



Short communication

Metallic iron for safe drinking water worldwide

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ABSTRACT

A new concept for household and large-scale safe drinking water production is presented. Raw water is successively filtered through a series of sand and iron filters. Sand filters mostly remove suspended particles (media filtration) and iron filters remove anions, cations, micro-pollutants, natural organic matter, and micro-organisms including pathogens (reactive filtration). Accordingly, treatment steps conventionally achieved with flocculation, sedimentation, rapid sand filtration, activated carbon filtration, and disinfection are achieved in the new concept in only two steps. To prevent bed clogging, Fe⁰ is mixed with inert materials, yielding Fe⁰/sand filters. Efficient water treatment in Fe⁰/sand filters has been extensively investigated during the past two decades. Two different contexts are particularly important in this regard: (i) underground permeable reactive barriers and (ii) household water filters. In these studies, the process of aqueous iron corrosion in a packed bed was proven very efficient for unspecific aqueous contaminant removal. Been based on a chemical process (iron corrosion), efficient water treatment in Fe⁰ beds is necessarily coupled with a slow flow rate. Therefore, for large communities several filters should work in parallel to produce enough water for storage and distribution. It appears that water filtration through Fe⁰/sand filters is an efficient, affordable, a flexible technology for the whole world.

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“The close link between scientific research and technical invention appears to be a new factor in the nineteenth century. According to Mumford, “the principal initiatives came, not from the inventor-engineer, but from the scientist who established the general law”. The scientist took cognizance both of the new raw materials which were available and of the new human needs which had to be met. Then he deliberately oriented his research toward a scientific discovery that could be applied technically. And he did this out of simple curiosity or because of definite commercial and industrial demands. Pasteur, for instance, was encouraged in his bacteriological research by wine producers and silkworm growers. . . . In the twentieth century, this relationship between scientific research and technical invention resulted in the enslavement of science to technique”.

Jacques Ellul 1954 [1]

1. Introduction

Universal access to safe drinking water is a challenge to the scientific community to which the responsibility is incumbent on

developing appropriate technologies. Safe drinking water must be globally available, e.g. drinking water for (i) citizens in all cities, (ii) holiday-makers and tourists in Bamena (Cameroon), Dighali (Bangladesh), or Fuheis (Jordan), and (iii) villagers in small communities worldwide. Adequate infrastructures for safe drinking water production certainly exist in most cities and in hotels for holiday-makers and tourists. In general, it can be roughly considered that water infrastructure is well developed in urban areas as opposed to rural areas where the infrastructure is either poorly developed or non-existent. Accordingly, the population to be urgently deserved with safe drinking water is the rural one [2–4].

Rural communities are not similar in their size, technical equipment and geographic distribution [5–11]. For example, in the Republic of South Africa close to five million people live in widely scattered remote small rural communities of often less than 100 people [11]. Similarly, areas of small island countries in the Pacific Ocean are made up of hundreds of scattered islands inhabited by few people [8,9]. In the developed world, it is a well-known fact that small and remote communities often lack adequate technical, managerial, and financial capacity for safe drinking water production [6,12,13]. For example, around 2003, there were about 1000 small municipal drinking water utilities in the Province of Quebec (Canada) whose waters were reported to frequently violate the provincial drinking water standards [6].

In many rural communities in the developing world, most people do not have paid employment. As a rule, any income comes

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from kindred in the family network that have jobs in the city or abroad. Most people live a sustainable agricultural, fishing or hunting existence and this paradigm of living results in little global influence [8,9,14]. However, global issues do impact on the villages, as their water is potentially contaminated with various imported manufactured substances including fertilizers, heavy metals, herbicides, insecticides, and pharmaceuticals [15,16]. Despite billions of dollars in aid, technology transfer, and local spending, inadequate progresses have been made in recent years in improving access to safe drinking water in the developing world [8]. It is presently not certain, whether the United Nations Millennium Development Goal of “halving by 2015, the proportion of people without sustainable access to safe drinking water” in 1990 will be achieved [17,18]. Even upon achievement, present technologies may still leave up to 600 million people without access to safe water in 2015 [4,19].

The presentation above clearly shows that providing people with safe drinking water is a human need of universal relevance. Therefore, efficient but affordable technologies are needed as the communities in need (small municipalities and villages) are characterized by their low-income [4,8,10,20]. Various technologies for safe drinking water provision are available but they are either cost-intensive or not applicable without electricity [11]. Accordingly, suitable technology should use low cost materials which are readily available and match or exceed the capability of conventional water treatment technologies: cue metallic iron (Fe^0).

1.1. Metallic iron in drinking water treatment plants

The last two decades have witnessed the establishment of Fe^0 as a powerful water remediation material for several classes of pollutants [21–25]. Fe^0 is currently used in groundwater remediation and wastewater treatment [25–29], and drinking water production at household level [30–36]. Despite existing patents on water treatment using Fe^0 in treatment plants [12,37,38], no concept comparable to the one presented here could be found. The process of Meng and Korfiatis [38] involves at least two other technical issues: (i) a vibration device to increase filtration efficiency in Fe^0 beds and (ii) the addition of oxidizing agents or coagulants to enhance the filtration efficiency in sand beds. The process of Santana [37] termed as “sulfur-modified iron” uses finely-divided Fe^0 in the presence of powdered S^0 (or MnS), followed by an oxidation step. The technical issues in both processes could cause managerial shortness in small communities. The chemical-free process for arsenic removal using a Fe^0 /sand filter presented by Gottinger [12] is closer to the one presented here. However, Gottinger’s invention is a pragmatic one and is theoretically designed for As only.

The present theoretical study is an extension of the recently presented concept of iron beds for safe drinking water production at household level [33,39,40], and community scale [41]. The technology uses Fe^0 to assist slow sand filtration. Contaminant removal is primarily due to size exclusion. Size exclusion is improved by volumetric expansion/compression cycles inherent to aqueous iron corrosion and the adsorptive nature of iron corrosion products [41]. The whole dynamic process of iron corrosion is responsible for the Fe^0 bed efficiency. Accordingly, the water flow velocity will be a function of the reactivity of the used material and the extent of contamination (contaminant nature and concentration). It can be emphasized that the water flow velocity is necessarily slow making Fe^0 filtration technology an appropriate technology for small communities [12,33,41]. For large communities several filtration units could be necessary to produce the daily required water volume. Alternatively, any large community can be subdivided in several small water districts (e.g. urban quarters). The presentation will start by recalling the main characteristics of natural waters that serve as source for drinking water production.

2. Characteristics of drinking water sources

Fresh waters or raw waters are natural waters (surface water, groundwater) commonly used as drinking water sources. The four main characteristics of raw waters are their content of: (i) pathogens (e.g. bacteria, fungi, helminths, parasites, protozoa, viruses), (ii) natural organic material (NOM), (iii) dissolved salt (salinity), and (iv) H^+ ions (pH value).

It is universally acknowledged that the greatest risks of water-borne disease are from pathogens. The microbial risk is mostly due to water contamination by human and/or animal feces [4,42–44]. The existence and dangers of pathogenic microbes in surface waters have been recognized for more than a century [45]. On the contrary, groundwaters (e.g. wells and springs) are naturally protected against contamination by pathogenic microbes. The protection is attributed to the filtration properties of subsurface soils and geologic strata. Accordingly groundwaters are generally less charged with pathogens [45,46].

NOM is ubiquitous in natural waters and can be present in dissolved, colloidal and/or particulate forms [47–49]. The dissolved and colloidal forms of NOM (DOM or fraction passing a 0.45- μm filter) are the most problematic and undesirable fractions of NOM with regard to water treatment (e.g. with granular activated carbon). DOM is a heterogeneous mixture of complex organic materials including humic substances, hydrophilic acids, proteins, lipids, carboxylic acids, polysaccharides, amino acids, and hydrocarbons. Due to its heterogeneous nature, a surrogate parameter such as total organic carbon (TOC) or dissolved organic carbon (DOC) is generally used to quantify DOM concentrations in water.

Salinity is a general term used to describe the levels of different salts such as sodium chloride, magnesium and calcium sulfates, and bicarbonates. The salinity (or hardness) of fresh waters is generally due to calcium and magnesium and may take values of up to 300 mg/L as CaCO_3 [47]. The salinity is primarily a measure of ionic conductivity of water and thus is important for sustaining aqueous Fe^0 corrosion (transport of Fe^{2+} from anodic sites).

The pH value is the most important characteristic of natural waters for the treatment with Fe^0 . As a rule, Fe^0 oxidative dissolution yields soluble Fe^{II} and Fe^{III} species at $\text{pH} < 4.0$ – 4.5 and precipitates of Fe^{II} , Fe^{III} and $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ at $\text{pH} > 4.5$ [50]. Water treatment by Fe^0 filters is only possible at $\text{pH} > 4.5$. [33] The pH value of natural waters may range from 6 to 10 [47]. Accordingly, dissolved iron precipitates as hydroxides or/and oxides in the vicinity of the Fe^0 surface forming an initially porous oxide film. Variations in pH can change both the surface charge distribution of iron hydroxides/oxides and the ionization of weak acid or bases (pK_a values), including DOM with various functional groups in its structure. The pH value can also impact the conformation of DOM components, and thus their adsorption onto the oxide scale on Fe^0 . Finally, if water is contaminated by metals and metalloids, their speciation, their complex formation tendency, solubility and thus affinity to iron oxides is strongly pH dependent.

In general, natural waters may be contaminated by: (i) natural organic matter (NOM and DOM), (ii) anthropogenic organic substances (fertilizers, pharmaceutical products, solvents), (iii) anthropogenic and geogenic inorganic substances (As, F, Fe, Mn, P, U) and (iv) micro-organisms (including bacteria and viruses). All these substances or substance groups should theoretically be efficiently removed in Fe^0 filters [33,51–56]. This theoretical prediction is validated by Fe^0 -based SONO filters designed for As which currently free water from more than 23 different metallic species, ammonia, bacteria, chloride, nitrates, and total coliform in Bangladesh and Nepal [30,55–57]. On the other hand, You et al. [35] and Diao and Yao [34] have explicitly demonstrated the suitability of Fe^0 to inactivate micro-organisms and removed them from water.

3. Metallic iron for drinking water treatment

Metallic iron is an emergent reactive material increasingly used for water treatment [25,29,33,36]. Fe⁰ is the most used reactive material in subsurface permeable reactive barriers [29,34,58]. It was originally used to remove redox-sensitive contaminants from groundwater [26,27,58–60]. It is commonplace to consider that the bare Fe⁰ surface reacts with the contaminants and converts them into non-toxic/less toxic species (Assumption 1). The validity of Assumption 1 automatically degrades all other reducing agents (co-reductants) to side-reductants. Co-reductants are primarily dissolved and adsorbed Fe^{II} and H₂. Assumption 1 further requires that the Fe⁰ surface must be accessible. Accordingly, the universal film on Fe⁰ is regarded as inhibitive for the process of contaminant reduction or reductive removal. The assumed inhibitive characteristic of the oxide film coupled to the large variation in the reactivity of used iron fillings (micro-scale Fe⁰) were amount the major reasons to introduce nano-scale Fe⁰ [61,62], and bimetallic materials [63,64]. Nano-scale Fe⁰ has been reported to have the potential to overcome these two problems. In fact, both the initial rates and the extent of contaminant reduction per mole of Fe⁰ is increased. However, despite infinitesimally small size, nano-scale Fe⁰ will also be covered by an oxide film such that expected, observed and reported increase reactivity is not necessarily coupled to direct reduction by Fe⁰ (electrons from Fe⁰).

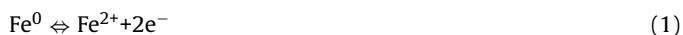
It has already been demonstrated that the oxide film on Fe⁰ is beneficial for the process of contaminant removal [51–54,65]. In fact, the oxide film acts as contaminant scavenger and the contaminant may be further chemically transformed (oxidized or reduced if applicable).

The presentation above clearly disprove the validity of Assumption 1 and corroborates results from other branches of science that iron corrosion is always coupled to oxide film formation at pH > 4.5. Iron corrosion continues under the film because the film is porous and permeable to water and other oxidizing agents [51,52,65–68]. More importantly, using Fe⁰ to assist sand filtration does not aim at inducing reductive transformations of contaminants, but to use the process of iron corrosion and the adsorptive properties of in situ generated iron oxides to sustain the filtration process. In other words, in Fe⁰ filters, Fe⁰ is oxidized by H₂O and corrosion products are used as trap for contaminants which could be chemically transformed. Depending on their nature and concentration, selected contaminants may influence (inhibit or sustain) the process of iron corrosion. For example, it is well-established that the incorporation of a cation into the structure of iron (oxyhydr)oxides alters the nucleation, crystal growth, and transformation [69]. This impact of the alteration on the further iron corrosion should be carefully characterized in laboratory and field investigations.

4. Mechanism of contaminant removal in Fe⁰ filters

4.1. Aqueous iron corrosion

Immersed reactive Fe⁰ corrodes due to differences in the electrical potential on anodic and cathodic sites on the Fe⁰ surface [70,71]. The metal oxidizes at the anode, where corrosion occurs according to Eq. (1):



Simultaneously, a reduction reaction occurs at cathodic sites. The typical cathodic processes are:



The electrons produced at anodic sites are conducted through the metal whilst the ions formed are transported via pore water (electrolyte).

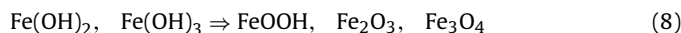
Fe²⁺ ions from Eq. (1) might be further oxidized (e.g. by O₂, MnO₂ or contaminants like CrO₄²⁻) to Fe³⁺ ions according to Eq. (4):



On the other hand, Fe³⁺ from Eq. (4) is an oxidizing agent for Fe⁰ (Eq. (5)):



Lastly, generated Fe²⁺ and Fe³⁺ will form hydroxides according to Eqs. (6) and (7) and the hydroxides will be progressively transformed to amorphous and crystalline oxides (Eq. (8)):



It is important to recall that, regardless from the size of the material, the formation and transformation of an oxide scale on Fe⁰ is a universal process (at pH > 4.5). Accordingly, the propensity of any Fe⁰ to aqueous corrosion is influenced by the nature of the oxide scale on its surface. The initial oxide scale is porous and permeable but may be transformed to an impervious layer mainly depending on the water chemistry [72]. In other words, an oxide scale begins to form immediately after Fe⁰ immersion and may facilitate or hinder corrosion, serving either as a barrier or as a path for ion exchange with the pore solution in the Fe⁰ filter.

It is also important to notice that the reactions after Eqs. (2)–(8) are considered as side reactions in the discussion of the process of contaminant reductive transformation by Fe⁰ (Fe⁰ is ideally oxidized by the contaminant). This simplification is not acceptable for at least two reasons: (i) even though a contaminant (e.g. Cr^{VI}) may be a stronger oxidizing agent for Fe⁰ than Fe²⁺, H⁺ and O₂, H₂O (H⁺) is present in very large stoichiometric abundance; (ii) even if the universal oxide scale is considered as a path for contaminant transport, it is a reactive path containing species (e.g. adsorbed Fe^{II}) which are sometimes more powerful reducing agents than Fe⁰ [73]. The next section discusses the mechanism of contaminant removal in Fe⁰ filters.

4.2. Mechanistic aspects of contaminant removal in Fe⁰ filters

4.2.1. Contaminant removing processes

Adsorption is characterized by the accumulation of substances at the interface between two phases (e.g. solid/liquid) due to chemical and physicochemical interactions. The solid on which adsorption occurs is called the adsorbent. In a Fe⁰/H₂O system, there are theoretically several adsorbents including Fe⁰, Fe(OH)₂, Fe(OH)₃, FeOOH, Fe₃O₄, Fe₂O₃, and green rust. However, apart from Fe⁰ and well crystallized phases (Fe₂O₃, Fe₃O₄), all other solid phases are in transformation. During the precipitation of Fe phases contaminants can be enmeshed. Whether precipitates are pure phases or not, there is no defined surface on which an inflowing contaminants should adsorb.

The transport of any contaminant (chemical, microbial and physical) in a Fe⁰ filter is primarily controlled by its physicochemical characteristics, the composition of the water, the characteristics of available adsorbents, and the water flow velocity. Two key contaminant characteristics are size and surface electrostatic properties. Key properties of Fe⁰ beds include water flow velocity which is coupled to pore size distribution, temperature, pH, and chemical/mineral composition of water. From a pure physical perspective, contaminant size, bed porosity and relative surface

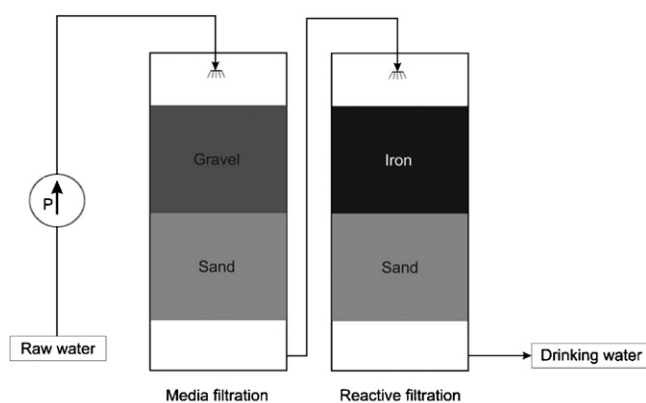


Fig. 1. Flow scheme of treatment concept. Potential materials are enumerated without care on their relative proportions. In the reactive filtration bed, sand and iron are mixed. The volumetric proportion of Fe^0 should not exceed 60%.

electrical properties of Fe species and contaminants are the most important factors governing the efficiency of a Fe^0 bed. Accordingly, large contaminants with higher affinity to Fe^0 species should be readily removed in Fe^0 beds. In other words, if adsorption was the most important mechanism, contaminant should be reduced (or oxidized) to yield species which should readily be adsorbed by Fe^0 species. However, the technology was developed to reductively degrade polar halogenated organic species (RX), ideally to non-polar organic species (RH). Actually, Fe oxides are mostly polar and will readily interact with other polar species. Given that reduced species are reported to be removed from the aqueous phase, it is obvious that adsorption on corrosion products alone cannot explain the reported efficiency of Fe^0 beds.

It should be explicitly pointed out, that the goal of water treatment for save water production is not contaminant chemical transformation (reduction or oxidation) but contaminant removal. Accordingly, even reduced contaminants (e.g. RH) must be removed from the aqueous phase. In other words, any contaminant and all its transformation products have to be removed from the aqueous phase. For example, the reductive transformation of carbon tetrachloride by Fe^0 has been reported to produce hexachloroethane, tetrachloroethane, trichloromethane, dichloromethane, carbon monoxide, carbon dioxide, and methane [74]. Apart from non toxic CO_2 , all these reaction products should be removed from water to obtain safe drinking water. Removal mechanisms in this context are adsorption, co-precipitation (also termed enmeshment, entrapment or sequestration), and volatilization.

This section has demonstrated that, from a pure semantic perspective contaminants are removed in $\text{Fe}^0/\text{H}_2\text{O}$ systems by adsorption, co-precipitation, and volatilization.

4.2.2. Bed porosity and porosity loss

A Fe^0 filtration bed is composed of one or several reactive zones of granular sand and Fe^0 particles (Fig. 1). The compact Fe^0 :sand mixture has a random porous structure. The manner with which the pore space is formed depends mainly on the arrangement of the granular particles [75,76]. While packing uniform spheres, the least compact and most compact arrangements are rhombohedral and cubic respectively. The pore size can be defined in terms of a length dimension (pore radius). Pore size in a packed bed is closely related with the size of the filter grains constituting the bed (e.g. Fe^0 and sand). The smaller the grains, the smaller the pore size.

The most important feature of Fe^0 filters is the evolution of the initial porosity with the extent of volumetric expansive Fe^0 corrosion [77] and its consequence for the process of contami-

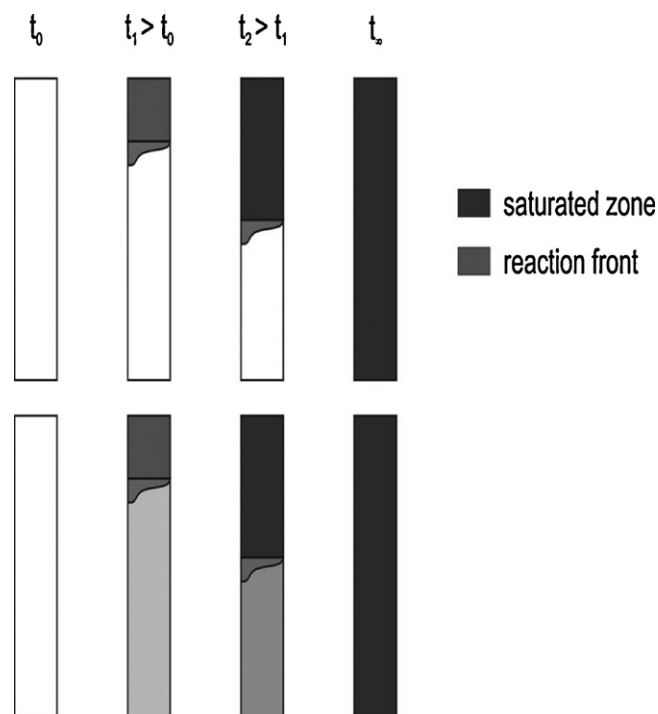


Fig. 2. Comparison of the evolution of contaminant loading in granular activated carbon (GAC – up) and Fe^0 (down) filters. The evolution of the GAC filters is virgin – preloaded (reaction front) and saturated carbon. For the Fe^0 filters a reaction front may exist due to increased O_2 in the influent but iron corrosion by H_2O (or H^+) occurs uniformly in the whole column.

nant removal. It has been shown that if a filter contents less than 50 vol.% of Fe^0 , no clogging (residual porosity = 0) will occur upon Fe^0 depletion [78]. In all the cases, a progressive diminution of pore radius will be observed. Assuming a purposeful selection of Fe^0 and sand grain size and a relevant Fe^0 volumetric ratio in a filter, the processes yielding contaminant removal in Fe^0 beds are discussed below.

4.2.3. Mechanism of contaminant removal in Fe^0 filters

In the conventional granular bed filtration (adsorptive filtration), contaminants have to be transported near the filter grains (e.g. activated carbon, metal oxide) by different transport mechanisms and then adhered to the grain surfaces by various attachment mechanisms for their successful removal [79,80]. Filtration is thus a complex process involving physico-chemical mechanisms and essentially depending on four major various factors: (i) filtration rate, (ii) media grain size, (iii) affinity of contaminant to bed media, and (iv) contaminant concentration. Depending from the media grain size and the size of the contaminant, a filtration bed may work as pure sieve (size exclusion). Size exclusion is used for example in rapid sand filtration for water clarification.

4.2.3.1. Adsorptive filtration and reactive filtration. Conventional filters contains adsorptive media (e.g. iron oxides) which are inert in water and posses a given adsorptive capacity for any contaminant. Accordingly, a contaminant breakthrough is observed when the adsorptive capacity of the material in the filter is exhausted. In a Fe^0 /sand bed on the contrary, iron oxides for contaminant adsorption are generated in-situ. Ideally, iron oxide generation through Fe^0 oxidation H_2O (or H^+) occurs uniformly in the whole bed (Fig. 2). Therefore, although a reaction front exists due to dissolve O_2 , salinity and probably contamination, virgin Fe^0 cannot be expected in a Fe^0 filter (reactive filtration). Accordingly at any date contami-

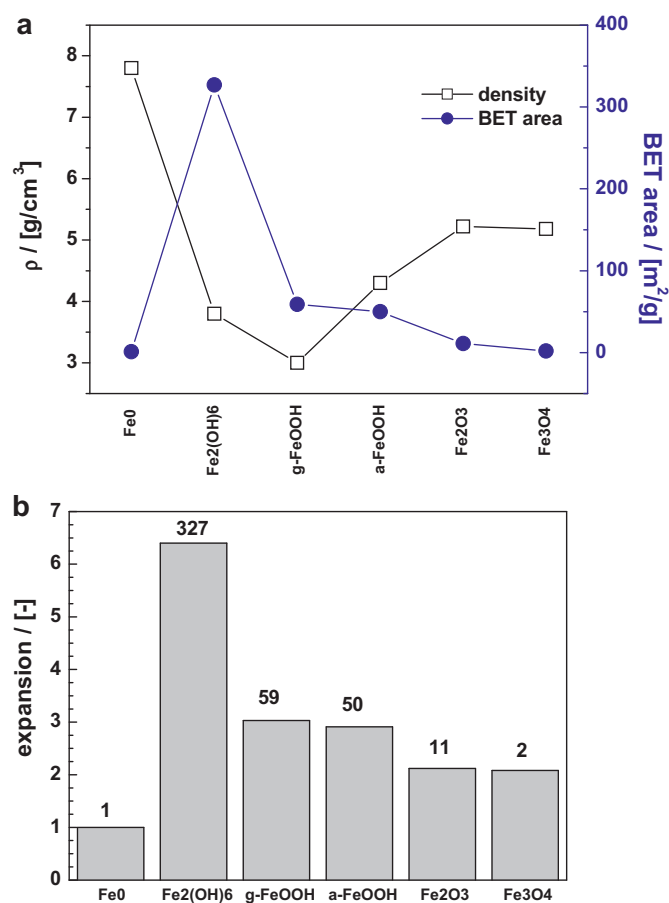
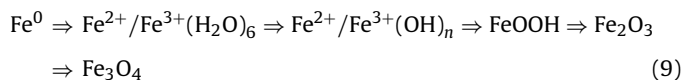


Fig. 3. Relative variation of density, specific surface area (SSA), and volume of Fe species during the process of iron corrosion. The values in (b) represent the SSA from Hanna [83]. Strictly any crystallization goes through dissolution, nucleation and aggregation. Intermediate species are of high specific area and even more voluminous than Fe₂(OH)₆.

nant removal occurs in the whole bed and iron corrosion proceeds in all three compartment of the bed. The best illustration for this is given by an experiment of Leupin and Hug [81]. The authors performed an As removal experiment with four identical filters in series containing each 1.5 g Fe⁰ and 60 g sand. The results showed that 36 L of water containing 500 μg As/L could be treated to below 50 μg/L arsenic. This performance resulted from multiple filtrations, showing that contaminant removal occurs in the whole bed. The difference between synthetic iron oxides and in-situ generated iron oxides (corrosion products) is excellently given by Sikora and Macdonald [82] and presented elsewhere in the context of safe drinking water production [33]. The further presentation will insist on the transformation of iron from its position in the metal lattice (Fe⁰) to its location in a crystallized corrosion products (e.g. FeOOH, Fe₂O₃, Fe₃O₄).

4.2.3.2. The volumetric expansion/compression cycle. The essential characteristic of a Fe⁰ filtration bed is the in-situ generation of very adsorptive iron hydroxides which are progressively transformed to amorphous and crystalline iron oxides. While filling the pore space, solid corrosion products necessarily reduce the pore radius, improving size exclusion but the most important feature is the dynamic nature of iron corrosion in the pore space (Fig. 3). Iron corrosion products could be regarded as “mercenaries” with the mission to trap contaminants in the pore space of the bed. Accordingly, contaminants should not be transported near the Fe⁰ grains to be removed.

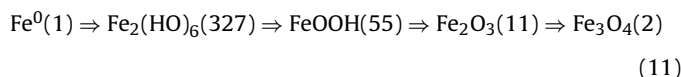
The cycle of a single atom (Fe⁰) in the process of iron corrosion can be given as follows:



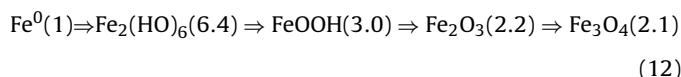
While only considering insoluble species the cycle is:



The transformation can also be represented in terms of variation of the specific surface area (SSA in m²/g – Fig. 3a). Selected representative values are given in parenthesis, Fe₂(HO)₆ stands for ferrihydrite [83].



The last alternative to represent the transformation is in terms volumetric expansion relative to Fe⁰ in the metal lattice. The coefficient of volumetric expansion given in parenthesis is equal to $V_{\text{oxide}}/V_{\text{Fe}}$ [77]. The following evolution is given (Fig. 3b):



The evolution of the surface area, the density and the coefficient of volumetric expansion clearly show that dissolved Fe first experiences an expansion than a compression. Focussing the attention on the initial stage (Fe⁰) and the final stage (FeOOH, Fe₂O₃ or Fe₃O₄) reveal an expansion which is definitively the reason for porosity loss. However, the whole dynamic process of iron corrosion should be considered. In particular, if there is not enough space for volumetric expansion, iron corrosion will stop. This is the very first argument against a 100% Fe⁰ reactive zone of 100% Fe⁰ filtration bed as used in the 3-Kolshi system [32,84,85]. Therefore, Leupin et al. [81,86] suggested the admixture of inert sand to Fe⁰ as an efficient tool to ameliorate the efficiency of iron filters. Recent calculation [78] suggested that a reactive zone with more than 60 vol.% Fe⁰ should be regarded as pure material wastage because corrosion will stop because of lack of space to proceed. It is important to notice that mixing Fe⁰ and inert materials (e.g. sand) is a prerequisite for long term reactivity (and permeability). Accordingly, the resulting economy in investment costs (costs for the corresponding 30 vol.% Fe⁰) could be regarded as beneficial side effects.

4.2.3.3. Expansion/compression cycles and contaminant removal. The transformations accompanying iron evolution from Fe⁰ to Fe^{II}/Fe^{III} in crystallized iron oxides may occurs in the presence of contaminants which may be trapped or enmeshed in the mass of corrosion products or be retained in the filter by size exclusion. The efficiency of a Fe⁰ filter for contaminant removal can be summarized in the following metaphor: *Instead of waiting for the contaminants to come to its surface, Fe⁰ injects corrosion products into the pore space for rapid and effective contaminant removal.* A further abstraction is to consider that the pore space is initially filled with porous amorphous iron hydroxides and oxides which are progressively transformed to more crystalline species.

It is important to note that the presentation above has not considered the nature of the contaminants (bacteria or virus, chemical or microbial, organic or inorganic). Accordingly, even contaminants with less adsorptive affinity to iron oxides like Mo^{VI} [87,88], will be transported in the filter by gravity and removed by pure size exclusion. Specific laboratory researches are nevertheless needed for such contaminants. These studies may check the possibility to add a layer of adequate reactive materials (e.g. MnO₂ or natural zeolite for Mo^{VI}) for the specific removal of such contaminants before or after Fe⁰ filtration.

5. The singularity of Fe⁰/H₂O systems

A natural water may contain three main types of contaminants that should be removed in any efficient treatment plant [19,43,44]: (i) chemical contaminants from natural or anthropogenic sources (organic and inorganic species), (ii) microbial contaminants which are the significant cause of water-borne diseases and is often associated with faecal matter, and (iii) physical contaminants such as taste, odour, colour, turbidity, and temperature. Physical aspects may not necessarily have any direct health effects but their presence in water may cause rejection by consumers.

5.1. A macroscopic view

Given the large array of available contaminants (charged/non-charged, negatively charged/positively negatively charged, polar/non-polar, reducible/non-reducible, small/large) the question arises how a Fe⁰/H₂O system could efficiently remove all these contaminants (at pH > 4.5). The answer is given by a profound observation of the evolution of Fe⁰ is aqueous solution, for example under anoxic conditions. Water (H₂O) is the most abundant and important oxidant and magnetite (Fe₃O₄) the main corrosion product. On the macroscopic scale, the original Fe⁰ is progressively transformed to crystalline oxides (Fe₃O₄). The original Fe⁰ surface is progressively covered by a Fe₃O₄ film. Magnetite films have a polycrystalline structure. The grain boundary diffusion coefficients of the reactant (H₂O) and products (H₂/H and Fe^{II}) moving through the corrosion film are between two and three orders of magnitude greater than the corresponding bulk diffusion coefficients. Therefore, grain boundary diffusion takes place rather than bulk diffusion ([89] and ref. therein). This is a major argument supporting the view that contaminant removal occurs within the oxide-film.

The rate-limiting step in process of Fe⁰ oxidative dissolution at pH > 4.5 being the diffusive transport of reactants and products through the layer of Fe₃O₄, the nature of the contaminant necessarily plays a secondary role. The thickness of the Fe₃O₄ film influences the inward diffusion of oxidants (H₂O, O₂, contaminants) and the outward diffusion of corrosion products (H/H₂, Fe^{II}), therefore, as the film grows, the rate of corrosion should become attenuated but also the rate of contaminant transport. Again, the nature of the contaminant is not yet addressed. Accordingly, contaminants are encapsulated within the oxide film irrespective from their intrinsic properties. It is evident that contaminants having stronger interactions with iron oxides will be sooner and stronger bounded. But chemical, microbial and physical contaminants are fundamentally removed. Properly dimensioning will certainly yield efficient water treatment. In other words, the relative affinity of contaminants for corrosion products may determine the bed thickness. To further understand the primarily unspecific nature of contaminant removal, the process or iron oxide generation will be considered on a microscopic scale.

5.2. A microscopic view

Iron oxyhydroxides (akaganeite, goethite, lepidocrocite), iron hydrous oxides (ferrihydrite, hydrohematite, maghemite) and iron oxides (hematite, magnetite) are known for their tendency to nucleate and grow on the surfaces of other phases [90]. In nature iron is leached as Fe^{II} from iron minerals (e.g. pyrite), nucleates and grows as Fe phases on the available surfaces. In an engineered Fe⁰/H₂O system, Fe^{II} is generated by the oxidative dissolution of Fe⁰, nucleation and growth occur at the Fe⁰ surface, the external or internal surface in-situ generated Fe phases (oxide scale) or the surface of additive materials (sand, pumice) [91].

At neutral pH (7.0) and under anoxic conditions, leached Fe^{II} has a relatively high solubility. The saturation concentration of the Fe^{II} species approaches 0.5 M (28 g/L) at room temperature. However, dissolved Fe concentrations drop below 10⁻¹² M (5.6 × 10⁻¹¹ g/L) if Fe^{II} is polymerized e.g. [Fe(OH)₂]_n or oxidized to Fe^{III} species [92]. This reaction results in the precipitation of Fe phases. Fe^{III} species (and Fe phases) can also form under anoxic conditions, for example, when water contents oxidizing species like NO₃⁻ or MnO₂. Fe^{II} oxidation and Fe phase formation is often catalyzed by microorganisms.

Fe^{III} phases which form from solution begin as small clusters that evolve into larger polymeric units with time, eventually reaching colloidal sizes [93]. Aggregation and/or crystal growth are necessarily coupled to the decrease in surface energy. All these processes occur millions of times in a Fe⁰ filter and in the presence of contaminants. As shown above contaminants are constrained to move to the oxide films of porous iron. Despite possible low affinity to the oxide film, contaminant could be retained by size exclusion. This size exclusion also happens hundreds of times in a Fe⁰ filters. Contaminants escaping in the entrance zone are possibly entrapped deeper in the filter. This argument supports the assertion that thicker beds will be necessary to satisfactorily remove contaminants with poor affinity to iron oxides.

5.3. Reactive filtration on Fe⁰ beds

The presentation above has strengthened the view that the efficiency of Fe⁰ filters is due to the progressive production of very reactive Fe phases that are in-situ further transformed. Accordingly, unlike in iron-coated system where the capacity of used iron oxides can be evaluated, a Fe⁰ filter is a system producing very reactive Fe⁰ which is in-situ transformed to less reactive comparable to coated ones. The less reactive species are comparative to coating but contaminants are removed during their formation.

6. Filter and plant design

6.1. Filter design

Fe⁰ filtration beds should remove trace amounts of chemical contaminants and pathogens from raw water to produce safe drinking water. The filter efficiency depends upon the purposeful selection of a reactive medium (Fe⁰) and the water flow velocity. The water flow velocity will depend on the intrinsic reactivity of Fe⁰ as the residence time should correspond to the time necessary to produce enough iron corrosion for contaminant removal by (i) adsorption, (ii) co-precipitation and (iii) size exclusion.

It should be explicitly said that the goal should never be to select (or manufacture) the most reactive material but a material which is reactive enough to produce enough water for the community in need within a reasonable time. For example, a Fe⁰ material that is not reactive enough for a water plant in Freiberg (Sachsen) or Krebeck in Germany could be satisfactorily for a plant in a tropical village in Indonesia, Malawi, Nigeria, Peru, Senegal or Zambia. Nevertheless having readily reactive materials has the advantage to offer a flexibility in selecting the amount to be used in individual cases. For example, only 35 vol.% of a very reactive material could be used under tropical conditions and up to 55 vol.% under temperate conditions. Varying the reactivity of Fe⁰ materials by varying their particle size from fine powders to large granules and chips will be a tool in optimising filtration efficiency.

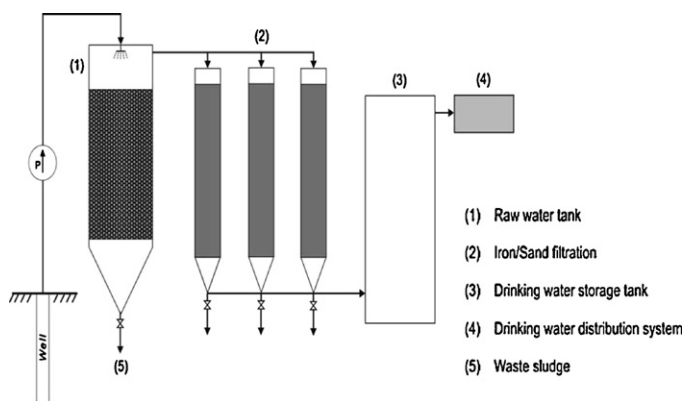


Fig. 4. Schematic diagram of a treatment plant. Media filtration can be performed before storage (raw water). Raw water is then filtered in Fe^0 filters and the filtrates are collected and stored in a drinking water tank for distribution.

6.2. Plant design

A water treatment plant based on Fe^0 bed filtration is very simple and similar to slow sand filtration for small communities. The simplest device is a single column containing layers of: (i) gravel and sand for water clarification (media filtration) and (ii) Fe^0 :sand for water treatment (reactive filtration). This device is similar to household Fe^0 -based SONO filters [30,94] which have been reported to function for more than five years. The long-term efficiency of SONO filters is certainly due to the porous nature of used composites. In fact, using non-porous Fe^0 was efficient but not sustainable [94] and mixing non-porous Fe^0 with inert materials has been theoretically [39] and experimentally [91] proven to sustain Fe^0 efficient filtration.

In the first stage, a good target for Fe^0 communities filters could be to design a filter which could be efficient for 12 months using locally available Fe^0 materials, e.g. construction steel. For larger communities, a device might comprise one or two sand filters (media filtration) and one or several iron filters (reactive filtration) in series (Figs. 1 and 4). A practical suggestion from experiences with 3-Kolshi filters in Bangladesh is to make small filters with 20 L/h flow and connect several in parallel to scale-up (Husam 2010, personal communication). For example if 100 L drinking water should be produced each hour (2400 L/day), 5 such small filters should be used in parallel (Fig. 4). The production plan may comprise a total of 25 small filters to assure continuous water production. Some filters could be fixed while others worked, for example for maintenance, repair or Fe^0 replacement.

Water for filtration could be first collected or pumped in a tank. Raw water is possibly chemically and microbially contaminated. Raw water is filtered through the Fe^0 /sand bed and contaminants are removed by several mechanisms including adsorption, co-precipitation, precipitation, size exclusion, volatilization and combinations thereof. Filtered water could be stocked in a tank for distribution. In pilot plans for large communities several sets of raw water/drinking water tanks should be linked by various embodied filtration beds (Fig. 5).

7. The economics of Fe^0 /sand beds

Fe^0 bed filtration as stand-alone remediation technology has already been proven affordable both at household [30,31,36] and at community [12,37,38] level. The costs are further reduced by admixing Fe^0 with inert materials [39,91] and eliminating some technical steps as discussed in Section 1.1. Accordingly the presentation will be limited in discussing the economics of Fe^0 beds for a small community.

Cost is a major factor in implementing Fe^0 filtration technologies and is necessarily site-specific. Factors determining water treatment cost in Fe^0 beds include: (i) the quality of freshwater, (ii) plant capacity, and (iii) construction costs. The realistic costs of Fe^0 /sand filters given by Gottinger [12] could be adopted here. The estimation is based on the evidence Fe^0 is the sole material to be bought. In Canada, Fe^0 filings can currently be obtained for under \$1.50/kg (1.12€/kg). The cost of manufacturing Fe^0 /sand filter is comparable to a biological activated carbon filter. The service life of a Fe^0 /sand filter (50 vol.% Fe^0) was estimated to be approximately 40 months (3.3 years) [12]. This yield to a treatment cost of <0.01\$/L (<0.01€/L) and includes filter installation, media, operation and maintenance costs.

It is not likely that any water treatment process addressing both chemical and microbial contamination could be cheaper than the one presented here. Calculations made for a model village in South Africa (125 inhabitants, 40 L water/person/day or 5000 L/day) showed that 200 kg Fe^0 could be sufficient to produce safe drinking water for 3 years. The cost for the 200 kg Fe^0 is only 224€. For comparison, a disinfection system recently presented as affordable for rural South Africa [11] has a capital cost of 900 R (82€) for the same population size, the monthly running cost for disinfection was up to 150 R (1800 R/year or 5400 R for 3 years, that is 570€ for 3 years). Thereby disinfection by chlorination has been proven harmful for humans [95–99]. This comparison confirms that Fe^0 /sand filtration beds represent an efficient and economically feasible option for safe drinking water production for small-scale utilities.

8. Concluding remarks

Fe^0 /sand filtration is an affordable technology for safe drinking water production at various scales: household, rural establishments (clinics, forestry stations, hospitals, hotels, schools), and small or large communities. Fe^0 /sand filtration is the ideal technology for remote villages in the developing world. Here inhabitants may lack money to purchase industrially manufactured Fe^0 (no income) but they possess the ancestral iron-making technology [100,101]. However, manufactured materials should be tested for reactivity and rural populations should be trained for filter design. It could be anticipated that, self produced safe drinking water will increase the self-confidence of these populations and contribute to reduce rural exodus. On the other hand the development and the implementation of the technology worldwide will render travel with bottle water superfluous. Moreover, Fe^0 /sand filters/beds are excellent candidates for safe drinking water in emergency situations (e.g. earthquakes, wars, tsunami) [78].

Fe^0 /sand filtration is equally a feasible option to successfully remove all target compounds from surface and groundwater: particles, natural organic matter, pathogens and micro-pollutants (including so-called emerging contaminants). Therefore, efforts should be made to use this chemical-free technology as the first choice everywhere. It could be expected that using Fe^0 /sand filtration as standard technology will be very beneficial for water works as iron oxides (the products of iron corrosion) are easy to recycle to Fe^0 . However, given the large spectrum of toxic substances enmeshed in the mass of corrosion products, the recycling task should be carefully addressed. In particular used household filter should be collected and professionally disposed (or recycled). This approach has the great advantage to control filter residue in regions where water is contaminated by toxic species like arsenic or uranium. On the other hand, recycling Fe -based materials (not only filter residues) for Fe^0 production will generate incomes in developing country while protecting the environment.

The probably strongest argument for the development of Fe^0 /sand filtration technology is the simplicity of the system. One

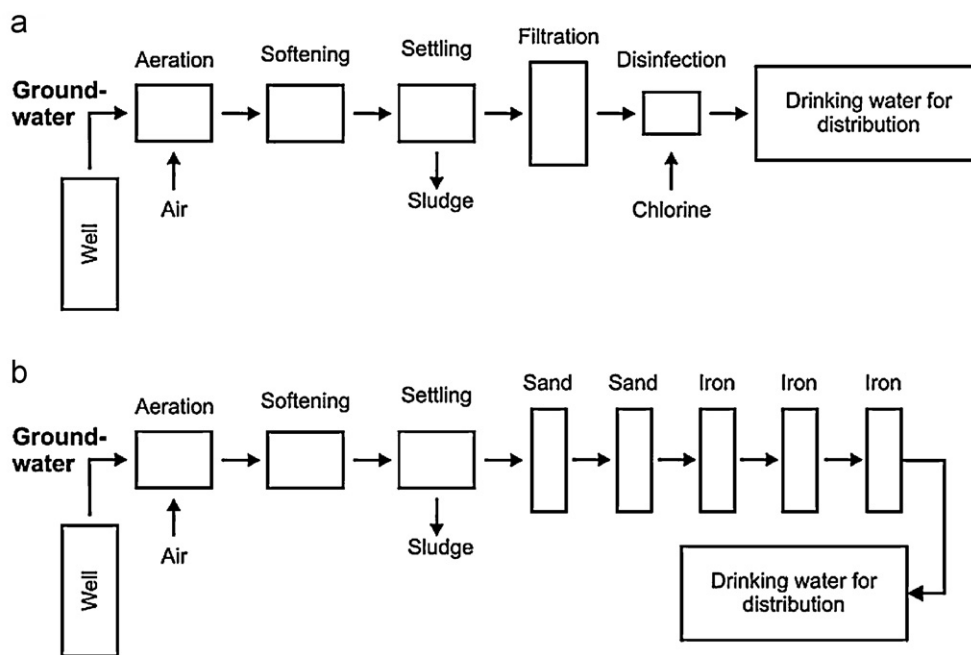


Fig. 5. Comparison of the processes of groundwater treatment in a conventional treatment plant and by Fe^0 beds. The number of sand and iron columns is arbitrary and does not reflect the actual configuration (parallel or series). Modified after Refs. [41,103].

should not care in parallel for membranes, granular activated carbon and chemicals (including disinfectants) but only on the stock of iron and sand, and the regeneration of the former. Finally, it can be speculated the success of the Fe^0 /sand technology for safe drinking water production will depend on the capacity of researchers to create new reactive Fe^0 materials and their capacity to find ways to control material reactivity in an affordable way.

Currently, there is an ongoing discussion on the suitability of localized solutions for safe drinking water production [102–104]. In the developed world, decentralized drinking water production units are progressively regarded as an efficient alternative to centralized production systems. This approach is discussed in analogy to the energy (and the communication) sector where decentralization has raised a surge in innovations and new market opportunities for a host of new and established companies [104]. In a similar way it could be expected that localized water treatment would produce new jobs, businesses, economic development, and quality of life. Efficient and affordable technologies for decentralized water treatment are needed to sustain the decentralization argumentation. The present communication and related works [12,33,39–41] have presented Fe^0 bed filtration as a serious candidate to be systematically assessed.

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