

Water Treatment Using Metallic Iron: A Tutorial Review

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Abstract:

Researchers and engineers using metallic iron (Fe⁰) for water treatment need a tutorial review on the operating mode of the Fe⁰/H₂O system. There are few review articles attempting to present systematic information to guide proper material selection and application conditions. However, they are full of conflicting reports. This review seeks to: (i) Summarize the state-of-the-art knowledge on the remediation Fe⁰/H₂O system, (ii) discuss relevant contaminant removal mechanisms, and (iii) provide solutions for practical engineering application of Fe⁰-based systems for water treatment. Specifically, the following aspects are summarized and discussed in detail: (i) Fe⁰ intrinsic reactivity and material selection, (ii) main abiotic contaminant removal mechanisms, and (iii) relevance of biological and bio-chemical processes in the Fe⁰/H₂O system. In addition, challenges for the design of the next generation Fe⁰/H₂O systems are discussed. This paper serves as a handout to enable better practical engineering applications for environmental remediation using Fe⁰.

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Review

Water Treatment Using Metallic Iron: A Tutorial Review

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Abstract: Researchers and engineers using metallic iron (Fe^0) for water treatment need a tutorial review on the operating mode of the $\text{Fe}^0/\text{H}_2\text{O}$ system. There are few review articles attempting to present systematic information to guide proper material selection and application conditions. However, they are full of conflicting reports. This review seeks to: (i) Summarize the state-of-the-art knowledge on the remediation $\text{Fe}^0/\text{H}_2\text{O}$ system, (ii) discuss relevant contaminant removal mechanisms, and (iii) provide solutions for practical engineering application of Fe^0 -based systems for water treatment. Specifically, the following aspects are summarized and discussed in detail: (i) Fe^0 intrinsic reactivity and material selection, (ii) main abiotic contaminant removal mechanisms, and (iii) relevance of biological and bio-chemical processes in the $\text{Fe}^0/\text{H}_2\text{O}$ system. In addition, challenges for the design of the next generation $\text{Fe}^0/\text{H}_2\text{O}$ systems are discussed. This paper serves as a handout to enable better practical engineering applications for environmental remediation using Fe^0 .

Keywords: iron corrosion products; laboratory experiments; pilot tests; removal mechanisms; water treatment; zero-valent iron

1. Introduction

The increased occurrence of micro-pollutants and pathogens in the hydrosphere is typically associated with population growth and increasing anthropogenic activities [1,2]. Historically, pollution of municipal water resources by human wastes was the starting point of industrial water treatment [1,3,4]. Public health and environmental concerns drive efforts to develop affordable, effective, and robust technologies for the removal of pollutants from water (water treatment). Related technologies are based on physical, chemical, electrical, thermal, and biological principles [5]. Filtration on fixed beds has been demonstrated as the most important one because of its wide range of applications [6,7] and ease of operation [8,9]. Adsorptive filtration is considered the most affordable water treatment technology due to the availability of a wide range of suitable adsorbents [5,6,8]. Adsorption also enables the removal of biological, chemical, and physical pollutants. However, adsorption has its limitations, such as finding suitable materials of high adsorption capacity [5,8,9]. For the past two or three decades, metallic iron (Fe^0) has been discussed in the literature as an affordable reactive material

for environmental remediation and decentralized safe drinking water provision [4]. However, the Fe^0 remediation technology is an old one [10].

As early as 1856, a household water filter using metallic iron (Fe^0) was patented [10]. Between 1881 and 1885, Fe^0 -based filters were successfully tested and used for the water supply of the city of Antwerp (Belgium) [10–13]. Afterwards, the city of Antwerp was supplied for some 30 years by water treated in a “revolving purifier”, a Fe^0 -based fluidized bed [13]. Thus, engineered Fe^0 -based systems for safe drinking water provision have a scientific history dating back to more than 160 years ago [14,15].

The long history of engineered Fe^0 -based systems for water treatment is not a continuous one [15]. Related systems have been abandoned and (partly) independently rediscovered several times [11,16–23]. In fact, after the first large scale applications in Antwerp and elsewhere [10–13], the Fe^0 technology was abandoned after World War I and there was no trace of it in the Western peer-reviewed scientific literature until 1951 [4,18]. On the other hand, the Harza Process (1986) [20] and all subsequent ones, including reactive barriers (1994), have not considered available knowledge from Western scientific journals [21–23]. Four examples will be given in a chronological order to illustrate the extent of confusion in the literature.

(i) Example 1: The Emmons Process

Lauderdale and Emmons [18] introduced the Emmons Process independently from past knowledge on using Fe^0 (steel wool (SW) or Fe^0 SW) for safe drinking water provision [15]. The Emmons Process is a compact unit designed at Oak Ridge National Laboratory (USA) to treat small volumes of radioactive polluted waters. This unit can be universally adapted for the following applications: (i) Emergency drinking water supply, and (ii) water supply in small communities. Lauderdale and Emmons [18] primarily added Fe^0 SW to remove ruthenium, “for which it had been found to be very effective”. They hypothesized that Fe^0 SW “serves both as a reducing agent and as a medium for the adsorption of radio-colloids”. The same authors also documented that radioactivity was not readily removed from the filter by washing it with water. Radioactive species were thus not removed by simple adsorption or “mechanical floc filtration” (i.e., pure size-exclusion). Another key observation by Lauderdale and Emmons [18] was that a band of rust appeared at the column inlet and progressed very slowly through the Fe^0 bed. The columns clogged rapidly if: (i) Extremely fine grade of Fe^0 SW was used, and/or (ii) fine iron filings were used. It was postulated that using a coarse grade of iron filings or other metals in granular form would enable the design of more robust and sustainable filtration systems. A year later, Lacy [24] successfully tested aluminum (Al^0), copper (Cu^0), and zinc (Zn^0) as alternative filter materials to Fe^0 . However, the relationship between Fe^0 type and clogging was not further investigated. Nearly 30 years later, the Harza Process has experienced the same challenge. Moreover, even 50 years later, Westerhoff and James [25] have faced the same problem without going to the basic fundamentals and looking for the scientific origin of this key observation [26,27]. It is interesting to note that using mathematical modeling (ref. [26]) could establish that the 1:3 Fe^0 :sand ratio used in the water works in Antwerp is the optimal ratio concealing efficiency and permeability in the long term.

(ii) Example 2: The Harza Process

The Harza Engineering Company patented in 1986 an Fe^0 -based process known as the Harza Process for the removal of toxic metals from wastewaters [28]. The Harza Process was successfully pilot-tested for treating selenium (Se)-polluted agricultural drainage water. The Harza Process involved filtering Se-polluted water through beds packed with iron filings (100% Fe^0) at controlled flow rates. Se removal was quantitative, but the filters clogged rapidly, thus the system was efficient but not sustainable. After three years of intensive research using several instrumental analytical tools, including Fourier transform infrared spectroscopy and Raman spectroscopy, the investigators realized that Se was removed by the action of in-situ generated iron oxyhydroxides, mostly at the inlet of the column. Adsorption and co-precipitation were the main removal mechanisms, even though some

redox reactions were possible [19]. One important observation of Anderson [19] was that the clogging behavior was not dependent upon the type of water flowing through the Fe^0 bed. Similar results were obtained whether Se was spiked to natural or to distilled waters. It is anticipated here that the bed clogging is an intrinsic property of Fe^0 , as aqueous iron corrosion is accompanied by volumetric expansion [29]. Accordingly, properly considering the Fe^0 mass balance in a porous system would have solved this problem [30,31].

(iii) Example 3: The SONO Arsenic Filter

Intensive research on using Fe^0 to treat water started around 1990 [32–34], when Fe^0 was clearly used as a stand-alone contaminant-removing agent. However, Khan et al. [21] used Fe^0 to increase the dissolved iron concentration and induce aqueous arsenic (As) removal by adsorption and co-precipitation. The resulting system, the SONO arsenic filter, was awarded the Grainger Challenge Gold Award [30]. While rationalizing the efficiency of SONO filter for As removal, Hussam and Munir [35] considered that inorganic As^{III} species are oxidized to As^{V} species, which are strongly adsorbed onto hydrous ferric oxide. This explanation is acceptable when focusing the attention on As, but cannot explain why more than 20 other species are removed by SONO filters [36]. In fact, the efficiency of Fe^0 -based systems to remove pathogens and chemical contaminants from water was documented more than a century earlier [15,37]. In view of the diversity of contaminants that have been reported to be quantitatively removed in $\text{Fe}^0/\text{H}_2\text{O}$ systems [38–40], it was stated that reduction is not likely to be a significant removal mechanism [41–44]. A decade after the first critical review severely questioning the reductive transformation concept [45], the view that Fe^0 is an own reducing agent under environmental conditions is still prevailing [46–48]. It appears that within the Fe^0 research community, there exists many individuals without adequate preparations to differentiate between chemical and electro-chemical reaction mechanisms. Yet, the viability and advancement of any scientific discipline largely depend on the quality of its investigators and the work they produce [49]. Considering its nature, this is a problem which cannot be resolved by some isolated research groups [43]. Therefore, the compilation of this tutorial review is a tool to make the problem better known to both the current and the future Fe^0 research community.

(iv) Example 4: Direct Versus Indirect Reduction Mechanisms

Hu et al. [50] characterized the reductive process of nitrate in the $\text{Fe}^0/\text{H}_2\text{O}$ system and concluded that “the indirect reduction of nitrate by hydrogen generated from the reaction between proton and metallic iron may be a major mechanism for the reduction of nitrate under the experimental conditions”. Although direct reduction by Fe^0 is thermodynamically possible, and even more favorable ($E^0 = -0.44$ V; [51]), indirect reduction by Fe^{II} species ($E^0 = 0.77$ V) is also favorable as the electrode potential for the reduction of NO_3^- is higher ($E^0 > 0.80$ V). Articles published after Hu et al. [50] have rarely tried to clarify the real mechanism of NO_3^- removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems, as reviewed by Vodyanitskii and Mineev [52]. They mostly just considered direct reduction, like the majority of available earlier works [46,47]. It is rather surprising that, nearly two decades after the work of Hu et al. [50], the indirect reduction mechanism is still being ignored by some in the Fe^0 research community. Indeed, this behavior seems to be the rule in the Fe^0 literature, and is a further motivation for the present tutorial review.

Examples 1 to 4 have clearly shown that information regarding the applicability of Fe^0 materials in the water treatment industry is conflicting and confusing. New information has been constantly added, independent from the available common database. As a consequence, some intrinsic impracticable designs have been published in the peer-reviewed literature [53,54]. Both references have not properly considered (i) the volumetric expansive nature of iron corrosion or (ii) the iron corrosion rate and its time-dependency. It is certain that many processes ridiculed by experts have been subsequently successfully applied [17]. However, the science of the system should be constantly considered. Systems (e.g., electrocoagulation) can work satisfactorily for decades before their operating mode

is established [55,56]. The $\text{Fe}^0/\text{H}_2\text{O}$ remediation system is no exception to this. The Fe^0 literature is full of systems, whose functionality is rationalized by challenging the mainstream iron corrosion science [57,58]. Clearly, the present tutorial review aims at demonstrating that concepts deeply rooted in the Fe^0 research community and generally taken for granted in daily research endeavors are not consistent with scientific principles. In such a context, aspects inherent to the established questionable concepts are investigated, rather than fundamentally questioning their benefit for science and engineering.

This work summarizes the science of aqueous iron corrosion and contrasts it with selected aspects of literature reports in order to improve the understanding of the interactions accounting for the removal of contaminants in $\text{Fe}^0/\text{H}_2\text{O}$ systems. The bulk of published monitoring studies lack sufficient detail with respect to study design, thus making conclusive interpretation of results difficult [59–62]. For example, Wilkin et al. [61,62] investigated Cr^{VI} and trichloroethylene removal in subsurface Fe^0 barriers without addressing the intrinsic characteristics (e.g., corrosion rate, extent of depletion) of the used materials. It is therefore imperative to routinely employ a ‘before’ and ‘after’ monitoring design to adequately assess potential impacts on selected operational parameters. Such a science-based understanding is crucial to design more efficient and sustainable Fe^0 -based remediation systems.

2. The Chemistry of the $\text{Fe}^0/\text{H}_2\text{O}$ system

A piece of metallic iron (Fe^0) rusts when it is exposed to humid air. Here, Fe^0 corrosion is caused by both water (H_2O) and atmospheric oxygen (O_2). In other words, under ambient conditions, Fe^0 corrodes to form a reddish-brown hydrated metal oxide ($\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O} = \text{rust}$) (Figure 1—top). Rust continually flakes off and exposes the Fe^0 surface to abundant oxygen and trace amounts of water (humidity) [63]. Under atmospheric conditions, both air oxygen and water are required for rust to form.

A piece of Fe^0 immersed in water under ambient conditions rusts differently than that in air. Here, water is abundant and dissolved O_2 is limited (8 mg L^{-1}). Under quiescent conditions, the Fe^0 surface is covered by layers of iron oxides in the sequence of increasing oxidation states: $\text{FeO}-\text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3$ (oxide scale). This oxide scale is equally not protective because of its structural differences [63–65]. The oxide scale also continually flakes off and exposes the Fe^0 surface to abundant water, but not likely to dissolve oxygen which has to diffuse through the oxide scale to reach the Fe^0 surface (Figure 1—bottom). If the immersing water is poor in O_2 (anoxic conditions), Fe^0 corrosion will occur at a lower kinetics and will be mostly made up of Fe_3O_4 . However, some Fe_2O_3 (and other Fe^{III} species) will be formed such that the oxide scale on Fe^0 is never an electrically conductive one [47,66,67].

Under atmospheric conditions, Fe^0 is oxidized to Fe^{2+} at an anodic site on the Fe^0 surface (e.g., a lattice defect), while O_2 is reduced to water at a different site on the Fe^0 surface (the cathode). Electrons are transferred from the anode to the cathode through the electrically conductive metal (Fe^0). Water is a solvent for the produced Fe^{2+} , and also acts as a salt bridge (electrolyte). Rust is formed by the subsequent oxidation of Fe^{2+} by atmospheric O_2 [68]. In other words, under atmospheric conditions, as long as the Fe^0 surface is not completely covered by an oxide scale, O_2 can be reduced to H_2O in an electro-chemical reaction (Figure 1—top). Here, the perfect interplay between the four components (anode, cathode, conductive metal, electrolyte) of an electro-chemical cell are depicted.

As a rule, under immersed conditions, dissolved O_2 cannot quantitatively reach the Fe^0 surface because the oxide scale acts as an O_2 diffusion barrier [45,68]. Thus, Fe^0 is corroded by water, while O_2 is reduced by Fe^{II} species. Clearly, iron corrosion is still an electro-chemical reaction, but in this instance, O_2 reduction is a chemical reaction (reduction by Fe^{II} species) (Figure 1—bottom).

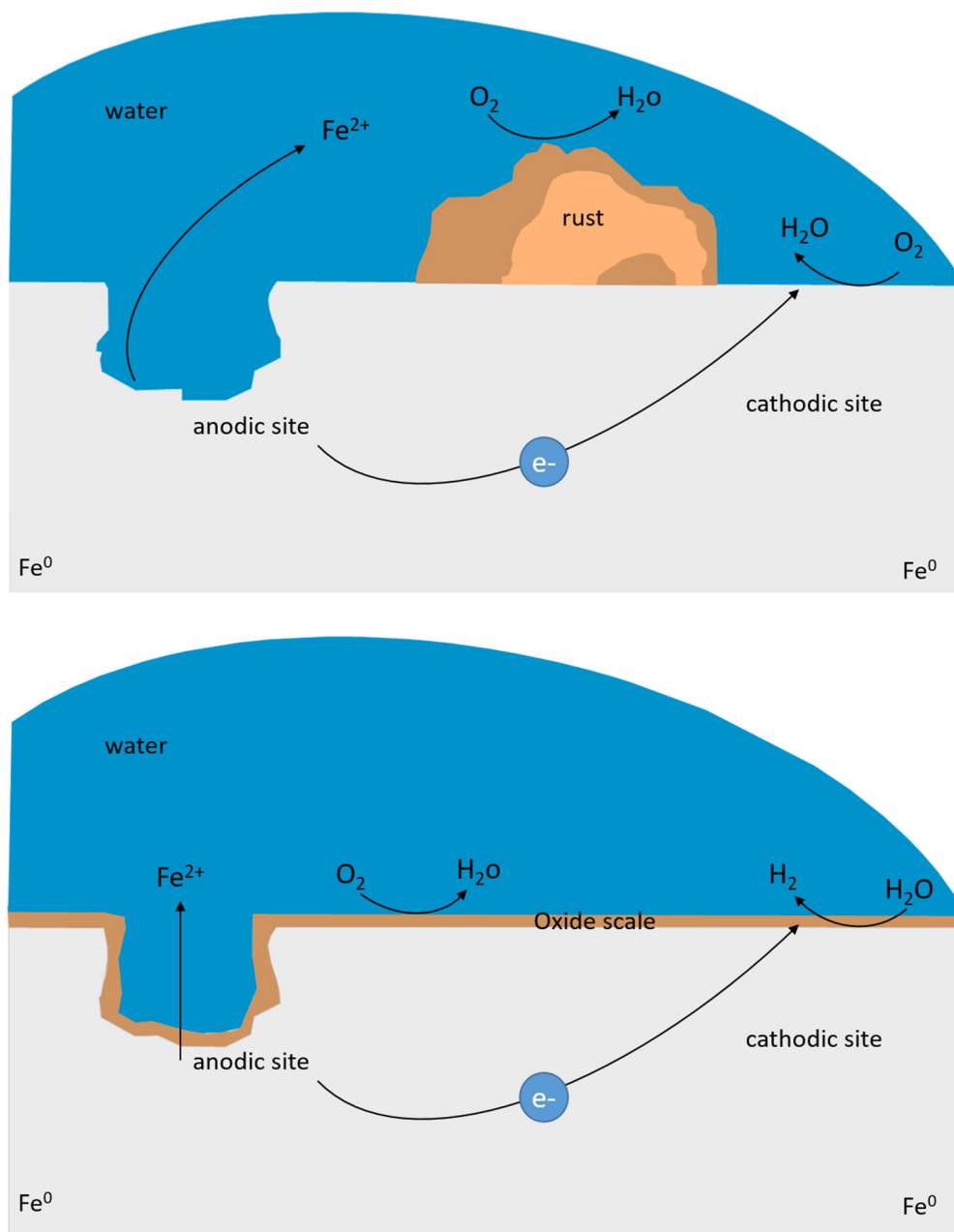


Figure 1. Sketch of the electro-chemical process of iron corrosion as influenced by the abundance of water and dissolved O_2 before (**top**) and after (**bottom**) the generation of a porous oxide scale. The porous oxide-film is a diffusion barrier to all dissolved species, including O_2 .

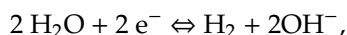
To illustrate what has been said, the reactions that occur at the anode and the cathode in each case will be presented together with the corresponding overall cell reaction.

In both cases, the anodic reaction is the oxidative dissolution of Fe^0 :



Under anoxic conditions, the cathodic reaction is certainly the reduction of water. Also, under immersed oxic conditions (presence of an oxide scale), the cathodic reaction may be the reduction of water:





It then follows that the overall cell reaction for immersed iron corrosion is:



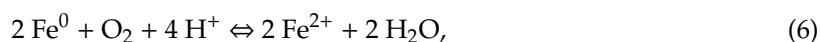
Actually, when O_2 or other oxidizing agents (e.g., reducible contaminants) are present, they are reduced by Fe^{II} species in a chemical reaction (Figure 1—bottom). Fe^0 corrosion by water (Equation (3)) is accelerated because Fe^{2+} is consumed (Le Chatelier's Principle). The electrode reaction for the reduction of oxygen reads as:



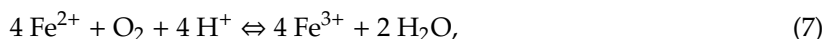
The electrode reaction for the oxidation of Fe^{2+} reads as:



Under atmospheric, non-immersed conditions, electrochemical reduction of O_2 by Fe^0 is possible according to Equation (6):



Under immersed conditions (oxide scale shields Fe^0), O_2 is reduced by Fe^{2+} according to Equation (7):



Similar to O_2 , all other reducible species must overcome the electrical non-conductive diffusive barrier (oxide scale) to reach the Fe^0 surface (Figure 1—bottom). Due to the non-conductive nature of the oxide scale, no quantitative electron transfer from the metal (Fe^0) to the possibly thereon adsorbed species is possible. Clearly, contaminant reduction in an $\text{Fe}^0/\text{H}_2\text{O}$ system is rarely (or even never) the cathodic reaction simultaneous to Fe^0 oxidation. This fundamental knowledge preceded the mechanistic discussion within the Fe^0 research community [69–71]. In fact, three years before Matheson and Tratnyek [69], Khudenko presented a concept for the cementation-induced oxidation-reduction of organics [72–74]. The method makes use of the following: (i) Electronegative sacrificial metals (e.g., Fe^0 or Al^0), (ii) a salt of a sufficiently electropositive metal (e.g., CuSO_4), and (iii) reagents for pH shift (e.g., pyrite or mineral acids) [72]. The redox transformation of target organics is induced as a parallel reaction to the cementation process. Clearly, aqueous Fe^0 oxidation is accelerated by Cu^{2+} reduction (cementation), and redox transformation of organics is induced by parallel reactions. Again, Fe^0 corrosion and redox transformation of organics are not simultaneous reactions [57,75,76]. Such reactions have been independently used over the years, the most recent example could be that of Xi et al. [48]. These authors used CuSO_4 to accelerate the kinetics of arsenic removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems. It is important to recall that As is removed by adsorption and co-precipitation [77,78]. Accordingly, rationalizing the efficiency of $\text{Fe}^0/\text{H}_2\text{O}$ systems for water decontamination by any electrochemical process involving the pollutants has been a huge mistake [69–71]. The electrochemistry-based reasoning implies the electrode potential of the couple $\text{Fe}^{\text{II}}/\text{Fe}^0$ ($E^0 = -0.44 \text{ V}$), representing the anodic half-reaction in the electrochemical cell. This is thermodynamically possible (E^0 values) but physically impossible because of the omnipresence of a non-conductive oxide scale. The next section recalls the fundamentals for an electrochemical cell and presents relevant influencing factors for their investigation.

3. Investigating the Electrochemical Corrosion in $\text{Fe}^0/\text{H}_2\text{O}$ Systems

For an electrochemical cell to be formed, the following four components must be available: (i) An anode where oxidation occurs, (ii) a cathode where reduction occurs, (iii) an external pathway to allow the flow of electrons, and (iv) a salt bridge (or a porous barrier) allowing ions to flow back and forth from the electrodes (anode and cathode) (Figure 1—top) [79–81]. In the context of remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems (immersed iron corrosion), anode and cathode are two different sites on the metal where Fe^0 is

dissolved to Fe^{2+} (Equation (1)) and H_2O reduced to H_2 (Equation (2)), respectively. Electron transfer is secured by the Fe^0 body and contaminated water is the electrolyte (ionically conducting medium). A constant connection is required among the four components for an electrochemical reaction to occur. As discussed in Section 2, the Fe^0 is constantly shielded by an oxide scale which is electronically non-conductive. This is the reason why quantitative contaminant reduction is never the cathodic reaction coupled to Fe^0 oxidative dissolution at the anode. Clearly, contaminant redox transformation in an $\text{Fe}^0/\text{H}_2\text{O}$ system is not an electrochemical, but a chemical process [57,75,76,82].

Another key feature of the remediation $\text{Fe}^0/\text{H}_2\text{O}$ system is a salt bridge (electrolyte), which is not always a 'free' aqueous solution, but a hydrated oxide scale, which is a porous barrier that allows the flow of anions and cations (Figure 1—bottom). The first consequence of this situation is that increasing ion mobility accelerates iron corrosion, and thus all related processes, including contaminant redox transformations. For this reason, fixing the experimental ionic strength while using high salt concentration is a huge conceptual mistake, as Fe^0 corrosion is accelerated in a manner that will not be reproduced in natural waters [82,83]. The authors of the present communication have been avoiding this mistake for two decades by using natural or tap water as background electrolytes while investigating the $\text{Fe}^0/\text{H}_2\text{O}$ system [84–86]. As $\text{Fe}^0/\text{H}_2\text{O}$ systems are used in a variety of field conditions (static to fluidized bed), it is understood that operational conditions in laboratory experimentations should correspond to the mimicked real situations [41,45,87,88]. In particular, experiments pertaining to improved understanding of Fe^0 -based filtration systems should be performed under conditions enabling the formation of oxide scale at the Fe^0 surface or in its vicinity [87]. On the contrary, the vast majority of experiments investigating the mechanism of contaminant removal in subsurface Fe^0 barriers have been performed under agitated/stirred and controlled conditions, mostly for relatively short experimental durations [41,45].

Summarizing, the proper investigation of remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems implies that experiments are performed under conditions relevant to field situations, including the experimental duration. The importance of the experimental duration is reflected by the dynamic nature of iron corrosion, which implies Fe^0 oxidation, $\text{Fe}(\text{OH})_x$ formation, polymerization and precipitation, Fe oxide crystallization, and subsequent formation of the oxide scale. The dynamic nature of Fe^0 corrosion is addressed in the next section.

4. The Dynamic Nature of the $\text{Fe}^0/\text{H}_2\text{O}$ System

In aqueous solutions, iron corrosion is relentless, thus "rust does not rest". This means that an immersed Fe^0 specimen corrodes until it is completely depleted. A better understanding of the long-term corrosion process could hold clues for engineering improved Fe^0 -based remediation systems. A variety of Fe^0 specimens have been tested and used for environmental remediation and water treatment [89–93]. However, these studies failed to pay particular attention to the iron corrosion rate [94,95]. The standard method for measuring the rate of corrosion entails immersing an Fe^0 specimen in a salt solution (e.g., NaCl), and then periodically monitoring the mass loss. This approach has been proven time-consuming and has presented an operational barrier for the development of new Fe^0 alloys, as test times of several months are necessary [96,97]. This evidence alone suggests that laboratory experiments pertinent to field Fe^0 barriers would have to last for months or years. This has not been the case in existing studies, as even column experiments just lasted for some weeks or months [41,45,75,76].

The most important reason why column experiments should last for months and years is that iron corrosion is a volumetric expansive process [29,98]. It is well known that the volume of each iron corrosion product (V_{oxide}) is larger than the volume of iron metal (V_{metal}). In the context of iron corrosion in steel reinforcing bars, it has been established that $2.1 \leq V_{\text{oxide}}/V_{\text{metal}} \leq 6.4$ [99,100]. Using this reasoning, Caré et al. [26] established that no Fe^0 filtration system containing more than 53% Fe^0 can be sustainable due to loss of porosity (and permeability) in the long term [27]. The reasoning assumed uniform spherical Fe^0 particles having an initial size of 1.2 mm and filling the packed-bed

with an initial porosity of 36%. To the best of the authors' knowledge, no field application has used such spherical Fe^0 particles, and measured initial porosity is often larger than 36%. However, it is evident that pure Fe^0 (100% Fe^0) beds are not sustainable. However, permeability loss and failure of Fe^0 barriers have been attributed to all possible arguments, but not really the expansive corrosion of Fe^0 [59,101,102]. An evident merit of considering the volumetric expansive nature of iron corrosion has been to end the discussion as to whether mixing Fe^0 and inert aggregates (e.g., gravel, MnO_2 , sand) is beneficial for packed beds. It was clearly established that mixing Fe^0 with other non-expansive aggregates is not a tool to reduce Fe^0 cost [103,104], but a prerequisite for sustainable filtration systems [26,27,105]. Specifically, mixing Fe^0 and non-expansive aggregates is meant to maintain porosity and permeability.

A further key feature of the dynamic nature of the $\text{Fe}^0/\text{H}_2\text{O}$ system is the differential reactivity of iron corrosion products (FeCPs) as they are produced and transformed in-situ [64,65,106]. Sikora and Macdonald [106] differentiated between aged and nascent FeCPs with respect to contaminant removal. Nascent FeCPs, or 'living FeCPs', are very reactive, while aged FeCPs are non-reactive and termed as 'dead FeCPs' [107,108]. It has already been discussed in detail that the dynamic nature of FeCP generation implies that contaminants are removed by adsorptive co-precipitation [41,43,45,109,110]. This corresponds to the view of Leffmann [17] that: "The most practical benefit of the application of electricity to water purification will come from the indirect methods in which the electrical energy used to produce an active disinfecting agent, and this is then applied to the water". The presentation, until now, has clearly demonstrated that $\text{Fe}^0/\text{H}_2\text{O}$ systems dynamically produce FeCPs for pollutant removal (water treatment). The dynamic nature of the system implies that their efficiency at any particular time depends on at least one key variable: The amount and the proportion of nascent FeCPs. For filtration systems, the extent of permeability loss should be considered as well [94,95].

5. Investigating the $\text{Fe}^0/\text{H}_2\text{O}$ System

The dynamic nature of the $\text{Fe}^0/\text{H}_2\text{O}$ system implies that the "bottle-point" technique, traditionally used to characterize the contaminant removal efficiency of adsorbing agents in batch systems [111,112], should be profoundly revisited. The main reason being that Fe^0 is a reactive material, producing adsorbing agents in-situ [20,21]. It is certain that discrepancies in published data are rationalized by the different experimental procedures employed by individual researchers [58,113,114]. Experimental procedures differ with respect to Fe^0 size and type, Fe^0 pre-treatment, Fe^0 particle size, Fe^0 dosage, volume of solution, shaking/stirring type and intensity, fraction of the bottles filled with solution, contaminant concentration, buffer application, and equilibration time [111,112,114]. In particular, the shaking/stirring type and intensity should not unnecessarily disturb the formation of an oxide scale on Fe^0 [88]. There has been no systematic study of the effects of operational parameters on the decontamination process using $\text{Fe}^0/\text{H}_2\text{O}$ systems [114]. Moreover, the nature of Fe^0 as an in-situ generator of contaminant scavengers (FeCPs) is yet to be recognized, as many researchers are still regarding it as a reducing agent (under environmental conditions) [34,46]. This section paves the way for the much needed systematic studies which would enable the realization of the huge potential of Fe^0 for environmental remediation and water treatment.

Investigating an $\text{Fe}^0/\text{H}_2\text{O}$ system implies that the four components (anode, cathode, conductive metal, electrolyte) of the electro-chemical iron corrosion are properly considered. The evidence that Fe^0 is covered by an electrically non-conductive oxide scale implies that (quantitative) electron transfer from the anode to the cathode is only possible for water, the solvent. All other oxidizing species must migrate across the oxide scale to reach a cathodic site where reduction would occur. For this reason, reductive transformations of any species in $\text{Fe}^0/\text{H}_2\text{O}$ systems should be regarded as a side effect (or a parallel reaction) of aqueous iron corrosion (Equation (3)) [19,41–45,72]. The presence of the oxide scale also implies that the electrolyte (contaminated water) is entrapped in a sort of porous barrier, where contaminant transport is an ion-selective process. It then follows that: (i) Quantitative contaminant transport depends on the relative surface charge of the oxide scale and one of the

contaminant (at a given pH value), and (ii) contaminant transport, and thus iron corrosion, is favored by all factors sustaining ionic migration.

The presentation until now suggests that there are three main groups of influencing factors for aqueous iron corrosion: (i) The nature of the electrodes (anode and cathode), (ii) the nature of the conductive metal (nature and proportion of alloying elements), and (iii) the nature of the electrolyte (pH value, temperature, and solution chemistry). It is understood that environmental remediation using Fe^0 is only possible in the pH ranges where the solubility of iron is low ($\text{pH} > 4.5$) [115–117]. The three groups of influencing factors are now discussed in some details. The impact of some common additives on the $\text{Fe}^0/\text{H}_2\text{O}$ system are also discussed.

5.1. The Nature of the Electrodes

Thermodynamically, an immersed Fe^0 specimen corrodes because there is a potential difference between two different sites at its surface. The site where Fe^0 is oxidized (Fe^{2+} is produced) is the anode, while the site where water (H^+) is reduced (H_2 is produced) is the cathode. In other words, in aqueous iron corrosion, electrons are transferred from Fe^0 to H_2O (Equation (3)). The tendency of Fe^0 to corrode in water is grounded in the difference in the electrode potential of the two involved redox couples: $\text{Fe}^{\text{II}}/\text{Fe}^0$ ($E^0 = -0.44$ V) and H^+/H_2 ($E^0 = -0.00$ V). $E^0 = -0.44$ V is the electrode potential of Fe^0 in all relevant reactive Fe^0 alloys. Accordingly, any difference in reactivity between different Fe^0 specimens is purely a kinetic issue, and depends mainly on the history of each individual specimen. Relevant parameters influencing the Fe^0 intrinsic reactivity include: The manufacturing process, the surface area, the size and the form of the particles, the alloying elements and their proportions. While the details of manufacturing conditions are typically not accessible to the researcher, all other parameters can be analytically determined [93,118,119]. It is essential to recall that all relevant parameters are interdependent and none of them could be proven superior in determining the reactivity of Fe^0 materials [89,92,120–122].

The evidence that $E^0 = -0.44$ V is the driving force for all Fe^0 materials implies that the nature of Fe^0 is a stand-alone variable in investigating the efficiency of Fe^0 for environmental remediation. The recent literature on “remediation Fe^0 ” reveals that this evidence has not been properly considered [91,93]. Moreover, there is still no standard protocol for characterizing the Fe^0 intrinsic reactivity and there exists no reference material to which new materials should be compared [122]. On the other hand, available Fe^0 materials are characterized for contaminant removal in parallel short-term experiments using pure adsorbents, including aged iron oxides [113,123,124]. For inert adsorbents (e.g., activated carbon, iron oxide, sand), an adsorption capacity is defined and gives the contaminant amount (e.g., mg) retained per unit adsorbent mass (g). The adsorption capacity (mg g^{-1}) enables the prediction of packed-bed adsorbents [111]. The adsorption capacity has been translated to the Fe^0 research, in a context where initial Fe^0 is not depleted, the used material is not characterized for its intrinsic reactivity, and the kinetics of iron corrosion (corrosion rate) is not known [94,95]. Accordingly, the adsorption capacity is used without any knowledge on the available adsorbent amount and its intrinsic reactivity. This is not a good starting point for the comparison of independent results, even obtained under similar experimental conditions.

Summarizing, this section clearly shows that various Fe^0 materials, including nano-scale Fe^0 and bimetallics, have been manufactured or selected and mostly reported to be successfully used for water treatment on a purely pragmatic basis. This is not a premise for progress in knowledge. Better systematic experimental work should be designed to rationalize the already documented success stories [30,31,35,61,62,125,126].

5.2. The Nature of the Conductive Metal

Conventional Fe^0 materials used for reductive transformation of contaminants often produce reaction products which are sometimes more toxic than the parent compounds [127]. On the other hand, the transformation process is slowed down as the natural oxide scale develops at the Fe^0 surface.

It is in this context that bimetallic systems were introduced, wherein a second metal is combined with Fe^0 [127,128]. The second metal primarily has three functions: (i) Acts as a hydrogenating catalyst, (ii) prevents the formation of the oxide film on the Fe^0 surface, and (iii) induces Fe^0 to release electrons due to the difference in reduction potentials [127,129,130]. However, the first function (hydrogenation catalyst) is questionable as H/H_2 has to migrate through the oxide film to the site where the contaminant is adsorbed (Figure 1—bottom). The second metal certainly disturbs the formation of the oxide scale [63–65], but cannot really prevent it in the long term. The property of the second metal to induce electron release from Fe^0 is a fundamental aspect and likely the most accurate (Section 3) [79,128,131].

As demonstrated by Noubactep [128] in the pH range of natural waters, the second metal primarily induces Fe^0 oxidative dissolution and accelerates—or at least sustains—the corrosion process, which in turn induces contaminant removal. Remember that Fe^0 is a generator of contaminant scavengers. Another aspect to consider at this stage is that processes based on chemical reactions are never stand-alone ones for water decontamination at low concentration levels. In fact, the concentration corresponding to the solubility limit is often larger than the permissible maximum contamination level (MCL). For example, the MCL for fluoride is 1.5 mg L^{-1} , while the concentration corresponding to the solubility limit of CaF_2 is about 8.0 mg L^{-1} [86,132]. Moreover, even reaction products of reducible species must be removed from the aqueous phase. This means that adsorption, co-precipitation, and adsorptive size-filtration are the dominant removal mechanisms for contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems, including those using bimetallic systems [128,133].

In summary, this section recalls that alloying Fe^0 to form bimetallic and multi-metallic systems are just a tool to sustain the reactivity of conventional $\text{Fe}^0/\text{H}_2\text{O}$ systems. Contaminants are transformed and removed by the same mechanisms [133,134]. An affordable bimetallic system that has been successfully tested is one entailing the addition of sulfur [123,135,136].

5.3. The Nature of the Electrolyte

The importance of water composition (including pH value and temperature) as operational and environmental variables on the efficiency of $\text{Fe}^0/\text{H}_2\text{O}$ systems is obvious. As a rule, the contaminants of concern are considered together with the pH value and the concentration of major ions, particularly anions (Cl^- , HCO_3^- , NO_3^- and SO_4^{2-}) [137–139]. Discrepancies among studies resulted mostly from the diversity of other operational variables like the Fe^0 intrinsic reactivity, Fe^0 dosage, the mixing rates, and experimental duration. It has already been stated that fixing the ionic strength with common salts is a conceptual mistake, as the ionic conductivity of the oxide scale is increased in a manner that will not be reproduced in nature.

The pH values are the most influencing factor as contaminant removal is only quantitative at $\text{pH} > 4.5$. Fortunately, this corresponds to the pH range of natural waters. However, because aqueous iron corrosion consumes acidity (Equation (3)), even industrial wastewaters with lower pH values can be efficiently treated [114,140]. On the other hand, the pH value of natural waters can be artificially fixed, for example, to 4.0 using H_2SO_4 , to optimize the efficiency of the $\text{Fe}^0/\text{H}_2\text{O}$ system [132]. The pH value also determines the surface charge of adsorbents (including sand and iron oxides) and the speciation of dissolved contaminants, and thus the efficiency of the system (Figure 2) [82,141].

The question arises how to test systems at laboratory scale in a way that results would be transferable to field situations. The conventional approach is to vary individual or single background ions. Another approach is to use a single natural water or tap water as a background electrolyte. More reliable approaches exist [142,143]; the one introduced by Heffron et al. [142] is to use four synthetic waters representing the ionic composition of a wide range of natural waters. These synthetic test waters mimicked low and high ionic concentrations for both surface and groundwater (Table 1). Using these model waters and systematically varying all relevant operational parameters would accelerate knowledge acquisition for the design of more robust and efficient systems. Ideally, each tested system is monitored for contaminant removal efficiencies, residual Fe concentration, and pH value.

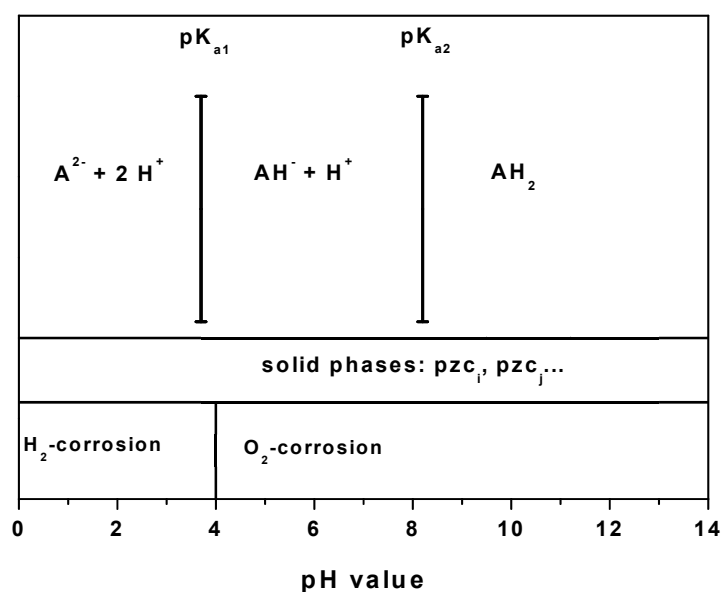


Figure 2. pH dependence of (i) the iron corrosion mechanism (i.e., hydrogen evolution, oxygen corrosion) and (ii) the specification of dissolved substances (A^{2-} , AH^- , AH_2). The solid phases existing in Fe^0/H_2O systems (mainly oxides) can be considered as poly-electrolytes. Each solid phase is characterized by an isoelectric point ($pHpzc = pzc =$ “point of zero charge”). Above the $pHpzc$, the solid oxide surface is negatively charged. AH_2 is a weak electrolyte with two acidity constants (pKa values). Similar to $pHpzc$ values, pKa values are the limit of the predominance ranges (A^{2-}/AH^- and AH^-/AH_2).

Table 1. Composition of the four water matrices used by Heffron et al. [142]. Ion concentrations are in $mmol L^{-1}$ (mM). The solutions were prepared using Milli-Q water and analytical grade reagents. The synthetic waters are SL (Surface Low), SH (Surface High), GL (Ground Low), and GH (Ground High). High and Low are related to the ionic strength (μ).

Matrix	$[Ca^{2+}]$ (mM)	$[Mg^{2+}]$ (mM)	$[Na^+]$ (mM)	$[Cl^-]$ (mM)	$[HCO_3^-]$ (mM)	$[SO_4^{2-}]$ (mM)	μ (mM)
SL	0.399	0.181	1.200	1.030	1.200	0.067	3.0
SH	0.898	0.333	1.950	2.000	1.950	0.229	5.9
GL	2.300	1.400	5.560	5.640	5.560	0.874	17.5
GH	2.920	1.780	22.800	18.900	9.090	2.100	39.0

5.4. The Impact of Selected Additives

Various aggregates have been added to granular Fe^0 to modify the efficiency of the Fe^0/H_2O system for water treatment. Typical aggregates include activated carbon [40], anthracite [144], gravel [144], magnetite [145], MnO_2 [58,146], pumice [95], sand [139,144], and zeolites [144]. While sand (inert) alone certainly increases the efficiency of Fe^0/H_2O systems, other more or less reactive aggregates have been introduced for the same purpose, but without systematic investigations demonstrating the corresponding concepts. For example, Huang et al. [145] reported that the co-presence of Fe^0 , Fe_3O_4 , and dissolved Fe^{II} creates a highly reactive system for molybdate removal. This is a tangible experimental observation. However, given that addition of both Fe_3O_4 and Fe^{II} enhances the Fe^0 efficiency, it is difficult to assess the specificity of this ternary system. Moreover, the named system should have been compared to the $Fe^0/sand/Fe^{II}$ system and the affordability of using Fe_3O_4 discussed. For illustration, two examples are: (i) Song et al. [147], who found out that in batch experiments, $Fe^0/sand$ systems were more efficient in removing aqueous Cr^{VI} than pure Fe^0 systems; and (ii)

Westerhoff and James [25], who reported that columns containing about 50% Fe⁰ (w/w) were more efficient at removing NO₃⁻ than pure Fe⁰ beds (100% Fe⁰). The rationale for this is that sand is in-situ coated with iron oxides that are better adsorbents for both negatively-charged HCrO₄⁻ and NO₃⁻ than the sand surface [85,148].

It is interesting to note that Noubactep et al. [82] initially used FeS₂ and MnO₂ as a tool to accumulate U^{VI} in the vicinity of Fe⁰, and to enhance its reductive precipitation by Fe⁰ [149]. However, the experimental observation in both cases was a delay of U^{VI} removal. In the Fe⁰/FeS₂ system, pyrite dissolution induced a pH shift and quantitative contaminant removal was observed only in systems exhibiting a final pH > 4.5. In the Fe⁰/MnO₂ system, MnO₂ reductive dissolution consumed Fe²⁺ from iron corrosion (Equation (3)), and U^{VI} removal was not quantitative until MnO₂ was depleted. Both observations suggest that there is no quantitative U^{VI} removal before iron hydroxides start to 'freely' precipitate [150]. It was clearly established that U^{VI} removal is not a property of 'reducing Fe⁰', but a consequence of aqueous iron corrosion in the presence of dissolved U^{VI}. This observation was generalized [41,45], and Fe⁰ was suggested as a suitable material for universal access to safe drinking water [107].

Overall, this section recalls that several efficient Fe⁰-based hybrid systems have been introduced and partly used over the years. The performance of these systems can be optimized based on the science of aqueous iron corrosion [113,151]. It should be noted that pre-washing Fe⁰ materials before use was also applied. This procedure solely frees the Fe⁰ surface from atmospheric corrosion products and thus accelerates 'free' precipitation of FeCPs [121,152].

6. Conclusions

The concept that contaminant removal in Fe⁰/H₂O systems is caused by aqueous iron corrosion (Equation (3)) is consistent with many experimental observations, including successful technical applications. It appears to be a generalization of "the cementation-induced oxidation-reduction" of dissolved compounds, which was demonstrated to be technically feasible in the early 1990s [72]. It is somewhat surprising to note that Khudenko [72]: (i) Published the findings in *Water Science and Technology* (IWA Publishing), an English language journal, which is expected to be widely read; and (ii) focused on organic compounds, but was almost completely ignored for 28 years of intensive research on the remediation Fe⁰. This review clearly delineates the important role of system analysis in understanding the efficiency of Fe⁰/H₂O systems for water treatment and environmental remediation.

During the past three decades, the field of "remediation using Fe⁰" has been expanding at an amazing speed. This didactic review indicates that field applications of the named systems are mostly not based on their scientific understanding. The question then arises: What is next? Some trends should emerge on the horizon, and they are well-aligned with other remediation systems.

First, paralleling the increased scope in treatability studies and field demonstrations, the quest to characterize the intrinsic reactivity of used materials has increased and even simpler protocols have been presented. As a consequence, it can be expected that both a standard protocol and a reference Fe⁰ material can be adopted in the coming years [108,122].

Second, the search for system design and operating principles has become popular [46,114,152–154]. This search has been a central theme in 'Fe⁰ remediation' for a long time [155,156], but has been hampered by considering Fe⁰ as a reducing agent. It appears that the next phase on this path is to consider the dynamic nature of the process of iron corrosion and its volumetric expansive nature [26,27]. Despite the availability of a sound theoretical concept [26,157], it might be that additional concepts must be developed to grasp design and operating features spanning sustainable Fe⁰-based systems.

Third, the community of remediation Fe⁰ is progressively recognizing the limitations of the reductive transformation concept [58,114]. Recognizing this deficiency implies that future developments should be based on long-term experiments (lab and pilot) to account for the long-term variability of the kinetics of iron corrosion and system clogging by iron corrosion products [94,95]. Particular attention should be paid to the non-linear relationship between Fe⁰ size and corrosion rate [158].

Summarizing, thousands of papers are available on water treatment by Fe⁰-based systems using batch systems. Some few of them apply column systems at laboratory, pilot, and field scales, including commercial-scale applications. Unfortunately, the whole effort was based on a pragmatic, experience-based approach which cannot enable any reliable prediction of the long-term performance of any system under actual environments. Therefore, it is time to move towards long-term, well-designed experiments which could enable knowledge-based Fe⁰ selection for the design of sustainable systems. There is a great need to explore more granular Fe⁰ materials for developing commercial-scale decentralized water treatment systems.

To the best of the authors' knowledge and experience, the future of Fe⁰ in water treatment is bright. Collaborative efforts of research and industry are needed to materialize a dream of economical and feasible decentralized water treatment technology. Only by working together will it be possible to achieve universal safe drinking water provision and global clean environment. The present tutorial review has revealed that a major obstacle on this path is of educational nature. There is practically no formalized corrosion education of scientists and professionals working on Fe⁰ in water treatment. Thus, this article presents an opportunity for universities, educational institutions, and professional associations to play a lighthouse role in this field.

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References

1. Howe, K.J.; Hand, D.W.; Crittenden, J.C.; Trussell, R.R.; Tchobanoglous, G. *Principles of Water Treatment*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2012; p. 674.
2. Tong, Y.; McNamara, P.J.; Mayer, B.K. Adsorption of organic micropollutants onto biochar: A review of relevant kinetics, mechanisms and equilibrium. *Water Res. Technol.* **2019**, *5*, 821–838. [[CrossRef](#)]
3. Parkes, E.A. *A Manual Practical Hygiene*, 7th ed.; P. Blakiston Son & Co.: Philadelphia, PA, USA, 1887; p. 766.
4. Noubactep, C.; Caré, S.; Crane, R. Nanoscale metallic iron for environmental remediation: Prospects and limitations. *Water Air Soil Pollut.* **2012**, *223*, 1363–1382.
5. Ali, I. Water treatment by adsorption columns: Evaluation at ground level. *Sep. Purif. Rev.* **2014**, *43*, 175–205. [[CrossRef](#)]
6. Shannon, M.A.; Bohn, P.W.; Elimelech, M.; Georgiadis, J.G.; Marinas, B.J.; Mayes, A.M. Science and technology for water purification in the coming decades. *Nature* **2008**, *452*, 301–310. [[CrossRef](#)] [[PubMed](#)]
7. Gonzalez-Perez, A.; Persson, K.M.; Lipnizki, F. Functional channel membranes for drinking water production. *Water* **2018**, *10*, 859. [[CrossRef](#)]
8. Ali, I. New generation adsorbents for water treatment. *Chem. Rev.* **2012**, *112*, 5073–5091. [[CrossRef](#)]
9. Chen, W.; Mo, J.; Du, X.; Zhang, Z.; Zhang, W. Biomimetic dynamic membrane for aquatic dye removal. *Water Res.* **2019**, *151*, 243–251. [[CrossRef](#)] [[PubMed](#)]
10. Bischof, G. On putrescent organic matter in potable water. *Proc. R. Soc. Lond.* **1877**, *26*, 258–261.
11. Anderson, W. On the purification of water by agitation with iron and by sand filtration. *J. Soc. Arts* **1886**, *35*, 29–38. [[CrossRef](#)]
12. Devonshire, E. The purification of water by means of metallic iron. *J. Frankl. Inst.* **1890**, *129*, 449–461. [[CrossRef](#)]
13. Tucker, W.G. The purification of water by chemical treatment. *Science* **1892**, *20*, 34–38. [[CrossRef](#)]

14. Mwakabona, H.T.; Ndé-Tchoupé, A.I.; Njau, K.N.; Noubactep, C.; Wydra, K.D. Metallic iron for safe drinking water provision: Considering a lost knowledge. *Water Res.* **2017**, *117*, 127–142. [[CrossRef](#)] [[PubMed](#)]
15. Hu, R.; Cui, X.; Gwenzi, W.; Wu, S.; Noubactep, C. Fe⁰/H₂O systems for environmental remediation: The scientific history and future research directions. *Water* **2018**, *10*, 1739. [[CrossRef](#)]
16. Bischof, G. On putrescent organic matter in potable water II. *Proc. R. Soc. Lond.* **1878**, *27*, 152–156.
17. Leffmann, H. Direct and indirect methods of electrical purification of water. *J. Frankl. Inst.* **1907**, *164*, 205–216. [[CrossRef](#)]
18. Lauderdale, R.A.; Emmons, A.H. A method for decontaminating small volumes of radioactive water. *J. Am. Water Work. Assoc.* **1951**, *43*, 327–331. [[CrossRef](#)]
19. Anderson, M.A. *Fundamental Aspects of Selenium Removal by Harza Process. Rep San Joaquin Valley Drainage Program*; US Dep Interior: Sacramento, CA, USA, 1989.
20. James, B.R.; Rabenhorst, M.C.; Frigon, G.A. Phosphorus sorption by peat and sand amended with iron oxides or steel wool. *Water Environ. Res.* **1992**, *64*, 699–705. [[CrossRef](#)]
21. Khan, A.H.; Rasul, S.B.; Munir, A.K.M.; Habibuddowla, M.; Alauddin, M.; Newaz, S.S.; Hussam, A. Appraisal of a simple arsenic removal method for groundwater of bangladesh. *J. Environ. Sci. Health A* **2000**, *35*, 1021–1041. [[CrossRef](#)]
22. Erickson, A.J.; Gulliver, J.S.; Weiss, P.T. Enhanced sand filtration for storm water phosphorus removal. *J. Environ. Eng.* **2007**, *133*, 485–497. [[CrossRef](#)]
23. Erickson, A.J.; Gulliver, J.S.; Weiss, P.T. Phosphate removal from agricultural tile drainage with iron enhanced sand. *Water* **2017**, *9*, 672. [[CrossRef](#)]
24. Lacy, W.J. Removal of radioactive material from water by slurring with powdered metal. *J. Am. Water Work. Assoc.* **1952**, *44*, 824–828. [[CrossRef](#)]
25. Westerhoff, P.; James, J. Nitrate removal in zero-valent iron packed columns. *Water Res.* **2003**, *37*, 1818–1830. [[CrossRef](#)]
26. Caré, S.; Crane, R.; Calabrò, P.S.; Ghauch, A.; Temgoua, E.; Noubactep, C. Modeling the permeability loss of metallic iron water filtration systems. *Clean—Soil, Air, Water* **2013**, *41*, 275–282.
27. Domga, R.; Togue-Kamga, F.; Noubactep, C.; Tchatchueng, J.B. Discussing porosity loss of Fe⁰ packed water filters at ground level. *Chem. Eng. J.* **2015**, *263*, 127–134. [[CrossRef](#)]
28. Harza Engineering Co. *Selenium Removal Study. Report to Panoche Drainage District*; Harza Engineering Co.: Firebaugh, CA, USA, 1986.
29. Pilling, N.B.; Bedworth, R.E. The oxidation of metals at high temperatures. *J. Inst. Met.* **1923**, *29*, 529–591.
30. Hussam, A. Contending with a development disaster: Sono filters remove arsenic from well water in Bangladesh. *Innovations* **2009**, *4*, 89–102. [[CrossRef](#)]
31. Chaudhari, S.; Banerji, T.; Kumar, P.R. Domestic and community-scale arsenic removal technologies suitable for developing countries. In *Water Reclamation and Sustainability*; Ahuja, S., Ed.; Elsevier: Amsterdam, The Netherlands, 2014; pp. 155–182.
32. Gillham, R.W.; O'Hannesin, S.F. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* **1994**, *32*, 958–967. [[CrossRef](#)]
33. Gillham, R.W. Development of the granular iron permeable reactive barrier technology (good science or good fortune). In *Advances in Environmental Geotechnics, Proceedings of the International Symposium on Geoenvironmental Engineering in Hangzhou, China*; Chen, Y., Tang, X., Zhan, L., Eds.; Springer: Berlin, Germany, 2010; pp. 5–15.
34. Rodrigues, R.; Betelu, S.; Colombano, S.; Masselot, G.; Tzedakis, T.; Ignatiadis, I. Elucidating the dechlorination mechanism of hexachloroethane by Pd-doped zerovalent iron microparticles in dissolved lactic acid polymers using chromatography and indirect monitoring of iron corrosion. *Environ. Sci. Pollut. Res.* **2019**, *26*, 7177–7194. [[CrossRef](#)] [[PubMed](#)]
35. Hussam, A.; Munir, A.K.M. A simple and effective arsenic filter based on composite iron matrix: Development and deployment studies for groundwater of Bangladesh. *J. Environ. Sci. Health A* **2007**, *42*, 1869–1878. [[CrossRef](#)] [[PubMed](#)]
36. Tuladhar, S.; Smith, L.S. SONO filter: An excellent technology for save water in Nepal. *Sophen* **2009**, *7*, 18–24.
37. Leaf, W.B. Method of Treating Water. U.S. Patent 2,447,511, 24 August 1948.
38. Bigg, T.; Judd, S.J. Zero-valent iron for water treatment. *Environ. Technol.* **2000**, *21*, 661–670. [[CrossRef](#)]

39. Henderson, A.D.; Demond, A.H. Long-term performance of zero-valent iron permeable reactive barriers: A critical review. *Environ. Eng. Sci.* **2007**, *24*, 401–423. [[CrossRef](#)]
40. Cundy, A.B.; Hopkinson, L.; Whitby, R.L.D. Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Sci. Tot. Environ.* **2008**, *400*, 42–51. [[CrossRef](#)] [[PubMed](#)]
41. Noubactep, C. Processes of contaminant removal in “Fe⁰–H₂O” systems revisited. The importance of co-precipitation. *Open Environ. Sci.* **2007**, *1*, 9–13. [[CrossRef](#)]
42. Gheju, M. Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems. *Water Air Soil Pollut.* **2011**, *222*, 103–148. [[CrossRef](#)]
43. Ghauch, A. Iron-based metallic systems: An excellent choice for sustainable water treatment. *Freib. Online Geosci.* **2015**, *32*, 1–80.
44. Touomo-Wouafo, M.; Donkeng-Dazie, J.; Btateu-K., B.D.; Tchatchueng, J.B.; Noubactep, C.; Ludvík, J. Role of pre-corrosion of Fe⁰ on its efficiency in remediation systems: An electrochemical study. *Chemosphere* **2018**, *209*, 617–622. [[CrossRef](#)] [[PubMed](#)]
45. Noubactep, C. A critical review on the mechanism of contaminant removal in Fe⁰–H₂O systems. *Environ. Technol.* **2008**, *29*, 909–920. [[CrossRef](#)] [[PubMed](#)]
46. Guan, X.; Sun, Y.; Qin, H.; Li, J.; Lo, I.M.C.; He, D.; Dong, H. The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: The development in zero-valent iron technology in the last two decades (1994–2014). *Water Res.* **2015**, *75*, 224–248. [[CrossRef](#)]
47. Noubactep, C. Metallic iron for environmental remediation: A review of reviews. *Water Res.* **2015**, *85*, 114–123. [[CrossRef](#)]
48. Xi, Y.; Luo, Y.; Zou, J.; Li, J.; Liao, T.; Zhang, L.; Wang, C.; Li, X.; Lin, G. Kinetics of arsenic removal in waste acid by the combination of CuSO₄ and zero-valent iron. *Processes* **2019**, *7*, 401. [[CrossRef](#)]
49. Tien, C. Remarks on adsorption manuscripts revised and declined: An editorial. *Sep. Purif. Technol.* **2007**, *54*, 277–278. [[CrossRef](#)]
50. Hu, H.-Y.; Goto, N.; Fujie, K.; Kasakura, T.; Tsubone, T. reductive treatment characteristics of nitrate by metallic iron in aquatic solution. *J. Chem. Eng. Jpn.* **2001**, *34*, 1097–1102. [[CrossRef](#)]
51. Atkins, P.W. *Physical Chemistry*; Oxford University Press: Oxford, UK, 1986.
52. Vodyanitskii, Y.N.; Mineev, V.G. Degradation of nitrates with the participation of Fe(II) and Fe(0) in groundwater: A review. *Eurasian Soil Sci.* **2015**, *48*, 139–147. [[CrossRef](#)]
53. Ngai, T.K.K.; Murcott, S.; Shrestha, R.R.; Dangol, B.; Maharjan, M. Development and dissemination of Kanchan™ Arsenic Filter in rural Nepal. *Water Sci. Technol. Water Supply* **2006**, *6*, 137–146. [[CrossRef](#)]
54. Kowalski, K.P.; Søgaard, E.G. Implementation of zero-valent iron (ZVI) into drinking water supply—Role of the ZVI and biological processes. *Chemosphere* **2014**, *117*, 108–114. [[CrossRef](#)] [[PubMed](#)]
55. Holt, P.K.; Barton, G.W.; Mitchell, C.A. The future for electrocoagulation as a localised water treatment technology. *Chemosphere* **2005**, *59*, 355–367. [[CrossRef](#)] [[PubMed](#)]
56. Noubactep, C.; Schöner, A. Metallic iron for environmental remediation: Learning from electrocoagulation. *J. Hazard. Mater.* **2010**, *175*, 1075–1080. [[CrossRef](#)] [[PubMed](#)]
57. Noubactep, C.; Makota, S.; Bandyopadhyay, A. Rescuing Fe⁰ remediation research from its systemic flaws. *Res. Rev. Insights* **2017**. [[CrossRef](#)]
58. Gheju, M.; Balcu, I. Sustaining the efficiency of the Fe(0)/H₂O system for Cr(VI) removal by MnO₂ amendment. *Chemosphere* **2019**, *214*, 389–398. [[CrossRef](#)] [[PubMed](#)]
59. Morrison, S.J.; Mushovic, P.S.; Niesen, P.L. early breakthrough of molybdenum and uranium in a permeable reactive barrier. *Environ. Sci. Technol.* **2006**, *40*, 2018–2024. [[CrossRef](#)]
60. Phillips, D.H.; Van Nooten, T.; Bastiaens, L.; Russell, M.I.; Dickson, K.; Plant, S.; Ahad, J.M.E.; Newton, T.; Elliot, T.; Kalin, R.M. Ten year performance evaluation of a field-scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene contaminated groundwater. *Environ. Sci. Technol.* **2010**, *44*, 3861–3869. [[CrossRef](#)] [[PubMed](#)]
61. Wilkin, R.T.; Acree, S.D.; Ross, R.R.; Puls, R.W.; Lee, T.R.; Woods, L.L. Fifteen-year assessment of a permeable reactive barrier for treatment of chromate and trichloroethylene in groundwater. *Sci. Tot. Environ.* **2014**, *468–469*, 186–194. [[CrossRef](#)] [[PubMed](#)]

62. Wilkin, R.T.; Lee, T.R.; Sexton, M.R.; Acree, S.D.; Puls, R.W.; Blowes, D.W.; Kalinowski, C.; Tilton, J.M.; Woods, L.L. Geochemical and isotope study of trichloroethene degradation in a zero-valent iron permeable reactive barrier: A twenty-two-year performance evaluation. *Environ. Sci. Technol.* **2019**, *53*, 296–306. [[CrossRef](#)] [[PubMed](#)]
63. Dickerson, R.E.; Gray, H.B.; Haight, G.P., Jr. *Chemical Principles*, 3rd ed.; Benjamin/Cummings Inc.: San Francisco, CA, USA, 1979; p. 944.
64. Lazzari, L. General aspects of corrosion. Chapter 9.1. In *Encyclopedia of Hydrocarbons*; Istituto Enciclopedia Italiana: Rome, Italy, 2008; Volume 5.
65. Nestic, S. Key issues related to modelling of internal corrosion of oil and gas pipelines—A review. *Corros. Sci.* **2007**, *49*, 4308–4338. [[CrossRef](#)]
66. Ritter, K.; Odziemkowski, M.S.; Gillham, R.W. An in situ study of the role of surface films on granular iron in the permeable iron wall technology. *J. Contam. Hydrol.* **2002**, *55*, 87–111. [[CrossRef](#)]
67. Odziemkowski, M. Spectroscopic studies and reactions of corrosion products at surfaces and electrodes. *Spectrosc. Prop. Inorg. Organomet. Compd.* **2009**, *40*, 385–450.
68. Stratmann, M.; Müller, J. The mechanism of the oxygen reduction on rust-covered metal substrates. *Corros. Sci.* **1994**, *36*, 327–359. [[CrossRef](#)]
69. Matheson, L.J.; Tratnyek, P.G. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* **1994**, *28*, 2045–2053. [[CrossRef](#)] [[PubMed](#)]
70. Roberts, A.L.; Totten, L.A.; Arnold, W.A.; Burris, D.R.; Campbell, T.J. Reductive elimination of chlorinated ethylenes by zero-valent metals. *Environ. Sci. Technol.* **1996**, *30*, 2654–2659. [[CrossRef](#)]
71. Weber, E.J. Iron-mediated reductive transformations: Investigation of reaction mechanism. *Environ. Sci. Technol.* **1996**, *30*, 716–719. [[CrossRef](#)]
72. Khudenko, B.M. Mechanism and kinetics of cementation processes. *Water Sci. Technol.* **1985**, *17*, 719–731. [[CrossRef](#)]
73. Khudenko, B.M. Mathematical models of cementation process. *J. Environ. Eng.* **1987**, *113*, 681–702. [[CrossRef](#)]
74. Khudenko, B.M. Feasibility evaluation of a novel method for destruction of organics. *Water Sci. Technol.* **1991**, *23*, 1873–1881. [[CrossRef](#)]
75. Noubactep, C. Flaws in the design of Fe(0)-based filtration systems? *Chemosphere* **2014**, *117*, 104–107. [[CrossRef](#)]
76. Noubactep, C. Research on metallic iron for environmental remediation: Stopping growing sloppy science. *Chemosphere* **2016**, *153*, 528–530. [[CrossRef](#)] [[PubMed](#)]
77. Lackovic, J.A.; Nikolaidis, N.P.; Dobbs, G.M. Inorganic arsenic removal by zero-valent iron. *Environ. Eng. Sci.* **2000**, *17*, 29–39. [[CrossRef](#)]
78. Su, C.; Puls, R.W. Arsenate and arsenite removal by zerovalent iron: Effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate and nitrate, relative to chloride. *Environ. Sci. Technol.* **2001**, *35*, 4562–4568. [[CrossRef](#)]
79. Snoeyink, V.L.; Jenkins, D. *Water Chemistry*; John Wiley & Sons: Hoboken, NJ, USA, 1980; p. 480.
80. Hamnett, A. The components of an Electrochemical Cell. In *Handbook of Fuel Cells—Fundamentals, Technology, Applications*; Vielstich, W., Lamm, A., Gasteiger, H., Eds.; John Wiley & Sons Ltd.: Chichester, UK, 2003; pp. 3–12.
81. Inzelt, G. Crossing the bridge between thermodynamics and electrochemistry. From the potential of the cell reaction to the electrode potential. *Chemtexts* **2014**, *1*, 2. [[CrossRef](#)]
82. Noubactep, C.; Meinrath, G.; Dietrich, P.; Merkel, B. Mitigating uranium in groundwater: Prospects and limitations. *Environ. Sci. Technol.* **2003**, *37*, 4304–4308. [[CrossRef](#)]
83. Gheju, M. Progress in understanding the mechanism of Cr^{VI} Removal in Fe⁰-based filtration systems. *Water* **2018**, *10*, 651. [[CrossRef](#)]
84. Miyajima, K.; Noubactep, C. Impact of Fe⁰ amendment on methylene blue discoloration by sand columns. *Chem. Eng. J.* **2013**, *217*, 310–319. [[CrossRef](#)]
85. Phukan, M.; Noubactep, C.; Licha, T. Characterizing the ion-selective nature of Fe⁰-based filters using azo dyes. *Chem. Eng. J.* **2015**, *259*, 481–491. [[CrossRef](#)]
86. Heimann, S.; Ndé-Tchoupé, A.I.; Hu, R.; Licha, T.; Noubactep, C. Investigating the suitability of Fe⁰ packed-beds for water defluoridation. *Chemosphere* **2018**, *209*, 578–587. [[CrossRef](#)] [[PubMed](#)]

87. Noubactep, C. Investigating the processes of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems. *Korean J. Chem. Eng.* **2012**, *29*, 1050–1056. [[CrossRef](#)]
88. Noubactep, C.; Schöner, A.; Sauter, M. Significance of oxide-film in discussing the mechanism of contaminant removal by elemental iron materials. In *Photo-Electrochemistry & Photo-Biology for the Sustainability*; Union Press: Somerville, MA, USA, 2012; pp. 97–122, ISBN-10 4946428615; ISBN-13 978-4946428616.
89. Miehr, R.; Tratnyek, G.P.; Bandstra, Z.J.; Scherer, M.M.; Alowitz, J.M.; Bylaska, J.E. Diversity of contaminant reduction reactions by zerovalent iron: Role of the reductate. *Environ. Sci. Technol.* **2004**, *38*, 139–147. [[CrossRef](#)] [[PubMed](#)]
90. Kim, H.; Yang, H.; Kim, J. Standardization of the reducing power of zero-valent iron using iodine. *J. Environ. Sci. Heal. A* **2014**, *49*, 514–523. [[CrossRef](#)] [[PubMed](#)]
91. Li, S.; Ding, Y.; Wang, W.; Lei, H. A facile method for determining the $\text{Fe}(0)$ content and reactivity of zero valent iron. *Anal. Methods* **2016**, *8*, 1239–1248. [[CrossRef](#)]
92. Lv, J.-f.; Tong, X.; Zheng, Y.-X.; Xie, X.; Huang, L.-y. Reduction of $\text{Cr}(\text{VI})$ with a relative high concentration using different kinds of zero-valent iron powders: Focusing on effect of carbon content and structure on reducibility. *J. Cent. South Univ.* **2018**, *25*, 2119–2130. [[CrossRef](#)]
93. Li, J.; Dou, X.; Qin, H.; Sun, Y.; Yin, D.; Guan, X. Characterization methods of zerovalent iron for water treatment and remediation. *Water Res.* **2019**, *148*, 70–85. [[CrossRef](#)]
94. Moraci, N.; Lelo, D.; Bilardi, S.; Calabrò, P.S. Modelling long-term hydraulic conductivity behaviour of zero valent iron column tests for permeable reactive barrier design. *Can. Geotech. J.* **2016**, *53*, 946–961. [[CrossRef](#)]
95. Noubactep, C. Predicting the hydraulic conductivity of metallic iron filters: Modeling gone astray. *Water* **2016**, *8*, 162. [[CrossRef](#)]
96. Benson, A.S.; Dietrich, A.M.; Gallagher, D.L. Evaluation of iron release models for water distribution system. *Crit. Rev. Environ. Sci. Technol.* **2011**, *42*, 44–97. [[CrossRef](#)]
97. Mohebbi, H.; Li, C.Q. Experimental investigation on corrosion of cast iron pipes. *Int. J. Corros.* **2011**, *1*, 383–389. [[CrossRef](#)]
98. Xu, C.; Gao, W. Pilling-Bedworth ratio for oxidation of alloys. *Mat. Res. Innov.* **2000**, *3*, 231–235. [[CrossRef](#)]
99. Caré, S.; Nguyen, Q.T.; L’Hostis, V.; Berthaud, Y. Mechanical properties of the rust layer induced by impressed current method in reinforced mortar. *Cement Concrete Res.* **2008**, *38*, 1079–1091. [[CrossRef](#)]
100. Zhao, Y.; Ren, H.; Dai, H.; Jin, W. Composition and expansion coefficient of rust based on X-ray diffraction and thermal analysis. *Corros. Sci.* **2011**, *53*, 1646–1658. [[CrossRef](#)]
101. Johnson, R.L.; Tratnyek, P.G.; Miehr, R.; Thoms, R.B.; Bandstra, J.Z. Reduction of hydraulic conductivity and reactivity in zero-valent iron columns by oxygen and TNT. *Ground Water Monit. Rem.* **2005**, *25*, 129–136. [[CrossRef](#)]
102. Johnson, R.L.; Thoms, R.B.; O’Brien Johnson, R.; Krug, T. Field evidence for flow reduction through a zero-valent iron permeable reactive barrier. *Ground Water Monit. Remediat.* **2008**, *28*, 47–55. [[CrossRef](#)]
103. Bi, E.; Devlin, J.F.; Huang, B. Effects of mixing granular iron with sand on the kinetics of trichloroethylene reduction. *Ground Water Monit. Rem.* **2009**, *29*, 56–62. [[CrossRef](#)]
104. Ulsamer, S. A Model to Characterize The Kinetics of Dechlorination of Tetrachloroethylene and Trichloroethylene by a Zero Valent Iron Permeable Reactive Barrier. Master’s Thesis, Worcester Polytechnic Institute, Worcester, UK, 2011; p. 73.
105. Noubactep, C.; Care, S.; Btatkeu-K., B.D.; Nanseu-Njiki, C.P. Enhancing the sustainability of household Fe^0 /sand filters by using bimetallics and MnO_2 . *Clean Soil Air Water* **2012**, *40*, 100–109. [[CrossRef](#)]
106. Sikora, E.; Macdonald, D.D. The passivity of iron in the presence of ethylenediaminetetraacetic acid I. General electrochemical behavior. *J. Electrochem. Soc.* **2000**, *147*, 4087–4092. [[CrossRef](#)]
107. Noubactep, C.; Schöner, A.; Wofo, P. Metallic iron filters for universal access to safe drinking water. *Clean Soil Air Water* **2009**, *37*, 930–937. [[CrossRef](#)]
108. Nanseu-Njiki, C.P.; Gwenzu, W.; Pengou, M.; Rahman, M.A.; Noubactep, C. $\text{Fe}^0/\text{H}_2\text{O}$ filtration systems for decentralized safe drinking water: Where to from here? *Water* **2019**, *11*, 429. [[CrossRef](#)]
109. Bojic, A.L.; Purenovic, M.; Bojic, D.; Andjelkovic, T. Dehalogenation of trihalomethanes by a micro-alloyed aluminium composite under flow conditions. *Water* **2007**, *33*, 297–304.
110. Bojic, A.L.; Bojic, D.; Andjelkovic, T. Removal of Cu^{2+} and Zn^{2+} from model wastewaters by spontaneous reduction–coagulation process in flow conditions. *J. Hazard. Mater.* **2009**, *168*, 813–819. [[CrossRef](#)]

111. Vidic, R.D.; Suidan, M.T.; Traegner, U.K.; Nakhla, G.F. Adsorption isotherms: Illusive capacity and role of oxygen. *Water Res.* **1990**, *24*, 1187–1195. [[CrossRef](#)]
112. Vidic, R.D.; Suidan, M.T. Role of dissolved oxygen on the adsorptive capacity of activated carbon for synthetic and natural organic matter. *Environ. Sci. Technol.* **1991**, *25*, 1612–1618. [[CrossRef](#)]
113. Naseri, E.; Ndé-Tchoupé, A.I.; Mwakabona, H.T.; Nansu-Njiki, C.P.; Noubactep, C.; Njau, K.N.; Wydra, K.D. Making Fe⁰-Based filters a universal solution for safe drinking water provision. *Sustainability* **2017**, *9*, 1224. [[CrossRef](#)]
114. Vollprecht, D.; Krois, L.-M.; Sedlazeck, K.P.; Müller, P.; Mischitz, R.; Olbrich, T.; Pomberger, R. Removal of critical metals from waste water by zero-valent iron. *J. Clean. Prod.* **2018**, *208*, 1409–1420. [[CrossRef](#)]
115. Wilson, E.R. The mechanism of the corrosion of iron and steel in natural waters and the calculation of specific rates of corrosion. *Ind. Eng. Chem.* **1923**, *15*, 127–133. [[CrossRef](#)]
116. Liu, X.; Millero, F.J. The solubility of iron in seawater. *Mar. Chem.* **2002**, *77*, 43–54. [[CrossRef](#)]
117. Lewis, A. Review of metal sulphide precipitation. *Hydrometallurgy* **2010**, *104*, 222–234. [[CrossRef](#)]
118. Lavine, B.K.; Auslander, G.; Ritter, J. Polarographic studies of zero valent iron as a reductant for remediation of nitroaromatics in the environment. *Microchem. J.* **2001**, *70*, 69–83. [[CrossRef](#)]
119. McGuire, M.M.; Carlson, D.L.; Vikesland, P.J.; Kohn, T.; Grenier, A.C.; Langley, L.A.; Roberts, A.L.; Fairbrother, D.H. Applications of surface analysis in the environmental sciences: Dehalogenation of chlorocarbons with zero-valent iron and iron-containing mineral surfaces. *Anal. Chim. Acta* **2003**, *496*, 301–313. [[CrossRef](#)]
120. Johnson, T.L.; Scherer, M.M.; Tratnyek, P.G. Kinetics of halogenated organic compound degradation by iron metal. *Environ. Sci. Technol.* **1996**, *30*, 2634–2640. [[CrossRef](#)]
121. Bhatke, B.D.; Miyajima, K.; Noubactep, C.; Caré, S. Testing the suitability of metallic iron for environmental remediation: Discoloration of methylene blue in column studies. *Chem. Eng. J.* **2013**, *215*, 959–968. [[CrossRef](#)]
122. Hu, R.; Ndé-Tchoupé, A.I.; Lufingo, M.; Xiao, M.; Nassi, A.; Noubactep, C.; Njau, K.N. The impact of selected pretreatment procedures on iron dissolution from metallic iron specimens used in water treatment. *Sustainability* **2019**, *11*, 671. [[CrossRef](#)]
123. Allred, B.J. Laboratory evaluation of zero valent iron and sulfur-modified iron for agricultural drainage water treatment. *Ground Water Monit. Rem.* **2012**, *32*, 81–95. [[CrossRef](#)]
124. Allred, B.J. Batch test screening of industrial product/byproduct filter materials for agricultural drainage water treatment. *Water* **2017**, *9*, 791. [[CrossRef](#)]
125. Neumann, A.; Kaegi, R.; Voegelin, A.; Hussam, A.; Munir, A.K.M.; Hug, S.J. Arsenic removal with composite iron matrix filters in Bangladesh: A field and laboratory study. *Environ. Sci. Technol.* **2013**, *47*, 4544–4554. [[CrossRef](#)]
126. Banerji, T.; Chaudhari, S. A cost-effective technology for arsenic removal: Case study of zerovalent iron-based nitro bombay arsenic filter in West Bengal. In *Water and Sanitation in the New Millennium*; Nath, K., Sharma, V., Eds.; Springer: New Delhi, India, 2017.
127. Suresh, S. Reductive remediation of pollutants using metals. *Open Waste Manag. J.* **2009**, *2*, 6–16. [[CrossRef](#)]
128. Noubactep, C. On the operating mode of bimetallic systems for environmental remediation. *J. Hazard. Mater.* **2009**, *164*, 394–395. [[CrossRef](#)] [[PubMed](#)]
129. Doong, R.A.; Wu, S.C. Reductive dechlorination of chlorinated hydrocarbons in aqueous solutions containing ferrous and sulfide ions. *Chemosphere* **1992**, *24*, 1063–1075. [[CrossRef](#)]
130. Grittini, C.; Malcomson, M.; Fernando, Q.; Korte, N. Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system. *Environ. Sci. Technol.* **1995**, *29*, 2898–3000. [[CrossRef](#)] [[PubMed](#)]
131. Noubactep, C. An analysis of the evolution of reactive species in Fe⁰/H₂O systems. *J. Hazard. Mater.* **2009**, *168*, 1626–1631. [[CrossRef](#)] [[PubMed](#)]
132. Heimann, S. Testing granular iron for fluoride removal. *Freiberg Online Geosci.* **2018**, *52*, 1–80.
133. Noubactep, C. The fundamental mechanism of aqueous contaminant removal by metallic iron. *Water* **2010**, *36*, 663–670. [[CrossRef](#)]
134. Ghauch, A.; Abou Assi, H.; Baydoun, H.; Tuqan, A.M.; Bejjani, A. Fe⁰-based trimetallic systems for the removal of aqueous diclofenac: Mechanism and kinetics. *Chem. Eng. J.* **2011**, *172*, 1033–1044. [[CrossRef](#)]
135. Fan, D.; Lan, Y.; Tratnyek, P.G.; Johnson, R.L.; Filip, J.; O'Carroll, D.M.; Garcia, A.N.; Agrawal, A. Sulfidation of iron-based materials: A review of processes and implications for water treatment and remediation. *Environ. Sci. Technol.* **2017**, *51*, 13070–13085. [[CrossRef](#)]

136. Qin, H.; Guan, X.; Bandstra, J.Z.; Johnson, R.L.; Tratnyek, P.G. Modeling the kinetics of hydrogen formation by zerovalent iron: Effects of sulfidation on micro- and nano-scale particles. *Environ. Sci. Technol.* **2018**, *52*, 13887–13896. [[CrossRef](#)] [[PubMed](#)]
137. Kim, J.S.; Shea, P.J.; Yang, J.E.; Kim, J.E. Halide salts accelerate degradation of high explosives by zerovalent iron. *Environ. Pollut.* **2007**, *147*, 634–641. [[CrossRef](#)] [[PubMed](#)]
138. Zhang, R.; Sun, H.; Yin, J. Arsenic and chromate removal from water by iron chips—Effects of anions. *Front. Environ. Sci. Eng. China* **2008**, *2*, 203–208. [[CrossRef](#)]
139. Bi, E.; Bowen, I.; Devlin, J.F. Effect of mixed anions (HCO_3^- - SO_4^{2-} - ClO_4^-) on granular iron (Fe^0) reactivity. *Environ. Sci. Technol.* **2009**, *43*, 5975–5981. [[CrossRef](#)] [[PubMed](#)]
140. Bartzas, G.; Komnitsas, K.; Paspaliaris, I. Laboratory evaluation of Fe^0 barriers to treat acidic leachates. *Min. Eng.* **2006**, *19*, 505–514. [[CrossRef](#)]
141. Kalin, M.; Wheeler, W.N.; Meinrath, G. The removal of uranium from mining waste water using algal/microbial biomass. *J. Environ. Radioact.* **2005**, *78*, 151–177. [[CrossRef](#)] [[PubMed](#)]
142. Heffron, J.; Marhefke, M.; Mayer, B.K. Removal of trace metal contaminants from potable water by electrocoagulation. *Sci. Rep.* **2016**, *6*, 28478. [[CrossRef](#)] [[PubMed](#)]
143. Xin, J.; Tang, F.; Yan, J.; La, C.; Zheng, X.; Liu, W. Investigating the efficiency of microscale zero valent iron-based in situ reactive zone (mZVI-IRZ) for TCE removal in fresh and saline groundwater. *Sci. Tot. Environ.* **2018**, *626*, 638–649. [[CrossRef](#)] [[PubMed](#)]
144. Ruhl, A.S.; Franz, G.; Gernert, U.; Jekel, M. Corrosion product and precipitate distribution in two-component $\text{Fe}(0)$ permeable reactive barriers. *Chem. Eng. J.* **2014**, *239*, 26–32. [[CrossRef](#)]
145. Huang, Y.H.; Tang, C.L.; Zeng, H. Removing molybdate from water using a hybridized zero-valent iron/magnetite/ $\text{Fe}(\text{II})$ treatment system. *Chem. Eng. J.* **2012**, *200*, 205–263. [[CrossRef](#)]
146. Bhatke, B.D.; Tchatchueng, J.B.; Noubactep, C.; Caré, S. Designing metallic iron based water filters: Light from methylene blue discoloration. *J. Environ. Manag.* **2016**, *166*, 567–573. [[CrossRef](#)]
147. Song, D.-I.; Kim, Y.H.; Shin, W.S. A simple mathematical analysis on the effect of sand in $\text{Cr}(\text{VI})$ reduction using zero valent iron. *Korean J. Chem. Eng.* **2005**, *22*, 67–69. [[CrossRef](#)]
148. Phukan, M. Characterizing the Fe^0/sand system by the extent of dye discoloration. *Freiberg Online Geosci.* **2015**, *40*, 1–70.
149. Gu, B.; Liang, L.; Dickey, M.J.; Yin, X.; Dai, S. Reductive precipitation of uranium (VI) by zero-valent iron. *Environ. Sci. Technol.* **1998**, *32*, 3366–3373. [[CrossRef](#)]
150. Noubactep, C.; Schöner, A.; Meinrath, G. Mechanism of uranium (VI) fixation by elemental iron. *J. Hazard Mater.* **2006**, *132*, 202–212. [[CrossRef](#)] [[PubMed](#)]
151. Makota, S.; Ndé-Tchoupé, A.I.; Mwakabona, H.T.; Tepong-Tsindé, R.; Noubactep, C.; Nassi, A.; Njau, K.N. Metallic iron for water treatment: Leaving the valley of confusion. *Appl. Water Sci.* **2017**. [[CrossRef](#)]
152. Gatcha-Bandjun, N.; Noubactep, C.; Loura-Mbenguela, B. Mitigation of contamination in effluents by metallic iron: The role of iron corrosion products. *Environ. Technol. Innov.* **2017**, *8*, 71–83. [[CrossRef](#)]
153. Bartzas, G.; Komnitsas, K. Solid phase studies and geochemical modelling of low-cost permeable reactive barriers. *J. Hazard. Mater.* **2010**, *183*, 301–308. [[CrossRef](#)] [[PubMed](#)]
154. Li, L.; Benson, C.H. Evaluation of five strategies to limit the impact of fouling in permeable reactive barriers. *J. Hazard. Mater.* **2010**, *181*, 170–180. [[CrossRef](#)] [[PubMed](#)]
155. Lee, G.; Rho, S.; Jahng, D. Design considerations for groundwater remediation using reduced metals. *Korean J. Chem. Eng.* **2004**, *21*, 621–628. [[CrossRef](#)]
156. McGeough, K.L.; Kalin, R.M.; Myles, P. Carbon disulfide removal by zero valent iron. *Environ. Sci. Technol.* **2007**, *41*, 4607–4612. [[CrossRef](#)]
157. Tepong-Tsindé, R.; Phukan, M.; Nassi, A.; Noubactep, C.; Ruppert, H. Validating the efficiency of the MB discoloration method for the characterization of $\text{Fe}^0/\text{H}_2\text{O}$ systems using accelerated corrosion by chloride ions. *Chem. Eng. J.* **2015**, *279*, 353–362. [[CrossRef](#)]
158. Ralston, K.D.; Birbilis, N. Effect of grain size on corrosion: A review. *Corrosion* **2010**, *66*, 075005–075005-13. [[CrossRef](#)]

