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References

[1] X. Guan, Y. Sun, H. Qin, J. Li, I.M. Lo, D. He, H. Dong, The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: the development in zero-valent iron technology in


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different surface coatings and water chemistry, Journal of Colloid and Interface


[27] Y. Xie, H. Dong, G. Zeng, L. Zhang, Y. Cheng, K. Hou, Z. Jiang, C. Zhang, J. Deng, The comparison of Se(IV) and Se(VI) sequestration by nanoscale zero-valent


[40] Y.H. Jo, S.H. Do, S.H. Kong, Persulfate activation by iron oxide-immobilized
MnO$_2$ composite: Identification of iron oxide and the optimum pH for degradations,


Fig. 1. (a) SEM image of nZVI-Ca(OH)$_2$ particles (sonication time: 0.5 h), (b) the corresponding EDS (sonication time: 0.5 h), (c) XRD analysis of nZVI-Ca(OH)$_2$ particles (sonication time: 0.5 h), and (d) the content of Ca(OH)$_2$ coated on the nZVI particles under different sonication time
Fig. 2. Effect of sonication time during synthesis of nZVI-Ca(OH)$_2$ on SMT removal by nZVI-Ca(OH)$_2$ activated PS (initial pH = 5; [SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-Ca(OH)$_2$] = 50 mg/L)
Fig. 3. (a) Effect of initial pH on the removal of SMT by nZVI-Ca(OH)$_2$ and (b) pH changes with time ([SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-Ca(OH)$_2$] = 50 mg/L)
Fig. 4. (a) Effect of nZVI-Ca(OH)\textsubscript{2} dosage on the removal of SMT and (b) pH changes with time in different nZVI-Ca(OH)\textsubscript{2} dosage systems (initial pH = 5; [SMT] = 0.025 mM; [PS] = 1 mM)
Fig. 5. (a) SMT removal by nZVI-Ca(OH)$_2$ in synthetic groundwater under different pH, and (b) pH changes with time in synthetic groundwater ([SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-Ca(OH)$_2$] = 50 mg/L)
Fig. 6. Effect of typical groundwater components of different concentrations (a: 1 mmol/L; b: 10 mmol/L) on the removal of SMT by nZVI-Ca(OH)\textsubscript{2} activated PS (initial pH = 5; [SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-Ca(OH)\textsubscript{2}] = 50 mg/L )
Fig. 7. (a) SMT removal by the aged nZVI-Ca(OH)$_2$ activated PS and (b) XRD patterns of aged particles (initial pH = 5; [SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-Ca(OH)$_2$] = 50 mg/L)
- nZVI-Ca(OH)$_2$ was used as an activator of PS for the degradation of SMT
- There was an optimum dosage of nZVI-Ca(OH)$_2$ for the activation of PS to degrade SMT
- nZVI-Ca(OH)$_2$ was efficient for PS activation in synthetic groundwater at pH 3-9
- The presence of high concentration of HCO$_3^-$ or SO$_4^{2-}$ greatly inhibited SMT removal
- The Ca(OH)$_2$ shell can protect the inner iron core from oxidation in the air.