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SHORT RESEARCH COMMUNICATION

Metallic iron for environmental remediation: the still overlooked iron chemistry

Minhui Xiao[1,2] · Rui Hu[1] · Ran Tao[2] · Xuesong Cui[2] · B. Konadu-Amoah[1] · Huichen Yang[2] · Arnaud Igor Ndé-Tchoupé[1] · Willis Gwenzi[3,4] · Chicgoua Noubactep[1,2,5,6,7,8] · Hans Ruppert[8]

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Abstract

Permeable reactive barriers (PRBs) containing metallic iron (Fe^0) as reactive materials are currently considered as an established technology for groundwater remediation. Fe^0 PRBs have been introduced by a field demonstration based on the fortuitous observation that aqueous trichloroethylenes are eliminated in Fe^0-based sampling vessels. Since then, Fe^0 has been tested and used for treating various biological (e.g. bacteria, viruses) and chemical (organic and inorganic) contaminants from polluted waters. There is a broad consensus on the view that "reactivity loss" and "permeability loss" are the two main problems hampering the design of sustainable Fe^0 systems. However, the view that Fe^0 is a reducing agent (electron donor) under environmental conditions should be regarded as a distortion of Corrosion Science. This is because it has been long established that aqueous iron corrosion is a spontaneous process and results in the Fe^0 surface being shielded by an oxide scale. The multi-layered oxide scale acts as a conduction barrier for electrons from Fe^0. Accordingly, "reactivity loss", defined as reduced electron transfer to contaminants, must be revisited. On the other hand, because "stoichiometric" ratios were considered while designing the first generation of Fe^0 PRBs (Fe^0 as reductant), "permeability loss" should also be revisited. The aim of this communication is to clarify this issue and reconcile a proven efficient technology with its scientific roots (i.e. corrosion science).

Keywords Adsorptive removal · Reactivity loss · Removal mechanisms · Size-exclusion · Zero-valent iron

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✉ Chicgoua Noubactep
cnoubac@gwdg.de

Minhui Xiao
xiaominhui@hhu.edu.cn

Rui Hu
rhu@hhu.edu.cn

Arnaud Igor Ndé-Tchoupé
ndetchoupe@gmail.com

Willis Gwenzi
wgwenzi@gast.uni-kassel.de; wgwenzi@yahoo.co.uk

Hans Ruppert
hrupper@gwdg.de

[1] School of Earth Science and Engineering, Hohai University, Fo Cheng Xi Road 8, Nanjing 211100, China

[2] Applied Geology, University of Göttingen, Goldschmidtstraße 3, D-37077 Göttingen, Germany

[3] Grassland Science and Renewable Plant Resources, Faculty of Organic Agricultural Science, University of Kassel, Steinstrasse 19, 37213 Witzenhausen, Germany

[4] Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB), Potsdam, Germany

[5] Department of Water and Environmental Science and Engineering, Nelson Mandela African Institution of Science and Technology, P.O. Box 447, Arusha, Tanzania

[6] Faculty of Science and Technology, Campus of Banekane, Université Des Montagnes, P.O. Box 208, Bangangté, Cameroon

[7] Centre for Modern Indian Studies (CeMIS), Universität Göttingen, Waldweg 26, 37073 Göttingen, Germany

[8] Department of Sedimentology & Environmental Geology, University of Göttingen, Goldschmidtstraße 3, 37077 Göttingen, Germany

Introduction

Dissolved species and pathogens are mostly quantitatively removed from aqueous solutions in the presence of metallic iron (Fe^0) (Devonshire 1890; Baker 1934). This century-old knowledge has been intensively applied during the past three decades in solving the challenges for a clean environment and safe drinking water (Wakatsuki et al. 1993; Henderson and Demond 2007; Chen et al. 2014; Ghauch 2015; Guan et al. 2015; Singh et al. 2023; Lawrinenko et al. 2023a). Despite such a broad application, an understanding of the science of the Fe^0 remediation technology has not yet been achieved (Cao et al. 2022; Lawrinenko et al. 2023b; Noubactep 2023). In particular, an understanding of the mechanisms of water decontamination in Fe^0/H_2O systems is useful for designing sustainable systems in practice (Comba et al. 2011; Fu et al 2014; Obiri-Nyarko et al 2014).

Mechanistic information regarding the operating mode of Fe^0/H_2O systems is conflicting. For example, Matheson and Tratnyek (1994) used slowly stirred batch experiments (≤ 15 rpm) to suggest that chlorinated carbons (RCl) are removed from aqueous solution mostly via reductive degradation mediated by electrons from Fe^0. Weber (1996) reported to have confirmed that reductive transformation by Fe^0 is a surface-mediated process while using 4-aminoazobenzene as a probe contaminant and a completely different experimental design. Weber (1996) also reported that the requirement that the contaminant contacts the Fe^0 surface for electron transfer can be circumvented by the addition of soluble electron mediators. Roberts et al. (1996) and several other authors made similar conclusion which finally led to the "broad concensus" (O'Hannesin and Gillham 1998) that Fe^0 oxidative dissolution is the anodic reaction occurring simultaneously to the cathodic reduction in the contaminant of interest (e.g. an electrochemical reaction). It should be pointed out that this reasoning is limited to reducible contaminants, while several other non-reducible species, including pathogens, have been quantitatively eliminated from the aqueous phase in the presence of Fe^0 (You et al. 2005; Henderson and Demond 2007; Noubactep 2007). Thus, the removal of non-reducible contaminants and microbes cannot be explained by the concept of reductive transformation or degradation.

In contrast, Lipczynska-Kochany et al. (1994) questioned the validity of the reductive transformation concept in a context where iron corrosion increases the pH value of the system and the universal oxide scale on Fe^0 impedes any (quantitative) electron transfer from the metal body. Similarly, Schreier and Reinhard (1994) found a lag time between the initiation of the reaction and the start of the degradation of chlorinated organic compounds in Fe^0/H_2O systems. Further results questioning the validity of the reductive transformation concept were presented by several authors including Cantrell et al. (1995), Warren et al. (1995), Fiedor et al. (1998), Qiu et al. (2000), Farrell et al. (2001), Lavine et al (2001), and Jiao et al. (2009).

While it is certain that the reductive transformation concept has never been univocally accepted/established, a cursory survey of the Fe^0 literature reveals that it is favoured by the large majority of active researchers investigating Fe^0/H_2O systems (Chen et al. 2014; Guan et al. 2015; Hu et al. 2021; Lawrinenko et al. 2023a). In particular, Lawrinenko et al. (2023a) recently attempted to reiterate the validity of the named concept while characterizing divergent views as "isolated misconceptions". The views reported by Lawrinenko et al. (2023a) contrast with recent developments that the observation that organic substances are reductively degraded in Fe^0/H_2O systems was not entirely new, rather, it has been known around 1990 as reported by Reynolds et al. (1990) (Hu et al. 2021; Konadu-Amoah et al. 2021). Moreover, the view that any dissolved species can exchange electrons with Fe^0 disproves a century-old knowledge that protons (H^+) and protons alone oxidize Fe^0 under environmental conditions ($pH > 4.5$) (Whitney 1903). Actually, the pioneers of the Fe^0 remediation technology have not considered Whitney (1903) and other ancient works like Gould (1982), Murphy (1988), Khudenko (1991), and Murphy (1991), while

Table 1 Bibliometric analysis of six important references pertinent to the understanding of the operating mode of Fe^0/H_2O systems using Google Scholar (https://scholar.google.de, Accessed 01.12.2022)

Reference	Total	Fe^0 lit	First cited	RGN	P
	(-)	(-)	(-)	(-)	(%)
Devonshire (1890)	64	62	2017	50	80.6
Whitney (1903)	139	21	2018	19	90.5
Baker (1934)	43	27	2017	24	88.9
Cutler (1987)	6	2	2017	0	0.0
Khudenko (1991)	39	24	2000	14	58.3
Reynolds et al. (1990)	260	212	1994	29	13.7
Gillham and O'Hannesin (1994)	1817	702	1994	43	6.1
Lipczynska-Kochany et al. (1994)	171	13	1995	34	26.2
Matheson and Tratnyek (1994)	1938	592	1995	63	10.6
Schreier and Reinhard (1994)	158	92	1995	31	33.7

For comparison, a bibliometric analysis of the first published peer-reviewed articles is added. It is seen that pioneering works were only discovered around 2017, 27 years after Reynolds et al. (1990). These works are predominantly ($P > 58\%$) referenced by our research group led by Dr. Noubactep (RGN). P in % represents the extent to which RGN has cited each reference relative to the total citation within the Fe^0 literature (Fe^0 lit.)

introducing their concept. Table 1 gives an overview of the extent to which six selected relevant pioneering scientific articles have been considered in the Fe^0 remediation literature. Khudenko (1991) utilized Cu^{2+} cementation by Fe^0 to generate Fe^{II} species (and H/H_2 species) for the reductive destruction of organics. This approach was rooted in the knowledge that direct electron transfer from Fe^0 is impossible (Whitney 1903; Khudenko 1985, 1987). In other words, it was established before 1994 that Fe^0 is corroded by an electrochemical mechanism while contaminants are reduced by a chemical mechanism.

Table 1 clearly shows that our research group (RGN) has largely considered the pioneering works with a citation rate varying from 6.1% for Gillham and O'Hannesin (1994) to 33.7% for Schreier and Reinhard (1994). Table 1 also reflects the fact that the reductive transformation concept was favoured (Sect. 1) as Gillham and O'Hannesin (1994) and Matheson and Tratnyek (1994) were roundly referenced 10 times more than Lipczynska-Kochany et al. (1994) and Schreier and Reinhard (1994). This selective citation is particularly evident considering that these papers were published in the same year (i.e., 1994). Another important feature reflected in Table 1 is that only a tiny fraction of published articles have referenced the original mechanistic works. In fact, recent bibliometric studies suggest that more than 10,000 scientific articles on "Fe^0 for water remediation" have been published since 1994 (Chen et al. 2019; Antia 2020; Li et al. 2021). Actually, Google Scholar covers also graduation thesis and technical documents.

Given the crucial importance of the actual reaction mechanisms for the design of sustainable Fe^0 remediation systems, the present work critically analyses the contaminant-free Fe^0/H_2O system to improve the mechanistic understanding of its operating mode. The presentation starts with a discussion of the chemistry of aqueous iron corrosion.

Aqueous iron corrosion: the Fe^0/H_2O system

Iron primarily exists in the environment in two oxidation states: (i) highly soluble Fe^{2+} (ferrous iron) and (ii) lowly soluble Fe^{3+} (ferric iron) (Langmuir 1997). Once immersed in water, reactive Fe^0 undergoes oxidative dissolution (corrosion) owing to its instability. It was demonstrated 120 years ago that aqueous iron corrosion under environmental conditions is an electrochemical process, whereby Fe^0 dissolves at an anode (Eq. 1) and proton (H^+ from water dissociation) reduction takes place at a cathode (Eq. 2) (Whitney 1903). Clearly, the knowledge that water (H^+) and only water (H^+) accepts electrons from Fe^0 (Eq. 3) is a century-old scientific fact.

$$Fe^0 \Leftrightarrow Fe^{2+} + 2\,e^- \tag{1}$$

$$2\,H^+ + 2\,e^- \Leftrightarrow H_2 \tag{2}$$

$$\Leftrightarrow Fe^0 + 2\,H^+ @ Fe^{2+} + H_2 \tag{3}$$

It should be highlighted that Whitney (1903) explicitly excluded the possibility that dissolved oxygen accepts electrons from Fe^0 (Eq. 1). This makes the following reaction (Eq. 4) impossible:

$$2Fe^0 + 4H^+ + O_2 @ 2Fe^{2+} + 2H_2O \tag{4}$$

As shown in Table 1, Whitney (1903) has been overlooked in the Fe^0 remediation literature until 2018. This means that the pioneers of the technology have performed incomplete literature research. This is unfortunate as the paper has been published twice: (i) in 1903 at the Journal of the American Chemical Society (original version) and (ii) in 1947 at CORROSION, The Journal of Science and Engineering. The textual reproduction was enriched with the mention: "Dr. W.R. Whitney's classical paper on the electrochemical principles of corrosion is reproduced here by courtesy of the American Chemical Society from that Society's 1903 journal. In recognition of Dr. Whitney's work in establishing this theory of corrosion, the National Association of Corrosion Engineers this year founded the Willis Rodney Whitney Award in the Science of Corrosion, and designated Dr. Whitney the first recipient of the award, presentation of which was made during the NACE award meeting in Chicago, III, April 7–10, 1947."

Dr. Whitney's theory negates the popular view that Fe^0 is corroded by water (Eq. 3) only under anoxic conditions (absence of O_2) (Matheson and Tratnyek 1994; Zhang et al. 2022). It also reiterates that under oxic conditions (presence of O_2), Fe^0 corrosion is accelerated because O_2 consumes Fe^{2+} for its reductive transformation (Eq. 5) (Le Chatelier Principle).

$$4Fe^{2+} + 4H^+ + O_2 @ 4Fe^{3+} + 2H_2O \tag{5}$$

In other words, the often-written reaction of Fe^0 oxidation by O_2 (under oxic conditions) (Eq. 4) should be regarded as impossible, even though it is still regarded as textbook knowledge. Once this misconception is fixed, scope exists for an agreement on the further transformations of ferrous and ferric ions to generate an oxide scale shielding the Fe^0 surface and slowing the kinetics of Fe^0 corrosion (Nesic 2007; Noubactep 2010). As evident from Eqs. 3 and 5, Fe^0 corrosion consumes H^+ and induces a significant increase in the pH value of the solution. A concomitant decline in solution redox potential (Eh) has been documented (Matheson and Tratnyek 1994; Singh et al. 2023). In other words, irrespective of the presence of any contaminant, the immersion of Fe^0 in a system may lead to the development of highly reducing conditions.

Another key feature from Whitney (1903, 1947) is that depending on the salinity of natural waters, for $pH > 4.5$, Fe^0 corrosion produces low-solubility hydroxides/oxides and more soluble salts (Antia 2020, 2022; Tao et al. 2023). The generation of iron hydroxides/oxides is certain as far as Fe^0 is reactive. However, the amount generated is unknown and cannot be estimated because the corrosion rate is unknown (non-constant and nonlinear) (Angst 2019; Yang et al. 2021, 2022). In a porous system, the extent of Fe^0 corrosion (spatially and temporally) depends on three key factors: (i) the relative solubility of hydroxides and salts, (ii) the concentration of dissolved O_2, and (iii) the residual porosity and the pore size distribution. For the proper discussion of the mechanisms of water decontamination using Fe^0/H_2O systems, it is essential to consider the relative abundance of Fe^0, O_2 and salts. Assuming that Fe^0 is available in stoichiometric abundance, for highly soluble salts (e.g. $FeCl_2$, $FeCl_3$), the extent of hydroxide precipitation depends on the time scale of Cl^- exhaustion (Antia 2020; Tao et al. 2023).

This section has reiterated the complexity of the contaminant-free Fe^0/H_2O system. The challenge for scientists is to properly investigate its changes with the numerous influencing factors, including: (i) Fe^0 intrinsic reactivity, (ii) water chemistry (electrolyte), (iii) water flow velocity (stagnant vs. convection), (iv) the presence of microorganisms, and (v) the presence of reactive phases (e.g. FeS_2, MnO_2) (Cao et al. 2022). In dynamic systems, the time-dependent properties of the porous medium (pore size and pore size distribution) must be considered as well (Wielinski et al. 2022). Clearly, it is about a holistic consideration of various interdependent dynamic processes such as Fe^0 corrosion, contaminant transport, chemical reactions, and particle transport (Bedrikovetsky 2008; Yang et al. 2021).

Investigating the remediation Fe^0/H_2O system

Section 2 recalls the major characteristics of the contaminant-free Fe^0/H_2O system which can be summarized in two points: (i) Fe^0 corrodes, and an oxide scale is generated in its vicinity (not really at its surface), and (ii) the extent of Fe^0 corrosion depends on various inter-related factors, including water chemistry (electrolyte's nature) and the available volume of pores (e.g. pore size and pore size distribution). In other words, polluted water (to be remediated) is just an electrolyte containing elevated concentrations of selected contaminants, typically in trace amounts (μg/L or mg/L). However, the electrolyte is just one component of an electrochemical cell. The three other components are: (i) the anode where Fe^0 is dissolved (to Fe^{2+}) and electrons are released, (ii) the uncorroded Fe^0 conducting the released electrons to the cathode, and (iii) the cathode where electrons from Fe^0 are exchanged (with protons) and molecular H_2 is generated (Groysman 2010; Noubactep 2014). At this stage of reasoning, four points need to be highlighted: (i) immersed Fe^0 corrodes also in the absence of O_2 and any contaminant (Fact 1), (ii) the oxide scale on Fe^0 acts as a diffusion barrier for O_2 and contaminants (Fact 2), (iii) the oxide scale on Fe^0 is non-conductive and acts as conduction barriers for electrons from Fe^0 (Fact 3), and (iv) Fe^{2+} and H_2 are standalone reducing agents (Fact 4). Facts 1–4 have been presented by Noubactep (2007, 2008) to refute the validity of the theory that Fe^0 donates electrons to any dissolved species. Attempts to falsify Noubactep's view to date were collectively limited to supporting the view introduced in the 1990s. For example, Lawrinenko et al. (2023a, 2023b) supported their views while citing Cutler (1987), Gillham and O'Hannesin (1994), and Matheson and Tratnyek (1994). These three articles are claimed to have provided "evidence for direct electron transfer and the corrosion of Fe^0 in contact with chlorinated hydrocarbons". However, as shown in Table 1, the two papers from 1994 have not considered Whitney (1903), while Cutler (1987) is rather a review article on the interactions of Al^0 with halogenated hydrocarbons. Clearly, since the rejection of the reductive transformation concept about 15 years ago, some colleagues have approved the alternative concept (Ghauch et al. 2011; Gheju 2011; Giles et al. 2011; Ghauch 2015; Sista et al. 2021; Gheju and Balcu 2019, 2023; Lan et al. 2023), while the large majority has overlooked it. Lawrinenko et al. (2023a) is the very first attempt to falsify the new concept.

Coming back to the contaminant-free Fe^0/H_2O system, and considering dissolved O_2 as a non-polluting contaminant, its reduction by Fe^{2+} (Eq. 4) induces concentration changes in the vicinity of Fe^0 and in the adjacent porous system. However, the dynamic relationships between these concentration changes and the extent of Fe^0 corrosion are complex and depend on many factors, including: (i) chemical reactions (e.g. O_2 reduction, oxide precipitation), (ii) local pore structure (e.g. size of Fe^0 and sand particles), and (iii) ionic transport, diffusion within the oxide scale, and advection in moving water. The presence of contaminants and site-specific microorganisms are two other complicating parameters (Angst 2019; Yang et al. 2021; Tao et al. 2023). Thus, it is impossible to root the understanding of the Fe^0/H_2O system on simple engineering approaches, merely based on the nature of the contaminant and its redox reactivity relative to the redox couple Fe^0/Fe^{II} ($E^0 = -0.44$ V) (Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994; Sarr 2001; Fu et al. 2014; Obiri-Nyarko et al. 2014; Lawrinenko et al. 2023a).

At this stage of reasoning, it should be highlighted that $E^0 = -0.44$ V, the electrode potential of the Fe^{II}/Fe^0 redox couple, is not the decisive factor to justify the use of Fe^0 in water treatment. The first reason for this is that the oxide scale is positively charged and will selectively attract negatively charged pollutants (Sato 2001; Miyajima 2012; Phukan et al. 2015). On the other hand, Al^0 ($E^0 = -1.66$ V), Mg^0 ($E^0 = -2.38$ V), and Zn^0 ($E^0 = -0.76$ V) are more powerful reducing agents than Fe^0 (Cutler 1987; Shreier and Reinhardt 1994; Warren et al. 1995). Proponents of the reductive transformation concept have not really considered this key aspect to explain why these metals are not used for the removal of contaminants in a similar way as Fe^0. Rather, their reasoning was limited to toxicity and cost issues. However, particularly, Al^0 and Zn^0 are not suitable for long-term operations because they just form one hydroxide each ($Al(OH)_3$ and $Zn(OH)_2$) and one oxide (Al_2O_3 and ZnO). The unit cells in Al and Al_2O_3 on the one side and that of Zn and ZnO on the other side are very similar to one another. Thus, Al_2O_3 adheres tightly to Al^0 beneath it, just as ZnO adheres tightly to Zn^0. In both cases, the oxidized surface provides a protective layer that prevents O_2 from getting to the underlying metal surface (Dickerson et al. 1979; Noubactep 2010). In contrast, the packing dimensions of Fe^0 and Fe oxides are not particularly close; thus, there is no tendency for an iron oxide layer to adhere to Fe^0. Accordingly, the oxide scale on Fe^0 constantly flakes off and exposes fresh Fe^0 surfaces for attack or corrosion (Dickerson et al. 1979). This is the reason why Fe^0 is a long-term source of iron oxides for water remediation (James et al. 1992; Wakatsuki et al. 1993; Jia et al. 2007; Bradley et al. 2011), and not a long-term source of electrons for the reductive transformation of selected species (Lawrinenko et al. 2023a) (Fig. 1).

Figure 1 recalls that both concepts recognized the formation of the oxide scale on Fe^0. On the one hand, the reductive transformation concept strives to explain why electron transfer from Fe^0 occurs despite the presence of the oxide scale (Scherer et al. 2000; Lawrinenko et al. 2023a). On the other hand, the alternative concept supported by the seminal work of Whitney (1903) argues that such an electrochemical reaction is impossible (Cao et al. 2022; Noubactep 2023). It is very important to recall that for the concentration ranges of natural water, chemical reduction is not even a relevant remediation mechanism for many substances, particularly when it comes to safe drinking water (Noubactep 2011; Heimann et al. 2018). The reason is that even reaction products have to be removed from the aqueous phase. However, the maximum contamination limit (MCL) is generally lower than the solubility limit (Kalin et al. 2005; Ndé-Tchoupé et al. 2015). For this reason, adsorption, co-precipitation, and size-exclusion as occurring in all Fe^0/H_2O systems are fundamental (Noubactep 2007, 2008; Ghauch et al. 2011; Gheju 2011; Giles et al. 2011; Noubactep 2011; Gheju and Balcu 2019; Sista et al. 2021).

Designing sustainable Fe^0 PRBs

The view that Fe^0 is an electron donor under environmental conditions has led to an empirical design of the first generation of Fe^0 PRBs. In fact, the stoichiometry of the reaction between Fe^0 and the contaminants of concern were considered (Sarr 2001), and a "safety factor" was used to "increase assurance of successful remediation" (Lawrinenko et al. 2023a). In this approach, mixing Fe^0 with non-expansive materials like pumice or sand was regarded as a " Fe^0 dilution" with cost benefits, but possible negative impacts on the efficiency of the resulting systems (Kenneke and McCutcheon 2003; Westerhoff and James 2003; Bi et al. 2009). Fe^0/sand mixtures were also used as pre-treatment systems to free inflowing water from dissolved O_2 such that the pure Fe^0 main treatment system could be fully anoxic (O_2 free) (Westerhoff and James 2003). Ironically, these efforts coexisted in the literature with the demonstration of the efficiency of Fe^0 PRBs using a Fe^0/sand mixture comprising 22% Fe^0 (w/w) (O'Hannesin and Gillham 1998).

Although differences in density between Fe^0 ($d = 7.6$ g/cm^3) and its corrosion products ($d < 5.2$ g/cm^3) have been previously considered in justifying permeability loss in Fe^0 PRBs (Liang et al. 2003, 2005), our research group led Dr.

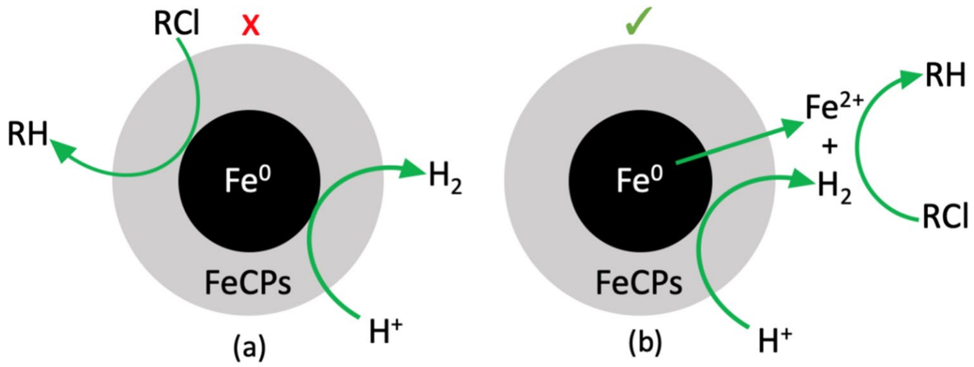

Fig. 1 Illustration of proposed hypotheses for contaminant (RCl) reduction in Fe^0/H_2O systems: (left) Fe^0 is oxidized by RCl and water (H^+) (Path 1), and (right) Fe^0 is oxidized by water (H^+) and RCl is reduced by Fe^{II} species and H_2 (Path 2). Path 1 is not feasible because the oxide scale is a conduction barrier for electrons from Fe^0. Path 2 is feasible and rooted in aqueous iron corrosion

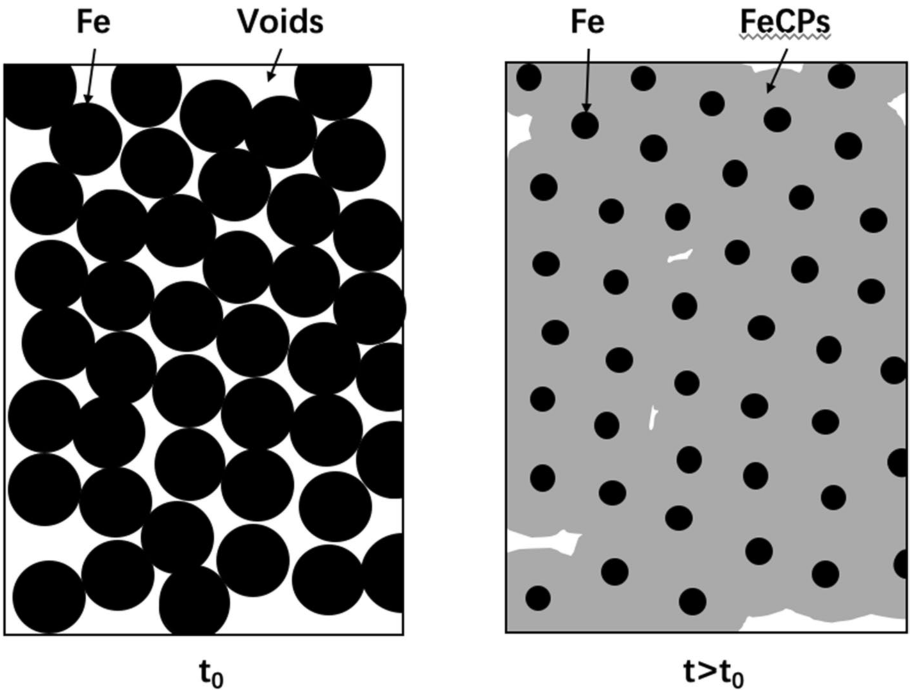

Fig. 2 Illustration of changes in the residual porosity in a bed filled with spherical Fe^0 particles: (left) at the start of the operation ($t_0 = 0$), and (right) sometimes later ($t > t_0$, but $t < t_\infty$) before Fe^0 complete exhaustion at t_∞. The time required for complete exhaustion (t_∞) depends on a diversity of factors, including Fe^0 intrinsic reactivity, initial porosity, water chemistry, and Fe^0 ratio

Noubactep was the first to properly consider the volumetric expansive nature of iron corrosion in designing Fe^0 filters (Noubactep and Caré 2010). Accordingly, replacing a fraction of Fe^0 in a filtration system with a non-expansive material (e.g. MnO_2, pumice, sand) is a tool to enable complete exhaustion of Fe^0 in the long-term (Moraci and Calabrò 2010; Noubactep et al. 2012; Caré et al. 2013; Bilardi et al. 2023). In 100% Fe^0 filters (Fig. 2), clogging occurs before Fe^0 exhaustion because of a lack of space for further dissolution. Figure 3 shows two systems, one with 100% Fe^0 and the other with 50% Fe^0 (vol/vol). Here, it is seen that the pure Fe^0 system clogs when the 50% Fe^0 has just lost 50% of its porosity. This reasoning implies that mixing Fe^0 and a non-expansive material is a tool to enable better material efficiency (avoid Fe^0 wastage), and a prerequisite for sustainability in terms of long-term permeability (Noubactep et al. 2012; Caré et al. 2013; Domga et al. 2015; Bilardi et al. 2023; Tao et al. 2023). Proponents of the reductive transformation concept have considered a decrease in the source of electrons (Fe^0 ratio) as a cause of declined system

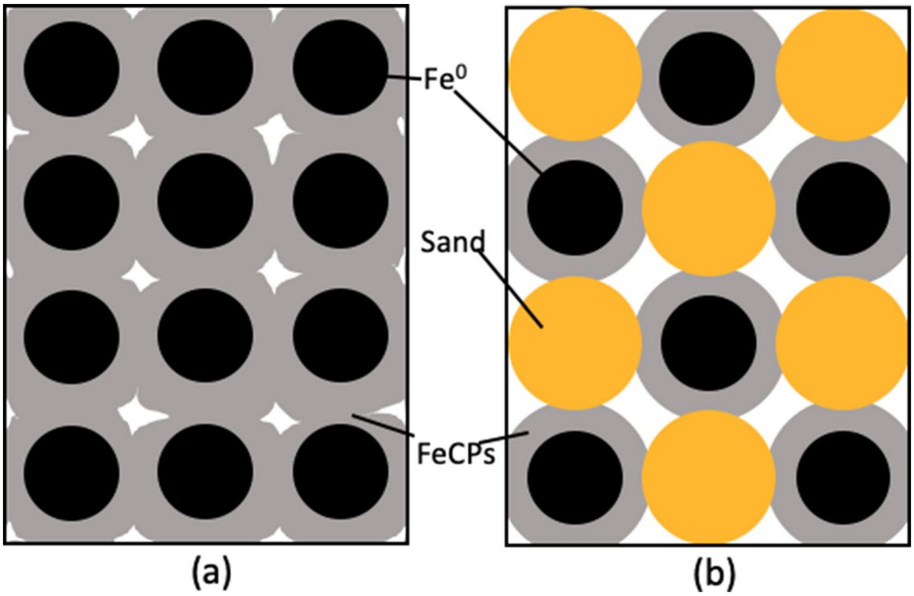

Fig. 3 Illustration of changes in the residual porosity in a bed filled with spherical particles: **a** 100% Fe^0, and **b** Fe^0/sand with 50% Fe^0 (vol/vol). The representation corresponds to a time (t) when the 100% Fe^0 is completely clogged. It is considered that the Fe^0/sand system has lost 50% of its initial porosity

performance for Fe^0 filters (Kenneke and McCutcheon 2003; Bi et al. 2009). Yet data from both batch and column studies show that admixing Fe^0 with non-expansive aggregates improves the performance of Fe^0/H_2O systems (Westerhoff and James 2003; Song et al. 2005; Moraci and Calabrò 2010; Miyajima 2012; Tepong-Tsindé et al. 2019; Gheju and Balcu 2023; Lan et al. 2023). Surprisingly, proponents of the reductive transformation concept have not yet revisited their theory in the light of this evidence (Wielinski et al. 2022; Lawrinenko et al. 2023a).

Another point of discrepancy between the two views is how to investigate spatio-temporal changes in Fe^0/H_2O systems. Proponents of the reductive transformation concept are still combining analytical tools to monitor changes in mineral phases in short-term experiments (some few weeks) (Wielinski et al. 2022), while our research group insists on the scarcity of long-term column studies (e.g. > 52 weeks, 1 year) (Tepong-Tsindé et al. 2019; Yang et al. 2022). In fact, using a pure thermodynamic approach (mass balance), the optimum Fe^0 ratio to avoid material wastage was determined as 25% (vol/vol) in hybrid Fe^0/sand systems (Miyajima 2012; Miyajima and Noubactep 2013). There is material wastage whenever Fe^0 is not completely exhausted as the system is clogged (Caré et al. 2013; Domga et al 2015). This is when the time to material exhaustion (t_∞) is lower than the time to clogging (t_{clog}). A Fe^0 volumetric ratio of 25% in a Fe^0/sand system roughly corresponds to (i) 50% Fe^0 (w/w) which has been used at several field installations (Henderson and Demond 2007; Guan et al. 2015) and (ii) the solution to the special case ($t_\infty = t_{clog}$, where clogging occurs promptly at Fe^0 complete exhaustion). The temporal issue that is the extent of porosity loss at any time (or time to clogging) is difficult or even impossible to address because the corrosion kinetics is not known and has even not been really investigated in the Fe^0 remediation context (Moraci et al. 2016; Noubactep 2016; Yang et al. 2022). Ironically, while Fe^0 oxidation by water is mostly considered as a side reaction, modelling efforts, since Mayer et al. (2001), are mainly rooted in its corrosion rate as determined by Dr. Eric J. Reardon 33 years ago (Reardon 1995).

A last fundamental design aspect to consider is how the expected decrease of the permeability will influence the long-term efficiency of Fe^0 PRBs. In fact, Fe^0 PRBs are designed to be more permeable than the surrounding aquifer material (O'Hannesin and Gillham 1998; Zhang et al. 2022; Plessl et al. 2023). However, despite mixing Fe^0 with non-expansive materials, the permeability of the reactive zone (Fe^0 PRB) will still decrease. Therefore, it makes sense to forecast specific cases, for example, when the initial PRB's permeability will decrease by one-quarter, one-third, or one-half. Considering such scenarios in the design phase would be useful for better monitoring of the system's performance (Yang et al. 2021, 2022).

Practical significance

The analysis in this study shows that under given operational conditions, Fe^0 can generate various amounts of FeCPs which are highly effective in removing many classes of contaminants from aqueous solutions (Bigg and Judd 2000; Henderson and Demond 2007; Cundy et al. 2008; Noubactep et al. 2009). Adsorption, co-precipitation, and size-exclusion (chromatographic effects) are the common underlying removal mechanisms, including for redox-active species. The robust design of sustainable Fe^0 PRBs depends on the profound understanding of how site-specific characteristics (e.g. O_2 availability, pH value, salinity) affect the long-term availability of FeCPs within the system (Naseri et al. 2017; Noubactep 2018; Tao et al. 2023). In other words, the analysis presented herein provides a new starting point for the conceptualization of future laboratory, pilot, and field-scale studies for the design of efficient and sustainable Fe^0 PRBs for groundwater remediation as well as systems to treat wastewater and Fe^0 filters for safe drinking water provision.

To the best of the authors' knowledge, only the research group of Dr. Vollprecht (starting later) has designed their whole experiments correctly and interpreted the results according to the state-of-the-art knowledge (Vollprecht et al. 2018, 2020; Sedlazeck et al. 2019, 2020). In retrospect, Vollprecht's articles on the "Ferrodecont Process" are built on Müller et al. (2014) entitled "Implementation of fluidized granulated iron reactors in a chromate remediation process". Müller et al. (2014) is nothing new, but an independent rediscovery of the Anderson Process as implemented in the 1880s in the waterworks of Antwerpten (Belgium) (Devonshire 1890; van Craenenbroeck 1998; Mwakabona et al. 2017; Antia 2020). Both processes (Anderson and Ferrodecont) are rooted in the evidence that in filtration systems, clogging is a special (or geometrical) effect occurring because space lacks to store the in-situ generated corrosion products (contaminant scavengers) (Caré et al. 2013; Domga et al. 2015; Bilardi et al. 2023).

Conclusions and a look ahead

This article presents a critical assessment of the state-of-the-art knowledge on the operating mode of engineered Fe^0-based systems for water remediation as used for safe drinking water supply, wastewater treatment, and environmental remediation. The following major conclusions are drawn:

Immersing a reactive Fe^0 specimen in (polluted) water at a pH value higher than 4.5 results in its oxidative dissolution by H^+ ions and the generation of solid iron corrosion products which act as contaminant scavengers. Fe^0 dissolution also generates standalone reducing agents (e.g. Fe^{II} oxides, Fe^{II}/Fe^{III} oxides, H_2) which may reduce selected contaminants by a chemical reaction. In other words, although Fe^0 corrosion in PRBs is an electrochemical process, oxidizing electrons are not supplied by any dissolved contaminant. This century-old knowledge has been overlooked for 28 years while discussing the mechanisms of contaminant removal in Fe^0/H_2O systems (Table 1).

Despite the discrepancy in the actual operating mode of engineered Fe^0-based systems, a well-documented advantage of these systems is that their decontamination efficiency can be maintained for decades (Phillips et al. 2010; Wilkin et al. 2014, 2019). This is an additional motivation to root this technology in its scientific background (i.e. iron corrosion).

The relationship between Fe^0 dissolution, porosity loss, and water decontamination is very complex. This is because of the numerous inter-related and partly dynamic influencing factors involved in the processes. Relevant influencing factors include: (i) the porous structure (e.g. size, distribution), (ii) the water chemistry (e.g. O_2 availability, pH value, salinity), (iii) water flow velocity, and (iv) the action of microorganisms. Thus, engineering or pragmatic approaches for understanding the mechanisms of water treatment using Fe^0/H_2O systems have proven unreliable. The scientific challenge for the coming years is to properly consider advances in numerical modelling (e.g. reactive transport modelling in porous media) to devise models capable of considering: (i) the spatio-temporal changes within the Fe^0/H_2O system at the pore-scale level, and (ii) the interdependence between the involved processes (e.g. chemical reactions, Fe^0 reactivity, Fe^0 ratio, and transport processes).

A concerted effort is needed to pave the way out of the current "valley of confusion" characterized by a high level of empiricism. It is hoped that based on the clarifications presented herein, new engineering tools will be developed to increase the effectiveness and reliability of the next generation of Fe^0 PRBs as an efficient and sustainable technology for groundwater remediation.

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Declarations

Conflict of interest The authors declare no confict of interest.

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