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1 **Ca(OH)₂ coated nanoscale zero-valent iron as a persulfate activator**
2 **for the degradation of sulfamethazine in aqueous solution**

3

4 **Junmin Deng^{1,2,3}, Haoran Dong^{1,2,*}, Long Li^{1,2}, Yaoyao Wang^{1,2}, Qin Ning^{1,2}, Bin**
5 **Wang^{1,2}, Guangming Zeng^{1,2}**

6 1. College of Environmental Science and Engineering, Hunan University,
7 Changsha, Hunan 410082, China.

8 2. Key Laboratory of Environmental Biology and Pollution Control (Hunan
9 University), Ministry of Education, Changsha, Hunan 410082, China

10 3. University of Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS,
11 ISCR-UMR6226, F-35000 Rennes, France

12 *Corresponding author. E-mail: dongh@hnu.edu.cn; Tel: (+86)-0731-88822778

13

14 **Abstract**

15 In this work, a novel composite, Ca(OH)₂ coated nanoscale zero-valent iron (denoted
16 as nZVI-Ca(OH)₂), was synthesized and used as an activator of persulfate for the
17 degradation of sulfamethazine (SMT). The effects of sonication time during
18 composite synthesis, pH, nZVI-Ca(OH)₂ dosage and typical groundwater components
19 were investigated by batch experiments. Sonication time during the synthesis of the
20 composite could affect the thickness of Ca(OH)₂ shell, however, it exerted no obvious

21 effect on SMT removal by nZVI-Ca(OH)₂ activated persulfate. The initial pH also had
22 insignificant effect on SMT removal in nZVI-Ca(OH)₂/persulfate system. There was
23 an optimum dosage of nZVI-Ca(OH)₂ composites for the activation of persulfate, and
24 the SMT removal efficiency decreased at both higher and lower dosage. The efficient
25 performance of nZVI-Ca(OH)₂ in synthetic groundwater was observed over a wide
26 pH range (3-9). However, with the presence of high concentration of HCO₃⁻ or SO₄²⁻,
27 SMT removal was inhibited greatly due to the quenching of radicals by HCO₃⁻ or
28 SO₄²⁻ and the buffering effect of HCO₃⁻. In addition, the longevity of nZVI-Ca(OH)₂
29 was also investigated. Even after 30 days of aging in the air, Fe⁰ could still be
30 detected in nZVI-Ca(OH)₂. Despite some loss of Fe⁰, the composites kept high
31 reactivity for activation of persulfate for SMT removal, which might be attributed to
32 the excellent activation ability of amorphous iron oxides. To sum up, the Ca(OH)₂-
33 shell can protect the inner iron core and consequently prolong the lifetime of nZVI.

34 **Keywords**

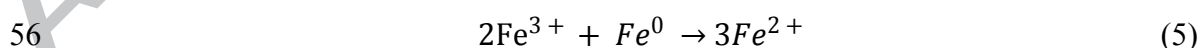
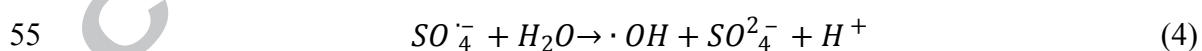
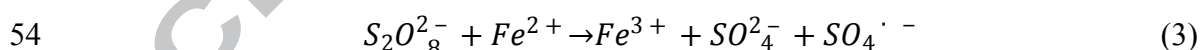
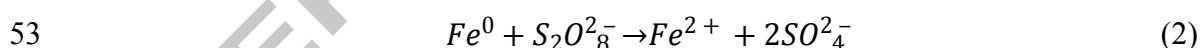
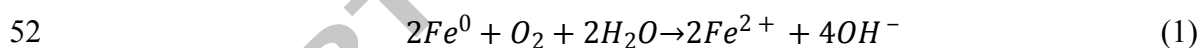
35 Calcium hydroxide; Surface coating; Nanoscale zero-valent iron; Persulfate;
36 Sulfamethazine

37 **Introduction**

38 In recent decades, nanoscale zero-valent iron (nZVI) has been widely applied in
39 water treatment and soil/groundwater remediation processes [1]. Due to its high

40 reactivity, nZVI has been applied to remove various environmental contaminants,
 41 such as chlorinated organic compounds and heavy metals [2-4]. Apart from directly
 42 using nZVI to reduce pollutant, nZVI can also perform heterogeneous catalysis in
 43 advanced oxidation system which is more effective for the treatment of refractory
 44 organic pollutants [5, 6]. Recently, nZVI has been reported to be an efficient activator
 45 of persulfate for the treatment of various organic contaminants [7-9].

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



57 However, strong magnetic attraction and van der Waals force between nZVI
 58 nanoparticles cause them to aggregate into larger size particles [12-18]. The increased
 59 size of these clusters results in a sharp decrease in surface area and poor dispersion of
 60 nZVI in aqueous solution [13,14]. Thus, to overcome the aggregation of nZVI,

61 researchers have attempted different stabilization methods for its effective
62 environmental application [12,19,20]. Some supporting materials (e.g., clay, zeolite
63 and biochar) and surface stabilizers (e.g., surfactant, synthetic or natural
64 macromolecule or polyelectrolyte) were chosen to stabilize nZVI [12]. However, the
65 issues concerning the effective release of reactive iron from the supporting material
66 and the reactivity loss after surface modification by surface stabilizer adsorption were
67 reported [15,21,22]. Besides the above supporters and organic stabilizers, one kind of
68 releasable inorganic shell ($\text{Ca}(\text{OH})_2$) on nZVI surface was developed [23]. It was
69 reported that the $\text{Ca}(\text{OH})_2$ coating layer can effectively enhance the stability and
70 mobility of nZVI. Depending on the solubility of $\text{Ca}(\text{OH})_2$, the $\text{Ca}(\text{OH})_2$ coating on
71 nZVI surface was supposed as a releasable shell during application for onsite
72 remediation, thus, it would not result in a reactivity loss of nZVI.

73 Given that one drawback in nZVI+persulfate system is that the activation
74 reactions usually proceed rapidly, resulting in self-quenching of radicals [24], it was
75 presumed that the moderately soluble $\text{Ca}(\text{OH})_2$ layer might control the persulfate
76 activation rate by nZVI. Up to date, no studies have applied the $\text{Ca}(\text{OH})_2$ coated nZVI
77 ($\text{nZVI-Ca}(\text{OH})_2$) for persulfate activation. In this study, $\text{nZVI-Ca}(\text{OH})_2$ composites
78 were synthesized for the activation of persulfate. Sulfamethazine (SMT) was chosen
79 as a model contaminant, not only because it is one of frequently detected
80 pharmaceutical compounds in aqueous environment, but the mechanism of SMT
81 degradation by sulfate radicals has been well established in many studies [25,26]. The

82 effects of critical factors such as coating thickness, initial pH, nZVI-Ca(OH)₂ dosage
83 and typical groundwater components were examined. Furthermore, aging experiments
84 were carried out to study the transformation of nZVI-Ca(OH)₂ in air and its reactivity
85 evolution with aging time.

86 2. Materials and methods

87 2.1. Chemicals

88 All chemicals used in this study were of analytical grade and used as received
89 without further purification. Sulfamethazine (SMT, ≥99%, w/w) was obtained from
90 Sigma Chemical Company (Beijing, China). HCl, NaOH, CaCl₂, FeCl₃ • 6H₂O, NaCl,
91 NaHCO₃, NaSO₄, NaBH₄, Na₂S₂O₈, ethanol and n-butanol were all purchased from
92 Damao Chemical Reagent Factory (Tianjin, China). Synthetic groundwater was
93 prepared according to our previous work [27], containing Na⁺ (230 mg/L), Ca²⁺ (32
94 mg/L), HCO₃⁻ (183 mg/L), SO₄²⁻ (96 mg/L) and Cl⁻ (234 mg/L).

95 2.2. Preparation of Ca(OH)₂ coated nZVI composites

96 nZVI was prepared following the liquid phase reduction method as described in
97 our previous study [15, 28]. In brief, with N₂ purging, 100 mL NaBH₄ solution (0.2
98 M) was added dropwise into 100 mL of a 0.05 M FeCl₃ solution with strong
99 mechanical stirring. After that, the suspension was stirred for another 30 min. Then
100 the synthesized nZVI particles were separated by a magnet, and washed three times

101 with ethanol. After vacuum dried at 60°C for 8 h, the nZVI particles were collected
102 and stored in sealing bags at 4°C in order to avoid oxidization before further
103 modification.

104 A surface precipitation method was employed to prepare Ca(OH)₂ coated nZVI
105 composites [23]. Firstly, CaCl₂ (0.025 M) and NaOH (0.05 M) solutions were
106 prepared with ethanol. Then, 600 mg nZVI particles were added into 200 mL NaOH
107 solution. After mixing in a sonication bath for 5 min, the CaCl₂ solution was quickly
108 introduced into the nZVI suspension. After that, the mixture was placed in a
109 sonication bath at 60 °C during the coating process. Then the Ca(OH)₂ coated nZVI
110 particles were magnetically separated from Ca(OH)₂ particles. These separated
111 particles were thoroughly washed with ethanol and vacuum dried. The synthesized
112 nZVI- Ca(OH)₂ particles were stored at 4°C before use.

113 **2.3. Batch experiments**

114 **2.3.1. SMT-removal experiments**

115 The SMT removal experiments were conducted in 250 mL glass bottles in the
116 dark. In a typical run, 250 mL SMT (0.1 mM) and 100 mL persulfate solutions were
117 introduced in 650 mL water to achieve a SMT concentration of 0.025 mM and
118 persulfate concentration of 1 mM. The reason for the use of higher concentration of
119 SMT (~ 6.9 mg/L) than the realistic concentration (~μg/L) in natural waters was to
120 facilitate the detection of SMT loss and examine the removal capacity of the oxidation

121 process. After adjusting the solution pH, the mixture was transferred to bottles (with
122 200 mL for each). Finally, nZVI-Ca(OH)₂ particles (10 mg) were added into the
123 bottles, and immediately transferred to a vapour bathing constant temperature vibrator
124 at 20.0 ± 0.2 °C for reaction up to 1 h. At predetermined time intervals, 1 mL of
125 samples were extracted from the suspension and filtered through 0.22-µm membranes,
126 and immediately quenched with 20 µL n-butanol (controlled experiments of SMT
127 removal quenched with n-butanol are shown in Fig. S1). During the reaction period,
128 the pH was monitored by using a pH meter (INESA, PHS-3C).

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

$$136 \quad \eta = \frac{C_0 - C_r}{C_0} \times 100\% \quad (6)$$

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

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

142 2.3.2. Aging experiments

143 Aging of nZVI-Ca(OH)₂ particles was carried out in the air at room temperature.
144 At certain intervals (5 d, 10 d, 20 d and 30 d), 100 mg of aged samples were collected,
145 characterized and applied for the successive SMT removal experiments under the
146 same condition as described above.

147 2.4. Characterization and analysis

148 The morphological images of nZVI-Ca(OH)₂ particles were recorded with a
149 scanning electron microscope (SEM, JSM-6700). Energy dispersive X-ray
150 spectroscopy (EDS) was coupled with SEM to examine the element on the particle
151 surface. The mass ratio of Ca(OH)₂ in the composite of nZVI-Ca(OH)₂ was measured
152 by analyzing the Fe and Ca concentration in acid-digestion solution of nZVI-Ca(OH)₂
153 with Atomic Absorption Spectrophotometer (AAS, PEAA700). The crystalline phases
154 were identified with an X-ray diffractometer (XRD, Philips Electronic Instruments).

155 3. Results and discussions

156 3.1. Characterization of nZVI-Ca(OH)₂ composites

157 The SEM image of nZVI-Ca(OH)₂ composite is presented in Fig. 1a. nZVI-
158 Ca(OH)₂ particles are in the size range of nanoscale with shape of sphere. These
159 particles existed in the form of chain-like aggregates. It is noticeable that these
160 nanoparticles were covered by a thin coating layer of several nanometer thickness,

161 which might be the $\text{Ca}(\text{OH})_2$ shell. Further EDS elemental analysis of $\text{nZVI-Ca}(\text{OH})_2$
162 shows a strong Fe peak and a weak Ca peak, indicating the existence of Ca on the
163 surface of composite (Fig. 1b).

164 The chemical components of $\text{nZVI-Ca}(\text{OH})_2$ were characterized by the XRD
165 (Fig. 1c). As observed, there is a strong peak at 44.5° which should be assigned to Fe
166 (0) [29, 30], while no obvious peaks of $\text{Ca}(\text{OH})_2$ were found. Similar phenomena
167 were also reported in other studies [23, 31], in which XRD was used to characterize
168 surface coated nZVI with $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, and it was found that neither
169 $\text{Ca}(\text{OH})_2$ nor $\text{Al}(\text{OH})_3$ was observed. This might be due to their low concentrations or
170 low degree of crystallinity.

171 In order to figure out the $\text{Ca}(\text{OH})_2$ content coated on nZVI , AAS was used to
172 determine the ratio of Fe and Ca after acid digestion of the $\text{nZVI-Ca}(\text{OH})_2$
173 composites. Fig. 1d shows the content of $\text{Ca}(\text{OH})_2$ coated on the nZVI particles under
174 different sonication time. It is clear that the sonication time did significantly affect the
175 coating thickness. The amount of $\text{Ca}(\text{OH})_2$ was 1.31% of the total weight after 0.5 h
176 coating, which rose to 10.19% after 4 h coating. To verify the effect of $\text{Ca}(\text{OH})_2$
177 coating on the mobility of nZVI particles, a simplified sand column test was carried
178 out and the results show that the $\text{Ca}(\text{OH})_2$ coating did improve the transport of nZVI
179 particles in porous media (Fig. S2). This is consistent with the finding in literature
180 [23]. However, no obvious difference was observed for the $\text{nZVI-Ca}(\text{OH})_2$ with
181 different amount of $\text{Ca}(\text{OH})_2$ (data not shown). In view of the effect of sonication time

182 on coating thickness, it may influence the reactivity of the composite, which will be
183 discussed in the following part. Overall, the results from SEM, EDS, XRD, AAS
184 analysis and mobility test, collectively, suggested the successful synthesis of nZVI-
185 $\text{Ca}(\text{OH})_2$ composite.

186 **3.2. Removal of SMT in nZVI- $\text{Ca}(\text{OH})_2$ /persulfate system**

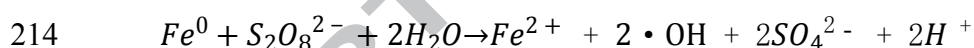
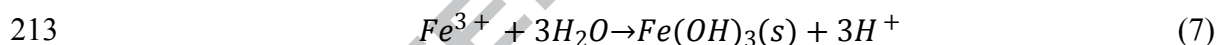
187 **3.2.1. Effect of sonication time**

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

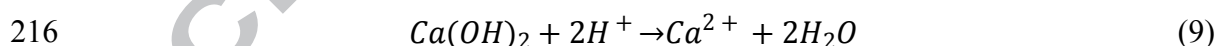
199 **3.2.2. Effect of initial pH**

200 SMT removal experiments were carried out at four different initial pH values, i.e. 3, 5,
201 7 and 9. As shown in Fig. 3a, the final removal efficiency as well as the removal

202 kinetics were much similar at initial pH from 3 to 9. In order to probe into the
 203 underlying mechanism, the changes of pH during reaction were monitored (Fig. 3b).
 204 Obviously, no matter at what initial pH value, the solution pH dropped dramatically
 205 (within 10 min) to around 3.5 and finally maintained in a very narrow pH range of 3.0
 206 to 3.2. This should be the reason for the similar SMT removal under various pH
 207 conditions. The sharp pH change may be due to the release of H^+ from the reaction of
 208 Fe^{3+} precipitation (Eq. 7) [11], the reaction between SO_4^{2-} and H_2O (Eq. 4) or the
 209 reaction of Fe^0 with persulfate (Eq. 8) [32]. Although the dissolution of the outside
 210 $Ca(OH)_2$ layer would consume protons and then cause a rise in solution pH (Eq. 9),
 211 the mass ratio of $Ca(OH)_2$ is extremely low (1.31%), the influence of $Ca(OH)_2$ layer
 212 on solution pH should be negligible.



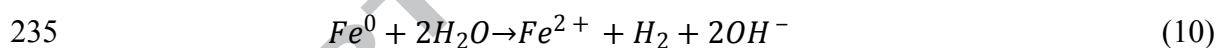
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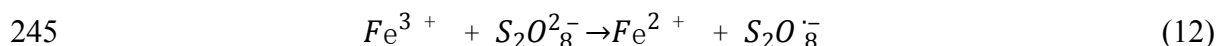
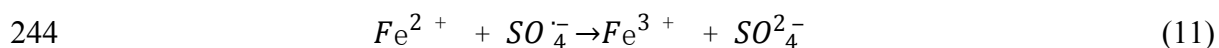
217 3.2.3. Effect of nZVI- $Ca(OH)_2$ dosage

218 The effect of nZVI- $Ca(OH)_2$ dosage on SMT removal was investigated over a
 219 range of 10–200 mg/L and the results are illustrated in Fig. 4a. The removal efficiency
 220 was 90.31%, 100%, 93.14% and 77.03% with the composite dosage of 10, 50, 100
 221 and 200 mg/L, respectively. With the increasing nZVI- $Ca(OH)_2$ dosage from 10 to 50
 222 mg/L, SMT removal efficiency was improved. This should be due to the generation of

223 more amounts of radicals with the existence of more iron ions in the solution. When
224 the dose was further increased up to 200 mg/L, the removal efficiency dropped
225 significantly to 77.03%. To find out the difference among the reaction systems with
226 varying nZVI-Ca(OH)₂ dosage, the pH changes with time in different systems were
227 measured (Fig. 4b). The pH changes in systems of 10 and 50 mg/L showed a similar
228 trend, i.e., a drastic drop in the first 5 min followed by a gradual slowdown. While the
229 systems of 100 and 200 mg/L displayed a very different way with pH increase after
230 the sharp decrease in the first 5 min. As discussed earlier, this sharp pH decrease was
231 mainly attributed to the release of H⁺ during the reactions. While for the system of
232 100 and 200 mg/L, the following pH rise may be due to the dissolution of excessive
233 nZVI-Ca(OH)₂ (Eq. 9 and Eq. 10). The rapid consumption of H⁺ and release of OH⁻
234 could lead to an increase in solution pH.



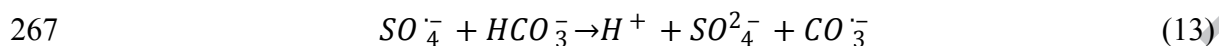
236 With the increase of nZVI-Ca(OH)₂ dosage from 50 mg/L to 200 mg/L, the
237 dissolution of excessive catalyst would cause a rise of solution pH as well as a break
238 out of ferrous ions. These ferrous ions could possibly have a scavenging effect on
239 radicals (Eq. 11), and thus lowering the removal efficiency of SMT [33]. Moreover,
240 the existence of dissolved iron could be just temporarily, under such pH condition,
241 they could easily tend to get hydrolysis [34]. According to Eq. 3, 11 and 12, the lack
242 of Fe²⁺/Fe³⁺ would inhibit the formation of sulfate radicals, and then further resulted
243 in a relative low removal efficiency of SMT [35].



246 3.2.4. Effect of typical groundwater components

247 In natural groundwater, there are many kinds of components that may have some
 248 effects on the contaminant removal process. In this study, experiments were carried
 249 out in synthetic groundwater under different pH conditions. As demonstrated in Fig.
 250 5a, SMT was removed efficiently at all pH values. However, the reaction rate at pH 9
 251 was much slower than that at other pH values. Specifically, the removal efficiency of
 252 SMT at pH 9 was just approximately 15.19% after reaction for 5 min, while around
 253 48.92%, 57.18% and 52.62% were obtained at pH 3, pH 5 and pH 7, respectively. The
 254 evolution of pH at different initial pH values was monitored (Fig. 5b). Different from
 255 the rapid pH drop in pure water condition, much less changes of pH were observed
 256 during the reaction in synthetic groundwater. This should be result from the good
 257 buffer capacity of HCO_3^- . Under alkaline condition, nZVI- $\text{Ca}(\text{OH})_2$ could hardly be
 258 dissolved and also it would be favorable for the precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$, thus, there
 259 would be less free iron ions existed in the system, resulting in the less activation of
 260 persulfate [36]. Pang et al. [36] reported that ultrasound irradiation could contribute to
 261 acceleration of ZVI corrosion and removal of passive films, resulting in high
 262 efficiency in peroxymonosulfate activation. Thus, the precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ could
 263 possibly be one reason for the slower removal rate of SMT at pH 9. Besides,
 264 bicarbonate can be a scavenger of sulfate radicals (Eq. 13). Although other radicals

265 (i.e. CO_3^{2-}) are generated from the scavenging reaction, they are quite unreactive
 266 compared to SO_4^{2-} toward most organic substrates in aqueous condition [37].



268 In addition, previous studies reported that SO_4^{2-} could also exhibit negative effect
 269 on the radical-based reactions [38]. SO_4^{2-} ions can form bonding with Fe^{2+} and Fe^{3+} ,
 270 producing complexes of $FeSO_4$ and $Fe_2(SO_4)_3$. These complex reactions reduced the
 271 concentration of free iron ions in the solution for activation of persulfate, thus
 272 inhibiting the removal of SMT.

273 To further identify the role of each individual component, SMT removal in the
 274 presence of single ions (i.e., HCO_3^- , SO_4^{2-} , Cl^- and Ca^{2+}) was examined respectively
 275 with different concentration. As shown in Fig. 6a, all these ions with a lower
 276 concentration (1 mmol/L) could barely affect the nZVI-Ca(OH)₂ performance on
 277 SMT removal. Only in the case of HCO_3^- , a slower removal rate was observed.
 278 However, after 60 min reaction time, the removal efficiency reached 100% in all
 279 reaction systems. When increasing the concentration to 10 mmol/L, the groundwater
 280 components showed very different impacts on the removal performance (Fig. 6b).
 281 Ca^{2+} and Cl^- had insignificant impact on SMT removal, while the presence of HCO_3^-
 282 or SO_4^{2-} substantially decreased the SMT removal. The results verified the previous
 283 assumption that the drop of SMT removal efficiency in synthetic groundwater was
 284 mainly due to the effect of HCO_3^- and SO_4^{2-} .

285 To sum up, the effect of these typical groundwater components at low

286 concentration were negligible, and even at higher concentration Cl^- and Ca^{2+} had little
287 effect on SMT removal. While HCO_3^- or SO_4^{2-} with higher concentration could inhibit
288 the degradation efficiency of SMT and the inhibiting effect of HCO_3^- was more
289 pronounced than the other ions at the same concentration.

290 3.2.5 Effect of particle aging

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

297 The reactivity of nZVI- $\text{Ca}(\text{OH})_2$ was associated with its surface composition,
298 XRD analysis was then conducted to identify the composition evolution and
299 crystalline change of nZVI- $\text{Ca}(\text{OH})_2$ with aging time. Fig. 7b shows the XRD patterns
300 of fresh and different aged nZVI- $\text{Ca}(\text{OH})_2$. It is noticeable that the peak of Fe^0 at
301 44.5° became weaker with aging time. But the Fe^0 peak can still be detected even
302 after 30 days of aging, indicating the existence of Fe^0 on the surface of particles after
303 30 days. Our previous study on Fe/Ni bimetal nanoparticles aging process reported
304 that the Fe^0 peak disappeared in just 5 days [29]. In comparison, it was clear that
305 coating nZVI with $\text{Ca}(\text{OH})_2$ did prolong its lifetime due to the protection of $\text{Ca}(\text{OH})_2$

306 outer shell. For the aged samples, peaks assigned to iron oxide were not detected,
307 which is quite different from the reported XRD patterns of aged nZVI. Typical aging
308 products of nZVI in oxic condition are goethite, maghemite, magnetite and
309 lepidocrocite [39]. Whilst, there were no iron oxides detected in the aging samples of
310 nZVI-Ca(OH)₂, which manifests that the corrosion of nZVI in nZVI-Ca(OH)₂ was not
311 significant and iron oxides were not existing in crystalline phase.

312 Even though there were some loss of Fe⁰ with aging, SMT removal efficiency
313 was barely influenced. This could possibly be attributed to the good persulfate
314 activation capacity of amorphous iron oxides [40]. Since both Fe⁰ and iron oxides can
315 activate persulfate, fresh and aged nZVI-Ca(OH)₂ samples showed similar
316 performance in the process of SMT degradation.

317 4. Conclusion

318 In this study, a thin Ca(OH)₂ shell was successfully coated on the surface of
319 nZVI particles. The thickness of Ca(OH)₂ is related to sonication time during
320 synthesis, the longer sonication time the more Ca(OH)₂ coated. Then, nZVI-Ca(OH)₂
321 composites were utilized as an activator of persulfate to remove SMT. The effects of
322 sonication time, pH, nZVI-Ca(OH)₂ dosage and typical groundwater components
323 were investigated. The following conclusions were made:

- 324 ● The sonication time and initial pH had little effect on SMT removal by
325 nZVI-Ca(OH)₂/persulfate system, while nZVI-Ca(OH)₂ dosage affected the

326 removal efficiency of SMT greatly. There was an optimum dosage of nZVI-
327 Ca(OH)_2 , at higher or lower dosage, the SMT removal was decreased.

328 ● nZVI- Ca(OH)_2 showed different performance in synthetic groundwater and
329 pure water over the pH range of 3-9. The effect of typical groundwater
330 components (Ca^{2+} , Cl^- , HCO_3^- and SO_4^{2-}) were examined respectively and it
331 was found that the groundwater ions at low concentration showed negligible
332 influence on SMT removal, but HCO_3^- and SO_4^{2-} at high concentration could
333 inhibit the SMT removal in a large degree.

334 ● Effect of aging time on the reactivity of nZVI- Ca(OH)_2 was investigated,
335 and it was found that the particles kept its reactivity even after 30 days of
336 aging. This suggests that coating nZVI with Ca(OH)_2 did prolong the
337 lifetime of nZVI.

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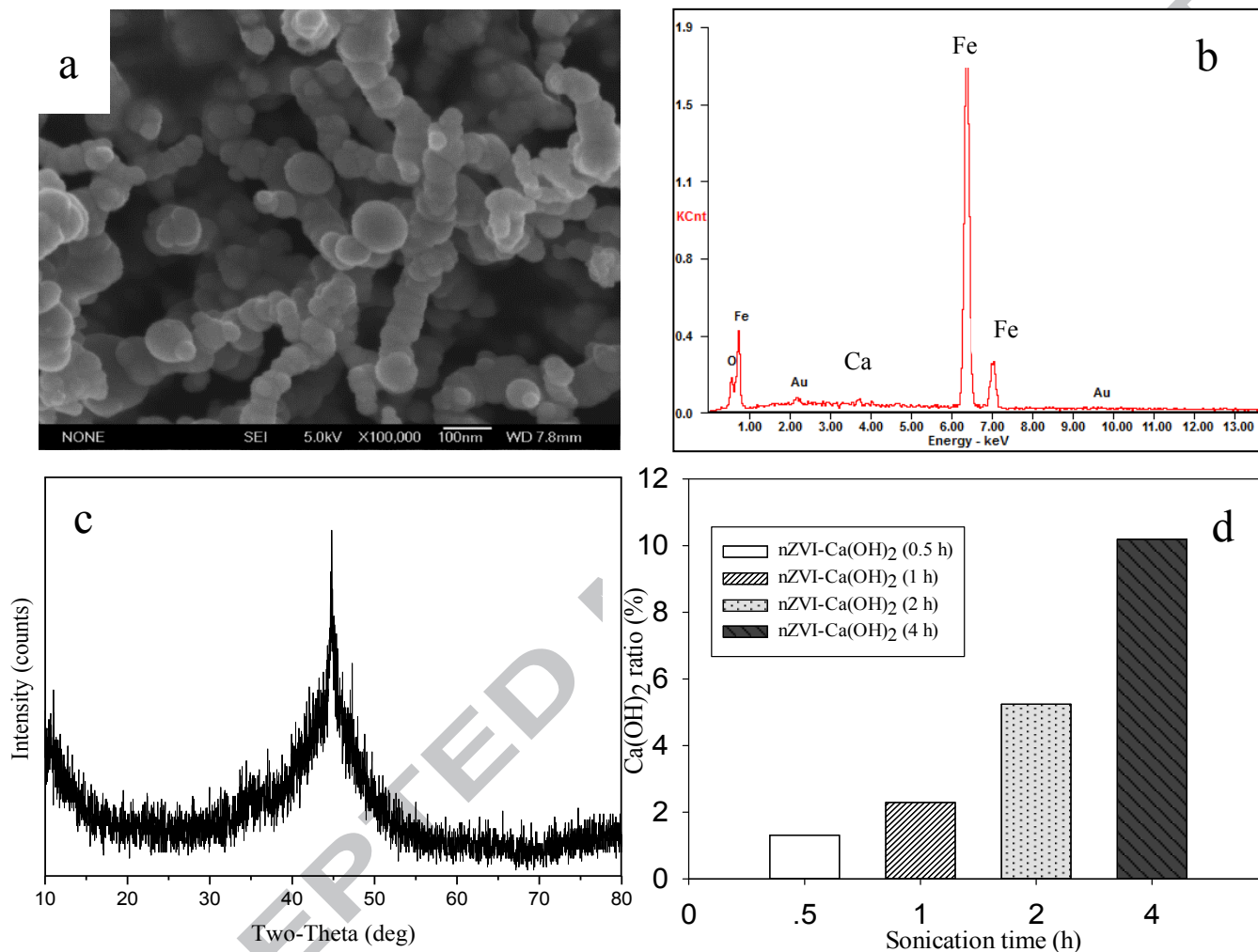
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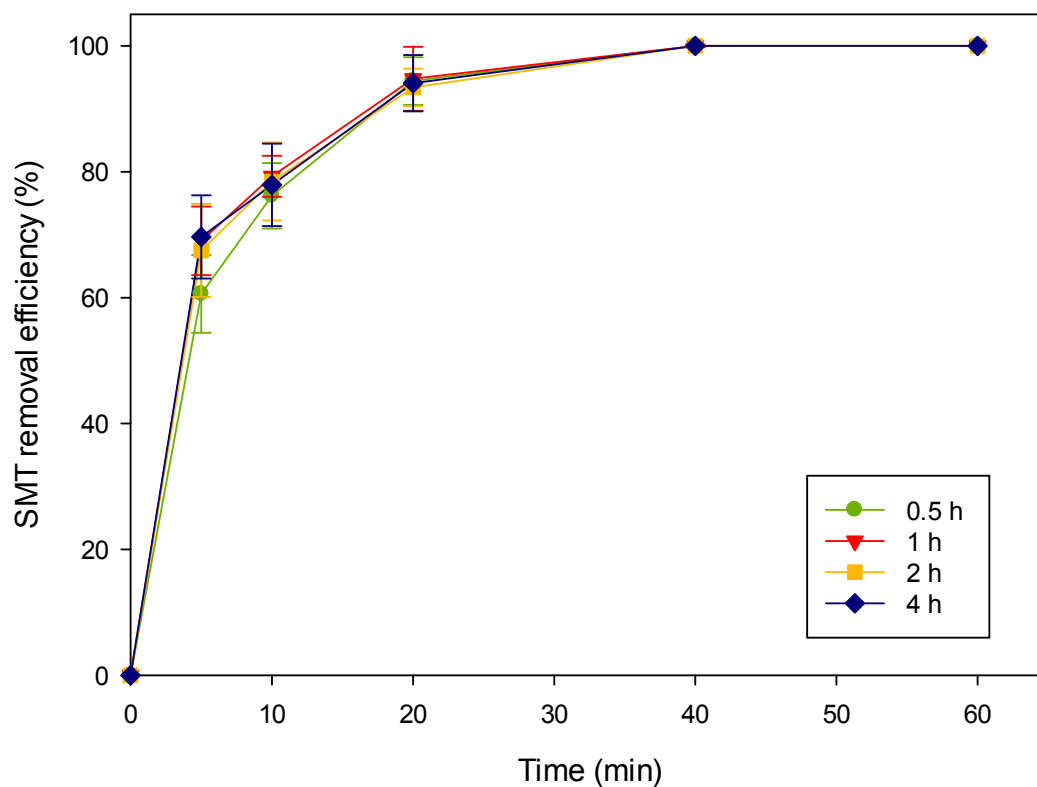
476 Fig. 1. (a) SEM image of nZVI-Ca(OH)₂ particles (sonication time: 0.5 h), (b) the

477 corresponding EDS (sonication time: 0.5 h), (c) XRD analysis of nZVI-Ca(OH)₂

478 particles (sonication time: 0.5 h), and (d) the content of Ca(OH)₂ coated on the nZVI

479 particles under different sonication time

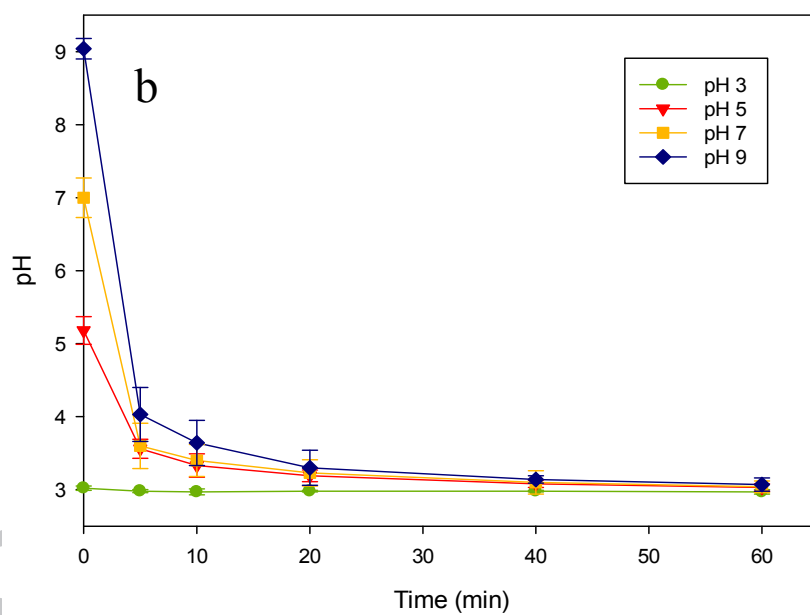
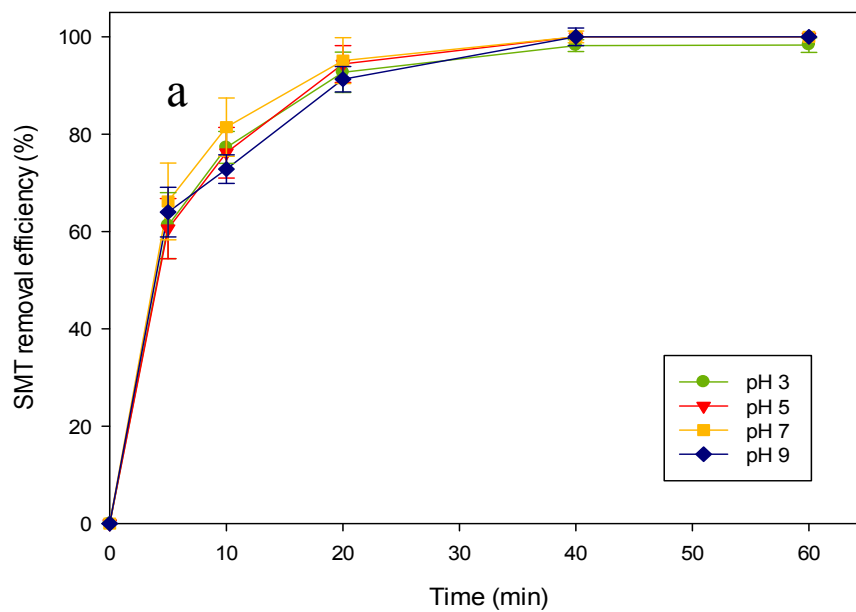
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482 Fig. 2. Effect of sonication time during synthesis of nZVI-Ca(OH)₂ on SMT removal483 by nZVI-Ca(OH)₂ activated PS (initial pH = 5; [SMT] = 0.025 mM; [PS] = 1 mM;484 [nZVI-Ca(OH)₂] = 50 mg/L)

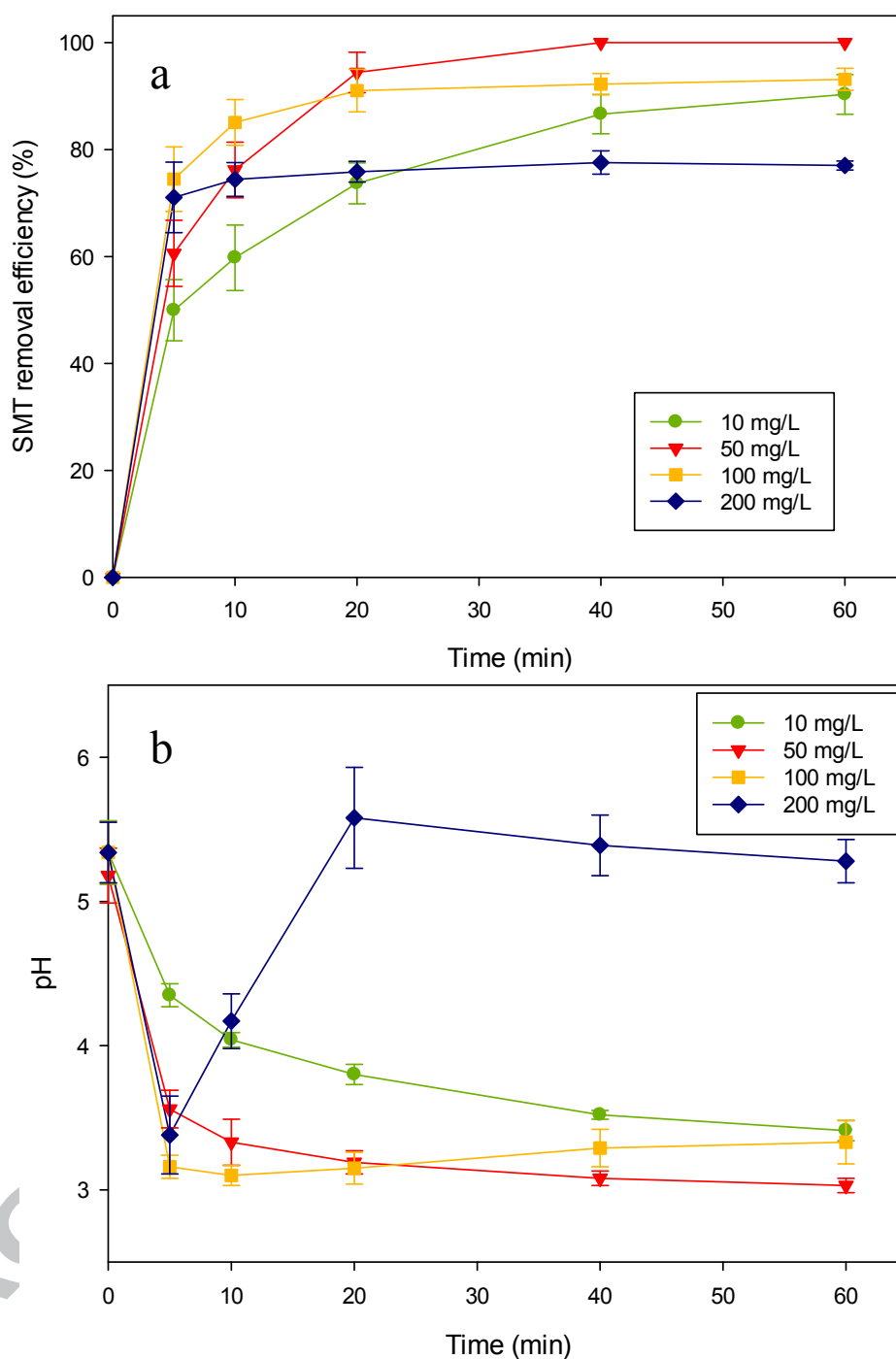
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488 Fig. 3. (a) Effect of initial pH on the removal of SMT by nZVI-Ca(OH)₂ and (b) pH489 changes with time ([SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-Ca(OH)₂] = 50 mg/L)



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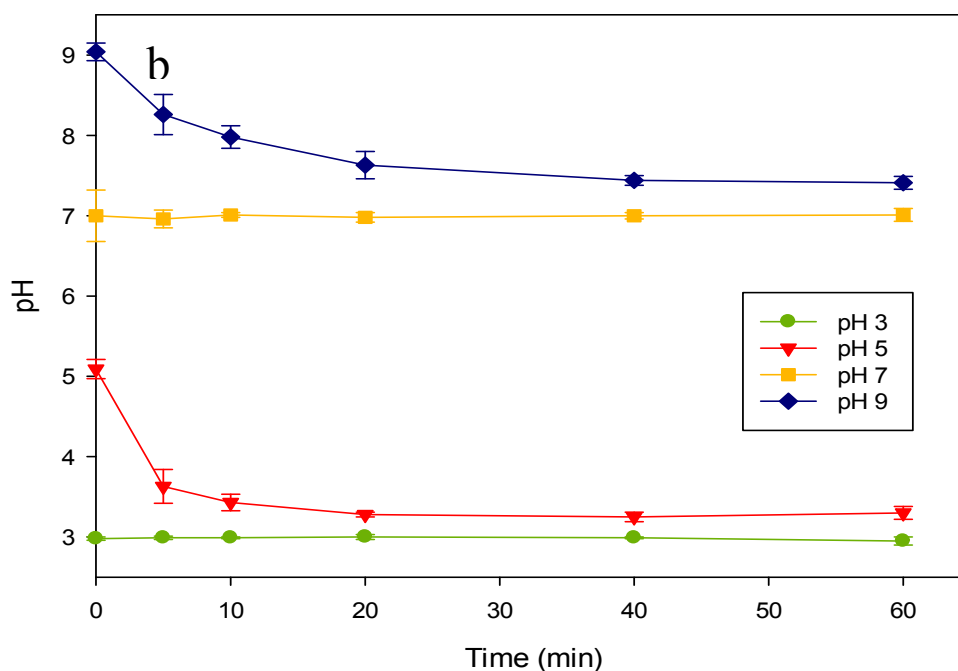
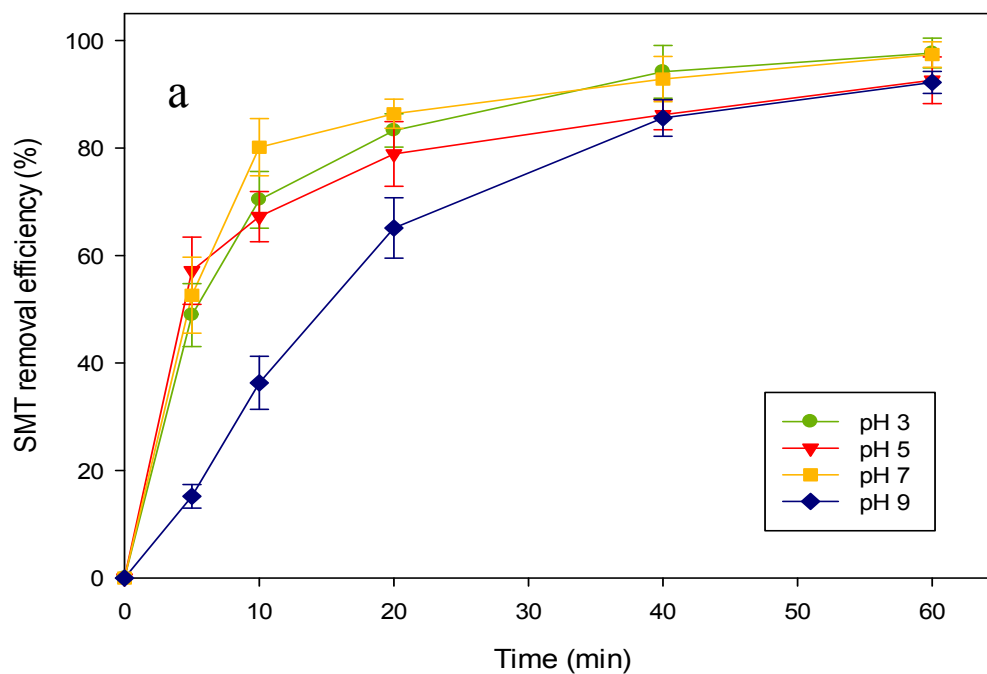
491 Fig. 4. (a) Effect of nZVI-Ca(OH)₂ dosage on the removal of SMT and (b) pH492 changes with time in different nZVI-Ca(OH)₂ dosage systems (initial pH = 5; [SMT]

493 = 0.025 mM; [PS] = 1 mM)

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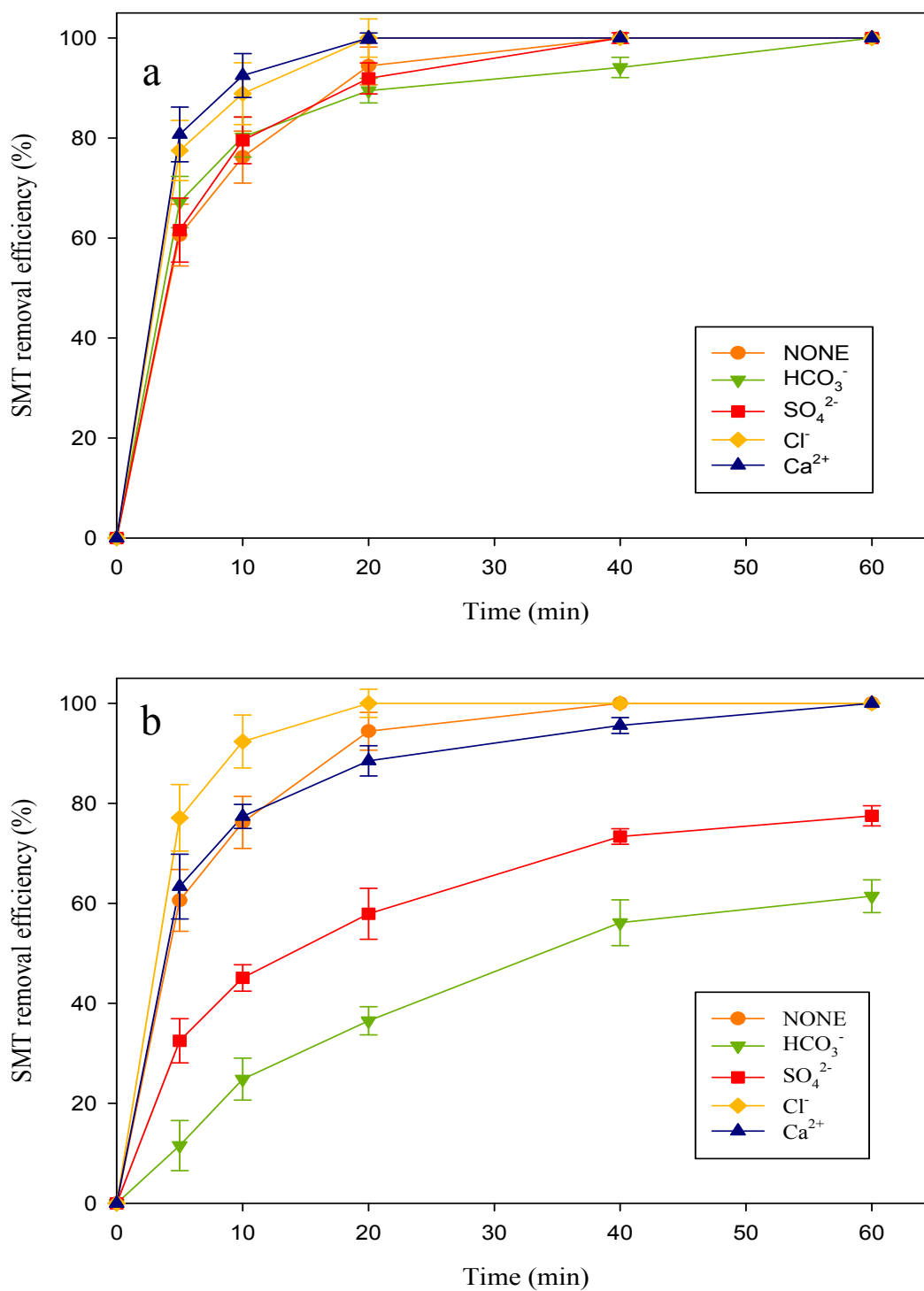


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498 Fig. 5. (a) SMT removal by nZVI-Ca(OH)₂ in synthetic groundwater under different

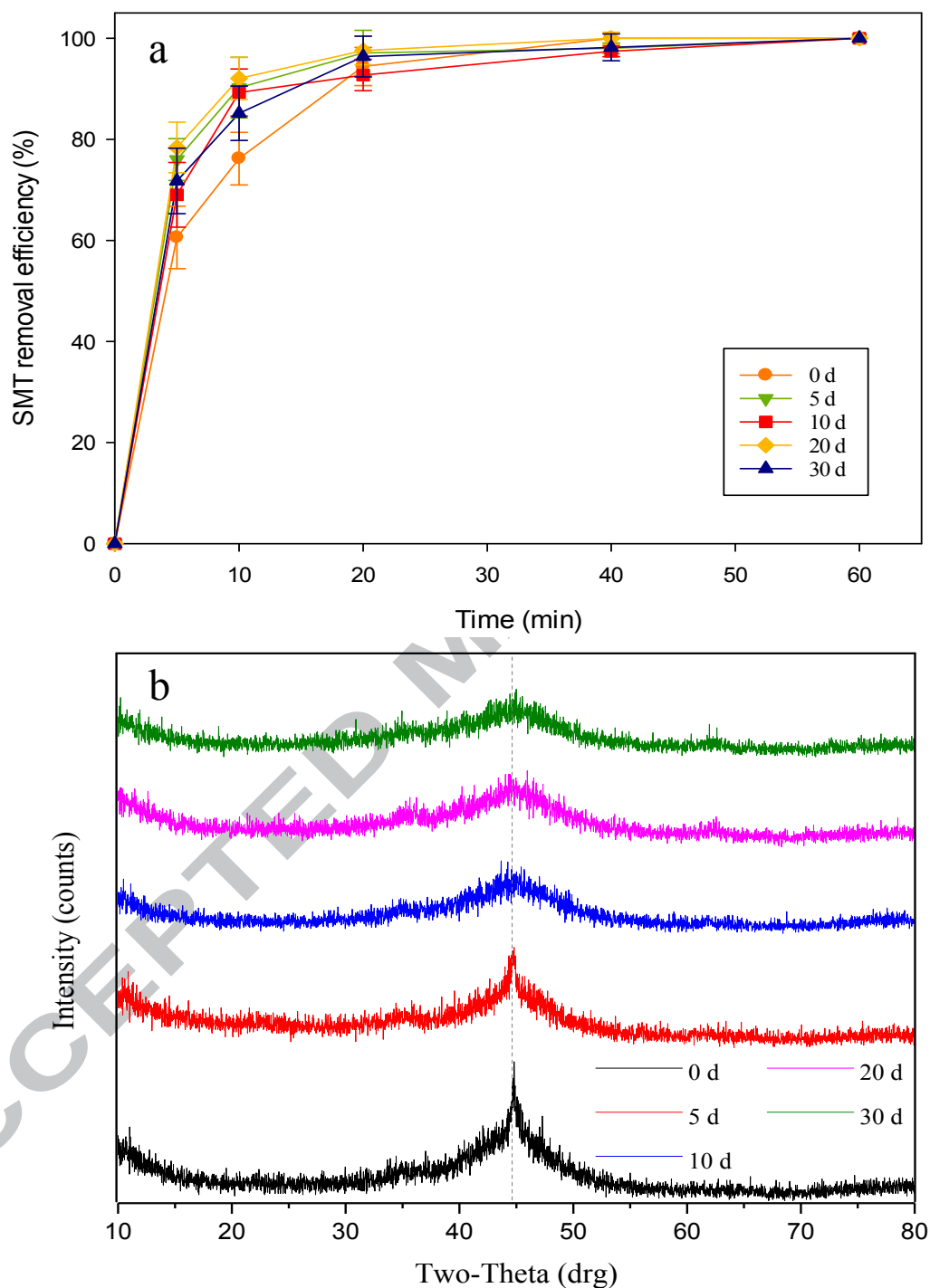
499 pH, and (b) pH changes with time in synthetic groundwater ([SMT] = 0.025 mM;

500 [PS] = 1 mM; [nZVI-Ca(OH)₂] = 50 mg/L)



501

502 Fig. 6. Effect of typical groundwater components of different concentrations (a: 1
 503 mmol/L; b: 10 mmol/L) on the removal of SMT by nZVI-Ca(OH)₂ activated PS
 504 (initial pH = 5; [SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-Ca(OH)₂] = 50 mg/L)
 505



506

507 Fig. 7. (a) SMT removal by the aged nZVI-Ca(OH)₂ activated PS and (b) XRD

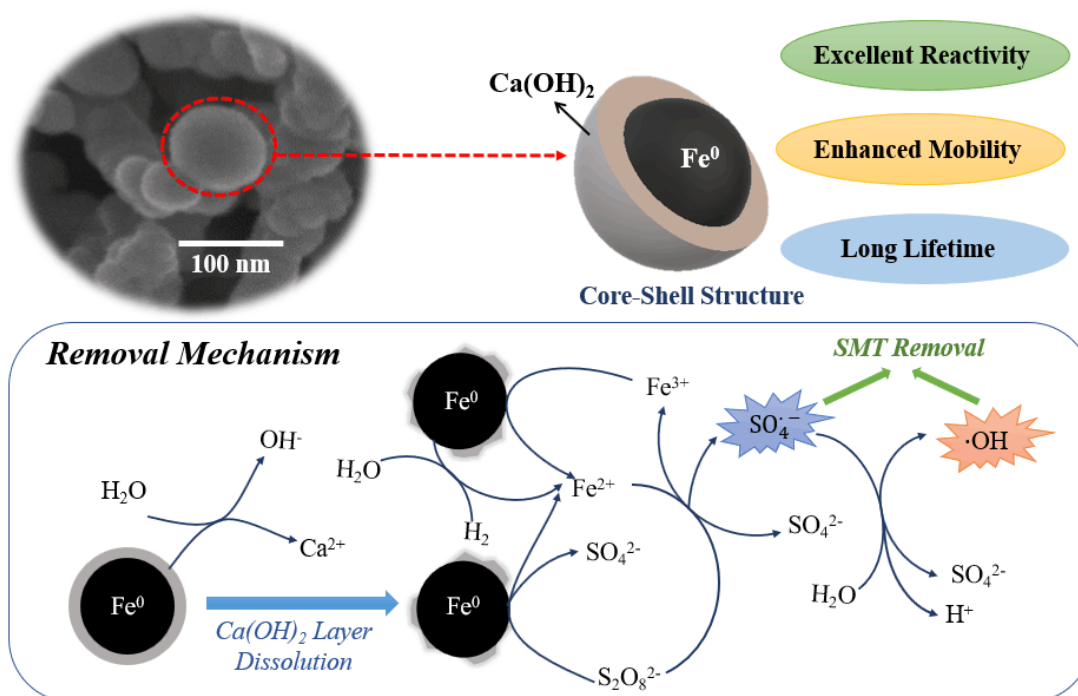
508 patterns of aged particles (initial pH = 5; [SMT] = 0.025 mM; [PS] = 1 mM; [nZVI-

509 Ca(OH)₂] = 50 mg/L)

510

- 511 ● nZVI-Ca(OH)₂ was used as an activator of PS for the degradation of SMT
- 512 ● There was an optimum dosage of nZVI-Ca(OH)₂ for the activation of PS to
- 513 degrade SMT
- 514 ● nZVI-Ca(OH)₂ was efficient for PS activation in synthetic groundwater at pH 3-9
- 515 ● The presence of high concentration of HCO₃⁻ or SO₄²⁻ greatly inhibited SMT
- 516 removal
- 517 ● The Ca(OH)₂ shell can protect the inner iron core from oxidation in the air

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520