

Concept Paper

Making Fe⁰-Based Filters a Universal Solution for Safe Drinking Water Provision

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Abstract: Metallic iron (Fe⁰)-based filtration systems have the potential to significantly contribute to the achievement of the United Nations (UN) Sustainable Development Goals (SDGs) of substantially improving the human condition by 2030 through the provision of clean water. Recent knowledge on Fe⁰-based safe drinking water filters is addressed herein. They are categorized into two types: Household and community filters. Design criteria are recalled and operational details are given. Scientists are invited to co-develop knowledge enabling the exploitation of the great potential of Fe⁰ filters for sustainable safe drinking water provision (and sanitation).

Keywords: design criteria; permeability loss; reactive filtration; revolving purifier; sponge iron; zero-valent iron

1. Introduction

Water pollution caused by chemical, microbial, and physical contamination is a worldwide health issue [1–14]. While microbes cause acute diseases (e.g., cholera, diarrhea, typhoid fever), chemicals mainly cause chronic diseases including cancer [4,9,11,14–19]. Physical contamination (e.g., color, suspended solids) is generally easy to remove. There are many classifications for chemical contaminants (e.g., (i) organic, inorganic, heavy metal, radioactive, (ii) conventional micro-pollutants vs. emerging contaminants like pesticides, pharmaceuticals, and personal care products (PPCPs)), among which water-soluble species can be collectively classified into three main groups: anionic, cationic, and neutral (nonionic). The next universal classification criterion is the size of the soluble species (small/medium/large). The presence of any contaminant in drinking water is a potential cause for concern as it might be toxic or be transformed into toxic species [4,19,20]. Therefore, the

development of efficient and affordable technologies for water treatment in developing countries, and specifically under remote and marginal living conditions, is urgently required.

Providing universal access to reliable, chemical- and pathogen-free water supplies is the ideal solution to water-borne illness [1,2,4,6,8,9,17,18,20–25]. This objective has not been achieved by previous efforts, including the Millennium Development Goals (MDGs; 2000–2015) [20]. In September 2015, the countries of the world identified goals and set targets to substantially improve the human condition by 2030. This was done by adopting the United Nations (UN) Sustainable Development Goals (SDGs). Goal 6 (one of the 17 SDGs) focuses explicitly on freshwater: “Ensure availability and sustainable management of water and sanitation for all” [26]. Accordingly, Goal 6 calls for improving water quality as well as protecting and restoring water-related ecosystems [10]. However, the goal does not explicitly include universal access to safe drinking water. This view gains importance, considering that in 13 years (by 2030) the countries of the world will evaluate the extent to which the UN SDGs have been achieved and set new goals/targets. This communication reiterates that universal access to safe drinking water is possible and feasible within one or two decades [27]. Thus, existing knowledge from the science of aqueous iron corrosion (Corrosion Science) needs to be effectively translated into practical solutions [27–30] by designing efficient filtration systems based on metallic iron (Fe^0 filters) for safe drinking water provision. This includes the use of established and recommended efficient slow sand filters (SSFs) and biosand filters (BSFs) [31,32], which can be optimized by amendment with Fe^0 [30,33]. Based on these studies, the long-lasting need for an appropriate, demand-based, affordable, efficient, and sustainable water treatment technology, which is additionally centered on local communities (not only in the developing world) has been scientifically resolved [26–30,33]. Means of universal, practical implementation are presented herein. An overview of recent achievements in using Fe^0 for decentralized safe drinking water provision is given first.

2. Current Knowledge on Using Fe^0 Filters for Decentralized Safe Drinking Water

2.1. General Aspects

Mwakabona et al. [33] recently discovered that using Fe^0 for safe drinking water provision both at a household level and at a larger scale is a technology more than 130 years old [33,34]. The presentation herein is focused on the named technology as derived from Fe^0 reactive walls for groundwater remediation [35–40]. The Fe^0 reactive wall technology was introduced in Canada during the early 1990s [35,37,38,40,41] as a reductive tool for the degradation of halocarbons from polluted plumes [42–48]. Fe^0 materials were then tested following a pragmatic case-by-case approach and their suitability for the removal of several classes of aqueous contaminants established [36,37,39,40,49,50]. Ex situ applications of Fe^0 filtration systems for water treatment were then introduced. Such systems could have considered two main subsurface characteristics prompt at introduction: (i) the prevalence of darkness and (ii) the prevalence of anoxic conditions (low oxygen levels; <2 mg/L) [51]. A profound understanding of the $\text{Fe}^0/\text{H}_2\text{O}$ system revealed that subsurface Fe^0 walls are sustainable mostly by virtue of the prevailing anoxic conditions keeping a reductive environment and favoring the generation of less voluminous Fe oxides (Fe_3O_4) [26–30]. Fe^0 ex situ applications include both domestic use (household level) [16,52,53], and middle–large size units (community level) [54–56].

Ex situ applications of Fe^0 filters for safe drinking water were mainly tested and applied in the context of arsenic (As) removal in South Asia, Southeast Asia, and Latin America [57–65]. Selected aspects of the corresponding literature have been reviewed [26,30,66] and actualized [27–29,50,67]. However, a complete review is still missing and information regarding the efficiency of Fe^0 filters for As removal is still conflicting [52,65].

2.2. Fundamental Aspects

High arsenite (As^{III}) levels and low iron concentrations make As removal from natural waters challenging. The issue is exacerbated by high phosphate and silicate concentrations in natural

waters [52]. Accordingly, oxidizing arsenite (As^{III} —not charged) to arsenate (As^{V} —negatively charged) and increasing the iron concentration are two common tools to improve As removal from natural waters. The second tool (increasing iron level) was the rationale that guided the first use of Fe^0 for As removal in filters [48,67] some 17 years ago. Despite the successful introduction of SONO filters [24,51] using solely a porous iron composite matrix (no oxidizing agent), it is still correctly reported that Fe^0 filters are not “as efficient for As^{III} removal as for As^{V} removal” [52]. Preliminary chemical oxidation of As^{III} is still suggested, tested and used [65–70]. However, the use of any chemical undermines the frugality of the technology. Tepong-Tsindé et al. [29] argued that quantitative removal of As^{III} and As^{V} by conventional Fe^0 filters is a pure design issue as properly selected materials would produce enough iron corrosion products to remove all available As species by adsorption, co-precipitation, and adsorptive size-exclusion. According to [29], the variability of experimental/operational conditions and the lack of a systematic designing approach are the main barriers to progress in Fe^0 research.

2.3. The Variability of Operational Conditions

The operational conditions of 12 representative studies testing Fe^0 for As removal in column experiments or pilot studies are presented herein (Table 1) to underline the crucial significance of the design issue. Considered studies were published in various journals between 2000 and 2016 [56,57,71–79]. Tables 2 and 3 show that system design differs in terms of the size of the columns, Fe^0 type, Fe^0 size, Fe^0 elemental composition, Fe^0 mass, Fe^0 ratio in the reactive layer (RZ, reactive zone), initial As concentration, initial pH value, flow rate, and duration of the experiments. Each parameter has been shown to be of great importance for the long-term efficiency of Fe^0 filters. However, the high degree of diversity among operational parameters renders inter-system comparability challenging [27–30,80,81].

Material selection should be the first step in designing a Fe^0 filter. As a rule of thumb, only readily corroded materials are used (e.g., no stainless steel). However, for the comparison of independent results, each material should be primarily characterized for its intrinsic reactivity. It has been clearly demonstrated that conventional parameters for the characterization of solid materials (e.g., specific surface area, particle size, elemental composition, adsorption capacity, surface structure) do not give a full picture of the intrinsic reactivity [82–85]. While the intrinsic reactivity has not been determined, Table 2 clearly shows that from the 12 selected studies, only one [77] specified the elemental composition of the used Fe^0 . In the broad Fe^0 literature, the specific surface area is being determined to define a system-independent descriptor [86,87]. This concept (k_{SA} concept) introduced in 1996 [86] was not successful but is still widely used [88,89]. Given that characterizing the intrinsic reactivity of Fe^0 materials is a prerequisite for discussing Fe^0 selection, the few available characterization tools [90–93] should be routinely used (Section 5.2).

Table 1. Summary of type and origin of Fe^0 materials used for As removal in column experiments in the 12 studies utilized herein for the discussion of the impact of design criteria and operational parameters on the performance of an Fe^0 household filter. “Nr” is the number referencing individual articles in Tables 2 and 3. EMPA refers to the Swiss Federal Laboratories for Materials Testing and Research.

Nr.	Anno	Ref.	Fe^0 Type	Origin
1	2016	[71]	Granular and powder	Shandong Kaitai Group Co., Ltd. (Shangong, China) and Sinopharm Chemical Shanghai Reagent Co., Ltd. (Shanghai, China)
2	2015	[72]	Nanoparticles	Nanoiron, s.r.o. (Czech Republic)
3	2015	[56]	Filings	n.s.
4	2014	[57]	Spiral coils	n.s.
5	2013	[73]	Steel wool	n.s.
6	2013	[74]	Iron-oxide-coated HBC	Synthesized from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
7	2013	[75]	Iron spikes and stainless steel	n.s.
8	2013	[76]	Filings	Fischer Scientific Co.
9	2005	[77]	Iron filings	U.S Metals Inc. (Mentune, IN, USA)
10	2005	[78]	Iron filings	EMPA (dubendorf, Switzerland)
11	2003	[79]	Iron filings	n.s.
12	2000	[70]	Iron chips (filings)	Renwick Ironworks, Kushtia (Bangladesh)

Table 2. Summary of iron characteristics used in the 12 selected studies. “SSA” is the specific surface area and “PD” the particle density, while HBC = Honeycomb Briquette Cinders. It is seen that the SSA, PD, particle size, and the elemental composition were seldom specified.

Nr.	Fe ⁰ Type	Size	SSA (m ² /g)	PD (g/cm ³)	Elemental	Composition
					Fe	C
1	Granular and powder	1 mm; 4.44–5.56 mm	n.s.	n.s.	n.s.	n.s.
2	Nanoparticles	50–60 nm	20–25	n.s.	n.s.	n.s.
3	Filings	n.s.	n.s.	n.s.	n.s.	n.s.
4	Spiral coils	n.s. (3–30 mm length)	n.s.	0.95	n.s.	n.s.
5	Steel wool	n.s.	n.s.	n.s.	n.s.	n.s.
6	Iron-oxide-coated HBC	n.s.	-	-	-	-
7	Iron spikes and stainless steel	n.s.	n.s.	n.s.	n.s.	n.s.
8	Filings	40 mesh	n.s.	n.s.	n.s.	n.s.
9	Iron filings	100 mesh	0.55	n.s.	95	1.2
10	Iron filings	n.s.	n.s.	n.s.	n.s.	≤0.17
11	Iron filings	n.s.	1	n.s.	n.s.	n.s.
12	Iron chips (filings)	n.s.	n.s.	n.s.	n.s.	low

Besides the Fe⁰ intrinsic reactivity, there is a need to consider the solution chemistry of the water to be treated. Luepin and Hug [77] investigated the effects of O₂ and the pH on As removal in Fe⁰ columns and reported a decrease of effluent As level with increasing initial O₂ level for short empty bed contact time (EBCT). For long EBCT, similar results were achieved, only at comparatively lower initial pH values (pH 5.0). Given that pH value and O₂ level are not independent parameters, the results of [77] suggest that some literature discrepancies are related to the insufficient consideration of the importance of some design parameters (here the thickness of the reactive zone or Fe⁰-based layer). The water flow velocity (residence time) co-influences such systems as well. Actually, the water flow velocity depends on several parameters including Fe⁰ reactivity (rate of production of solid corrosion products), Fe⁰ size and shape, the Fe⁰ proportion in the reactive zone, and the thickness of the reactive zone.

Table 3 evidences a high variability in all considered operational parameters. For example, the initial As level varied from 0.02 to 100 mg/L and the Fe⁰ varied mass from 0.4 to more than 3000 g. The column dimensions and the tested water flow velocity also varied widely, but the most obvious variability was observed in the duration of the experiments (18 min to 224 h). Given that the kinetics of Fe⁰ corrosion is never linear, there is no way to extrapolate results from short-term experiments to real-world situations (months and years). The large diversity in system design coupled with the variability in Fe⁰ characteristics render comparison of independent results challenging or even impossible. This evidence justifies the frequency of discrepancy in the literature [92,94] and underlines the need for a more systematic approach [26–30,69]. Figure 1 presents the breakthrough curve for pure adsorbents (e.g., activated carbons) and raises questions regarding the predictability of the efficiency of Fe⁰ filters.

In summary, the development of efficient ex situ Fe⁰-based systems for safe drinking water provision has been impaired by an exceedingly pragmatic research approach [26–30]. The huge potential of Fe⁰ filters as a reliable, affordable, and efficient technology is yet to be exploited for households and small communities. The effort engaged herein aims to redirect research for Fe⁰ filters and establish a common base for pilot testing.

Table 3. Summary of some experimental conditions used for the column experiments in the 12 selected articles. X stands for the used contaminant and [X] for its concentration. ID is the inner diameter of the column, L its length, and RZ the thickness of the reactive zone. The numbers (Nr.) are related to relevant references as specified in Table 1.

Nr.	X	[X] (mg/L)	Fe ⁰ (g)	Dimension			Porosity (%)	PH (—)	Duration	Flow Rate
				ID (cm)	L (cm)	RZ (cm)				
1	Sb(V), Cd(II), Hg(II) and As(V)	0.2 for each	100.0	1.8	40.0	0.1	n.s.	7.5	224 d	2300 BV/8.0 min EBCT
2	Iopromide	200.0	0.4	2.5	15.0	n.s.	n.s.	6.6–7.3	75 min	8.5 m/d
3	As(III) and As(V)	0.5 for each	2.5	n.s.	n.s.	3–5	n.s.	7.0	n.s.	0.75–1.0 L/h
4	As	0.02	n.s.	31.0	n.s.	120.0	86.0	7.1–7.5	45 m	10,000 L/h
5	As(V)	0.3	47.0	4.0	0.1	n.s.	n.s.	n.s.	90 h	<600 mL/h
6	As(III) and As(V)	0.2 for each	n.s.	7.0	65.0	n.s.	n.s.	7.1	24 d	7502.2 mL/h
7	As	0.04–0.26	2200 and 1813	14.0	n.s.	n.s.	n.s.	6.5–8.5	105 d	0.189 m/h
8	As	70.0	17.2	n.s.	30.0	n.s.	n.s.	4–7	7 h	1.8 L/h
9	As(III)	0.09	150	2.5	17.8	11.6	n.s.	6.0	9 h	30 mL/min
-	As(V)	85	600	5.1	17.8	11.3	n.s.	5.0	56 d	200 mL/d
-	As(III) and As(V)	50 and 100	400	3.8	17.8	13.6	n.s.	6.0	200 d	700 mL/d
10	As(III)	0.5	6	1	n.s.	1	3.5–4	7.0	n.s.	1 L/h
11	As(III)	0.35	73,000–74,300	30	n.s.	127	n.s.	6.0–6.3	>18 m	2722 L/d
12	As(III) and As(V)	0.8 and 1.1	3000	n.s.	n.s.	n.s.	n.s.	6.8	n.s.	6.2 L/h

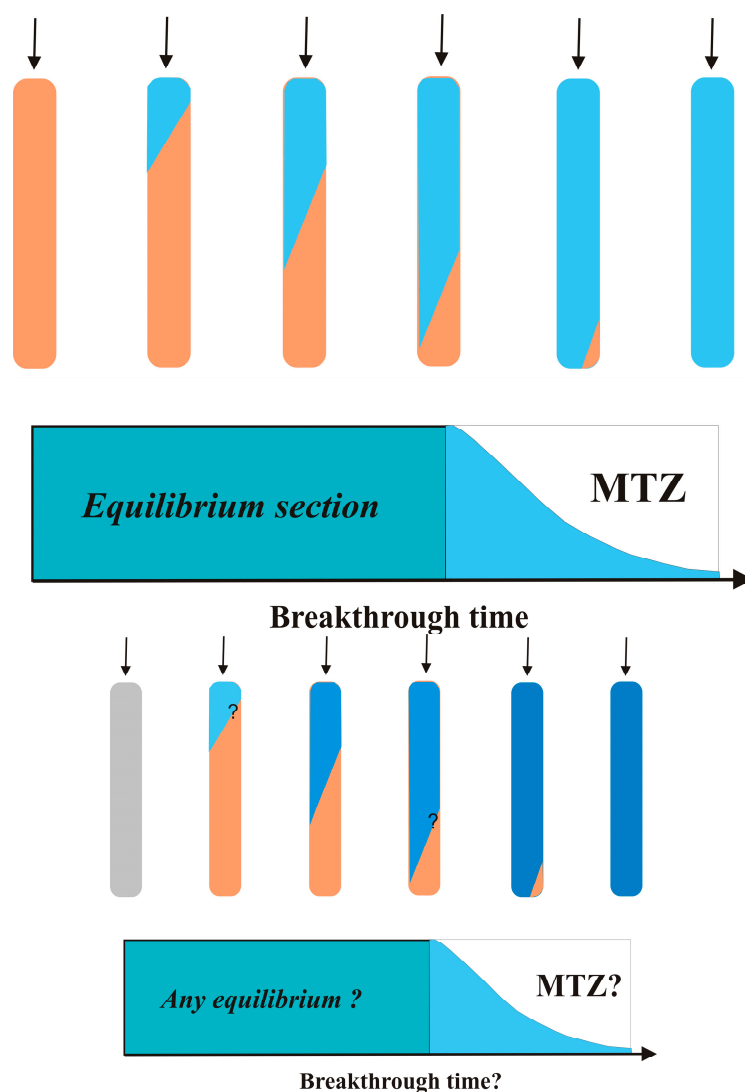


Figure 1. Concentration and breakthrough profiles in packed beds of pure adsorbents and Fe^0 filters. The adsorption breakthrough behavior (**top**) is well understood and the unusual effects widely characterized. For Fe^0 filters (**bottom**) this knowledge is yet to be confirmed.

3. The Affordability of Fe^0 -Amended Sand Filters

One major argument against universal access to safe drinking water in the short term is the high capital cost of piped supply systems, which are still regarded as the default option [4,8,9,95]. Current cost estimations are based on universal safe piped water for many developing regions. Accordingly, household water treatment and safe storage (HWTS) practices like boiling, chlorination, or filtration are collectively regarded as an interim solution [95–97]. Ojomo et al. [8] reported on controversies surrounding the question of whether HWTS practices yield improvements in drinking water quality and reductions in diarrheal disease [97–99]. In particular, it was argued that studies claiming the efficiency of HWTS practices were assessed over too short a duration [99]. However, these reports are not based on the instrumental analysis of treated water, making this discussion questionable, as only biological and chemical water analyses should be used to determine the water quality: the presence, level, and nature of contamination [11,27].

The success of HWTS practices in treating water (e.g., eliminating pollution) has been randomly interchanged with “the success in preventing diarrheal disease,” mostly for children under five. This oversimplification is no longer acceptable [28]. Diseases are potentially caused by many other factors

including sudden changes in the diet or the natural growth process [100]. On the other hand, the most common HWTS practice (disinfection by boiling or chlorination) addresses only biological contamination [33]. In other words, a child drinking water polluted with As, F, or U (the three ‘natural inorganic killers’) will not suffer from any diarrheal disease, but the water s/he is drinking is not safe. Therefore, relating the efficacy of HWTS methods to the frequency of diarrheal diseases is misleading. Additionally, HWTS definitively has the potential to improve water safety, but does not address water accessibility [101–103]. Nevertheless, because affordable methods for water accessibility are increasingly available (rainwater harvesting, solar pump), HWTS is not just a “partial and interim solution to unsafe water” [8], but a potentially reliable stand-alone solution for sustainable, safe drinking water [17,26–28,30,103].

The affordability of Fe⁰ filters results from the evidence that they rely on two universally available materials: Fe⁰ and sand. As stated in Section 1, amending conventional BSFs with Fe⁰ reactive layers will make them efficient at removing (i) pathogens in the BSF part and (ii) ‘excess’ pathogens and micro-pollutants in the reactive layers. Moreover, the BFS should precede Fe⁰ layers and acts as an O₂-scavenger to enable the operation of Fe⁰ layers under subsurface-like anoxic conditions (Section 2). Conventionally, the Fe⁰ reactive layer is made up of sand and Fe⁰, wherein the volumetric proportion of sand should exceed 50% [80,81]. In practice, sand can be partly or totally replaced by other available and affordable natural minerals like anthracite, MnO₂, or pumice [104–108]. These inert (e.g., anthracite, pumice) or reactive, but non-expansive (MnO₂) materials primarily serve as a storage surface for in situ generated corrosion products (in situ coating) [109], and thus as an adsorptive surface for inflowing contaminants. This is the fundamental mechanism of contaminant removal in Fe⁰/H₂O systems [33]. The role of MnO₂ in sustaining the efficiency of Fe⁰ filters was explained as follows [105–110]: MnO₂ uses Fe²⁺ from Fe⁰ oxidative dissolution by water (Equation (1)) for its reductive dissolution (Equation (2)):



MnO₂ works as an Fe²⁺ scavenger and thus a sustaining reaction after Equation (1) according to the Lechatelier Principle. Despite stoichiometric disadvantage, small amounts of MnO₂ will act as a catalyst because MnOOH is permanently recycled into MnO₂ [110]. This catalytic aspect has been put forward to rationalize the sustainability of SONO arsenic filters [17,25,53].

Some existing efficient Fe⁰ filters have been built by local populations without any particular skills and are maintained by them [56,111–113]. As an example, the community-scale Fe⁰ arsenic filter developed at the Indian Institute of Technology Bombay (IITB filter) [56,113] uses commercial iron nails. Each community filter contains some 10 kg of iron nails and should work for about five years. Fe⁰ filters use the same construction materials as any other filtration systems (e.g., biochar, biosand, activated carbon). As an example, Kearns [114] used commercially available 200-liter high-density polyethylene (HDPE) drums to build biochar-based filtration systems in Thailand. The same drums could be used for Fe⁰ filters. For IITB-like filters, 10 kg of iron nails are needed; 10 kg of iron nails every five years is certainly affordable. However, ‘iron nails’ is not a well-characterized class of Fe⁰ materials [92,115,116]. This makes the transferability of results achieved with IITB filters difficult.

4. The Efficiency of Fe⁰ Filters

The removal of many contaminants from natural water to meet drinking water standards is difficult as a result of their high solubility in water. Common decentralized water treatment technologies such as adsorptive filtration, boiling (pasteurizing), chlorination, ceramic filtration, membrane filtration (e.g., reverse osmosis (RO)), biosand filtration (BSF), and solar water disinfection (SODIS) are either energy-intensive (RO) or restrictive under marginal living conditions due to high complexity (chlorination), the possible production of toxic byproducts (chlorination), and the small

spectrum of contaminants addressed (boiling, BSE, chlorination, SODIS) [1,117]. Adsorptive filtration is considered the most affordable, reliable, and effective means for decentralized safe drinking water production [17,118]. Further arguments for adsorptive filtration include its simplicity, ease of operation, economic feasibility, recyclability of adsorbents, and the availability of a wide range of adsorbents such as activated carbon, metal oxides, and zeolites. Despite the large spectrum of available adsorbents, it is still challenging to find efficient, readily available, economically feasible, and high-adsorption capacity materials for field applications. In recent years, Fe^0 has been established as an in situ generator of hydroxides and oxides for water treatment (Section 2) [3,21,26,119,120].

The in situ generation of metal oxides for the removal of aqueous biological and chemical contaminants was known prior to the era of Fe^0 filters [121–130]. Despite their inherently engineered nature (fabrication costs), Fe^0 -based materials are abundantly available and are sometimes low in cost [130,131]. Fe^0 in the forms of granulated iron (chips, fillings, nails, plates), iron powder, nanoscale iron (nano- Fe^0), sponge iron, steel wool, etc. has been widely used to remove aqueous contaminants. At pH values of natural waters (6.0–9.0), Fe^0 filters are basically ion-selective as the surface of iron (hydr)oxides (iron corrosion products, FeCPs) shielding Fe^0 is positively charged [132–134]. Accordingly, Fe^0 filters are more suitable for the removal of negatively charged species (e.g., fluoride and arsenates/AsV). However, regardless of their surface charge and molecular size, contaminants are (i) physically sequestered or enmeshed during the precipitation of FeCPs (co-precipitation) [125–127,135–137], and/or (ii) removed from the aqueous phase by size exclusion. Size exclusion is mediated by the volumetric expansive nature of iron corrosion ($V_{\text{oxide}} > V_{\text{iron}}$) [80,81,138,139]. This implies that contaminant removal by size exclusion is constantly improved during the filter lifespan (provided the system does not get clogged). Therefore, well-designed Fe^0 filters efficiently remove all classes of aqueous contaminants in a single-stage process by a synergy between adsorption, co-precipitation, and size-exclusion [26–30,33,140].

A major challenge of the Fe^0 filtration technology is to select the appropriate material capable of efficiently treating polluted water within an appropriate packed-bed. None of the tested/used Fe^0 material classes (e.g., iron fillings, iron nails, steel wool) is homogeneous in term of intrinsic reactivity or efficiency for contaminant removal. Accordingly, despite 27 years of extensive research, information is lacking to confidently select Fe^0 materials to be used in filters for safe drinking water provision [44,92–94]. This evidence makes the design of Fe^0 filters challenging.

5. Designing Efficient Fe^0 Filters

A critical understanding of past design efforts made in the arena of Fe^0 filters is a fundamental prerequisite for future research. Considerable information on contaminant removal by Fe^0 filters is available (Sections 2 and 3), but randomly scattered in the literature [3,141–146]. Three concise review articles have been recently presented to catalyze further advancements [26,27,52]. Hence, this section focuses on conceptual aspects.

5.1. General Aspects

Fe^0 fixed beds are a reactive filtration technology. Like adsorptive filtration, it is expected to be an extremely versatile technology. Adsorptive filtration has proved to be the least expensive treatment option for many water treatment applications [16,52,147,148]. Research over the past three decades has demonstrated the suitability of Fe^0 filters to quantitatively remove a wide variety of pathogens and toxic chemicals [17,25,53,71,116,119,142,144–146,149]. Its suitability on a specific application depends on costs as they relate to the amount of Fe^0 consumed.

5.2. Fe^0 Characteristics: Form, Size, and Intrinsic Reactivity

Determining the Fe^0 amount to be used in an application is a challenging task for at least two reasons: (i) Fe^0 is not the contaminant-removing agent but rather the generator of contaminant collectors, (ii) contaminant collectors are in situ generated and further transformed in a highly

dynamic process. Reason 1 implies that, unlike inert adsorbents (e.g., granular activated carbons), the determination of the “specific adsorption capacity” for Fe^0 materials is not easy and cannot be derived from short-term adsorption isotherms [52,147]. The ‘adsorption capacity’ gives the maximum amount of each contaminant that can be removed per unit weight (usually in grams) of adsorbing material (Fe^0 is not one such). When additionally considering that the initial reaction products (Fe^{II} and H/H_2 species) are further transformed to a variety of hydroxides and oxides (Reason 2) and that each Fe^0 reacts with its own reaction kinetics (intrinsic reactivity), it becomes evident that selecting the appropriate Fe^0 for a specific application is a challenging task [52,86,93,150–152]. Tested and used reactive Fe^0 exists in several sizes and forms, including iron fillings, iron nails, scrap iron, sponge iron, and steel wool. Materials of each class have been positively tested for contaminant removal without any effort to link individual materials to specific applications. Moreover, a common tool to characterize the intrinsic reactivity of Fe^0 materials is still missing [45,92,93].

5.3. Characteristics of the Admixing Aggregates

The next important feature for the design of Fe^0 filters arises from the evidence that pure Fe^0 systems (100% Fe^0) are not sustainable [28,29,80–82]. In fact, iron corrosion is a volumetric expansive process as each iron corrosion product (hydroxide, oxide) is at least 2.1 times larger than the parent atom ($V_{\text{oxide}} > V_{\text{iron}}$) [80,81,138,139,153]. Therefore, Fe^0 should be mixed with at least one non-expansive aggregate (e.g., gravel, pumice, sand) [80,81,152]. The nature and proportion of the appropriate aggregate is an important operational parameter for the design of Fe^0 filters. Each aggregate has adsorptive affinity to individual contaminants but another criterion for their selection is the high surface area to volume ratio (porosity) as the accessible porous system may enable the accumulation of in situ generated corrosion products and thus delay permeability loss [80,81,150].

To summarize, from a purely material perspective, the efficiency of a Fe^0 filter depends on (i) the intrinsic reactivity of the used Fe^0 , (ii) the form and size of used Fe^0 , (iii) the nature of the admixing aggregate, and (iv) the Fe^0 :aggregate ratio. It appears that material selection is crucial for the functionality and sustainability of Fe^0 filters. Regardless of the Fe^0 type used, it is applied for the mitigation of the extent of contamination from polluted water. Accordingly, besides the nature of the contaminant, the characteristics of the polluted water (solution chemistry) should be considered as well.

5.4. Impact of Solution Chemistry

As a polluted stream passes through a Fe^0 filter, a dynamic condition develops that should produce a decrease in the contaminant concentration from the initial to the final level, ideally lower than the maximum contamination level (MCL). When the contamination level starts off higher than MCL, there is a “breakthrough.” In adsorptive filtration, the breakthrough corresponds to the exhaustion of the capacity of used adsorbent (breakthrough capacity) [147,148]. For Fe^0 filters, however, breakthrough may/should be observed before Fe^0 is exhausted. This is because there is no real ‘removal front’ and Fe^0 is oxidized in all parts of the filter, even in the absence of contaminants and dissolved O_2 . For this reason, all parameters influencing aqueous water corrosion must be considered and their impact of the decontamination process discussed. In essence, such parameters influence the dissolution of Fe^0 , the solubility of iron, the formation of the oxide scale on Fe^0 , and the permeability of the oxide scale [154,155].

The decontamination with Fe^0 is affected by various interrelated chemical and physical characteristics of the water. These parameters include: (i) pH value, (ii) nature and extent of contamination, (iii) nature and extent of co-solutes (e.g., NO_3^- , PO_4^{3-}), (iv) presence of organic matter, (v) availability of dissolved O_2 , and (vi) availability of CO_2 . From the relevant parameters, the pH value and the availability of dissolved O_2 will be commented on in some detail. The nature of the contamination is a site-specific issue. However, for a concept paper, the four most common contaminants can be considered: arsenic, bacteria, fluoride, and uranium.

5.4.1. Impact of pH Value

Fe^0 oxidative dissolution rates are faster at lower pH values (abundance of H^+ —Equation (1)) than at higher pH values. For safe drinking water provision, especially in the developing country, the water source should have a $\text{pH} > 5.0$. Because Fe^0 is the source of contaminant collectors, the real contaminant scavengers are low-soluble iron corrosion products and their solubility is low at $\text{pH} > 4.5$ [156]. The surface of iron oxides and hydroxides is positively charged in the pH range of interest, suggesting that negatively charged contaminants will be more efficiently removed. In other words, because of the ion-selective nature of the $\text{Fe}^0/\text{H}_2\text{O}$ system at $\text{pH} > 5.0$, the most important impact of the pH value is its impact on the contaminant speciation. The large majority of available studies have not properly discussed this aspect (Sections 2 and 3).

5.4.2. Impact of O_2 Level

O_2 accelerates the initial kinetics of Fe^0 oxidative dissolution but its most important impact is indirect as it cannot quantitatively reach the shielded O_2 surface. The O_2 level might favor the formation of a thick oxide scale on Fe^0 (lowering the oxidation kinetics) as well as the cementation of Fe^0 particles and other aggregates (yielding permeability loss). It appears that the effect of O_2 level is situation-dependent, even within the same system. Accordingly, it is not surprising that controversial reports have been published (Section 2).

A certain impact of O_2 is on the nature of in situ generated iron hydroxides and oxides. When O_2 is abundantly available, more voluminous compounds are generated (Fe^{III} oxides/hydroxides). The net result is a rapid porosity loss yielding system clogging (permeability loss). When the system is clogged, it becomes useless despite the remaining Fe^0 amount. For this reason, a sure way to sustain Fe^0 filters is to operate at low O_2 levels (e.g., $[\text{O}_2] < 2.0 \text{ mg/L}$) [33]. Fortunately, such conditions are achieved in biosand filters (BSF). This means that using a BSF as pre-treatment unit for a Fe^0 filter is advantageous [26–30].

5.5. Design Considerations

The oxidative dissolution of Fe^0 and the associated reactions are not instantaneous. In other words, the generation of contaminant collectors needs time. Fe^0 filters should be designed such that contaminant removal is completed within the bed for the selected flow velocity [26–30,122–126]. As the rate of aqueous Fe^0 corrosion is not a constant function of the time, and each Fe^0 has its own intrinsic reactivity, the prediction of the efficiency of each filter goes through pilot testing. Another key factor is the expected change of the hydraulic properties (permeability) of Fe^0 filters during their operation. The question arises: which testing approach would enable the achievement of reliable results that may be regarded as system-independent?

The efficiency of a Fe^0 filter for As removal has illustrated the complexity of the issue (Section 2). The efficiency depends on the following five parameters: (i) the pH value determining the ion selectivity of the filter, (ii) the redox speciation of As (As^{III} , As^{V} or $\text{As}^{\text{III}}/\text{As}^{\text{V}}$ ratio), (iii) the As concentration and the concentrations of all other species interfering with As adsorption by competing for adsorption sites, modifying surface charges, or modifying As and Fe solubility, (iv) porosity and pore size distribution of iron precipitates (and aggregates), and (v) the hydraulic conductivity of the filter as influenced by in situ generated contaminant collectors.

5.6. Approach for the RSM Modeling

The presentation herein has reiterated the availability of limited guidance for the Fe^0 selection for designing efficient Fe^0 filters. However, Fe^0 is the heart of the system and the efficiency of each system depends on the (i) initial kinetics of Fe^0 corrosion (corrosion rate) and (ii) its time-dependent change, which is not a linear function ([28] and refs. cited therein). Accordingly, the determination of the corrosion rate of various Fe^0 materials under relevant field conditions is urgently needed [89].

The next section (Section 6) will present a protocol for the characterization of steel wool as Fe^0 material for drinking water production at a community level. Steel wool is selected for its worldwide availability [25,131] and the rapid kinetics of its corrosion [127,128].

The illustrative RSM model herein will discuss the effects of Fe^0 type (four samples), the nature of the contaminants (As, bacteria, F, U) (four species), flow rate (0.2 to 2.4 mL/min) (five values), bed height (10 to 70 cm) (5 values), and initial fluoride concentration (2 to 15 mg/L) (five values) on the efficiency of Fe^0 filters.

6. Testing Steel Wool as a Starting Fe^0 Material

To illustrate the design practice of Fe^0 filters, a procedure to systematically test a system based on steel wool is discussed in this section. Three cylindrical columns (Column 1 through 3) with a diameter (D) of 15 cm and a height (H) of 100 cm are used (Figure 2). The bed volume of this filter is 17.7 L ($V = \pi \times D^2 \times H/4$). The first and third columns are filled with fine sand ($d < 0.4$ mm). The first (Column 1) is basically a conventional BSF, whereas the second (Column 3) fixes dissolved Fe from the Fe^0 -based column (in situ coating) to optimize decontamination. Column 2 contains a 70 cm thick reactive layer sandwiched between two layers of fine sand. Accordingly, the volume of the reactive layer is 12.4 L. Table 4 summarizes the volumes of sand and Fe^0 to be taken to build six different reactive layers. In each case the corresponding masses should be documented as well as the effective depth of the reactive zone. The pure Fe^0 (100%) reactive zone is only to be tested for porous (e.g., foam/sponge) and filamentous (e.g., steel wool) materials.

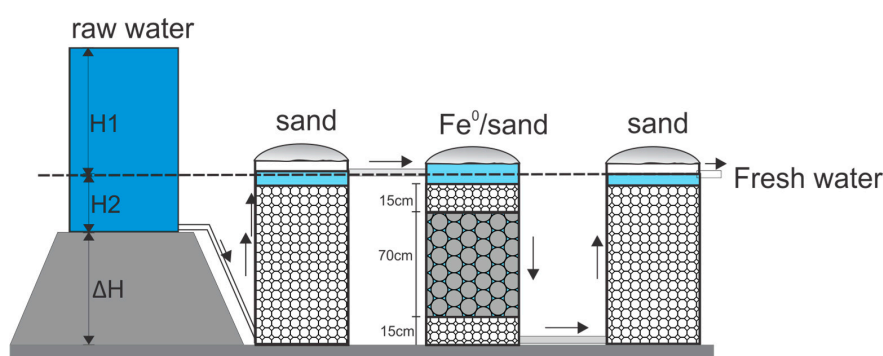


Figure 2. Concept of water treatment train based on filtration on granular Fe^0 (Fe^0/sand) and including at least one sand filter. The sand filter is either a roughing filter or a biosand filter. Treated water is stored for distribution.

Table 4. Guide for the implementation of a 70 cm thick reactive zone. The apparent volume occupied by the Fe^0 material is used as reference and the actual volume of the reactive zone should be documented. The corresponding masses of sand and Fe^0 should be documented as well.

Fe^0 (v. %)	V_{iron} (L)	V_{sand} (L)	m_{iron} (g)	m_{sand} (g)	Fe^0 (w. %)
100.0	12.4	0.0	x_0	0.0	100.0
75.0	9.3	3.1	x_1	y_1	z_1
50.0	6.2	6.2	x_2	y_2	z_2
25.0	3.1	9.3	x_3	y_3	z_3
10.0	1.2	11.1	x_4	y_4	z_4
5.0	0.6	11.8	x_5	y_5	z_5

6.1. Natural Water as a Complex Design Parameter

Natural waters are contaminated and eventually polluted due to three main inherent processes [5,20]: (i) atmospheric particle dissolution, (ii) rock weathering, and (iii) soil leaching. Increasing human

population, industrialization, and the use of fertilizers and manufactured materials (including metal-based ones) have worsened water pollution due to weathering and leaching. It is necessary that the quality of any water source (e.g., lake, river, well) is checked to establish its (drinking) quality.

Irrespective of the presence of any toxic contamination (pollution), details about conventional physico-chemical parameters should be documented. These parameters include acidity (pH value), alkalinity (HCO_3^-), chloride (Cl^-), color, dissolved organic carbon (DOC), dissolved oxygen (O_2), electrical conductivity (EC), hardness (Ca^{2+} , Mg^{2+}), nitrate (NO_3^-), phosphate (PO_4^{3-}), potassium (K^+), sodium (Na^+), sulfate (SO_4^{2-}), temperature, and turbidity. Although the enumerated parameters are not mutually exclusive, it is seen that up to 14 parameters are necessary to characterize a water source. The relevance of the measurement of individual parameters arises from the evidence that measured EC values give an idea of the salinity of the water but no idea about the actual nature of dissolved ions (co-solutes).

This sub-section recalls that each water body is unique in its nature [157,158] and that the water quality is not limited to the nature and extent of contamination. In the context of using Fe^0 for water treatment, a pollutant (e.g., As, F, U) is just one of the operational parameters capable of influencing iron corrosion by (i) enhancing/inhibiting the kinetics of Fe^0 oxidative dissolution, (ii) influencing the process of oxide scale formation, (iii) influencing the ionic conductivity of the oxide scale, and (iv) influencing the porosity/permeability of the oxide scale [159–165].

Apart from the pH value, it is not yet established whether selected parameters (including the nature and extent of contamination) are more significant than others for the process of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems. Accordingly, designing Fe^0 filters based solely on the extent of contaminant removal at selected initial pH values is a highly qualitative task. Natural waters do contain different types of dissolved, suspended, and microbiological contaminants. Suspended contaminants are successfully removed in roughing filters [22]. To obtain reliable design criteria for Fe^0 filters, the extent to which inherent water contents influence iron corrosion should be established. Only once this task is accomplished can rules of thumb for site-specific design be developed.

6.2. Design Criteria

The principal design criteria for Fe^0 filters are (alphabetically): (i) depth of the reactive zone, (ii) extent (and nature) of water contamination (including dissolved O_2 and co-solutes) (Section 2), (iii) Fe^0 intrinsic reactivity, (iv) media depth and size (all aggregates including Fe^0 ; number of columns), (v) proportion of Fe^0 within the reactive zone, (vi) required treatment level, and (vii) water flow velocity (residence time). The performance of the filter is assessed by monitoring changes in the (i) concentrations of relevant species including contaminants and iron, (ii) hydraulic conductivity (permeability), (iii) pH value, and (vi) electrical conductivity.

6.3. Preparing and Implementing Media in Fe^0 Filters

Sand is first sieved through a series of sieves to be separated into its different grain sizes. This operation is essential because the filtration rate is influenced by grain size and the grain size distribution. Only the fraction <2.0 mm is used. The fraction 0.2 to 0.4 mm can be used for the BSFs (columns 1 and 3, Figure 1), the fraction 1.0 to 2.0 to support the reactive zone (column 2, Figure 1), and the fraction 0.4 to 1.0 mm used in the reactive zone. Sieved sand is then washed to remove fine silt, clay, and other impurities that the media may contain. Store the washed sand in a protected dry area away from possible human or animal contamination.

Fe^0 is also sieved and the fraction lower than 2.0 mm used. Filamentous steel wool is chopped into pieces less than 2 cm in length. It should be ensured that the Fe^0 does not contain grease and/or toxic species (perform appropriate cleaning/washing, if applicable). Table 5 summarizes the characteristics of commercial steel wool that should be systematically tested in long-term experiments. It is obvious that homogeneously mixing fine grade steel wool with sand will be a difficult task in rural conditions.

Accordingly, only coarser materials, for instance with widths >50 μm , will be suggested for testing (four materials: 60, 75, 90, and 100 μm).

Table 5. The eight typical levels of abrasiveness (grade) of steel wool and their width. The grade is determined by the thickness of the wire of which the wool is made of. Stainless steel wool is not considered herein. (www.steelwooldirect.com).

Grade	0000	000	00	0	1	2	3	4
Name	Finest	Extra Fine	Fine	Medium Fine	Medium	Medium Coarse	Coarse	Extra Coarse
d (Inch)	0.0010	0.0015	0.0018	0.0020	0.0025	0.0030	0.0035	0.0047
d (mm)	0.03	0.04	0.04	0.05	0.06	0.08	0.09	0.10
d (μm)	25	35	40	50	60	75	90	100

6.4. Simulating Testing Practice: RSM Model

In this section, the statistical framework of experiments is simulated to understand the methodology of designing a filter. As the effective parameters influencing filter design according to concerning dilemma may vary from place to place and from one investigator to another, the parameters are simplified according to the following considerations. Section 6.1 listed 14 parameters relevant for water quality (Table 6); Section 6.2 listed seven principal design criteria (see also Table 7) and three major monitoring parameters. Section 6.3 suggested four steel wool materials to be tested. From the design criteria, the intrinsic reactivity of Fe^0 (steel wool in Table 5 or k_{EDTA} value in Table 6) [94], the media depth and size, the proportion of Fe^0 within the reactive zone (Table 4), the required treatment level (e.g., WHO guidelines), and the initial water flow velocity (mediated by ΔH in Figure 1) can be considered as fixed. The nature and extent of water contamination are also fixed for any specific case (Section 6.1).

As shown in Table 6, many variables as well as their interactions might influence the design of an efficient Fe^0 filter. For this reason, the conditions need to be optimized. Unfortunately, the conventional methods for optimization are “one factor at a time” approaches that frequently fail to identify the variables that give rise to the optimum response because the effects of factor interactions are not taken into account in such procedures. These procedures are time-consuming and require a large number of experiments. They are also incapable of reaching truly optimal conditions due to ignoring such interactions among variables [166–168]. In order to overcome these problems, a multivariate statistical design approach could be adopted through RSM, which is a multivariate statistical tool that uses quantitative data from appropriate experiments to solve multivariate equations.

Table 6. Initial variables for the design of Fe^0 filters. Temperature and turbidity are not considered. Based on a single Fe^0 material (k_{EDTA} value), it is seen that more than 45 variables should be considered to design a filter.

No.	Parameter (x)	Unit	Variables	Comments
1	Acidity (pH value)	-	6.0, 7.0, 8.0, 9.0	pH of natural waters
2	Alkalinity (HCO_3^-)	mg/L	5, 10, 20, 35, 50	no
3	Dissolved oxygen (O_2)	mg/L	1.0, 2.0, 4.0, 6.0, 8.0	Relevant natural waters
4	Hardness (Ca^{2+} , Mg^{2+})	mg/L	5.0, 7.5, 10.0, 15.0, 20.0	Relevant natural waters
5	Electrical conductivity (EC)	$\mu\text{Sv}/\text{cm}$	50, 150, 300, 450, 200	Relevant natural waters
6	Depth of the reactive zone (RZ)	cm	10, 20, 30, 50, 70	For a 100 cm length column
7	Extent and nature of contamination	μM	water quality	Including co-solutes
8	Initial concentration of fluoride	mg/L	1.0, 4.0, 8.0, 12.0, 20.0	As example for the RSM model
9	Fe^0 intrinsic reactivity	k_{EDTA}	n.a.	A standard approach is missing
10	Fe^0 proportion within the RZ	%	5, 10, 25, 40, 60	Higher values not to be tested
11	Nature of aggregates (e.g., Fe^0 , sand)	n.a.	n.a.	Inert or reactive; non expansive
12	Required treatment level	MCL	Requested water quality	Not considered in RSM model
13	Size of Fe^0	μm	250, 500, 1000, 2000	The diameter is meant
14	Size of other aggregates (e.g., gravel, sand)	mm	0.25, 0.50, 1.0, 2.0, 4.0	The diameter is meant
15	Water flow velocity	mL/min	0.5, 1.0, 2.5, 5.0, 10.0	Fixed by the daily need

Table 7. Summary of the operational factors retained for the RSM modeling. The parameters selected are the most globally monitored for the quality of natural waters.

No.	Parameter	Minimum	Maximum
1	Nature of contaminant (e.g., fluoride)	1	20
2	(%) Fe ⁰ volumetric proportion	5	50
3	Hydraulic conductivity (mL/min)	0.5	10
4	(−) pH value	6	9
5	Electrical conductivity (μS/cm)	50	200

Compared to conventional optimization methods, RSM is introduced as an economic and time-saving instrument because it can provide more information from fewer experiments [169]. In addition, the estimates of the effects of each factor are more precise, the interaction between factors can be estimated systematically, and there is experimental information in a larger region of the factor space, which improves the prediction of the response in the factor space by reducing the variability of the estimates of the response [170]. In addition, the main aim of RSM is to find the optimal response, and it has been widely used to describe the interactive and synergistic effects among experimental variables as well as to work on the optimization of operation conditions [171–174].

Over the last few decades, many researchers have been using various design of experiment (DoE) techniques in RSM including two-level full factorial design (FFD) [175], Box–Behnken design (BBD) [176], and Central Composite Design (CCD) [177] to predict the ultimate response. CCD was first studied by Box and Wilson in 1951 and is still the most popular design for experiments. CCD has three groups of design points that are codified to summarize the data and ease of statistical calculations: (i) two-level factorial design points (2^k), consists of all possible combinations of the +1 and −1 codified levels of the factors, (ii) axial or star points ($2k$) codified as $(\alpha = (2^k)^{1/4})$ have all of the factors set to 0, the midpoint, except one factor, which has the value $\pm \alpha$, and (iii) center points are points with all levels set to coded level 0 [178].

The total number of experiments is calculated by the following equation:

$$N = 2^k + 2k + n_c \quad (3)$$

where k is the number of factors and n_c the number of central points, which is calculated by the following equation:

$$n_c = (\sqrt{n_F} + 2)^2 - n_F - 2k, \quad (4)$$

where n_F is the number of factorial points and k is calculated by the following equation:

$$k = \left((k+3) + (9k^2 + 14k - 7)^{\frac{1}{2}} \right) / (4(k+2)) \quad (5)$$

The methodology mainly involves a quadratic model to explain the behavior of the system. This model is flexible and covers all linear, non-linear, and interaction effects between the factors [179]. The quadratic polynomial equation is as follows:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j \neq i}^k \beta_{ij} x_i x_j + \varepsilon, \quad (6)$$

where y is the predicted response, β_0 is the offset term, β_i is the i th linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the ij th coefficient, and ε is the error or residual value. Solving this equation and calculating the coefficients are done by using the least squares method. The fitness of the given models can be tested by ANOVA statistics (R^2 , adjusted R^2 , F-test and t-test) and residuals analysis. As Bezera et al. [180] introduced RSM as a tool for optimization in analytical chemistry, this kind of design experiment has been widely used by different researchers in order to optimization of water and soil remediation [166,173,181–183] or designing different types of water filters [184,185]. The experimental design and statistical analysis of the data were done by Design-expert10 statistical software.

In this study, the design of experiments is simulated by considering five factors; the total number of experiments will be 32, which is more economic and time-saving compared to 50 for a full-factorial design (Table 8).

Table 8. Central composite design experiments. Φ = Hydraulic conductivity.

StdOrder	RunOrder	PtType	Blocks	[F [−]]	[Fe ⁰]	Φ	pH	EC
				(mg/L)	(vol. %)	(%)	(—)	(μ S/cm)
1	1	1	1	5.75	16.25	2.875	6.75	162.5
2	2	1	1	15.25	16.25	2.875	6.75	87.5
3	3	1	1	5.75	38.75	2.875	6.75	87.5
4	4	1	1	15.25	38.75	2.875	6.75	162.5
5	5	1	1	5.75	16.25	7.625	6.75	87.5
6	6	1	1	15.25	16.25	7.625	6.75	162.5
7	7	1	1	5.75	38.75	7.625	6.75	162.5
8	8	1	1	15.25	38.75	7.625	6.75	87.5
9	9	1	1	5.75	16.25	2.875	8.25	87.5
10	10	1	1	15.25	16.25	2.875	8.25	162.5
11	11	1	1	5.75	38.75	2.875	8.25	162.5
12	12	1	1	15.25	38.75	2.875	8.25	87.5
13	13	1	1	5.75	16.25	7.625	8.25	162.5
14	14	1	1	15.25	16.25	7.625	8.25	87.5
15	15	1	1	5.75	38.75	7.625	8.25	87.5
16	16	1	1	15.25	38.75	7.625	8.25	162.5
17	17	−1	1	1.00	27.50	5.250	7.50	125.0
18	18	−1	1	20.00	27.50	5.250	7.50	125.0
19	19	−1	1	10.50	5.00	5.250	7.50	125.0
20	20	−1	1	10.50	50.00	5.250	7.50	125.0
21	21	−1	1	10.50	27.50	0.500	7.50	125.0
22	22	−1	1	10.50	27.50	10.000	7.50	125.0
23	23	−1	1	10.50	27.50	5.250	6.00	125.0
24	24	−1	1	10.50	27.50	5.250	9.00	125.0
25	25	−1	1	10.50	27.50	5.250	7.50	50.0
26	26	−1	1	10.50	27.50	5.250	7.50	200.0
27	27	0	1	10.50	27.50	5.250	7.50	125.0
28	28	0	1	10.50	27.50	5.250	7.50	125.0
29	29	0	1	10.50	27.50	5.250	7.50	125.0
30	30	0	1	10.50	27.50	5.250	7.50	125.0
31	31	0	1	10.50	27.50	5.250	7.50	125.0
32	32	0	1	10.50	27.50	5.250	7.50	125.0

7. Discussion

7.1. Calling for Co-Development

Slow sand filters (SSFs), as first built in Scotland by John Gibb of Paisley in 1804, are the conventional form of filtration for safe drinking water provision [98,157]. Biosand filters (BSFs) are an adaptation of traditional SSFs for water treatment at the household and small community levels. BSFs mostly remove pathogens and unpleasant taste from water by virtue of biological processes taking place in a sand column ‘covered’ with a biofilm (termed as *Schmutzdecke*). These filtration systems have no specific vocation for the removal of chemical contaminations (e.g., As, F, U) [22,26,30,186]. A particular feature of BSFs is that dissolved oxygen is consumed in the upper layer of the filter, some 10 cm under the resting water (*Schmutzdecke*). The BSF is recommended by the World Health Organization (WHO) for decentralized water treatment in the developing world. Efforts to optimize the efficiency of biosand filters are undergoing [30,57,186–192].

An established way to improve the efficiency of a BSF is to amend it with metallic elements (Al⁰, Fe⁰, Zn⁰) [126,130,131,189,193–195]. Depending on the intrinsic reactivity of the used Fe⁰, the extent of water contamination, the size of the filter, and water flow velocity, a relative small volumetric Fe⁰ ratio (e.g., <10%) could yield efficient long-term water treatment. Even in the case of larger Fe⁰ ratios, the sustainability of the system is proven by the fact that the Fe⁰ layer works under anoxic

conditions as O_2 is consumed in the BSF [30,80,81]. In other words, the combination BSF/ Fe^0 filter promises sustainability. Given that (i) Fe^0 characterization [92], (ii) Fe^0 design [29], and (iii) BSF construction [187,190] are all frugal in nature, the science of universal safe drinking water provision using Fe^0 materials is established. Thus, systematic material characterization and site-specific design would complete the studies needed for implementation.

Arguably, this work can be performed anywhere in the world. The originality of the approach is that a global concept is presented that can be applied to specific contexts. The scientific or technical experts need to be informed on local priorities, needs, and opportunities [10]. These local conditions are perfectly known to water professionals who are now collaborating with (international) researchers, for example in the framework of an established consortium. There are several effective ways for individuals to coordinate their special skills and expertise to meet the challenge posed by the UN SDGs. Two examples from Germany include (i) the short- and long-term appointments from German Academic Exchange Service (DAAD) and (ii) support by programs of the German Federal Ministry of Education and Research (BMBF) that focus on sustainable development.

Herewith scientists are called to collaborate with water professionals in the field to fill the pressing gaps to achieve universal safe drinking water provision. The same technology will be modified for sanitation for a healthier world.

7.2. The Science of the Universality of Fe^0 Filters

Methods to tackle water pollution are based on biological, chemical, physical, and thermal principles. Methods based on thermal principles include boiling, distillation, and pasteurization. The most important are [17]: adsorption, boiling, coagulation, crystallization, distillation, electrolysis, evaporation, filtration, flotation, ion exchange, oxidation, pasteurization, precipitation, reduction, reverse osmosis, sedimentation, and solvent extraction. Relevant oxidation and reduction processes are biological, chemical, or electrochemical in nature. From the listed technologies, filtration on packed-beds of adsorbents (adsorptive filtration) and reverse osmosis are considered as the best [16,52,147]. Among them, adsorptive filtration is the most applicable due to its ease of operation and is also considered a universal water treatment technology [16].

The scientific rationale for the universality of adsorptive filtration is that chemical methods (e.g., oxidation, precipitation, reduction) are collectively limited by the equilibrium constant. Reasoning on the case of a simple salt (AB), which is dissolved to A^{n+} and B^{n-} , the equilibrium constant (K_s) is given by Equation (7):

$$K_s = [A^{n+}] \times [B^{n-}]. \quad (7)$$

If A^{n+} is the pollutant, the water is satisfactorily treated by pure chemical precipitation (not co-precipitation) only if $[A^{n+}] = [K_s]^{1/2}$ is less than the maximum contamination level (MCL) for the species A. It is well documented that this is rarely the case [27,196,197]. For this reason, as far as safe drinking water is concerned, chemical methods alone are not satisfactory. Their performance should be enhanced by at least one filtration step. The suitability of each filtration technology depends on the adsorbing material and its affinity for the pollutant. This makes adsorptive filtration necessarily selective and thus multi-barriers are applied to treat multi-contaminated water sources [18,198]. Note that, in coagulation and flotation, adsorbents are formed in situ to accumulate contaminants (e.g., A^{n+}) and the contaminant-laden flocs (precipitates) are eliminated during subsequent filtration by size exclusion.

The suitability of Fe^0 filters to treat multi-contaminated waters (as a stand-alone solution) arises from the fact that two non-selective mechanisms are involved in the removal process: co-precipitation and size-exclusion (beside selective adsorption) [26,52,132]. Noubactep and colleagues [199–201] have demonstrated that the dynamic nature of the process of in situ generation and precipitation of iron oxides implies that colloidal forms remove species without affinity to iron oxides to an unpredictable extent. For this reason, upon proper design, Fe^0 filters will be efficient at removing even very small species that would have needed high pressure (electricity) to be eliminated by reverse osmosis. Thus,

well-designed Fe^0 filters certainly ameliorate the biological and chemical quality of natural water, which makes Fe^0 filters a technology of choice in contexts where analytical instrumentation is lacking. However, universal analytical quality control should remain the goal [28].

7.3. Fe^0 Filters for Pathogen Removal

The biocidal property of Fe^0 was discovered and applied in Western Europe as early as the 19th century, when the outbreak of disease was connected to water quality [33,122,123]. Fe^0 was shown effective at turning even sewage water potable within an appreciably short contact time ([33] and refs. cited therein). Interestingly, research over the past 15 years has demonstrated that Fe^0 filters are a cost-effective option helping utilities meet their multiple water treatment goals [142–146,202–205]. Pilot studies have confirmed the potential achievement of this goal [206]. Accordingly, the question of whether Fe^0 filters are efficient at removing pathogenic contamination from water is clearly answered in the affirmative. However, the design question remains as for chemical contamination (Section 4): how to evaluate the long-term performance of Fe^0 filters while taking into account the effects of relevant operational variables? Operational variables include the presence of natural organic matter (NOM) and the pH value. Answering these two questions would enable researchers to (i) design sustainable Fe^0 filters for actual water treatment plants and (ii) understand changes in filter performance over time, as affected by the water chemistry.

The discussion on the operating mode of Fe^0 filters for pathogen removal is ongoing despite two important facts [207–211]: (i) Bojic et al. [130] have demonstrated that producing metal oxides from a Fe-micro-allowed Al^0 is an efficient tool to remove bacteria from water, and (ii) You et al. [194] have demonstrated that Fe^0 filters remove viruses from water. Because Fe^0 filters also remove NOM, they automatically help prevent the formation of disinfection byproducts (DBPs). This knowledge is an independent proof of the efficiency of Fe^0 filters as a powerful, stand-alone, non-oxidant-based technology to control the microbial contamination of water. Using Fe^0 filters would additionally avoid the challenges of (i) financing oxidant-based technologies and (ii) controlling DBPs. In other words, Fe^0 filters are compact devices helping us solve a daunting challenge facing water utilities: controlling microorganisms without dealing with DBPs or residual disinfectant level. In addition, they are more affordable and easy to install and operate.

7.4. Spent Media: Dispose or Recycle?

The presentation herein implies that spent materials from Fe^0 filters are a matrix of (i) residual Fe^0 and (ii) iron oxyhydroxides entrapping contaminants. The first piece of good news is that quantitative contaminant release from spent material under environmental conditions is not likely as iron oxyhydroxides are not dissolved by natural waters [54,212,213]. The second piece of good news is that iron oxyhydroxides are the raw material for iron making [214]. These key characteristics of the element Fe and its water chemistry make Fe^0 filters a green technology. Additionally, contaminant recovery from the spent material is possible and should be investigated on a case-by-case basis. Thus, it is essential to take the aspect of ‘contaminant recovery’ into consideration in the design equation. In essence, this recovery aspect is not new, as Tseng et al. [127] used steel wool [Fe^0] to ‘adsorb’ cobalt-60 (^{60}Co) from sea water some 35 years ago [28]. ^{60}Co was then recovered from corrosion products and analytically determined.

Properly disposing of spent materials is always possible, as well as for toxic pollutants, including radioactive ones. However, recycling is basically only universally possible for organic pollutants as they will be burnt off during heating. For inorganic pollutants the decision will be taken on a case-by-case basis but the recovery of the pollution should make the residual material recyclable. Intensive research is needed on all involved aspects. However, given the urgency of meeting the UN SDGs, efficient filters are needed and spent materials can be either disposed of or stocked until a recovering technology is made available.

7.5. Limitations of Fe⁰ Filters

Fe⁰ has a high potential to induce the removal of various aqueous contaminants by adsorption, co-precipitation, and size exclusion; as recalled herein, a systematic investigation will enable the successful implementation of Fe⁰ filters, which should include recycling filters' wastes and recovering pollutants. The most critical factors are discussed in Section 6. It appears that Fe⁰ filtration technology has no real limitations. No chemical additives are needed (chemistry free), no sophisticated accessories are needed (simplicity), no electrical power is needed (energy-free), installation and maintenance can be performed by the owner (household or community), and the design is demand-oriented (e.g., the size of the community). The evidence that Fe⁰ filters are prone to fouling will be tackled by increasing the frequency of unit replacement or using short-living Fe⁰-materials. All these reasons make Fe⁰ filters the ideal solution for developing countries as there is no constraint for implementation other than locally available materials and manpower.

The culture of filter maintenance and Fe⁰ regeneration will be established in an intern dynamic. The technical viability (proof of concept) [26,121–126,215–221] and economic feasibility are already demonstrated [54,201]. The environmental and social acceptance of the technology in the community can be considered a given as the technology is developed locally. However, advice and knowledge transfer can be acquired in collaboration with other groups, including scientific ones. Considering the significant advancements made in research on 'Fe⁰ for environmental remediation and water treatment' over the past three decades [26–30,52,76,116,146,222–229] as the cornerstone for a universal sustainable solution to a long-lasting crisis, the universal provision of safe drinking water is no longer an 'elusive goal' [7]; Fe⁰ filtration provides a solution, specifically for the developing world [229,230].

8. Design Your Fe⁰ Filter

Fe⁰ filters for households and small communities are presented as a further development of the biosand filter (BSF) [26–30,56,111–113,229]. BSF is neither standardized nor patented [22,111,230]. The BSF is considered one of the most promising household water treatment methods but the demonstration of its suitability and efficiency is impaired by two key factors: (i) The quality of treated water is not routinely analytically assessed and (ii) overarching designing or manufacturing and quality control guidelines do not exist. The challenge of accessing equipment for water analysis as a cornerstone for achieving the UN SDGs is obvious [11,28]. This section summarizes the efforts achieved in designing consistently high-quality Fe⁰ filters. If an open collaboration in designing Fe⁰ starts now, it will be easy to identify areas where manufacturing and quality control guidelines are needed. The presentation is limited to three key issues: (i) The nature of used Fe⁰ materials, (ii) the design of the treatment units, and (iii) quality control practices.

8.1. Nature of Fe⁰ Materials

Available studies suggest that improper Fe⁰ selection can affect the performance of locally designed Fe⁰ filters to the point where their ability to produce safe drinking water is compromised. The historical example of the Kanchan arsenic filter [111,112] is well documented [30]. The variability in the efficiency of designed filters implies that the iron nails used were of different intrinsic reactivity. Smith et al. [229] recently presented a comparison of two different iron-nail-based Fe⁰ filters for arsenic removal in China: (i) the original Kanchan arsenic filter (SONO-style) and (ii) a modification in which the nails are embedded in the upper sand layer (before the fine sand layer). The filter with embedded nails was found to be more efficient. However, this result is only qualitative as different iron nails would show different results and there is no tool to correlate the obtained results to those of Smith et al. [229]. During the last 20 years, sporadic efforts to characterize the intrinsic reactivity of Fe⁰ materials have been presented [83,84,90,91,93,94,115,116,224]. However, only the methods of Reardon [90] (H₂ evolution) and Noubactep (Fe⁰ dissolution in EDTA) [84] are really simple and affordable. Fe⁰ dissolution in EDTA further presents the advantage that it used very small amounts of

materials and lasted for just four days. Recently, Bhatkeu et al. [45,92] further developed the EDTA method and demonstrated an excellent correlation of k_{EDTA} values and the extent of methylene blue discoloration from aqueous solutions. Accordingly, the routine determination of k_{EDTA} values is proposed as a tool to characterize the intrinsic reactivity of Fe^0 materials and ease discussion of results from various sources.

8.2. Design of Fe^0 Treatment Units

A starting rule of thumb for designing Fe^0 could be: “Design an efficient BSF and add a Fe^0 -based unit (new filter or a reactive zone in the BSF) [30]. Then increase the water flow velocity and control the biological and chemical quality of the filtered water.” Accordingly the reference system is a BSF operating under the same conditions. By altering the current filter design, it will be possible to identify the range of parameters that can be changed while still having an improved BSF filter. It is essential to recall that the experiments should last for at least six months. Results obtained at lab scale demonstrate the viability of the system and could be directly used to design household Fe^0 filters. These results are the cornerstone for the design of pilot tests for scalable community treatment plants. However, lab and current pilot tests are lasting just for a few weeks or months [67,231–233]. This is not acceptable given the non-linearity of the kinetic of iron corrosion [89].

8.3. Assessing the Efficiency of Fe^0 Filters

Designing an efficient Fe^0 filter could be regarded as ascertaining whether the flow rate of a BSF could be increased after the addition of a Fe^0 unit without sacrificing filter effectiveness in terms of pathogen removal while inducing satisfactory chemical decontamination. Thus, once the specific design variables are identified, the task remaining is to monitor the quality of filtered water as result of the performed alteration.

The research method can be summarized as: “Take a BSF as reference system and create new filter designs by changing one of relevant design variables (Section 5). Then produce the new designs (e.g., in triplicate along with three control BSF). Finally, pass the model solution or the local natural water through the filters daily, and test the filtrates once a week (or twice a month) for at least six months.” Original and filtrated natural waters should be tested for electrical conductivity, flow rate, iron concentration, major ions (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Cl^- , HCO_3^- , PO_4^{3-} , SO_4^{2-}) pH value, total coliforms (TC), and turbidity. Additionally, natural waters should be monitored for arsenic, fluoride, and uranium, which have been revealed as global killers.

The large variability in water sources, Fe^0 materials, and design options raises concerns about the consistency and quality of locally produced Fe^0 filters, especially in the absence of standardized quality control procedures. If the approach presented herein is adopted widely, areas where designing/manufacturing guidelines are needed would soon be identified and this would contribute to consistently high-quality Fe^0 filters. The next logical step is to identify areas where further research is needed to refine design recommendations. A significant goal can be to guide the development of a best-practice manual that describes science-based recommendations for quality-controlled Fe^0 filters worldwide.

8.4. Local Candle Fe^0 Filters

8.4.1. General Aspects

Candle-style Fe^0 filters (Figure 3) can be locally manufactured, based on local knowledge. Using locally affordable materials would ensure the affordability of the resulted filters. One key benefit is the ability to adjust efficiency by manipulating the number of candles in each filtration system. It is understood that such candle filters may require plastic parts and some type of adhesive that are not yet locally available. Nevertheless, the candle Fe^0 filter would still be an appropriate solution because resulting problems are related to leakage and/or replacing broken parts and not to water treatment.

Moreover, the introduction of such candles would galvanize the development of the market for such additional materials or even their local production in the short/long term. Once locally designed and produced candle Fe^0 filters are established, their efficiency would be improved in a locally induced development dynamic. Clearly, the comparison of first-generation local Fe^0 candles with commercial filters does not give a fair sense of their suitability. All that is needed is (i) the readiness to improve own systems with a systematic approach, (ii) an initially efficient system, and (iii) a clear indication for users as to when to replace the candle.

It is essential to recall that ‘old’ systems like BSF or ceramic filters are still in development [186,190–192,234,235]. Accordingly, being a ‘complication’ of BSF, many design-related topics are yet to be addressed in further research efforts. Understanding some of the specific causes of Fe^0 filter failures will help to optimize the cost-effectiveness of the Fe^0 filtration technology as a whole [26]. Long-term studies are needed to warrant sustainable Fe^0 filters. Finally, locally manufactured candle Fe^0 filters could encourage the recycling of filter wastes.

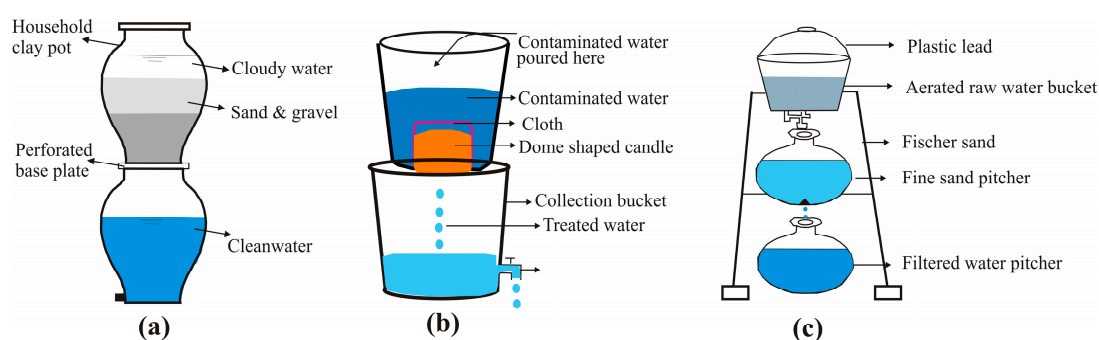


Figure 3. Schematic representation of three candle-type filters. A candle is either a container like in a Brita filter, a bucket like in a n-Kolshi filter (a,c) or simply the hollow portion of a domestic candle filter (filled with adsorbent materials) (b).

8.4.2. Design Aspects

Using Fe^0 materials in domestic candle-type filters has been experimentally tested but not used in practice for the reasons elucidated herein (Section 2). In essence, the n-Kolshi systems ($n = 2$ or 3), largely tested in Bangladesh and Nepal, are candle Fe^0 filters as they can be regarded as “candles” whose hollow parts (here a Kolshi) are filled with Fe^0 . For example, [73] tested cast-iron filings and steel wool (SW) in domestic candle-type filters. Due to the large difference in density, the tested candle could contain 176 g of fillings and just 47 g of SW. As breakthrough (initial concentration: 300 $\mu\text{g/L}$) was observed after 6.0 L in the fillings filter and only 1.5 L in the SW filters (per run of intermittent filtration). The authors speculated that using three candles in series would enable the treatment of 18.0 and 4.5 L of water per filtration run, respectively. As demonstrated herein (see also [56]), this speculation is not acceptable as the kinetics of Fe^0 corrosion is not linear. Moreover, the candles were completely filled with Fe^0 (100%), meaning that even with a supposedly linear rate of iron corrosion, permeability loss will soon occur and at different extents for individual materials [80,81]. This example demonstrates that only long-term systematic experiments will determine the feasibility of Fe^0 candle filters for water treatment at the household level. While it is certain that candle filters will be efficient, the main issue to address is the Fe^0 selection and its proportion in the candle. The service life of the candle is to be determined experimentally until enough data is available for the establishment of some correlations (e.g., long-term reactivity). The next section specifies some key issue for sustainable candle Fe^0 filters.

8.4.3. Sustainability Aspects

It is frustrating to observe that even recent reports are not unanimous as to whether candle-type Fe^0 filters are viable or not [56,69]. In essence, a newly designed Fe^0 filter can be compared to a highly permeable sand filter, which is characterized by a high level of interconnectivity between the inter-granular voids (pores). Once the corrosion process starts, the pores are progressively filled by iron corrosion products [80,81]. Thus, the effective porosity decreases because the proportion of voids in which water flows decreases. In other words, permeability loss in Fe^0 filters is fundamentally due to reduced interconnectivity. Unconnected pores are often called dead-end pores. The non-sustainability of conventional Fe^0 filters is thus due to increased dead-end pores [28,30,80,81].

Material particle size and shape, Fe^0 ratio, Fe^0 intrinsic reactivity, the height of the reactive zone (Fe^0 layer), and packing arrangements are among the factors that determine the occurrence of dead-end pores (Section 2). In addition, the porosity of the admixing aggregates (e.g., gravel, MnO_2 , pumice) also impacts the water flow. The large array of significant operational parameters impacting the efficiency and sustainability of Fe^0 filters and the absence of a systematic approach to assess the efficiency of such filters explain why, despite 17 years (from 2000 onwards) of intensive research, controversial reports are still published [56,69,236]. To end this frustration, systematic investigations with well-characterized materials are needed [237,238].

9. Concluding Remarks

To gain acceptance, each stand-alone water treatment technology should quantitatively remove a broad range of contaminants at an economical cost and in an environmentally benign manner. Reports on Fe^0 filters over the last two decades have shown encouraging results as Fe^0 filters remove a wide variety of aqueous chemical and microbial contaminants. However, the major factor that limits the acceptance of Fe^0 filters is the pragmatic (practical rather than theoretical considerations of the reactivity of Fe^0) approach with which related research has been performed. The presentation herein has reiterated the reasons for the efficiency of Fe^0 filters and presented ways to make them a universal solution for decentralized safe drinking water provision. The experiment could start by testing commercial steel wool at the community level.

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