

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, an flexible technology for the whole world.

26 **Keywords:** Contaminant removal, Conventional treatment, Iron bed, Media filtration,
27 Reactive filtration, Zerovalent iron.

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

40

Jacques Ellul 1954 [1]

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43 **1 Introduction**

44 Universal access to safe drinking water is a challenge to the scientific community to which
45 the responsibility is incumbent on developing appropriate technologies. Safe drinking water
46 must be globally available, e.g. drinking water for (i) citizens in all cities, (ii) holiday-makers
47 and tourists in Bamena (Cameroon), Dighali (Bangladesh), or Fuheis (Jordan), and (iii)
48 villagers in small communities worldwide. Adequate infrastructures for safe drinking water
49 production certainly exist in most cities and in hotels for holiday-makers and tourists. In
50 general, it can be roughly considered that water infrastructure is well developed in urban areas
51 as opposed to rural areas where the infrastructure is either poorly developed or non-existent.
52 Accordingly, the population to be urgently deserved with safe drinking water is the rural one
53 [2-4].

54 Rural communities are not similar in their size, technical equipment and geographic
55 distribution [5-11]. For example, in the Republic of South Africa close to five million people
56 live in widely scattered remote small rural communities of often less than 100 people [11].
57 Similarly, areas of small island countries in the Pacific Ocean are made up of hundreds of
58 scattered islands inhabited by few people [8,9]. In the developed world, it is a well-known
59 fact that small and remote communities often lack adequate technical, managerial, and
60 financial capacity for safe drinking water production [6,12,13]. For example, around 2003,
61 there were about 1,000 small municipal drinking water utilities in the Province of Quebec
62 (Canada) whose waters were reported to frequently violate the provincial drinking water
63 standards [6].

64 In many rural communities in the developing world, most people do not have paid
65 employment. As a rule, any income comes from kindred in the family network that have jobs
66 in the city or abroad. Most people live a sustainable agricultural, fishing or hunting existence
67 and this paradigm of living results in little global influence [8,9,14]. However, global issues
68 do impact on the villages, as their water is potentially contaminated with various imported

69 manufactured substances including fertilizers, heavy metals, herbicides, insecticides, and
70 pharmaceuticals [15,16]. Despite billions of dollars in aid, technology transfer, and local
71 spending, inadequate progresses have been made in recent years in improving access to safe
72 drinking water in the developing world [8]. It is presently not certain, whether the United
73 Nations Millennium Development Goal of "halving by 2015, the proportion of people without
74 sustainable access to safe drinking water" in 1990 will be achieved [17,18]. Even upon
75 achievement, present technologies may still leave up to 600 million people without access to
76 safe water in 2015 [4,19].

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

85 **1.1 Metallic iron in drinking water treatment plants**

86 The last two decades have witnessed the establishment of Fe^0 as a powerful water remediation
87 material for several classes of pollutants [21-25]. Fe^0 is currently used in groundwater
88 remediation and wastewater treatment [25-29], and drinking water production at household
89 level [30-36]. Despite existing patents on water treatment using Fe^0 in treatment plants
90 [12,37,38], no concept comparable to the one presented here could be found. The process of
91 Meng and Korfiatis [38] involves at least two other technical issues: (i) a vibration device to
92 increase filtration efficiency in Fe^0 beds and (ii) the addition of oxidizing agents or coagulants
93 to enhance the filtration efficiency in sand beds. The process of Santina [37] termed as
94 "sulfur-modified iron" uses finely-divided Fe^0 in the presence of powdered S^0 (or MnS),

95 followed by an oxidation step. The technical issues in both processes could cause managerial
96 shortness in small communities. The chemical-free process for arsenic removal using a
97 Fe^0 /sand filter presented by Gottinger [12] is closer to the one presented here. However,
98 Gottinger's invention is a pragmatic one and is theoretically designed for As only.

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

113 **2. Characteristics of drinking water sources**

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

118 It is universally acknowledged that the greatest risks of waterborne disease are from
119 pathogens. The microbial risk is mostly due to water contamination by human and/or animal
120 feces [4,42-44]. The existence and dangers of pathogenic microbes in surface waters have

121 been recognized for more than a century [45]. On the contrary, groundwaters (e.g. wells and
122 springs) are naturally protected against contamination by pathogenic microbes. The protection
123 is attributed to the filtration properties of subsurface soils and geologic strata. Accordingly
124 groundwaters are generally less charged with pathogens [45,46].

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

133 Salinity is a general term used to describe the levels of different salts such as sodium chloride,
134 magnesium and calcium sulfates, and bicarbonates. The salinity (or hardness) of fresh waters
135 is generally due to calcium and magnesium and may take values of up to 300 mg/L as CaCO_3
136 [47]. The salinity is primarily a measure of ionic conductivity of a water and thus is important
137 for sustaining aqueous Fe^0 corrosion (transport of Fe^{2+} from anodic sites).

138 The pH value is the most important characteristic of natural waters for the treatment with Fe^0 .
139 As a rule, Fe^0 oxidative dissolution yields soluble Fe^{II} and Fe^{III} species at $\text{pH} < 4.0 - 4.5$ and
140 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
141 possible at $\text{pH} > 4.5$. [33] The pH value of natural waters may range from 6 to 10 [47].
142 Accordingly, dissolved iron precipitates as hydroxides or/and oxides in the vicinity of the Fe^0
143 surface forming an initially porous oxide film. Variations in pH can change both the surface
144 charge distribution of iron hydroxides/oxides and the ionization of weak acid or bases (pKa
145 values), including DOM with various functional groups in its structure. The pH value can also
146 impact the conformation of DOM components, and thus their adsorption onto the oxide scale

147 on Fe^0 . Finally, if water is contaminated by metals and metalloids, their speciation, their
148 complex formation tendency, solubility and thus affinity to iron oxides is strongly pH
149 dependant.

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

160 **3 Metallic iron for drinking water treatment**

161 Metallic iron is an emergent reactive material increasingly used for water treatment [25,29,
162 33,36]. Fe^0 is the most used reactive material in subsurface permeable reactive barriers
163 [29,34,58]. It was originally used to remove redox-sensitive contaminants from groundwater
164 [26,27,58-60]. It is commonplace to consider that the bare Fe^0 surface reacts with the
165 contaminants and converts them into non-toxic/less toxic species (Assumption 1). The
166 validity of Assumption 1 automatically degrades all other reducing agents (co-reductants) to
167 side-reductants. Co-reactants are primarily dissolved and adsorbed Fe^{II} and H/H_2 . Assumption
168 1 further requires that the Fe^0 surface must be accessible. Accordingly, the universal film on
169 Fe^0 is regarded as inhibitive for the process of contaminant reduction or reductive removal.
170 The assumed inhibitive characteristic of the oxide film coupled to the large variation in the
171 reactivity of used iron fillings (micro-scale Fe^0) were amount the major reasons to introduce
172 nano-scale Fe^0 [61,62], and bimetallic materials [63,64]. Nano-scale Fe^0 has been reported to

173 have the potential to overcome these two problems. In fact, both the initial rates and the extent
174 of contaminant reduction per mole of Fe^0 is increased. However, despite infinitesimally small
175 size, nano-scale Fe^0 will also be covered by an oxide film such that expected, observed and
176 reported increase reactivity is not necessarily coupled to direct reduction by Fe^0 (electrons
177 from Fe^0).

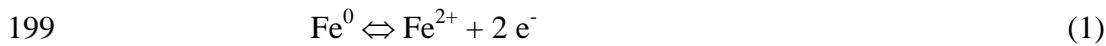
178 It has already been demonstrated that the oxide film on Fe^0 is beneficial for the process of
179 contaminant removal [51-54,65]. In fact, the oxide film acts as contaminant scavenger and the
180 contaminant may be further chemically transformed (oxidized or reduced if applicable).

181 The presentation above clearly disprove the validity of Assumption 1 and corroborates results
182 from other branches of science that iron corrosion is always coupled to oxide film formation
183 at $\text{pH} > 4.5$. Iron corrosion continues under the film because the film is porous and permeable
184 to water and other oxidizing agents [51,52,65-68]. More importantly, using Fe^0 to assist sand
185 filtration does not aim at inducing reductive transformations of contaminants, but to use the
186 process of iron corrosion and the adsorptive properties of in situ generated iron oxides to
187 sustain the filtration process. In other words, in Fe^0 filters, Fe^0 is oxidized by H_2O and
188 corrosion products are used as trap for contaminants which could be chemically transformed.
189 Depending on their nature and concentration, selected contaminants may influence (inhibit or
190 sustain) the process of iron corrosion. For example, it is well-established that the
191 incorporation of a cation into the structure of iron (oxyhydr)oxides alters the nucleation,
192 crystal growth, and transformation [69]. This impact of the alteration on the further iron
193 corrosion should be carefully characterized in laboratory and field investigations.

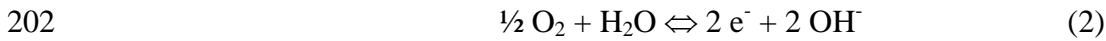
194 **4 Mechanism of contaminant removal in Fe^0 filters**

195 **4.1 Aqueous iron corrosion**

196 Immersed reactive Fe^0 corrodes due to differences in the electrical potential on anodic and
197 cathodic sites on the Fe^0 surface [70,71]. The metal oxidizes at the anode, where corrosion
198 occurs according to equation 1:

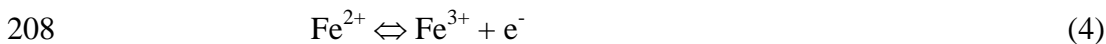


200 Simultaneously, a reduction reaction occurs at cathodic sites. The typical cathodic processes
201 are:



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

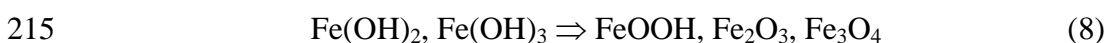
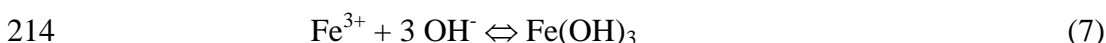
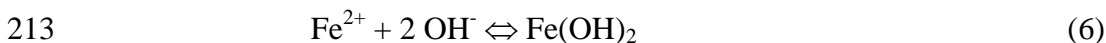
206 Fe^{2+} ions from Eq. 1 might be further oxidized (e.g. by O_2 , MnO_2 or contaminants like CrO_4^{2-})
207 to Fe^{3+} ions according to equation 4:



209 On the other hand, Fe^{3+} from Eq. 4 is an oxidizing agent for Fe^0 (Eq. 5):



211 Lastly, generated Fe^{2+} and Fe^{3+} will form hydroxides according to equations 6 and 7 and the
212 hydroxides will be progressively transformed to amorphous and crystalline oxides (Eq. 8):



216 It is important to recall that, regardless from the size of the material, the formation and
217 transformation of an oxide scale on Fe^0 is an universal process (at $\text{pH} > 4.5$). Accordingly, the
218 propensity of any Fe^0 to aqueous corrosion is influenced by the nature of the oxide scale on its
219 surface. The initial oxide scale is porous and permeable but may be transformed to an
220 impervious layer mainly depending on the water chemistry [72]. In other words, an oxide
221 scale begins to form immediately after Fe^0 immersion and may facilitate or hinder corrosion,
222 serving either as a barrier or as a path for ion exchange with the pore solution in the Fe^0 filter.

223 It is also important to notice that the reactions after equations 2 through 8 are considered as
224 side reactions in the discussion of the process of contaminant reductive transformation by Fe^0
225 (Fe^0 is ideally oxidized by the contaminant). This simplification is not acceptable for at least
226 two reasons: (i) even though a contaminant (e.g. Cr^{VI}) may be a stronger oxidizing agent for
227 Fe^0 than Fe^{3+} , H^+ and O_2 , H_2O (H^+) is present in very large stoichiometric abundance; (ii)
228 even if the universal oxide scale is considered as a path for contaminant transport, it is a
229 reactive path containing species (e.g. adsorbed Fe^{II}) which are sometimes more powerful
230 reducing agents than Fe^0 [73]. The next section discuss the mechanism of contaminant
231 removal in Fe^0 filters.

232 **4.2 Mechanistic aspects of contaminant removal in Fe^0 filters**

233 **4.2.1 Contaminant removing processes**

234 Adsorption is characterized by the accumulation of substances at the interface between two
235 phases (e.g. solid/liquid) due to chemical and physicochemical interactions. The solid on
236 which adsorption occurs is called the adsorbent. In a $\text{Fe}^0/\text{H}_2\text{O}$ system, there are theoretically
237 several adsorbents including Fe^0 , $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, FeOOH , Fe_3O_4 , Fe_2O_3 , and green rust.
238 However, apart from Fe^0 and well crystallized phases (Fe_2O_3 , Fe_3O_4), all other solid phases
239 are in transformation. During the precipitation of Fe phases contaminants can be enmeshed.
240 Whether precipitates are pure phases or not, there is no defined surface on which an inflowing
241 contaminants could adsorb.

242 The transport of any contaminant (chemical, microbial and physical) in a Fe^0 filter is
243 primarily controlled by its physico-chemical characteristics, the composition of the water, the
244 characteristics of available adsorbents, and the water flow velocity. Two key contaminant
245 characteristics are size and surface electrostatic properties. Key properties of Fe^0 beds include
246 water flow velocity which is coupled to pore size distribution, temperature, pH, and
247 chemical/mineral composition of water. From a pure physical perspective, contaminant size,
248 bed porosity and relative surface electrical properties of Fe species and contaminants are the

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

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

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

270 **4.2.2 Bed porosity and porosity loss**

271 A Fe^0 filtration bed is composed of one or several reactive zones of granular sand and Fe^0
272 particles (Fig. 1). The compact Fe^0 :sand mixture has a random porous structure. The manner
273 with which the pore space is formed depends mainly on the arrangement of the granular
274 particles [75,76]. While packing uniform spheres, the least compact and most compact

275 arrangements are rhombohedral and cubic respectively. The pore size can be defined in terms
276 of a length dimension (pore radius). Pore size in a packed bed is closely related with the size
277 of the filter grains constituting the bed (e.g. Fe⁰ and sand). The smaller the grains, the smaller
278 the pore size.

279 The most important feature of Fe⁰ filters is the evolution of the initial porosity with the extent
280 of volumetric expansive Fe⁰ corrosion [77] and its consequence for the process of contaminant
281 removal. It has been shown that if a filter contains less than 50 vol-% of Fe⁰, no clogging
282 (residual porosity = 0) will occur upon Fe⁰ depletion [78]. In all the cases, a progressive
283 diminution of pore radius will be observed. Assuming a purposeful selection of Fe⁰ and sand
284 grain size and a relevant Fe⁰ volumetric ratio in a filter, the processes yielding contaminant
285 removal in Fe⁰ beds are discussed below.

286 **4.2.3 Mechanism of contaminant removal in Fe⁰ filters**

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

296 **4.2.3.1 Adsorptive filtration and reactive filtration**

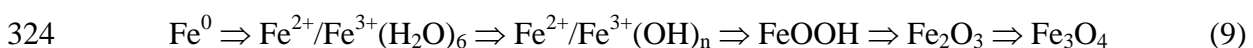
297 Conventional filters contain adsorptive media (e.g. iron oxides) which are inert in water and
298 possess a given adsorptive capacity for any contaminant. Accordingly, a contaminant
299 breakthrough is observed when the adsorptive capacity of the material in the filter is
300 exhausted. In a Fe⁰/sand bed on the contrary, iron oxides for contaminant adsorption are

301 generated in-situ. Ideally, iron oxide generation through Fe^0 oxidation H_2O (or H^+) occurs
 302 uniformly in the whole bed (Fig. 2). Therefore, although a reaction from exists due to dissolve
 303 O_2 , salinity and probably contamination, virgin Fe^0 can not be expected in a Fe^0 filter
 304 (reactive filtration). Accordingly at any date contaminant removal occurs in the whole bed
 305 and iron corrosion proceeds in all three compartment of the bed. The best illustration for this
 306 is given by a experiment of Leupin and Hug [81]. The authors performed an As removal
 307 experiment with four identical filters in series containing each 1.5 g Fe^0 and 60 g sand. The
 308 results showed that 36 L of water containing 500 μg As/L could be treated to below 50 μg /L
 309 arsenic. This performance resulted from multiple filtrations, showing that contaminant
 310 removal occurs in the whole bed. The difference between synthetic iron oxides and in-situ
 311 generated iron oxides (corrosion products) is excellently given by Sikora and Macdonald [82]
 312 and presented elsewhere in the context of safe drinking water production [33]. The further
 313 presentation will insist on the transformation of iron from its position in the metal lattice (Fe^0)
 314 to its location in a crystallized corrosion products (e.g. FeOOH , Fe_2O_3 , Fe_3O_4).

315 **4.2.3.2 The volumetric expansion/compression cycle**

316 The essential characteristic of a Fe^0 filtration bed is the in-situ generation of very adsorptive
 317 iron hydroxides which are progressively transformed to amorphous and crystalline iron
 318 oxides. While filling the pore space, solid corrosion products necessarily reduce the pore
 319 radius, improving size exclusion but the most important feature is the dynamic nature of iron
 320 corrosion in the pore space (Fig. 3). Iron corrosion products could be regarded as
 321 “mercenaries” with the mission to trap contaminants in the pore space of the bed.
 322 Accordingly, contaminants should not be transported near the Fe^0 grains to be removed.

323 The cycle of a single atom (Fe^0) in the process of iron corrosion can be given as follows:



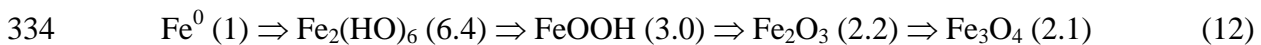
325 While only considering insoluble species the cycle is:



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



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



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

349 **4.2.3.3 Expansion/compression cycles and contaminant removal**

350 The transformations accompanying Fe⁰ transformation to crystallized iron oxides may occurs
351 in the presence of contaminants which may be trapped or enmeshed in the mass of corrosion
352 products or be retained in the filter by size exclusion. The efficiency of a Fe⁰ filter for

353 contaminant removal can be summarized in the following metaphor: *Instead of waiting for the*
354 *contaminants to come to its surface, Fe⁰ injects corrosion products into the pore space for*
355 *rapid and effective contaminant removal.* A further abstraction is to consider that the pore
356 space is initially filled with porous amorphous iron hydroxides and oxides which are
357 progressively transformed to more crystalline species.

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

365 **5 The singularity of Fe⁰/H₂O systems**

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

373 **5.1 A Macroscopic view**

374 Given the large array of available contaminants (charged/non-charged, negatively
375 charged/positively negatively charged, polar/non-polar, reducible/non-reducible, small/large)
376 the question arises how a Fe⁰/H₂O system could efficiently remove all these contaminants (at
377 pH > 4.5). The answer is given by a profound observation of the evolution of Fe⁰ in aqueous
378 solution, for example under anoxic conditions. Water (H₂O) is the most abundant and

379 important oxidant and magnetite (Fe_3O_4) the main corrosion product. On the macroscopic
380 scale, the original Fe^0 is progressively transformed to crystalline oxides (Fe_3O_4). The original
381 Fe^0 surface is progressively covered by a Fe_3O_4 film. Magnetite films have a polycrystalline
382 structure. The grain boundary diffusion coefficients of the reactant (H_2O) and products (H_2/H
383 and Fe^{II}) moving through the corrosion film are between two and three orders of magnitude
384 greater than the corresponding bulk diffusion coefficients. Therefore, grain boundary
385 diffusion takes place rather than bulk diffusion ([89] and ref. therein). This is a major
386 argument supporting the view that contaminant removal occurs within the oxide-film.

387 The rate-limiting step in process of Fe^0 oxidative dissolution at $\text{pH} > 4.5$ been the diffusive
388 transport of reactants and products through the layer of Fe_3O_4 , the nature of the contaminant
389 necessarily plays a secondary role. The thickness of the Fe_3O_4 film influences the inward
390 diffusion of oxidants (H_2O , O_2 , contaminants) and the outward diffusion of corrosion products
391 (H/H_2 , Fe^{II}), therefore, as the film grows, the rate of corrosion should become attenuated but
392 also the rate of contaminant transport. Again, the nature of the contaminant is not yet
393 addressed. Accordingly, contaminants are encapsulated within the oxide film irrespective from
394 their intrinsic properties. It is evident that contaminants having stronger interactions with iron
395 oxides will be sooner and stronger bounded. But chemical, microbial and physical
396 contaminants are fundamentally removed. Properly dimensioning will certainly yield efficient
397 water treatment. In other words, the relative affinity of contaminants for corrosion products
398 may determine the bed thickness. To further understand the primarily unspecific nature of
399 contaminant removal, the process of iron oxide generation will be considered on a
400 macroscopic scale.

401 **5.2 A Microscopic view**

402 Iron oxyhydroxides (akaganeite, goethite, lepidocrocite), iron hydrous oxides (ferrihydrite,
403 hydrohematite, maghemite) and iron oxides (hematite, magnetite) are known for their
404 tendency to nucleate and grow on the surfaces of other phases [90]. In nature iron is leached

405 as Fe^{II} from iron minerals (e.g. pyrite), nucleates and grows as Fe phases on the available
406 surfaces. In a engineered Fe⁰/H₂O system, Fe^{II} is generated by the oxidative dissolution of
407 Fe⁰, nucleation and growth occur at the Fe⁰ surface, the external or internal surface in-situ
408 generated Fe phases (oxide scale) or the surface of additive materials (sand, pumice) [91].

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

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

425 **5.3 Reactive filtration on Fe⁰ beds**

426 The presentation above has strengthened the view that the efficiency of Fe⁰ filters is due to the
427 progressive production of very reactive Fe phases that are in-situ further transformed.
428 Accordingly, unlike in iron-coated system where the capacity of used iron oxides can be
429 evaluated, a Fe⁰ filter is a system producing very reactive Fe⁰ which is in-situ transformed to

430 less reactive comparable to coated ones. The less reactive species are comparative to coating
431 but contaminants are removed during their formation.

432 **5. Filter and plant design**

433 **5.1 Filter design**

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

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

450 **5.2 Plant design**

451 A water treatment plant based on Fe⁰ bed filtration is very simple and similar to slow sand
452 filtration for small communities. The simplest device is a single column containing layers of:
453 (i) gravel and sand for water clarification (media filtration) and (ii) Fe⁰:sand for water
454 treatment (reactive filtration). This device is similar to household Fe⁰-based SONO filters
455 [30,94] which have been reported to function for more than five years. The long-term

456 efficiency of SONO filters is certainly due to the porous nature of used composites. In fact,
457 using non-porous Fe⁰ was efficient but not sustainable [94] and mixing non-porous Fe⁰ with
458 inert materials has been theoretically [39] and experimentally [91] proven to sustain Fe⁰
459 efficient filtration.

460 In the first stage, a good target for Fe⁰ communities filters could be to design a filter which
461 could be efficient for 12 months using locally available Fe⁰ materials, e.g. construction steel.
462 For larger communities, a device might comprises one or two sand filters (media filtration)
463 and one or several iron filters (reactive filtration) in series (Fig. 1, Fig. 4). A practical
464 suggestion from experiences with 3-Kolshi filters in Bangladesh is to make small filters with
465 20 L/h flow and connect several in parallel to scale-up (Hussam 2010, personal
466 communication). For example if 100 L drinking water should be produce each hour (2400
467 L/day), 5 such small filters should be used in parallel (Fig. 4). The production plan may
468 comprise a total of 25 small filters to assure continuous water production. Some filters could
469 be fixed while others worked, for example for maintenance, reparation or Fe⁰ replacement.

470 Water for filtration could be first collected or pumped in a tank. Raw water is possibly
471 chemically and microbially contaminated. Raw water is filtered through the Fe⁰/sand bed and
472 contaminants are removed by several mechanisms including adsorption, co-precipitation,
473 precipitation, reduction, size exclusion and combinations thereof. Filtered water could be
474 stocked in a tank for distribution. In pilot plans for large communities several sets of raw
475 water/drinking water tanks should be linked by various embodied filtration beds (Fig. 5).

476 **6 The economics of Fe⁰/sand beds**

477 Fe⁰ bed filtration as stand-alone remediation technology has already been proven affordable
478 both at household [30,31,36] and at community [12,37,38] level. The costs are further reduced
479 by admixing Fe⁰ with inert materials [39,91] and eliminating some technical steps as
480 discussed in section 1.1. Accordingly the presentation will be limited in discussing the
481 economics of Fe⁰ beds for a small community.

482 Cost is a major factor in implementing Fe⁰ filtration technologies and is necessarily site-
483 specific. Factors determining water treatment cost in Fe⁰ beds include: (i) the quality of
484 freshwater, (ii) plant capacity, and (iii) construction costs. The realistic costs of Fe⁰/sand
485 filters given by Gottinger [12] could be adopted here. The estimation is based on the evidence
486 Fe⁰ is the sole material to be bought. In Canada, Fe⁰ filings can currently be obtained for
487 under \$1.50 / kg (1.12 €/kg). The cost of manufacturing Fe⁰/sand filter is comparable to a
488 biological activated carbon filter. The service life of a Fe⁰/sand filter (50 vol-% Fe⁰) was
489 estimated to be approximately 40 months (3.3 years) [12]. This yield to a treatment cost of <
490 0.01 \$/L (< 0.01 €/L) and includes filter installation, media, operation and maintenance costs.
491 It is not likely that any water treatment process addressing both chemical and microbial
492 contamination could be cheaper than the own presented here. Calculations made for a model
493 village in South Africa (125 inhabitants, 40 L water/person/day or 5,000 L/day) showed that
494 200 kg Fe⁰ could be sufficient to produce safe drinking water for 3 years. The cost for the 200
495 kg Fe⁰ is only 224 €. For comparison, a disinfection system recently presented as affordable
496 for rural South Africa [11] has a capital cost of 900 R (82 €) for the same population size, the
497 monthly running cost for disinfection was up to 150 R (1,800 R/year or 5,400 R for 3 years,
498 that is 570 € for 3 years). Thereby disinfection by chlorination has been proven harmful for
499 humans [95-99]. This comparison confirms that Fe⁰/sand filtration beds represent an efficient
500 and economically feasible option for safe drinking water production for small-scale utilities.

501 **7 Concluding remarks**

502 Fe⁰/sand filtration is an affordable technology for safe drinking water production at various
503 scales: household, rural establishments (clinics, forestry stations, hospitals, hotels, schools),
504 and small or large communities. Fe⁰/sand filtration is the ideal technology for remote villages
505 in the developing world. Here inhabitants may lack money to purchase industrially
506 manufactured Fe⁰ (no income) but they possess the ancestral iron-making technology
507 [100,101]. However, manufactured materials should be tested for reactivity and rural

508 populations should be trained for filter design. It could be anticipated that, self produced safe
509 drinking water will increase the self-confidence of these populations and contribute to reduce
510 rural exodus. On the other hand the development and the implementation of the technology
511 worldwide will render travel with bottle water superfluous. Moreover, Fe⁰/sand filters/beds
512 are excellent candidates for safe drinking water in emergency situations (e.g. earthquakes,
513 wars, tsunami) [78].

514 Fe⁰/sand filtration is equally a feasible option to successfully remove all target compounds
515 from surface and groundwater: particles, natural organic matter, pathogens and micro-
516 pollutants (including so-called emerging contaminants). Therefore, efforts should be made to
517 use this chemical-free technology as the first choice everywhere. It could be expected that
518 using Fe⁰/sand filtration as standard technology will be very beneficial for water works as iron
519 oxides (the products of iron corrosion) are easy to recycle to Fe⁰. However, given the large
520 spectrum of toxic substances enmeshed in the mass of corrosion products, the recycling task
521 should be carefully addressed. In particular used household filters should be collected and
522 professionally disposed (or recycled). This approach has the great advantage to control filter
523 residue in regions where water is contaminated by toxic species like arsenic or uranium. On
524 the other hand, recycling Fe-based materials (not only filter residues) for Fe⁰ production will
525 generate incomes in developing country while protecting the environment.

526 The probably strongest argument for the development of Fe⁰/sand filtration technology is the
527 simplicity of the system. One should not care in parallel for membranes, granular activated
528 carbon and chemicals (including disinfectants) but only on the stock of iron and sand, and the
529 regeneration of the former. Finally, it can be speculated the success of the Fe⁰/sand
530 technology for safe drinking water production will depend on the capacity of researchers
531 create new reactive Fe⁰ materials and their capacity to find ways to control material reactivity
532 in an affordable way.

533 Currently, there is an ongoing discussion on the suitability of localized solutions for save
534 drinking water production [102-104]. In the developed world, decentralized drinking water
535 production units are progressively regarded as an efficient alternative to centralized
536 production systems. This approach is discussed in analogy to the energy sector where
537 decentralization has raised a surge in innovations and new market opportunities for a host of
538 new and established companies [104]. In a similar way it could be expected that localized
539 water treatment would produce new jobs, businesses, economic development, and quality of
540 life. Efficient and affordable technologies for decentralized water treatment are needed to
541 sustain the decentralization argumentation. The present communication and related works
542 [12,33,39-41] have presented Fe⁰ bed filtration as a serious candidate to be systematically
543 assessed.

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548 **References**

- 549 [1] J. Ellul, *The technological society*. New York: Vintage Books. (1964), cited by ref. [20]
550 [2] J. Albert, J. Luoto, D. Levine, End-User Preferences for and Performance of Competing
551 POU Water Treatment Technologies among the Rural Poor of Kenya. *Environ. Sci. Technol.*
552 44 (2010) 4426–4432.
553 [3] G. Concha, K. Broberg, M. Grandr, A. Cardozo, B. Palm, M. Vahter, High-level exposure
554 to lithium, boron, cesium, and arsenic via drinking water in the Andes of northern Argentina.
555 *Environ. Sci. Technol.* 44 (2010) 6875–6880.
556 [4] T.F. Clasen, Household water treatment and the millennium development goals: Keeping
557 the focus on health. *Environ. Sci. Technol.* (2010) doi: 10.1021/es1018674.

- 558 [5] J.B. Braden, P.C. Mankin, Economic and financial management of small water supply
559 systems: Issue Introduction. *J. Contemp. Water Res. Ed.* 128 (2004) 1–5.
- 560 [6] H.D. Coulibaly, M.J. Rodriguez, Development of performance indicators for small
561 Quebec drinking water utilities, *J. Environ. Manag.* 73 (2004) 243–255.
- 562 [7] J. Maras, Economic and financial management capacity of small water systems, *J.*
563 *Contemp. Water Res. Ed.* 128 (2004) 31–34.
- 564 [8] W.J. Smith Jr, The place of rural, remote and least-wealthy small islands in international
565 water development: the nexus of geography–technology sustainability in Chuuk State,
566 Federated States of Micronesia, *The Geogr. J.* 174 (2008) 251–268.
- 567 [9] W.J. Smith Jr, Improving access to safe drinking water in rural, remote, and least wealthy
568 small islands: Non-traditional methods in Chuuk State, Federated States of Micronesia,
569 *Int. J. Environ. Waste Manag.* 10 (2009) 167–189.
- 570 [10] M.N.B. Momba, C.L. Obi, P. Thompson, Survey of disinfection efficiency of small
571 drinking water treatment plants: Challenges facing small water treatment plants in South
572 Africa, *Water SA* 35 (2009) 485–494.
- 573 [11] D.L. Key, J.D. Key, G. Okolongo and M. Siguba, *Development of a small-scale electro-*
574 *chlorination system for rural water supplies*. Report No. 1442/1/09 to the Water
575 Research Commission, (ISBN 978-1-77005-916-0), 2010.
- 576 [12] A.M. Gottinger, Master thesis, University of Regina (Saskatchewan, Canada), 2010.
- 577 [13] A.M. Gottinger, D.J. Wild, D. McMartin, B. Moldovan and D. Wang, *Development of an*
578 *iron-amended biofilter for removal of arsenic from rural Canadian prairie potable*
579 *water*, In: *Water Pollution X*. A.M. Marinov and C.A. Brebbia, Eds.; WIT Press:
580 Ashurst, Southampton, 2010, 333–344.
- 581 [14] S.F. Bagi, Small rural communities’ quest for safe drinking water, *Rural America* 17
582 (2002) 40–46.

- 583 [15] K. Ballschmiter, R. Hackenberg, W.M. Jarman, R. Looser, Man-made chemicals found
584 in remote areas of the world: The experimental definition for POPs, *Environ. Sci. Pollut.*
585 *Res.* 9 (2002) 274–288.
- 586 [16] O. Osibanjo, *Organochlorines in Nigeria and Africa*. In *The Handbook of Environmental*
587 *Chemistry Vol. 3, Part O*, H. Fiedler (ed.), Springer-Verlag Berlin Heidelberg, 2003,
588 321–354.
- 589 [17] A. Loftus, Rethinking political ecologies of water, *Third World Quart.* 30 (2009) 953–
590 968.
- 591 [18] E. Gerlach, R. Franceys, "Standpipes and beyond" - a universal water service dynamic. *J.*
592 *Int. Dev.* (2009), doi 10.1002/jid.1567.
- 593 [19] WHO/UNICEF, *Progress on sanitation and drinking-water 2010 update*, Geneva,
594 Switzerland: WHO/UNICEF 2010.
- 595 [20] W.J. Smith Jr., Geographic research in water resources: a vibrant research agenda for the
596 next 20 years, *J. Contemp. Water Res. Ed.* 142 (2009) 83–89.
- 597 [21] R.W. Gillham, *Cleaning halogenated contaminants from groundwater*, U.S. Pat.
598 5266213, 1992.
- 599 [22] D.W. Blowes, C.P. Ptacek, *System for treating contaminated groundwater*. U.S. Patent
600 5362394, 1994.
- 601 [23] S.F. O'Hannesin, R.W. Gillham, Long-term performance of an in situ "iron wall" for
602 remediation of VOCs *Ground Water* 36 (1998) 164–170.
- 603 [24] M.M. Scherer, S. Richter, R.L. Valentine and P.J.J. Alvarez, *Rev. Environ. Sci. Technol.*,
604 *Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean*
605 *up*, 30 (2000) 363–411.
- 606 [25] A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable
607 reactive barriers: a critical review, *Environ. Eng. Sci.* 24 (2007), 401–423.

- 608 [26] A.B. Cundy, L. Hopkinson, R.L.D. Whitby, Use of iron-based technologies in
609 contaminated land and groundwater remediation: A review, *Sci. Tot. Environ.* 400
610 (2008), 42–51.
- 611 [27] R. Thiruvengkatachari, S. Vigneswaran, R. Naidu, Permeable reactive barrier for
612 groundwater remediation, *J. Ind. Eng. Chem.* 14 (2008), 145–156.
- 613 [28] J.P. Muegge, P.W. Hadley, An evaluation of permeable reactive barrier projects in
614 California, *Remediation* 20 (2009), 41–57.
- 615 [29] D.H. Phillips, T. Van Nooten, L. Bastiaens, M.I. Russell, K. Dickson, S. Plant, J.M.E.
616 Ahad, T. Newton, T. Elliot and R.M. Kalin, Ten year performance evaluation of a field-
617 scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene
618 contaminated groundwater, *Environ. Sci. Technol.* 44 (2010), 3861–3869.
- 619 [30] A. Hussam, A.K.M. Munir, A simple and effective arsenic filter based on composite iron
620 matrix: Development and deployment studies for groundwater of Bangladesh, *J.*
621 *Environ. Sci. Health A* 42 (2007), 1869–1878.
- 622 [31] T.K.K. Ngai, R.R. Shrestha, B. Dangol, M. Maharjan, S.E. Murcott, Design for
623 sustainable development – Household drinking water filter for arsenic and pathogen
624 treatment in Nepal, *J. Environ. Sci. Health A* 42 (2007), 1879–1888.
- 625 [32] E. Awuah, R.T. Morris, P.A. Owusu, R. Sundell, J. Lindstrom, Evaluation of simple
626 methods of arsenic removal from domestic water supplies in rural communities,
627 *Desalination* 248 (2009), 42–47.
- 628 [33] C. Noubactep, A. Schöner, P. Woafu, Metallic iron filters for universal access to safe
629 drinking water, *Clean* 37 (2009), 930–937.
- 630 [34] M. Diao, M. Yao, Use of zero-valent iron nanoparticles in inactivating microbes, *Water*
631 *Res.* 43 (2009), 5243–5251.
- 632 [35] Y. You, J. Han, P.C. Chiu, Y. Jin, Removal and inactivation of waterborne viruses using
633 zerovalent iron. *Environ. Sci. Technol.* 39 (2005), 9263–9269.

- 634 [36] M.I. Litter, M.E. Morgada, J. Bundschuh, Possible treatments for arsenic removal in
635 Latin American waters for human consumption, *Environ. Pollut.* 158 (2010), 1105–
636 1118.
- 637 [37] P.F. Santina, *Method for removing toxic substances in water*, US Pat. 5575919, 1996.
- 638 [38] X. Meng, G.P. Korfiatis, *Iron powder and sand filtration process for treatment of water*
639 *contaminated with ...* - US Pat. 6,942,807, 2005.
- 640 [39] C. Noubactep, S. Caré, Enhancing sustainability of household water filters by mixing
641 metallic iron with porous materials, *Chem. Eng. J.* 162 (2010), 635–642.
- 642 [40] C. Noubactep, S. Caré, Dimensioning metallic iron beds for efficient contaminant
643 removal, *Chem. Eng. J.* 163 (2010) 454–460.
- 644 [41] C. Noubactep and A. Schöner, Metallic iron: dawn of a new era of drinking water
645 treatment research? *Fresen. Environ. Bull.* 19 (2010), 1661–1668.
- 646 [42] N.J. Ashbolt, Microbial contamination of drinking water and disease outcomes in
647 developing regions, *Toxicology* 198 (2004), 229–238.
- 648 [43] WHO, *Guidelines for drinking-water quality*. vol. 1. 3rd ed. Geneva, Switzerland: World
649 Health Organization, 2004.
- 650 [44] UNICEF, *Unicef handbook on water quality*. United Nations Children's Fund, New
651 York, 2008.
- 652 [45] J.B. Robertson, S.C. Edberg, Natural protection of spring and well drinking water against
653 surface microbial contamination, I. Hydrogeological parameters. *Crit. Rev. Microbiol.*
654 23 (1997), 143–178.
- 655 [46] S.C. Edberg, H. Leclerc, J. Robertson, Natural protection of spring and well drinking
656 water against surface microbial contamination. II. Indicators and monitoring parameters
657 for parasites. *Crit. Rev. Microbiol.* 23 (1997), 179–206.

- 658 [47] T. Karanfil, *Activated carbon adsorption in drinking water treatment*, In *Activated*
659 *Carbon Surfaces*. In *Environmental Remediation* T.J. Bandosz (editor). *Interf. Sci.*
660 *Technol.* 7 (2006), 345–373.
- 661 [48] P. Le Cloirec and C. Faur, *Adsorption of organic compounds onto activated carbon –*
662 *applications in water and air treatments*, In *Environmental Remediation* T.J. Bandosz
663 (editor). *Interf. Sci. Technol.* 2006, 7, 375–419.
- 664 [49] W. Zhu, J. Graney, K. Salvage, *Land-use impact on water pollution: elevated pollutant*
665 *input and reduced pollutant retention*, *J. Contemp. Water Res. Ed.* 139 (2008), 15–21.
- 666 [50] G.W. Whitman, R.P. Russel, V.J. Altieri, *Effect of hydrogen-ion concentration on the*
667 *submerged corrosion of steel*. *Indust. Eng. Chem.* 16 (1924), 665–670.
- 668 [51] C. Noubactep, *Processes of contaminant removal in “Fe⁰–H₂O” systems revisited. The*
669 *importance of co-precipitation*, *Open Environ. J.* 1 (2007), 9–13.
- 670 [52] C. Noubactep, *A critical review on the mechanism of contaminant removal in Fe⁰–H₂O*
671 *systems*, *Environ. Technol.* 29 (2008), 909–920.
- 672 [53] C. Noubactep, *The suitability of metallic iron for environmental remediation*, *Environ.*
673 *Progr.* (2009), doi: 10.1002/ep.10406.
- 674 [54] C. Noubactep, A. Schöner and M. Sauter, *Significance of oxide-film in discussing the*
675 *mechanism of contaminant removal by elemental iron materials*. In *"Photo-*
676 *Electrochemistry & Photo-Biology for the Sustainability"*; S. Kaneco, B. Viswanathan,
677 H. Katsumata (Eds.), Bentham Science Publishers 2010, 1, 34–55.
- 678 [55] M. Shafiquzzaman, M.S. Azam, I. Mishima, J. Nakajima, *Technical and social*
679 *evaluation of arsenic mitigation in rural Bangladesh*, *J. Health Popul. Nutr.* 27 (2009),
680 674–683.
- 681 [56] S. Tuladhar, L.S. Smith, *SONO filter: An excellent technology for save water in Nepal.*
682 *SOPHEN* 7 (2009), 18–24.

- 683 [57] S. Tuladhar, Er.B. Man Shakya, *A study on the performance of SONO filter in reducing*
684 *different drinking water quality parameters of ground water: A case study in Ramgram*
685 *municipality of Nawalparasi District, Nepal*. Paper presented at the Regional
686 Conference on Appropriate Water Supply, Sanitation and Hygiene (WASH) Solution for
687 Informal Settlements and Marginalized Communities, Kathmandu, Nepal, May 19-21,
688 (2010), 297–310.
- 689 [58] J.L. Jambor, M. Raudsepp, K. Mountjoy, Mineralogy of permeable reactive barriers for
690 the attenuation of subsurface contaminants. *Can. Miner.* 43 (2005), 2117–2140.
- 691 [59] R.W. Gillham, S.F O’Hannesin, Enhanced degradation of halogenated aliphatics by zero-
692 valent iron, *Ground Water* 32 (1994), 958–967.
- 693 [60] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron
694 metal. *Environ. Sci. Technol.* 28 (1994), 2045–2053.
- 695 [61] C.-B. Wang, W.-X. Zhang, Synthesizing nanoscale iron particles for rapid and complete
696 dechlorination of TCE and PCBs. *Environ. Sci. Technol.* 31 (1997), 2154–2156.
- 697 [62] W.-x. Zhang, Nanoscale iron particles for environmental remediation: An overview. *J.*
698 *Nanopart. Res.* 5 (2003), 323–332.
- 699 [63] R. Muftikian, Q. Fernando, N. Korte, A method for the rapid dechlorination of low
700 molecular weight chlorinated hydrocarbons in water, *Water Res.* 29/10 (1995), 2434–
701 2439.
- 702 [64] N. Korte, L. Liang, R. Muftikian, C. Grittini, Q. Fernando, The dechlorination of
703 hydrocarbons: Palladised iron utilised for ground water purification. *Platinum Metals*
704 *Rev.* 41 (1997), 2–7.
- 705 [65] A. Ghauch, H.A. Assi, A. Tuqan, Investigating the mechanism of clofibric acid removal
706 in Fe^0/H_2O systems, *J. Hazard. Mater.* 176 (2010), 48–55.
- 707 [66] C. Noubactep, A. Schöner, Fe^0 -based alloys for environmental remediation: Thinking
708 outside the box, *J. Hazard. Mater.* 165 (2009), 1210–1214.

- 709 [67] M. Stratmann, J. Müller, The mechanism of the oxygen reduction on rust-covered metal
710 substrates, *Corros. Sci.* 36 (1994), 327–359.
- 711 [68] S. Nestic, Key issues related to modelling of internal corrosion of oil and gas pipelines –
712 A review, *Corros. Sci.* 49 (2007), 4308–4338.
- 713 [69] S. Mitsunobu, Y. Takahashi, Y. Terada, M. Sakata, Antimony(V) incorporation into
714 synthetic ferrihydrite, goethite, and natural iron oxyhydroxides. *Environ. Sci. Technol.*
715 44 (2010), 3712–3718.
- 716 [70] D. Talbot and J Talbot, *Corrosion Science & Technology*. CRC Press LLC, Boca Raton,
717 New York, Washington, London. 1998, 406 pp.
- 718 [71] E. Zitrou, J. Nikolaou, P.E. Tsakiridis, G.D. Papadimitriou, Atmospheric corrosion of
719 steel reinforcing bars produced by various manufacturing processes. *Const. Build.*
720 *Mater.* 21 (2007), 1161–1169.
- 721 [72] R.E. Dickerson, H.B. Gray and G.P. Haight Jr., *Chemical Principles*, 3. Edition,
722 Benjamin/Cummings Inc. London, Amsterdam, 1979, 944 pp.
- 723 [73] A.F. White, M.L. Peterson, Reduction of aqueous transition metal species on the surfaces
724 of Fe(II)-containing oxides. *Geochimica et Cosmochimica Acta* 60 (1996), 3799–3814.
- 725 [74] J.S. Alvarado, C. Rose, L. LaFreniere, Degradation of carbon tetrachloride in the
726 presence of zero-valent iron. *J. Environ. Monit.* 12 (2010) 1524–1530.
- 727 [75] S. Vigneswaran, J.-S. Chang Effect of media pore size distribution on deep-bed filtration,
728 *Sep. Technol.* 1 (1991), 259–266.
- 729 [76] A. Nur, G. Mavko, J. Dvorkin, D. Galmudi, Critical porosity; a key to relating physical
730 properties to porosity in rocks. *The Leading Edge* 17 (1998), 357–362.
- 731 [77] S. Caré, Q.T. Nguyen, V. L'Hostis, Y. Berthaud, Mechanical properties of the rust layer
732 induced by impressed current method in reinforced mortar, *Cement Concrete Res.* 38
733 (2008), 1079–1091.

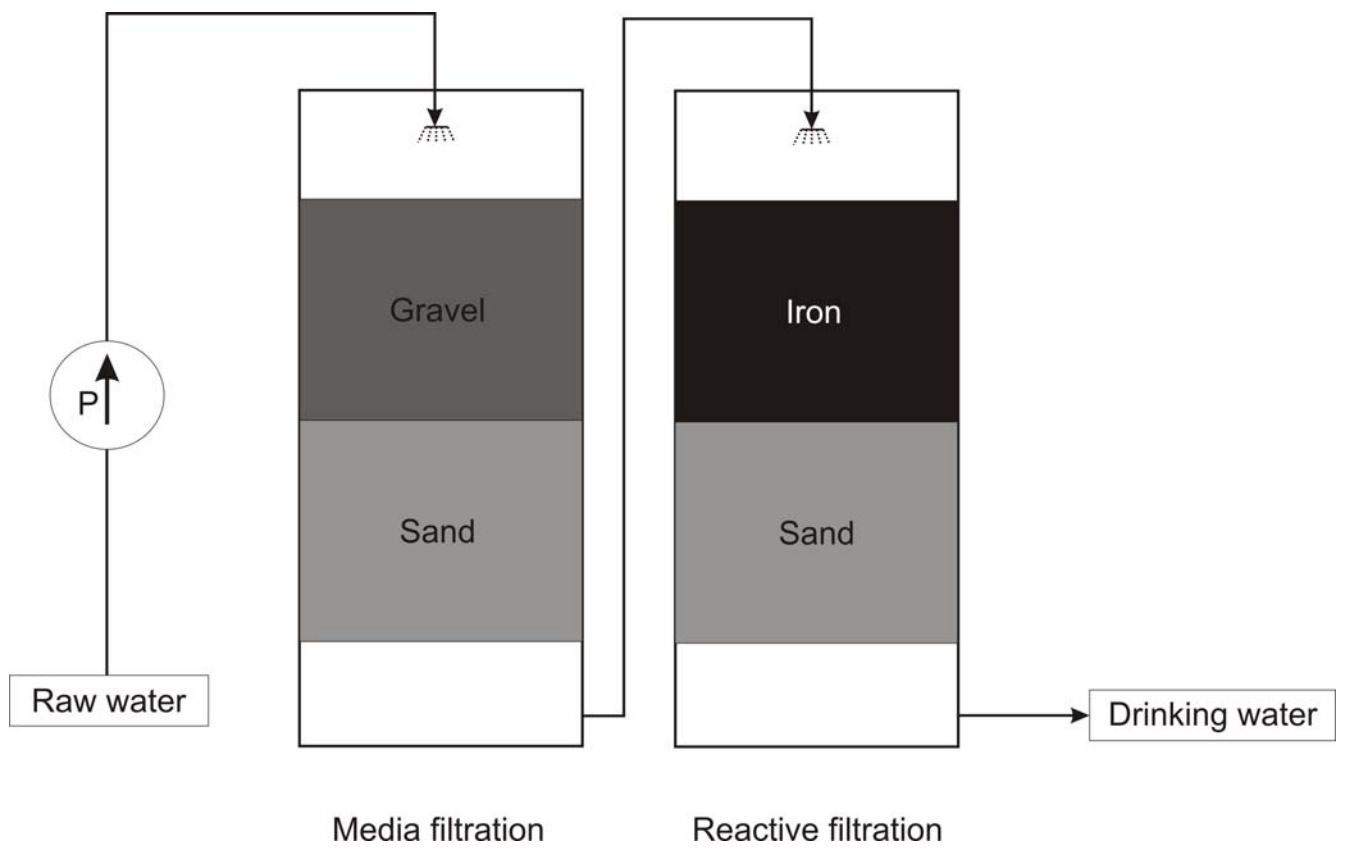
- 734 [78] C. Noubactep, S. Caré, F. Togue-Kamga, A. Schöner, P. Woafu, Extending service life
735 of household water filters by mixing metallic iron with sand. *Clay* (2010)
736 doi:10.1002/clen.201000177.
- 737 [79] U.K. Manandhar, S. Vigneswaran, Effect of media size gradation and varying influent
738 concentration in deep-bed filtration: Mathematical models and experiments. *Sep.*
739 *Technol.* 1 (1991), 178–183.
- 740 [80] A. Santos, P.H.L. Barros, Multiple particle retention mechanisms during filtration in
741 porous media. *Environ. Sci. Technol.* 44 (2010), 2515–2521.
- 742 [81] O.X. Leupin, S.J. Hug, Oxidation and removal of arsenic (III) from aerated groundwater
743 by filtration through sand and zero-valent iron, *Wat. Res.* 39 (2005) 1729–740.
- 744 [82] E. Sikora, D.D. Macdonald, The Passivity of Iron in the Presence of
745 Ethylenediaminetetraacetic Acid I. General Electrochemical Behavior, *J. Electrochem.*
746 *Soc.* 147 (2000), 4087–4092.
- 747 [83] K. Hanna, Sorption of two aromatic acids onto iron oxides: Experimental study and
748 modeling, *J. Colloid Interf. Sci.* 309 (2007), 419–428.
- 749 [84] A.H. Khan, S.B. Rasul, A.K.M. Munir, M. Habibuddowla, M. Alauddin, S.S. Newaz, A.
750 Hussam, Appraisal of a simple arsenic removal method for groundwater of Bangladesh.
751 *J. Environ. Sci. Health A35* (2000), 1021–1041.
- 752 [85] A.K.M. Munir, M. Habibuddowla, M. Alauddin, A. Hussam and A.H. Khan, *Evaluation*
753 *of performance of Sono 3-Kolshi filter for arsenic removal from groundwater using zero*
754 *valent iron through laboratory and field studies.* In: Ahmed, F.M.A., Adeel, A.M.Z.
755 (Eds.), *Technologies for Arsenic Removal from Drinking Water*, vol. 1.1. BUET, UNU,
756 Dhaka, 2001, p. 177–189.
- 757 [86] O.X. Leupin, S.J. Hug, A.B.M. Badruzzaman, Arsenic removal from Bangladesh tube
758 well water with filter columns containing zerovalent iron filings and sand. *Environ. Sci.*
759 *Technol.* 39 (2005), 8032–8037.

- 760 [87] S.J. Morrison, D.R. Metzler, B.P. Dwyer, Removal of As, Mn, Mo, Se, U, V and Zn
761 from groundwater by zero-valent iron in a passive treatment cell: reaction progress
762 modeling. *J. Contam. Hydrol.* 56 (2002), 99–116.
- 763 [88] S.J. Morrison, P.S. Mushovic, P.L. Niesen, Early Breakthrough of Molybdenum and
764 Uranium in a Permeable Reactive Barrier. *Environ. Sci. Technol.* 40 (2006), 2018–2024.
- 765 [89] J. Peña, E. Torres, M.J. Turrero, A. Escribano, P.L. Martín, Kinetic modelling of the
766 attenuation of carbon steel canister corrosion due to diffusive transport through
767 corrosion product layers. *Corros. Sci.* 50 (2008) 2197–2204.
- 768 [90] G.A. Waychunas, C.S. Kim, J.F. Banfield, Nanoparticulate iron oxide minerals in soils
769 and sediments: unique properties and contaminant scavenging mechanisms. *J. Nanopart.*
770 *Res.* 7 (2005) 409–433.
- 771 [91] N. Moraci, P.S. Calabrò, Heavy metals removal and hydraulic performance in zero-
772 valent iron/pumice permeable reactive barriers. *J. Environ. Manag.* 91 (2010) 2336–
773 2341.
- 774 [92] C.F. Baes, R.E. Mesmer, *The hydrolysis of cations*, John Wiley & Sons, New York
775 (1976) 489 pp.
- 776 [93] J.M. Combes, A. Manceau, G. Calas, J.Y. Bottero, Formation of ferric oxides from
777 aqueous solutions: A polyhedral approach by X-ray absorption spectroscopy: I.
778 Hydrolysis and formation of ferric gels. *Geochim. Cosmochim. Acta* 53 (1989) 583–
779 594.
- 780 [94] A. Hussam, Contending with a development disaster: SONO filters remove arsenic from
781 well water in Bangladesh. *Innovations* 4 (2009), 89–102.
- 782 [95] S. Li, S.G.J. Heijman, J.Q.J.C. Verberk, J.C. van Dijk, An innovative treatment concept
783 for future drinking water production: fluidized ion exchange – ultrafiltration –
784 nanofiltration – granular activated carbon filtration. *Drink. Water Eng. Sci.* 2 (2009),
785 41–47.

- 786 [96] J.J. Rook, Formation of haloforms during chlorination of natural waters. *Water*
787 *Treatment Exam.* 23 (1974), 234–243.
- 788 [97] J. Rook, Chlorination reactions of fulvic acids in natural waters. *Environ. Sci. Technol.*
789 11 (1977), 478–482.
- 790 [98] M.A. El-Dib, R.K. Ali, THMs formation during chlorination of raw Nile River water,
791 *Water Res.* 29 (1995), 375–378.
- 792 [99] J.W. Li, Z. Yu, X. Cai, M. Gao, F. Chao, Trihalomethanes formation in water treated
793 with chlorine dioxide, *Water Res.* 30 (1996), 2371–2376.
- 794 [100] L.M. Pole, Decline or survival? Iron production in West Africa from the seventeenth to
795 the twentieth centuries. *J. African Hist.* 23 (1982), 503–513.
- 796 [101] B. Prakash, Metallurgy of iron and steel making and blacksmithy in ancient India.
797 *Indian J. History Sci.* 261 (1991), 351–371.
- 798 [102] S.P. Dix, Onsite wastewater treatment: a technological and management revolution.
799 *Water Eng. Manag.* 148 (2001) 24–29.
- 800 [103] B. Tansel, New technologies for water and wastewater treatment: A survey of recent
801 patents. *Recent Pat. Chem. Eng.* 1 (2008) 17–26.
- 802 [104] S. Slaughter, Improving the sustainability of water treatment systems: Opportunities for
803 innovation. *Solutions* 1 (2010) 42–49.
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804 **Figure 1**

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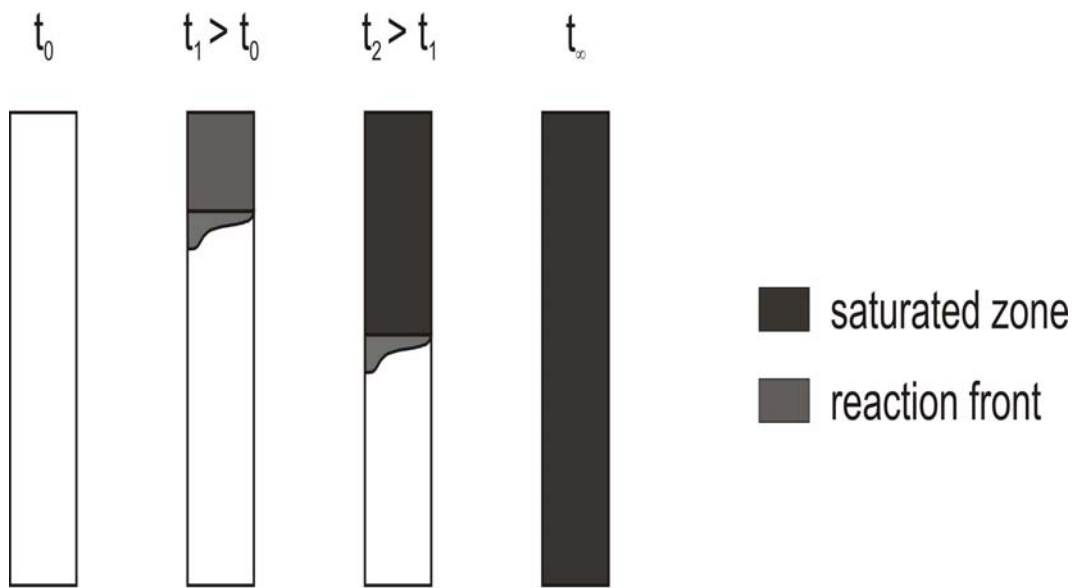
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808 **Figure 2**

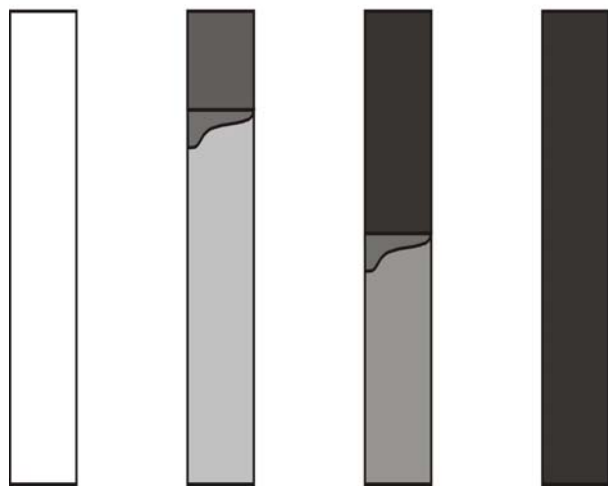
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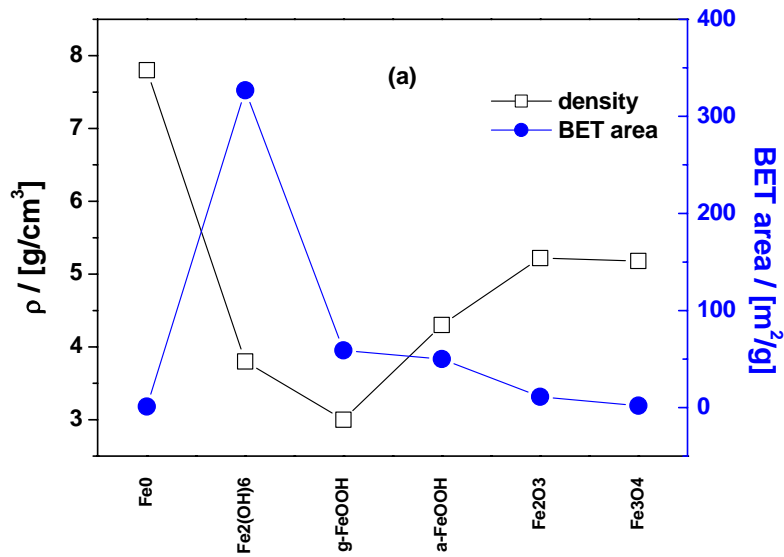
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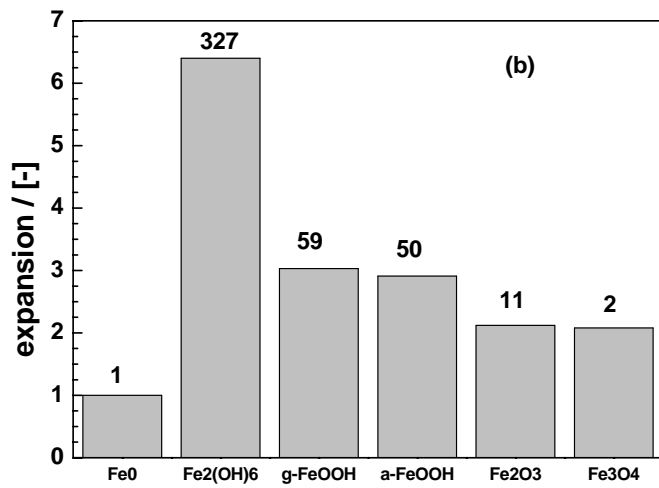
812 **Figure 3**

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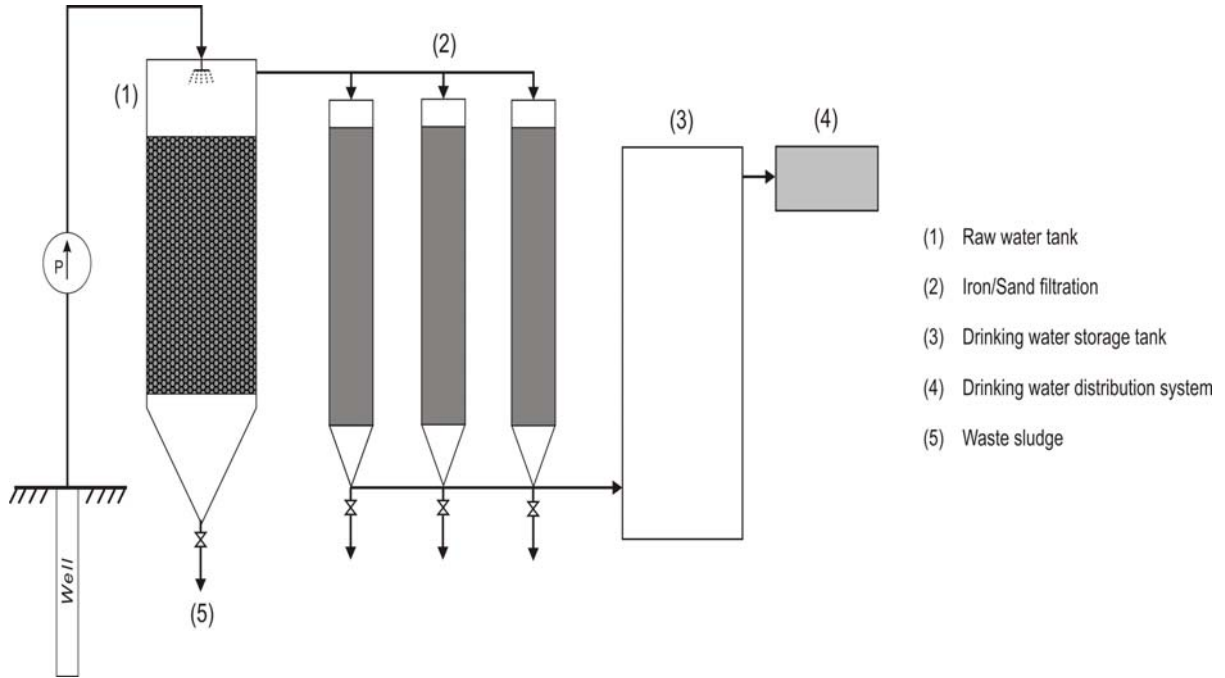
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818 **Figure 4**

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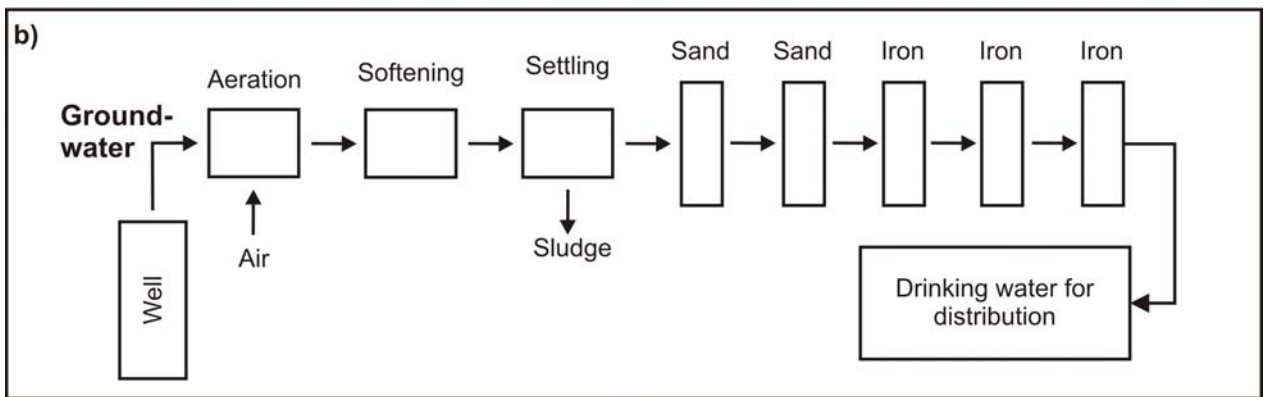
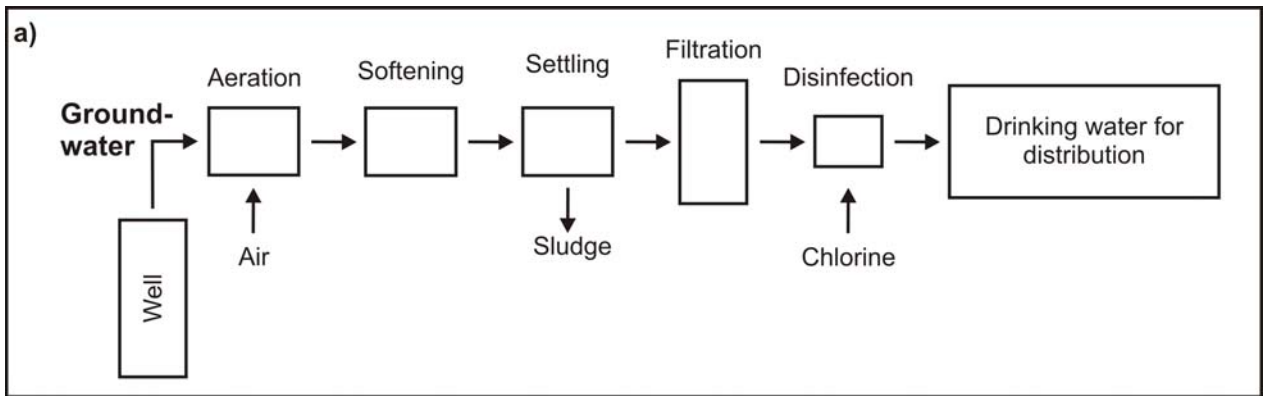
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824 **Figure 5**

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829 **Figure captions**

830

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

834

835 **Figure 2:** Comparison of the evolution of contaminant loading in granular activated carbon
836 (GAC - up) and Fe^0 (dawn) filters. The evolution of the GAC filters is virgin - preloaded
837 (reaction front) and saturated carbon. For the Fe^0 filters a reaction front may exist due to
838 increased O_2 in the influent but iron corrosion by H_2O (or H^+) occurs uniformly in the whole
839 column.

840

841 **Figure 3:** Relative variation of density, specific surface area (SSA), and volume of Fe species
842 during the process of iron corrosion. The values in (b) represent the SSA from Hanna [83].
843 Strictly any crystallization goes through dissolution, nucleation and aggregation. Intermediate
844 species are of high specific area and even more voluminous than $\text{Fe}_2(\text{OH})_6$.

845

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

849

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