An Analysis of the Evolution of Reactive Species in Fe^0/H_2O Systems

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Abstract

Aqueous contaminant removal in the presence of metallic iron (e.g. in Fe^0/H_2O systems) is characterized by the large diversity of removing agents. This paper analyses the synergistic effect of adsorption, co-precipitation and reduction on the process contaminant removal in Fe^0/H_2O systems on the basis of simple theoretical calculations. The system evolution is characterized by the percent Fe^0 consumption. The results showed that contaminant reduction by Fe^0 is likely to significantly contribute to the removal process only in the earliest stage of Fe^0 immersion. With increasing reaction time, contaminant removal is a complex interplay of adsorption onto iron corrosion products, co-precipitation or sequestration in the matrix of iron corrosion products and reduction by Fe^0, Fe^{II} or H_2/H. The results also suggested that in real world Fe^0/H_2O systems, any inflowing contaminant can be regarded as foreign species in a domain of precipitating iron hydroxides. Therefore, current experimental protocols with high contaminant to Fe^0 ratios should be revisited. Possible optimising of experimental conditions is suggested.

Keywords: Adsorption; Co-precipitation; Iron Reactivity; Reduction; Zerovalent iron.

Capsule: A Fe^0/H_2O system should be regarded as a domain of precipitating iron oxides.

Introduction

Widespread groundwater contamination has prompted intensive efforts to find efficient and affordable remediation technologies. Recently, the introduction of in situ permeable reactive barriers for groundwater remediation [1,2] has attracted the attention of environmental researchers. Permeable reactive barriers consist of a cost-effective material which functions as

a contaminant removing agent. The contaminated groundwater flows toward the barrier, which contains a removing agent. The groundwater passing through a reactive barrier is ideally completely freed from contaminants [3-5].

In the last two decades metallic iron (Fe^0) has been extensively used in remediation schemes to effectively remove a wide variety of inorganic and organic contaminants in reactive barriers [3-6]. Ideally, Fe^0 is oxidized only from the oxidized form of the contaminant (Ox) which reduction yields a corresponding reduced form (Red) (Eq. 1 - Tab. 1). Unfortunately, water is present in stoichiometric abundance (solvent), and is corrosive to Fe^0 both under anoxic (Eq. 2) and oxic (Eq. 3) conditions ([7] and ref therein). Fe^{II} species resulting from Eq. 1 to Eq. 3 may be oxidized to Fe^{III} species by molecular O_2 or other available oxidants (Ox_1: contaminant, MnO_2) (Eq. 4a,b). Under anoxic conditions, H_2 from Eq. 2 may reduce the contaminant (Eq. 5). The process of H_2O reduction by Fe^0 obviously reduces the efficiency of the decontamination process (H_2O as concurrent for contaminant) and also increases the pH of the system, promoting the formation of iron hydroxides (Eq. 6 and 7). Iron hydroxides are then transformed through dehydration and recrystallisation to various iron oxides depending on the geochemical conditions [3,8,9]. Iron (hydr)oxides are good adsorbent for several contaminants (Eq. 9). During their precipitation, iron hydroxides may sequestrate contaminant in their matrix (Eq. 10).

The presence of iron hydroxides and other ferrous and ferric oxides (Eq. 6 to 8) causes passivation of the Fe^0 surface [3,8-10]. As an oxide layer is formed on the Fe^0 surface, a contaminant should migrate across the film to adsorb on the Fe^0 surface and undergo reduction. Alternatively, the oxide layer should be electronic conductive to warrant electron transfer [11,12]. On the other hand Fe^{II} adsorbed on a mineral surface (structural Fe^{II} or $Fe^{II}_{(s)}$) has been reported to be a very strong reducing agent, suggesting that beside Fe^0 and H_2, dissolved Fe^{II} and structural Fe^{II} are further contaminant reducing agents in Fe^0/H_2O systems (table 1).

53 The ongoing discussion over the relative importance of adsorption and reduction on the

54 process of contaminant removal in Fe^0/H_2O systems [3,9-14] illustrates the challenge in

55 assessing the environmental relevance of laboratory results. The potential of Fe^0/H_2O systems

56 for reductive transformation of various contaminants is well-established. However, the precise

57 mechanism and the extent of reductive transformation remains controversial and has been

58 recently kindled by considering the importance of contaminant co-precipitation [15,16].

59 The most important feature characterizing a Fe^0/H_2O system is that the weight fraction of iron

60 corrosion products increases from zero at the beginning of the experiment to more or less

61 higher proportions depending on the reaction progress (Fe^0 consumption). The large changes

62 in the solid composition during the reaction certainly influence the mass transfer of species to

63 the Fe^0/H_2O interface and thereby play a significant role in the determination of reaction rates.

64 However, as corrosion products are not inert, they actively participate to contaminant

65 removal. The present communication aims at using theoretical calculations (computer-based

66 analysis without numerical simulation) to better understand the reactivity of Fe^0/H_2O systems

67 toward contaminant removal. Clearly, simulations for a well-thought-out experimental plan

68 will be given. From the simulation results, a discussion of the suitability of experimental

69 conditions will be given. The main goal is to purchase researchers with a solid guidance for

70 purposeful experimental design for the investigation of Fe^0/H_2O systems.

71 **Background**

72 Contaminant removal in Fe^0/H_2O systems is neither a purely chemical/electrochemical

73 reduction nor a purely physical adsorption process. Rather, it is the result of a complex

74 interplay of processes (adsorption, co-precipitation, reduction) dependent on Fe^0 type

75 (intrinsic reactivity), temperature, water chemistry, hydrodynamic conditions, and microbial

76 community. The literature is overwhelmingly dominated by studies considering Fe^0 as the

77 primary reductant for contaminants (direct reduction) [4-6,11,12,17]. It has been recently

78 suggested that the chemical reactivity of Fe^0 (iron corrosion) has not been properly considered

79   while using Fe^0 as remediation medium [15,16]. In fact, as discussed above, the Fe^0 reactivity

80   yielding contaminant removal is not necessarily an intrinsic property (reduction by electrons

81   from Fe^0). Contaminant removal could be mostly associated with primary (Fe^{II}, H/H_2) and

82   secondary (iron oxyhydroxides) iron corrosion products. This suggests that the effectiveness

83   of Fe^0 for abiotic contaminant removal might be mostly related to the above-enumerated

84   process-specific factors (temperature, water chemistry, and hydrodynamic conditions) [15].

85   Furthermore, the presence of other substances ("electron shuttles"), and impurities with

86   catalytic effects might be important for the process of contaminant removal in Fe^0/H_2O

87   systems [4,12]. The next section discusses the relative importance of the reactive species in

88   Fe^0/H_2O systems.

Evolution of reactive species in a Fe^0/H_2O system

90   A Fe^0/H_2O system is primarily made up of elemental iron (Fe^0) and an aqueous solution

91   (H_2O). Considering for simplification, that Fe^0 is initially freed from atmospheric corrosion

92   products (e.g. acid washed and vacuum dried), the initial system (t = 0) contains only Fe^0 as

93   reactant (adsorbent and/or reductant) for dissolved species (including contaminants). Aqueous

94   iron oxidation (immersed corrosion) is known to be effective both under anoxic and oxic

95   conditions [18,19], yielding at the term a layer of primarily non-protective oxide film on Fe^0

96   [20,21]. Therefore, from the early stage of iron immersion on, the impact of in situ generated

97   reactants (Fe^{II}, H/H_2, iron hydroxides and oxides) should be properly discussed. Moreover,

98   once the oxide film is formed it constitutes a physical barrier shielding the Fe^0 surface from

99   dissolved species [15,22,23]. To reach the Fe^0 surface any dissolved species has to move

100   across the oxide film. With regard on the quantitative evolution of reactive species in Fe^0/H_2O

101   systems, a purposeful system analysis has not been performed by the pioneers of the iron

102   barrier technology. In fact, they mostly considered the low potential (-0.44 V) of the redox

103   couple Fe^{II}/Fe^0 to explain the observed contaminant reduction in Fe^0/H_2O systems [11,12].

104   However, a survey of the electrode potentials of the redox couples of iron (-0.44 V for

105 Fe^{II}/Fe^0 and -0.35 to -0.65 V for $Fe^{III}_{(s)}/Fe^{II}_{(s)}$ [24]) suggests that, from a pure thermodynamic

106 perspective, in some circumstances (E < -0.44 V), contaminant reduction by $Fe^{II}_{(s)}$ might be

107 more favourable than reduction by electrons from Fe^0. From a pure qualitative perspective it

108 can be concluded that investigations of contaminant reduction by Fe^0 (direct reduction) have

109 to be performed under conditions where the interferences of all other removal processes

110 (adsorption, co-precipitation and indirect reduction) are absent or minimal. This premise

111 implies, that the formation of Fe corrosion products should be kept as low as possible.

112 Therefore, (i) too large Fe^0 loadings should be avoided and for a given Fe^0 loading, (ii) too

113 intensive mixing operations should be avoided. The next section will illustrate this on a

114 quantitative perspective.

115 **Quantification of Reactive Species in a Fe^0/H_2O System**

116 To demonstrate the importance of in situ generated reactants on the process of contaminant

117 removal in Fe^0/H_2O systems, lets consider contaminant removal experiments with 0 to 50 g L$^-$

118 ^{1} of an iron-based alloy (Fe^0 material) containing 92 % Fe. The experiments are performed at

119 pH > 4 in 20 mL of an aqueous solution containing a reducible contaminant (Ox) which

120 reduced form (Red) is harmless or low soluble. Whether Red remains in solution or not, is it

121 operationally considered in this work as removed. The aqueous speciation of Ox and Red and

122 thus their affinity to adsorptive surfaces is necessarily pH dependant. At pH > 4 the iron

123 surface is covered by insoluble oxide layers [18,22]. Whether the contaminant is reduced or

124 not, it might be removed from the aqueous phase by adsorption and/or co-precipitation

125 [15,25-27]. Therefore, "contaminant removal" and "contaminant reduction" should never be

126 interchanged randomly. Moreover, when a contaminant is effectively reduced the exact

127 reduction mechanism (direct or indirect) is difficult to access. In the field the situation is

128 exacerbated by microbial mediated reduction. The question arises whether it is possible to

129 distinguish between adsorption, co-precipitation, and reduction in laboratory experiments.

Adsorption, Co-precipitation, or Reduction?

Figure 1 depicts the results of the simulation of contaminant removal by: (i) direct reduction (Fig. 1a), (ii) physical adsorption (Fig. 1b), and (iii) co-precipitation (Fig. 1c) when 1 to 10 % of the initial amount of iron has reacted ($n_0/100$ to $n_0/10$). Reduction by $Fe^{II}_{(aq)}$, $Fe^{II}_{(s)}$, H_2/H (indirect reduction) is not considered for simplification. For comparison, a reference system without Fe^0 addition (blank) is presented. It is assumed that the contaminant is reduced by Fe^0 in a 1:1 ratio (**assumption 1**), that each mole of contaminant is adsorbed by two moles of FeOOH (**assumption 2**), and that each mole of contaminant is co-precipitated with four moles of $Fe(OH)_2$ or $Fe(OH)_3$ (**assumption 3**), FeOOH and $Fe(OH)_2$ resulting from Fe^0 oxidation. Assumption 2 is made to account for large molecules while assumption 3 is somewhat arbitrary but intends to considered the non-specific nature of co-precipitation (simple sequestration or entrapment, physical process). The simulated systems contains 100 μmoles of contaminant in 20 mL (5 mmol L^{-1}). This corresponds for instance to 260 mg L^{-1} Cr^{VI}, 1.190 mg L^{-1} U^{VI}, 562.5 mg L^{-1} chlorophenol, or 1.596 mg L^{-1} methylene blue. This initial concentration is roughly one order of magnitude higher than those currently used in removal experiments for natural waters and wastewaters. Such a large initial concentration was nevertheless used to evidence the abundance of corrosion products relative to available amounts of contaminant.

From Fig 1a it can be seen that under given experimental conditions, contaminant reduction (assumption 1) is quantitative for all tested extents of Fe^0 consumption (1 to 10 %) for Fe^0 loadings equal or higher than 35 g L^{-1}. At the same time, at least 57 % of the initial available contaminant could have been removed by pure adsorption (assumption 2) onto FeOOH (Fig 1b) and 29 % by non-specific co-precipitation (assumption 3) with $Fe(OH)_2$ (Fig 1c). As soon as corrosion products ($Fe(OH)_2$, $Fe(OH)_3$) start to precipitate they inevitably adsorb Fe^{II} from continuously corroding Fe^0 yielding more reductive adsorbed Fe^{II} (so-called structural Fe^{II}) for contaminant reduction. Figure 1b clearly shows that for 10 % Fe^0 consumption ($n_0/10$)

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more than 80 % of the initial amount of contaminant could be removed from the aqueous solution by pure physical adsorption for all tested Fe^0 loadings ($5 \geq$ g L^{-1}). From Fig. 1c it can be seen that at least 42 % could be removed by co-precipitation with in-situ formed corrosion products. These results suggest that when a 5 mmol L^{-1} contaminant solution is treated by 5 g L^{-1} Fe^0 (containing 92 % Fe), and only 10 % of the used Fe^0 reacts, contaminant removal by (i) direct reduction, or (ii) pure adsorption onto in situ generated corrosion products may be quantitative (> 80 % removal efficiency). In the same time the contribution of co-precipitation for contaminant removal could be more than 40 %. The minimal resulting percent molar ratio Fe/Ox is 60 %. This means that less than 40 % contaminant in a matrix of initially amorphous iron oxide matrix. Therefore, when a too high Fe^0 loading is used in an experiment, distinguishing the mechanism responsible for contaminant removal is a very complex issue (see below). Furthermore, because contaminants (Ox) and reduction products (Red) might co-precipitate with iron corrosion products, the extent of contaminant reduction is difficult to assess. Moreover, because removed Ox and Red are partly sequestrated in the matrix of iron corrosion products a purposeful mass balance can only be done if corrosion products are completely digested. Contrary to the simulated case of this work (5 g L^{-1} Fe^0), studies using less than 20 g L^{-1} Fe^0 are scarce. Furthermore, experiments are sometimes performed under high mixing conditions (up to 500 min^{-1}) [28,29], possibly yielding a larger extent of Fe^0 consumption (> 10 %) for tested experimental durations and thus data that are more difficult to interpret as shown in the next section.

Chemical transformation vs. physical processes

To further evidence the importance of experimental conditions for the significance of expected results, the processes in a Fe^0/H_2O system can be abstractly considered independent and subdivided into chemical transformations (contaminant reduction, iron hydroxide precipitation) and physical processes (contaminant adsorption, contaminant co-precipitation). With respect to contaminant removal, all chemical transformations are called reduction and

182 physical processes are called fixation (Fig. 2). Fixation is thus the sum of adsorption and co-

183 precipitation while only direct reduction is considered. Figure 2 shows clearly that for 1 %

184 material consumption (Fig. 2a) the extends for contaminant fixation and contaminant

185 reduction are very closed for all Fe^0 loadings. Therefore, if the studied contaminant is reduced

186 to a low soluble species (e.g. U^{VI} to U^{IV}), contaminant removal is twice larger than

187 contaminant reduction. For organic contaminant the result is quite the same as the processes

188 are considered independent, the difference is that reduced species remain in the aqueous phase

189 and the strength of contaminant fixation may be lower. For 10 % material consumption (Fig.

190 2b), both contaminant reduction and contaminant fixation are quantitative (100 %). This result

191 corroborates the statement that low Fe^0 loadings should be used when reduction is to be

192 investigated. This operation targets at avoiding large amounts of corrosion products. But

193 which real world situation should be simulated by low Fe^0 loadings or low amounts of iron

194 (hydr)oxides?

195 Although the iron wall technology is demonstrably efficient, the presentation above

196 demonstrates that reported experiments are disconnected from reality. In fact, the main

197 conclusion from the hitherto presentation is that in nature, contaminants flowing into a

198 Fe^0/H_2O system are foreign species in a system of precipitating iron oxide (**statement 1**). This

199 situation is illustrated by Fig. 3. Figure 3 shows the evolution of the molar ratio contaminant

200 to Fe (Ox/Fe) in the simulated batch systems as function of the Fe^0 loading. It can be seen that

201 when the Fe^0 consumption varies from 1 to 10 % the Ox/Fe-values vary from 86 to 6 %.

202 Material consumption of 1 to 5 % can be attributed to the initial stage of the barrier

203 installation, with increasing service life Fe^0 consumption will increase to reach 100 % at

204 depletion. Therefore, systems with high Ox/Fe-values (e.g. > 25 %) are not likely to be

205 encountered in nature where diluted contaminated waters come in contact with an iron bed

206 (Fe^0 covered with an oxide layer). However, systems with high Ox/Fe-values are the most

207 currently investigated in the laboratory, particularly in batch experiments. In long term

208   column experiments with significantly low initial contaminant concentrations on the contrary

209   relevant results can be achieved.

210   In conclusion, theoretical calculation demonstrates that contaminant removal in Fe^0/H_2O

211   systems is necessarily a synergistic effect of adsorption, co-precipitation and reduction. The

212   resulting removal extent is much more than that of their separate effects. While adsorption

213   and reduction have been largely considered, co-precipitation has been mostly overseen (in

214   particular for organic species). The theoretical calculation shows that to properly investigate

215   contaminant reduction, investigations should be performed under conditions where corrosion

216   products are minimal: e.g. early stage of Fe^0 immersion and under experimental conditions

217   avoiding rapid corrosion. Moreover, results from such investigations will only be of

218   qualitative value because in field Fe^0/H_2O systems, corrosion products are abundantly present

219   before contaminant inflow.

220   **Improved Experimental Conditions**

221   Typically, factors controlling Fe^0 consumption (Fe^0 reactivity) have been treated

222   independently and with use of a variety of methodologies, for example: hydrogen production

223   [30,31]; Fe^0 oxidative dissolution in ethylenediaminetetraacetic acid - EDTA [32,33] or more

224   commonly, the extend of contaminant removal [34,35]. Experimental measurements of

225   aqueous contaminant removal coupled to Fe^0 consumption are usually normalized to Fe^0

226   specific surface area [36]. However, the Fe^0 area is only one of numerous reactivity factors.

227   Therefore, it is difficult to compare published kinetic data. To circumvent this inherent

228   difficulty, the analysis in this study has considered the percent Fe^0 consumption. It is obvious

229   that the kinetic of consumption depends on several factors [11,32,34,37] like Fe^0 size (nm,

230   μm, mm), Fe^0 composition (C, Cr, Ni contents), water temperature, water chemistry, and

231   hydrodynamic conditions. All these factors will influence the nature and crystallinity of

232   formed corrosion products and possibly the strength of contaminant fixation. However, for the

233   present discussion considers solely the abundance of Fe^0 corrosion products.

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234 To minimize the abundance of iron corrosion products in a Fe^0/H_2O system, the following

235 operations can be undertaken: (i) use the lowest possible Fe^0 loading (e.g. < 5 g L^{-1}); (ii) work

236 under non-disturbed conditions (mixing speed 0 min^{-1}) or low mixing conditions (e.g. $<$

237 critical value to be identified in preliminary studies); (iii) used a less reactive material; (iv)

238 work at low temperature (e.g. 15 °C). From the discussion above, it is evident that the

239 minimization of the abundance of iron corrosion products is a tool to investigate the role of

240 Fe^0 on the process of contaminant reduction. Because in a real world reactive wall corrosion

241 products are available and abundant prior to contaminant inflow, a more purposeful approach

242 is to characterize the process of contaminant removal in the $Fe^0/Fe_xO_y/H_2O$, Fe_xO_y

243 representing the in situ generated oxide film on Fe^0. For this purpose the systems could be

244 preconditioned by several ways to obtain different amounts of Fe_xO_y in the starting systems.

245 The simplest way is to allow oxide film formation in time series, for example 0 to 6 weeks

246 before the beginning of the experiment (t = 0; time of contaminant addition) with an acid-

247 washed Fe^0. After a given reaction time (t $>$ 0; e.g. three weeks) the extent of contaminant

248 removal and the strength of contaminant fixation can be purposefully discussed. In discussing

249 the strength of contaminant fixation, it should be kept in mine that a co-precipitated

250 compound can only be released when iron (hydr)oxide is dissolved.

251 **Conclusions**

252 This study has presented an analysis of the evolution of reactive species in Fe^0/H_2O systems

253 with relative little attention on published results. The discussion is performed on a relevant

254 case study for Fe^0 conversion/consumption varying from 1 to 10 %. Although the commonly

255 cited reaction for reducible contaminant removal in Fe^0/H_2O systems is given by Eq. 1 (also

256 see table 1), the simulations of this study demonstrated that direct reduction by Fe^0 is only one

257 of three potential contaminant reducing mechanisms and is not always the more favourable on

258 a pure thermodynamic perspective. Furthermore, contaminant adsorption and co-precipitation

259 always occur (table 1)

$$Fe^0 + Ox \Rightarrow Fe^{II} + Red \qquad\qquad (1)$$

The oxidative dissolution of Fe^0 (iron corrosion) yielding aqueous contaminant removal has been extensively studied by environmental scientists during the past two decades. However, previous studies have generally concentrated on systems with high contaminant abundance (relative to Fe corrosion products). Such systems are non-representative for field situations as a rule. Therefore, existing models for designing iron barriers and predicting their long-term performance are based on results from inappropriate experimental conditions. Consequently, these models should be revisited. When revisiting available models, the first key question to address is, what are the processes relevant at the interface $Fe^0/Fe_xO_y/H_2O$? Experimental work on this issue is required before geochemical remediation strategies with Fe^0 be effectively revisited.

This article has demonstrated the importance of appropriate system analysis as a scientific method [38] prior to cost-intensive experimentations. The presented geochemical system analysis clearly indicates that in a real world Fe^0/H_2O system, any contaminant can be regarded as foreign species in an "ocean" of iron oxides (**statement 1**). Statement 1 should be used as primary point of departure for the future investigations and/or for re-evaluation of the abundant literature on environmental remediation with metallic iron.

Acknowledgments

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370

370 **Table 1**: Survey of reactive species for contaminant removal in a Fe^0/H_2O system. Fe^0,

371 $Fe^{II}_{(aq)}$, $Fe^{II}_{(s)}$, and H_2 are possible reducing agents; iron hydroxides and oxides ($Fe(OH)_2$,

372 $Fe(OH)_3$, $FeOOH$, Fe_2O_3, Fe_3O_4) are adsorbing agents. Additionally contaminants may be co-

373 precipitated by precipitating iron (hydr)oxides. Water is a concurrent for contaminants for Fe^0

374 oxidation. Ox the oxidized form of a contaminant yield Red upon reduction. Ox_1/Red_1 is

375 another redox couple present in the system (e.g. O_2/OH^- or MnO_2/Mn^{II}).

Reaction			Eq.
$Fe^0 + Ox$	$\Leftrightarrow$	$Fe^{2+} + Red$	[1]
$Fe^0 + 2 H_2O$	$\Leftrightarrow$	$Fe^{2+} + H_2 + 2 OH^-$	[2]
$2 Fe^0 + O_2 + 2 H_2O$	$\Leftrightarrow$	$2 Fe^{2+} + 4 OH^-$	[3]
$Fe^{II}_{(aq)} + Ox_1$	$\Leftrightarrow$	$Fe^{III}_{(aq)} + Red_1$	[4a]
$Fe^{II}_{(s)} + Ox_1$	$\Leftrightarrow$	$Fe^{III}_{(s)} + Red_1$	[4b]
$H_2 + Ox$	$\Leftrightarrow$	$H^+ + Red$	[5]
$Fe^{2+} + 2 OH^-$	$\Leftrightarrow$	$Fe(OH)_2$	[6]
$Fe^{2+} + 3 OH^-$	$\Leftrightarrow$	$Fe(OH)_3$	[7]
$Fe(OH)_2, Fe(OH)_3$	$\Rightarrow$	$FeOOH, Fe_2O_3, Fe_3O_4$	[8]
$Fe_xO_y + Ox$	$\Leftrightarrow$	$Fe_xO_y\text{-}Ox$	[9]
$Ox + n\ Fe_x(OH)_y^{(3x-y)}$	$\Rightarrow$	$Ox[Fe_x(OH)_y^{(3x-y)}]_n$	[10]

376
377

378

378   **Figure 1**
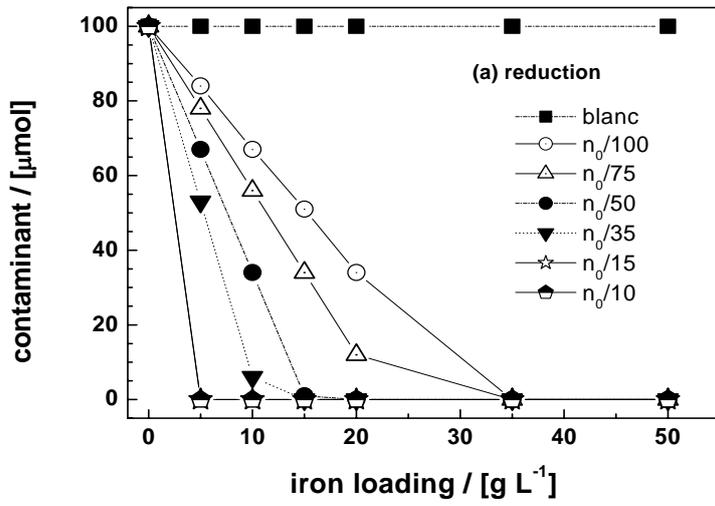
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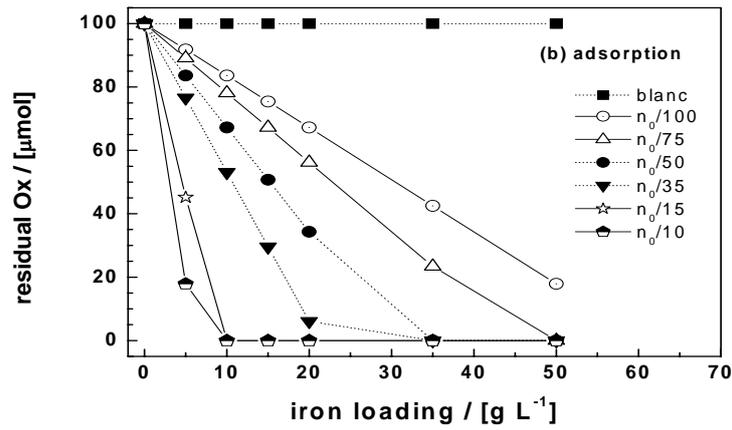
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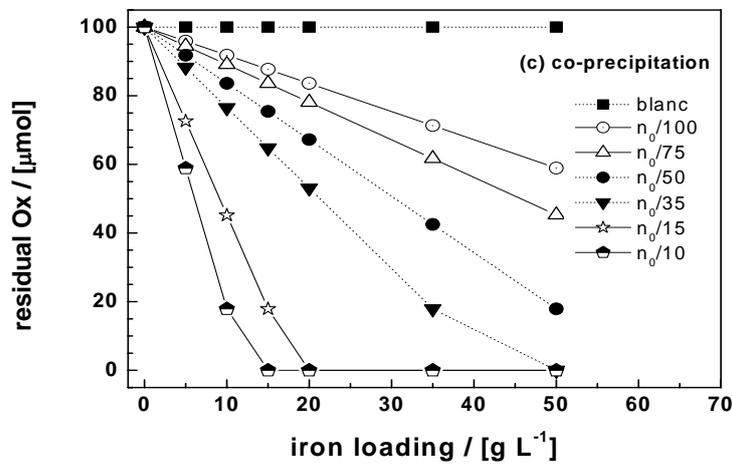
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383

383   **Figure 2**
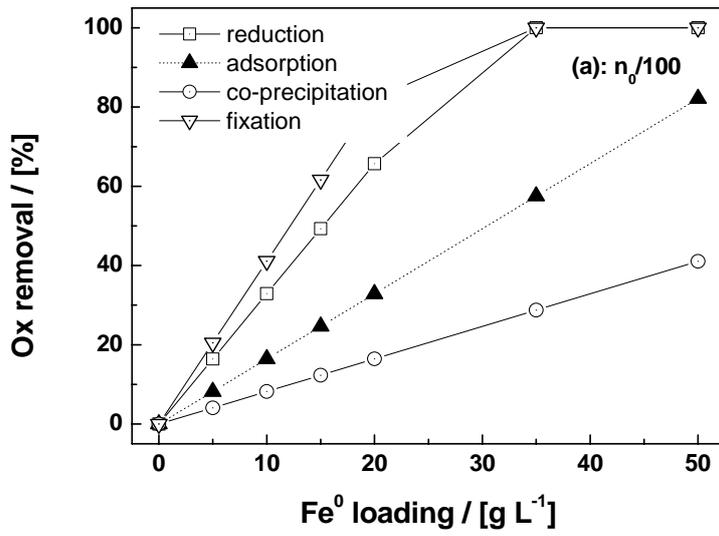
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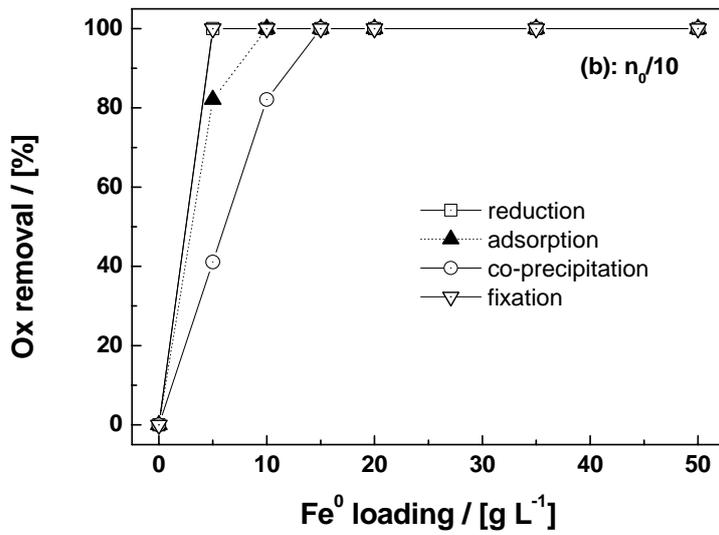
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387

387 **Figure 3**

388
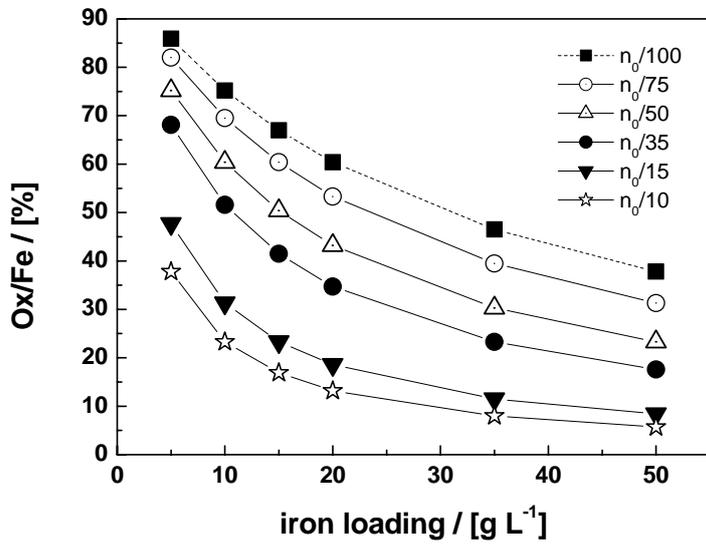
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390

390　**Figure Captions**

391

392　**Figure 1**: Evolution of contaminant removal by direct reduction through elemental iron (a),

393　　　and its corrosion products: adsorption (b) and co-precipitation (c) in a batch

394　　　system as a function of Fe^0 loading. Amorphous FeOOH is taken as the model

395　　　corrosion product. It is assumed that each mole of the reducible contaminant

396　　　adsorbs onto two moles of FeOOH and each mole of contaminant co-precipitates

397　　　with four moles of FeOOH. The lines are not fitted functions, they simply

398　　　connected points to facilitate visualization.

399

400　**Figure 2**: Comparison of the extent of contaminant (Ox) removal by direct reductive

401　　　transformation (reduction by Fe^0) and physical processes (fixation = adsorption +

402　　　co-precipitation) in the simulated system as function of Fe^0 mass loading for 1 %

403　　　(a) and 10 % (b) Fe^0 consumption. It is assumed for simplifications that

404　　　adsorption, co-precipitation, and reduction are independent contaminant removal

405　　　processes. Indirect reduction (Fe^{II}, H_2/H) is also not considered.

406

407　**Figure 3**: Evolution of molar ratio contaminant to iron (Ox/Fe) in the simulated batch systems

408　　　as a function of Fe^0 loading. The simulation are performed for Fe^0 consumption

409　　　varying from 1 % ($n_0/100$) to 10 % ($n_0/10$) and a contaminant concentration

410　　　yielding 100 μM substance in 20 mL solution. The lines are not fitted functions,

411　　　they simply connected points to facilitate visualization.

412