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Single-step removal of Hexavalent chromium and phenol using meso zerovalent iron

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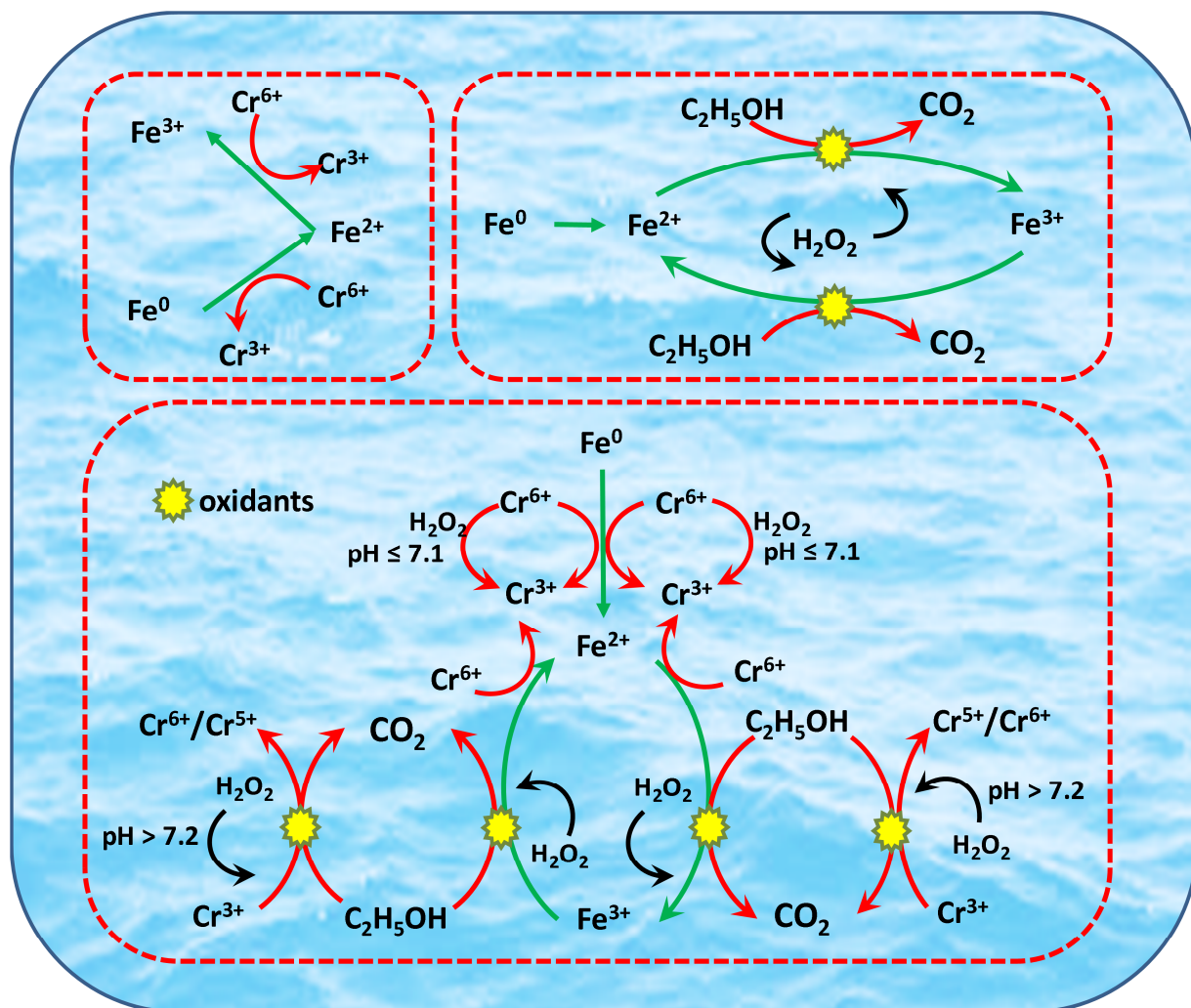
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Dr. Devasena M: Writing - Review & Editing, Visualization

Prof. Indumathi M Nambi: Supervision, Resources

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Graphical Abstract

Proposed mechanism of mZVI-mediated coupled Cr^{6+} and phenol
removal

1 **SINGLE-STEP REMOVAL OF HEXAVALENT CHROMIUM AND**
2 **PHENOL USING MESO ZEROVALENT IRON**

3
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18 **ABSTARCT**

19 Novel meso-zero valent iron (mZVI) was investigated for treating complex wastewater
20 containing toxic heavy metal Cr^{6+} and organic compound phenol. This study is first of its kind
21 illustrating coupled removal in single-step with H_2O_2 playing a major role as an oxidant and
22 reductant. The mechanism involved was electron transfer from $\text{Fe}^{0/2+}$ to Cr^{6+} resulting in $\text{Fe}^{2+/3+}$
23 which in turn was consumed for phenol oxidation returning as Fe^{2+} into the system for further
24 Cr^{6+} reduction. While comparing, single-step simultaneous removal of Cr^{6+} and phenol
25 showed better performance in terms of pollutant removal, $\text{Fe}^{2+/3+}$ recurrent reaction and
26 precipitation generation, double-tep sequential removal performed better in iron active-
27 corrosion time. It was also observed that the entire redox cycle of Cr^{6+} - Cr^{3+} - Cr^{6+} was reusable
28 for co-contaminant phenol degradation at all pH with the recurrence of Fe^{2+} - Fe^{3+} - Fe^{2+} . The
29 proposed technique was checked for its viability in a single batch reactor and the complex
30 chemistry of the reactions are unfolded by conducting chemical speciation and mass balance
31 study at every stage of reaction. The unique functioning of mZVI was proven with micro-
32 analysis of ZVI's surface and compared with granular ZVI, cZVI. The results obtained from
33 this study open the door for a safer and cleaner single treatment system in removing both toxic
34 heavy metals and organic compounds from contaminated surface water, groundwater and many
35 such industrial effluents.

36 **KEYWORDS**

37 Coupled organic and heavy metal removal, sequential and simultaneous treatment, single-step
38 treatment, chromium and phenol, Fenton like reaction, meso-zero valent iron, series and
39 coupled removal.

40

41 **HIGHLIGHTS**

- 42 • Study of gZVI & mZVI based coupled toxic organic compound & heavy metal removal
- 43 • Beneficial single-step treatment synchronizing Cr⁶⁺ reduction & phenol oxidation
- 44 • More pollutant removal/unit mZVI, with least unwanted iron-sludge even at neutral pH
- 45 • pH-focus chemical speciation, mass balance & radical study at every stage of reaction
- 46 • Scrap Fe recycled mZVI in *in/ex-situ* Cr & phenol removal without buffer/stabilizer

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59 **1 INTRODUCTION**

60 Highly complex industrial wastewater discharged with a multitude of toxic organic and
61 inorganic compounds necessitates a robust and sustainable technique for simultaneous
62 degradation of mixed pollutants(Aksu and Gonen, 2006; Bekkouche et al.,2012; Bokare and
63 Choi, 2011; Ciesla et al.,2007;Deng and Stone, 1996; Elovitz and Fish, 1994; Katsoyiannis et
64 al.,2008; Mahlambi et al.,2015).Hexavalent chromium (Cr^{6+}) and phenol co-exist in painting,
65 printing ink, leather and textile industrial discharges apart from dumpsite leachates. Together,
66 they exhibit compounded toxic effects resulting in increased complexity and remediation
67 expenses (Elovitz and Fish, 1994; Golbaz et al.,2014; Kumar et al.,2017; Lee et al.,2003;
68 Lu,2000; Zang et al.,2015). Physico-chemical treatment technologies such as adsorption and
69 chemical precipitation merely transfer the pollutants from one phase to another without
70 detoxifying them (Jorgensen,1979; Manahan, 2011, 1999, 1997). Biological treatment, on the
71 other hand, suffers from slow rate of removal, sensitive microbial kinetics and in many cases
72 result in incomplete removal of pollutants (Massoud et al.,2009; Rajasulochana and Preetha,
73 2016; Todd and Josephson, 1996).There are no single-step removal treatment techniques
74 available for the removal of heavy metals and organic compounds. Iron enabled Fenton's
75 phenol oxidation and Cr^{6+} reduction is extensively studied for separate heavy metal and organic
76 pollutant removal but not for the complex wastewater containing both. Over the past decades,
77 usage of zero-valent iron (ZVI) which acts as the source for Fe^{2+} has gained popularity in
78 removing organic contaminant but fails often due to the choice of either granular or nano ZVI
79 as reactive media. The reasons for lack of field accomplishment could be the limitations
80 associated with iron corrosion rate, longevity and sustenance of the system(Cao et al., 2013;

81 Jiang et al., 2015; Jiao et al., 2009; Mu et al.,2004; Noubactep, 2008; Noubactep and Care,
82 2010; Ryu et al., 2011; Shi et al., 2018; Vilardi et al.,2019; Yao et al.,2019; Yoon et
83 al.,2011).This necessitates selecting an alternative form of ZVI that performs better in pollutant
84 removal and overcomes the shortcomings of granular-ZVI (gZVI) and nano ZVI
85 (nZVI)(Ambika et al.,2016; Noubactep and Care, 2010; Obiri et al.,2014; Reynolds et al.,2013;
86 Yuet et al.,2019). The authors proved the efficacy of meso-ZVI (mZVI) for separate removal
87 of phenol in comparison with coarse/nano ZVI (Ambika et al.,2016) and observed better
88 degradation efficiencies even at circum-neutral pH. Separate Cr^{6+} reduction using mZVI also
89 showed excellent results and encouraged to investigate the coupled removal of phenol and
90 Cr^{6+} .

91 The present work is the first of its kind in bringing out the potentialities of mZVI to achieve
92 coupled removal of Cr^{6+} and phenol as a single step in an unbuffered system. The chemical
93 reactions amongst Cr, phenol and Fenton's reagent may be complex, but the treatment system
94 is believed to be relatively simple with adjustment only with the pH of the solution and dose of
95 H_2O_2 added. It is hypothesized that ferrous and ferric forms of iron generated during the redox
96 reaction could recycle between Cr^{6+} reduction and Fenton's phenol oxidation and satiate the
97 entire process devoid of external addition of zero valent iron. It is essential to understand the
98 potential of mZVI in coupled removal of a heavy metal and an organic compound aiming zero
99 leaching and effective contaminant removal devoid of secondary sludge formation.

100 The objectives of this study were to i) to understand the catalytic activity of mZVI
101 during Cr^{6+} reduction and phenol oxidation; ii) to evaluate the separate Cr^{6+} and phenol
102 removal, sequential and single-step simultaneous (S^3) mode's efficiency in Cr^{6+} and phenol
103 removal, including variation in pH; iii) to investigate the kinetic model fitting with Cr^{6+} and

104 phenol removal in separate, sequential and S³ of treatment iv) to evaluate the reuse of mZVI
105 and quantify typical number of cycles until exhaustion of active sites. Since mZVI was
106 employed for the first time for coupled removal of organic and inorganic aqueous
107 contaminants, the insights from this study are expected to alleviate the secondary sludge
108 formation and extra addition of ZVI during the treatment of highly complex mixed wastewater
109 generated from industries. The mode and efficiency of pollutant removal, reaction kinetic rates,
110 utilization of Fe⁰/Fe²⁺/Fe³⁺, Fe²⁺/Fe³⁺ cycling, activeness of the system and Fe/Cr precipitation
111 were determined by performing a series of batch experiments.

112 2 METHODOLOGY

113 2.1 CHEMICALS AND MATERIALS

114 Major chemicals that were used in this study were potassium dichromate (K₂Cr₂O₇), phenol
115 (C₆H₅OH) and hydrogen peroxide (H₂O₂ 30%). All solutions were prepared using Millipore
116 water. The mZVI (D₅₀ ~20.9 μm, specific surface area ~2.101 m²/cc, crystalline size based on
117 Scherrer equation 17 nm) were obtained by grinding 2 mm gZVI in a high energy planetary
118 ball mill (Fritsch P5) for 10 h (Ambika et al.,2016). The surface composition of mZVI
119 analyzed by Energy Dispersive Spectroscopy (EDS) showed that the surface primarily
120 comprised of 98% of pure iron (Fe) and trace amounts of Silica (Si).

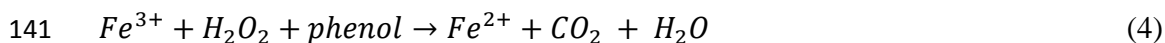
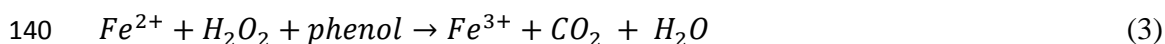
121 2.2 EXPERIMENTAL PROCEDURE AND ANALYTICAL METHODS

122 All experiments were carried out in 100 mL glass beakers stirred in an orbital shaker at
123 a stirring velocity of 150 rpm for 60 min. Unless otherwise stated, Cr⁶⁺ were fixed at 2 mg/L,
124 phenol at 5 mg/L and mZVI at 20 mg/L. The H₂O₂ concentration varied between 1.58 mM to

125 9.5 mM. All experiments were carried out in the ambient laboratory atmosphere at room
 126 temperatures between 25 °C and 30 °C.

127 Three types of experiments were carried out as indicated in Fig. S1, representing separate,
 128 sequential and simultaneous modes of Cr⁶⁺ reduction and phenol oxidation. A first set of
 129 experiments were done as shown in Fig. S1(a-b) under independent-mode showing separate
 130 removal of phenol and Cr⁶⁺ with the same concentration of mZVI, resembling ZVI mediated
 131 Cr⁶⁺ reduction and Fenton's phenol oxidation.

132 The two-step sequential removal of Cr⁶⁺ and phenol as shown in Fig.S1(c) was investigated
 133 with synthetic wastewater with the concentration ratio of Cr⁶⁺, phenol and mZVI maintained as
 134 2:5:20. The experiments were started with mZVI assisted Cr⁶⁺ reduction. Post Cr⁶⁺
 135 stabilization as in reactions (1) and (2), phenol transformation as Fenton reactions (3) and (4)
 136 was investigated with respect to addition of predetermined moles of H₂O₂ in the same reactor.
 137 Presence of residual H₂O₂ was quenched with sodium sulphite before further analysis.



142 Third set of experiments was conducted to depict single step simultaneous (S³) mode, where
 143 Cr⁶⁺, phenol, mZVI and H₂O₂ were added in the same order to promote simultaneous removal
 144 of the pollutants as shown in Fig. S1(d).

145 In all the above-said three experiments, the pollutant removal capacity of mZVI was quantified
146 by multiple use of ZVI or repeated addition of Cr^{6+} or/and phenol after stabilization of
147 Cr^{6+} /phenol in the previous use based on the design of experiments. All the three types of
148 experiments were conducted at Britton Robinson buffered system which maintained the
149 desired pH between 3 to 10, to confirm the reaction mechanism (Reynolds et al.,2013). The
150 details of the preparation of the buffer is given in supplementary material. Influence of
151 increased Cr^{6+} concentration during phenol removal and vice versa was also demonstrated as
152 distinct experiments. Auxiliary experiments with the different combinations of
153 $\text{Fe}^{0/2+/3+}/\text{Cr}^{6+/3+}/\text{phenol}/\text{H}_2\text{O}_2$ were conducted to confirm the kinetics and mechanisms involved
154 in the coupled pollutant removal.

155 Similar experiments were carried out parallelly, using 20 (mZVI concentration) and 2000 mg/L
156 of gZVI (depicting the same surface area of 20 mg/L of mZVI) as the catalyst to compare the
157 efficiency of mZVI in folds and to reason out the unique performance by mZVI. At regular
158 intervals, aliquots were collected and analyzed for pollutants and Fe speciation.

159 Quantitative analysis of phenol was done using high performance liquid chromatography
160 (HPLC), Dionex USA equipped with a diode array detector and C-18 μm HPLC column
161 (L=250 mm, dia. 4.6 mm). Total iron and Fe^{2+} was analyzed using UV-Vis spectrophotometer
162 by modified ferrozine method (Keenan and Sedlak, 2008). The concentrations of residual Fe^0
163 and total Fe in solid and aqueous phase were measured. Both solid and aqueous phase Fe^{2+}
164 were analyzed and Fe^{3+} was found by subtracting the Fe^{2+} concentration from total Fe
165 concentration in respective phases. Mass balance was checked by comparing the measured
166 total iron with initial mZVI concentration. Similar analysis and mass balance were done for Cr
167 by measuring total Cr and Cr^{6+} by UV spectrophotometer by diphenyl carbazide method

168 (Ansaf et al.,2016). The radicals were measured using respective quenching agents (Ambika et
169 al.,2016; Henry and Donahue,2011; Lloyd et al.,1997). Electron Microscopy (Nikon eclipse
170 LV100, Japan) images of the surface and cross-section of ZVIs were captured during and at the
171 end of experiments.

172 **3 RESULTS AND DISCUSSION**

173 **3.1 SYSTEM PERFORMANCE**

174 The results are discussed in terms of pollutant removal efficiency, utilization of mZVI, $\text{Fe}^{2+/3+}$
175 cycle and Fe precipitation in separate, sequential and S^3 -mode of treatment systems. In the first
176 place, the results reinstate the fact that the Fenton's oxidative mineralization of an organic
177 compound coupled with removal of any inorganic compound requires the contribution of non-
178 selective, highly reactive $\cdot\text{OH}$ radicals and the activity of Fe ions even in neutral/alkaline
179 conditions. This is in accordance with an earlier report about the origin of $\cdot\text{OH}$ in Fenton
180 reaction (Bremner et al.,2006; Lloyd et al.,1997). The stability of the redox states of inorganic
181 compound over a wide pH range also influences the coupled removal (Kabdasli et al.,2010;
182 Segura et al.,2013; Vilardi et al.,2019), especially in the study pH range 3 to 10. The batch
183 tests in this study witnessed the dual-role of H_2O_2 as both an oxidant and reductant depending
184 on pH of the aqueous solution promoting both the reduction of Cr^{6+} to Cr^{3+} and oxidation of
185 phenol which are explained in detail in the following sections. The concentrations of dissolved
186 Fe and Cr ions at the end of the experiments were below detectable limit (0.001 mg/L)
187 indicating that there is no dissolution of trace pollutants in the system. Fig. 1(a-d) shows the
188 first three cycles of mZVI and its transformation in separate Cr^{6+} , separate phenol, sequential
189 and S^3 treatment modes.

190 When the redox capability of mZVI was checked, both sequential and S³-modes showed 1.3 to
191 3.3 times better pollutant removal rate than separate Cr⁶⁺ and phenol removal for the entire pH
192 range as represented in Fig. 1(a-d). . The experimental results, obtained by repeated cycles,
193 with an initial concentration of 2 mg/L of Cr⁶⁺, 5 mg/L of phenol and 20 mg/L mZVI and
194 circum-neutral pH are shown in Fig. 2(a-c). In the first cycle, half-life of Cr⁶⁺ reduction was
195 achieved in a time span of 5 min while the subsequent cycle took 150 min. The redox reactions
196 occurred simultaneously as well as sequentially with the aid of Fe^{0/2+/3+} and ·OH radicals and
197 both modes showed enhanced utilization of mZVI by about 21% at circumneutral pH as
198 indicated in Fig. 2(b). Electron transfer from Fe⁰ to Cr⁶⁺ resulting in Cr³⁺ along with phenol
199 degradation was found to be the main process in separate, sequential and S³-modes. Compared
200 to the sequential-mode, number of ZVI reuse (number of cycles) was higher in the S³-mode
201 due to the effectual recycling of Fe^{2+/3+} ions. About 20% to 50% of enhancement in number of
202 mZVI reuses was observed in the pH range of 3 to 10. The results are supported by statements
203 given by (Fu et al.,2013; Liu et al.,2006; Vilaridi et al.,2019) who proved that only catalysts
204 regeneration could improve the Cr⁶⁺ reduction efficiency and in this study the regeneration
205 happened through cyclic reactions between Fe²⁺ and Fe³⁺ through Cr⁶⁺ reduction and Fenton,
206 and Fenton like oxidation as represented in reactions (1-4)

207 More number of mZVI usages was observed in coupled-S³-mode followed by sequential and
208 separate modes during Cr⁶⁺ reduction, whereas the order of S³>separate>sequential-mode was
209 observed during phenol oxidation. This is due to the two facts, firstly, the dual role of H₂O₂ as
210 an oxidant and reductant depends on the pH condition and secondly, the change in route of
211 pollutant removal mechanism and synergistic effect of radical generation in the system that
212 will be discussed in the following sections. The Fe speciation of the stabilized system (no more

213 removal) as shown in Fig. 2(a-b) demonstrated that (i) the sustenance of the coupled removal
214 depends on the concentration of Fe^{2+} , especially at least 0.02 mg/L of Fe^{2+} must be present in
215 the current system for further $Fe^{2+/3+}$ cycling. Below this Fe^{2+} concentration, no coupled
216 pollutant removal was observed (ii) both sequential and S^3 treatment modes enhanced the
217 utilization of mZVI by 21% and 8% respectively at pH 7 and 10 as indicated in Fig. 2(b)
218 precipitation of Fe was delayed about 5 to 10 times after pH 7 due to the synergistic effect of
219 Cr^{6+} reduction and Fenton phenol oxidation in the separate-mode. All the above observations
220 prove that $Fe^{2+/3+}$ recycling is working best for S^3 than sequential mode, particularly during
221 Cr^{6+} reduction at low pH and phenol oxidation at alkaline pH with effective utilization of mZVI
222 (Fig. 2(a-b)).

223 This crucial finding that mZVI can be reused without regeneration makes mZVI a successful
224 reactive media during S^3 -mode of phenol and Cr^{6+} removal in field applications. Compared
225 with the sequential removal, S^3 -mode removed 1.3 to 1.9 and 1.6 to 3.33 times more Cr^{6+} and
226 phenol, respectively from pH 3 to 10 as shown in Fig. 2(a). Good removal of phenol and Cr^{6+}
227 were obtained for independent separate modes for first 2-3 cycles; however, mZVI active sites
228 exhausted quickly showing a smaller number of mZVI reuse cycles as indicated in Fig. 1(a-b)
229 and Fig. 2(a).

230 Another set of experiments were done where predetermined amount of H_2O_2 in incremental
231 supply of about 1.513 to 1.1 times (Fig. S3 and Table S1) was added. The auxiliary addition of
232 H_2O_2 was to satisfy the dual role played by H_2O_2 as a reductant (at $pH \leq 7.1$) and as an oxidant
233 for the entire pH range. It was expected that in an unbuffered S^3 -mode, the redox cycling of
234 Cr^{3+}/Cr^{6+} and Fe^{2+}/Fe^{3+} cycling can be achieved in repeated cycles in a single-batch reactor
235 without regenerating Cr^{3+} and without addition of mZVI. This hypothesis was again confirmed

236 with the results obtained from the auxiliary experiments as in Fig. S4, by measuring Fe and Cr
237 speciation at different reaction times.

238 All experiments aimed to remove Cr^{6+} and phenol from aqueous solution proved that the S^3 -
239 mode of batch operation to be efficient and most sustainable and hence preferred because of
240 the following reasons i) The use of mZVI reactive media after many cycles without
241 regeneration of Fe ion was found to be higher in S^3 -mode, say at pH 3 the number of recycles
242 obtained for Cr^{6+} reduction were 8, 9, and 13, and at pH 7, the same were found to be 3, 5, and
243 6 for separate, sequential and S^3 modes, respectively. Hence Cr^{6+} reduction with co-
244 contaminant phenol degradation can be achieved without extra addition of mZVI compared to
245 the other two systems; ii) H_2O_2 was used as a reductant in acidic condition to form Cr^{3+} and as
246 an oxidant at neutral or near alkaline pH oxidizing phenol and regenerating
247 Cr^{6+} simultaneously. (the details are explained in next section). This method avoids the overall
248 treatment cost expected in sequential or separate removal where pH adjustment must be made
249 for obtaining the same results; iii) The existing theory that maintaining acidic pH conditions
250 alone can promote contaminant removal can be ruled out considering the satisfactory
251 performance in terms of Fe utilization (47% to 66%) and pollutant removal (18% to 42%) at
252 circumneutral pH. In addition, dissolved iron concentration was also reduced at this pH
253 showing a residual concentration of less than 0.005 mg/L for all the conducted experiments.
254 Also, there was no dissolution of Cr^{6+} even though the solubility of Cr^{6+} is high in aqueous
255 solutions, iv) The redox reactions can occur simultaneously as well as sequentially with the
256 help of Fe^{2+} and generated oxidants. $\text{Fe}^{2+/3+}$ recycling was found to be working better for S^3 -
257 mode than sequential-mode, during Cr^{6+} reduction at low pH and phenol oxidation at alkaline
258 pH conditions with effective utilization of mZVI. In the S^3 -mode, Cr^{6+} reduction and phenol

259 oxidation depended on Fenton's process and the reaction rates increased with time making
260 multiple cycles possible in a short span of time. For an instance, separate, sequential and S³
261 mode took 4, 3 and 0.5 h, respectively for complete oxidation of phenol at pH 7 as shown in
262 Fig. 1(b-d) and the resultant first order kinetic rates were 0.025, 0.033 and 0.053 min⁻¹,
263 respectively as given in Table S(b-d).

264 Whereas, the sequential removal experiments experienced limited cycle as listed in Table
265 S2(c), as pH gets increased under acidic pH conditions (upto pH 7.5) and addition of H₂O₂ was
266 needed to complete the reaction besides Cr⁶⁺ conversion being very slow and v) Cr⁶⁺ removal
267 with simultaneous phenol degradation can be achieved without extra addition of mZVI and pH
268 adjustment. Above all, the sustenance of the simultaneous removal depends on the
269 concentration of Fe²⁺, a least of 0.02 mg/L of Fe²⁺ must be present in the current system for
270 further Fe^{2+/3+} cycling. Below this Fe²⁺ concentration, there was no S³-mode of pollutants.

271 **3.2 ROLE OF MZVI**

272 Ball milled mZVI acted as an effective reactive material and has provided a new dimension in
273 overcoming the limited usage of ZVI and the major factors hindering the sustainability of
274 Fenton's process in groundwater remediation. Compared to bulk gZVI, mZVI was capable of
275 45-68% of better and consistent phenol degradation in separate-mode (Ambika et al.,2016; Fu
276 et al.,2013; Kabdasli et al.,2010; Keenan and Sedlak.,2008; Neyens and Baeyens,2003; Obiri et
277 al.,2014) with lesser secondary sludge production. Similar results were observed with separate
278 Cr⁶⁺ reduction systems as well. With mZVI, the system experienced an initial lag time and
279 subsequent delay in reaction at all pH conditions. The initial lag time of 5 to 10 min was
280 observed between mZVI addition and phenol or Cr⁶⁺ removal which is exactly the time needed

281 for the generation of iron corrosion products such as Fe^{2+} and FeOOH for its action on
282 pollutants (Fig. 1(a-d)). In many situations, it is advantageous to delay the reaction and allow a
283 small lag time for effective interaction between the contaminant and ZVI. In case of gZVI, the
284 lag time was 0.5 to 1 h which further hinders the initiation of reaction and offered required
285 time enabling the precipitation. Compared to gZVI mediated experiments (Fig. S2), mZVI are
286 found to be better in Fe utilization by 48 -68%, improved the interaction between Fe^{2+} ions and
287 H_2O_2 by 25-32% promoted good radical generation by 12-48%, and effective $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycling
288 by 50-70%, along with 88% less precipitation and only less than 2% unreacted mZVI and
289 meagre sludge production. The kinetic rates of different systems using gZVI (2000 mg/L
290 depicting the same specific area as 20 mg/L of mZVI) was represented in Table S3 and Fig.
291 2(d-f) for three different modes of experiments, shows that gZVI performed about 10 folds
292 lesser than mZVI (Table S2(a-c)). The experiments conducted with 20 mg/L of gZVI resulted in
293 lethargic removal of pollutants in 24 h that showed minimum 1000 times lesser kinetic rates
294 than mZVI, and hence the discussion on that experiments were omitted.

295 Though Cr^{6+} reduction can be achieved with mere H_2O_2 in pH controlled systems, addition of
296 mZVI as reactive media enhances Cr^{6+} reduction and minimises Cr precipitation, as $\text{Cr}(\text{OH})_3$
297 particularly in the presence of an aromatic organic compound like phenol. This may be the
298 reason for thin passive layer associated with mZVI. During this transformation, suggested
299 mechanism of phenol removal included formation of ferric oxyhydroxide [$\text{Fe}(\text{OH})_3$] from
300 oxidation of mZVI and oxidation by Cr^{6+} itself.

301 With mZVI, the reduced Cr^{3+} may get incorporated into the growing surface oxide phase
302 rendering Cr^{3+} inert and unreactive at low pH (Namkung et al., 2008; Nayens and Baeyens,
303 2003). Typically, $\text{Fe}(\text{III})$ and Cr^{3+} are likely to form $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ complex which obstructs

304 precipitation and Fe(0) passivation in case of mZVI (Pan et al.,2017). Acidic pH enhanced iron
305 dissolution by 22% resulting in $\cdot\text{OH}$ radical production and 7% more in the solution than on
306 the mZVI's surface. All these were missing in gZVI due to its reluctant corrosion.

307 The other major factor affecting the pollutant removal is the probability of contact between the
308 catalyst $\text{Fe}^{0/2+/3+}$ and contaminates Cr^{6+} or phenol which is controlled by the thickness and
309 nature of surface passivation. Fig. 3(a-c) shows the microscopic images of surface and cross-
310 sections (c/s) of mZVI and gZVI during and at the end of experiments. It is well known that
311 the Fe/Cr oxide precipitation and further passive layer formation decide the diffusion of Fe^{2+}
312 ions from core ZVI towards the aqueous contaminant solution for its removal. Fig. 3(a) shows
313 spongy precipitation and presence of thin ($\sim 2 \mu\text{m}$) and micro-porous passive layer structure in
314 mZVI which favoured Fe^{2+} dissolution, and pore-scale and bulk-liquid electron transfer
315 reactions. With gZVI, it was hardened precipitation and non-porous thick passive layer (~ 100
316 μm) which hampered the reactions. As a whole, the ability of Fe^{2+} ions to transport through the
317 passive layer is likely to happen only with mZVI. The slow and continuous release of Fe^{2+} may
318 allow easy and consistent contaminant migration across the newly formed iron oxide. Unlike
319 gZVI, where passivation ensues soon after the reaction, mZVI continuously released Fe^{2+} and
320 thereby enhanced contaminant removal under all pH conditions albeit at a lower rate. This
321 microscopic images of gZVI and mZVI supported and validated the experimental data and
322 speculations of the crucial performance of mZVI compared to the PRB-applied gZVI.

323 It is also well-known fact that Cr^{6+} reduction would occur within the matrix of iron corrosion
324 products besides the reduction reactions on the undissolved ZVI surface which takes own time
325 to form (Jiao et al.,2009; Liu et al.,2006; Mielczarski et al.,2005; Noubactep.,2008; Obiri et
326 al.,2014; Ryu et al.,2011; Yang et al.,2018; Yao et al.,2019; Yoon et al., 2011; Zhang et

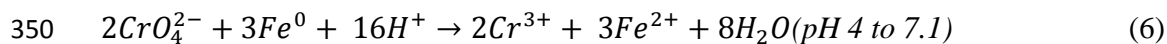
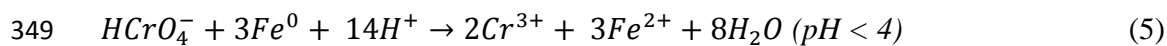
327 al.,2019). At low pH, removal of phenol may be due to the adsorption or the complex
328 formation of phenol with the newly formed surface ferric oxide phase (Namkung et al.,2008;
329 Nayens and Baeyens, 2003). However, this study observed no adsorption and no changes in pH
330 value during reductive transformation proving that $\cdot\text{OH}$ concentration and catalytic activity of
331 mZVI dominated the entire coupled process.

332 3.3 REACTION MECHANISM AND KINTEICS

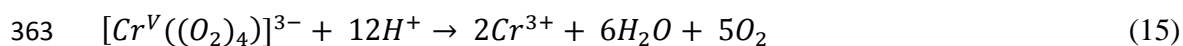
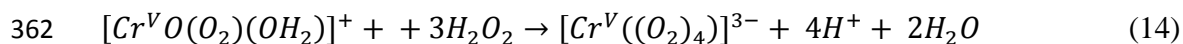
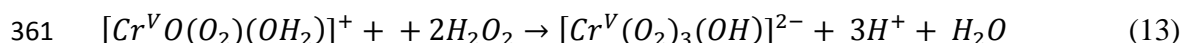
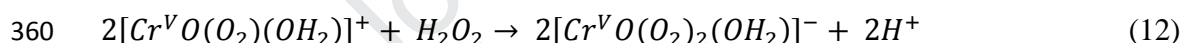
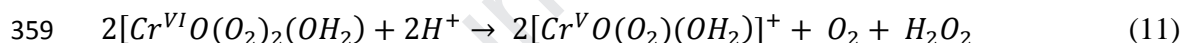
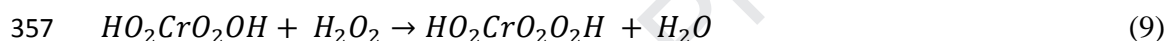
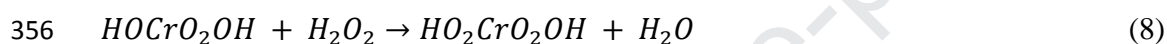
333 Cr^{6+} reduction can occur via the reactions (5-22) dominated by the form of Cr^{6+} at different
334 pHs. The coupled mode of treatment exhibited no change in pH of the solution during reaction
335 time as shown in Fig. 1(c-d) and hence no change in removal percentage of the Cr^{6+} and phenol
336 between buffered and unbuffered system. The predominance diagram of Cr-H₂O showed that
337 HCrO_4^- being the dominant form of Cr^{6+} till pH 6.8 and CrO_4^{2-} for neutral and alkaline pH
338 conditions. The pe-pH relationship shown in Table S4 also reinstates that the form of Cr^{6+} is an
339 influencing factor in transformation of the contaminant.

340 At $\text{pH} \leq 4$, pe for $\text{HCrO}_4^-/\text{Cr}^{3+}$ is greater than $\text{H}_2\text{O}_2/\text{O}_2$ proving that Cr^{6+} is the better oxidant
341 than H_2O_2 and Cr^{6+} underwent reduction to Cr^{3+} . With 1.5 mM H_2O_2 , the system witnessed
342 92.1%, 66%, 22.8%, 3.89% and 0.03% Cr^{6+} reduction at pHs 3, 4, 6, 7 and 7.1 respectively. The
343 reduction reaction at pH 4 to 7.1 is because of the presence of CrO_4^{2-} species in aqueous
344 solution for which the pe value of $\text{CrO}_4^{2-}/\text{Cr}^{3+} > \text{H}_2\text{O}_2/\text{O}_2$ till pH 7.1. There was neither Cr^{6+}
345 evolution from Cr^{3+} observed for the next 24 h for $\text{pH} \leq 7.1$ nor Cr^{6+} reduction after $\text{pH} > 7.1$
346 detected by H_2O_2 (pe values for $\text{CrO}_4^{2-}/\text{Cr}^{3+} < \text{H}_2\text{O}_2/\text{O}_2$).

347 The remaining Cr^{6+} removal is taken by the electron transfer reactions from $\text{Fe}^{0/2+}$ as shown in
348 reactions (5 and 6) (Anah and Astrini, 2017; Pouloupoulou et al.,1997).

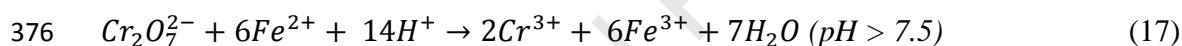
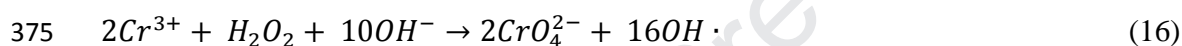


351 Mauriziopettine *et al* proposed an intermittent formation of highly unstable Cr^{5+} species in
 352 H_2O_2 enabled Cr^{6+} reduction subsequently converted to stable Cr^{3+} form through one-electron
 353 transfer reactions from a coordinated peroxo-group to the central chromium, which is probably
 354 facilitated by protonation as indicated in reactions (7-15) (Pettine et al.,2002).



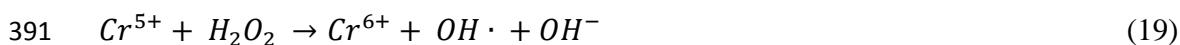
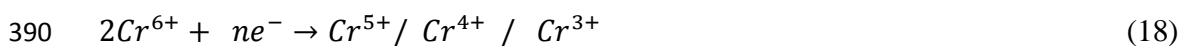
364 The pe-pH relationship of different species of Cr^{6+}/Cr^{3+} , H_2O_2/O_2 pairs as shown in Table S4
 365 figured out the reducing action of H_2O_2 on Cr^{6+} .

366 At pH>7.1, where the form of Cr⁶⁺ subsequently shifts to Cr₂O₇²⁻, H₂O₂ was found to be
 367 superior as an oxidant compared to Cr⁶⁺ species. (At pH<4, Cr⁶⁺ performed better as an oxidant
 368 than H₂O₂). At circumneutral pH of 7, newly formed Cr³⁺ exhibited maximum oxidative
 369 capacity and regenerated Cr⁶⁺. At this point, through Cr³⁺-Cr⁶⁺-Cr³⁺-Cr⁶⁺ cyclic reaction is
 370 important due to the formation of ·OH radicals. The influence of Fe²⁺ determines the fate of
 371 Cr⁶⁺ under typical groundwater conditions where pH is circumneutral. For this reason, Cr³⁺
 372 formed from Cr⁶⁺ reduction which can easily be precipitated as insoluble Cr(OH)₃ at neutral
 373 and alkaline pH, was regenerated to soluble Cr⁶⁺ leaving no Cr⁶⁺ concentration in the aqueous
 374 solution according to reactions (16 and 17).



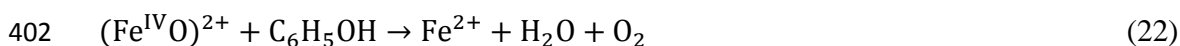
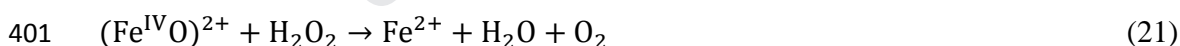
377 The resultant Cr⁶⁺ was immediately reduced by Fe²⁺ present in the system and hence no
 378 shuttling back of Cr⁶⁺ was observed. Fe²⁺ fixes the fate of Cr⁶⁺ under typical groundwater
 379 conditions where pH>7.2. The Fe²⁺ enabled Cr⁶⁺ reduction rate was one order more than H₂O₂
 380 mediated Cr³⁺ oxidation. When phenol is present as a co-contaminant, ·OH radical generated by
 381 Cr^{3+/6+} cycles offers additional treatment efficiency. It was observed that 1.5 mM H₂O₂ can
 382 oxidize 0.088%, 6.06%, 5.24%, 3.25% of Cr⁶⁺ at pH 7.2, 7.5, 8 and 10, when 2 mg/L of Cr³⁺
 383 was added and the respective phenol removal was 0.019%, 1.25%, 3.88% and 2.46%. Hence
 384 Cr⁶⁺ via Fenton-like activation of H₂O₂ favors the phenol removal in coupled Cr⁶⁺ and phenol
 385 removal at circum-neutral and alkaline pH (Bakac and Espenson, 1983). Using Cr⁶⁺ for
 386 Fenton-like activation of H₂O₂ favors the purpose of coupled removal. Also, it was observed
 387 that a sequential of chromium intermediates like Cr⁴⁺ and Cr⁵⁺ may directly react with H₂O₂

388 and produce powerful $\cdot\text{OH}$ radicals again to oxidize phenol as indicated in reactions (Bakac
389 and Espenson, 1983; Luo et al., 1996; Liu et al., 2001; Shi et al 1994).



392 Though the above reactions are strongly favored at acidic pH, the reactive chromium
393 intermediates were formed in wide pH range and hence the oxidation of phenol was achieved
394 even in neutral and near-alkaline conditions (Bokare and Choi, 2011). Hence using Cr^{6+} for
395 Fenton-like activation of H_2O_2 favors the purpose of coupled removal.

396 It is also possible that at circum-neutral pH of 7, the nonselective $\cdot\text{HO}$ radical was
397 replaced by a highly selective Ferryl radical (20 to 22) that promoted oxidation of phenol.
398 Beyond neutral pH, degradation rate of phenol decreased with decreased reactivity of Cr^{3+} with
399 H_2O_2 .



403 When surface $\cdot\text{OH}$ radicals become too weak to participate in the degradation process, Ferryl
404 radical was found to play an important role and is reported to have a longer lifetime in solution
405 even in the absence of H_2O_2 . The role of H_2O_2 on the redox cycling of $\text{Cr}^{3+}/\text{Cr}^{6+}$ and
406 $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycling for coupled removal of chromium and phenol without pH adjustment, without

407 regenerating Cr^{3+} and without addition of mZVI was thus verified in S^3 -mode and represented
 408 in the graphical abstract.

409 The mechanism was verified by two additional experiments as given in Fig. 2(c), (i) Excess
 410 phenol and maintaining the same concentration of Cr^{6+} and mZVI and (ii) Excess chromium
 411 and same amount of phenol and mZVI. The first case represented the negative effect of phenol
 412 concentration on Cr^{6+} reduction, where the excess phenol than typical (5 mg/L) was used,
 413 Fe^{2+} was exhausted for radical production and hence only a scanty supply of electrons or role as
 414 Cr^{6+} reducing agent was observed. With Cr^{6+} being excess, phenol oxidation was less at acidic
 415 and neutral pH owing to the fact H_2O_2 was trying to satisfy only Cr^{6+} reduction. At alkaline
 416 pH, $\cdot\text{OH}$ production and phenol oxidation occurred with the help of newly formed Cr^{3+} (Bokare
 417 and Choi, 2010; Shi and Dalai, 1994). The whole mechanism was verified by conducting
 418 different sets of experiments as detailed in Fig. S4.

419 Reaction kinetics were obtained for separate, sequential and S^3 -mode of both contaminants.
 420 The reduction rates of Cr^{6+} and oxidation rates of Phenol were characterised by pseudo first
 421 order rate equation. The data are expressed in terms of the first order rate constant (min^{-1}).
 422 However, in the S^3 -mode, the reaction rates increased with time making multiple cycles
 423 possible in a short span of time. The kinetic constant was reduced from the first value of 0.203
 424 min^{-1} to lower values in the subsequent treatment cycles (Table S2(a-c)).

425 The pseudo first order equation of the reductive transformation of Cr^{6+} in this study is given as

$$426 \quad \frac{dC}{dt} = -K_{pseudo}C \quad (23)$$

$$427 \quad K_{pseudo}C = K[radical] \quad (24)$$

428 It can be seen from the associated kinetic data that reduction of chromium fitted fairly
429 well with the pseudo first order equation at stoichiometric conditions ($r^2 > 0.989$) with increased
430 rates at acidic pH. The rate constant in this study is therefore in proportion to solution $\cdot\text{OH}$
431 radical concentration. At alkaline pH, radical production and phenol oxidation occurred with
432 the help of newly formed Cr^{3+} . The kinetic data also provides a non-linear plot since the
433 reaction rates were not proportional to the increase in Cr^{6+} concentration.

434 **4 CONCLUSIONS**

435 Cr^{6+} reduction and phenol degradation were investigated in gZVI and mZVI mediated
436 Fenton's system as separate, sequential and S^3 mode of experiments. More catalysis i.e. about
437 16.2 mg/L Cr^{6+} reduction and 48 mg/L of phenol removal was observed in S^3 -mode at pH 3
438 using 20 mg/l of mZVI and 1.5 mM of H_2O_2 whereas separate-mode removed 8 mg/L Cr^{6+} and
439 36 mg/L phenol and doubled the Cr^{6+} reduction and 25% increase in phenol removal. Electron
440 transfer from $\text{Fe}^{0/2+}$ to Cr^{6+} resulting in $\text{Fe}^{2+/3+}$ which in turn was consumed for phenol
441 oxidation returning Fe^{2+} back into the system for further Cr^{6+} reduction being the governing
442 mechanism showed best results when the contaminants were treated simultaneously rather than
443 separately or sequentially. At circumneutral pH of 7, H_2O_2 promotes reduction of Cr^{6+} to Cr^{3+}
444 where Cr^{3+} exhibits maximum oxidative capacity and regenerates Cr^{6+} . Cr in turn helps phenol
445 oxidation with reactive mZVI and powerful $\cdot\text{OH}$ radicals. The results recommend coupled and
446 S^3 redox mode compared to sequential or separate removal of pollutants under nearly natural
447 subsurface conditions. The reduction of Cr^{6+} depends upon the solution pH and nature of
448 mZVI particle rather than the presence of aromatic organic compound like phenol. However,
449 the reduction was more pronounced in the presence of phenol because of the synergistic effect.
450 The convincing results of coupled removal of phenol and Cr^{6+} should be encouraged to

451 incorporate redox reactions into transport models when assessing the fate of Cr⁶⁺ and phenols
452 in the environment.

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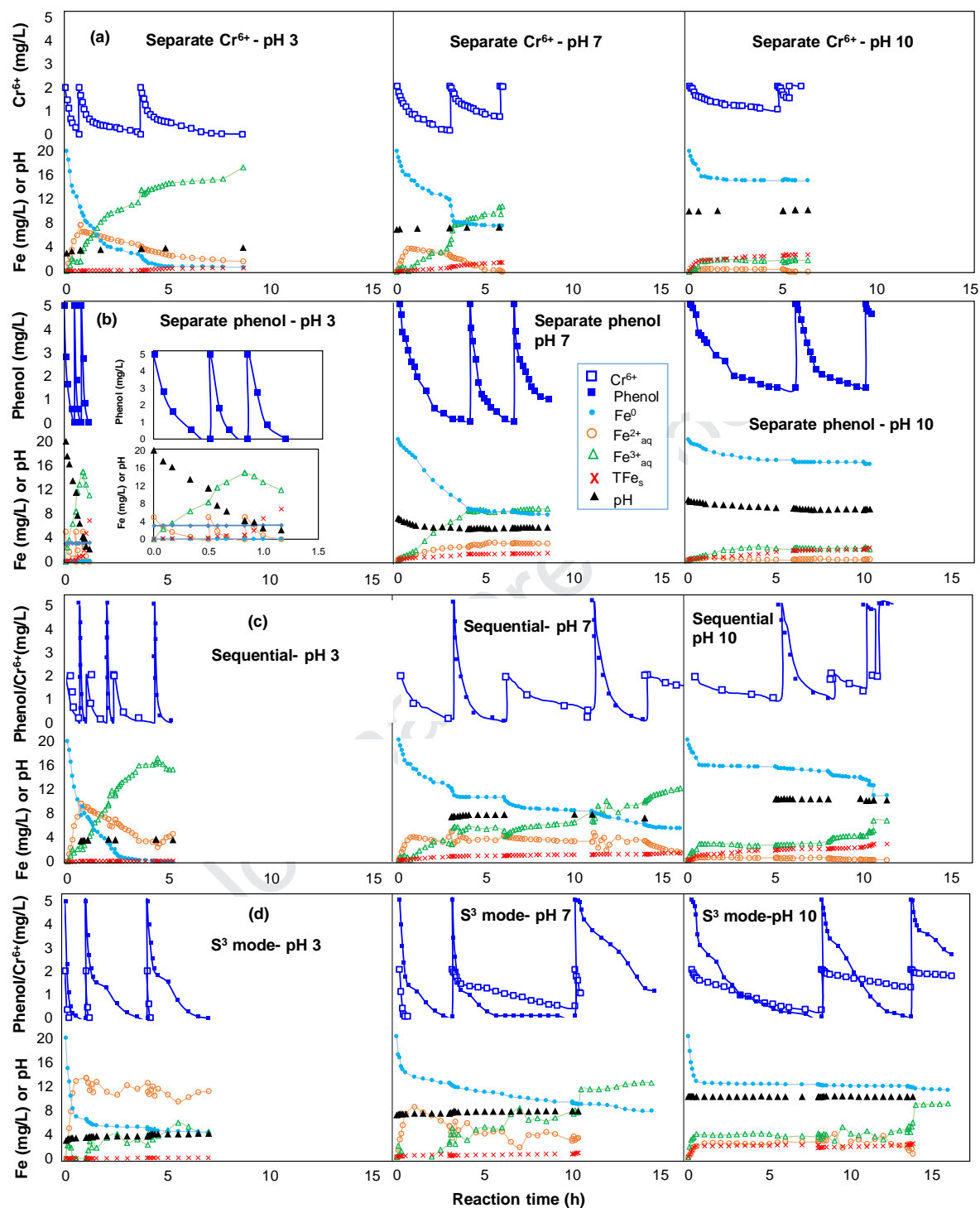
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FIGURE AND TABLES

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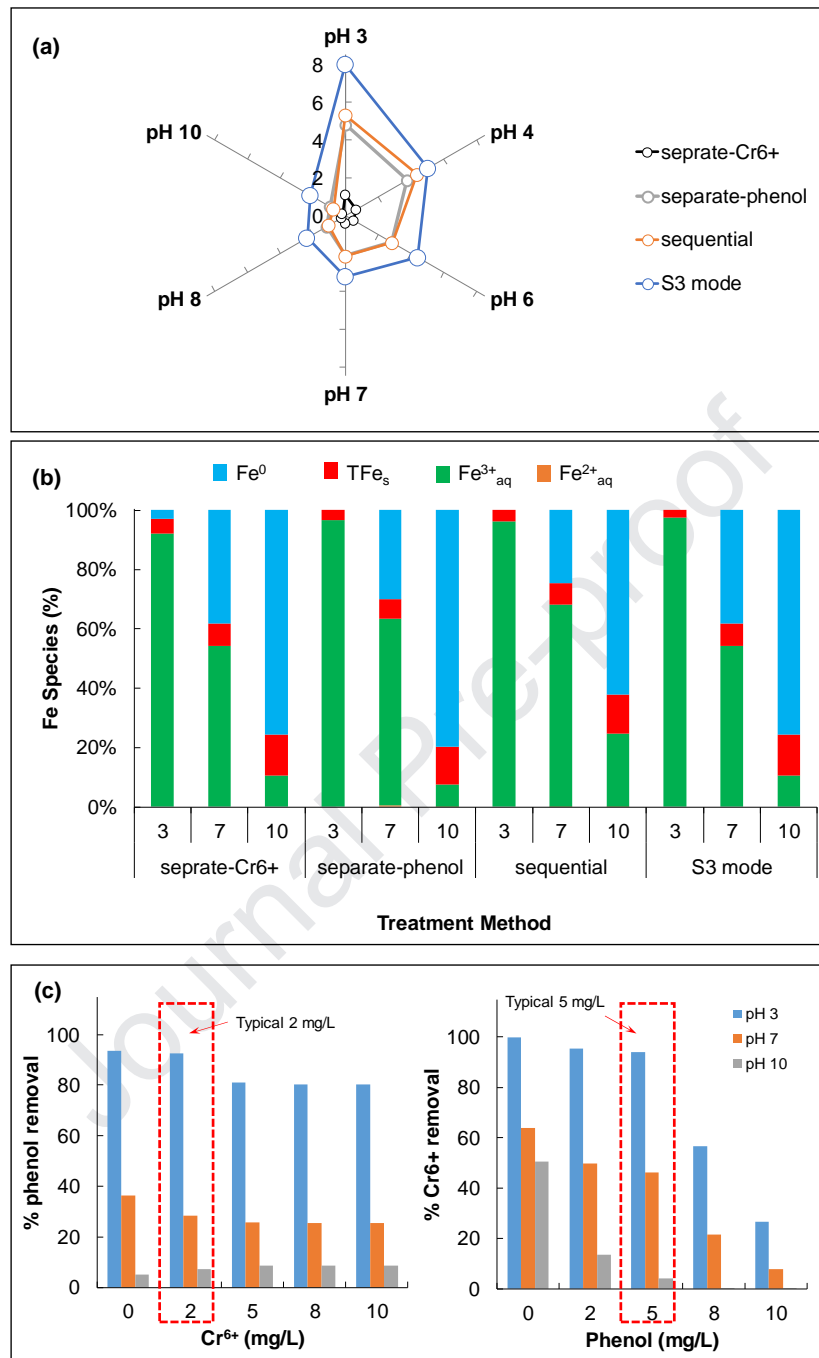
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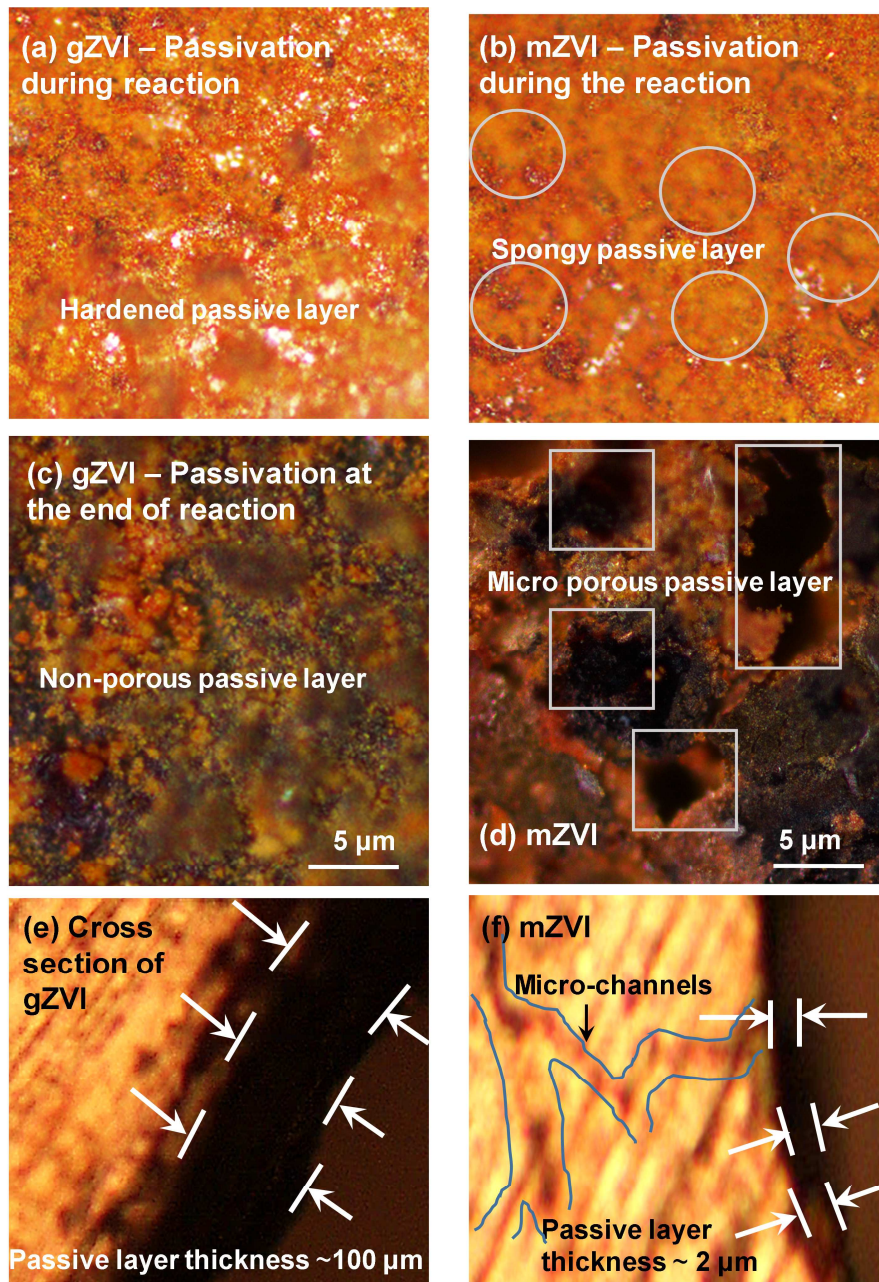
675 Fig. 1 Cr^{6+} removal and Fe transformation in different modes, mZVI=20 mg/L, Cr^{6+} =2

676 mg/L, phenol=5 mg/L



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678 Fig. 2 (a) Pollutant removal capacity of mZVI during different modes, (b)
 679 Transformation of mZVI during different modes, (c) Effect of change in concentration of Cr⁶⁺
 680 and phenol in phenol and Cr⁶⁺ removal, respectively in S³ mode (constant Cr⁶⁺=2 mg/L,
 681 constant phenol=5 mg/L), mZVI=20 mg/L, Cr⁶⁺=2 mg/L, phenol=5 mg/L.



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Fig. 3

Microscopic images of the surfaces and cross-sections of gZVI and mZVI

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HIGHLIGHTS

- Study of gZVI & mZVI based coupled toxic organic compound & heavy metal removal
- Beneficial single-step treatment synchronizing Cr⁶⁺ reduction & phenol oxidation
- More pollutant removal/unit mZVI, with least unwanted iron-sludge even at neutral pH
- pH-focus chemical speciation, mass balance & radical study at every stage of reaction
- Scrap Fe recycled mZVI in *in/ex-situ* Cr & phenol removal without buffer/stabilizer

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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