Tracing the Scientific History of Fe^0-Based Environmental Remediation Prior to the Advent of Permeable Reactive Barriers

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Abstract: The technology of using metallic iron (Fe^0) for in situ generation of iron oxides for water treatment is a very old one. The Fe^0 remediation technology has been re-discovered in the framework of groundwater remediation using permeable reactive barriers (PRBs). Despite its simplicity, the improvement of Fe^0 PRBs is fraught with difficulties regarding their operating modes. The literature dealing with Fe^0 remediation contains ambiguities regarding its invention and its development. The present paper examines the sequence of contributions prior to the advent of Fe^0 PRBs in order to clarify the seemingly complex picture. To achieve this, the current paper addresses the following questions: (i) What were the motivations of various authors in developing their respective innovations over the years?, (ii) what are the ancient achievements which can accelerate progress in knowledge for the development of Fe^0 PRBs?, and (iii) was Fe^0 really used for the removal of organic species for the first time in the 1970s? A careful examination of ancient works reveals that: (i) The wrong questions were asked during the past three decades, as Fe^0 was premised as a reducing agent, (ii) credit for using Fe^0 for water treatment belongs to no individual scientist, and (iii) credit for the use of Fe^0 in filtration systems for safe drinking water provision belongs to scientists from the 1850s, while credit for the use of Fe^0 for the removal of aqueous organic species does not belong to the pioneers of the Fe^0 PRB technology. However, it was these pioneers who exploited Fe^0 for groundwater remediation, thereby extending its potential. Complementing recent achievements with the chemistry of the Fe^0/H$_2$O system would facilitate the design of more sustainable Fe^0-remediation systems.

Keywords: corrosion products; dissolved oxygen; permeable reactive barriers; water treatment; zero-valent iron

1. Introduction

The world is facing a problem of continuously decreasing availability of fresh water [1]. This is because natural water resources are progressively polluted with anthropogenic chemicals, including chlorinated hydrocarbons [2,3]. Previous efforts to remediate polluted groundwater have culminated in the development of permeable reactive barriers (PRBs) [4–6]. PRBs are subsurface filters filled with appropriate materials to treat through-flowing polluted waters. PRBs containing granular metallic iron (Fe^0) have been demonstrated as an economically-feasible, environmentally friendly, and technologically simple approach for groundwater remediation [6–11]. In addition, PRBs are applicable to a broad range of chemical species, and are less vulnerable to environmental conditions [7,8,11,12].

The development of the Fe^0 PRB technology is currently believed to be fraught with two major difficulties: Reactivity loss and permeability loss [8,11]. Both aspects are inherent to aqueous iron corrosion and occur everywhere, unless appropriate countermeasures are developed [11,13,14]. Reactivity loss is perceived as the decrease of electron transfer from Fe^0 to contaminants over time caused by the formation of an oxide scale on the Fe^0 surface (or in its vicinity). On the one hand, a quantitative electron transfer is impaired by the non-conductive nature of the named oxide scale. On the other hand, permeability loss is perceived as filling the pore space of Fe^0-based filters mainly by foreign precipitates (e.g., $CaCO_3$) or mixed precipitates (e.g., $FeCO_3$). However, at pH > 4.5, aqueous iron corrosion is a volumetric expansive process [15–17], meaning that the very first cause of permeability loss is pore filling with iron oxides and hydroxides [18,19]. Luo et al. [18] have recently demonstrated porosity loss in a Fe^0 filter fed by deionised water (no contaminant, no foreign minerals).

The presentation until now demonstrates that the development of the Fe^0 PRB technology has been based on considering Fe^0 as a reducing agent. This view implies that iron corrosion by water (the solvent) is a side reaction. The net result is an underestimation of the importance of pore filling by solid iron corrosion products (FeCPs). Considering Fe^0 as a reducing agent has culminated in the introduction of the electron efficiency concept (EE concept) [20,21]. The EE concept aims at optimizing the Fe^0 amounts in PRBs in order to avoid material wastage. The EE concept characterizes the redistribution of electrons from Fe^0 to dissolved O_2, target contaminants, and co-contaminants (e.g., NO_3^-). The EE concept frontally contradicts the fact that contaminant reductive transformation and Fe^0 oxidative dissolution are not simultaneous processes (electrochemical reaction) [22–24]. There is thus a need to clarify the root role of Fe^0 in PRBs and related filtration systems (Section 8).

The purpose of this paper is to examine the literature dealing with using Fe^0 in aqueous systems prior to the advent of Fe^0 PRBs in order to clarify its role in the decontamination process. In particular the following three questions will be answered: (i) What were the motivations of previous workers in using Fe^0 in their innovations?, (ii) what are the ancient achievements which can accelerate progress in knowledge for the development of Fe^0 PRBs?, and (iii) was Fe^0 really used for the removal of organic species for the first time in the 1970s, as alleged by the pioneers of the Fe^0 PRBs [25]? Answering these three questions will evaluate the accuracy of the literature review at the starting point of the Fe^0 PRB technology. Particularly, whether or not Fe^0 is a reducing agent under environmental conditions.

2. Methodology

The literature reviewed herein corresponds to the one published in the peer-reviewed literature prior to the advent of Fe^0 PRBs [26–29]. No systematic review is performed, rather, studies relevant in answering the research questions were selected. Metal recovery with cementation using Fe^0 [30,31] and heavy metal removal from industrial wastewaters [32,33] are not considered. The use of Fe^0 in organic synthesis [34] is just considered to specify the reaction conditions which do not correspond to environmental conditions. Typically, organic synthesis by metals (including Fe^0) occurs in acidic aqueous solutions (pH < 7.0) and at elevated temperatures (e.g., > 30 °C) [34–36].

3. Fe^0 in Organic Synthesis: The Béchamp Reduction

Reduction of organics with metals has been known for many decades, but there is no commonly accepted theory of the process. A general agreement exists that hydrogen species are involved in these reductive transformations. In these reactions, double-bonds are broken; halogen atoms are replaced by hydrogen or removed entirely with formation of double bonds; while nitrile, thiocyanide, and other nitrogen and sulfur-containing groups are destroyed [36]. The oldest known reaction involving Fe^0, and used on an industrial scale is probably the synthesis of aniline after the Béchamp reduction [37,38].

The Béchamp reduction (Béchamp process) implies the chemical reduction of aromatic nitro compounds to amines in the presence of Fe^0 and in dilute acid (iron and acid). In the original version of the Béchamp process, nitrobenzene was used to produce aniline in the presence of iron filings or shavings in a dilute hydrochloric acid. It was postulated that reduction was mediated by Fe^0 (electrons from the metal body), and that a slightly acidic pH value was needed (optimum $5.5 \leq$ pH ≤ 6.6) [39]. However, over the years, it was discovered that the reaction was more or less quantitative in organic acids (e.g., HCOOH) and even in NaCl. This implies that Fe^{2+} ions (stabilized by Cl$^-$) are able to induce the reduction of nitrobenzene. For details, interested readers are referred to annual reviews on "Amination by reduction" published between 1951 and 1961 by Jesse Werner in Industrial and Engineering Chemistry (American Chemical Society) [35,38]. For the current presentation, it suffices to recall that: (i) The reactants are pre-heated and then passed through a suitable heated reactor, (ii) ferrous salts could also initiate the chemical reduction of aromatic compounds, and (iii) aniline is removed both from the reaction vapors and the bulk solution (not at the Fe^0 surface). Moreover, lower aniline recovery was explained by its occlusion in the matrix of solid iron corrosion products (FeCPs) as the final pH values were constantly higher than 5.0 [39,40].

Summarizing, the century-old Béchamp reduction reveals that organics can be quantitatively reduced by Fe^{2+} ions in the bulk solution, but at elevated temperatures (e.g., > 50 °C). In other words, Fe^0 is "just" a generator of Fe^{2+} for the reductive transformation of nitrobenzene, and the reaction is possibly catalyzed by Fe^0 and solid FeCPs (e.g., Fe(OH)$_2$, Fe(OH)$_3$), and the reaction products are quantitatively available in the bulk solution. In the Fe^0 remediation technology, pollutants (e.g., nitrobenzene) and reaction products (e.g., aniline) must be removed from the aqueous phase. This is particularly true for safe drinking water provision. However, as a rule, in the concentration range of natural waters, chemical reduction is not a contaminant removal mechanism. In fact, the residual concentrations of the parent chemical and reaction products as per the equilibrium constant, are larger than the maximum permissible contamination level in most of the cases [41].

4. Fe^0 for Safe Drinking Water Provision

In his historical textbook on water treatment, Davis [42] highlighted the following materials as potentially suitable for safe drinking water provision in filtration systems: Animal charcoal, bricks, carbonide of iron, coke, compressed sponge, porous tiles, sand, spongy iron, unglazed earthenware, and wood charcoal. From this list, two materials are Fe^0-based: Carbonide of iron and spongy iron. Spongy iron was explicitly described for its capacity for "removal and destruction of organic matter". Filtration systems are often operated under ambient conditions (about 20 °C) and without pH adjustment. In other words, as early as the end of the 19th century, Fe^0 was used for the abiotic or chemical destruction of organic matter and nitrates under environmental conditions [43]. Remember that pioneers of the Fe^0 PRBs have traced this process back to the 1970s. Admittedly, organics of concern were not halogenated carbons, but the ancient literature on water treatment using the Fe^0 system remains largely unexploited [44]. The three known ancient Fe^0-based systems for safe drinking water provision will be briefly presented in this section.

4.1. The Bischof Process

In 1871, Prof. Gustav Bischof (Glasgow) patented a system for water treatment at the household level using spongy iron as a reactive material [45,46]. Porous spongy iron or sponge iron corresponds to direct reduction of iron and was the best innovation in efforts to use Fe^0-materials in a decentralized water treatment as summarized by Mwakabona et al. [44]. The Bischof process was then tested and used for the water supply of the city of Antwerp (Belgium) (10,000 m^3 d^{-1}) between 1881 and 1883 [42,47]. The Bischof process (Figure 1) could efficiently supply the city with safe drinking water for 18 months without any perturbation or need for maintenance. However, after 18 months, the filters experienced clogging and could no longer produce enough water to cover the needs of the 200,000 inhabitants. Hence, it became necessary to adopt a more rapid system: The revolving purifier or Anderson process [47,48].
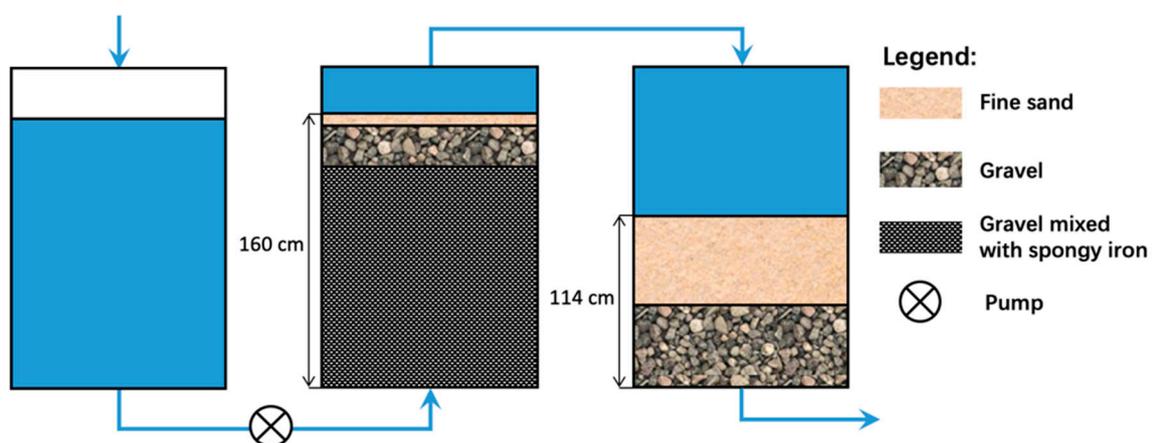

Figure 1. Schematic diagram of the Bischof's spongy iron filter as described by Davis [42]. Arrows show the direction of water flow.

A careful examination of the origin of filter clogging clearly traced it to the Fe^0/gravel layer (Figure 1) [42]. In this layer, gravel and Fe^0 particles were cemented to a compact mass which locally reduced the interconnectivity of available pore spaces and the hydraulic conductivity (permeability) of the whole filter. The rationale for the use of the volumetric Fe^0/gravel ratio of 1/3 (25% Fe^0) was not given in Davis [42] and could not be found in the original works of Bischof [45,46]. The volumetric expansive nature of iron corrosion was also not yet discovered by then. However, the implementation of the Bischop process in Antwerp had clearly demonstrated that Fe^0-based filters are prone to clogging caused by iron corrosion. Since the Fe^0 proportion matters, it can be postulated that higher Fe^0 ratios (e.g., 50, 75, or 100%) would have yielded less sustainable Fe^0 filter systems (less than 18 months of service life).

4.2. The Anderson Process

In 1885, Anderson patented the "revolving purifier" and used it in Antwerp to replace the spongy iron filters [42,47,48]. The revolving purifier entails vigorously churning up the polluted water for up to 5 min with Fe^0 filings or shavings in a cylinder. During this time, iron hydroxides precipitate and occlude contaminants, including organic matters. The flocs are then removed in a subsequent filtration on gravel and sand. In other words, the Anderson process roughly corresponds to coagulation/flocculation, wherein flocs are not generated by iron salts but are in situ produced from Fe^0. It is obvious that the Bischof process relies on the same principles, with the subtle but important difference that iron precipitation occurs in the vicinity of Fe^0 particles and not in the bulk solution. The subsequent Emmons process intuitively used this evidence. The Anderson process could produce up to 20,000 m^3 d^{-1} in Antwerp.

4.3. The Emmons Process

Around 1950, the US Atomic Energy Commission initiated research to thoroughly investigate the decontamination of water polluted with radionuclides at a decentralized level. The tested methods included adsorption, coagulation, distillation, and ion exchange. While investigating adsorptive methods, Lauderdale and Emmons [49] found that steel wool (Fe^0 SW) was capable of quantitatively removing radioactivity from the aqueous phase. This observation led to the investigation of powdered metals (e.g., Al^0, Cu^0, Fe^0, Zn^0) as an alternative to Fe^0 SW for the removal of radioactivity from water [50].

The patented Emmons process [51] was a promising water treatment technology for decentralized safe drinking water provision. It entails using a mixed bed ion exchange in conjunction with another bed filled with Fe^0 SW, clay, and activated carbon. However, the systems were outcompeted by pure ion exchange systems, partly because of its selectivity towards negatively charged radionuclides [52,53]. The merit of the Emmons process was to reiterate the crucial importance of permeability loss in Fe^0-based filters, while revealing the importance of multi-barrier systems to account for the specificities of individual contaminants.

The presentation of the ancient Fe^0 technology for safe drinking water demonstrates that already in the 1950s, Fe^0 and other elemental metals (e.g., Al^0, Cu^0, Fe^0, Zn^0) were demonstrated as powerful reactive materials for the removal of nitrate, organic substances, pathogens, and radionuclides from polluted waters. The corresponding filtration systems, working under ambient conditions (e.g., O_2 level, temperature), were plagued by permeability loss certainly due to solid FeCPs [42,49]. However, the volumetric expansive nature of iron corrosion as demonstrated by Pilling and Bedworth [15] was not considered in solving the clogging problem. Instead, Lauderdale and Emmons [49] used a grade 0 (d = 50 μm) Fe^0 SW and suggested the use of coarser Fe^0 SW or granular Fe^0 (d > 50 μm) to avoid (or delay) clogging. Oldright et al. [32] partly justified permeability loss of Fe^0 filters by larger Pb^{2+} ions replacing Fe^{2+} in filters. This plausible argument has equally not considered the volumetric expansion of Fe.

5. Fe^0 for Agricultural Wastewater

The need for an affordable solution for wastewater treatment, particularly water containing high levels of phosphate is a classic example of how technology can be rediscovered in different contexts. For example, Section 4 has already pointed out how the Emmons process was discovered independently from the Bischof process. In 1992, while seeking for applicable and cost-effective solutions for phosphate removal from wastewaters, George Frigon suggested Fe^0 SW as a good material to in situ generate "oxides" for phosphate removal [54]. In this communication, this tool will be operationally termed the Frigon process. One key advantage of the Frigon process is that, Fe^0 SW is readily available and is acceptable "from an engineering viewpoint". In 2007, Andrew J. Erickson independently presented the Frigon process [55–57] where sand was used as admixing material instead of peat similar to the Frigon process. The Erickson process is particularly interesting because it was introduced more than a decade after the advent of the Fe^0 PRB technology, but was introduced as a stand-alone technology. Only in the further development of the Erickson process was the knowledge from the Fe^0 PRB considered [56,57]. For example, it was suggested that Fe^0 SW was replaced by the granular Fe^0. Another interesting feature of the Erickson process is that, it used only less than 5% by weight of Fe^0 SW and was efficient for years without any clogging problems [56].

Another field of application where Fe^0 presented promising results is that of Se removal from agricultural drainage water. Filtration on Fe^0 beds was investigated as a feasible, cost-effective, and practical alternative to biological precipitation, flow-through wetlands, ion-exchange, microalgal-bacterial treatment, reverse osmosis, solar ponds, and volatilization [58]. In 1985, the Harza Engineering Company tested a pilot-scale process using iron filings in flow-through beds to remove Se from agricultural drainage water (Harza process) [59]. Se removal was quantitative, but the testing was discontinued because the columns quickly cemented with precipitates (FeCPs). It was first postulated that Fe^0 reduces Se^{VI} to Se^{IV}
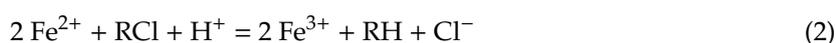
and Se^0. Further studies conclusively demonstrated that Se was not reduced by Fe^0 (no electrochemical mechanism), but rather, by Fe^{II} species generated in situ [60]. Anderson [60] also demonstrated that Se was removed by adsorption onto and co-precipitation with FeCPs, despite the observed chemical reduction. The tested filter beds contained 100% Fe^0 and were very efficient at removing Se, but were not sustainable due to clogging. Testing the Harza process has demonstrated that Fe^0 filtration can decrease Se concentrations to very low values and suggested that the Harza process "might be useful as a polishing step following microbial treatment" [58]. However, the Erickson process suggests that decreasing the Fe^0 proportion in the beds (e.g., 25% *v/v*) would make the Harza process a stand-alone sustainable technology for selenium removal.

6. Fe^0 for Domestic and Industrial Wastewaters

Previous sections have demonstrated the ability of Fe^0 filters to treat water polluted with organic matter, phosphate, and nitrate, which are three main components of human wastes. Thus, Fe^0 filters are also a good candidate for the decentralized treatment of domestic wastewaters. Conventional methods for decentralized domestic wastewater treatment include lagoons, sand filters, and wetlands. However, these technologies presented numerous drawbacks, such as evaporation of huge quantities of valuable water, generation of significant odor, and high demand for land. Additionally, their treatment performance depends on seasonal variations and require frequent maintenance operations [61,62].

In 1993, Wakatsuki et al. [61] presented in the English peer-reviewed literature a system first published between 1989 and 1991 in Japanese (*Jpn. J. Soil Sci. Plant Nutri.*). Then, the new Fe^0-based wastewater treatment technology is termed as a multi-soil-layering (MSL) system. In a MSL system, Fe^0 in soil is oxidized to ferrous ions which in situ coat the available surface (e.g., in zeolite layers), and are oxidized further to ferric iron which can fix phosphate ions. Fe^0 oxidation consumes oxygen and contributes to the development of anaerobic conditions. The MSL system has been successfully tested for domestic wastewater treatment in several countries over the past 30 years [62–64]. Compared to the other alternatives discussed earlier, the MSL technology is very cost effective and has an effective service life estimated to be more than 20 years. The MSL system has several advantages, including (i) occupies a small area, (ii) has a high hydraulic capacity, (iii) simple maintenance and no frequent clogging, and (iv) requires no energy [62]. Therefore, the MSL system has the potential to become a sustainable domestic wastewater treatment option in low-income communities in the developing countries. MSL are very flexible systems which can be selectively designed with available materials. Their huge potential in achieving universal sanitation cannot be overemphasized.

The very last important aspect of the ancient Fe^0 literature is the concept for wastewater treatment presented in 1991 by Michael Boris Khudenko. Khudenko [36] suggested the use of cementation using Fe^0 as a tool to reductively degrade organics in wastewaters. Clearly, a copper salt (e.g., $CuSO_4$) was used to oxidize Fe^0 (Equation (1)) to produce Fe^{II} species, which in turn reduce organics in a parallel (not simultaneous) reaction (Equation (2)). Contaminant degradation is optimal at lower pH values (H^+ consumption), and its extent depends on the Cu^{2+} concentration, among other parameters. The Fe^0 PRB literature has mostly considered that contaminants are reduced by Fe^0 (Equation (3)), while Fe^0 corrosion by water (Equation (4)) has been regarded as a side reaction.

$$Fe^0 + Cu^{2+} = Cu^0 + Fe^{2+} \tag{1}$$

$$2\,Fe^{2+} + RCl + H^+ = 2\,Fe^{3+} + RH + Cl^- \tag{2}$$

$$Fe^0 + RCl + H^+ = Fe^{2+} + RH + Cl^- \tag{3}$$

$$Fe^0 + 2\,H^+ = Fe^{2+} + H_2 \tag{4}$$

The most trivial argument against Equation (3) is the presence of a non-conductive oxide scale shielding the Fe^0 surface, hence electron transfer from Fe^0 to the contaminant is impossible [65]. On the other hand, chemical reduction according to Equation (3) was documented in the Béchamp process

(Section 3). In other words, before the mechanistic discussion initiated by Matheson and Tratnyek [28] in the framework of research for Fe^0 PRBs, the scientific literature had already presented evidence that at a pH value of natural waters, contaminants are quantitatively removed in well-designed Fe^0/H_2O systems. As demonstrated herein, Fe^0 is corroded by water (Equation (4)), while contaminants are reduced in parallel reactions (Equation (2)) (Section 8).

7. Significance for the Fe^0 PRB Technology

In the early 1990s, groundwater remediation using PRBs filled with Fe^0 has been demonstrated as an applicable technology. In such systems, Fe^0 is used as a reducing agent, mostly for chlorinated organics (RCl). It is "preferred" that Fe^0 is oxidized only from the reduction of target contaminants (RCl). Unfortunately, water (H_2O), dissolved oxygen (O_2), and other reducible species (including NO_3^-) are ubiquitous in most natural waters, and have the ability to corrode or sustain the corrosion of Fe^0 as well. Additionally, the abundance of water (the solvent) coupled with the low concentrations of contaminants imply that Fe^0 is mostly corroded by water, even under anoxic conditions (absence of O_2) (Section 8). Moreover, the evidence that Fe^0 is permanently shielded by an electronically non-conductive oxide-scale definitively excludes Fe^0 oxidation by any contaminant as a relevant reaction path [65]. In other words, before the advent of Fe^0 PRBs, it was established that in Fe^0/H_2O systems, quantitative reductive transformations of contaminants are possible, but through a chemical reaction path: The electrons are not from Fe^0 (Section 3).

The present communication highlights that Fe^0 is not an electron donor under environmental conditions. In other words, Fe^0 oxidative dissolution is not the cathodic reaction simultaneous to the reductive transformation of any dissolved species (including O_2 and NO_3^-). Yet, the whole Fe^0 PRB technology is built on this mistaken premise! Thus, the prevailing paradigm for the Fe^0 PRB technology is built on the confusion between an electrochemical process (reduction by Fe^0) and a resulting chemical process (reduction in the presence of Fe^0). The presentation above suggests that it would have sufficed to properly consider Khudenko's work [36] to avoid three decades of confusing reports. The evidence that there is a direct proportionality between the extent of Fe^0 oxidation and the abundance of Fe^{II} (and H_2) species in a Fe^0/H_2O system has added to the confusion.

The brief glimpse of the Fe^0 remediation technology prior to the advent of Fe^0 PRB may help the research community move out of the "valley of confusion" [66]. In strictly limiting the presentation to the time before 1994, an appreciation of the accuracy of literature review accompanying the introduction of the technology is enabled. Gillham [25] gives an excellent overview of the development of the Fe^0 PRB technology. It is explicitly said that Reynolds et al. [67] have observed the disappearance of halogenated hydrocarbons in Fe^0-based vessels, and that reductive transformation was postulated as a plausible mechanism. Efforts to assess the novelty of the discovery went back to a patent by Sweeny and Fischer [68]. The clear answer published in 1991 by Khudenko [36] was unfortunately overseen. The net result, three decades later, is that restoring the scientific truth in the maze of several papers based on half-true results is a very challenging issue.

Table 1 summarizes the processes considered in this study, while specifying their key features. It is seen that Fe^0 was used as an own reducing agent only in the synthetic organic chemistry (Béchamp process). The Béchamp process occurs in a dilute acid (pH < 7.0) and at elevated temperatures, up to 100 °C [35,38]. Thus, prior to the advent of the Fe^0 PRB technology, Fe^0 had already been used for contaminant removal under environmental conditions, but mostly as a generator of contaminant scavengers. In the 1980s, the Harza process first assumed Se(VI) reduction, but later demonstrated that Se removal was achieved by adsorption and co-precipitation. Lastly, the Khudenko process used a Cu^{2+} salt to oxidize Fe^0 and reduce organic species in parallel chemical reactions. Khudenko [36] was ignored by the pioneers of the Fe^0 PRB technology as well.

Table 1. Chronological overview of processes relevant for the discussion of the mechanism of contaminant removal in Fe^0/H_2O systems.

Process	Anno	Rationale for Using Fe^0	Species of Concern	Reference
Béchamp process (*)	1854	Reducing agent	Nitro phenols	[37]
Bischof process	1871	Generator of adsorbents	Color, pathogens, nitrate	[45]
Anderson process	1885	Generator of flocs	Color, pathogens, nitrate	[48]
Emmons process	1951	Generator of adsorbents	Radionuclides	[49]
Harza process	1986	Generator of adsorbents	Selenium	[59]
Wakatsuki process	1989	Generator of adsorbents	Organics, nutrients	[61]
Khudenko process	1991	Generator of reducing agents	Organics	[36]
Frigon process	1992	Generator of adsorbents	Phosphate	[54]
Fe^0 PRBs	1994	Reducing agent	Chlorinated hydrocarbons	[28]

(*) The Béchamp process corresponds to the organic synthesis and occurs in an acidic solution and at elevated temperatures.

The other important features from Table 1 is that, prior to the advent of the Fe^0 PRB technology, Fe^0 had already been used to remove all classes of contaminants from aqueous solutions, including: Biological, chemical, and physical ones. Thus, already in 1990, Fe^0 could have been introduced as a filter material for universal safe drinking water provision upon proper literature review. The way forward is to forget that Fe^0 is a reducing agent and consider that, in a filtration system, each oxidized Fe^0 atom contributes to porosity loss, and consequently, permeability loss.

The very last thing to address is the often reported reactivity loss of Fe^0 materials [11]. Reactivity loss is mistakenly regarded as the decrease in the kinetics of electron transfer to contaminants caused by the formation of the oxide scale on Fe^0. Without any in-depth discussion, it can be stated that, reactivity loss is not really a problem because it has occurred during the 18 months of successful operation of the Bischof process in Antwerp [47]. Reactivity loss is also currently occurring in systems that have been operating for more than two decades now [69,70]. In essence, reactivity loss is an intrinsic characteristic of Fe^0, which is yet to be properly considered in the Fe^0 PRB literature [71]. Reactivity loss is the expression of the non-linear nature of the kinetics of iron corrosion [71–73]. In particular, Antia [73] recently presented the most complete review on the history of the Fe^0 technology. The conclusion reads as: "The current global commercial market for Fe^0-based technologies is small, with perhaps < 350,000 m^3 d^{-1} being treated in surface based reactors and PRBs. If the technology can be commercialized for any of these purposes, then the future global commercial market for Fe^0-based technologies may exceed several million m^3 d^{-1}". There is no doubt, that clarifying the mechanism of contaminant removal will accelerate the process of designing more efficient systems. The next section clarifies the state-of-the-art knowledge as to offer a (common) starting point for future investigations.

8. Shaping the Design of Better Fe^0-Based Systems

The presentation until now has insisted on past mistakes due to an incomplete literature review. In this effort, it has been demonstrated that the Fe^0 technology has been independently rediscovered at least three times (Emmons process, Frigon process, and Erickson process, Table 1). There are three recent peer-reviewed articles presenting the history of the Fe^0 technology [44,73,74]. Thereby, ref. [74] is limited to the water supply of the city of Antwerp (Belgium) using both the Bischof and the Anderson Processes. Specifically, ref. [73] summarizes the Fe^0 technology and presents its current status with specific reference to the patent literature. Concerning its use for potable water provision, refs. [44] and [73] pointed out the particular suitability of Fe^0 for households and small communities.

Regardless of the history of the Fe^0 technology, a careful analysis of the fate of Fe^0, contaminants, and their reaction products always enables the design of efficient and sustainable systems. All what is then needed is to perform experiments under conditions relevant to field applications. For example, experiments pertaining to Fe^0 PRBs and any filtration system must be performed under conditions enabling the precipitation of FeCPs in the vicinity of Fe^0. Quiescent batch experiments have been

proven excellent for this purpose around 2007 [75,76]. Moreover, batch system stirred at less than 100 rpm can still offer relevant results [77]. However, most experiments are still performed at higher stirring intensities and subsequent results are used to design filtration systems [10–12]. On the other hand, little efforts have been directed at analyzing the fate of Fe^0, including the consideration of the Fe mass balance [78].

The Fe^0 technology is grounded on iron corrosion by water (Equation (4)). Equation (4) implies that one mole of Fe^0 is corroded by two moles of water to produce one mole of Fe^{2+} and one mole of H_2 gas. In essence, each Fe^0 specimen is a different material with its own intrinsic reactivity [79]. Similarly, each polluted water is unique in its characteristics (pH value, water chemistry) [80]. Both these factors make the comparison of independent results very challenging. However, avoidable mistakes have been made. The most important being to consider that iron corrosion by water is a side reaction. The extent of the mistake is presented herein. For this purpose, a polluted water at pH 7 ($[H^+] = 10^{-7}$ mol L^{-1}) saturated with oxygen ($[O_2] = 8$ mg L^{-1} or 2.5×10^{-4} mol L^{-1}) is considered [81]. The redox couples present in such systems are: Fe^{II}/Fe^0 ($E^0 = -0.44$ V); Fe^{III}/Fe^{II} ($E^0 = 0.77$ V); H^+/H_2O ($E^0 = 0.00$ V); and O_2/OH^- ($E^0 = 0.81$ V).

For the oxidative dissolution of Fe^0, the reaction with the highest difference between the E^0 values (E (V) = E^0 + 0.44) is the most favorable. This corresponds theoretically to the O_2 reduction. This argument seems to be supported by the relative concentrations of involved species: $[H^+] = 10^{-7}$ mol L^{-1} and $[O_2] = 2.5 \times 10^{-4}$ mol L^{-1}; $[Fe^{2+}] = 8.9 \times 10^{-6}$ mol L^{-1}; and $[Fe^{3+}] = 8.9 \times 10^{-6}$ mol L^{-1} [81]. However, the low concentration of H^+ (10^{-7} mol L^{-1}) corresponds to a dynamic equilibrium. This implies that Fe^0 is permanently dissolved by water and the generated Fe^{2+} either precipitates or is further transformed. Thus, the effective concentration of H^+ is 55.5 mol L^{-1}. In other words, from a pure thermodynamic perspective, Fe^0 corrosion by water is always quantitative. The kinetics of the reaction depends on the Fe^0 intrinsic reactivity and the solution chemistry [79,81]. On the other hand, the oxide scale resulting from quantitative iron corrosion by water shields the Fe^0 surface, making it inaccessible to O_2. The comparison of the E^0 values show that Fe^{2+} can be chemically oxidized by O_2. This communication posits that the improper consideration of water as a solvent is the root cause of the conflicting reports in the Fe^0 remediation literature.

It is very important to recall that even under ambient anoxic conditions, electronic conductive oxide scales are not formed on Fe^0 [65,82]. Accordingly, no electron transfer from Fe^0 to O_2 and any dissolved species (e.g., contaminant) is possible [82]. Thus, all available models based on direct reduction have underestimated the extent of Fe^0 consumption as twice more Fe^0 is needed to produce the assumed amount of electrons for contaminant reduction (Fe^{II} to Fe^{III} exchanges only one mole of electrons). If it is additionally considered that relevant contaminants have at best intensify iron corrosion [83], it becomes clear, that the focus should be on investigating the process of iron corrosion by water as influenced by the presence of contaminants [75,76]. More than a decade after this peer-reviewed view, only recently corresponding approaches were published [84,85]: Sand is spiked with Fe^0 to achieve quantitative contaminant removal in the long term.

Summarizing the work presented by Ullah et al. [85], the authors have not started by considering any stoichiometry, but are just testing how to disperse Fe^0 in sand to achieve quantitative removal by adsorption, co-precipitation, and size-exclusion in the long term. The premise is that in situ coating of sand with FeCPs will induce quantitative contaminant removal. This corresponds to the idea behind the Bischof, the Emmons, the Erickson, and the Frigon processes (Table 1). The future of the Fe^0 depends on the ability of researchers to couple this "Fe^0 dispersion" with the characteristic of Fe^0 materials. Results summarized by Antia [73] suggest that porous materials (e.g., sponge iron) have been used in the most sustainable systems [44,86,87]. Accordingly, efforts to develop more sustainable systems should go through manufacturing porous materials tailored for water treatment. A viable alternative is to test the available filamentous Fe^0 materials such as steel wool (SW) [79]. In fact, Bradley et al. [88] realized that a Fe^0 SW with a diameter of 25 μm was depleted in household filters after six months of operation while Tepong–Tsindé et al.[89] observed no depletion of a coarser Fe^0 SW

(50 μm) after one year of operation. The results of refs. [88] and [89] suggest that only well-structured systematic investigations will enable the advent of science-based sustainable Fe^0-based systems to fill the market gap as described by Antia [73].

9. Concluding Remarks

Prior to the advent of Fe^0 PRBs, the development of Fe^0-based remediation systems was the result of a tortuous process in which all important steps were made: (i) Fe^0 was established as an in situ generator of contaminant scavengers, (ii) Fe^0 was recognized as a volumetric expansive process, and (iii) aqueous iron corrosion was exploited to mediate quantitative reduction of inorganic and organic species. Accordingly, the attribution of the discovery of "reducing Fe^0" to pioneers of Fe^0 PRBs is clearly incorrect unless the real mechanism of documented reductive transformation is not considered. The Fe^0 PRB literature has mostly considered that contaminant reductive transformation is the cathodic reaction simultaneous to Fe^0 oxidative dissolution (electrochemical cell). This assumption makes Fe^0 oxidation by water a side reaction and neglects the accompanying porosity loss. This mistaken view has culminated in the development of the electron efficiency concept to characterize the distribution of electrons from Fe^0 to all available oxidizers (contaminants of concern, co-contaminants and dissolved O_2). Given that there is no electron transfer from Fe^0 to any dissolved species, it is fair to state that the Fe^0 PRB literature has been answering or asking the wrong questions for three decades. However, even though the wrong questions were asked, past and current efforts have been successful in developing highly valuable tools which can now be adjusted. The advent of Fe^0 PRBs has created an unprecedented boom in research for water treatment using Fe^0 materials and revived forgotten aspects such as safe drinking provision and wastewater treatment. Now, by focusing the energy and resources on the right questions, it is expected that systematic research will soon enable the exploitation of the opportunities of the remediation Fe^0/H_2O system, as suggested by Antia [73].

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