



Metallic Iron for Environmental Remediation: The Fallacy of the Electron Efficiency Concept

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The suitability of remediation systems using metallic iron (Fe⁰) has been extensively discussed during the past 3 decades. It has been established that aqueous Fe⁰ oxidative dissolution is not caused by the presence of any contaminant. Instead, the reductive transformation of contaminants is a consequence of Fe⁰ oxidation. Yet researchers are still maintaining that electrons from the metal body are involved in the process of contaminant reduction. According to the electron efficiency concept, electrons from Fe⁰ should be redistributed to: i) contaminants of concern (COCs), ii) natural reducing agents (e.g., H₂O, O₂), and/or iii) reducible co-contaminants (e.g. NO₃⁻). The electron efficiency is defined as the fraction of electrons from Fe⁰ oxidation which is utilized for the reductive transformations of COCs. This concept is in frontal contradiction with the view that Fe⁰ is not directly involved in the process of contaminant reduction. This communication recalls the universality of the concept that reductive processes observed in remediation Fe⁰/H₂O systems are mediated by primary (e.g., Fe^{II}, H₂) and secondary (e.g., Fe₃O₄, green rusts) products of aqueous iron corrosion. The critical evaluation of the electron efficiency concept suggests that it should be abandoned. Instead, research efforts should be directed towards tackling the real challenges for the design of sustainable Fe⁰-based water treatment systems based on fundamental mechanisms of iron corrosion.

Keywords: contaminant removal, electron efficiency, environmental remediation, zero-valent iron, safe drinking water

INTRODUCTION

Metallic iron (Fe⁰), also termed as zero-valent iron (ZVI) is widely considered as a cost-effective reducing agent for organic pollutants in groundwater (Henderson and Demond 2007; Guan et al., 2015; Cao et al., 2020; He et al., 2020). The Fe⁰-based permeable reactive barrier (PRB) technology for groundwater remediation is rooted on this premise (Gillham 2008; Chen et al., 2019; Xiao et al., 2020a; Xiao et al., 2020b; He et al., 2020; Wang et al., 2022). Fe⁰ has also been successfully used for the removal of various inorganic contaminants (e.g. As, NO₃⁻) and pathogens (e.g., bacteria, viruses) from polluted waters (Richardson and Nicklow 2002; Henderson and Demond 2007; Gheju 2011;

TABLE 1 | An overview of the most important discoveries regarding the reduction mechanisms in Fe⁰/H₂O system shown in the form of a timeline. For the discussion herein, it suffices to consider two facts: i) ref. [6] has not considered previous works, and ii) the results of [6] was disproved by ref. [10].

Time	Event	Ref.
1854	Fe ⁰ reduces aromatic nitro compounds to amines	[1]
1877	Fe ⁰ water filters are presented in the scientific literature	[2]
1903	Whitney established that water is the sole oxidant for Fe ⁰ under environmental conditions	[3]
1988	Fe ⁰ is used for the reduction of inorganic micro-pollutants	[4]
1991	Fe ⁰ is used for the indirect reduction of organic micro-pollutants Fe ⁰ is oxidized by Cu ²⁺	[5]
1994	Direct reductive transformation of RCl by Fe ⁰ is claimed CCl ₄ is one of the probe contaminants	[6]
1995	Direct reductive transformation of RCl by Fe ⁰ is questioned	[7]
1998	Direct reductive transformation of RCl by Fe ⁰ is favored It is explicitly recognized as a “broad consensus”	[8]
2007	Direct reductive transformation of RCl by Fe ⁰ is theoretically refuted	[9]
2009	Direct reductive transformation of CCl ₄ by Fe ⁰ is experimentally disproved	[10]

[1] = Popat and Padhiyar (2013); [2] = Bischof (1877); [3] = Whitney, 1903; [4] = Murphy (1988); [5] = Khudenko (1991); [6] = Matheson and Tratnyek (1994); [7] = Warren et al. (1995); [8] = Gillham and O' Hanesin, 1994; [9] = Noubactep (2007); [10] = Jiao et al. (2009).

Guan et al., 2015; Cao et al., 2020; Kim et al., 2021; Noubactep, 2021). However, these applications are mainly perceived to be derived from the Fe⁰ PRB technology for organic pollutants (Obiri-Nyarko et al., 2014; Naseri et al., 2017). The concept that Fe⁰ is an electron donor under environmental conditions has never been experimentally established (Warren et al., 1995; Farrell et al., 2001; Lavine et al., 2001; Jiao et al., 2009; Naseri et al., 2017; Cao et al., 2020; Hu et al., 2020; Noubactep, 2022). For example, while investigating the reductive dechlorination of carbon tetrachloride (CT) in Fe⁰/H₂O systems, Jiao et al. (2009) clearly demonstrated that reducing electrons are not from Fe⁰, although iron corrosion was helpful for CT reductive dechlorination. Their conclusions read as: “The inherent relationship between the dechlorination of CT and the corrosion of iron is attributed to the fact that the adsorbed hydrogen atoms produced during the iron corrosion process are necessary for the dechlorination process of CT.” **Table 1** summarizes some key arguments presented in the broad scientific literature prior to the advent of the recent Fe⁰ remediation technology, and disproving the reductive transformation concept.

The idea that organic pollutants are reductively transformed by Fe⁰ was introduced in the scientific literature by Reynolds et al. (1990). Scientists from the University of Waterloo (Canada) were investigating the potential for sampling bias caused by sorption of chlorinated organic species to materials commonly used in groundwater sampling (Lee et al., 2004; Gillham 2008; Cao et al., 2020). Their results revealed losses of chlorinated organic contaminants from water samples in contact with Fe⁰-based vessels. Hence, reductive dechlorination was proposed as the most likely reaction path (Reynolds et al., 1990; Gillham 2008). This observation coincided with a period when geochemists were looking for suitable materials for the realization of the concept of groundwater remediation using PRBs as introduced in the 1980s by McMurty and Elton (1985). In other words, Fe⁰ was considered a reducing agent (or an electron donor) for organic pollutants, because their reductive transformation was observed in its presence, in the Fe⁰/H₂O system. This coincidence was misinterpreted as a scientific fact and still prevails (Cao et al., 2020; Thakur et al.,

2020; Noubactep, 2022). Investigations by Matheson and Tratnyek (1994) and Weber (1996) have been reported to confirm these observations. Moreover, it was claimed that the observation that organic pollutants can be reduced in Fe⁰/H₂O systems was novel (Matheson and Tratnyek, 1994; Gillham 2008). Unfortunately, the then available seminal works of Khudenko (1985), Khudenko (1987), and Khudenko (1991) frontally contradict the claimed novelty (Cao et al., 2020). In particular, in the paper entitled, “Feasibility evaluation of a novel method for destruction of organics” (Khudenko, 1991), Boris Michael Khudenko demonstrated that Cu²⁺ cementation by Fe⁰ can be used to induce the reductive degradation of organic pollutants (**Table 2**). Clearly, Fe⁰ is oxidized by Cu²⁺ and reaction products (Fe^{II} and H₂ species) act as reducing agents for the (organic) contaminants of concern (COCs). In other words, Fe^{II} species resulting from iron corrosion are used for the “destruction of organics.” Factually, H₂ and H species also resulting from iron corrosion are reducing agents as demonstrated by Jiao et al. (2009).

Table 2 summarizes the experimental conditions and results of Khudenko (1991) with regard to the Fe⁰/H₂O system. In Khudenko (1991)'s work, an aqueous solution of Direct Yellow 12 was acidified to an initial pH value of 4.5 using H₂SO₄. Two parallel experiments were performed differing in the addition or non-addition of 100 mg L⁻¹ Cu²⁺ (CuSO₄). Used Fe⁰ was a 1 m long iron wire of 0.2 mm in diameter. The filtrate was stirred by a magnetic stirrer. Results demonstrated that with Cu²⁺ addition, complete discoloration was achieved within 2.5 min, while the system without Cu²⁺ could not be discolored at all after 60 min of stirring. More Fe⁰ was consumed in the absence of Cu²⁺ than with Cu²⁺. The second experiment was conducted with a wastewater from finishing operations of a textile mill. The wastewater had a rosy color, and an initial pH value of 8.0. Addition of Cu²⁺ alone changed the color to dark blue suggesting formation of Cu²⁺ complex. Cementation with Fe⁰ and Cu²⁺ resulted in 98.5% color removal, while the process without copper resulted in just 10% color removal (**Table 2**).

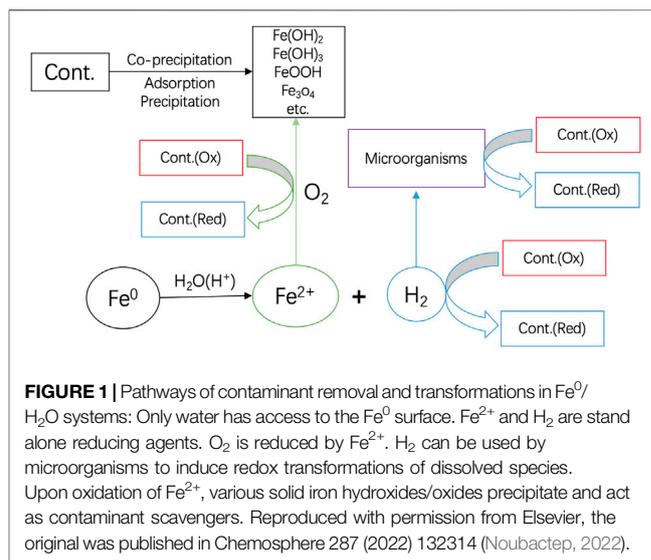
It is surprising that 3 years after the brilliant concept of Khudenko (1991) and its validation using both synthetic and

TABLE 2 | Summary of experimental conditions and results for the Fe⁰/H₂O systems investigated by Khudenko (1991). pH₀ = initial pH, [X] = concentration of X, pH = final pH, E = per cent removal efficiency, n.s.: not specified.

Pollutant	pH ₀ (-)	[Cu ²⁺] (mg L ⁻¹)	Stirring time (min)	pH (-)	Fe loss (mg)	E (%)
Direct Yellow 12	4.5	100.0	2.5	4.5	28.5	100.0
Direct Yellow 12	4.5	0.0	60.0	5.3	45.3	0.0
Industrial wastewater	8.0	100.0	n.s.	n.s.	n.s.	98.5
Industrial wastewater	8.0	0.0	n.s.	n.s.	n.s.	10.0

real wastewater, Matheson and Tratnyek (1994) introduced the contradiction without proving Khudenko (1991) wrong. In fact, Matheson and Tratnyek (1994) did not even consider that earlier work by Khudenko (1991). Bigg and Judd, 2000 were the first scientists to cite Khudenko (1991), 2 years after the report that the concept that, Fe⁰ is a reducing agent was a “broad consensus” (O’Hannesin and Gillham, 1998). It is also surprising that the view of Matheson and Tratnyek (1994) was claimed to be experimentally validated (Roberts et al., 1996; Weber, 1996) and is still favored by the majority of active researchers on the remediation Fe⁰/H₂O system (Naseri et al., 2017; Xiao et al., 2020a; Xiao et al., 2020b; Cao et al., 2020; Hu et al., 2020; Hu et al., 2021; Noubactep, 2022). Accordingly, the whole mechanistic discussion is based on the idea that there is some electron transfer from the Fe⁰ bulk material to COCs, which are potentially transformed into non-toxic or less toxic species (He et al., 2020). The extent of this reaction was conventionally evaluated using the reaction rate constant *k* (kobs or kSA) (Johnson et al., 1996; McGeough et al., 2007). However, according to Liu et al. (2013) this is inappropriate because the extent of iron corrosion and the proportion of electrons used for the transformation of COCs should be considered to assess the economics of the system. In other words, the goal was to avoid superfluous Fe⁰ dosages which impede the economics of the designed systems (Wu et al., 2014; Shufen et al., 2018, He et al., 2020). During the past 8 years, an important number of papers has been published on the suitability of the electron efficiency concept (EE concept). He et al. (2020) give an excellent overview on the topic, and, interested readers are referred to this very recent review article.

To this point, the presentation has highlighted that the EE concept is intrinsically wrong, because Fe⁰ does not play any significant role in the process of contaminant reductive transformation in Fe⁰/H₂O systems (Whitney, 1903; Jiao et al., 2009; Noubactep, 2022). In fact, while Jiao et al. (2009) have proven Matheson and Tratnyek (1994) wrong, Whitney (1903) had already established that under environmental conditions, Fe⁰ is oxidized only by protons (H⁺), even in the presence of dissolved oxygen (O₂) and carbonic acid (H₂CO₃) (Table 1). The present communication aims at demonstrating the fallacy of the EE concept in order to avoid its further propagation. The presentation starts with chemistry of the Fe⁰/H₂O system, followed by a historical overview on water treatment using Fe⁰, and ends with a critical evaluation of the usefulness of the EE concept.



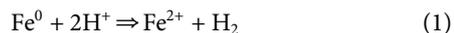
THE CHEMISTRY OF THE FE⁰/H₂O SYSTEM

Aqueous iron corrosion is an electrochemical process which needs four compartments to occur: an anode, a cathode, a conductor and an electrolyte (Landolt, 2007; Groysman, 2010). In the remediation Fe⁰/H₂O system, the conductor is the metal body (Fe⁰), the electrolyte is the polluted water, the anode is an area of the Fe⁰ surface where oxidative dissolution occurs (releasing ferrous iron–Fe²⁺), and the cathode is an area of the Fe⁰ surface where electrons left behind by Fe²⁺ are transferred to a reducible species. A key feature of this process is that, the reactions at the anode and the cathode occur simultaneously, and the prerequisite is that the electrolyte must be in contact with both the anode and the cathode (Landolt, 2007; Noubactep, 2014; Noubactep, 2016).

Aqueous iron corrosion proceeds as follows: i) Fe⁰ is oxidatively dissolved at the anode to release Fe²⁺, ii) the generated Fe²⁺ ions migrate in the polluted water (electrolyte), and iii) then electrons left behind by Fe²⁺ are transferred through the metal body (conductor) to a reducible species at the cathode. It is crucial to underline that electrons are transported from the anode to the cathode by Fe⁰. Electron transfer to any adsorbed species only occurs if there is no conduction barrier at the Fe⁰ surface (Landolt, 2007; Nescic, 2007; Lazzari, 2008; Groysman, 2010). It is well-known that, at pH > 4.5, an oxide scale forms on the Fe⁰ surface and shields it from dissolved species, including

dissolved O_2 (Stratmann and Müller, 1994; Lazzari, 2008). For the EE concept to be applicable, it means that the universal oxide scale on Fe^0 should be electronically conductive, which is not the case in Fe^0/H_2O systems (Noubactep 2007; Noubactep, 2008; Noubactep, 2014; Noubactep, 2016). **Figure 1** summarized the pathways of contaminant removal and transformations in Fe^0/H_2O systems.

The electrochemical reaction for aqueous iron corrosion is depicted in Eq. 1:



Eq. 1 shows that iron corrosion consumes protons, thereby increasing the pH value. This means that adding protons (acidification) is a powerful tool to intensify iron corrosion where it is needed, for example for H_2 evolution (Ndé-Tchoupé et al., 2020). However, for environmental remediation, a pH shift to lower values is not typically envisaged such that a pH increase occurs as a rule (Lipczynska-Kochany et al., 1994; Matheson and Tratnyek, 1994; Schreier and Reinhard, 1994; Hu et al., 2021). This pH increase favours the formation of ferrous hydroxides [$Fe(OH)_2$], which polymerize and precipitate at the surface of Fe^0 or in its vicinity (Eq. 2). When dissolved oxygen (O_2) is present, ferric hydroxides [$Fe(OH)_3$] are formed as well. In the real world, whether the conditions are anoxic or oxic, iron corrosion generates an oxide scale which permanently shields its surface and is made up of several oxides and hydroxides (Odziemkowski and Simpraga, 2004). The process of oxide scale formation and transformation is a dynamic one (Odziemkowski et al., 1998; Sikora and Macdonald, 2000; Nescic, 2007; Lazzari, 2008; Groysman, 2010). It is certain that no electronically conductive oxide scale can be formed at the Fe^0 surface under environmental conditions (Nescic, 2007; Lazzari, 2008). In other words, the oxide scale, acting as diffusion barrier for contaminants and dissolved O_2 , also represents a conductive barrier for electrons from Fe^0 . For this reason, electrons from the metal body cannot (quantitatively) reduce any initially dissolved species (contaminants and O_2) (**Figure 1**) (Stratmann and Müller, 1994; Noubactep 2007; Noubactep, 2008; Jiao et al., 2009; Noubactep, 2013; Noubactep, 2015; Noubactep, 2019; Hu et al., 2020). Clearly, the EE concept is built on a thinking mistake. Accordingly, scientists propagating this concept are justifying their own mistakes by citing past mistakes. The EE concept would have been valid to some extent, if the oxide scale was not present. That is under acidic conditions (pH < 4.5) which is not the pH range of environmental remediation (Gillham 2008; Ghauch, 2015). The barrier nature of the oxide film implies that all reductive transformations are mediated by corrosion products (e.g., Fe^{II} , H/H_2 , Fe_3O_4 , green rust). However, contaminant removal is mediated by adsorption onto and co-precipitation with solid iron corrosion products (FeCPs). In fixed beds, size-exclusion is the other relevant removal mechanism (Noubactep, 2007; Noubactep, 2008).

The Fe^0 research community is reminded of a famous quote by Mahatma Gandhi “An error does not become truth by reason of

multiplied propagation, nor does truth become error because nobody sees it.” Contextualizing this to the Fe^0 literature, the highlighted mistake (error) has been propagated since the time the work of Khudenko (1991) was ignored. Despite several efforts by our group pointing out this conceptual mistake (Noubactep 2007, Noubactep, 2008; Noubactep, 2010a; Noubactep, 2010b; Noubactep, 2014; Noubactep, 2016), the truth has been ignored for 1 decade already (Xiao et al., 2020a; Xiao et al., 2020b; Cao et al., 2020; Cao et al., 2021a; Cao et al., 2021b; Cao et al., 2021c; Cao et al., 2021d; Hu et al., 2021; Noubactep, 2022). However, an accurate fundamental understanding of processes governing contaminant removal is critical in the design and operation of Fe^0 -based systems. This is particularly important given that Fe^0 based remediation systems have wide practical applications. These applications have been discussed in earlier papers (Naseri et al., 2017; Antia, 2020, Huang et al., 2021a), thus, a detailed review is beyond the scope of the present paper. In summary, typical applications of Fe^0 -based remediation systems documented in literature include: i) decentralized safe drinking water provision in low-income settings (Huang et al., 2021b; Mueller et al., 2021), ii) industrial wastewater treatment systems (Li et al., 2019; Kulkarni et al., 2020), iii) recovery of heavy metals from industrial effluents (Vollprecht et al., 2018; Calabrò et al., 2021; Noubactep, 2021), iv) urban stormwater treatment (Rahman et al., 2013; Tian et al., 2019), v) treatment of drainage water from agroecosystems (Das et al., 2017; Lanet et al., 2021), vi) subsurface permeable reactive barriers (PRBs) for remediation of contaminated groundwater (Thakur et al., 2020; Njaramba et al., 2021, Wang et al., 2022), and vii) treatment of domestic wastewater (Wakatsuki et al., 1993; Latrach et al., 2018).

The next section gives some selected examples on how the past decade has ignored available knowledge.

HISTORICAL OVERVIEW OF THE Fe^0 REMEDIATION TECHNOLOGY

Fe^0 has been used in the following applications: i) H_2 production, ii) food packaging, iii) laboratory demonstration (e.g., practicals), iv) drinking water conservation, v) mining activities (e.g., copper cementation), and vi) safe drinking water provision for many decades/centuries (Davis, 1891; Bafghi et al., 2008; Noubactep, 2010a; Noubactep, 2013; Mwakabona et al., 2017; Antia, 2020; Cao et al., 2020; Noubactep, 2020; Rangan et al., 2020; Huang et al., 2021a). This section presents the various uses of the Fe^0/H_2O system for water treatment in a historical perspective. Interested readers are referred to a recent overview summarizing 160 years of Fe^0 technology based mainly on patent literature (Antia, 2020).

Fe^0 for Drinking Water Provision

Fe^0 has been used for safe drinking water provision for a very long time (Bischof, 1877; Davis, 1891; van Craenenbroeck, 1998; Mwakabona et al., 2017; Antia, 2020; Noubactep, 2020). Ancient textbooks reveal that this technology was commonplace in West England in the 1850s (Davis, 1891).

Bischof (1873) gives an overview of the ancient efforts for the design of household water filters culminating in the design of spongy iron filters. In 1881, spongy iron filters were successfully pilot tested in Antwerp (Belgium), and could enable the supply of drinking water to 200,000 inhabitants for 18 months without any maintenance (Mwakabona et al., 2017; Antia, 2020; Cao et al., 2020).

Spongy iron filters were used to treat yellow-colored water contaminated with pathogens (Devonshire, 1890; Antia, 2020). The yellow coloration reveals that organic substances were present in water. Fe⁰ was said to be oxidized by dissolved O₂, and contaminants were removed by adsorption and occlusion (co-precipitation). In other words, contaminants were removed by mechanisms similar to that in the flocculation process, with the only difference that flocs were not formed in a bulk solution but in the vicinity of individual Fe⁰ grains (Figure 1) (Bojic et al., 2009). The design of Fe⁰ filters were not based on the stoichiometry of any chemical reaction, but on the probability to generate enough “flocs” on time to address the extent of water contamination.

Household and community drinking water treatment systems working on the same principles were independently designed later (Antia, 2020). Available designs include; i) the Anderson Process (Devonshire, 1890; van Craenenbroeck, 1998), ii) the Emmons Process (Lauderdale and Emmons, 1951; Lacy, 1952), iii) the SONO arsenic filters (Hussam and Munir, 2007; Neumann et al., 2013) and iv) the IITB (Indian Institute of Technology Bombay, India) arsenic filters (Chaudhari et al., 2014; Banerji and Chaudhari, 2017). It is important to point out that, in all these designs, iron corrosion products (FeCPs) for contaminant scavenging are generated without any addition of chemicals. Designs using common oxidants (e.g. H₂O₂, O₃) to intensify iron corrosion were also presented (e.g., Gottinger et al., 2013; Kowalski and Søgaard, 2014; Tepong-Tsindé et al., 2015). Evidently, these findings show that the formation of flocs or FeCPs is critical for contaminant removal, and reaction stoichiometry is not critical in the design and operation of these filters.

Fe⁰ for Wastewater Treatment

Fe⁰ has been used for wastewater treatment for many decades (Obiri-Nyarko et al., 2014; Antia, 2020; Lanet et al., 2021). Applications encompass the recovery of important elements (Vollprecht et al., 2018; Vollprecht et al., 2020), and the treatment of wastewaters from domestic (Wakatsuki et al., 1993), industrial (Oldright et al., 1928; Gould, 1982; Vollprecht et al., 2020), and agricultural sources (Anderson, 1989; James et al., 1992; Erickson et al., 2007). In all these applications, FeCPs serve as contaminant scavengers and the systems are designed to produce enough scavengers. Again, no reaction stoichiometry is needed, and the major reason is that the long-term kinetics of iron corrosion in each individual case is not known (Lufingo et al., 2019; Ndé-Tchoupé et al., 2020; Lanet et al., 2021; Noubactep, 2022).

The presentation until now shows that Fe⁰ based remediation systems have been designed and mostly satisfactorily operated for the past 170 years. During the time before the advent of the PRB

technology (1990), efforts to rationalize the efficiency of the systems using reaction stoichiometry were scarce. For example, Gould (1982) found that, in their systems, more Cr^{VI} was reduced than predicted by the cementation process (electrons from Fe⁰). The same author speculated that some Cr^{VI} was reduced by *in-situ* generated H₂ and pointed out that Fe^{II} species also reduce Cr^{VI} (Gheju, 2018).

Fe⁰ for PRBs

Research on Fe⁰ PRBs started around 1990 (Gillham 2008). In 1994, the four first peer-reviewed articles were published by four research groups in three different journals (Gillham and O'Hannesin, 1994; Lipczynska-Kochany et al., 1994; Matheson and Tratnyek, 1994; Schreier and Reinhard, 1994) (Supplementary Table S1). Supplementary Table S1 summarizes their current bibliometric evaluation according to SCOPUS Web of knowledge and Table 3 summarizes their experimental conditions. This section demonstrates that the four papers have already revealed all important issues for the discussion of the invalidity of the EE concept. In particular, Schreier and Reinhard (1994) tested both Fe⁰ and Mn⁰, while Lipczynska-Kochany et al. (1994) used a pyrite mineral (FeS₂) to delay the precipitation of FeCPs in the vicinity of Fe⁰.

The common feature of the four papers is that they were investigating the reductive degradation of chlorinated hydrocarbons in the presence of Fe⁰. It was clear to all of the investigators that FeCPs will form, and influence the reductive process. Among other results, Schreier and Reinhard (1994) observed a lag time in the process of contaminant reduction in Fe⁰/H₂O systems. In biological systems, for example, a lag time is the time necessary to induce the synthesis of appropriate enzymes (Schreier and Reinhard, 1994). Such lag periods were repeatedly reported in the literature over the years (e.g., Huang et al., 1998; Noubactep et al., 2003; Hao et al., 2005; Cao et al., 2021a; Cao et al., 2021b; Cao et al., 2021c; Cao et al., 2021d). In Fe⁰/H₂O systems, the lag time is indicative of the time required for the generation of FeCPs following Fe⁰ immersion into a polluted water. Proponents of the reductive transformation concept, and the EE concept, often do not provide a rational reason for the lag time.

The currently well-accepted model for the lag time was summarized in a recent review article (Sun et al., 2016). It stipulates that, the lag time corresponds to the time to transform the outer Fe₂O₃ layer, an air-formed oxide scale into Fe₃O₄. In fact, commercial Fe⁰ specimens used in water treatment are covered by a pre-existing oxide scale consisting of an inner Fe₃O₄ layer and an outer Fe₂O₃ layer. The inner layer is electronically conductive by virtue of the semi-conductive nature of Fe₃O₄ (band gap: 0.11 eV) (Odziemkowski and Simpraga, 2004; Huang and Zhang, 2005). However, electron transport is hindered by the outer non-conductive Fe₂O₃ layer. According to this model, contaminant reductive transformation starts when the reduction of the Fe₂O₃ layer is completed.

The crucial role of *in-situ* generated FeCPs in adsorbing contaminants (Charlet et al., 1998; Furukawa et al., 2002) and their role in mediating contaminant reduction was demonstrated (White and Peterson, 1996). However, little attention was paid to

TABLE 3 | Summary of some experimental conditions used for batch experiments in the four first peer-reviewed articles using metallic iron (Fe⁰) for contaminant removal. Chlorinated hydrocarbons were used with various initial concentrations. CT stands for carbon tetrachloride. "Citation" is the number of independent citations (excluding self-citations) according to Scopus (www.scopus.com: February 25, 2021).

Reactant	Vessel	Volume (ml)	Iron (g L ⁻¹)	Shaking (rpm)	Duration (h)	Conditions	Citation (-)	Ref.
4 RX	Serum bottles	60	16.7	15	12	anoxic	1,147	[1]
14 RX	Glass hypovials	40	250.0	2	500	oxic	1,015	[2]
CT	Vials	25	200.0	175	1	oxic	110	[3]
6 RX	Glass bottles	250	20.0	0	1800	anoxic	88	[4]

[1] = Matheson and Tratnyek (1994), [2] = Gillham and O' Hanesin, 1994, [3] = Lipczynska-Kochany et al. (1994), and [4] = Schreier and Reinhard (1994).

the role of primary iron corrosion products (e.g. Fe^{II}, H/H₂, Fe₃O₄, green rusts) as sole relevant source of electrons to mediate chemical reduction (**Figure 1**) (Jiao et al., 2009; Noubactep, 2010b; Noubactep, 2011; Cao et al., 2021a; Cao et al., 2021b). Another important observation of Schreier and Reinhard (1994) was that in experiments conducted at room temperature with Fe⁰, reductive transformations ceased abruptly after some 28 days. The Citation-values in **Table 3** suggest that Lipczynska-Kochany et al. (1994) and Schreier and Reinhard (1994) have not continued working on the remediation Fe⁰/H₂O system (**Supplementary Table S1**). The two other research groups have continuously worked on this field for at least 2 decades (Jeen et al., 2013; Fan et al., 2017). This is a plausible explanation for the fact that the research community could have widely accepted the mistake that contaminant removal is an electrochemical reaction represented by **Eq. 3**:



Table 3 summarized some relevant experimental conditions of the first four peer-reviewed articles on the remediation Fe⁰/H₂O system. A total of 14 chlorinated hydrocarbons (RCl) were tested. Carbon tetrachloride (CT) was tested in 3 works. The tested RCl initial concentrations varied widely. It is seen that different experimental procedures were employed. While Fe⁰ powder (20 and 100 mesh) was used in individual works, there were huge differences in the used mass loading (17–250 g L⁻¹), the nature and the volume of the reaction vessels, the mixing intensities (2–175 rpm), the availability of dissolved O₂, and the experimental duration (1 h–75 days). It has been clearly demonstrated that these differences in the experimental designs are responsible for reported discrepancies (Devlin and Allin, 2005; Henderson and Demond 2007; Gheju 2011; Ghauch, 2015; Guan et al., 2015). Efforts towards more reliable experimental conditions were discussed and constantly actualized for example from 1999 to 2011 by The Interstate Technology and Regulatory Council (www.itrcweb.org) (ITRC, 2011). However, the key factor that the formation of oxide scales in the vicinity of Fe⁰ should be favored has received little attention (Devlin and Allin, 2005; Noubactep, 2008; Cao et al., 2021b). This premise implies that only quiescent or very slow-mixed batch experiments would produce results relevant for the design of filters (Noubactep et al., 2009). As concerning column experiments, low-flow-rate conditions should be observed

(Colabro et al., 2021). These conditions enable the Fe²⁺ concentration to increase in the vicinity of Fe⁰ and eventually attain the saturation concentration. In batch experiments, beside quiescent conditions, limited testing volume favor a rapid formation of oxide scales on Fe⁰. The oxide scale ultimately exerts rate control through the control of reactant diffusion transport kinetics (Devlin and Allin, 2005; Noubactep, 2008; Cao et al., 2020; Noubactep 2020; Cao et al., 2021a).

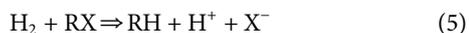
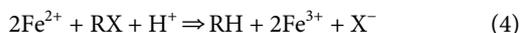
The presentation until now shows that a great deal of work has been done under test conditions that do not permit formation of the universal oxide scale on Fe⁰. Accordingly, reproducible results could be obtained but they are by no means relevant for field conditions. These obvious problems of relevance of results has also favor the introduction of the EE concept which is vehemently refuted herein.

FALSIFYING THE REDUCTIVE TRANSFORMATION CONCEPT

The present work intends to disprove the view that Fe⁰ is a reducing agent under environmental conditions. This section revisits Matheson and Tratnyek (1994) in the perspective of assessing whether or not their conclusions were supported by any methodical approach. The clear experimental observation is that there is reductive transformation of chlorinated methanes (RCl) in Fe⁰/H₂O systems (Reynolds et al., 1990; Gillham and O' Hanesin, 1994; Matheson and Tratnyek, 1994). The question is whether Matheson and Tratnyek (1994) have given a molecular level understanding of this process or established the reaction mechanism. This information is very important for the design of sustainable Fe⁰/H₂O systems and was even the objective of their investigations (Matheson and Tratnyek, 1994). The history of science teaches that the most powerful advances in surface phenomena (including catalysis) are those that improve the ability to predict the efficiency of engineered systems (Buskirk and Baradaran, 2009). As recently recalled by Scott (2019), the fundamental understanding of the mechanisms of chemical reactions broadens the range of accurate predictions.

Any postulated reaction mechanism is a working hypothesis, whose predictions must be compared with experimental observations (Scott, 2019). Following this principle, Matheson and Tratnyek (1994) considered three possible pathways to justify the RCl

reduction in $\text{Fe}^0/\text{H}_2\text{O}$ systems: i) reductive dehalogenation by Fe^0 (Eq. 3) which is equivalent to Fe^0 oxidation by RCl (RCl = oxidizing agent, electrochemical mechanism) (Pathway 1), ii) reductive dehalogenation by Fe^{2+} (Eq. 4) which is equivalent to Fe^{2+} oxidation by RCl (chemical mechanism) (Pathway 2), and iii) reductive dehalogenation by H^+ (Eq. 5) which is equivalent to H^+ oxidation by RCl (chemical mechanism) (Pathway 3). These three mechanisms are all consistent with the named experimental observation. However, the reaction stoichiometry and the corrosion rate are not known, making the discussion with the spectral signatures of reactants, intermediates and products highly speculative. A profound analysis by Lee et al. (2004) revealed that “no carbon balances between reactants and products have ever been successfully done for many chlorinated hydrocarbons, which indicates that reduction pathways of metal-mediated reactions are not fully understood yet.” The statement by Lee et al. (2004) is just another hint for the lack of concrete evidence on the reductive transformation concept. The lack of mass-balance disproves the concept in the sense that reduction is not necessarily quantitative as the missing fraction of carbon is rather enmeshed in the matrix of iron corrosion products (co-precipitation) (Eusterhues et al., 2011; Noubactep, 2011). However, in mechanistic discussions, co-precipitation is mostly considered relevant for metallic species (Henderdon and Demond 2007; Colabro et al., 2021). The lack of mass-balance collectively questions the validity of the three postulated mechanisms.



The most important feature from Matheson and Tratnyek (1994) is the approach they used to rule out reduction after Pathway 2 and Pathway 3: Uncatalyzed reduction by dissolved H_2 or Fe^{2+} . They performed control experiments with H_2 -saturated water and a 100 mg L^{-1} FeCl_2 over 15 days in the absence of Fe^0 and could not observe any dehalogenation. They acknowledged that it was “difficult to exclude the possibility that adsorbed Fe^{2+} or nascent hydrogen” from Eq. 1 “may be participating in the dehalogenation reaction.” Additionally, the amendment of $\text{Fe}^0/\text{H}_2\text{O}$ systems with external Fe^{2+} or H_2 did not impact RCl reduction. Finally, the addition of 0.5 mM ethylenediaminetetraacetic acid (EDTA) had no effect on the RCl dehalogenation rate. EDTA was supposed to fix Fe^{2+} , avoid hydroxide precipitation and keep the Fe^0 surface free for RCl electrochemical reduction. Matheson and Tratnyek (1994) concluded on the basis of the presented experiments, that “reductive dehalogenation directly coupled with oxidative dissolution of the metal” (Pathway 1) was the “dominant process.” It is very important to note that Matheson and Tratnyek (1994) have just initiated a discussion, but just 2 years later, Weber (1996) claimed to have confirmed the electrochemical nature of contaminant reduction in $\text{Fe}^0/\text{H}_2\text{O}$ systems. This section seeks to convince the reader that this concept was not established by any scientific approach.

In the absence of mass balance, Matheson and Tratnyek (1994) could not establish the mechanism of RCl reduction. However, there are two more intriguing facts: i) Fe^0 oxidation by water is not discussed, and ii) water is just considered as a

proton source for reaction after Eq. 3. The presentation of the authors textually reads, alkyl halides “can also be reduced by iron. In the presence of a proton donor like water, they typically undergo reductive dehalogenation.” This means that the seminal work of Whitney (1903) was ignored as well as thousands of works describing corrosion as resulting from the presence of water, including impurities in natural oil (Brondel et al., 1994) and atmospheric humidity (Stratmann and Müller, 1994). Moreover, there is no iron corrosion in dry (H_2O free) chlorinated solvents (Rhodes and Carty, 1925; Archer, 1979). Fe^0 corrosion by H_2O (including moisture) and no Fe^0 corrosion by dry RCl clearly indicates that more attention should have been paid to water as corroding agent in the Fe^0 remediation literature (Ghauch, 2015; Cao et al., 2021b; Noubactep, 2022).

The extent to which it is possible to confirm a reaction mechanism is an issue that has preoccupied researchers in the chemical sciences for many decades (Brenner, 2010; Scott, 2019). In Geology, it is recommended to generate and test multiple working hypotheses in scientific inquiry to guard against drawing premature conclusions (Chamberlin, 1890). The science philosophers Karl Popper and Thomas Kuhn further asserted that scientific hypothesis must be falsifiable, or refutable (Scott, 2019). Following this approach, experiments should be designed to test the viability of multiple proposed reaction mechanisms. A mechanistic hypothesis can be falsified, resulting in its modification or even abandonment (Scott, 2019). Because the reaction mechanism of Matheson and Tratnyek (1994) was falsified by Jiao et al. (2009) it should be abandoned. Moreover, because their concept has not properly considered the redox reactivity of water ($E^0 = 0.00 \text{ V}$), the concept was false at the introduction.

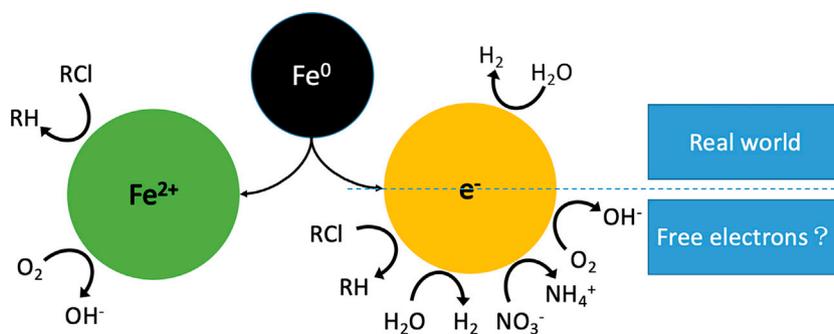
This section calls authors to exercise vigilance to avoid making claims that a proof exists where it does not. To enable progress in the design of sustainable $\text{Fe}^0/\text{H}_2\text{O}$ systems, attempts should be made to discredit rather than prove available mechanistic concepts (Scott, 2019). Louis Pasteur once formulated the following advice: “When you believe you have found an important scientific fact, and are feverishly curious to publish it, constrain yourself for days, weeks, years sometimes, fight yourself, try and ruin your own experiments, and only proclaim your discovery after having exhausted all contrary hypotheses” (Scott, 2019).

THE ELECTRON EFFICIENCY CONCEPT: REDOX AND MASS BALANCE PERSPECTIVES

Electron efficiency is defined as the fraction of total electrons from Fe^0 that are used in the reduction of COCs (Eq. 3). The presentation until now has demonstrated that no single electron from Fe^0 can be transferred to COCs because of the presence of the universal oxide scale which is never electronically conductive (Table 4). If electrons from Fe^0 were transferred to any COC, there would have not been a lag time between the start of the experiment and the start of reductive transformation of COCs (Schreier and Reinhard, 1994; Huang et al., 1998; Hao et al., 2005;

TABLE 4 | Summary of the key factors affecting changes in Fe⁰/H₂O systems and their implication for the validity of the electron efficiency concept (EE concept).

Process in Fe ⁰ /H ₂ O	Remarks	Description
Anodic Fe ⁰ dissolution Fe ²⁺ migration away from the Fe ⁰ surface	Driven by the electrode potential of the redox couple Fe ^{II} /Fe ⁰ : E ⁰ = -0.44 V Facilitated by the ionic conduction of the polluted water	All Fe ⁰ materials have virtually the same reactivity Saline water is more corrosive than fresh water
Transport of electrons to cathodic sites	Driven by the electronic conduction of used Fe ⁰ , and depends on its intrinsic reactivity	Fe ⁰ /S better than Fe ⁰
Electron transfer at cathodic sites	Driven by the difference of the electrode potential relative to E ⁰ = -0.44 V	O ₂ (E ⁰ = 0.84 V) reacts better than H ₂ O (E ⁰ = 0.00 V)
Formation of an iron oxide scale on Fe ⁰	The oxide scale acts as a barrier for electron transfer. The oxide scale also acts as a diffusion barrier for dissolved species	Only water access the Fe ⁰ surface. The EE concept is not valid.

**FIGURE 2** | Pathways of contaminant transformations in Fe⁰/H₂O systems. In the real world, only water has access to the metal surface. Fe²⁺ and H₂ are stand alone reducing agents. O₂ and RCl are reduced by Fe²⁺. The scenario of the EE concept corresponds to free electrons within the Fe⁰/H₂O system, which is an absurdity.

Cao et al., 2021d). Consequently, COCs, O₂ and co-contaminants are reduced by Fe^{II}, H₂, Fe₃O₄, green rust, and other reducing species generated in the Fe⁰/H₂O system (Figure 2). For simplification, it can be assumed that reductive transformations are mainly mediated by Fe²⁺ and H₂ from Eq. 1.

Eq. 1 implies that the oxidation of 1 mole of Fe⁰ produces 1 mole of Fe²⁺ and 1 mole of H₂. Fe²⁺ can donate one electron and H₂ two electrons. This means that the electrochemical oxidation of 1 mole of Fe⁰ by water (H⁺ or H₂O—the solvent), indirectly produces 3 moles of electrons for the reduction of O₂, NO₃⁻ and all other oxidizing agents. In other words, the EE concept has better considered how the 3 moles of electrons are distributed. In this laborious effort, the mass balance of all involved species must be performed, starting with that of iron, which implies the need for experiments entailing the controlled dissolution of FeCPs. To the best of the authors' knowledge, such a work has not been published. It is very strange, that mechanistic discussions have been performed without complete mass balance for 3 decades (Lavine et al., 2001; Lee et al., 2004; Noubactep, 2011; Cao et al., 2021c). Yet mass balance analysis is critical for proving the validity of the EE concept.

Another important feature about the EE concept is the way it addresses the electrode redox potential. The electrode potential of the Fe^{II}/Fe⁰ redox couple (E⁰ = -0.44 V) is not relevant to explain the reduction potential of the system towards individual contaminants. Instead, the potential of the couples Fe^{III}/Fe^{II} and H⁺/H₂, both in adsorbed and

dissolved states are considered. For Fe^{II}, it has been demonstrated that, while dissolved Fe^{II} is far less powerful than Fe⁰, adsorbed Fe^{II}, also referred to as structural Fe^{II} is sometimes more powerful than Fe⁰: -0.65 ≤ E⁰ (V) ≤ -0.34 (White and Peterson, 1996). This last argument demonstrates that reduction of COCs is favourable, but this reduction of COCs is a chemical process as demonstrated for example by Khudenko (1991) and Jiao et al. (2009).

The last important feature about the EE concept is its usefulness. Reactivity loss and permeability loss are the two main challenges of the Fe⁰ remediation technology (Henderson and Demond 2007; Ghauch, 2015; Guan et al., 2015; Cao et al., 2020). Avoiding material wastage is certainly a noble goal, but it should start when the intrinsic reactivity of each relevant material is documented, and its long-term changes characterized (Ndé -Tchoup é et al., 2020). This presents a challenge, because the current situation is that Fe⁰ materials are not characterized, and their long term behaviour has not been really investigated (Li et al., 2019; Lufingo et al., 2019; Ndé -Tchoup é et al., 2020). For example, steel wool (d ≤ 90 μm), iron wire (d = 200 μm) and iron nails (d > 200 μm) are just tested as "Fe⁰ materials" in independent researches (Tepong-Tsindé et al., 2019).

In summary, evidence shows that: i) the EE concept fails to account for the lag time widely reported in Fe⁰/H₂O systems, ii) the application of the EE concept is not based on any iron mass balance, iii) the EE concept disregards the decade old doubts on

the reducing nature of Fe^0 , and iv) the EE concept does not contribute to solve the two major design issues for $\text{Fe}^0/\text{H}_2\text{O}$ systems (i.e., reactivity loss and permeability loss).

REVISITING REACTIVITY LOSS AND PERMEABILITY LOSS

The two major problems of Fe^0 -based filters as documented from laboratory experiments, large-scale experiments and field implementations are reactivity loss and permeability loss (Guan et al., 2015; Cao et al., 2020). This corresponds to the state-of-the-art knowledge as summarized 14 years ago by Henderson and Demond (2007). Since then, the research community is divided in two schools. Some few researchers have realized that the dynamic nature of the $\text{Fe}^0/\text{H}_2\text{O}$ system implies a different approach of investigation (Ghauch, 2015) while the large majority is still considering that isolated instrumental characterizations would help to understand the system. Clearly, the still praised monitoring of physical changes of Fe^0 features using sophisticated tools including X-ray microcomputer tomography have not mediated the expected understanding of the technology as a whole. In other words, changes of Fe^0 surface, Fe^0 particle size, nature of expanding FeCPs, the reducing porosity can be experimentally documented. However, all these observations are collectively only static snap-shots and their measurements are inaccurate. Therefore, they cannot enable the generation of non-trivial models of the dynamic processes within $\text{Fe}^0/\text{H}_2\text{O}$ systems (Santisukkasaem and Das, 2019), especially as these occur over an enormous range of time scales (from few seconds to some 2 decades) (Gillham 2008; Wilkin et al., 2014; Cao et al., 2020).

Reactivity Loss

The present paper posits that the consideration of wrong reactions and improper descriptors has been a major problem the Fe^0 literature. This section clarifies this key issue. A parent compound (e.g., RX) reductively transformed in a $\text{Fe}^0/\text{H}_2\text{O}$ system has been assumed to be transformed by electrons from the Fe^0 body according to Eq. 3 (Section *Fe⁰ for PRBs*). A pseudo-first-order model is applied to describe the transformation of RX (Eq. 6). The natural logarithmic transformation of Eq. 6 yields a linear equation with the first-order rate constant k_{obs} as slope (Eq. 7) (Reardon, 1995; Velimirovic et al., 2013). Usually, the mass normalized rate constants (k_M , $\text{L g}^{-1} \text{h}^{-1}$) and specific surface area normalized rate constants (k_{SA} , $\text{L m}^{-2} \text{h}^{-1}$) are used to account for the Fe^0 mass and/or the Fe^0 surface area in the systems

$$C = C_0 * e^{-k_{\text{obs}} * t} \quad (6)$$

$$\ln(C/C_0) = -k_{\text{obs}} * t \quad (7)$$

where C is the concentration at any time and C_0 is the initial concentration of RX, k_{obs} is the pseudo-first-order rate constant (h^{-1}) and t (h) is the reaction time. In essence, rooting the reasoning on the available mass loading of Fe^0 particles (g L^{-1}) and/or their surface area concentration ($\text{m}^2 \text{L}^{-1}$) is a bright idea. However, the mistake made in considering Eq. 3 is not corrected.

Eq. 6 contents no single parameter related to water which clearly oxidizes Fe^0 according to the definition of the EE concept (Liu et al., 2013). However, in trying to account for the “fraction of electrons” used to reduce water, the EE concept has replicated the same mistake. Therefore, the EE concept is not able to address the problem of reactivity loss. Reactivity loss has been documented for H_2 generation (Eq. 1) in the absence of any contaminant (Reardon, 1995; Tang et al., 2017; Qin et al., 2018). In fact, reactivity loss is the “natural” time-dependent decrease of the kinetics of iron corrosion (Romanoff, 1957; Melchers and Petersen, 2018). As an intrinsic characteristic, reactivity loss can never be suppressed (Miyajima and Noubactep, 2015). In other words, reactivity loss has occurred in Fe^0 reactive barriers satisfactorily operating for decades (O’Hannesin and Gillham, 1998; Guan et al., 2015; Wilkin et al., 2019). These systems are still efficient because their designs (e.g., Fe^0 characteristics, Fe^0 amount, Fe^0 :aggregate ratio, flow velocity) are somehow favorable. The rationale for their efficiency or the failure of other systems (e.g., Morrison et al., 2006; Ngai et al., 2007) is yet to be investigated.

Efforts to overcome “reactivity loss” are numerous, and include the following: i) increasing the available reactive surface area by using either porous materials (Hussam and Munir, 2007) or nano-sized Fe^0 (Zhang, 2003), ii) creating galvanic cells by alloying Fe^0 mostly in bimetallic materials (e.g. Fe^0/Pd^0 , Fe^0/Ni^0), and iii) admixing Fe^0 with reactive aggregates (e.g., Fe^0/FeS_2 , $\text{Fe}^0/\text{Fe}_3\text{O}_4$, Fe^0/GAC , Fe^0/MnO_2) (Bojic et al., 2009; Btatkeu et al., 2014a; Btatkeu et al., 2014b; Dong et al., 2018; Han et al., 2019; Hu et al., 2021). GAC stands for granular activated carbon. Although GAC is chemically inert, it can create galvanic cells with Fe^0 to alleviate its surface passivation (Gatcha-Bandjun et al., 2014; Dong et al., 2018). However, it is evident that none of these efforts has attempted to correct the original mistake. The documented enhanced efficiency is just due to increased iron corrosion or increased “electron density” (Noubactep and Caré, 2010; Noubactep et al., 2012). The proof for this statement is that admixing Fe^0 with inert aggregates (e.g., $\text{Fe}^0/\text{gravel}$, Fe^0/sand) yields a more efficient system than the pure Fe^0 system (Song et al., 2005; Btatkeu et al., 2014a; Btatkeu et al., 2014b). Accordingly, testing activated carbon, metal oxides and other reactive materials without a reference system (e.g., Fe^0/sand) can only give qualitative results. It is thus not surprising that the reaction mechanisms and removal pathways using metal oxides assisted Fe^0 -based systems have not been investigated (Dong et al., 2018; Hu et al., 2021).

Permeability Loss

Permeability loss describes the time-dependent decrease of the hydraulic conductivity of Fe^0 -based filter (Caré et al., 2013, Domga et al., 2015, Cao et al., 2020, Antia, 2020, Njaramba et al., 2021). While considering Fe^0 as the reducing agent and corrosion by water as a side reaction, permeability loss has been mainly attributed to the precipitation of foreign species evolving for instance CO_3^{2-} or HCO_3^- (Henderson and Demond 2007; Henderson and Demond, 2011; Santisukkasaem and Das, 2019).

However, the fact that contaminants are likely reduced by Fe^{II} species which are transformed to Fe^{III} ones, suggest that (at least) twice more Fe^0 is needed as suggested by the stoichiometry of Eq. 3: 1 mole of Fe^0 exchanges 2 moles of electrons and 1 mole of Fe^{2+} only 1 mole of electrons. At $\text{pH} > 4.5$, each oxidized Fe^0 atom is transformed to an iron hydroxide or oxide which volume is at least twice larger than that of the parent metal (Caré et al., 2008; Zhao et al., 2011; Caré et al., 2013; Domga et al., 2015; Yang et al., 2021; Noubactep, 2022). In other words, before considering the contribution of any foreign species (e.g., Ca^{2+} , CO_3^{2-} , HCO_3^-) in the process of permeability loss, the own contribution of iron corrosion should be properly discussed. The contribution of iron corrosion to permeability loss is obvious and has been firstly experimentally documented by Luo et al. (2013) using deionized water (Yang et al., 2021). Properly considering the expansive nature of iron corrosion has prompted Domga et al. (2015) to recommend only hybrid systems (e.g., Fe^0/sand) for sustainable filters. According to Naseri et al. (2017), in testing a Fe^0 system, the main interest should be to check whether the designed system generated enough contaminant scavengers for efficient water treatment, regardless from the redox properties or even the chemical nature of the pollutants. It is recalled that Fe^0 filters also remove pathogens (You et al., 2005; Bradley et al., 2011; Tepong-Tsindé et al., 2019; Kulkarni et al., 2020) and many other species without redox properties (Richardson and Nicklow 2002; Henderson and Demond 2007; Ullah et al., 2020).

STARTING A NEW AREA IN Fe^0 RESEARCH

The core problem of the Fe^0 remediation literature is that tools such as the first-order rate constants (k_{obs}) or the specific reaction rate first-order constants (k_{SA}) premised on the misconception that Fe^0 is a reducing agent have had an adverse effect on its development. The EE concept is such a questionable tool. Rather than help the Fe^0 research community to exploit the mainstream corrosion science, these inappropriate tools have isolated the community to a modern knowledge system, reasoning circularly on an avoidable mistake introduced by some few individuals nearly 3 decades ago. Yet despite several efforts highlighting the mistakes, the scientific community continues to propagate the same errors (Xiao et al., 2020a; Xiao et al., 2020b; Cao et al., 2020; Hu et al., 2020; Cao et al., 2021a; Cao et al., 2021b; Hu et al., 2021). Consequently, in terms of progress the Fe^0 remediation technology has not progressed much in the last decade, a scenario referred to as the “lost decade” (Noubactep, 2019). The Fe^0 research community cannot afford to further lose time by further perpetuating the errors of yesteryear, hence the need to root any further research on the correct mechanistic understanding of iron corrosion (Makota et al., 2017; Cao et al., 2020; Hu et al., 2021; Huang et al., 2021). Therefore, to design better systems, there is no other option besides the following: i) to come back to the historical work of Khudenko (1991) as a starting point, and ii) consider progress made by some few research groups during the last decades (Gheju, 2011; Ghauch, 2015; Noubactep, 2015). It is only on the basis of this consideration that research on designing efficient and sustainable Fe^0 will progress in the next coming decades.

Notably, abandoning the view that Fe^0 is an environmental reducing agent will not fix everything at once. It will take time to acquire relevant data pertaining to the specificity and long-term kinetics of iron corrosion as used in environmental remediation and water treatment. Further, it takes time for research funding institutions to adapt their funding practices to support a research in which pilot tests shall last for years exceeding the 2–3 years typical of most funded research project. It is particularly obvious that the common 2 or 3 years grants are not suitable for such research efforts. It is important to bear in mind that, Fe^0 remediation research is going back to its roots: Corrosion Science (Whitney, 1903; Howard, 1910; Dickerson et al., 1979; Nescic, 2007).

The change in strategic direction suggested in this communication is seemingly controversial, because it refutes the consensus of the late 1990s (Gillham and O’ Hannesin, 1994). However, the consensual approach has not worked during the past 2 decades, resulting in unsatisfactory technical systems (Morrison et al., 2006; Ngai et al., 2007; Comba et al., 2011; Mueller et al., 2011; Kowalski and Søgaard, 2014; Bretzler et al., 2020; Ogata et al., 2020; Huang et al., 2021b; Mueller et al., 2021). There is no alternative to abandoning the misleading concept for mere conveniences since the aspirations of younger scientists are yet to be met.

A further argument against the “reducing Fe^0 ” is presented by Ito and colleagues (Satur et al., 2007; Tabelin et al., 2017a; Tabelin et al., 2017b; Seng et al., 2019; Parka et al., 2020). It took 1 decade to Ito and his collaborators to establish Fe^0 addition as the most promising tool to suppress pyrite oxidation under environmental conditions (Seng et al., 2019). The idea of the so called carrier-microencapsulation (CME) technique, developed during the second half of the 2000s (Satur et al., 2007), is to coat pyrite with a layer of metal hydroxide or oxide, in order to stop mineral oxidative dissolution which causes acid mine drainage (AMD) (Tabelin et al., 2017a; Tabelin et al., 2017b). Several Al, Fe and Ti complexes with organics were tested over the years but were not really specific to FeS_2 in mine tailings and waste rocks. The bright idea, based on the electrochemistry of Fe^0 ($E^0 = -0.44 \text{ V}$) and FeS_2 ($E^0 = 0.25 \text{ V}$), was that, in a Fe^0/FeS_2 mixture, Fe^0 is the anode and dissolved Fe^{2+} migrates to the cathode (FeS_2) which is passivated upon formation of an oxide scale. Seng et al. (2019) have verified this sound hypothesis using Al^0 and Fe^0 . Interested readers are referred to the related publications. For the presentation herein, it suffices to recall that the semi-conductives properties of FeS_2 have been regarded as the reason for enhanced efficiency of Fe^0/FeS_2 systems (Xiao et al., 2020a; Xiao et al., 2020b; Hu et al., 2021). It is obvious that thermodynamics is not all but the results of Sheng et al. (2019) are a further call to revisit the operating mode of remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems.

The research group of the corresponding author and some few others have been working according to a new paradigm for a decade and have already achieved some good results than can be summarized as: i) Fe^0 is not the source of electrons for the reduction of any contaminant. Tested species include organic (e.g., diclofenac, utriafol) and inorganic (e.g., Cr, Se) compounds (Gheju, 2011; Gheju, 2018; Gheju and Balcu, 2019), ii) the $\text{Fe}^0/\text{H}_2\text{O}$ system is ionic selective, negatively charged species are

favoured (Phukan et al., 2015; Phukan et al., 2016), iii) only hybrid filtration systems (e.g., Fe⁰/pumice, Fe⁰/sand) are sustainable (Ghauch, 2015; Noubactep, 2016), iv) each Fe⁰ has a different corrosion rate which is never constant (Btatkeu et al., 2013; Lufingo et al., 2019; Hildebrant et al., 2020), and v) Fe⁰ filters are a special case of “corrosion in porous media” (Ndé-Tchoupé et al., 2018; Yang et al., 2021). Yang et al. (2021) have recently introduced the most really holistic attempt to predict the service life of Fe⁰ filters. They considered for the first time the Faraday’s law to tentatively predict the time to clogging. The limitation is that there are no reliable corrosion rates available, this limitation is common to all branches of science investigating corrosion in porous media, including corrosion of reinforcing steel in concrete (Caré et al., 2008; Zhao et al., 2011; Stefanoni et al., 2018; Stefanoni et al., 2019). Therefore, long-term data for iron corrosion are needed (Noubactep, 2022).

CONCLUDING REMARKS

Fe⁰/H₂O systems have a long history of application in environmental remediation and water treating, and several new applications are emerging. However, the Fe⁰ technology suffers from a number of misconceptions and mistakes pertaining to the mechanisms of contaminant removal. In the current communication, evidence was presented highlighting the mistakes of the electron efficiency concept, based on the misunderstanding that contaminant removal occurs according to reaction stoichiometry involving Fe⁰ as electron donor (electrochemical mechanism). A number of lines of evidence were presented to demonstrate the invalidity of the EE concept, including: i) the lag time widely reported in Fe⁰/H₂O systems, ii) the universal formation of a non-conductive oxide layer that acts as a barrier for electron transfer, and iii) lack of mass balance data confirming its validity. Despite these limitations, and several studies demonstrating more plausible mechanisms based on iron corrosion, the bulk of the Fe⁰ research community continues to propagate the k_{SA} , k_{obs} and electron efficiency concepts. As a result, Fe⁰ research has been nearly stagnant for the past 2 decades, a scenario that has constrained the development of robust and efficient Fe⁰/H₂O systems. Hence, this communication highlighted the need for a paradigm shift

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from flawed historical concepts, to a future where the design of the next generation of Fe⁰ is rooted on sound fundamental principles based on the science of iron corrosion. The suggested approach would enable an improved exploitation of the capacity of Fe⁰ technology beyond its actual stand as summarized by Antia (2020). To achieve this, a critical evidence based on the reactivity and long-term kinetics of Fe⁰ is needed, and research to generate such evidence requires long-term funding commitments.

AUTHOR CONTRIBUTIONS

Conception (RH and CN), developing the original idea (RH, CN, AN, and VC), literature review (all), supervision (RH, CN and WG), redaction and revisions (all).

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SUPPLEMENTARY MATERIAL

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