Metallic iron for water treatment: A critical review

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Abstract

Water treatment with metallic iron (Fe\textsuperscript{0}) is still based on the premise that Fe\textsuperscript{0} is a reducing agent. An alternative concept stipulates that contaminants are removed by adsorption, co-precipitation and size-exclusion in a reactive filtration process. This article underlines the universal validity of the alternative concept. It is shown that admixing non-expansive material to Fe\textsuperscript{0} as a pre-requisite for sustainable Fe\textsuperscript{0}-based filtration systems. Fe\textsuperscript{0}-based filters are demonstrated an affordable, appropriate and efficient decentralized water treatment technology.

Keywords: Media filtration, Size-exclusion, Water treatment, Zerovalent iron.
Fe-based alloys (elemental iron, Fe⁰ materials or zerovalent iron) have been found to be effective for removing a wide range of compounds from water. Studies on the successful removal of organic and inorganic chemicals [1-16] and pathogens [17-21] have been widely published and reviewed [22-30]. However, reports on the mechanism of contaminant removal have not been univocal. For more than a decade reductive transformations (degradation of organics and precipitation of inorganics) have been regarded as the fundamental mechanism of contaminant removal in Fe⁰/H₂O systems [3,31-34]. But the literature contains many contradictory findings regarding the processes of aqueous contaminant removal in the presence of Fe⁰. Reported discrepancies include the nature of reaction products [35], the extent of contaminant reduction [36,37], the actual reducing agents (Fe⁰, Fe^[II] or H/H₂) [12,38] and the relative importance of adsorption and reduction [37]. These conflicting findings suggest that reductive transformations may not be as important as currently considered. Nevertheless, a ‘broad consensus’ on reductive transformations persists in the literature despite parallel acknowledgment that the real mechanisms of contaminant removal have not yet been completely elucidated [6,24,32-34,39-41].

Recently, a new concept was introduced stating that contaminants are fundamentally adsorbed onto and co-precipitated with insoluble Fe⁰ oxides and hydroxides [42,43]. As for any subject on which there is a difference of opinion, it is pertinent to compare the concepts with the hope of finding the truth in the matter.

2 Reduction or adsorption/co-precipitation?

If contaminants are mostly reduced in Fe⁰/H₂O systems (concept 1), then one should consistently explain why this is possible at the long-term despite the oxide film formation (layer insoluble Fe⁰ oxides and hydroxides) and transformation at the surface of Fe⁰. It is important to notice in this regard, that the model for oxide film formation, that was compatible with progressive contaminant reduction [23] was proven unrealistic [44].
If contaminants are primarily adsorbed and co-precipitated \textbf{(concept 2)} within the oxide film, then one must simply sustain iron corrosion to ensure contaminant removal.

\textbf{Concept 1} gave birth to the iron reactive barrier technology as only reducible species (mostly chlorinated compounds) were considered \cite{1,3,6,31}. However, reaction products for many chlorinated hydrocarbons have not been clearly identified \cite{35,45,46}. Moreover, Fe$^0$ consumption, oxide film formation on the clean Fe$^0$ surface, and rise of pH inevitably accompany the removal processes \cite{47-49}. Due to these inherent properties of Fe$^0$-mediated reactions, the contaminant removal rate should necessarily decrease with increasing Fe$^0$ consumption yielding contaminant breakthrough. As this was not observed as the rule, \textbf{concept 2} is more close to the reality. Therefore, future researchers should follow \textbf{concept 2}. That is working on ways and means to sustain Fe$^0$ reactivity which automatically yields contaminant adsorption and co-precipitation \cite{48,50-54}.

It is essential to recall that reality (to be found out) is the action of nature under relevant conditions. Accordingly calling a technology ‘passive’ is not related to ‘no action’ but no external input of energy. In other words, active technologies need external energy input to initiate/support the action of nature (the reality). The challenge is to find out, how the nature works. Finding out how nature works is knowledge acquisition. The question here is “how are contaminants removed in Fe$^0$/H$_2$O systems?”

\textbf{2.1 Reduction is not a removal mechanism}

In water treatment, chemical reactions are used to facilitate contaminant elimination by one or several removal mechanisms \cite{55,56}. Relevant removal mechanisms are: (i) adsorption, (ii) co-precipitation, (iii) precipitation, (iv) size-exclusion and (v) volatilisation. All water treatment methods are based on these five mechanisms.

For water treatment at a specific site, it is important to identify the treatment method that is the most suitable: efficient, affordable and applicable. The treatment system that is best for a particular situation depends mostly on the nature and the concentration of contaminants and the
operational requirements of the system. As a rule, a combination of treatment methods is more
effective. A practical example is the chemical reduction of Cr\textsuperscript{VI} to Cr\textsuperscript{III} at pH value < 4, followed
by an increase of the pH to values > 6.0 for which Cr\textsuperscript{III} precipitates as Cr(OH)\textsubscript{3}.
The example of chromium (atomic number: 24) is very illustrative as chromium and iron (atomic
number: 26) are two heavy metals. In other words, aqueous Cr\textsuperscript{III} is only quantitatively removed
when precipitation is favourable, e.g. at pH > 6.0 \cite{57}.

2.2 Iron solubility and contaminant removal
Iron is a potential contaminant for water. Its maximum contaminant level (MCL) is 0.3 mg/L or
5.4 μM \cite{58}. Accordingly, while using Fe-based reactive material (e.g. Fe\textsuperscript{0}, FeS, FeS\textsubscript{2}) in water
treatment systems, care must be taken for the residual iron concentration to remain below 0.3
mg/L. This requirement delineates the importance of pH dependant Fe solubility of the process of
contaminant removal (Fig. 1).

In Fig. 1, literature experimental data for the solubility curve of Fe(OH)\textsubscript{3} and FeS are represented
together with the line for the MCL for Fe (5.4 μM) \cite{59,60}. It is seen that Fe\textsuperscript{II} is by far more
soluble than Fe\textsuperscript{III} at all pH values. For pH > 5.5, Fe\textsuperscript{II} concentration is at most comparable to MCL
suggested that Fe\textsuperscript{0} is only applicable at pH > 5.5. Clearly, if pH ≤ 4.5 (e.g. acid mine drainage),
an pH enhancement should precede Fe\textsuperscript{0} application. It should be noticed that Fe\textsuperscript{0} corrosion is
always coupled with a pH increased: H\textsuperscript{+} consumption (Eq. 1) or OH\textsuperscript{-} production (Eq. 2). Thus for
systems at pH 4.0-4.5 the technology can be tested \cite{61}.

\begin{equation}
\text{Fe}^0 + 2 \text{H}^+ \Rightarrow \text{Fe}^{2+} + \text{H}_2 \quad (1)
\end{equation}

\begin{equation}
\text{Fe}^0 + 2 \text{H}_2\text{O} \Rightarrow \text{Fe}^{2+} + 2 \text{HO}^- + \text{H}_2 \quad (2)
\end{equation}

Because Fe\textsuperscript{0} is oxidized by water (Eq. 2) and water is a solvent a Fe\textsuperscript{0}/H\textsubscript{2}O should be regarded as a
zone of precipitating iron oxides and hydroxides \cite{62}. During this precipitation, available foreign
species (including contaminants) are inevitably enmeshed in the mass of precipitates (co-
precipitation). Resulting precipitates are in turn potential adsorbents for biological and chemicals
contaminants. Therefore, adsorption and co-precipitation are definitively the fundamental
processes of aqueous contaminant removal in the presence of reactive Fe$^0$. In a Fe$^0$ bed, size-
exclusion is the third important process (‘reactive filtration’) [62-65]. A porous bed of granular
materials primarily removes dissolved molecules (e.g. size exclusion chromatography) and
suspended components (e.g. sand filtration) based on their molecular sizes and shapes. The
molecular sieve properties of used (porous) materials is exploited. In all cases volatilisation may
occur (if applicable) but chemical precipitation is not likely to occur given that contaminants are
usually present in trace amounts [66,67].

2.3 What went wrong?

2.3.1 The aqueous Fe$^0$ reactivity

The major problem with the introduction of the Fe$^0$ remediation technology is that no critical
survey of the data available on iron corrosion was done [30,63]. Ideally, the results of such a
survey should have been linked for all possible hypotheses. Then well-designed experiments under
strictly controlled conditions should have been performed to uncover the observed process of
contaminant removal.

On the other hand, reactive Fe$^0$ was tested under the same experimental conditions as inert
adsorbents and conflicting results were reported [68-70]. Tested adsorbents included activated
carbon, coal, hematite, goethite, lignite, lime, magnetite, peat, sawdust. For example, based on
their previous works on the efficiency of several industrial materials for uranium removal [68],
Morrison et al. [69] tested Fe$^0$ and concluded that Fe$^0$ was the most efficient material for their
purpose. In contrast, Indelicato [70] compared Fe$^0$ and granular activated carbon (GAC) for the
removal of chlorinated compounds from groundwater and concluded that GAC was superior to
Fe$^0$. It is obvious, that these articles have overseen the key aspect that the efficiency of Fe$^0$
primarily depends on the (long-term) kinetics of iron corrosion under the experimental conditions.
It should be recalled that Fe$^0$ reactive barriers were primarily designed for large volumes of low
contaminated water (micro-pollutants) flowing slowly through Fe$^0$ beds. Under such conditions,
the kinetics of iron corrosion and the residence time of water within the beds may be sufficient to
generate enough corrosion products for quantitative contaminant removal. In contrast, the
adsorptive capacity of adsorbents is maximal at the beginning of the experiment. Provided that the
water flow velocity is satisfactory, adsorptive filtration (e.g. GAC) could be efficient where
reactive filtration with Fe$^0$ is not efficient.

The key issue is not the relative efficiency but the appropriateness of each class of materials. If
this issue is properly addressed, then an appropriate design could be achieved. The results of
Miyajima [71] have recently clarified the relationship between ‘intrinsic reactivity’ and ‘removal
efficiency’. Summarized, the intrinsic reactivity is an invariable characteristic of a material that
does not depend on its amount or the operational conditions. The efficient of a material
characterizes the extent to which the material can remove a given contaminant under defined
operational conditions. In other words, ‘efficiency’ and ‘reactivity’ should never be randomly
interchanged.

2.3.2 The origin of the mistake

A careful look on the first 4 peer-reviewed articles on Fe$^0$ [1-4] (Table 1) suggests that a
systematic investigation of all observed phenomena would have avoided the mistake of
considering Fe$^0$ as a reducing agent. For example, the observed time lag for contaminant removal
reported by Schreier and Reinhard [4] is consistent with the view that (at pH > 4.5) contaminants
are removed by adsorption and co-precipitation (concept 2). This time lag thus corresponds to the
time necessary for the in-situ production of removing agents (Fe$^{II}$/Fe$^{III}$ hydroxides and oxides). On
the other hand, the necessity to sustain chemical reduction by an addition of pyrite as reported by
Lipczynska-Kochany et al. [2] depicted a clear concern that there would be a problem with
chemical reduction (e.g. reductive degradation) at pH values relevant for natural waters. It is
important to notice that reactive pyrite is added by Lipczynska-Kochany et al. [2] as a long-term
pH shifting agent and not as an own-reducing agent as successfully tested for example by
Kriegman-King and Reinhard [72,73]. Both these articles [2,4] were almost ignored (less than 70
citations each as referred to Table 1) and the idea presented above were not further investigated.
The article of Matheson and Tratnyek [3], one of the favoured (Table 1), has recently been granted as 2011 Outstanding Publication Award from the Association of Environmental Engineering and Science Professors (AEESP). The AEESP is made up of professors in academic programs throughout the world who provide education in the sciences and technologies of environmental protection. In fact, this article [3] is currently among the most cited articles published at Environmental Science & Technology. However, the theory propagated by this article is based on a wrong interpretation of good experimental observations as discussed in section 2.1. In other words, the current paradigm for the rationalization of the operating mode of Fe\textsubscript{0}/H\textsubscript{2}O remediation systems is unstable. Paradigm refers to all knowledge about which there is agreement in science.

2.3.3 The propagation of the mistake

Having met an agreement on a false premise, researchers have been reporting on findings (i) disagreeing 150 years intensive research on aqueous iron corrosion [74-76], (ii) disagreeing good results of synthetic organic chemistry [30], (iii) neglecting the voluminous work available from the hydrometallurgy, and the petroleum industry [75-79], and (iv) not able to explain why non-reducible contaminants are quantitatively removed in Fe\textsubscript{0}/H\textsubscript{2}O systems [30,42,43]. It is important in this regard to notice that Fe\textsuperscript{0} is also used for oxidative conversion of aqueous contaminants [13]. However, contaminant oxidation is also not a removal mechanism (section 2.1).

Besides the improper consideration of available results from other branches of science two other key factors have contributed to maintain confusion on the mechanism of contaminant removal in Fe\textsubscript{0}/H\textsubscript{2}O systems: (i) the use of inappropriate experimental conditions and (ii) the failure to use sequential extraction while making mass balances.

2.3.4 Inappropriate experimental conditions

There is actually no standard experimental protocol for the investigation of processes in Fe\textsubscript{0}/H\textsubscript{2}O systems. Available results are not really comparable [80,81]. In particular the used mixing operations (agitating, shaking, stirring) have disturbed the process of oxide film formation yielding
possibly reproducible results under well-designed laboratory conditions. These conditions are however difficult to reproduce in the subsurface [30].

2.3.5 Non-conclusive mass balance

No convincing carbon balances between reactants and products have ever been successfully done for many chlorinated hydrocarbons [45]. This means that organic contaminants that have disappeared from the aqueous phase are mostly considered chemically reduced. The situation is similar for inorganic contaminants for which speciation experiments have been mostly made without efforts to reductively dissolve iron corrosion products [82]. In other words, available results from geochemistry have equally not been properly considered. In fact, reductive dissolution of iron (and manganese) oxides is integral part of all sequential extraction schemes [83-85]. For example, Ma and Rate [84] used ammonium oxalate for amorphous iron/manganese oxides and hydroxylamine hydrochloride for crystalline iron/manganese oxides. As far as the author could ascertain, only Kishimoto et al. [86] have chemically reduced iron corrosion products for mechanistic demonstration. Previous research articles have used reducing agents to demonstrate the stability of removed contaminants [87,88].

3 Discussion

The presentation above has acknowledged that the concept of contaminant reductive transformation as removal mechanism in Fe\(^0\)/H\(_2\)O is clearly inadequate for explaining many experimental and field observations. Furthermore, irreversible contaminant removal which could result from contaminant co-precipitation with iron corrosion products has been mistakenly regarded as contaminant reductive transformation. However, the actual reactive wall design (e.g. wall sizing) is based on this concept [39,89-91]. Therefore, it is urgent to reconsider available data and models [92,93]. Moreover, further research work should be performed under adequate experimental conditions, including non-disturbed conditions of slow mixing regimes in batch experiments [30,81]. More research under relevant conditions is needed before the concept of
contaminant co-precipitation can be fully understood and predicted. Considering its nature, this is a challenge which can only be properly addressed by several research groups.

Finally, it must be explicitly said that the concept of contaminant co-precipitation is not a contradiction but an extension of the reductive transformation concept. The new concept explains better why various contaminants are continuously removed in Fe$^0$/H$_2$O systems despite “passivation” of the Fe$^0$ surface [52,94]. Adsorbed and co-precipitated contaminants can be further reduced [42,43]. Based on this knowledge, Fe$^0$-based filtration systems (including reactive walls) can be better designed [71,93]. The next section presents Fe$^0$ as a universal material for safe drinking water provision at small scale.

4 Metallic iron for safe drinking water provision

The conventional approach for safe drinking water provision is to treat natural water in a treatment plant and distribute through a pipeline network to the population [95,96]. One of the most severe shortcomings of this approach is that any sudden interruption (e.g. disasters: floods, droughts, quakes, tsunamis, hurricanes) could leave thousands of people without drinking water supply for some days or weeks. There is a current trend for decentralized solutions for safe drinking water supply [56,64,95-98].

4.1 Basic requirements for decentralized water supply solutions

Centralized waterworks are sophisticated systems with high demand of energy, skilled operation personnel and chemicals [55,96,99]. To be applicable worldwide, a water supply system must be (i) efficient, (ii) affordable and (iii) applicable in small and secluded remote areas (including islands) without electricity grid and possibly without (enough) skilled personnel [94,98,100-104]. Presently only chlorination, coagulation, filtration, solar disinfection, ceramic filters and biosand filters fulfil these basic criteria [56,103]. However, chlorination and coagulation need skilled personnel and should never be performed by illiterates (e.g. in developing countries). Solar disinfection can not address chemical contamination and the efficiency for both ceramic and biosand filters for virus removal was shown non satisfactory [97]. In other words, there is
presently no simple, efficient and affordable technology for water supply in low-income remote communities. One exception is the recently developed “WaterBackpack” at the University of Kassel (Germany) [97]. The “WaterBackpack” is a “small, transportable and easy to use dead-end membrane filtration unit for basic water supply” for small communities in the range of 200 up to 500 people [97]. The “WaterBackpack” is suitable for critical situations like natural disasters (e.g. earthquakes, tsunami) or wars (refugee camps). The need for sustainable, affordable safe drinking water technologies for low-income communities persists. Some of these communities have only so few inhabitants (down to less than 10 persons) for who the current version of “WaterBackpack” is not appropriate even though it could be affordable (around Euro 700).

4.2 Concept of Fe⁰ for safe drinking water provision

The suitability of metallic iron for decentralized drinking water provision arises from two main reasons: (i) metallic iron is widely available; iron filings can be produced locally even in poor localities (so-called ‘indigenous iron’) at low-cost or no money expense and (ii) water corrodes Fe⁰ to strongly adsorbing iron hydroxides and oxides [49,105-114]. As demonstrated above these iron precipitates should be regarded as collectors in a sand filter [115,116]. Accordingly, biosand filters should be amended with Fe⁰ to yield efficient gravity filters. The design of Fe⁰ filters has been discussed in several recent articles [52,116] and will not be repeated here.

The heart of the Fe⁰ filter is a suitable reactive Fe⁰ which should be mixed to an inert material (e.g. anthracite, gravel, pumice, sand) or a reactive but not expansive material (e.g. MnO₂, TiO₂) in a reactive zone [53]. The reactive zone should be sandwiched between two biosand filters (BSFs) (Fig. 2) [117]. The first BSF scavenges O₂ and removes pathogens and the second removes dissolved iron from the reactive zone. It can be anticipated that to each Fe⁰ (intrinsic reactivity) will correspond a thickness (Hₑz) of the reactive zone and a thickness (HₑBSF₂) of the second fine sand layer. The concept presented here can be realized at any corner of this world at several scales. With regard on the developing world, this is not a technology transfer in the conventional sense
[102], but a ‘knowledge sharing’ that could enable research institutions in the developing world to solve a long lasting problem by local initiatives.

The concept is affordable and applicable because: (i) no chemicals is needed, (ii) no energy is needed (gravity filtration), (iii) no (skilled) operation personnel is needed, and (iv) no intensive maintenance is needed. The sole need is a concept for recycling iron for new filters.

5 Further applications of Fe⁰ in environmental remediation

The knowledge, that Fe⁰ is used to produce reactive species is not unique to Fe⁰ filters. For example, Gould [118] used Fe⁰ as reducing agent for Cr⁶⁺, but their results demonstrated that more Cr⁶⁺ is reduced than predicted by the stoichiometry of the reaction between Fe⁰ and Cr⁶⁺. In this case, Fe²⁺ and H₂ are efficient reducing agents for Cr⁶⁺ (Table 2). In another example, Bafghi et al. [119] used powdered Fe⁰ as Fe²⁺ generator for the reductive dissolution of MnO₂. Their results showed that Fe⁰ is superior to Fe²⁺-bearing materials “as far as dissolution rate and efficiency were concerned”. In a third example, Chen et al. [120] positively investigated the potential of nano-Fe⁰ for hydrogen generation. In a fourth example, Biswas and Bose [121] successfully tested Fe⁰ as source of H₂ for autotrophic denitrification. In a fifth example, Fe⁰- and Fe²⁺-bearing materials are used as cost-effective oxygen scavengers to protect oxygen-sensitive foods from oxidation [122-124]. The idea is to eliminate or reduce the levels of oxygen inside packs. The working mechanism is the reaction of iron (Fe⁰, Fe²⁺) with oxygen in the container to form Fe³⁺ oxides [124]. These five examples show clearly that Fe⁰ can efficiently be used as parent material to produce useful species for different purposes. In Fe⁰/sand filters, Fe⁰ is used as generators for colloids which adsorb and/or enmesh contaminants during their precipitation. In other words, Fe⁰ is used to improve filtration which is basically a size-exclusion process [99]. Accordingly, the removal of very small particles (e.g. viruses) is not guaranteed by small pore sizes like in membrane filtration [97,103] but by the dynamic process of aqueous iron corrosion [47,64,65].

The geochemistry of iron in general and the behaviour of iron minerals in soils with regards to contaminant removal [125,126] suggest that Fe⁰ can be used as progressive source for slow release
of Fe (hydr)oxides in several remediation scenarios [127]. Relevant applications include: (i) remediation of contaminated groundwater, (ii) production of safe drinking water, (iii) treatment of industrial and agricultural wastewater, (iv) treatment of hospital effluents, (v) improvement of water quality in aquifers, (vi) improvement of river bank filtration, (vii) treatment of contaminated soils, and (viii) optimisation of artificial aquifer recharge. The material to be used in each application depends on the suitable operational conditions. However, it can be anticipated that a large array of materials with different reactivity should be available. Therefore, a standard protocol for the characterization of the intrinsic reactivity of Fe⁰ materials is urgently needed.

Depending on their intrinsic reactivity, materials could be classified with respect to their suitable application; e.g. Fe⁰ for safe drinking water, Fe⁰ for soil treatment, Fe⁰ for irrigation water, Fe⁰ for drainage water, Fe⁰ for river bank filtration…

6 Concluding remarks

The universality of the view that Fe⁰ is not a reducing agent is delineated. Regarding Fe⁰ as a generator of ‘contaminant collectors’ [116] has enabled the conceptual design of Fe⁰-amended slow sand filters (Fe⁰ SSFs) which are yet to be realized. A Fe⁰ SSF has a large potential for application to small-scale systems, in particular in low-income communities worldwide: (i) it is totally chemistry free, (ii) it is simple to design, (iii) it is easy in operation and maintenance, (iv) it is cost effective and (v) it is reliable upon proper design. Innovative designs of the reactive zones (e.g. use of Fe⁰-composites, Fe⁰/MnO₂, Fe⁰/pumice) will increase the sustainability of Fe⁰ filtration beds [54,128].

Intensive research with column and pilot studies are necessary to verify and optimise the presented concept. In this effort, the proper consideration of the volumetric expansive nature of iron corrosion should be carefully considered. In particular, lowering the concentration of dissolved O₂ at the inlet of the filter is a key issue (Table 3). The proper disposal of spent media as well as the recycling of used materials should be considered during the testing stage.
The knowledge that Fe$^0$ is not a reducing agent is also essential for the further development of the iron wall technology for groundwater remediation. In fact, considering the volumetric expansive nature of iron corrosion [74,76,129,130], the question as whether mixing Fe$^0$ and inert materials (e.g. gravel, sand) is beneficial or not [40,71, 131-133] is now definitively solved. Mixing Fe$^0$ and non-expansive materials is even a pre-requisite for system sustainability [134]. Accordingly, a reactive wall containing a zone with 100 % Fe$^0$ is not viable. Consequently, the rationale for the sustainability of reactive walls with a pure Fe$^0$ layer [24,27,66] is yet to be elucidated. A plausible explanation is that used materials were not very reactive. In such a constellation the reactivity of the wall could be sustained by an array of abiotic and biotic reductive reaction recycling Fe$^{\text{III}}$ to Fe$^{\text{II}}$ [135]. The impact of chemical reaction within the barrier is the progressive generation of colloids for contaminant ‘collection’. Without recycling, Fe$^{\text{II}}$/Fe$^{\text{III}}$ colloids are irreversibly transformed to less/non reactive crystalline forms [134,136-138]. As regarding the failure cases [66,70,139,140], it can be anticipated that used materials were very reactive under site specific conditions. Verifying this hypothesis is a challenge for the scientific community and an opportunity to further develop the already established remediation technology.

Acknowledgments

The original manuscript was improved by the insightful comments from Florence Tsagué Assopgoum (University of Siegen/Germany).

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Table 1: Overview on important results of the four first published peer-reviewed articles on the Fe\(^0\)/H\(_2\)O system in 1994 and the number of their citations in Scopus (2012/09/10). [X stands for contaminant; RCl is a chlorinated hydrocarbon].

<table>
<thead>
<tr>
<th>Reference</th>
<th>Systems</th>
<th>X</th>
<th>Findings</th>
<th>Citations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matheson et al. [2]</td>
<td>Fe(^0)/H(_2)O</td>
<td>CH(_3)Cl(_y)</td>
<td>Degradation mostly by Fe(^0)</td>
<td>682</td>
</tr>
<tr>
<td>Gillham et al. [1]</td>
<td>Fe(^0)/H(_2)O</td>
<td>RCl</td>
<td>Enhanced degradation</td>
<td>650</td>
</tr>
<tr>
<td>Schreier et al. [4]</td>
<td>Fe(^0)/H(_2)O</td>
<td>C(_2)Cl(_4)</td>
<td>Partial degradation with lag time</td>
<td>70</td>
</tr>
<tr>
<td>Lipczynska-Kochany [3]</td>
<td>Fe(^0)/FeS(_2)/H(_2)O</td>
<td>CCl(_4)</td>
<td>FeS(_2) sustains degradation</td>
<td>56</td>
</tr>
</tbody>
</table>
Table 2. Some relevant reactions involved in Cr\textsuperscript{VI} removal in the system Fe\textsuperscript{0}/H\textsubscript{2}O. It can be seen that Fe\textsuperscript{0} and its both secondary reaction products (Fe\textsuperscript{2+}, H\textsubscript{2}) can reduce Cr\textsuperscript{VI}. Fe\textsuperscript{0} is oxidized by water (H\textsuperscript{+}), Fe\textsuperscript{3+}, dissolved O\textsubscript{2} and Cr\textsuperscript{VI}. Ternary reaction products (FeOOH, Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}) are involved in the process of Cr removal (adsorption). Whether reduced or not Cr is enmeshed in the mass of Fe precipitates or adsorbed at their surface.

<table>
<thead>
<tr>
<th>Reaction equation</th>
<th>( E^0 )</th>
<th>Eq.</th>
</tr>
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<tbody>
<tr>
<td>Fe\textsuperscript{0} \rightleftharpoons Fe\textsuperscript{2+} + 2 e\textsuperscript{-}</td>
<td>-0.44</td>
<td>(1)</td>
</tr>
<tr>
<td>2 H\textsuperscript{+} + 2 e\textsuperscript{-} \rightleftharpoons H\textsubscript{2}</td>
<td>0.00</td>
<td>(2)</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+} + e\textsuperscript{-} \rightleftharpoons Fe\textsuperscript{2+}</td>
<td>0.77</td>
<td>(3)</td>
</tr>
<tr>
<td>O\textsubscript{2(aq)} + 2 H\textsubscript{2}O + 4 e\textsuperscript{-} \rightleftharpoons 4 OH\textsuperscript{-}</td>
<td>0.81</td>
<td>(4)</td>
</tr>
<tr>
<td>CrO\textsubscript{4}\textsuperscript{2-} + 8 H\textsuperscript{+} + 3 e\textsuperscript{-} \rightleftharpoons Cr\textsuperscript{3+} + 4 H\textsubscript{2}O</td>
<td>1.51</td>
<td>(5)</td>
</tr>
<tr>
<td>Fe(OH)\textsubscript{3} ⇒ ( \alpha\text{-}, \beta\text{-} )FeOOH, Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}</td>
<td></td>
<td>(6)*</td>
</tr>
<tr>
<td>FeOOH + Cr\textsuperscript{VI(aq)} \rightleftharpoons FeOOH–Cr\textsuperscript{VI(adsorbed)}</td>
<td></td>
<td>(10)</td>
</tr>
</tbody>
</table>

*non stoichiometric
Table 3: Coefficient of volumetric expansion ($\eta$) of relevant iron species. The reference ($\eta = 1$) is Fe$^0$ with a molar volume ($V_m$) of 7.6 cm$^3$/mol. $x_{Fe}$ is the stoichiometry of Fe in the solid phase. It is seen that the largest volumetric expansion occurs under oxic conditions ($\eta = 4.53$ for ferric hydroxide). $V_m$ values are adopted from Henderson and Demond [66].

<table>
<thead>
<tr>
<th>Solid phase</th>
<th>Name</th>
<th>$V_m$ (cm$^3$/mol)</th>
<th>$x_{Fe}$</th>
<th>$\eta$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^0$</td>
<td>Iron metal</td>
<td>7.6</td>
<td>1.0</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>FeOOH</td>
<td>Goethite</td>
<td>20.3</td>
<td>1.0</td>
<td>2.67</td>
<td>167</td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td>Ferrous hydroxide</td>
<td>26.4</td>
<td>1.0</td>
<td>3.47</td>
<td>247</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Maghemite</td>
<td>29.1</td>
<td>2.0</td>
<td>1.91</td>
<td>91</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>Siderite</td>
<td>29.3</td>
<td>1.0</td>
<td>3.86</td>
<td>286</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Hematite</td>
<td>30.1</td>
<td>2.0</td>
<td>1.98</td>
<td>98</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>Ferric hydroxide</td>
<td>34.4</td>
<td>1.0</td>
<td>4.53</td>
<td>353</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Magnetite</td>
<td>45.0</td>
<td>3.0</td>
<td>1.97</td>
<td>97</td>
</tr>
<tr>
<td>Fe$^{II}<em>{4}Fe^{III}</em>{2}$(OH)$_{12}$CO$_3$.2H$_2$O</td>
<td>Carbonate green rust</td>
<td>176.3</td>
<td>6.0</td>
<td>3.87</td>
<td>287</td>
</tr>
</tbody>
</table>
Figure Caption

**Figure 1**: Comparison of the solubility limit of iron with the EPA maximum contaminant level (0.3 mg/L or 5.4 μM). Data for Fe$^{III}$ solubility (0.01 M NaCl at 25°C) are from Liu and Millero [59] while data for Fe$^{II}$ solubility are from Rickard [60]. Although the experiments are performed under different conditions, it can be seen that iron solubility is minimal between pH 5.5 and 10. This is necessarily the pH range of water treatment using Fe$^{0}$ and other Fe-bearing materials.

**Figure 2**: Schematic diagram of a three compartments Fe$^{0}$-amended biosand filter (BSF). The first and the third columns are conventional BSF. The thickness of column 2 (reactive zone) depends on the intrinsic reactivity of used Fe$^{0}$ (after ref. [117]).