

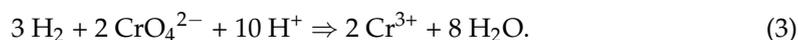
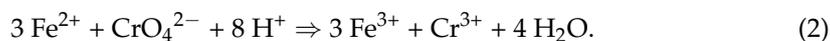
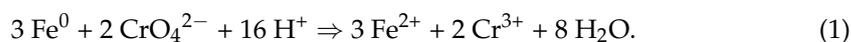
1. Introduction

The eradication of waterborne diseases (e.g., cholera, typhoid fever) through proper water and waste management was achieved in industrialized nations during the 19th century [1,2]. The paradigm accounting for this achievement can be summarized in three points: (i) protect still clean water sources, (ii) avoid any further water pollution, and (iii) treat/reuse polluted waters [2]. For more than 170 years, it has been well established that the provision safe drinking water and the management of wastes eliminate waterborne diseases [2,3]. This understanding of how to eliminate waterborne diseases virtually represents the greatest achievement for public health [3]. However, access to safe drinking water and proper sanitation is still a dream for millions of people worldwide as aptly captured in the United Nations Sustainable Development Goals [4]. In particular, Goal 6 strives to “ensure availability and sustainable management of water and sanitation for all”. Actually, it is questionable whether Goal 6 will be achieved within the remaining period of less than a decade, particularly in the developing world [5,6], and there is a broad consensus that the main challenge is financial in nature [7,8].

Arguably, safe drinking water provision cannot be achieved without money. However, the question is how much money and which technologies should be used? Available cost estimations are essentially rooted in the “big is beautiful” paradigm, which is based on centralized systems, while regarding decentralized systems as low-technology and/or short-term bridging alternatives [9]. On the contrary, the “small is beautiful” or decentralized approach [10] has not yet received due attention [11–14]. The decentralized approach, comprising do-it-yourself (D-I-Y) solutions, advocates for the use of local materials, labor, and skills (not only) for safe drinking water supply [10,15–17]. Using the wording of Roy and Hartigan [16], it is about “empowering the rural poor to develop themselves”. This effort includes using harvested rainwater (arsenic free) instead of buying reportedly affordable commercial filters for arsenic removal [15]. At the start of the SDGs era, Hering et al. [18] published a timely “call for synthesis of water research to achieve the Sustainable Development Goals by 2030”. The present communication strives for such a synthesis for the design of metallic iron-based filtration systems (Fe^0 filters). The presentation is limited to the sustainability in terms of long-term permeability.

Metallic iron (Fe^0) has been industrially used for water treatment since the 1850s with the first patent secured in 1857 [3,19–22]. However, over the years, Fe^0 filters have been designed on a pragmatic basis, often without critical evaluation of the published works to enable the advancement of the technology [23–31]. Accordingly, although it was known before 1883 that Fe^0 filters clog because of cementation between gravel/sand and Fe^0 particles [3,19,32], the post-1990 research on Fe^0 filtration continued using pure Fe^0 beds (100% Fe^0) [33,34]. Moreover, pretreatment zones with up to 50% Fe^0 (w/w) were tested as oxygen scavengers [34–36]. This occurred despite the fact that, under field conditions, quantitative contaminant removal in a field Fe^0 reactive permeable reactive barrier containing only 22% Fe^0 (w/w) was reported [23,37,38]. This confusion motivated the first efforts to systematically test hybrid Fe^0 /aggregate systems [39]. Mixing sand with Fe^0 was regarded as “ Fe^0 dilution” with potential negative impacts on the extent of decontamination [24,39–41]. Interestingly, some “diluted systems” performed better than pure Fe^0 systems [24,39,42,43]. For example, Song et al. [42] reported on the enhancement of Cr(VI) reduction in Fe^0 /sand systems relative to Fe^0 alone. Obviously, the presence of sand and its subsequent coating by nascent iron hydroxide resulted in the removal of Cr(VI) via adsorption. Thus, the results of Song et al. [42] can be regarded as an unexploited opportunity to question the importance of direct reduction reactions (electrons from Fe^0) in the process of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems. An understanding of the real reaction mechanism is critical for the discussion of changes in the hydraulic conductivity, hereafter referred to as permeability loss. This is because the stoichiometry of the decontamination process has been used to model the service life of Fe^0 filters [44]. Accordingly, assuming effective reductive transformations, it makes a significant difference

whether the reducing electrons (for Cr^{VI} , for example) come from Fe^0 (Equation (1)), Fe^{II} (Equation (2)), or H_2 (Equation (3)).



For example, comparing Equations (1) and (2) shows that the reduction of 2 mol of CrO_4^{2-} requires 3 mol of Fe^0 (Equation (1)—electrochemical reaction) or 6 mol of Fe^{2+} (Equation (2)—chemical reaction). However, the electrochemical reaction is impossible under environmental conditions because the electron transfer is hindered by the nonconductive oxide layer on Fe^0 [31,45]. In other words, using reactions similar to Equation (1) to predict the service life of Fe^0 filters [44,46] is faulty [29,30]. When it is additionally considered that Fe^0 is corroded only by H^+ [29,45,47–49], it becomes evident that the proper discussion of the permeability loss of Fe^0 is yet to be started [29–31]. Admixing Fe^0 and various aggregates is part of these efforts [25,27,34,50,51].

This work presents the suitability of Fe^0 /aggregate systems, including the fundamental principles, achievements, and potential applications, as a prerequisite for sustainable Fe^0 filters. Specifically, the value of Fe^0 /sand as a reference system in assessing the suitability of other aggregates (e.g., FeS_2 , MnO_2 , pumice, wood chips) is discussed. Lastly, future research directions using appropriate characterization tools including the MB method are highlighted.

2. The Remediation Fe^0 /Aggregate Filtration System and Its Proper Investigation

2.1. Historical and Fundamental Aspects

Water treatment by filtration is a very old technology [3,19–22,52–54]. The five main operational parameters for the success of a filter to treat a given polluted water are (i) the volume and quality of water to be produced per unit time (e.g., day), (ii) the nature (e.g., charcoal, Fe^0 , gravel) and the characteristics of the filtering media (e.g., form, reactivity, porosity, size), (iii) the used amount of filtering media (e.g., size of filter, number of filters in series), (iv) the nature and extent of pollution (e.g., co-solutes, contaminants of concern, pH value), and (v) the water flow velocity, which in turn determines the contact time. Additionally, it is preferable that filter media are cost-effective and capable of being easily recycled [23,52,55]. Over the decades, the technology of filtering polluted water through porous beds filled with adsorbents has been established in many areas of environmental engineering, including drinking water provision [11,56,57], mine water treatment [58–60], and stormwater treatment [61–63]. A common feature for all filtration systems is clogging (permeability loss) resulting from the accumulation of colloids, contaminants, and suspended particles [36,64–66]. Fe^0 filters are characterized by the in situ generation of colloids [31], meaning that, even without any inflow of contaminants and suspended particles, Fe^0 filters may clog, depending on the (kinetics and) extent of Fe^0 corrosion by water [67–69].

Notter [52] stated that spongy iron (a porous Fe^0) was undoubtedly the best medium for water filters and added that “its action is not so rapid as charcoal”. Baker [3,19] recalled that Fe^0 generates coagulants or flocs for contaminant scavenging. This then implies that the efficiency of Fe^0 filters for water treatment depends on the kinetics and extent of flocs generation within the porous structure. The same flocs fill the initial porosity and are responsible for reported permeability loss [68,70]. For this reason, the discussion of the process of permeability loss of Fe^0 filters should have started by addressing the time-dependent reduction in the initial porosity as Fe^0 corrodes [30,31,68,70].

A survey of the history of Fe^0 filters reveals tangible observations made before 2010 that would have led to the proper consideration of the contribution of iron corrosion to the process of permeability loss (Table 1). In particular, Oldright et al. [54] recommended many

thin Fe⁰ beds in series, rather than a thicker one with the same amount of sponge iron, to avoid material wastage. They rationalized their recommendations by the larger volume of lead (Pb⁰) replacing iron (Fe⁰) in the porous system. These authors could have considered the volumetric expansive nature of iron corrosion at pH values > 4.5 as reported 25 years before by Whitney [45].

Table 1. Timeline of the main experimental observations relating the importance of porosity loss due to iron corrosion before 2010.

Year	Main Results	References
1882	Spongy iron filters are clogged at the water works of Antwerp (Belgium) because of cementation of iron and gravel.	[71]
1903	Whitney reported on the expansive volumetric nature of iron corrosion.	[45]
1923	Pilling and Bedworth established the rule of the volumetric expansive nature of iron corrosion.	[72]
1928	Bed clogging is attributed to Fe replacement by Pb.	[54]
1951	It is observed that column clogging occurs rapidly if fine iron filings are used in place of the steel wool. Using extremely fine grade of steel wool should also be avoided.	[73]
1986	Filtration beds containing 100% iron filings are very efficient at removing selenium from drainage water, but clogging occurs very rapidly.	[74]
1992	Using steel wool as Fe ⁰ source for phosphate removal, it is demonstrated that Fe ⁰ /peat performed better than Fe ⁰ /sand.	[75]
1993	Filtration systems containing 10% to 25% Fe ⁰ particles (iron fillings) mixed with pelletized jute do not experience any permeability loss.	[76]
2001	Fe ⁰ /pyrite filters are essentially more efficient for water treatment than pure Fe ⁰ filters.	[24]
2007	Filtration systems containing less than 5% Fe ⁰ (steel wool) do not experience any permeability loss.	[77]
2000–2009	Household arsenic filters with pure Fe ⁰ layers are mostly efficient but not sustainable due to clogging. Only filters using porous materials (CIM = composite iron material) were sustainable.	[78]
2009	TCE removal rates are higher in an 85% Fe ⁰ filter than in the 100% system.	[39]

Table 1 shows that, in addition to sand and gravel, which are considered standard admixing agents [33], researchers have considered other aggregates including jute, peat, and pyrite. It is certain that peat was used as another potential remediation material for PO₄³⁻. However, the aspect of sustained permeability should have received more attention. This is particularly true because systems using pelletized jute [76] and peat [75] experienced no permeability loss. It can be postulated that bio-aggregates (e.g., jute, peat, wood chips) are better than compact minerals (e.g., gravel, sand) for sustained permeability. This is because bio-aggregates are likely to undergo decomposition over time, thereby improving the porosity and permeability of the system and offsetting the effects of cementation.

However, a number of knowledge gaps still exist on the use of bio-aggregates in Fe⁰/H₂O systems. First, it is unclear whether the oxidation of bio-aggregates will generate adequate porosity to sustain the Fe⁰/H₂O system in the long term. Second, limited data are available on the depletion of O₂ concentration in water passing through a column packed with bio-aggregates/Fe⁰ mixture. Thus, the impacts of the depletion in O₂ concentration, coupled with the potential release of organic compounds on the organoleptic properties (e.g., taste, odor) of the treated water, are currently unknown. These gaps call for systematic studies to investigate and identify the appropriate bio-aggregate and their mixing ratios.

Table 1 is limited to the period before 2010 as it corresponds to the date that the research group of Dr. Noubactep started its systematic investigation on hybrid Fe^0 systems. Two very comprehensive review articles were also published in 2010 [79,80], retrospectively demonstrating the confusion on the suitability of hybrid Fe^0 /aggregate systems for sustainable systems. In particular, Fe^0 /aggregate systems were used as “equalization zones” [80–83], “pretreatment zones” [33,35,81], or “sacrificial pretreatment zones” [80] to optimize the efficiency of the pure Fe^0 “reactive zone”. The very first result of Noubactep and colleagues published in 2010 was that using porous Fe^0 materials like sponge iron or porous composites yields more sustainable systems [84,85]. For the same reasons, using pumice instead of sand yields more sustainable filters. The rationale is that the internal pores of individual grains are good reservoirs for in situ generated FeCPs [84,86]. On the other hand, the rationale for Fe^0 /sand being more sustainable than pure Fe^0 is that there are less expansive Fe^0 particles in the system compared to the pure Fe^0 system (a fraction is replaced by non-expansive sand), thus delaying clogging (Figure 1). Upon clogging, the residual amount of unreacted Fe^0 is pure material wastage [68,70]. In other words, the expression “ Fe^0 dilution” for hybrid systems is a thinking mistake. Of course, there are fewer Fe^0 particles in hybrid systems, but it is rather a prerequisite for sustainability and optimal material usage [68,70]. This means that using pretreatment Fe^0 /sand zones [79–83] was a thinking mistake as quantitative contaminant removal has been reported in such systems for more than one century, even when porous Fe^0 (e.g., spongy iron) was used [3,10]. Figure 2 summarizes the types of filters that have been tested, including the layered hybrid system (Figure 2b).

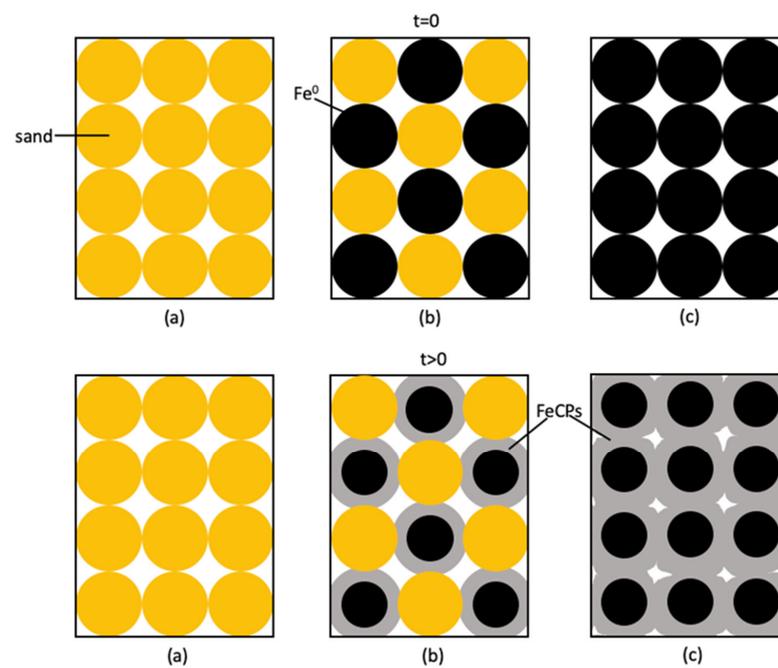


Figure 1. Schematic representation of the cross-section of three different filters containing (a) sand alone, (b) Fe^0 /sand (1:1), and (c) Fe^0 alone. The pure Fe^0 systems completely clog when the Fe^0 /sand system has just experienced 50% porosity loss. In all three systems, permeability loss due to inflowing colloids and suspended particles is also possible.

The presentation at this point recalls that only mixed layer hybrid systems (Figure 2c) are sustainable; however, as pointed out by Domga et al. [68], pure Fe^0 filters can still be designed for particular uses, for instance, in an emergency. In such cases, modular designs comprising at least one Fe^0 filter are recommended, and selected Fe^0 units can be regularly replaced, for example, on a monthly basis. For water supply of households and small communities, however, more sustainable systems are required; a rule of thumb is to

develop systems capable at operating for 6 to 12 months without maintenance [57,87–89]. The remaining discussion focuses on the suitability of admixing aggregates.

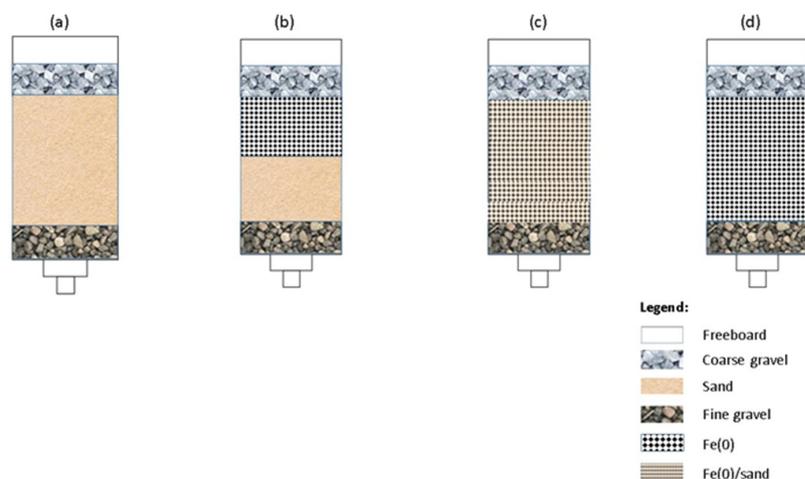


Figure 2. Sketch of layered and mixed Fe^0 /sand filters for water treatment: (a) sand alone (reference), (b) layered Fe^0 /sand, (c) mixed Fe^0 /sand, and (d) Fe^0 alone (negative reference).

2.2. Investigating the Remediation Fe^0 /Aggregate Filtration System

The mechanisms of contaminant removal in Fe^0 filters are adsorption, coprecipitation, and size exclusion [90–92]. No mechanistic discussion is considered herein as the focus is on the extent (and the kinetics) of pore filling by in situ generated FeCPs. The presentation in Section 2.1 indicated that the efficiency of Fe^0 filters with regard to contaminant removal varies as a function of several interdependent experimental setups, including the properties of used Fe^0 materials and the nature of admixing aggregates. Although the kinetics and extent of FeCPs generation in each system depend on the intrinsic reactivity of used Fe^0 materials, this section is virtually limited to the nature of the aggregate. In other words, it is virtually considered that Fe^0 and aggregates are from the same sizes (Figure 1), and that polluted water has the same chemistry. Thus, only the nature of the aggregate is discussed. Table 2 gives an overview of the main aggregates that have been used to date.

Table 2. Representative materials used as aggregates in Fe^0 /aggregate systems.

Aggregate	Rationale for Use	Comments	Reference
Biochar	Adsorbs and accumulates contaminants	Also used as support for nano- Fe^0	[93]
Fe oxides	Adsorbs and accumulates contaminants	Fe_3O_4 is used the most	[94]
Fe sulfides	Shifts pH to lower values	FeS_2 is used the most	[95]
GAC	Builds galvanic cells with Fe^0	GAC coating with FeCPs will hinder electron transfer	[96]
Lapillus	Stores FeCPs	Pores are not interconnected	[97]
Mn oxides	Sustains Fe^0 corrosion	Extends Fe^0 filter's service life	[98]
Peat	Accumulates contaminants	More efficient than sand	[75]
Pozzolan	Stores FeCPs	More efficient than sand	[99]
Pumice	Stores FeCPs	Pores are not interconnected	[100]
Sand	Reduces the Fe^0 cost	Reference additive	[39]
Wood chips	Accumulates contaminants	Mostly used in PO_4^{3-} removal	[101]
Zeolite	Accumulates contaminants	Also used as support for nano- Fe^0	[102]

Table 2 lists 12 different materials that demonstrated in individual studies a significant impact on the efficiency of hybrid systems relative to pure Fe^0 . Discrepancies between studies are obvious because the employed Fe^0 materials were not characterized, although testing methods were made available for decades [103–106]. On the other hand, each aggregate is tested as an independent success story without any effort to have an operational reference system (e.g., Fe^0/sand). To the best of the authors' knowledge, only Ndé-Tchoupé et al. [106] used Fe^0/sand systems as a reference to discuss the suitability of $\text{Fe}^0/\text{pozzolan}$. Therefore, it is a tangible fact that no normalization of published data is possible. This sad situation is illustrated herein by the Fe^0/FeS_2 system from a historical perspective.

Pyrite (FeS_2) was introduced in the Fe^0 remediation literature as a pH-shifting agent by Lipczynska-Kochany et al. [107]. The objective was to address “the deactivation of the metal surface” which was reported to be a barrier to the practical application of the then considered new technique. Between 1995 and 2005, many other researchers reported on the improved efficiency of Fe^0/FeS_2 system relative to pure Fe^0 [23,79–81,108–111]. In particular, Wolfe and Cipollone [23] secured a patent for remediation Fe^0/FeS_2 systems. Later on, Henderson and Demond [65] used a pure Fe^0 bed length of 25 cm to investigate permeability and concluded that Fe^0 filters are not sustainable. Henderson and Demond [112] concluded that FeS-based filters are better than Fe^0 ones with regard to permeability loss. This conclusion was based on four lines of evidence: (i) their excellent literature review [36], (ii) the results with the pure Fe^0 filters [65], (iii) results of a 25 cm bed of FeS-coated sand [112], and (iv) geochemical modeling. However, the same authors [65,112] considered inflowing groundwater and not expansive iron corrosion as the cause of permeability loss. Additionally, no Fe^0/FeS system was investigated.

Since 2018, more systematic investigations on the suitability of the Fe^0/FeS systems were made available [95,113–115]. However, they have not considered past efforts, the duration of the experiments was too short, and the used Fe^0 and FeS materials were poorly characterized [116]. Additionally, the discussion of the operating mode of FeS_2 in improving the efficiency of $\text{Fe}^0/\text{H}_2\text{O}$ systems is biased by considering Fe^0 as a reducing agent under operational conditions [116–118]. The results of Hu et al. [116] support that FeS_2 (i) delays (not suppresses) the pH increase in $\text{Fe}^0/\text{H}_2\text{O}$ systems, and (ii) boosts the production of reactive Fe^{2+} . However, their results clearly demonstrated that any discussion supporting the electron transfer from Fe^0 is highly speculative and even wrong because, despite pH decrease, quantitative contaminant removal was only observed when the final pH value was not higher than 4.5 [117,118]. Thus, arguments such as “ FeS_2 activates the Fe^0 surface through replacing partially the passive oxide film with iron sulfide (FeS)” [113] are not acceptable. There is even evidence that the addition of Fe^0 to pyrite can suppress its oxidation over the time [119,120]. In other words, the documented enhanced efficiency of FeS-amended $\text{Fe}^0/\text{H}_2\text{O}$ systems should be further investigated to optimize their use in modular systems. The frequency of exchanging Fe^0/FeS units depends on the characteristics of used aggregates.

To sum up, despite 30 years of intensive investigations on the remediation Fe^0/FeS system, available knowledge is largely fragmented [116–118]. The situation is not better for all other aggregates, including sand. Therefore, real systematic investigations with well-characterized Fe^0 and aggregates are needed to optimize the design of efficient Fe^0 filters for safe drinking water provision, wastewater treatment, and environmental remediation [30,121].

2.3. Investigating $\text{Fe}^0/\text{Aggregate}$ Systems

The presentation until now has intentionally paid little attention to the nature of contaminants. This is because, regardless of the nature of contaminants, water treatment in $\text{Fe}^0/\text{H}_2\text{O}$ systems entails Fe^0 corrosion in porous systems under aqueous conditions [122,123]. Thus, the nature and the level of contamination are just other operational parameters [25,30,121]. Cognizant of this fact, the methylene blue method (MB method) was introduced one decade

ago to characterize the extent of Fe^0 corrosion as reflected by the availability of its corrosion products [43,124]. The MB method exploits the differential adsorptive affinity of positively charged MB onto sand (negatively charged) and iron oxides (FeCPs positively charged; charge exclusion). Accordingly, when two Fe^0 specimens are to be compared for their intrinsic reactivity, it suffices to take a certain amount of each (e.g., 100 g) mix it to the same volume of sand and investigate the extent of MB discoloration in both systems. The more reactive material is the one that exhibits the lowest MB discoloration efficiency. The rationale is that the more the surface of sand is coated with in situ generated FeCPs, the lower the extent of MB discoloration (charge exclusion) will be [25–28].

The MB method, in its current form, will certainly work for SiO_2 -based aggregates (e.g., gravel, pozzolan, pumice) [99]. The MB method was also successfully applied for FeS_2 [111–113] and MnO_2 [98,125–127]. However, particularly for carbon-based aggregates, the MB method should be assessed and, eventually, appropriate amendments or alternatives could be developed. Unlike minerals (e.g., gravel, sand), carbon-based aggregates do not induce MB discoloration via purely electrostatic interactions [128]. However, in the case of strong affinity, two simple complementary tools can be adopted: (i) lengthening the experimental duration to investigate the system upon the exhaustion of the adsorptive capacity of the tested aggregate, and (ii) using lower amounts of the aggregate to achieve early contaminant breakthrough. In all cases, long-term experiments have to be performed [29,30]. Because only column tests are of concern, tested systems are relevant for household water filters with the results being immediately transferable to commercial filters (prototypes).

Many household Fe^0 filters have been presented during the past 20 years, including the Kanchan arsenic filter (KAF) in Nepal [129–132]. KAF designs can be used to test the concepts presented herein and facilitate the transfer of achieved results. While the KAF is still using up to 5 kg of iron nails, a recent investigation found out that only 300 g of steel wool could provide safe drinking water for 1 year without significant permeability loss [57,89]. One important result from Tepong-Tsindé [57] is that suitable small-size Fe^0 materials dispersed in a sand matrix can corrode to exhaustion. One objective of outstanding investigations is to assess to what extent the combination of reactive additives and coarser Fe^0 materials would enable comparable efficiency. In these efforts, the investigation of the probability that biodegradable aggregates (e.g., wood chips) degrade in the long term and leave behind room or pores for expansive FeCPs should be an explicit objective. The additional synergetic effects of Fe^0 and microorganisms on the decontamination process is well documented [133]. One important result of the proposed investigations will be testing various materials under comparable experimental conditions. Provided that the tested materials are thoroughly characterized, this will ensure that a database for relevant materials will be available soon. From this database, a range of hybrid Fe^0 /aggregate systems for various applications will be made available, for example, Fe^0/MnO_2 for drinking water, Fe^0/FeS_2 for wastewater, and Fe^0 /peat for phosphate removal. Perhaps none of the resulting efficient systems will be really new, but identifying appropriate Fe^0 /aggregate systems for specific remediation applications will be a major achievement. However, the rationale for their design, including their service life, will need to be established in a systematic manner, i.e., the path to transform the current drawbacks of this affordable technology to its established limit. For example, Fe^0 filters which are efficient only for 6 months [134] should be replaced. Such a filter working only for 6 months is no longer a drawback. Much labor is required to replace an exhausted filter, which is rather a limitation. For example, by using a different grade of steel wool, i.e., a coarser one, the filter of Bradley [134] could work for 1 year [57,89]. In a modular system [12,13], this means that the Fe^0 unit is replaced yearly instead of twice a year.

3. Economics of Fe^0 Filters

In concerted efforts for self-reliance in sustainable water management worldwide with respect to using affordable and efficient green technologies, Fe^0 filters potentially have a

significant role to play. Over the past 170 years, Fe⁰ filters have been successfully used for safe drinking water provision at micro (household), medium (small community), and large (city) scales [22]. They have also been successfully used for the on-site treatment of stormwater, as well as agricultural, domestic, and industrial wastewaters [135–141]. Their ability to perform well under environmental conditions coupled with the universal availability of cheap Fe⁰ materials (e.g., iron nails, steel wool) [87] makes them an affordable option that is significantly different from conventional water filters (e.g., charcoal, zeolite). The major difference is that, unlike other filter systems, the central component of the Fe⁰ filter system (i.e., Fe⁰) does not need to be locally activated/fabricated or specially imported. The realization of the potential of Fe⁰ filters has been hampered by current trends to obtain faster results while using as few resources as possible [142].

The aforementioned trends have misled scientists to overlook the paramount importance of the nonconstant and nonlinear kinetics of iron corrosion (corrosion rate). Thus, the net result is that several systems were proven efficient in short-term laboratory and pilot tests, but failed in field applications. The lack of long-term testing is also the reason why permeability loss due to iron corrosion has largely been underestimated.

Despite their promise, Fe⁰ filters have so far failed to attain the expected widespread adoption within low-income communities [29,143–147]. To be commercially viable, the costs of producing, marketing, and distributing Fe⁰ filters should be covered by the purchase price paid for the product by the consumer. Bretzler et al. [148] recently gave an overview of the state-of-the-art knowledge on the development of Fe⁰ filters for safe drinking water provision for low-income communities. The most widely used Fe⁰ filters so far are the SONO arsenic filters (SAFs) developed in Bangladesh employing a proprietary porous composite iron matrix (CIM) [78,146,149,150] and the Kanchan arsenic filter (KAF) developed in Nepal employing commercial iron nails [129]. SAFs have been more successful than the KAF and are often considered as the basis for designing alternative Fe⁰ filters [146,148]. Reproducing SAFs without using a porous Fe⁰ material like CIM is challenging [86]. Iron coils, iron filings, iron nails, iron shavings/scrap, and steel wool have been tested and used as alternatives [57,89]. Iron nails and steel wool are the most widely used Fe⁰ alternative sources. One ton (1000 kg) of iron nails costs up to 1000 USD [148], meaning that, if 5 kg of iron nails are used for each alternative Fe⁰ filter, one ton will enable manufacturing 200 Fe⁰ filters. Thus, 1000 USD is the money expense (not the price) for 200 Fe⁰ filters in the “small is beautiful” approach advocated herein. With 1000 USD, just some 20 SAF filters can be bought (50 USD / unit) [146]. In other words, by adapting the DIY approach, 10 times more filters are produced, with the additional advantage that the maintenance is operated locally. Tepong-Tsindé [57] recently designed Fe⁰ filters containing only 0.3 kg of a commercial steel wool, but these were more efficient for drinking water treatment than systems containing 5 kg iron nails. These two examples clearly show that there is room to optimize Fe⁰ consumption and water treatment.

4. Conclusions

This communication demonstrated that considering the intrinsic nature of Fe⁰ (volumetric expansion at pH > 4.5), only hybrid Fe⁰/aggregate systems are sustainable from a purely thermodynamic perspective (filling the initial porosity). For the kinetics of the process (time to permeability loss), the long-term reactivity of relevant Fe⁰ must be investigated. This task is yet to be started as all known Fe⁰ characterization tools last for just some few days or weeks. This short timeframe solely corresponds to the initial corrosion rate, but provides no insights into long-term performance and permeability loss. However, the technical expertise from 170 years and the newly established science of Fe⁰ filters, together with the opportunity to exchange Fe⁰ units in modular water treatment trains, make the immediate design of efficient Fe⁰ filters possible. It is predicted that the number and adoption of decentralized Fe⁰-based water treatment systems will increase exponentially once an improved understanding of the long-term corrosion rate of readily available materials is achieved. To achieve this, more collaborative work is needed among the research

community, funding agencies, practitioners such as nongovernmental organizations, and decision- and policymakers in the water, sanitation, and hygiene (WASH) sector.

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References

1. Hamlin, C. *A Science of Impurity: Water Analysis in Nineteenth Century Britain*; University of California Press: Berkeley, CA, USA; Los Angeles, CA, USA, 1990.
2. 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.
3. Baker, M.N. *The Quest for Pure Water: The History of Water Purification from the Earliest Records to the Twentieth Century*; American Water Works Assn.: New York, NY, USA, 1948; p. 527.
4. UN SDGs. Transforming Our World: The 2030 Agenda for Sustainable Development. Resolution Adopted by the UN General Assembly. 2015. Available online: <https://sustainabledevelopment.un.org/post2015/transformingourworld> (accessed on 4 December 2021).
5. He, Z.; Bishwajit, G.; Zou, D.; Yaya, S.; Cheng, Z.; Zhou, Y. Burden of Common Childhood Diseases in Relation to Improved Water, Sanitation, and Hygiene (WASH) among Nigerian Children. *Int. J. Environ. Res. Public Health* **2018**, *15*, 1241. [[CrossRef](#)]
6. Li, P.; Wu, J. Drinking water quality and public health. *Expo. Health* **2019**, *11*, 73–79. [[CrossRef](#)]
7. Hope, R.; Ballon, P. Global water policy and local payment choices in rural Africa. *NPJ Clean Water* **2019**, *2*, 21. [[CrossRef](#)]
8. Hope, R.; Thomson, P.; Koehler, J.; Foster, T. Rethinking the economics of rural water in Africa. *Oxford Rev. Econ.* **2020**, *36*, 171–190. [[CrossRef](#)]
9. Domènech, L. Rethinking water management: From centralised to decentralised water supply and sanitation models. *Doc. D'anàlisi Geogràfica* **2011**, *57*, 293–310. [[CrossRef](#)]
10. Schumacher, E.F. *Small is Beautiful: Economics as if People Mattered*; Harper & Row: New York, NY, USA, 1973; p. 324.
11. Moropeng, R.C.; Budeli, P.; Mpenyana-Monyatsi, L.; Momba, M.N.B. Dramatic reduction in diarrhoeal diseases through implementation of cost-effective household drinking water treatment systems in Makwane Village, Limpopo Province, South Africa. *Int. J. Environ. Res. Public Health* **2018**, *15*, 410. [[CrossRef](#)]
12. Huang, Z.; Nya, E.L.; Cao, V.; Gwenzi, W.; Rahman, M.A.; Noubactep, C. Universal access to safe drinking water: Escaping the traps of non-frugal technologies. *Sustainability* **2021**, *13*, 9645. [[CrossRef](#)]
13. Kearns, J.; Dickenson, E.; Aung, M.T.; Joseph, S.M.; Summers, S.R.; Knappe, D. Biochar water treatment for control of organic micropollutants with UVA surrogate monitoring. *Environ. Eng. Sci.* **2021**, *38*, 298–309. [[CrossRef](#)]
14. Nya, E.L.; Feumba, R.; Fotsing-Kwetché, P.R.; Gwenzi, W.; Noubactep, C. A hybrid model for achieving universal safe drinking water in the medium-sized city of Bangangté (Cameroon). *Water* **2021**, *13*, 3177. [[CrossRef](#)]
15. Roy, J. Economic benefits of arsenic removal from ground water—A case study from West Bengal, India. *Sci. Total Environ.* **2008**, *397*, 1–12. [[CrossRef](#)]
16. Roy, B.; Hartigan, J. Empowering the rural poor to develop themselves: The barefoot approach. *Innovations* **2008**, *3*, 67–93. [[CrossRef](#)]
17. Banerji, T.; Chaudhari, S. A cost-effective technology for arsenic removal: Case study of zerovalent iron-based IIT Bombay arsenic filter in West Bengal. In *Water and Sanitation in the New Millennium*; Nath, K., Sharma, V., Eds.; Springer: New Delhi, India, 2017; pp. 127–137.
18. Hering, J.G.; Maag, S.; Schnoor, J.L. A call for synthesis of water research to achieve the sustainable development goals by 2030. *Environ. Sci. Technol.* **2016**, *50*, 6122–6123. [[CrossRef](#)] [[PubMed](#)]
19. Baker, M.N. Sketch of the history of water treatment. *J. Am. Water Works Assoc.* **1934**, *26*, 902–938. [[CrossRef](#)]
20. Van Craenenbroeck, W. Easton & Anderson and the water supply of Antwerp (Belgium). *Ind. Archaeol. Rev.* **1998**, *20*, 105–116.
21. 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](#)]

22. Antia, D.D.J. Water treatment and desalination using the eco-materials $n\text{-Fe}^0$ (ZVI), $n\text{-Fe}_3\text{O}_4$, $n\text{-Fe}_x\text{O}_y\text{H}_z[\text{mH}_2\text{O}]$, and $n\text{-Fe}_x[\text{Cation}]_n\text{O}_y\text{H}_z[\text{Anion}]_m[\text{rH}_2\text{O}]$. In *Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications*; Kharissova, O.V., Ed.; Springer Nature: Basel, Switzerland, 2020. [CrossRef]
23. Wolfe, N.L.; Cipollone, M.G. Remediation of environmental contaminants using a metal and a sulfur-containing compound. *Int. J. Occup. Med. Environ. Health* **2001**, *14*, 241–248.
24. Zhang, P.; Simunek, J.; Bowman, R.S. Nonideal transport of solute and colloidal tracers through reactive zeolite/iron pellets. *Water Resour. Res.* **2004**, *40*, W04207. [CrossRef]
25. Miyajima, K. Optimizing the design of metallic iron filters for water treatment. *Freiberg Online Geosci.* **2012**, *32*, 1–60.
26. Miyajima, K.; Noubactep, C. Effects of mixing granular iron with sand on the efficiency of methyleneblue discoloration. *Chem. Eng. J.* **2012**, *200–202*, 433–438. [CrossRef]
27. Miyajima, K.; Noubactep, C. Impact of Fe^0 amendment on methylene blue discoloration by sand columns. *Chem. Eng. J.* **2013**, *217*, 310–319. [CrossRef]
28. Miyajima, K.; Noubactep, C. Characterizing the impact of sand addition on the efficiency of granular iron for water treatment. *Chem. Eng. J.* **2015**, *262*, 891–896. [CrossRef]
29. Yang, H.; Hu, R.; Ndé-Tchoupé, A.I.; Gwenzi, W.; Ruppert, H.; Noubactep, C. Designing the next generation of Fe^0 -based filters for decentralized safe drinking water treatment. *Processes* **2020**, *8*, 745. [CrossRef]
30. Yang, H.; Hu, R.; Ruppert, H.; Noubactep, C. Modeling porosity loss in Fe^0 -based permeable reactive barriers with Faraday's law. *Sci. Rep.* **2021**, *11*, 16998. [CrossRef]
31. Noubactep C: Should the term 'metallic iron' appear in the title of a research paper? *Chemosphere* **2022**, *287*, 132314. [CrossRef] [PubMed]
32. Anderson, W. On the purification of water by agitation with iron and by sand filtration. *J. Soc. Arts* **1886**, *35*, 29–38. [CrossRef]
33. Westerhoff, P.; James, J. Nitrate removal in zero-valent iron packed columns. *Water Res.* **2003**, *37*, 1818–1830. [CrossRef]
34. Njaramba, L.K.; Park, J.-B.; Lee, C.-S.; Nzioka, A.M.; Kim, Y.-J. Permeable reactive barriers with zero-valent iron and pumice for remediation of groundwater contaminated with multiple heavy metals. *Environ. Eng. Sci.* **2021**, *38*, 245–255. [CrossRef]
35. Mackenzie, P.D.; Horney, D.P.; Sivavec, T.M. Mineral precipitation and porosity losses in granular iron columns. *J. Hazard. Mater.* **1999**, *68*, 1–17. [CrossRef]
36. 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]
37. Gillham, R.W.; O'Hannesin, S.F. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* **1994**, *32*, 958–967. [CrossRef]
38. O'Hannesin, S.F.; Gillham, R.W. Long-term performance of an in situ "iron wall" for remediation of VOCs. *Ground Water* **1998**, *36*, 164–170. [CrossRef]
39. Bi, E.; Devlin, J.F.; Huang, B. Effects of mixing granular iron with sand on the kinetics of trichloroethylene reduction. *Ground Water Monit. Remed.* **2009**, *29*, 56–62. [CrossRef]
40. Kaplan, D.I.; Gilmore, T.J. Zero-valent iron removal rates of aqueous Cr(VI) Measured under flow conditions. *Water Air Soil Pollut.* **2004**, *155*, 21–33. [CrossRef]
41. 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, MA, USA, 2011; p. 73.
42. Song, D.-I.; Kim, Y.H.; Shin, W.S. A simple mathematical analysis on the effect of sand in Cr(VI) reduction using zero valent iron. *Korean J. Chem. Eng.* **2005**, *22*, 67–69. [CrossRef]
43. Konadu-Amoah, B.; Ndé-Tchoupé, A.I.; Hu, R.; Gwenzi, W.; Noubactep, C. Investigating the $\text{Fe}^0/\text{H}_2\text{O}$ systems using the methylene blue method: Validity, applications and future directions. *Chemosphere* **2021**, 132913, in press. [CrossRef] [PubMed]
44. Sarr, D. Zero-valent-iron permeable reactive barriers—How long will they last? *Remediation* **2001**, *11*, 1–18.
45. Whitney, W.R. The corrosion of iron. *J. Am. Chem. Soc.* **1903**, *25*, 394–406. [CrossRef]
46. ITRC (Interstate Technology & Regulatory Council). *Permeable Reactive Barrier: Technology Update. PRB-5*; PRB: Technology Update Team; Interstate Technology & Regulatory Council: Washington, DC, USA, 2011. Available online: www.itrcweb.org (accessed on 5 December 2021).
47. Hu, R.; Cui, X.; Gwenzi, W.; Wu, S.; Noubactep, C. $\text{Fe}^0/\text{H}_2\text{O}$ systems for environmental remediation: The scientific history and future research directions. *Water* **2018**, *10*, 1739. [CrossRef]
48. Hu, R.; Gwenzi, W.; Sipowo-Tala, V.R.; Noubactep, C. Water treatment using metallic iron: A tutorial review. *Processes* **2019**, *7*, 622. [CrossRef]
49. Hu, R.; Ndé-Tchoupé, A.I.; Cao, V.; Gwenzi, W.; Noubactep, C. Metallic iron for environmental remediation: The fallacy of the electron efficiency concept. *Front. Environ. Chem.* **2021**, *2*, 677813. [CrossRef]
50. 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]
51. Florea, A.F.; Lu, C.; Hansen, H.C.B. A zero-valent iron and zeolite filter for nitrate recycling from agricultural drainage water. *Chemosphere* **2022**, *287*, 131993. [CrossRef]
52. Notter, J.L. The purification of water by filtration. *Br. Med. J.* **1878**, *2*, 556–557. [CrossRef]
53. Tucker, W.G. The purification of water by chemical treatment. *Science* **1892**, *20*, 34–38. [CrossRef]

54. Oldright, G.L.; Keyes, H.E.; Miller, V.; Sloan, W.A. Precipitation of lead and copper from solution on sponge iron. *BuMines B* **1928**, *281*, 131.
55. Ali, I. Water treatment by adsorption columns: Evaluation at ground level. *Sep. Purif. Rev.* **2014**, *43*, 175–205. [[CrossRef](#)]
56. Siwila, S.; Brink, I.C. A small-scale low-cost water treatment system for removal of selected heavy metals, bacteria and particles. *Water Pract. Technol.* **2018**, *13*, 446–459. [[CrossRef](#)]
57. Tepong-Tsindé, R. Designing and Piloting a household filter for the peri-urban population of Douala (Cameroon). *Freiberg Online Geosci.* **2021**, *61*, 1–90.
58. Sasaki, K.; Nukina, S.; Wilopo, W.; Hirajima, T. Removal of arsenate in acid mine drainage by a permeable reactive barrier bearing granulated blast furnace slag: Column study. *Mater. Trans.* **2008**, *49*, 835–844. [[CrossRef](#)]
59. Komnitsas, K.; Bazdanis, G.; Bartzas, G.; Sahinkaya, E.; Zaharaki, D. Removal of heavy metals from leachates using organic/inorganic permeable reactive barriers. *Desalination Water Treat.* **2013**, *51*, 3052–3059. [[CrossRef](#)]
60. Westholm, L.J.; Repo, E.; Sillanpää, M. Filter materials for metal removal from mine drainage—A review. *Environ. Sci. Pollut. Res.* **2014**, *21*, 9109–9128. [[CrossRef](#)] [[PubMed](#)]
61. Kandra, H.; McCarthy, D.T.; Fletcher, T.D.; Deletic, A. Assessment of clogging phenomena in granular filter media used for stormwater treatment. *J. Hydrol.* **2014**, *512*, 518–527. [[CrossRef](#)]
62. Kandra, H.S.; Deletic, A.; McCarthy, D. Assessment of impact of filter design variables on clogging in stormwater filters. *Water Resour. Manag.* **2014**, *28*, 1873–1885. [[CrossRef](#)]
63. Kandra, H.; Callaghan, J.; Deletic, A.; McCarthy, D. Investigation of biological clogging in stormwater filters. *J. Environ. Eng. ASCE* **2015**, *141*, 1–8. [[CrossRef](#)]
64. Yao, K.-M.; Habibian, M.T.; O'Melia, C.R. Water and waste water filtration: Concepts and applications. *Environ. Sci. Technol.* **1971**, *5*, 1105–1112. [[CrossRef](#)]
65. Henderson, A.D.; Demond, A.H. Impact of solids formation and gas production on the permeability of ZVI PRBs. *J. Environ. Eng.* **2011**, *137*, 689–696. [[CrossRef](#)]
66. Reddy, K.R.; Dastgheibi, S.; Comeselle, C. Mixed versus layered multi-media filter for simultaneous removal of nutrients and heavy metals from urban stormwater runoff. *Environ. Sci. Pollut. Res.* **2021**, *28*, 7574–7585. [[CrossRef](#)]
67. Noubactep, C. Metallic iron for water treatment: A critical review. *Clean—Soil Air Water* **2013**, *41*, 702–710. [[CrossRef](#)]
68. 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](#)]
69. Noubactep, C. Predicting the hydraulic conductivity of metallic iron filters: Modeling gone astray. *Water* **2016**, *8*, 162. [[CrossRef](#)]
70. 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. [[CrossRef](#)]
71. Devonshire, E. The purification of water by means of metallic iron. *J. Frankl. Inst.* **1890**, *129*, 449–461. [[CrossRef](#)]
72. Pilling, N.B.; Bedworth, R.E. The oxidation of metals at high temperatures. *J. Inst. Metals.* **1923**, *29*, 529–591.
73. 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](#)]
74. Anderson, W. Purification of water by iron on a large scale. *J. Soc. Arts* **1883**, *32*, 963. [[CrossRef](#)]
75. 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](#)]
76. Wakatsuki, T.; Esumi, H.; Omura, S. High performance and N, P removable on-site domestic wastewater treatment system by multi-soil-layering method. *Water Sci. Technol.* **1993**, *27*, 31–40. [[CrossRef](#)]
77. 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](#)]
78. Hussam, A. Contending with a development disaster: Sono filters remove arsenic from well water in Bangladesh. *Innovations* **2009**, *4*, 89–102. [[CrossRef](#)]
79. 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](#)]
80. 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](#)]
81. Kenneke, J.F.; McCutcheon, S.C. Use of pretreatment zones and zero-valent iron for the remediation of chloroalkenes in an oxic aquifer. *Environ. Sci. Technol.* **2003**, *37*, 2829–2835. [[CrossRef](#)]
82. McMahan, P.; Dennehy, K.; Sandstrom, M. Hydraulic and geochemical performance of a permeable reactive barrier containing zero-valent iron. *Ground Water* **1999**, *37*, 396–404. [[CrossRef](#)]
83. Phillips, D.; Gu, B.; Watson, D.; Roh, Y.; Liang, L.; Lee, S. Performance evaluation of a zerovalent iron reactive barrier: Mineralogical characteristics. *Environ. Sci. Technol.* **2000**, *34*, 4169–4176. [[CrossRef](#)]
84. Noubactep, C.; Caré, S. Dimensioning metallic iron beds for efficient contaminant removal. *Chem. Eng. J.* **2010**, *163*, 454–460. [[CrossRef](#)]
85. Noubactep, C.; Caré, S. Enhancing sustainability of household water filters by mixing metallic iron with porous materials. *Chem. Eng. J.* **2010**, *162*, 635–642. [[CrossRef](#)]

86. Rahman, M.A.; Karmakar, S.; Salama, H.; Gactha-Bandjun, N.; Btatkeu, K.B.D.; Noubactep, C. Optimising the design of Fe⁰-based filtration systems for water treatment: The suitability of porous iron composites. *J. Appl. Solution Chem. Model.* **2013**, *2*, 165–177.
87. Noubactep, C.; Schöner, A.; Woafu, P. Metallic iron filters for universal access to safe drinking water. *Clean Soil Air Water* **2009**, *37*, 930–937. [[CrossRef](#)]
88. Noubactep, C.; Schöner, A. Metallic iron: Dawn of a new era of drinking water treatment research? *Fresenius Environ. Bull.* **2010**, *19*, 1661–1668.
89. Tepong-Tsindé, R.; Ndé-Tchoupé, A.I.; Noubactep, C.; Nassi, A.; Ruppert, H. Characterizing a newly designed steel-wool-based household filter for safe drinking water provision: Hydraulic conductivity and efficiency for pathogen removal. *Processes* **2019**, *7*, 966. [[CrossRef](#)]
90. Noubactep, C. The fundamental mechanism of aqueous contaminant removal by metallic iron. *Water SA* **2010**, *36*, 663–670. [[CrossRef](#)]
91. Noubactep, C. Aqueous contaminant removal by metallic iron: Is the paradigm shifting? *Water SA* **2011**, *37*, 419–426. [[CrossRef](#)]
92. Noubactep, C. Metallic iron for environmental remediation: A review of reviews. *Water Res.* **2015**, *85*, 114–123. [[CrossRef](#)] [[PubMed](#)]
93. Zhang, X.; Wu, Y. Application of coupled zero-valent iron/biochar system for degradation of chlorobenzene-contaminated groundwater. *Water Sci. Technol.* **2017**, *75*, 571–580. [[CrossRef](#)]
94. Huang, Y.H.; Tang, C.; Zeng, H. Removing molybdate from water using a hybridized zero-valent iron/magnetite/Fe(II) treatment system. *Chem. Eng. J.* **2012**, *200–202*, 257–263. [[CrossRef](#)]
95. Lü, Y.; Li, Z.; Li, J.; Chen, K.; Dong, H.; Shou, J.; Li, Y. Synergetic effect of pyrite on Cr(VI) removal by zero valent iron in column experiments: An investigation of mechanisms. *Chem. Eng. J.* **2018**, *349*, 522–529. [[CrossRef](#)]
96. Tseng, H.H.; Su, J.G.; Liang, C. Synthesis of granular activated carbon/zero valent iron composites for simultaneous adsorption/dechlorination of trichloroethylene. *J. Hazard Mater.* **2011**, *192*, 500–506. [[CrossRef](#)] [[PubMed](#)]
97. Bilardi, S.; Calabrò, P.S.; Moraci, N. The removal efficiency and long-term hydraulic behaviour of zero valent iron/lapillus mixtures for the simultaneous removal of Cu²⁺, Ni²⁺ and Zn²⁺. *Sci. Tot. Environ.* **2019**, *675*, 490–500. [[CrossRef](#)]
98. Dong, G.; Huang, L.; Wu, X.; Wang, C.; Liu, Y.; Liu, G.; Wang, L.; Liu, X.; Xia, H. Effect and mechanism analysis of MnO₂ on permeable reactive barrier (PRB) system for the removal of tetracycline. *Chemosphere* **2018**, *193*, 702–710. [[CrossRef](#)]
99. Ndé-Tchoupé, A.I.; Makota, S.; Nassi, A.; Hu, R.; Noubactep, C. The suitability of pozzolan as admixing aggregate for Fe⁰-based filters. *Water* **2018**, *10*, 417. [[CrossRef](#)]
100. Moraci, N.; Calabrò, P.S. Heavy metals removal and hydraulic performance in zero-valent iron/pumice permeable reactive barriers. *J. Environ. Manag.* **2010**, *91*, 2336–2341. [[CrossRef](#)] [[PubMed](#)]
101. Wilopo, W.; Sasaki, K.; Hirajima, T. Contribution of sheep manure bacteria in the immobilization of arsenic from groundwater using zero-valent iron. *J. SE Asian Appl. Geol.* **2010**, *2*, 1–11.
102. Fronczyk, J. Properties of reactive materials for application in runoff water treatment systems. *J. Ecol. Eng.* **2020**, *21*, 185–197. [[CrossRef](#)]
103. Reardon, J.E. Anaerobic corrosion of granular iron: Measurement and interpretation of hydrogen evolution rates. *Environ. Sci. Technol.* **1995**, *29*, 2936–2945. [[CrossRef](#)]
104. Noubactep, C.; Meinrath, G.; Dietrich, P.; Sauter, M.; Merkel, B. Testing the suitability of zerovalent iron materials for reactive Walls. *Environ. Chem.* **2005**, *2*, 71–76. [[CrossRef](#)]
105. Lufingo, M.; Ndé-Tchoupé, A.I.; Hu, R.; Njau, K.N.; Noubactep, C. A novel and facile method to characterize the suitability of metallic iron for water treatment. *Water* **2019**, *11*, 2465. [[CrossRef](#)]
106. Ndé-Tchoupé, A.I.; Hu, R.; Gwenzi, W.; Nassi, A.; Noubactep, C. Characterizing the reactivity of metallic iron for water treatment: H₂ evolution in H₂SO₄ and uranium removal efficiency. *Water* **2020**, *12*, 1523. [[CrossRef](#)]
107. Lipczynska-Kochany, E.; Harms, S.; Milburn, R.; Sprah, G.; Nadarajah, N. Degradation of carbon tetrachloride in the presence of iron and sulphur containing compounds. *Chemosphere* **1994**, *29*, 1477–1489. [[CrossRef](#)]
108. Butler, C.E.; Hayes, F.K. Factors influencing rates and products in the transformation of trichloroethylene by iron sulfide and iron metal. *Environ. Sci. Technol.* **2001**, *35*, 3884–3891. [[CrossRef](#)]
109. Noubactep, C.; Meinrath, G.; Dietrich, P.; Merkel, B. Mitigating uranium in groundwater: Prospects and limitations. *Environ. Sci. Technol.* **2003**, *37*, 4304–4308. [[CrossRef](#)]
110. Noubactep, C.; Meinrath, G.; Merkel, J.B. Investigating the mechanism of uranium removal by zerovalent iron materials. *Environ. Chem.* **2005**, *2*, 235–242. [[CrossRef](#)]
111. Noubactep, C.; Schöner, A.; Meinrath, G. Mechanism of uranium (VI) fixation by elemental iron. *J. Hazard Mater.* **2006**, *132*, 202–212. [[CrossRef](#)] [[PubMed](#)]
112. Henderson, A.D.; Demond, A.H. Permeability of iron sulfide (FeS)-based materials for groundwater remediation. *Water Res.* **2013**, *47*, 1267–1276. [[CrossRef](#)] [[PubMed](#)]
113. Du, M.; Zhang, Y.; Hussain, I.; Du, X.; Huang, S.; Wen, W. Effect of pyrite on enhancement of zero-valent iron corrosion for arsenic removal in water: A mechanistic study. *Chemosphere* **2019**, *233*, 744–753. [[CrossRef](#)]
114. Lü, Y.; Li, J.; Li, Y.; Liang, L.; Dong, H.; Chen, K.; Yao, C.; Li, Z.; Li, J.; Guan, X. The roles of pyrite for enhancing reductive removal of nitrobenzene by zero-valent iron. *Appl. Catal. B Environ.* **2019**, *242*, 9–18. [[CrossRef](#)]

115. Du, M.; Zhang, Y.; Zeng, X.; Kuang, H.; Huang, S. Enhancement of ballmilling on pyrite/zero-valent iron for arsenic removal in water: A mechanistic study. *Chemosphere* **2020**, *249*, 126130. [[CrossRef](#)] [[PubMed](#)]
116. Hu, R.; Cui, X.; Xiao, M.; Gwenzi, W.; Noubactep, C. Characterizing the impact of pyrite addition on the efficiency of Fe⁰/H₂O systems. *Sci. Rep.* **2021**, *11*, 2326. [[CrossRef](#)]
117. Xiao, M.; Hu, R.; Cui, X.; Gwenzi, W.; Noubactep, C. Understanding the operating mode of Fe⁰/Fe-sulfide/H₂O systems for water treatment. *Processes* **2020**, *8*, 409. [[CrossRef](#)]
118. Xiao, M.; Cui, X.; Hu, R.; Gwenzi, W.; Noubactep, C. Validating the efficiency of the FeS₂ method for elucidating the mechanisms of contaminant removal using Fe⁰/H₂O systems. *Processes* **2020**, *8*, 1162. [[CrossRef](#)]
119. Seng, S.; Tabelin, C.B.; Kojima, M.; Hiroyoshi, N.; Ito, M. Galvanic microencapsulation (GME) using zero-valent aluminum and zero-valent iron to suppress pyrite oxidation. *Mater. Trans.* **2019**, *60*, 277–286. [[CrossRef](#)]
120. Tabelin, C.B.; Park, I.; Li, X.; Seng, S.; Villacorte-Tabelin, M.; Igarashi, T.; Ito, M.; Hiroyoshi, N. Development of advanced pyrite passivation strategies towards sustainable management of acid mine drainage. *IOP Conf. Ser. Earth Environ. Sci.* **2019**. [[CrossRef](#)]
121. Naseri, E.; Ndé-Tchoupé, A.I.; Mwakabona, H.T.; Nanseu-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](#)]
122. Noubactep, C. Processes of contaminant removal in “Fe⁰-H₂O” systems revisited. The importance of co-precipitation. *Open Environ. Sci.* **2007**, *1*, 9–13. [[CrossRef](#)]
123. Noubactep, C. A critical review on the mechanism of contaminant removal in Fe⁰-H₂O systems. *Environ. Technol.* **2008**, *29*, 909–920. [[CrossRef](#)] [[PubMed](#)]
124. Btatkeu, K.B.D.; Olvera-Vargas, H.; Tchatchueng, J.B.; Noubactep, C.; Caré, S. Determining the optimum Fe⁰ ratio for sustainable granular Fe⁰/sand water filters. *Chem. Eng. J.* **2014**, *247*, 265–274. [[CrossRef](#)]
125. Btatkeu, K.B.D.; Olvera-Vargas, H.; Tchatchueng, J.B.; Noubactep, C.; Caré, S. Characterizing the impact of MnO₂ on the efficiency of Fe⁰-based filtration systems. *Chem. Eng. J.* **2014**, *250*, 416–422. [[CrossRef](#)]
126. Cao, V.; Alyoussef, G.; Gatcha-Bandjun, N.; Gwenzi, W.; Noubactep, C. The key role of contact time in elucidating the mechanism of enhanced decontamination by Fe⁰/MnO₂/sand systems. *Sci. Rep.* **2021**, *11*, 12069. [[CrossRef](#)]
127. Cao, V.; Alyoussef, G.; Gatcha-Bandjun, N.; Gwenzi, W.; Noubactep, C. The suitability of methylene blue discoloration (MB method) to investigate the Fe⁰/MnO₂ system. *Processes* **2021**, *9*, 548. [[CrossRef](#)]
128. Attia, A.A.; Girgis, B.S.; Fathy, N.A. Removal of methylene blue by carbons derived from peach stones by H₃PO₄ activation: Batch and column studies. *Dye. Pigment.* **2008**, *76*, 282–289. [[CrossRef](#)]
129. 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](#)]
130. Ogata, R.; Dangol, B.; Sakamoto, M. Sustainability assessment of long-term, widely used household Kanchan Arsenic Filters in Nepal. *J. Environ. Sci. Health Part A Tox Hazard Subst. Environ. Eng.* **2020**, *55*, 517–527. [[CrossRef](#)]
131. Huang, Z.; Cao, V.; Nya, E.L.; Gwenzi, W.; Noubactep, C. Kanchan arsenic filters and the future of Fe⁰-based filtration systems for single household drinking water supply. *Processes* **2021**, *9*, 58. [[CrossRef](#)]
132. Mueller, B.; Dangol, B.; Ngai, T.K.K.; Hug, S.J. Kanchan arsenic filters in the lowlands of Nepal: Mode of operation, arsenic removal, and future improvements. *Environ. Geochem. Health* **2021**, *43*, 375–389. [[CrossRef](#)]
133. Huang, J.; Ye, Y.; Fu, Z.; Dun, W.J.; Wang, Y.; Fang, L.; Ye, S.; Ye, X.; Jin, J.; Hu, Q.; et al. Synergetic effects of zero-valent iron and Morganella morganii on the removal of Cr(VI) from Wastewater. *Nat. Environ. Poll. Tech.* **2019**, *18*, 871–877.
134. Bradley, I.; Straub, A.; Maraccini, P.; Markazi, S.; Nguyen, T.H. Iron oxide amended biosand filters for virus removal. *Water Res.* **2011**, *45*, 4501–4510. [[CrossRef](#)] [[PubMed](#)]
135. Zorgani, A.E.; Cibati, A.; Trois, C. Assessment of a natural iron-based sand for the removal of nitrate from water. *Water Air Soil Pollut.* **2016**, *227*, 1–11.
136. Al-Hashimi, O.; Hashim, K.; Loffill, E.; Cebašek, T.M.; Nakouti, I.; Faisal, A.A.H.; Al-Ansari, N. A Comprehensive Review for Groundwater Contamination and Remediation: Occurrence, Migration and Adsorption Modelling. *Molecules* **2021**, *26*, 5913. [[CrossRef](#)]
137. Amoako-Nimako, G.K.; Yang, X.; Chen, F. Denitrification using permeable reactive barriers with organic substrate or zero-valent iron fillers: Controlling mechanisms, challenges, and future perspectives. *Environ. Sci. Pollut. Res.* **2021**, *28*, 21045–21064. [[CrossRef](#)]
138. Cao, V.; Alyoussef, G.; Gatcha-Bandjun, N.; Gwenzi, W.; Noubactep, C. Characterizing the impact of MnO₂ addition on the efficiency of Fe⁰/H₂O systems. *Sci. Rep.* **2021**, *11*, 9814. [[CrossRef](#)]
139. Gong, L.; Qiu, X.; Cheng, D.; Hu, Y.; Zhang, Z.; Yuan, Q.; Yang, D.; Liu, C.; Liang, L.; He, F. Coincorporation of N and S into zero-valent iron to enhance TCE dechlorination: Kinetics, electron efficiency, and dechlorination capacity. *Environ. Sci. Technol.* **2021**, *55*, 16088–16098. [[CrossRef](#)]
140. Huang, J.; Jones, A.; Waite, T.D.; Chen, Y.; Huang, X.; Rosso, K.M.; Kappler, A.; Mansor, M.; Tratnyek, P.G.; Zhang, H. Fe(II) redox chemistry in the environment. *Chem. Rev.* **2021**, *121*, 8161–8233. [[CrossRef](#)]
141. Natarajan, P.; Gulliver, J.S.; Arnold, W.A. Iron filings application to reduce lake sediment phosphorus release. *Lake Reserv. Manag.* **2021**, *27*, 143–159. [[CrossRef](#)]
142. Berthod, A.; Armstrong, D.W. Future perspectives for ionic liquids. In *Ionic Liquids in Analytical Chemistry*; American Chemical Society: Washington, DC, USA, 2022. [[CrossRef](#)]

143. 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](#)] [[PubMed](#)]
144. Anderson-Coughlin, B.L.; Litt, P.K.; Kim, S.; Craighead, S.; Kelly, A.J.; Chiu, P.; Sharma, M.; Kniel, K.E. Zero-valent iron filtration reduces microbial contaminants in irrigation water and transfer to raw agricultural commodities. *Microorganisms* **2021**, *9*, 2009. [[CrossRef](#)] [[PubMed](#)]
145. Sun, J.; Tian, A.; Feng, Z.; Zhang, Y.; Jiang, F.; Tang, Q. Evaluation of zero-valent iron for Pb(II) contaminated soil remediation: From the analysis of experimental mechanism hybrid with carbon emission assessment. *Sustainability* **2021**, *13*, 452. [[CrossRef](#)]
146. Kundu, D.K.; Mol, A.P.J.; Gupta, A. Failing arsenic mitigation technology in rural Bangladesh: Explaining stagnation in niche formation of the Sono filter. *Water Pol.* **2016**, *18*, 1490–1507. [[CrossRef](#)]
147. Smith, K.; Li, Z.; Chen, B.; Liang, H.; Zhang, X.; Xu, R.; Li, Z.; Dai, H.; Wei, C.; Liu, S. Comparison of sand-based water filters for point-of-use arsenic removal in China. *Chemosphere* **2017**, *168*, 155–162. [[CrossRef](#)]
148. Bretzler, A.; Nikiema, J.; Lalanne, F.; Hoffmann, L.; Biswakarma, J.; Siebenaller, L.; Demange, D.; Schirmer, M.; Hug, S.J. Arsenic removal with zero-valent iron filters in Burkina Faso: Field and laboratory insights. *Sci. Tot. Environ.* **2020**, *737*, 139466. [[CrossRef](#)]
149. 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](#)]
150. Singh, S.K. An analysis of the cost-effectiveness of arsenic mitigation technologies: Implications for public policy. *Int. J. Sust. Built Environ.* **2017**, *6*, 522–535. [[CrossRef](#)]