

Review

Metallic Iron for Environmental Remediation: Starting an Overdue Progress in Knowledge

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Abstract: A critical survey of the abundant literature on environmental remediation and water treatment using metallic iron (Fe^0) as reactive agent raises two major concerns: (i) the peculiar properties of the used materials are not properly considered and characterized, and, (ii) the literature review in individual publications is very selective, thereby excluding some fundamental principles. Fe^0 specimens for water treatment are typically small in size. Before the advent of this technology and its application for environmental remediation, such small Fe^0 particles have never been allowed to freely corrode for the long-term spanning several years. As concerning the selective literature review, the root cause is that Fe^0 was considered as a (strong) reducing agent under environmental conditions. Subsequent interpretation of research results was mainly directed at supporting this mistaken view. The net result is that, within three decades, the Fe^0 research community has developed itself to a sort of modern knowledge system. This communication is a further attempt to bring Fe^0 research back to the highway of mainstream corrosion science, where the fundamentals of Fe^0 technology are rooted. The inherent errors of selected approaches, currently considered as countermeasures to address the inherent limitations of the Fe^0 technology are demonstrated. The misuse of the terms “reactivity”, and “efficiency”, and adsorption kinetics and isotherm models for Fe^0 systems is also elucidated. The immense importance of $\text{Fe}^0/\text{H}_2\text{O}$ systems in solving the long-lasting issue of universal safe drinking water provision and wastewater treatment calls for a science-based system design.

Keywords: adsorption capacity; decentralized water supply; electrochemical reaction; inconsistent view; sand filtration; wastewater treatment; zero-valent iron

1. Introduction

Metal corrosion is one of the most important problems in industry, transport and agriculture [1–4]. Understanding metal corrosion comprises its detection (e.g., analytical, visual), its monitoring (e.g., mass loss, H₂ evolution) and its long-term characterization under various field conditions [4,5]. The corrosion research aims at determining the durability of metallic structures under operational conditions (e.g., oil and gas pipelines, tanks) and revealing the mechanisms of corrosion process [5,6]. This mechanism can be chemical, electrochemical or mixed [1]. Various tools have been used to characterize the corrosion resistance of different metals under various application conditions [4]. The overall result is the availability of integrated approaches to assess and predict the corrosion processes and thus the longevity of metallic structures (e.g., buried pipes) [3,4]. However, the frequency and sudden nature of metallic pipe failures worldwide indicate the inadequacy of current knowledge related to the longevity of buried metallic pipes.

Metallic iron (Fe⁰) used as a reactive material in subsurface permeable reactive barriers is comparable to iron pipes with three major differences: (i) corrosion is welcome because it is a rather useful process [7–9], (ii) a reactive wall is ideally permanently water saturated, and (iii) the length of used particles (<5 cm) is tiny compared to pipes which are up to 12 m in length. On the one hand, Fe⁰ specimens used in water treatment comprise steel wool with thickness varying between 25 and 90 μm [10,11]. On the other hand, the length of these particles is comparable to the wall thickness of iron pipes (2–4 mm). There has been no real system analysis for remediation Fe⁰ materials with the aim to outline the differences making their peculiar characteristics. In addition, traceably deriving the longevity of remediation Fe⁰ specimens from Fe⁰ pipes is impossible because of the differences highlighted.

The remediation Fe⁰ was termed as zero-valent iron (ZVI). This acronym is perhaps the first problem of this still innovative technology. A literature research with “zero-valent iron” as keyword would never reveal the ancient literature on Fe⁰ for water treatment [12–16]. Indeed, no research group until 2017 has referenced a single article from the ancient use of Fe⁰ in water treatment [17,18]. In chemistry, metallic elements are characterized by their oxidation state, the one of Fe⁰ is zero (0). Upon oxidation, Fe⁰ is transformed to Fe^{II}, Fe^{III} or Fe^{IV} species. Under environmental conditions, only Fe^{II} and Fe^{III} species are stable. The oxidation of Fe⁰ to Fe^{II} is a redox process characterized by an electrode potential whose value is TM0.44 V [1]. According to the first principle of chemical thermodynamics, Fe⁰ can be oxidized by oxidizing agents from each redox couple having a higher electrode potential (E⁰ > TM0.44 V). Water (H₂O or H⁺) is a relevant oxidizing agent for Fe⁰ under environmental conditions. The electrode potential for the redox couple H⁺/H₂ is 0.00 V. Fe⁰ immersed in (contaminated or polluted) water is corroded to form H₂ and Fe^{II} (and mixed Fe^{II}/Fe^{III}) species which are stand-alone reducing agents [19–26]. Clearly, it is not surprising that selected species undergo reductive transformations in an Fe⁰/H₂O system [19,26–29]. The application of metallic iron in water treatment dates back to the 1890s (Table 1). Suspended matter then left to settle

Table 1. Historical application of metallic iron in water treatment (modified from Mwakabona et al. [17]).

Age/Time	Material	Usage	Target Impurities	Application	Reference
Pre-1850	Old iron nails	Shaken with impure water	Suspended matter then left to settle	Used in West England	[30,31]
1850–1900	Iron plates/wires (1857)	Suspended in flowing impure	Suspended matter water	Tested but not widely applied	[13,31,32]
	Magnetic carbide/ Iron oxide	Filter media	Suspended matter/microbes	Widely applied household scale filters	[12,13,31]

Table 1. Cont.

Age/Time	Material	Usage	Target Impurities	Application	Reference
	Polarite	Filter media	Suspended matter/colour/microbes	Household filters	[32,33]
	Spongy iron	Filter media	Suspended matter/colour/microbes/chemical contaminants	Household and large scale filters	[30,31,34,35]
	Iron fillings	Agitated in the evolving purifier	Suspended matter/colour/microbes	Large scale in treatment plants	[31,34,35]
1900–1950	Iron fillings	Agitated in the revolving purifier	Suspended matter/colour/microbes/chemical contaminants	Large scale in treatment plants	[16,31,35,36]
1950–1990	Steel wool	Filter media	Radionuclides	Widely tested household scale filters	[37]
	Iron fillings	Filter media	Selenium from agricultural drainage water	Field scale	[38]
	Iron fillings	Static or dynamic	Halogenated hydrocarbons	Concept	[39]
Post–1990s	Iron fillings, steel wool	Filter media	Phosphate from agricultural drainage water	Field scale	[40,41]
	Iron fillings	Filter media	Domestic wastewater	Field scale	[42]
	Al ⁰ /Fe ⁰ composite	Filter media or batch systems	Pathogen and chemical removal	Laboratory demonstration	[43]
	Iron fillings	Filter media	Pathogen removal	Laboratory demonstration	[44]
	Iron nails	Filter media	Kanchan Arsenic filter	Field scale	[45,46]
	Composite iron matrix	Filter media	SONO Arsenic filter	Field scale	[47]
	Metallic iron	Reactive media in PRBs	Chemical contaminants	Field scale	[22,23,48,49]
	Metallic iron	Filter media or batch systems	All classes of contaminants	Concept	[50]
	Metallic iron	Filter media	<i>E. coli</i> and <i>Listeria monocytogenes</i> removal from surface water for irrigation	Field scale	[51,52]

Table 1 presents a summary of the historical applications of metallic iron in water treatment. The history of Fe⁰ application in environmental remediation has been the subject of several papers by our research group. Comprehensive research on Fe⁰ for water treatment revealed that the generation of iron hydroxides and oxides (iron corrosion products or FeCPs) is the root cause of contaminant removal in Fe⁰/H₂O systems [22,23,25,26,53,54]. For example, arsenic [55], carbon tetrachloride [29], chromium [56], fluoride [57,58], hexachloroethane [59], methylene blue [60], methyl orange [61], Orange II [62], phosphate [63], selenium [64] and zinc [65] are all removed in Fe⁰/H₂O systems despite their differences in charge, redox-reactivity and size.

A critical research review article from 2008 [54] established that adsorption, co-precipitation and size-exclusion were the fundamental mechanisms of contaminant removal in Fe⁰/H₂O systems. Yet to date, 13 years later, researchers are still trying to establish the mechanisms by which aqueous contaminants are removed in the presence of Fe⁰ [59,63,64,66,67]. Unfortunately, none of them has proven the alternative concept [53,54,68] wrong, and most of them are considering Fe⁰ as the electron donor for observed transformations (electrochemical reaction) [69–71]. Moreover, “contaminant

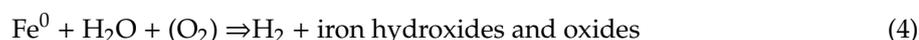
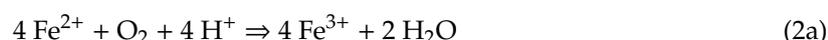
reduction” and “contaminant removal” are mostly randomly interchanged. Therefore, a better argumentation is still needed to convincingly explain the in-depth knowledge on the mechanisms causing contaminant removal in Fe⁰/H₂O systems. Another important application of Fe⁰ materials entails using Fe⁰ to induce a pH shift and/or enhance microbial processes involved in methane production in anaerobic digesters [72–75]. This aspect is not considered herein as it is not focused on contaminant removal as discussed in Section 2.

This paper presents a profound analysis of the Fe⁰/H₂O system and derives the leading causes and factors influencing its efficiency for water treatment. Relevant factors include: (i) the Fe⁰ specimen including its form and size (intrinsic reactivity), (ii) the water chemistry including the nature of contaminants, the presence of dissolved O₂ and the pH value, (iii) the contact time (flow velocity or mixing intensity), and (iv) the Fe⁰ amount and its proportion in the reactive mixture (thickness of the reactive layer or number of columns). Contaminants are explicitly considered within water chemistry, one of the four main groups of factors influencing iron corrosion. The approaches conventionally adopted to investigate these factors, the major findings, the limitations and the knowledge gaps are presented. It is argued that no progress in knowledge is possible before the research community agrees on the key issue that Fe⁰ is not a reducing agent (under field conditions).

2. The Fe⁰/H₂O System

2.1. Overview of Fundamental Aspects

There is a transfer of electrons from the Fe⁰ body (solid state) to the Fe⁰/H₂O interface whenever a piece of a reactive Fe⁰ specimen is immersed in an aqueous solution (Fe⁰/H₂O system) [1,5,6,76]. This occurs because Fe⁰ is not stable under environmental conditions or because the redox couple H⁺/H₂ (E⁰ = 0.00) is higher than that of Fe^{II}/Fe⁰ (E⁰ = 0.44) in the electrochemical series [1,22–26]. Equation (1) reveals that the oxidative dissolution of Fe⁰ by protons (H⁺) and Equation (1a) considers that protons are from water (H₂O ⇌ H⁺ + HO⁻). Fe(OH)₂ from Equation (1b) tends to polymerize and precipitate but can also be oxidized to even lower soluble Fe(OH)₃ by dissolved O₂ for example (Equation (2a)). Fe(OH)₂ and Fe(OH)₃ are polymerized and further transformed to various hydroxides and oxides (FeCPs) (Equation (3)) [1,21,77]. The different iron corrosion products (FeCPs) depict different adsorptive affinities for dissolved species [77–79]. Equation (4) summarizes the process of aqueous iron corrosion.



In summary, Equation (4) recalls that immersing a reactive Fe⁰ in water can be universally used to generate H₂, Fe²⁺ and various Fe^{II}, Fe^{III} and Fe^{II}/Fe^{III} hydroxides and oxides. Equation (1) demonstrates that Fe⁰ is a scavenger of humidity (H₂O), while Equation (2) demonstrates the O₂ scavenging nature of Fe⁰. These two scavenging characteristics have been exploited in several industrial applications [80–82]. For example, Fe⁰ is used as desiccant in food packaging [81]. In the Fe⁰ remediation literature, the best illustration for the nature of the Fe⁰/H₂O system as generator of FeCPs is perhaps the excellent research article by Furukawa et al. [83]. These authors used several analytical tools to demonstrate the presence of ferrihydrite, green rust, magnetite and lepidocrocite in an Fe⁰/H₂O system. More importantly, they conclude that an Fe⁰/H₂O system is a temporally and spatially heterogeneous geochemical environment. Concerning the spatial heterogeneity, Furukawa et al. [83] specified that magnetite (Fe₃O₄) is generated

in the vicinity of Fe^0 , whereas ferrihydrite ($\text{Fe}(\text{OH})_3$) precipitates away from the Fe^0 surface. This conclusion corroborates ancient findings [84] and recalls that even under oxic external conditions, there is a progressive O_2 depletion culminating into anoxic conditions in the vicinity of Fe^0 . In this context, Stratmann and Müller [85] clearly demonstrated that oxygen is reduced by Fe^{II} species within the oxide scale (chemical reaction), while Fe^0 is oxidized by water (electrochemical reaction).

This section has recalled that, before Fe^0 complete depletion, an $\text{Fe}^0/\text{H}_2\text{O}$ system is a dynamic and heterogeneous system containing Fe^0 and all its corrosion products (Equation (4)). Accordingly, even the most accurate measurements and the most precise observations are just a static snap-shots of dynamic processes within the system. The situation is exacerbated by the evidence that, the processes occur over an enormous range of timescales ranging from some few minutes or hours in laboratory investigations to months and years in field applications [86–88]. This communication insists on the fact that the frequency of discrepant reports in the scientific literature is rooted on an insufficient system analysis. In this regard, an accurate system analysis constitutes the theory of the system. The theory of the $\text{Fe}^0/\text{H}_2\text{O}$ system, in turn, is like a guide to constrain the choice of the model. The theory that some contaminants are reduced by electrons from Fe^0 (electrochemical mechanism) is flawed as water, even present as humidity or moisture do corrode iron [1]. In fact, even deionized water corrodes iron [89]. Figure 1 depicts the interactions of contaminants with solid phases in a pure adsorbent system and the Fe^0 -based system.

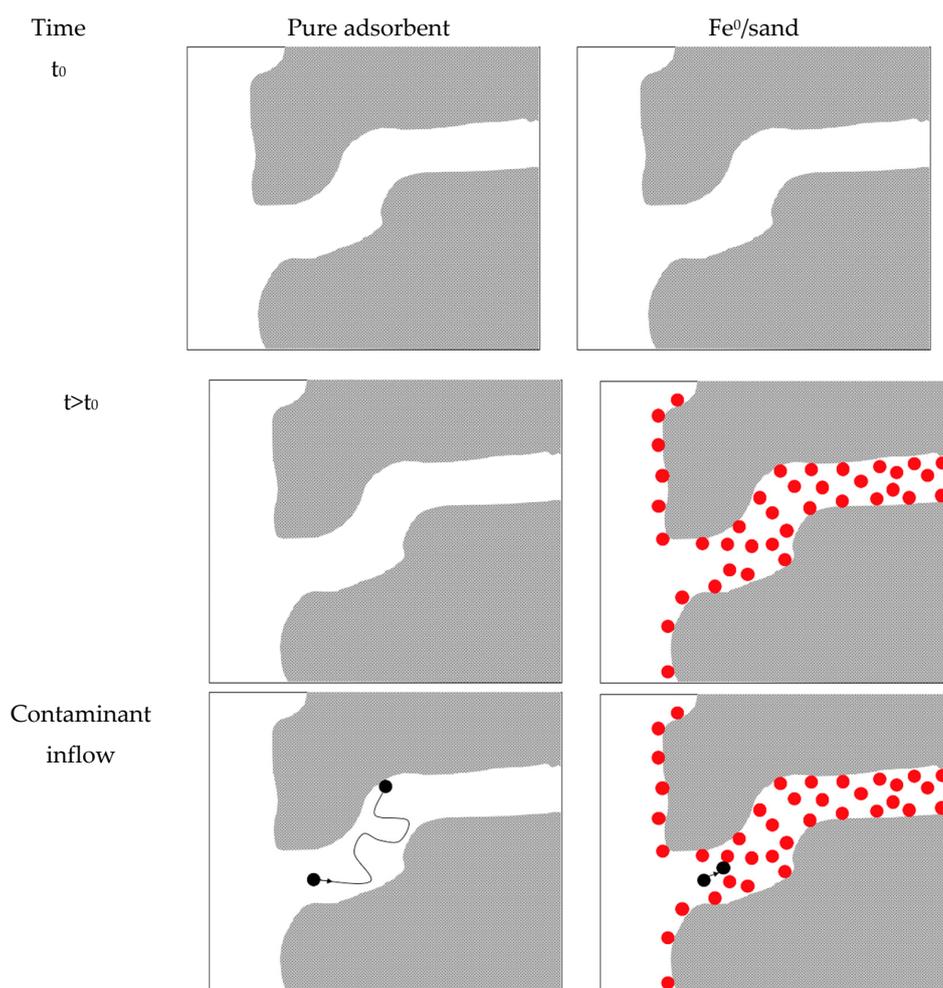


Figure 1. Schematic diagram comparing the interactions of contaminants (black points) with solid phases in a pure adsorbent system (left) and the Fe^0 -based system (right). The red points represent iron corrosion products (FeCPs) which are either coated on solids or suspended in the pore solution.

2.2. Oxide Scale on Fe⁰ and the Decontamination Process

The universal oxide scale on iron metal (at pH > 4.5) is still regarded by the majority of active researchers on remediation Fe⁰ as a disturbing factor compromising the electron transfer from the metal body (reactivity loss) [90–92]. This view contradicts the evidence that a lag time between the start of experiments and reductive transformation is reported in the literature [93,94]. This time corresponds to the quantitative generation of FeCPs, which act as contaminant scavengers. This means that relevant reducing agents are generated in situ. Another problem of the Fe⁰ literature is that “contaminant removal” and “contaminant reduction” are randomly interchanged, while no real mass balance of the contaminants has been presented [53,54,95]. On the contrary, contaminants that are not recovered are assumed to be chemically reduced [68–70].

A look at the mechanism of oxide scale formation reveals that it cannot be electronically conductive. In fact, the initial scale is very porous and cannot transfer electrons because air and water are not electronically conductive (an aqueous solution can be ionic conductive—electrolyte). In subsequent stages, available pores are filled with nascent FeCPs, but they are never uniform and the oxide scale is a mixture of iron hydroxides and oxides [5]. An oxide scale made up of Fe₃O₄ alone would have been electronically conductive. However, such an Fe₃O₄ scale cannot exist under natural conditions (immersed Fe⁰). All other FeCPs are at best semi-conductors and cannot relay electrons from Fe⁰ under natural conditions. Clearly, reports justifying the reductive efficiency of Fe⁰/H₂O systems using the semi-conductive nature of FeCPs are mistaken [96]. This assertion encompasses the Fe⁰/pyrite/H₂O system, whose efficiency is mainly justified by the semi-conductive nature of FeS species [97–99].

The oxide scale on Fe⁰ is definitively a diffusion barrier for all dissolved species, including the pollutants. It is also the contaminant scavenger such that electrochemical corrosion of immersed Fe⁰ induces the generation of contaminant scavengers and other reducing agents. Thus the generation of solid FeCPs is a necessary process which has the (perceived negative) side effect of being expansive. Thus, designing an efficient and sustainable system requires answering the question: how long can FeCPs be generated to satisfactorily treat water while keeping a reasonable hydraulic conductivity (permeability)?

2.3. Chemical Aspects

As discussed earlier (Section 2.1), Fe²⁺ from Equation (1) is transformed to ferrous hydroxide (Fe(OH)₂) and ferric hydroxide (Fe(OH)₃) which have a strong tendency to form colloids of particles that normally carry a positive charge [62,100,101]. These minerals are further transformed to other Fe^{II}/Fe^{III} minerals (e.g., Fe₂O₃, FeOOH, green rust) exhibiting different affinities to dissolved species. The nature of oxides in each individual system depends on the intrinsic reactivity of the used Fe⁰ material and the environmental conditions [5,79]. For example, two different Fe⁰ specimens corroding under the same environment will not necessarily produce the same iron oxides, because the composition of the oxide scale depends on the relative kinetics of Fe⁰ dissolution and Fe hydroxide precipitation, which in turn depends on the solution chemistry, including the pH value, dissolved ions and the salinity [5,6,102]. On the other hand, in-situ generated free Fe²⁺ are adsorbed to the surface of available minerals to form the so-called structural Fe^{II} with a reducing power far larger than that of the free Fe²⁺ ($E^0 < 0.77$ V) and sometimes stronger than Fe⁰ ($E^0 < -0.44$ V) [103]. The availability of several reducing agents in the Fe⁰/H₂O system, and especially from structural Fe^{II}, partly stronger than Fe⁰ implies that the electrochemical series of metal alone cannot predict the chemistry of the system.

2.4. Physical Aspects

The volumetric expansive nature of iron corrosion is the most important physical phenomenon occurring in Fe⁰/H₂O systems [104]. There is expansion because the parent metal (Fe⁰) produces in-situ both: (i) H₂, occupying a volume about 3100 times larger [26,105], and (ii) each solid oxide and hydroxide is at least twice larger in volume than Fe⁰ ($V_{\text{oxide}} > V_{\text{iron}}$) [106,107]. For example, the specific

density of magnetite (Fe_3O_4) is about one half that of iron (Fe^0). It implies that after corrosion a space twice larger than the initial space is occupied [108–110]. While it can be assumed that H_2 escapes from each open system, no free expansion of oxides in porous systems (e.g., water filters, reactive walls) can be assumed [26]. External or internal free expansion occurs in metallic pipes [111,112] and on the walls of steel canister for radioactive waste repositories [110,113]. On the contrary, free expansion cannot be expected in steel-reinforced concrete structures [108,109]. Table 2 presents a comparison of iron corrosion parameters in Fe^0 remediation to that of water pipes and reinforced concrete. Accordingly, considering expansive iron corrosion, which culminates into permeability loss is an essential design parameter for porous $\text{Fe}^0/\text{H}_2\text{O}$ systems (Fe^0 filters). For each Fe^0 filter, the temporal production of both H_2 and oxide is decisive for the long-term efficiency and the permeability of the system [105,107,114,115].

Table 2. Comparison of iron corrosion parameters in Fe^0 remediation to that of water pipes and reinforced concrete.

Parameter	Water Piping	Reinforced Concrete	Fe^0 Remediation
Iron corrosion	Destructive	Destructive	Constructive
Environment	Unknown soil	Known concrete	Known mixture
Fe size	several meters	some cm	<5 mm
	some cm thick	some mm	<2 mm
Rust expansion	Minor or no issue	major issue	major issue
Corrosion effect	Pipe damage	cracking	permeability loss
Linear corrosion	Conservative	non applicable	Absurd
Knowledge status	Quite good	Quite good	Rather poor
Service life	>50 years	>50 years	Up to 30 years
Reference	Enning et al. [2]	Caré et al. [108]	Hu et al. [26]

Another key feature in investigating the remediation $\text{Fe}^0/\text{H}_2\text{O}$ system is that, at $\text{pH} > 4.5$, the Fe^0 surface is permanently covered by an oxide scale. The oxide scale acts both as: (i) conduction barrier for electrons from the metal body, and (ii) physical barrier for dissolved species, including O_2 and pollutants of concern [22–26,53,54]. The net result is that Fe^0 is oxidized by water (electrochemical reaction—Equation (1)), and O_2 and dissolved contaminants are reduced by reducing species present in the oxide scale (Fe^{II} and $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ species, H_2) (chemical reaction). Again, any reasoning based on the electrochemical series of elements is a misuse of chemical thermodynamic, as the physics of the system, specifically the expansive nature of iron corrosion and its electronically non-conductive nature are simply ignored.

2.5. Kinetic Aspects

Aqueous corrosion of Fe^0 materials under environmental conditions ($\text{pH} > 4.5$) is an electrochemical process involving iron dissolution at the anode and H_2 evolution at the cathode (Equation (1)). This electrochemical reaction is accompanied by the formation of an oxide scale on Fe^0 which is not protective as a rule [6,116–118]. In general, oxide scale growth and its protectiveness depend primarily on the precipitation rate of iron hydroxides [5,102]. As the Fe^0 surface corrodes under the initial scale, corrosion continuously undermines the scale. Voids are created and are progressively filled up by the ongoing hydroxide precipitation. The relative rate of (i) Fe^0 oxidative dissolution and (ii) hydroxide precipitation in the Fe^0 vicinity determine the protectiveness of the oxide scale. According to Nesic [5], when the rate of hydroxide precipitation exceeds the rate of Fe^0 dissolution, a dense protective oxide scale is formed. Conversely, when Fe^0 dissolution undermines the new oxide scale faster than hydroxide precipitation can fill the voids, a porous and non-protective scale forms.

There are several factors influencing the iron corrosion rate, including the intrinsic reactivity of a material and the solution chemistry. The solution chemistry includes the presence of dissolved O_2 , contaminants and other (mostly) ubiquitous species. In particular, two different Fe^0 specimens may exhibit different degree of protectiveness under the same operational conditions. The most important feature to consider is that the corrosion rate is never linear. Thus, a linear extrapolation of the initial corrosion rates of Fe^0 specimens in engineered systems can give an inaccurate estimation of its service life. However, for remediation systems, the non-linear nature of the corrosion kinetics implies a decrease in efficiency. Again, results from pipe corrosion or wall corrosion cannot be transferred to remediation Fe^0/H_2O systems. However, it is certain that the semi-permeable nature of the oxide scale allows significant and continuous corrosion over long time periods (“rust never rest”). In this context, Roh et al. [119] reported of buried iron pieces from World War I still corroding in the subsurface. Thus, the objective of the Fe^0 remediation is to couple this long-term corrosion with efficient contaminant removal [7,88,118,120,121].

2.6. Investigating the Fe^0/H_2O System

The extent and kinetics of Fe^0 oxidative dissolution are the result of the following: (i) the nature of metal (intrinsic reactivity), and (ii) the interactions between Fe^0 and the environment in which it is placed [76,122–125]. Therefore, (i) a change of material, and/or (ii) a change in environment results in changes in the rate and the extent of corrosion. In this study, the influence of the environment is considered at micro-scale, specifically what is happening on the Fe^0 surface, in its vicinity or over short distances (within the oxide scale). The oxide/water interface is also considered, but the volume of the solution is not. The aqueous phase is regarded as a reservoir of pollutants and co-solutes, while being the principal Fe^0 oxidizing agent [126,127].

Laboratory and pilot-scale investigations are usually conducted in order to obtain reliable information on the interactions of metallic devices with particular operational environments [128,129]. Laboratory tests are designed to simulate some relevant field situations. Laboratory studies are mostly aimed at obtaining data in a more convenient way and in a shorter time [123,124,130]. They also provide mechanistic information for field applications. However, short-term laboratory experiments are always a simplification and this should be borne in mind when interpreting achieved results [76,129,131,132]. Given the diversity of operational parameters that have been proven to influence iron corrosion from individual studies, one can be overwhelmed by their number and the fact that each material is unique in its corrosion behaviour [11,124,125,133]. Therefore, a first attempt toward a systematic investigation of relevant influencing factors goes through the consideration of the electrochemical nature of aqueous iron corrosion.

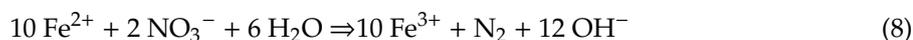
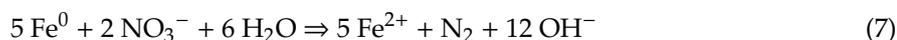
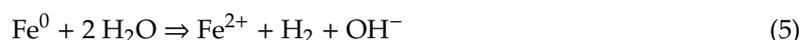
Fe^0 is a good conductor of electricity, and its electrochemical aqueous corrosion depends on the conductive nature of the solution in which it is immersed [1,76]. Understanding the corrosion processes helps in selecting Fe^0 materials necessary for designing sustainable systems. Therefore, the best way to design a sustainable system is to consider the fundamentals of iron corrosion at the design stage. This section highlights the knowledge of corrosion principles and the importance of the environment and materials for field design. The four compartments necessary for continuous Fe^0 corrosion are: (i) an anodic region on Fe^0 where the metal is oxidized and releases Fe^{2+} (leaving two electrons behind), (ii) an electrolyte to transport released Fe^{2+} away from the anode, (iii) a cathode where the simultaneous reductive transformation coupled to iron oxidation occurs, and (iv) the Fe^0 body transporting electron from the anode to the cathode. In an Fe^0/H_2O system, the anode and the cathode are different sites on the same Fe^0 specimen. In the conventional remediation technology, the size of Fe^0 particles is generally small (<5 mm). The four compartments must be electronically connected for the electrochemical process to proceed. This means that if Fe^0 is covered by an oxide scale, the scale must be conductive to warrant the transfer of electrons from the metal body to the oxidizing agent within the oxide scale or at the oxide/ H_2O interface.

A Fe⁰/H₂O system is made up of two interfaces: (i) Fe⁰/oxide and (ii) oxide/H₂O. Because the oxide scale is never electronically conductive and is a diffusion barrier to many species, only water can quantitatively reach the Fe⁰ surface. The net result is that Fe⁰ oxidative dissolution is an electrochemical reaction (water is reduced) but all other observed/reported chemical reduction occur within the oxide film or at the oxide/H₂O interface [53,54,127]. For the Fe⁰/H₂O remediation system, it means that contaminants are not reduced by electrons from Fe⁰. This has important implications on the operating principles of Fe⁰/H₂O systems: first, using the electrochemical series to predict the reductive transformation of any species has been a mistake, and second, using the stoichiometry of any electrochemical reaction involving Fe⁰ is also a mistake. Accordingly, contaminants are ‘just’ dissolved species, capable of modifying: (i) the conductive properties of the electrolyte (H₂O), (ii) the ion conductivity of the oxide scale, and (iii) formation and the transformation of the oxide scale.

3. An Overview of the Mistakes of Past Efforts

3.1. Contaminant Removal Mechanisms

The major mistake of the Fe⁰ remediation literature has been to consider that relevant contaminants are reduced by an electrochemical reaction (electrons from the metal) [134–136]. This section summarizes the extent of the confusion using a paper by Kamolpornwijit and Liang [137]. This paper is selected because it considered past efforts in understanding the service life of Fe⁰ filters and performed long-term experiments (>400 days). Kamolpornwijit and Liang [137] considered porosity loss during nitrate (NO₃⁻) removal in an Fe⁰ barrier. The following reactions were considered:



Equation (5) corresponds to Equation (1) and represents aqueous iron corrosion, an electrochemical reaction. Direct electron transfer from Fe⁰ to NO₃⁻ yielding NH₄⁺ (Equation (6)) or N₂ (Equation (7)) are only possible if the oxide scale on Fe⁰ is electronically conductive. Because an electronically conductive oxide scale does not exist under immersed conditions, Equations (6) and (7) are wrong. In discussing their results, Kamolpornwijit and Liang [137] considered that the H₂ volume they measured corresponds to the stoichiometry of Equation (5). Comparing this H₂ volume to the N₂ volume after Equation (7), they concluded that the contribution of water to the corrosion of iron is minimal. In chemical terms, this is erroneous as Equation (5) shows that 5 moles of Fe⁰ release only 1 mole of N₂. Whether N₂ escapes from the system or not, the 5 moles of Fe²⁺ are further oxidized and or precipitated within the Fe⁰ filter and filling the initial porosity. In reality, it is 10 moles of Fe⁰ that are needed to release one mole of N₂ (Equation (8)).

One major problem of the Fe⁰ literature has been the discussion of the reaction mechanism without mass balance considerations [31,95,138]. Complete mass balance analysis comprises the one of iron, which is admittedly a difficult task as the system is highly dynamic. However, the analysis made herein for nitrate reduction clearly demonstrates the wrongness of the view that Fe⁰ is corroded by NO₃⁻. On the other hand, the importance of FeCPs in inducing porosity loss is demonstrated. If the discussion of the porosity loss starts with the assumption that one mole of N₂ corresponds to 10 moles of corroded and expanded Fe⁰, a better evaluation of changes in the porosity will be achieved. Kamolpornwijit and Liang [137] is also an excellent illustration on how in-situ generated FeCPs are not properly considered while exotic species like CaCO₃ or the flow regime (convection versus laminar) are given key role in pore filling and permeability loss. In essence, if a contaminated water is rich in carbonates a pre-treatment unit for their removal can be used such that decontamination units are

HCO_3^- free. Thus, given the expansive nature of iron corrosion, loss of permeability and porosity even occurs in aqueous systems without CaCO_3 .

Another important feature from Kamolpornwijiit and Liang [137] is that, in case nitrate is reduced to NH_4^+ , regardless of the real mechanisms, NH_4^+ must be removed from the aqueous phase. This removal occurs by adsorption, co-precipitation and size-exclusion [53,54]. These three mechanisms represent the fundamental mechanisms of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems [26,67]. It is essential to recall that chemical reduction and even chemical precipitation are not relevant contaminant removal mechanisms in the concentration ranges relevant to natural waters [111,139]. In particular, for safe drinking water provision, physical methods (e.g., adsorption, filtration, ion exchange) are always mandatory to cope with the stringent regulations. As an example, water defluoridation by chemical precipitation yields an equilibrium fluoride concentration of about 8 mg L^{-1} according to the solubility of CaF_2 [57,58]. This value is far larger than the maximum permissible contamination level of 1.5 mg L^{-1} for drinking water. Coming back to the $\text{Fe}^0/\text{H}_2\text{O}$ system, available results show limited removal extent for fluoride while various removal extents for several contaminants depicting no redox reactivity in the systems has been documented. For this reason, a more rational approach is to consider that all species can be removed regardless of their redox potential, and identify exceptions on a case by case basis. In this regard, recent results by Hildebrant et al. [140] have confirmed that fluoride removal is low, but less reactive materials (EDTA test) comparatively remove more fluoride. This last observation corroborates the view that there is no single Fe^0 material for all situations and calls for more systematic investigations to identify appropriate Fe^0 materials for specific remediation applications.

The lack of systematic investigations has also affected the selection of Fe^0 materials used for pathogen removal [141–146]. Using various Fe^0 materials and very different experimental conditions, discrepant results have been reported [141,146]. Lu et al. [142] can be regarded as a perfect reflection of the state-of-the-art knowledge. The same authors investigated the mechanism of nitrate reduction and iron cycling by an iron-reducing bacteria strain (strain CC76) and metallic iron. They reported that the strain CC76 was able to utilize Fe^{2+} (from iron corrosion) as electron donor for the nitrate removal. More importantly, they observed that Fe^0 inhibited the growth of strain CC76 in the early stage of the operation. This observation corresponds to CC76 removal by Fe^0 . However, the authors also reported that after the initial stage, strain CC76 was able “to tolerate” the presence of Fe^0 , meaning that no or less removal was achieved. This phase corresponds to a decrease in the kinetics of iron corrosion as discussed above and has been described in microbially-influenced corrosion [2]. If we recall the work of Kamolpornwijiit and Liang [137] primarily investigating nitrate removal in an abiotic $\text{Fe}^0/\text{H}_2\text{O}$ system, it then becomes apparently clear that the major source of discrepancy in the literature is the insufficient system analysis. Like with chemical contaminants, all pathogens will be removed in a well-designed system. For a filtration system, the key questions to address are: (i) which Fe^0 material, in what amount, and for which contaminant and water? and (ii) with which filtration depth, for which flow velocity and for which operational duration? Another key aspect to consider is the nature of the aggregates (e.g., gravel, MnO_2 , pumice, sand) to be mixed with Fe^0 and the Fe^0 proportion in the mixture [107,114]. These aspects are yet to be addressed in the Fe^0 remediation literature, but are critical for the design and field application of the technology. Table 3 presents a synthesis of current knowledge including the mistakes, and proposed refinements for future studies on Fe^0 remediation.

Table 3. Summary of synthesis of current knowledge and proposed refinements for future studies on Fe⁰ remediation.

Previous Study	Synthesis	Refinement for Future Studies
	Electrochemical reduction	Chemical reduction
	Protons as concurrent Fe ⁰ oxidizer	Protons as sole oxidizing agents for Fe ⁰
Decontamination mechanism	Adsorption as possible mechanism	Adsorption as fundamental mechanism
	Co-precipitation as possible mechanism	Co-precipitation as fundamental mechanism
	Size-exclusion rarely considered	Size-exclusion as fundamental mechanism
Driving force	E ₀ value = −0.44 V	Affinity to iron oxides and hydroxides
Selectivity	E ₀ value of the contaminant	Surface charge and size
	H ₂ evolution	Fe ⁰ dissolution in 1,10-Phenanthroline
Material selection	Removal efficiency for selected species	Fe ⁰ dissolution in EDTA
	Physical characterization tools	Not really useful
	Fe ⁰ dissolution in complexing agents	Phen test as candidate for standard method
Batch experiments	Shaken or stirred	Quiescent or shaken at < 100 rpm
	Lasting for some hours to days	Lasting for some weeks to months
	Mostly lasting for some few months	Lasting for at least six months
	Many contain only Fe ⁰	Never contain more than 50% (vol/vol) Fe ⁰
Column/field experiments	Some accelerated column experiments	Never artificially accelerated iron corrosion
System modelling	Based on the stoichiometry of an electrochemical reduction reaction	Consider protons as the sole oxidizers of Fe ⁰ Consider porosity loss related to each Fe ⁰ atom

3.2. Reactivity and Efficiency

In the Fe⁰ remediation literature the terms “reactivity” and “efficiency” are mostly randomly interchanged. This has introduced confusion in the evaluation of independent results. In an effort to resolve this confusion the notion of “electron efficiency” has been introduced [147,148]. The electron efficiency (in %) is defined as the proportion of electrons from Fe⁰ oxidation that is used for the target reduction reaction, for example for nitrate reduction by Kamolpornwijiit and Liang [137] (Section 3.1). In this approach, electrons used to reduce water (Eq. 1) or dissolved O₂ are considered as “excess electrons” or avoidable electron wastage [148]. In other words, the main reaction is devalued to a side effect. Contrary to this still prevailing approach [92], the present work and related ones [149–153] recall that aqueous iron corrosion (Equation (1)) is not an unwanted reaction leading to an extra consumption of Fe⁰, but Equation (1) produces Fe^{II} species and H₂, which are responsible for the documented chemical reduction and FeCPs which are responsible for contaminant removal and permeability loss [105–107].

Each Fe⁰ material is characterized by its intrinsic reactivity while each system is characterized by its efficiency for water treatment [154–156]. According to Miyajima and Noubactep [156], the efficiency is the expression of reactivity in a given system. This means that changing the Fe⁰ material modifies the efficiency. Conversely, an Fe⁰ material proven efficient in a system could be useless in another

system. In the quest of more efficient systems for water treatment, several Fe⁰ materials and groups of materials (e.g., bimetallics, iron nails, nano-Fe⁰, scrap iron, sponge iron, steel wool) have been tested and used for water treatment (Table 1). These efforts have been rendered difficult by a mistaken system analysis [157,158] and the evidence that most comparative works are based on testing materials for the removal of individual contaminants [159–162]. Lufingo et al. [11] recently discussed approaches that can be considered as universal as they are based on the stoichiometry of Equation (1): (i) H₂ evolution [163,164] and (ii) Fe²⁺ production [11,159]. They concluded that iron dissolution in a dilute solution of 1,10-Phenanthroline (2 mM) (Phen test) is the best available tool to characterize the intrinsic reactivity of Fe⁰ materials (Section 4).

3.3. Misuse of Adsorption Isotherms and Kinetic Models

Several studies investigating contaminant removal by Fe⁰ materials have applied isotherm and kinetic models initially developed for materials where contaminant removal occurs via adsorption [131, 132,165,166]. A detailed discussion of the various adsorption isotherm and kinetic models, including assumptions and equations are presented in earlier reviews [132]. A comprehensive review of the limitations associated with the applications of such models to Fe⁰ systems is the subject of another paper, hence is beyond the scope of the current study. Briefly, the extension of such models to Fe⁰ materials is problematic for the following reasons: first, unlike adsorbents such as activated carbon whose surface area is readily available for adsorption at the beginning of the experiment (time $t_0 = 0$; Figure 1), Fe⁰ systems are highly dynamic and equilibrium is rarely achieved in such systems (i.e., rust never rests), while the total reactive sites contributing to contaminant removal is not exactly known (Figure 1). Thus, most assumptions for such models are not valid for Fe⁰ materials. Second, as discussed earlier, contaminant removal in Fe⁰ systems does not occur solely via adsorption. In view of this, the application of adsorption models to Fe⁰ systems constitute another fundamental error in Fe⁰ literature. Yet despite a number of reviews highlight the mistakes, misuse and inconsistencies in the use of adsorption kinetic and isotherm models [53,54,67–71,131,132], the problem persists. Thus there is need to develop models for contaminant removal in Fe⁰ systems that takes into account the iron corrosion phenomena and the fundamental mechanisms responsible for contaminant removal as highlighted in the current review.

Reference [157] severely questioned the validity of specific rate constants (k_{SA}) in Fe⁰/H₂O systems. These rate constants are based on the stoichiometry of contaminant reduction by electrons from the metal body (Fe⁰) and are not considering the interactions of contaminants within the oxide scale [167]. As discussed in Section 2.2, the Fe⁰ surface is not accessible to all contaminants. Even k_{obs} values (which are normalized to the surface area to obtain k_{SA}) currently used in the literature are erroneous as they are rooted on the wrong reaction. However, the most severe mistake has been to use the adsorption capacity for Fe⁰ which is considered a reducing agent. Moreover, an adsorption capacity is determined in a system where the reactive agent is not completely depleted.

4. Selection and Characterization of Fe⁰ Materials

As discussed above, the scientific reason for using all Fe⁰ materials (e.g., granular iron and bimetallics, iron filings, iron nails, iron wire, nano-Fe⁰, scrap iron, steel wool) in water treatment is the electrode potential of the redox electrode Fe^{II}/Fe⁰: $E^0 = -0.44$ V. Clearly, all reactive Fe⁰ materials have the same redox potential. The intrinsic reactivity of individual Fe⁰ specimens depends on a myriad of factors from which some are not readily accessible to the researcher. Relevant influencing factors include: alloying elements, Fe⁰ form, manufacturing processes, metallography, Fe⁰ grain size, surface area, and surface oxidation state. Accordingly, each Fe⁰ material has its own intrinsic reactivity which should be characterized in order to better understand how it is influenced by operational conditions to induce the intended remediation goal.

The long history of using Fe⁰ for technical chemical applications, including water treatment reveals that there has always been efforts to select appropriate materials for individual applications.

For example, the porous “spongy iron” (sponge iron or direct reduced iron) was proven more suitable in filtration systems than dense materials [12,13,168]. Similarly, multi-metallic systems and nanoscale materials were recently developed to address (recalcitrant) contaminants that were less sensitive to treatment with granular materials [169]. For completeness, it should be stated that there is no Fe⁰ material for all situations such that one should rationally select appropriate materials for each specific application. For example, while treating water in fluidized systems (Anderson Process), dense materials were better than sponge iron [13,168]. Similarly, Hildebrandt et al. [140] reported that Fe⁰ materials of low reactivity according to the EDTA test exhibited a better efficiency for fluoride removal. The question arises how to select the right Fe⁰ specimen for a given application? This calls for the development of standardized protocols for selection and characterization of Fe⁰ materials for various applications.

It is unfortunate that material selection has not received the due attention given its central role for the technology. Lufingo et al. [11] recently gave an overview of the available tools for the characterization of the intrinsic reactivity of Fe⁰ specimens. These authors based their work on an excellent review article by Li et al. [162] and insisted on the quantification of Fe²⁺ from Equation (1). According to Lufingo et al. [11], quantifying Fe²⁺ or H₂ evolution from Equation (1) are the best tools to characterize the intrinsic reactivity. However, quantifying both Fe²⁺ and H₂ in natural systems suffers from the high reactivity of those primary corrosion products within the system, including their adsorption onto FeCPs and their action as own reducing agents. Clearly, measured amounts of Fe²⁺ and H₂ represent an excess quantity and cannot be strictly used to quantify iron corrosion (at pH values >4.5). These considerations clearly show that the H₂ evolution method [163,164] is an approximation, while the EDTA method [170] is disturbed by dissolved O₂. All other methods are contaminant-specific, and thus of low value [133,160,161]. Lufingo et al. [11] then proposed iron dissolution in a dilute (2 mM) 1,10-Phenanthroline solution (Phen test) as a facile method free from the inherent shortcomings of all available methods.

In terms of affordability and applicability, the Phen test is currently the best available method to characterize the intrinsic reactivity of Fe⁰ specimens. The test lasts for less than 36 hours and characterizes the initial kinetics of Fe⁰ dissolution. It is suggested as a candidate for a standard method and is immediately useful for material selection (screening) and quality control [11]. Each Fe⁰ specimen is characterized by its k_{Phen} value which reflects its initial dissolution at the pH value of natural waters but without the interaction of the oxide scale. The k_{Phen} values for nine steel wool specimens (Fe⁰ SW) presented by Lufingo et al. [11] were such that $0.07 \leq k_{\text{Phen}} (\mu\text{g h}^{-1}) \leq 1.30$. This shows a ratio of reactivity of 18.5 for Fe⁰ SW specimens which are often tested as a uniform class of materials compared to granular materials for example. Hildebrandt et al. [10,140] presented the k_{EDTA} values for 13 reactive Fe⁰ SW and one granular Fe⁰ as $3.7 \leq k_{\text{EDTA}} (\mu\text{g h}^{-1}) \leq 130.8$. The lowest k_{EDTA} value corresponds to granular Fe⁰, suggesting a reactivity ratio of up to 36 between Fe⁰ SW and granular Fe⁰. No data comparing k_{Phen} values for Fe⁰ SW and granular Fe⁰ are yet available. However, it is certain that the Phen test provides a confidence Fe⁰ screening tool and is non-contaminant-specific. Therefore, if a significant body of k_{Phen} data and data for characterized Fe⁰ specimens for the removal of selected representative contaminants (or contaminant groups) are made available, then site-specific treatability studies would then be required only to fine-tune design criteria for the optimal performance of remediation Fe⁰/H₂O systems.

Our research group has long recognized the need for systematic characterization of Fe⁰ materials in terms of their intrinsic reactivity and efficiency. The idea followed by this research group as summarized herein is to characterize the Fe⁰ reactivity and the efficiency of Fe⁰/H₂O systems in a pollutant-independent-manner. The alternative is to agree on probing pollutants while using standard protocols. A reference Fe⁰ material would also be necessary. The use of EDTA and Phen tests to characterize the intrinsic reactivity has already been discussed. The efficiency of the Fe⁰/H₂O system is characterized using the methylene blue (MB) discoloration method (MB method) [60]. Herein, the low affinity of MB for FeCPs is used to trace the abundance of in-situ generated iron oxides in comparatively

long-term experiments [62,101,159,171]. The Phen test provides a reliable guidance in selecting Fe⁰ from the large catalog of available materials and to control the quality of newly manufactured ones. On the other hand, the MB method provides a reliable guidance for the characterization of the efficiency of Fe⁰/H₂O systems. Selected probing agents enable the discussion of the results, and orange II, methyl orange and reactive red 120 were positively tested in this regard [61,62]. Recent results by Hildebrandt et al. [140] suggest that fluoride could be the next candidate for affordable probing reagent. In fact, it was found that fluoride removal is more efficient by low reactive Fe⁰ specimens.

5. Future Perspectives and Potential Applications

5.1. Investigating the Fe⁰/H₂O System

The findings on which future research should be rooted must be based on the evidence that the oxide scale on iron is a diffusion barrier and shall never be disturbed in ways that are not reproduced under field situations [22,23,53,54,56,124,126,127,171–175]. This has been the motivation for adopting quiescent bath experiments as a more suitable approach to investigate processes occurring in Fe⁰ permeable reactive barriers some two decades ago [20]. Then and now, most research groups consider the shaking intensity as a relevant operational parameter to be investigated almost in all instances without a quiescent system as a reference. However, there is no given convincing reason for the chosen mixing intensities tested in these experiments [124,125].

In 2005, Devlin and Allin [173] designed a glass-encased magnet batch reactor (GEM reactor) to investigate the impacts of selected anions on the efficiency of granular Fe⁰ in removing aqueous contaminants using 4-chloronitrobenzene as a probe molecule. This design aimed to achieve a better comparability between results of different experiments by fixing the stirring method and the stirring rates [169,173]. Using this approach, all experiments should be conducted in the GEM reactor to ensure that the granular iron remains stationary while the solution is stirred. Noubactep et al. [124,127] later demonstrated that, while using a rotary shaker, the shaking intensity should never be larger than 100 rpm. Given that a stirring device (including the GEM reactor) can be difficult to acquire by low-income laboratories, quiescent experiments can be adopted as a rule [171].

Quiescent batch experiments have also been adopted for the determination of the initial corrosion rate of Fe⁰ in EDTA (k_{EDTA}) and Phen (k_{Phen}). Herein, the experiments are stopped before solution saturation, meaning that Fe⁰ specimens are characterized under conditions where no oxide scale is available. Contrary to the prevalent approach [152–164], Fe⁰ specimens are not characterized for any contaminant removal efficiency [176,177]. Solution saturation corresponds to [Fe] values equivalent to the stoichiometry of iron complexation (e.g., [Fe] = 112 mg L⁻¹ for 2 mM EDTA). Lufingo et al. [11,120,121] recently compared the EDTA and the Phen test and established the superiority of the Phen test, which is additionally more affordable.

Another key feature of the remediation Fe⁰/H₂O system is related to the oxide scale. The omnipresent oxide scale on Fe⁰ is positively charged under natural conditions (pH > 5.0) [62,100,101,178]. Thus, the Fe⁰/H₂O system is an ion-selective one and preferentially removes negatively charged species like bacteria [142,146]. One original idea has been to characterize the discoloration of methylene blue (MB) by Fe⁰/sand/H₂O systems (MB method). The MB method is grounded on an historical work by Mitchell et al. [178], who observed that sand adsorbs less MB when it is coated with iron oxide. Thus, mixing the same mass of different Fe⁰ specimens with the given mass of a sand specimen, and allowing them to equilibrate for the long-time in a MB solution enable the differentiation of the Fe⁰ reactivity of various materials [62,101,176,177]. As a rule, the most reactive material produces the largest amount of iron hydroxides, which, in turn, in-situ coat sand and thus discolors MB the least. MB is thus not a model contaminant, but an operational tracer [171,177]. To ease the interpretation of results, methylene orange (MO) [61,176] or Orange II [62,101] can be used as anionic dyes since they have molecular sizes similar to that of MB. Phukan et al. [62,101,176]

additionally used reactive red 120 which is also an anionic dye, but is much larger in size than MO and Orange II.

One key advantage of the MB method is that it enables a visual observation of preferential flow within a reasonable time scale (some weeks) [62]. In designing an Fe⁰-based filtration systems, a decrease in hydraulic conductivity (permeability loss) is expected, and an early contaminant breakthrough will be observed due to preferential flow [179–183]. Mineral precipitation is particularly intense in the entrance zone of the filter [181], but the created preferential pathways are extended throughout the whole water column [179,181]. The investigation of the process of creation and extension of preferential pathways has been analytically very challenging [181–183]. On the basis of observations using the MB method [176,177], changes generated in the entrance zone can be better followed and considered in modelling efforts. This last aspect is crucial for the development of the technology as it has been convincingly demonstrated that models currently predicting the service life of Fe⁰ filters are rooted on a wrong premise [114,115].

5.2. Designing the Next Generation Filter

The determination of the amount of a given Fe⁰ which long-term corrosion kinetics would allow a designed Fe⁰/aggregate system to satisfactorily treat a given water for a certain time frame (e.g., 12 months) can be regarded as a routine work. This routine engineering application is however complicated by the complexity of the iron corrosion process and mistakes in past research as outlined herein. One major thinking mistake has been to consider that admixing Fe⁰ with sand (the most used aggregate) would alter the decontamination kinetics [90,183,184]. Thus, admixing with sand has been mainly considered as an economic tool to save Fe⁰ costs and the negative effects on the resulting system discussed [185]. It has been recently demonstrated that only hybrid Fe⁰ systems are sustainable [105–107].

Several hybrid systems have been successfully tested for water treatment including Fe⁰/activated carbon [184], Fe⁰/Fe₃O₄ [185], Fe⁰/MnO₂ [186], Fe⁰/pyrite [99] and Fe⁰/sand [187]. While inert sand alone has clearly improved the efficiency of Fe⁰ systems [188], the efficiency of other tested aggregates was attributed to the specific materials. The Fe⁰/sand is regarded as in-situ sand coating [141]. It is certain that other materials will be similarly covered by FeCPs. Thus, it is questionable whether the systems really operate as described.

Rephrasing Notter [189], the success of an Fe⁰ filter depends on four main factors: (i) the quantity and quality of the water to be produced (e.g., daily), (ii) the intrinsic reactivity of used Fe⁰, (iii) the nature of the contaminant(s), and (iv) the availability of Fe⁰ material (to renew exhausted systems). This key principle remains unchanged, one century later. All that is needed are systematic investigations that take each Fe⁰ and each water source as a stand-alone design parameter.

The laboratory procedures used to characterize and evaluate Fe⁰-based systems in batch and column experiments vary considerably among studies. For example, some studies use agitated batch experiments to investigate contaminant removal by Fe⁰ [126,127], while others used batch experiments operated in quiescent mode, which is closer to field conditions [61]. This makes direct comparison of results among studies problematic, and could lead to misleading conclusions about the performance of Fe⁰ materials. Therefore, there is a need to develop standardized protocols for the evaluation of Fe⁰ material in both batch and column experiments. In the case of batch experiments, such protocols should include specifying the particle/grain size, tests for determination of material reactivity (e.g., EDTA, Phen tests), liquid/solid ratio, sampling frequency and duration of experiment. For column experiments, such protocols should specify filter depth, duration of experiment, grain size of filter material and chemical properties of test solution to be used, while accounting for potential interference among solutes. Besides developing dedicated pristine Fe⁰ materials for the water treatment industry, scope also exists to use Fe⁰ material generated as wastes from other industries. Similarly, iron oxide-rich spent sludge from Fe⁰-based water treatment systems can be used as raw materials in other industries such as the production of pigments (e.g., iron oxide red) [190], and even as filter material in the construction

industry. This cyclic flow of iron materials between the water treatment industry and other industrial processes could form part of a circular economy. Filter wastes may also be regenerated and recycled to new Fe⁰ material, and then used in other industry when they contain toxic contaminants such as As or U. The recycling of filter wastes in other industries may require detailed environmental risk assessments, including the evaluation of contaminant leaching and potential ecotoxicological effects.

5.3. Field Applications of Fe⁰-Based Systems

Fe⁰-based systems present unprecedented opportunities for wastewater treatment and safe drinking water provision especially in low-income countries, including those in Africa (Table 4) [144,157,191–201]. In fact, the use of Fe⁰-based systems (e.g., the Bishof Process) for clean water provision has a long history dating back to the 19th century [13,14,202]. The history of Fe⁰-based drinking water treatment systems is discussed in detail in earlier review papers [17,18,122]. Recently, our research group has proposed the integration of Fe⁰-based systems in rainwater harvesting systems as a low-cost technology for decentralized drinking water provision, in what is known as the Kilimanjaro Concept [192–194].

Table 4. Potential field applications of Fe⁰-based systems in drinking water and wastewater treatment. The given reference refers to the oldest known application.

Field of application	Remarks	References
<i>A: Safe drinking water provision:</i>		
1. Centralized safe drinking water systems	Both filter beds and fluidized beds are used	[168]
2. Decentralized water treatment for small communities	Steel wool is used against radionuclides	[37,154]
3. Household filters against arsenic	Traditional filters are amended with iron nails	[45,46]
4. Household filters against pathogens	Biosand filters are amended with Fe ⁰ materials	[141]
5. Community-scale Fe ⁰ -based systems against arsenic	Natural water equilibrates with iron nails and flocs are filtered on gravel	[191]
6. Decentralized rainwater harvesting systems for drinking provision	Fe ⁰ filters are efficient to remediate expected contaminants	[192–194]
<i>B: Wastewater treatment systems:</i>		
1. Decentralized domestic wastewater treatment	A Fe ⁰ unit is implemented mostly to remove PO ₄ ³⁻	[42,195]
2. Wastewater for agriculture and aquaculture	Iron filings are used in filter beds to remove Se	[196,197]
3. Industrial wastewaters/effluents	Sponge iron is used to precipitate Cu and Pb from industrial wastes	[198]
4. Constructed Wetlands for Wastewater Treatment	Granular iron is added to reactive materials	[79,199]
5. Urban stormwater treatment	Fe ⁰ is amended to other media to optimize the treatment of runoff water	[200,201]

Fe⁰-based systems also have potential applications in domestic and industrial wastewater treatment systems (Table 4). For example, the Harza Process [27,203] has been used to remove Se from agricultural drainage water. Rahman et al. [200] and Fronczyk et al. [201] proposed the amendment of treatment media for runoff infiltration trenches/pits with granular Fe⁰. In addition, Fe⁰-based systems have been used to treat both domestic [204] and industrial wastewaters [205,206], including acid mine drainage [24,207]. Available studies suggest that Fe⁰ can be added as filter media in constructed

wetlands designed to treat urban stormwater and industrial wastewaters [199]. However, a lot remains to be done to further develop and disseminate Fe⁰-based technologies for wastewater treatment and decentralized safe water provision in developing countries, which such low-cost technologies are most needed. Considering that the bulk of studies are limited to laboratory scale applications, there is need to optimize the Fe⁰-based systems and evaluate them under field conditions.

6. Summary and Conclusions

The corrosion of iron in remediation Fe⁰/H₂O systems is an electrochemical process, coupling Fe⁰ oxidative dissolution to the reduction of water (protons) and to no other available oxidizing agent, including dissolved O₂. This is because the universal oxide scale on Fe⁰ acts as diffusion barrier to dissolved species and a conduction barrier to electrons from the metal body. In other words, water is the sole chemical which can remove electrons from the Fe⁰ surface. Fe⁰ oxidation and water reduction must not necessarily occur at the same locality. The spatial separation of oxidative (anodic) and reductive (cathodic) reactions is possible as the metal body allows the free flow of electrons from anodic to cathodic sites. The tendency of Fe⁰ to give off electrons (Equation (1)) is the same for all Fe⁰-based materials ($E^0 = -0.44$ V). This makes material selection and characterization critical in designing sustainable Fe⁰/H₂O systems.

The need to characterize Fe⁰ materials in terms of intrinsic reactivity and efficiency is critical for the design and operation Fe⁰/H₂O systems, a subject that has been addressed by our research group. Specifically, EDTA and Phen tests were used to characterize the intrinsic reactivity of Fe⁰ materials. In this regard, the Phen test is considered an affordable and appropriate method that provides a reliable guidance in selecting Fe⁰ from the large catalog of available Fe⁰ materials and to control the quality of newly manufactured ones. The efficiency of the Fe⁰/H₂O system is characterized using the methylene blue (MB) discoloration method, while other probing agents investigated include orange II, methyl orange and reactive red 120.

The most characteristic issue of remediation Fe⁰ is the small size (<5 mm) of used materials. Assuming uniform corrosion, the corrosion rates for progressive Fe⁰ oxidation should be normalized to the individual particles. In other words, expression like mmol year⁻¹ should be expressed as mmol year⁻¹ particle⁻¹ or mmol year⁻¹ grain⁻¹. The next important issue will be to consider the non-linear kinetics of the corrosion rate such that the service life of a designed system can be deduced knowing the size of used particles and the long-term corrosion rate. Once this is known, considering the expansive nature of iron corrosion would help to design sustainable systems. The choice of the admixing aggregates (e.g., gravel, MnO₂, pumice, sand) and the mixing ratios are to be investigated on a case-by-case basis.

A better understanding of the long-term corrosion of relevant Fe⁰ materials under site-specific conditions is envisioned to ultimately aid in the design of affordable, applicable and efficient remediation Fe⁰/H₂O systems. Applications of Fe⁰-based systems include; (i) a large variety of water treatment systems, (ii) household and small-scale water treatment plants, including rainwater harvesting systems for drinking water supply, (iii) decentralized domestic wastewater treatment, (iv) urban stormwater, agricultural and industrial wastewater treatment, and (v) as filter media in constructed wetlands. Addressing the key knowledge gaps highlighted here, and extending Fe⁰-based systems to other application domains such as wastewater treatment for agriculture are focal research areas in our group, which brings together collaborators from various countries.

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