REVIEW ARTICLE

Realizing the potential of metallic iron for the mitigation of toxics: flee or adapt?

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Abstract

Metallic iron (Fe^0) has been increasingly used to remove toxics from water over the past three decades. However, the idea that metallic iron (Fe^0) is not an environmental reducing agent has been vigorously refuted. Researchers presenting their findings in a scientific journal have to accept the burden of proving that their argument has any validity. This 30-year-lasting discussion within the Fe^0 remediation community is alien to electro-chemists, as it is a century-old knowledge. Nevertheless, the peer-reviewed literature on "remediation using Fe^0" seems to be dominated by evaluators thinking that Fe^0 is a reducing agent. This communication challenges the view that Fe^0 donates any electron to any dissolved species. The sole goal is to reconcile a proven efficient technology with its scientific roots and enable the design of better Fe^0 remediation systems.

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Metallic iron for environmental remediation

Permeable reactive barriers (PRBs) as an effective remediation technology for polluted groundwater were introduced in the 1980s (McMurty and Elton 1985). Upon careful design and installation, PRBs remediate groundwater polluted with diverse contaminants, including chlorinated hydrocarbons, nutrients, and trace metals (Bigg and Judd 2000; Blowes et al. 2000; Thiruvenkatachari et al. 2008; Obiri-Nyarko et al. 2014; Courcelles 2015). Metallic iron (Fe^0) has been tested the most as a filling material for PRBs (Warner 2015; Gheju 2018). The suitability of Fe^0 for groundwater remediation is due to the negative value of the electrode potential of the Fe^{II}/Fe^0 redox couple ($E^0 = -0.44$ V) (Nesic 2007). This makes Fe^0 a potential reducing agent for many dissolved species ($E^0 > -0.44$ V), and even for water ($E^0 = 0.00$ V) (Thiruvenkatachari et al. 2008; Courcelles 2015). Water is the solvent and thus stoichiometrically very abundant (55.5 mol L^{-1}). At pH ranges above 5.0, the reaction between Fe^0 and water produces an oxide layer (oxide scale) close to the Fe^0 surface which is of fundamental importance for the efficiency of Fe^0 PRBs. In other words, the oxide scale on Fe^0 does act as a contaminant scavenger (Obiri-Nyarko et al. 2014; Gheju 2018). Despite three decades of intensive investigations, the mechanistic discussion on the operation mode of Fe^0/H_2O systems is still on-going (Warner 2015; Cai et al. 2021).

In 1994, Matheson and Tratnyek published highly counter-intuitive findings that metallic iron (Fe^0) could be oxidized by dissolved contaminants at circum-neutral pH values. Their results were reported to be confirmed two years later by Weber (1996). Since then, environmental scientists are mostly considering Fe^0 as a reducing agent for relevant aqueous species, including chlorinated organics (RCl) (O'Hannesin and Gillham 1998). RCl reductive transformation is considered to be a cathodic half-reaction occurring simultaneously with the anodic Fe^0 oxidative dissolution (Eq. 1):

$$Fe^0 + RCl + H^+ \Rightarrow Fe^{2+} + RH + Cl^- \tag{1}$$

Any researcher familiar with the Fe^0 remediation technology will confirm that this is the state-of-the-art knowledge (Obiri-Nyarko et al. 2014; Gheju 2018; Chen et al. 2019; Thakur et al. 2020). Any reader interested in following the path of the paradigm from Reynolds et al. (1990) is encouraged to read Gillham (2008). In fact, Reynolds et al. (1990) fortuitously found that trichloroethylene disappeared in Fe^0-based vessels (Lee et al. 2004; Gillham 2008). This is virtually considered as the starting point for the Fe^0 remediation technology which is now 30 years old and widely recognized as a competent alternative technology for remediation of contaminated groundwater (Lee et al. 2004; Gillham

2008; Chen et al. 2019; Thakur et al. 2020) and the provision of safe drinking water (Giles et al. 2011; Neumann et al. 2013; Huang et al. 2021a, b). In this paper, we contrast the misconception of Matheson and Tratnyek (1994) to the fundamental science of aqueous iron corrosion (Fe^0/H_2O system) (Whitney 1903).

The science of the Fe^0/H_2O system

In 1903, Willis Rodney Whitney established the science of the Fe^0/H_2O system which convincingly demonstrated that, at pH above 4.5 and under immersed conditions, only water can oxidize Fe^0 by an electrochemical mechanism according to Eq. 2 (Whitney 1903):

$$Fe^0 + 2H^+ \Rightarrow Fe^{2+} + H_2 \tag{2}$$

In particular, Whitney (1903) demonstrated two important facts: (1) carbonic acid (H_2CO_3) accelerates corrosion by supplementing protons (H^+) in Eq. 2 and intensifying water dissociation, and (2) dissolved oxygen (O_2) accelerates corrosion by consuming Fe^{2+} and favoring the forward reaction in Eq. 2 (i.e., Le Chatelier's principle). In other words, all reports on direct aqueous Fe^0 corrosion by O_2 are faulty. In terms of chemistry, H_2CO_3 and O_2 enhance iron corrosion by an indirect mechanism or following the Le Chatelier's principle. O_2 reduction by Fe^{2+} is given by Eq. 3 (Stratmann and Müller 1994):
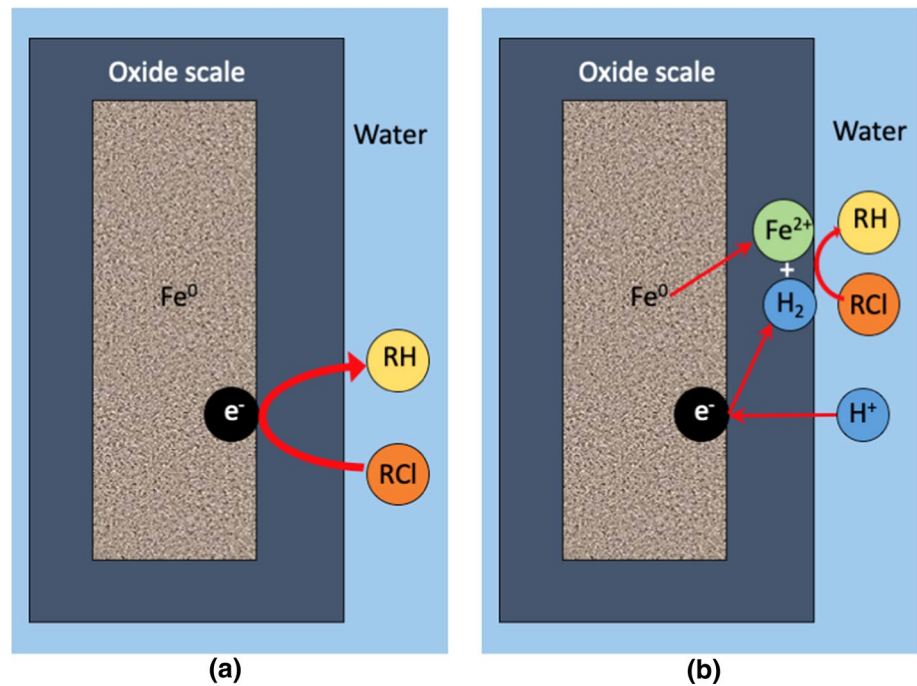
$$4\,Fe^{2+} + O_2 + 2\,H^+ \Rightarrow 4\,Fe^{3+} + 2\,OH^- \tag{3}$$
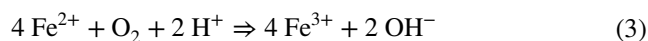
This is basic knowledge of a chemist. Similarly, the chemical reduction of RCl by Fe^{II} species should be written as in Eq. 4 (Fig. 1):

$$2\,Fe^{2+} + RCl + H^+ \Rightarrow 2\,Fe^{3+} + RH + Cl^- \tag{4}$$
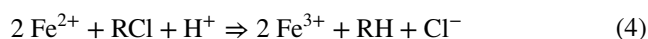
For the sake of simplicity, the pH-dependent speciation of Fe ions (Fe^{II} and Fe^{III}) is not considered in Eqs. 3 and 4. To this point, the presentation demonstrates that the view that under environmental conditions (pH > 4.5) the reductive transformation of RCl in the presence of Fe^0 is an electrochemical reaction (Fig. 1a) is contrary to basic chemistry textbook knowledge (Fig. 1b). Thus, the Fe^0 remediation literature has distorted the basic science of aqueous iron corrosion. In this regard, the Fe^0 remediation research community has perpetuated and propagated the mistake for years now despite various efforts drawing attention to this error as summarized by Hu et al. (2020). This mistake is attributed to insufficient literature review as the seminal paper by Whitney (1903) was then 91 years old. Recent trends in journal editorial and review processes emphasizing the review and

Fig. 1 Schematic representation of possible mechanisms of contaminant (RCl) reduction by metallic iron (Fe⁰): **a** electrochemical reaction (impossible) and **b** chemical reaction (science-based concept)

without any hint on the controversy existing in the literature with respect to the mechanisms of contaminants removal in Fe^0/H_2O systems (Noubactep 2014; Thakur et al. 2020). This communication is not addressing the related controversies; interested readers are referred to the following five representative articles: Gheju and Balcu (2011), Ghauch (2015), Noubactep (2014), Hu et al. (2021b), and Konadu-Amoah et al. (2022).

The mistaken path of the recent Fe^0 remediation research

Fe^0 has been industrially employed for water treatment since the 1850s (Tucker 1892; Baker 1934, 1948; Van Craenenbroeck 1998; Mwakabona et al. 2017). Selected outstanding patents were: (1) Medlock (1857) producing iron oxide by merely suspending iron rods in water; (2) Spencer (1857) using magnetic carbide of iron in household filters; (3) Bischof (1870) using spongy iron initially in household filters; (4) Anderson (1880) using iron fillings in a revolving cylinder (revolving purifier); and (5) Sellers (1890) using suspended iron rods while making the rods revolve. In particular, the Bischof process and the Anderson process were put into use in some cities, but the total number of plants remained small and all were soon abandoned after the First World War (Baker 1948). In fact, no Fe^0-based water treatment plant seems to have survived the First World War (Van Craenenbroeck 1998). This ancient use of Fe^0 was not considered in the post-1990 literature until 2017 (Mwakabona et al. 2017; Antia 2020). The reason why the ancient Fe^0

citation of recent literature have also contributed to the current scenario where researchers exclude "old" but correct knowledge, while simultaneously introducing conceptual errors. Clearly, researchers trying to restore the integrity of science now bear the burden of proof and face resistance from experts (e.g., grant referees and journal reviewers). However, those researchers have basically no proofs to bring as they are just correcting an error which has been propagated over the years. The error has developed to be an "acceptable truth" by virtue of mere repeated citations, but it is common knowledge that repeating an error does not make it the truth (Noubactep 2019). In addition, active researchers may also have the tendency to become attached to their ideas no matter how flawed they might be. Such a situation has made publishing on "Fe^0 for water remediation" becoming an irrational discussion among scientists, rather than a rational competition among ideas underpinned by fundamental scientific knowledge (Chamberlin 1897; Fudge 2014).

For contaminant removal in Fe^0/H_2O systems, there should be a recognizable and universal reality based on scientific principles. In this case, it is about the corrosion science of metallic iron in aqueous environments. To reach a new reality, "good explanations should rise out of the ashes of those (assumptions) shown to be false" (Fudge 2014). Accordingly, scientists seeking to reach the "recognizable and universal reality" on the fate of contaminants in Fe^0/H_2O systems should strive to entertain the two theories given above as concurrent hypotheses and find out which one enables a better explanation of their experimental results. This is currently not the case as even "critical" reviews are written

water treatment technology failed has never been scientifically investigated. From Baker (1948), it is clear that filtration systems failed because of cementation of gravel/sand and iron causing clogging, while fluidized systems were initially very efficient but not sustainable.

The key result of the ancient use of Fe^0 for water treatment is that it was an attempt at achieving coagulation (Baker 1948). Fe^0 was used to generate flocs for the collection of dissolved pollutants and suspended substances. This technology was independently rediscovered in the 1950s by Lauderdale and Emmons (1951), who used steel wool to generate iron oxides for the removal of radionuclides from drinking water. In other words, before 1990, Fe^0 has never been used as a reducing agent under environmentally relevant conditions (pH > 4.5). For lower pH values, the solubility of iron is higher and the Fe^0 surface is accessible to dissolved species, but such conditions rarely occur in nature (Ghauch 2015). It is the pH range of cementation (Noubactep 2010a, b), which is a clearly distinct process.

Cementation using Fe^0 is a heterogeneous process in which dissolved metallic ions (e.g., Cu^{2+}) are reduced to an element (e.g., Cu^0) at the Fe^0 surface (Khudenko 1991). Section 2 has already recalled that no single species other than H^+ can initiate iron corrosion under environmental conditions. This was the starting point of our research group to establish the science of the Fe^0/H_2O system. Recent bibliometric analysis of "Fe^0 research for environmental remediation from 2000 to 2019" suggests that our research group is the most prolific with respect to research on Fe^0/H_2O systems (Chen et al. 2019; Li et al. 2021). Table 1 summarizes the milestones of our contribution to establish the renewed aspects of Fe^0/H_2O systems.

Table 1 shows that our research group has presented a different path to systematically investigate the Fe^0/H_2O system. The focus was not on individual contaminants (e.g., biological, inorganic, and organic) and the extent of their removal. Rather, the time-dependent changes of the extent of the decontamination capacity of the systems were

Table 1 Timeline of the main contributions to establish the science of the Fe^0/H_2O system from 2007 onwards

Year	Event	References
2007	A very critical literature review on the Fe^0/H_2O systems is presented. Reactivity loss and permeability loss are the main issues in these systems	Henderson and Demond (2007)
2007–2010	The importance of electrochemical reduction in Fe^0/H_2O systems is questioned	Noubactep (2007, 2008, 2009a, 2010a, b)
2008–2009	The impact of operational conditions in batch studies is elucidated. Shaking and stirring at intensity > 75 rpm generate results that are not representative for filtration systems (e.g., subsurface permeable reactive barriers)	Noubactep (2009b, 2011)
2011	Electrochemical contaminant reduction in Fe^0/H_2O system is radically refuted	Noubactep (2011)
2010–2013	The impact of admixing agents in column studies is investigated. Only hybrid systems with a Fe^0 volumetric ratio < 50% are sustainable	Noubactep and Caré (2010), Miyajima and Noubactep (2012, 2013)
2012–2015	There is no reactivity loss in Fe^0/H_2O systems. The "natural" decrease in the corrosion rate has been misinterpreted as loss of reactivity	Noubactep (2014)
2013–2015	The ion-selective nature of Fe^0/H_2O systems is demonstrated	Phukan et al. (2015, 2016)
2015	Available review articles on the Fe^0/H_2O system are critically reviewed: Only some few research groups are rooting their reasoning on the fundamental science of aqueous iron corrosion	Noubactep (2014)
> 2016	The importance of corrosion rate on the efficiency of Fe^0/H_2O systems is discussed. Success stories have fortunately used appropriate Fe^0 (e.g., reactivity, size) in an appropriate mixing ratio	Noubactep (2016), Yang et al. (2021)
> 2014	The role of two reactive materials (FeS_2 and MnO_2) in enhancing the efficiency of Fe^0/H_2O systems is elucidated. Both materials control the availability of free Fe corrosion products (e.g., contaminant scavengers)	Btatkeu-K et al. (2014), Xiao et al. (2020a), Cao et al. (2021), Hu et al. (2021a)
> 2012	Development and application of the methylene blue method for the visualization of the dynamic processes within the Fe^0/H_2O system	Miyajima and Noubactep (2012, 2013), Phukan et al. (2015, 2016), Btatkeu-K et al. (2016), Xiao et al. (2020b), Konadu-Amoah et al. (2022)

characterized (Noubactep 2014). Moreover, batch experiments were mostly performed under quiescent conditions and lasted for up to four months. Because only some two or three research groups had adopted quiescent conditions, results are not really comparable to other published data and no profound discussion was possible. A key aspect was the development of the methylene blue method (MB method) which is the sole available tool to characterize the dynamics within the Fe^0/H_2O system without relying on a specific contaminant (Btatkeu-K et al. 2016; Konadu-Amoah et al. 2022). The MB method assesses the availability of iron corrosion products (FeCPs), or the extent of iron corrosion as influenced by selected operational parameters. For example, for column studies, the time to contaminant breakthrough has never been a key evaluation parameter. Rather, systems were designed for rapid breakthrough such that their behavior after breakthrough can be characterized for the longest experimental duration (Miyajima and Noubactep 2013; Konadu-Amoah et al. 2022).

Before 2007, tools to characterize the Fe^0 intrinsic reactivity were already presented as summarized in one of the papers (Btatkeu-K et al. 2016). It was also clear to us that there is no quantitative contaminant removal in Fe^0/H_2O systems until enough oxides are precipitated. Given that even recent review articles are still presenting Fe^0 as a (strong) reducing agent (Huang et al. 2021a, b), it is fair to state that collaborators within the research community still fail to understand the fundamentals of iron corrosion under aqueous conditions. For sure, this includes all actors: researchers, reviewers, and editors. While this may sound harsh, it is critical that past errors are corrected to ensure that the industry of water treatment using Fe^0 cannot continue to deny its flaws, while expecting interested funders and investors to commit resources to fund research on Fe^0/H_2O systems. In summary, researchers are still using a paradigm that attempts to violate the first law of thermodynamics (conservation of mass).

The real tragedy of the Fe^0 remediation technology has been a wrong system analysis (Noubactep 2009a), as demonstrated by the electron efficiency concept. The expression "electron efficiency" was introduced in an effort to avoid Fe^0 wastage by optimizing the proportion of electrons from Fe^0 used for the reductive transformation of a target contaminant (e.g., RCl) (Hu et al. 2021b). Regarding RCl, the electron efficiency characterizes the relative quantity of electrons transferred from Fe^0 to RCl, where relevant competing electron receptors are co-contaminants (e.g., NO_3^-), dissolved O_2, and water. Before the advent of the Fe^0 remediation technology, however, it was already clear that no electron transfer to NO_3^-, O_2, and RCl is possible (Sect. 2). The fallacy of the electron efficiency concept was demonstrated in a recent paper (Hu et al. 2021b).

A good literature review (Sect. 2), coupled with a proper system analysis restores the scientific truth. The three major mistakes as extracted from Huang et al. (2021a, b) are:

1. Acknowledging the non-stoichiometric nature of decontamination reactions while using pseudo-first-order rate constants (k_{obs}, k_M, k_{SA}) or the corresponding half-lives ($t_{1/2}$) to describe the systems.
2. Considering that any Fe^0/H_2O interface exists, including within pits, crevices, or equivalent defects in the oxide scale on Fe^0. Direct electron transfer from Fe^0 to contaminants (electrochemical reduction) supposedly occurs at such sites. Because the formation of an oxide scale is spontaneous, it occurs also at defects such that there is always a Fe^0/oxides interface. Note that the oxide scale acts as a conductive barrier for electrons from Fe^0 and a diffusion barrier for contaminants. Thus, contaminants can accumulate at the oxides/H_2O interface.
3. Improperly considering the kinetics of iron corrosion which is non-constant, and nonlinearly varies with the time (Nesic 2007). While the dynamics of the Fe^0/H_2O system has been often addressed, very few experiments have lasted for more than three months (Westerhoff and James 2003; Jha and Bose 2005; Yamashita and Yamamoto-Ikemoto 2008, 2014; Zheng et al. 2019), meaning that available data just reflect the initial corrosion rate yet they are used to design and model field applications and long-term performance (Jeen et al. 2009).
4. A typical feature of a redox reaction is an exchange of electrons between at least two reaction partners; oxida-

Table 2 Summary of the key features happening in a classical electrochemical cell (Daniell cell) compared to the electrochemical corrosion of water. It is seen that the oxide scale blocks electron transfer, making electrochemical reduction in any contaminants (e.g., RCl) impossible

	Daniell cell	Remediation	Comments
Anode	Zn^0	Fe^0	Zn^0 is oxidized to Zn^{2+} in Daniell cell Fe^0 is oxidized to Fe^{2+} by polluted water
Cathode	Cu^0	Fe^0	Cu^0 is deposited in Daniell cell H^+ is reduced in polluted water
Conductor	Wire	Fe^0/oxide	The wire transfers electrons from Zn^0 to Cu^{2+} The oxide scale hinders electron transfer to dissolved species including RCl
Electrolytes	Salt bridge	Polluted water	The salt bridge transport cations to replace Cu^{2+} Anions are transported to neutralize Zn^{2+} cations

tion and reduction always occur simultaneously. Table 2 illustrates this for the Daniell cell which involves Cu^{2+} reduction by Zn^0. For the Fe^0 remediation technology, the contaminants are the oxidizing agent while Fe^0 is the reducing agent. Thus, contaminant and Fe^0 together form the corresponding redox pair. The question arises: Is contaminant reduction a chemical (electrons from Fe^{II} or H species) or an electrochemical reaction (electrons from Fe^0)? Both types of reactions are possible because of the negative value of the Gibbs energy ($\Delta G^0 < 0$). In other words, the thermodynamics alone cannot help to disclose the real mechanism of contaminant reductive degradation in Fe^0/H_2O systems. Chemical reduction requires that the reaction partners come close together (< 4 Å or 0.4 nm). On the other hand, electrochemical reactions occur between distant partners under the prerequisite that they are both electronically and ionically conductive and coupled together (Table 2). Clearly, for a contaminant to be electrochemically reduced by Fe^0, electrons should flow from Fe^0 to the contaminant. Unfortunately, the Fe^0 surface is permanently covered by a non-conductive oxide scale (Lee et al. 2004; Nesic 2007; Gheju 2018; Hu et al. 2020) and no electrochemical interaction with any contaminant is possible (Hu et al. 2021b).

The future of Fe^0-based filtration systems

The view that Fe^0 is a reducing agent for contaminant reduction under environmental conditions is faulty as demonstrated in Sects. 2 and 3. The main problem of Fe^0 filters is the time-dependent decrease in its permeability (Lauderdale and Emmons 1951; Antia 2020). There are many contributing factors to permeability loss, but the most important one is the volumetric expansive nature of iron corrosion. Volumetric expansion implies that each oxide is at least twice larger in volume than the parent metal ($V_{oxide} > 2\ V_{iron}$). The question arises: How much oxide is generated in a Fe^0 filter per unit time? Answering this question requires that the corrosion rate of the used Fe^0 specimens is known. However, this is not the case, and too little efforts have been directed at characterizing the reactivity of Fe^0 materials (Li et al. 2019; Lufingo et al. 2019). This is very unfortunate in a context where it is well-documented that the Fe^0 corrosion rate can vary over several orders of magnitude (Melchers and Petersen 2018). Equations 1 and 4 demonstrate that twice more Fe^0 is consumed for the reduction of RCl than it would have been in an electrochemical reaction (Eq. 1). Given the low solubility of Fe^{II} and Fe^{III} in water at pH above 4.5, this implies at least twice more oxides to fill the pores and induce permeability loss as

has been assumed until now. When finally considering that only protons (H^+) oxidize Fe^0, it becomes clear that pore filling by iron corrosion products must be considered before any other operating factors (e.g., foreign precipitates; suspended particles; and even H_2 generation). In other words, despite three decades of intensive research efforts to characterize the long-term permeability of Fe^0 filters, satisfactorily results are lacking because the system analysis underlying past efforts was not holistic. For instance, in the majority of the studies, the Fe^0 materials used were only poorly or never characterized with respect to their intrinsic reactivity (e.g., long-term corrosion rate). In other studies, high agitation rates that are not representative of operating conditions of the Fe^0 remediation systems were used (Lee et al. 2004; Gheju and Balcu 2011; Ghauch 2015). Thus, a systematic comparison of results among studies is problematic.

It may be surprising to read that investigating the contribution of expansive iron corrosion to the process of permeability loss in Fe^0 permeable reactive barriers (Fe^0 PRBs) is an innovation. This becomes obvious, however, when it is recognized that no single contaminant can oxidize Fe^0, while current models for predicting the operation of Fe^0 PRBs are mostly based on the stoichiometry of an electrochemical reaction between Fe^0 and the contaminants of concern (Sarr 2001; Lee et al. 2004; Santisukkasaem and Das 2019). Thus, such models are premised on the wrong scientific principle. For more than a decade, admixing sand or non-expansive aggregates with Fe^0 was considered as "material dilution" with possible negative impacts on the decontamination process (Bi et al. 2009; Konadu-Amoah et al. 2022). Around 2010, it was proved that only hybrid systems (e.g., Fe^0/sand) can be sustainable, making "material dilution" rather a prerequisite for sustainability (Domga et al. 2015). In other words, Fe^0 filtration systems are yet to be properly considered as a special case of "electrochemical dissolution of metals in porous media." In such porous systems, the corrosion rate also depends on the pore size distribution (Bi et al. 2009).

The last important feature to be considered for the next generation Fe^0 PRBs is the validity of the design prerequisite that PRBs must have a higher hydraulic conductivity than the surrounding aquifer (Lauderdale and Emmons 1951; Gillham 2008). It is certain that the hydraulic conductivity of any Fe^0 PRB will decrease with time (Stefanoni et al. 2019). This raises the question, what will happen when the wall and the surrounding porous environment have the same permeability? To the best of the authors' knowledge, this issue has never been addressed in the Fe^0 remediation literature.

A call to change course

The credibility of Fe^0-based remediation system as a technology depends essentially on the quality of the work that researchers produce. The fact that a distortion of corrosion science has been prevailing in the Fe^0 literature for three decades must be a concern to the scientific community. During the last decade, the situation has worsened to the extent that journal editors and grant referees rejected manuscripts or proposals questioning the current paradigm with the summary comment "*not relevant*" or "*lack of novelty.*" For manuscripts, the authors can migrate from one journal to another until they find more understanding and open-minded editors and reviewers. For grant proposals, however, there is almost no such chance, because the "best experts" or grant reviewers could be the same scientists who introduced and perpetuated the named mistakes. In a context of stiff competition for grant money, a single negative referee is often enough for a proposal rejection. Therefore, researchers or research groups submitting novel findings or proposals anchored on the fundamental principles of iron corrosion science either have to: (1) find alternative publication outlets or funding agencies (i.e., flee), or (2) conform to the current flawed or erroneous concepts (i.e., adapt). This is a fundamental problem which cannot be resolved by a few individuals (Tien 2007; Hu et al. 2021b; Konadu-Amoah et al. 2022). By making the problem better known to the public and the research community, the present authors hope to contribute to its solution. It is also our proposal that journal editorial boards and reviewers should avoid further acceptance of manuscripts further perpetuating or propagating the fundamental mistake highlighted here. This approach could redeem the Fe^0 remediation technology from its current conceptual errors (Hu and Noubactep 2018, 2019; Hu et al. 2018, 2019, 2020; Noubactep 2022). In fact, that was the motivation for writing this short communication. It should be recalled that good results have refuted the reductive transformation concept in its initial phase (from 1994 to 2001) (Lipczynska-Kochany et al. 1994; Qiu et al. 2000; Lavine et al. 2001; Lee et al. 2004), but were collectively ignored. In particular, Lavine et al. (2001) used differential pulse polarography to simultaneously monitor the disappearance of nitrobenzene and the appearance of Fe^{2+}. Their results could not confirm any electrochemical mechanism for the observed nitrobenzene reduction in the investigated Fe^0/H_2O system. Lavine et al.'s (2001) study was published in Microchemical Journal (Elsevier) which is mainly devoted to analytical chemistry. Yet 21 years later, this excellent article has been referenced only some 131 times according to Google Scholar (scholar.google.com, accessed: 13/03/2022). Clearly, Lavine et al.'s (2001) study has not been really considered within the Fe^0 remediation literature. Several other thought-provoking articles have experienced the same fate (Lipczynska-Kochany et al. 1994; Farrell et al. 1999; Furukawa et al. 2002; Purenović et al. 2004; Lee et al. 2004; Jiao et al. 2009; Noubactep 2010a, b; Giles et al. 2011; Gheju and Balcu 2011, Fudge 2014). In particular, Furukawa et al. (2002) suggested that the abundance of FeCPs in Fe^0/H_2O systems implies their systematic consideration in all mechanistic discussions. On the other hand, Jiao et al. (2009) traceably demonstrated that the reductive transformation of carbon tetrachloride (CCl_4) in the presence of Fe^0 was the result of chemical interactions of CCl_4 with primary iron corrosion products (e.g., H_2 and Fe^{2+}).

The way forward is to consider that the following statement has never been proven false "In 1888, Crum Brown pointed out that iron remained free from rust in an atmosphere of oxygen, carbon dioxide, and water vapor so long as liquid water was prevented from condensing on its surface" (Friend 1906). Moreover, this knowledge is yet to be properly considered in the Fe^0 remediation literature where Fe^0 is constantly immersed, meaning that less O_2 and CO_2 are available compared to atmospheric conditions.

Questioning the prevailing flawed concept

The present work is a further attempt to question the premise that "Fe^0-induced contaminant removal is initiated by the direct electron transfer from Fe^0 to substrates" (Kang and Choi 2009). The named premise was proved inconsistent many years ago by Noubactep (2007, 2008), but this has been largely ignored by active researchers while journal and grant referees are accusing the authors for citing only their own papers to support the new concept. Kang and Choi (2009) anticipated resistance for the new concept using the following wording "this argument is hardly acceptable since the role of the direct electron transfer in Fe^0-mediated reactions is well-established and generally accepted among the research community." It seems that there is no other way to demonstrate the fallacy of the reductive transformation concept than to question the experimental design of Matheson and Tratnyek (1994) and its ability to support their conclusions.

Matheson and Tratnyek (1994) recognized that determining the relative importance of three reductive mechanisms is essential to predict the performance of related remediation systems: (1) reduction by electrons from Fe^0 (direct reduction), (2) reduction by electrons from Fe^{II} species (indirect reduction), and (3) reduction by electrons from H_2 (indirect reduction). Unfortunately, already in their theoretical analysis, Matheson and Tratnyek (1994) had under-estimated or overlooked the importance of indirect reduction because there was a need for an effective catalyst to support reduction through Fe^{II} and H_2. The same authors further considered

that Fe^0 is oxidized by dissolved O_2 under oxic conditions and by H_2O under anoxic conditions. Yet it was known that even under oxic conditions, O_2 cannot diffuse to the Fe^0 surface and is oxidized within the oxide scale by Fe^{II} species (Stratmann and Müller 1994).

Other inconsistencies of the demonstration by Matheson and Tratnyek (1994) include the following considerations: (1) that water acts as proton donor to enable the reduction of RCl, (2) that because the addition of external Fe^{2+} or H_2 had not significantly affected the rate of CCl_4 dehalogenation under their experimental condition, indirect reduction can be ruled out, and (3) that complexing Fe^{II} with ethylenediaminetetraacetic acid (EDTA) would impact CCl_4 reduction by Fe^0. EDTA is a ligand which forms very stable complexes with Fe^{III}, meaning that a proper discussion should consider the electrode potential of the redox couple $Fe^{III}EDTA/Fe^{II}EDTA$. All these important aspects were not considered by Matheson and Tratnyek (1994) in the mechanistic discussion of their findings.

The development of concepts for understanding processes leading to decontamination in Fe^0/H_2O systems requires a careful analysis of all the contributing physicochemical processes (Lee et al. 2004; Noubactep 2009a; Taylor and Ke 2021; Hu et al. 2021b). Relevant processes include: (1) mass transport from the polluted water to the Fe^0 vicinity, (2) chemical and electrochemical reactions at the Fe^0/oxide interface, within the oxide scale, and at the oxide/H_2O interface, (3) compositional and microstructural changes in Fe^0 and the in-situ generated and transforming oxide scale, and (4) the dynamic interactions of solutes, including pollutants with the oxide scale (Nesic 2007; Wen et al. 2012; Gheju 2018; Barrera et al. 2018; Hu et al. 2021b; Taylor and Ke 2021). These processes

are highly dynamic, while some maybe close to equilibrium, and heavily dependent upon environmental variables such as hydrodynamic conditions, pH value, the presence of impurities in the used Fe^0 material, and the ambient temperature. Clearly, designing laboratory experiments to support field installations of Fe^0 PRBs is a very challenging task that shall not be further complicated by avoidable biases (Lee et al. 2004; Hu et al. 2021b). In particular, mixing conditions (mass transfer rate) used in the large majority of batch experiments in treatability studies influence mass transfer in a manner that is not representative of field Fe^0 PRBs (Lee et al. 2004; Noubactep 2008; Noubactep et al. 2012). The existence of such a fundamental vagueness imposes difficulties in determining an appropriate Fe^0 amount and a thickness for the PRB (Sarr 2001).

Finally, Table 3 summarizes and illustrates four key perceptions in favor of the reductive transformation concept and the corresponding disproving counter-arguments. Table 3 is also regarded as the summary of this communication.

Conclusions

This communication recalls that under environmental conditions the following occur in the Fe^0/H_2O system:

1. Fe^0 is oxidized by water and by water alone,
2. Fe^{2+}, H_2, and other species like green rust or Fe_3O_4 reduce contaminants (and O_2),
3. Twice more Fe^0 is needed to produce the number of electrons for the reduction by Fe^{2+} compared to the case where Fe^0 would have been the reducing agent, and

Table 3 Assumptions and counter-arguments for the reductive transformation of contaminants in Fe^0/H_2O systems

Assumptions for reductive transformation	Counter-arguments against the reductive transformation concept
RCl reduction is an electrochemical process (Matheson and Tratnyek 1994; Weber 1996)	Oxide scale is a non-conductive barrier; thus, electron transfer is blocked
	RCl must diffuse across the oxide scale to the Fe^0 surface. This migration cannot be quantitative
A fraction of electrons from Fe^0 is transferred to RCl (electron efficiency concept) (Liu et al. 2013)	No RCl can receive electrons from Fe^0 (Hu et al. 2021b)
	RCl is reduced by an indirect mechanism (Jiao et al. 2009)
Shaking or stirring experimental vessels in batch studies accelerates mass transfer (Lee et al. 2004)	In field Fe^0 PRBs, diffusion controls all transport processes in the vicinity of Fe^0 (Hu et al. 2021b)
The Fe^0 amount for a PRB can be determined from the stoichiometry of the electrochemical reaction between Fe^0 and RCl (Sarr 2001)	Non-reducible contaminants such as Zn^{2+} (Njaramba et al. 2021) and methylene blue (Konadu-Amoah et al. 2022) have been quantitatively removed in Fe^0/H_2O systems
	Contaminants and O_2 are exclusively reduced by an indirect mechanism (Whitney 1903; Hu et al. 2021b)
	The volumetric expansive nature of the corrosion process must be considered (Caré et al. 2013; Domga et al. 2015; Yang et al. 2021; Tao et al. 2022)

RCl stands for a reducible halogenated hydrocarbon ($E^0 > -0.44$ V)

4. Because of the very low solubility of Fe^{II} and Fe^{III} species, iron oxides and hydroxides must precipitate close to the Fe^0 surface and cannot migrate far. Iron oxides are larger in volume than Fe^0 and will progressively fill the pores. For these reasons, expansive iron corrosion should be considered first when discussing the process of permeability loss.

All these aspects were strongly neglected in the Fe^0 remediation research in the past three decades.

A survey of publications on "groundwater remediation" (Chen et al. 2019) and "remediation using Fe^0" (Thakur et al. 2020) shows increasing publication numbers. This confirms the importance of the subject of study and its relevance to industrial technology. The impressive publication record should have made any member of the community proud in this robust state of affairs (Tien 2007). However, the evidence that the large majority of these publications are propagating a mistake and that a circular reasoning is deveoped in the community is very disappointing. The present communication is a call for the Fe^0 remediation research community to look critically at their past and future results, and then embark a new path anchored on well-established scientific principles (i.e., aqueous corrosion of Fe^0, iron corrosion in porous media).

Declarations

Conflict of interest The authors declare no conflict of interest.

Institutional review board statement Not applicable.

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