

1 **Metallic iron: dawn of a new era of drinking water treatment research?**

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9 **Abstract**

10 The goal of water treatment in water works is safe drinking water production. Various
11 technological options are available to this end. However, many conventional water treatment
12 technologies are too expensive for extensive deployment in rural communities worldwide.
13 Research over the past two decades has demonstrated the efficiency of metallic iron (Fe^0) for
14 the aqueous removal of a wide range of chemical and microbial contaminants (e.g. bacteria,
15 chlorinated organics, dyes, emerging contaminants, heavy metals, radionuclides, viruses). The
16 prevailing concept considers that the mechanism of Fe^0 remediation varies depending on the
17 contaminant of interest. This concept was recently revisited and Fe^0 was proven an universal
18 material for water treatment. As a consequence Fe^0 filtration beds are proposed in this
19 communication to replace ultra-filtration, nano-filtration, and disinfection units in water
20 works. It is anticipated that the success of Fe^0 filtration beds in producing safe drinking water
21 in large scale will depend on the ability of researchers to produce adequate reactive materials.
22 Target experimental work is needed to confirm and extend the applicability of this affordable
23 method.

24 **Key words:** Emerging contaminants; Micro-pollutants; Safe drinking water; Zerovalent iron.

25 **Capsule:** Filtration on Fe^0 beds could replace ultra-filtration, nano-filtration, and disinfection
26 units in water treatment plants.

27

27 **1 Introduction**

28 The goal of water treatment is the production of safe drinking water for proper distribution.
29 Conventional water treatments with coagulation, rapid sand filtration, granular activated
30 carbon filtration, and disinfection (chlorination, ozonation or ultraviolet radiation) have been
31 proven inefficient for the quantitative removal of several micro-pollutants from surface waters
32 [1-3]. The situation is exacerbated by the occurrence of so-called emerging contaminants of
33 unknown property and toxicity [4-7]. Emerging contaminants are mostly pharmaceuticals and
34 personal care products. Approximately 3,000 different pharmaceutical ingredients are used in
35 the EU today, including painkillers, antibiotics, antidiabetics, beta-blockers, contraceptives,
36 lipid regulators, antidepressants, antineoplastics, tranquilizers, impotence drugs and cytostatic
37 agents [4]. As a consequence alternative and innovative water treatment concepts are under
38 development [1,6]. For example, a new treatment four-stages-concept was recently proposed
39 in the Netherlands: (i) fluidized ion exchange (FIEX), (ii) ultrafiltration (UF), (iii)
40 nanofiltration (NF), (iv) granular activated carbon filtration (GAC) [2]. The FIEX process
41 removed calcium and other divalent cations; the UF membrane removed particles and micro-
42 organisms; and the NF membrane and GAC removed natural organic matter (NOM) and
43 micro-pollutants. The results of a pilot study showed successful removal of most micro-
44 pollutants. However, very polar substances with a molecular weight lower than 100 Daltons
45 could not be quantitative removed. These substances are too small to be rejected by the NF
46 (size exclusion), and too polar to be quantitatively adsorbed by the GAC. Therefore, a process
47 is needed to quantitatively remove both small and polar substances from water. Water
48 filtration on metallic iron is a serious candidate as will be shown later. The technology of
49 water filtration on metallic iron will first be presented.

50 **2. Water filtration on metallic iron**

51 In early 1990 metallic iron (Fe^0) was introduced as reducing agent for groundwater
52 remediation in permeable reactive barriers (iron walls). Fe^0 was proved particularly efficient

53 for the decontamination of halogenated organic compounds [8-10]. Subsequent studies have
54 confirmed the efficiency of Fe^0 for quantitative removal of several substances including
55 nitrate, bromate, chlorate, nitro aromatics compounds, pathogens, pesticides, arsenic,
56 chromium, copper, lead, triazoles, uranium, and zinc [9-14]. Although successful removal of
57 reducible (e.g. Cr^{VI} , lindane) and non reducible (e.g. Zn^{II} , triazoles) contaminants was
58 reported, the initial premise of reductive transformation is still prevailing. However, there is
59 clear evidence that contaminants are basically removed by an unspecific mechanism
60 [12,15,16].

61 The unspecific nature of the processes yielding aqueous contaminant removal by Fe^0 is
62 confirmed by reports on successful removal of more than 20 different species (including
63 bacteria and viruses) in Fe^0 -based filters (3-Kolshi and SONO filters) designed for arsenic
64 removal at the household level in South East Asia [17-19]. The qualitative aspect of the
65 efficiency of Fe^0 materials for contaminant removal in iron walls and household filters is the
66 motivation for this communication. The most important output is that Fe^0 is an efficient filter
67 material to quantitatively remove all contaminants including small size and polar species
68 which have been shown difficult to remove in conventional water treatment plants.

69 **3. Suitability of Fe^0 bed for water treatment plants**

70 The voluminous literature on "remediation with corroding iron" is characterized by the
71 overwhelming number of parameters which have been shown to affect the process of aqueous
72 contaminant removal in the presence Fe^0 [20-25]. These parameters include the nature of the
73 contaminant, the pH of the solution, the nature of Fe^0 (e.g. carbon steel, cast iron, direct
74 reduced iron), the size of Fe^0 (mm, μm , nm), the temperature, the water flow velocity, the
75 water salinity, the presence of oxidizing agents (e.g. O_2), the character of the oxide scales on
76 Fe^0 . The importance of all these factors was traceably demonstrated from isolated sets of
77 experiments. However, due to lack of a standard experimental protocol, available results
78 could be collectively regarded as qualitative as they are not comparable to each other [22-25].

79 Taken together, results from Fe⁰-based filters (field walls and household filters) demonstrate
80 the suitability of Fe⁰ beds for the removal of all possible contaminants from water. This
81 statement is supported by the fact that some parameters (e.g. bed depth, Fe⁰ type, flow
82 velocity) could be adjusted for performance optimization. Another argument to support this
83 view is that field Fe⁰ walls have quantitatively removed species (e.g. 1,2-dichloroethane and
84 dichloromethane), which were proven to be not treatable by Fe⁰ in batch studies [26].
85 Accordingly, the mechanism of contaminant removal in Fe⁰ beds is different from that which
86 is investigated in batch studies.

87 **4 Mechanism of contaminant removal in Fe⁰ beds**

88 Despite two decades of intensive research, there is no agreement on the fundamental
89 mechanisms of aqueous contaminant removal in the presence of reactive Fe⁰. The prevailing
90 concept considering Fe⁰ as a reducing agent was shown inconsistent with many experimental
91 observations [12,15]. The new more consistent concept considers adsorption and co-
92 precipitation as the fundamental mechanism of aqueous contaminant removal in the presence
93 of Fe⁰ (adsorption/co-precipitation concept) [12,15]. The adsorption/co-precipitation concept
94 is not yet accepted by the scientific community as recently discussed [25,27]. The new
95 concept was recently validated by Ghauch et al. [16] while investigating aqueous clofibric
96 acid removal in the presence of Fe⁰. Nevertheless, even newer works explicitly disprove the
97 adsorption/co-precipitation concept without any convincing argument [28,29]. Moreover, the
98 new concept is even falsified. As an example, the authors of ref. [28] considered that the
99 validity of the adsorption/co-precipitation concept means that “degradation of chlorinated
100 organics is unimportant because some metals are removed mainly by sequestration”.
101 However, the adsorption/co-precipitation concept considers that chlorinated organics (RCl)
102 are certainly adsorbed and co-precipitated. RCl reduction certainly occurs to some unknown
103 extent and reduction is not likely to be mediated by electrons from of Fe⁰ as adsorbed Fe^{II} and
104 adsorbed H are more accessible than Fe⁰ and partly more powerful than Fe⁰ [12,15].

105 Although the adsorption/co-precipitation concept is not yet univocally accepted, it is
106 considered as actual state-of-the-art knowledge and used for the further presentation. For the
107 sake of clarity the process of aqueous iron corrosion will be briefly recalled.

108 **4.1 Aqueous iron corrosion**

109 Aqueous iron oxidative dissolution in water (aqueous iron corrosion) is an electrochemical
110 process. Aqueous iron corrosion is a heterogeneous reaction characterized by the spontaneous
111 dissolution of iron (yielding dissolved Fe^{II} or Fe^{III} – Tab. 1). Iron oxidation is driven by any
112 oxidative species which standard electrode potential (E^0) is higher than -0.44 V (E^0 of the
113 couple $\text{Fe}^{\text{II}}/\text{Fe}^0$). Table 1 shows clearly, that H^+ ($E^0 = 0.00\text{ V}$), Fe^{3+} ($E^0 = 0.77\text{ V}$) and
114 dissolved O_2 ($E^0 = 0.81\text{ V}$) are oxidizing agents for Fe^0 (and H_2 is a reducing agent for Fe^{III}).
115 Accordingly, in a contaminant-free aqueous solution, Fe^0 is oxidized. Resulting Fe^{II} and Fe^{III}
116 are hydrolysed, and precipitated (Eq. 8-10). The kinetic of iron corrosion is controlled mainly
117 by diffusion-convection of oxidizing agents from the bulk solution towards the metal surface
118 (and reciprocally). At $\text{pH} > 4.5$, the Fe^0 surface is always covered by an oxide scale.

119 **4.2 Contaminant removal in batch systems**

120 It was found that mixing operations have a negative effect on identifying the real mechanism
121 of contaminant removal by Fe^0 [16,22,23,25,30,31]. In fact, mixing disturbs the formation of
122 the universal oxide scale in the vicinity of Fe^0 . As state above, the universal oxide scale serves
123 as a diffusion barrier for contaminants. Accordingly, if a contaminant exhibits a poor
124 adsorptive affinity to the oxide scale, it will not readily diffuses into the oxide scale where it
125 could be enmeshed or further transformed (oxidized or reduced, if applicable). However,
126 mixing batch systems disturbs the spatial disposition of the oxide scale relative to Fe^0 . In
127 particular, the Fe^0 surface is rendered accessible to all contaminants, regardless their affinity
128 to the iron corrosion products (“fluidized cells”). These conditions, however, are not
129 reproduced in nature.

130 Under stagnant and slow-mixing conditions, dissolved species (including contaminants) are
131 adsorbed or/and enmeshed during the process of the oxide scale formation. Adsorbed and
132 enmeshed species could be further chemically transformed as discussed above. It is certain
133 that the kinetics of aqueous removal of various species will depend on their relative affinities
134 to the oxide scale. However, all species will be removed as they are in trace quantity in a
135 domain of precipitating iron [32,33]. This is the first argument suggesting Fe^0 as universal
136 materials for save water production. It is very important to note that contaminants are neither
137 exclusively removed by Fe^0 nor the oxide scale. Contaminants are quantitatively removed
138 during the dynamic process of oxidative dissolution yielding a transforming oxide scale [27].
139 Table 2 gives an overview on contaminant classes that have been successfully removed from
140 aqueous solutions by Fe^0 . In a column system size exclusion is added to the described
141 dynamic process.

142 **4.3 Contaminant removal in column systems**

143 The mechanism of contaminant removal in Fe^0 beds was recently elucidated [27,43]. A Fe^0
144 packed bed initially contents an inter-granular volume (pore volume) which ideally, should
145 never been totally filled by in situ generated iron corrosion products (long-term permeability).
146 A Fe^0 bed in its initial stage of implementation is comparable to a sand filter for the removal
147 of suspended solids by size exclusion (media filtration). The filtration efficiency depends on
148 the sand particle size. The suitability of Fe^0 as reactive medium for drinking water filters
149 relies on two essential characteristics: (i) the interactions of corroding iron with contaminants
150 (adsorption, co-precipitation/enmeshment as for batch systems), and (ii) the improved size
151 exclusion by virtue of the expansive nature of iron corrosion. The improved size exclusion is
152 due to the fact that generated iron corrosion products are at least 2.1 times larger in volume
153 than Fe^0 in the metallic lattice [27,43,44].
154 An essential feature of corroding iron for contaminant removal in Fe^0 beds are the
155 expansion/contraction cycles accompanying iron oxide formation from Fe^0 . In fact, each Fe^0

156 (SSA < 2 m²/g) is first oxidized to nebulous hydrated iron hydroxides having specific surface
157 areas (SSA) larger than 500 m²/g. The hydrated hydroxides are then progressively
158 transformed to amorphous and crystalline oxides (Fe(OH)₃, Fe₂O₃, Fe₃O₄, FeOOH) (SSA <
159 40 m²/g) [45]. To illustrate the transformations yielding to contaminant
160 sequestration/trapping, the evolution of three iron atoms from the Fe⁰ material will be
161 discussed. The space between the individual atoms is neglected for simplifications.
162 Three atoms Fe⁰ will be first oxidized to 3 Fe^{II} species and may further be oxidized to 3 Fe^{III}
163 species. Then, the hydrolysed species will be transformed to colloidal species (SSA > 500
164 m²/g) before they aggregate and crystallize to one Fe₃O₄, 1.5 Fe₂O₃ or 3 Fe(OH)₂, Fe(OH)₃ or
165 FeOOH (Tab. 1). Calculations (not presented here) clearly showed volumetric expansion
166 relative to 3 Fe⁰ for all iron oxides except magnetite for which a volume reduction of 30 %
167 was noticed [27]. However, even magnetite is a final stage of a transformation going through
168 voluminous colloidal, amorphous and highly adsorptive species.
169 Considering for simplifications only Fe⁰ and the crystalline forms of the oxides, the
170 coefficient of volumetric expansion (V_{oxide}/V_{iron}) varies from 2.1 for Fe₃O₄ (magnetite) to 4.2
171 for Fe(OH)₃ (bernalite) [27,44]. As stated above, dissolved Fe first experienced volumetric
172 expansion, and then contraction in the inter-granular space of a filter. The transformation
173 sequence: Fe⁰ – hydroxides – amorphous oxides – crystalline oxides probably occurs in the
174 presence of trace amounts of contaminants. In particular, the "nebulous" hydroxide can be
175 considered as an instantaneous spider-like web which traps contaminants in the inter-granular
176 space in the filter. Sequestered contaminants could be further chemically transformed.
177 This presented mechanism does not consider the nature of the contaminant and in particular
178 its reactivity with Fe⁰. Contaminants are transported to the bed and within the bed by gravity
179 (or other hydrodynamic forces) and are primarily removed from the aqueous phase by
180 adsorption and/or co-precipitation. This explains why non reducible and reducible
181 contaminants are removed (Tab. 2) and suggests that upon proper design Fe⁰ beds will

182 produce safe drinking water at several scales (households, small communities, large cities). It
183 is very important to note that in this scheme no energy is needed, apart from the energy to
184 pump water from wells into the Fe^0 beds. This makes Fe^0 bed filtration ideal for developing
185 countries where shortages in water production are sometimes due to lack of energy power
186 [46]. The complete absence of chemicals (including disinfecting agents) is a further key
187 advantage. It could be anticipated that Fe^0 beds is primarily for small water treatment plants.
188 However, several small urban quarters drinking water production units using Fe^0 beds could
189 produce enough water for large cities.

190 **5 Innovative iron filters**

191 An inherent problem of Fe^0 filter beds is porosity/permeability loss due to the expansive
192 nature of iron corrosion [44]. The volumetric expansion of corroding iron is presented in the
193 present communication as a useful tool to improve (slow) sand filtration efficiency. In other
194 words, Fe^0 filters are regarded as Fe^0 assisted sand filtration [47]. Accordingly, calculated
195 amounts of Fe^0 are added to sand to warrant quantitative (abiotic) contaminant removal while
196 keeping acceptable water flow velocity. Calculations (not presented here) assuming Fe_3O_4 as
197 sole corrosion products demonstrated that, regardless from the filter size, a 51:49 (vol:vol)
198 Fe^0 /quartz mixture is clogged upon Fe^0 depletion. Accordingly, a long-term efficient Fe^0 filter
199 should contain less than 51 vol-% Fe^0 . Considering that the oldest Fe^0 reactive barrier initially
200 contained only 8.8 vol-% (22 wt-%) Fe^0 [8] and efficiently removed the target contaminant
201 for more than 10 years, it could be anticipated that Fe^0 volumetric ratios of 30 to 40 % (60 to
202 70 vol-% sand) might satisfactorily treat water for several months. It is certain that the actual
203 used Fe^0 proportion will depend on its intrinsic reactivity and the extent of the contamination.
204 The presentation above confirms that mixing sand to iron is a prerequisite for long-term
205 efficient Fe^0 filters. Previous efforts [48,49] to sustain Fe^0 reactivity by mixture with sand
206 were not really rationalized as expressing the proportion of Fe^0 by a weight percent is not
207 consistent with the fact that pore volume availability is discussed (expansive nature of iron

208 corrosion filling the pore space in the filter). Moreover, despite Fe⁰:sand mixtures the porosity
209 of the Fe⁰ filters was sustained by the application of a source of vibratory energy and/or an
210 auger system [50]. It should be acknowledged that some few authors have properly
211 rationalized the used Fe⁰/sand volumetric ratios [47,51-53]. However, the discussion was not
212 based on the available volume for in-situ generated corrosion products.

213 Provided proper material selection, Fe⁰ filters could satisfactorily render raw waters safe for
214 drinking without any addition of chemicals. The three major operating parameters to be
215 addressed on a site specific basis are: (i) Fe⁰ selection, (ii) bed depth, (iii) water flow velocity.
216 In other words, pilot studies should focus at determining Fe⁰ type (e.g. particle size), bed's
217 length, and water flow velocity.

218 **5.1 Iron filter design**

219 Innovative Fe⁰ filters for drinking water production at community level are very flexible in
220 their design. The simplest design is a single bed containing layers of gravel, pebble, sand,
221 “sand + Fe⁰”, and fine sand. The actual Fe⁰ bed size depends on the size of the population to
222 be served or the volume of water to be produced daily. Single beds are necessarily good for
223 very small communities (e.g. up to 100 people). For larger communities the device
224 could/should comprise separate beds of gravel, pebble, and sand for media filtration, and Fe⁰
225 beds (containing one or more layers of “Fe⁰ + sand”) for the removal of dissolved substances.
226 Here, the system may comprise several Fe⁰ beds in series (Fig. 1) and each bed may contain:
227 (i) the same Fe⁰ material in a certain Fe⁰:sand ratio, (ii) various layers of the same Fe⁰
228 material with different Fe⁰:sand ratios, or (iii) various Fe⁰ materials (e.g. differing in their
229 particle size).

230 **6 Discussion**

231 Generally, safe drinking water is obtained either from surface water or groundwater after
232 several treatment steps (Tab. 3). The goal is to remove pathogens, dissolved, and suspended
233 substances [2,6,46]. The treatment processes may include (i) flocculation, (ii) sedimentation,

234 (iii) media filtration, (iv) ion exchange, (v) carbon adsorption, (vi) membrane filtration, and
235 (vii) disinfection. The first three named treatment processes remove colloidal and suspended
236 solids and the subsequent processes remove dissolved substances. Water disinfection is
237 achieved by chlorination, ozonation, or ultraviolet radiation. The actual drinking water
238 treatment scheme depends on the source water characteristics.

239 Generally, surface water is characterized by high contents of suspended solids and organic
240 matter. Accordingly, pre-sedimentation, coagulation or coarse filtration processes are
241 generally used for water treatment followed by disinfection. On the other side, groundwater is
242 characterized by high contents of salts, organics, or gasses. Therefore, groundwater is aerated
243 to remove dissolved gasses followed by softening to remove dissolved salts prior to
244 disinfection. Regardless of the water source, there could be a need to further remove dissolved
245 organics. In this case air stripping, ion exchange, carbon adsorption, or membrane filtration
246 processes may be used [6].

247 The presentation above has demonstrated the suitability of corroding iron in a filter to remove
248 contaminants which are conventionally removed in several treatment steps: ion exchange,
249 carbon adsorption, membrane filtration and disinfection [43,47]. Accordingly, after the
250 removal of colloidal and suspended solids (media filtration), filtration on a properly designed
251 Fe^0 system will free water from dissolved substances and pathogens. In other words,
252 processes achieved by ion exchange, carbon adsorption, membrane filtration, and disinfection
253 could be achieved in Fe^0 beds (Tab. 3). Moreover, emerging contaminants which are not
254 quantitatively removed in conventional water treatment plants are successfully removed in
255 Fe^0 beds (Tab. 2). Therefore, Filtration through Fe^0 beds is a promising technology for safe
256 drinking water production in water works. The technology is necessarily limited to raw waters
257 having a pH value larger than 4.5. For lower pH values, iron solubility is increased and
258 dissolved iron is transported out of the column. The consequence is increased
259 porosity/permeability with time and thus decreased bed efficiency. Remember that size

260 exclusion at $\text{pH} > 4.5$ is improved by precipitating iron oxides progressively filling the intra-
261 particular space in the filter (pore volume).

262 **7 Concluding remarks**

263 The present communication has presented a new concept for water treatment in beds of
264 metallic iron (Fe^0). An efficient removal of particles, natural organic matter, pathogens and
265 micro-pollutants is possible using only sand filtration and filtration on Fe^0 beds (Fig. 1). The
266 concept is inspired by (i) recent reports on efficient removal of contaminants from several
267 classes by Fe^0 in iron walls [10] and in household filters [19], and (ii) the profound
268 understanding of the mechanisms of contaminant removal in Fe^0 filters [12,15,16,27].

269 Provided the use of appropriated Fe^0 materials and proper bed design, all classes of
270 substances will be removed in Fe^0 beds. It can be anticipated that event nourishing element
271 (e.g. Ca, Mg) will be removed from water such that the contaminant free water could need
272 addition of selected nutrients to be healthy. A clear advantage of Fe^0 beds is that no chemical
273 is added and iron oxides is the sole wastes which could be recycled to produce new Fe^0
274 materials.

275 Actually, Fe^0 beds (household filters and field reactive barriers) have been successfully used
276 under conditions of slowly corroding iron. Under these conditions, microbial mechanisms
277 assist the process of contaminant removal and the kinetics of iron corrosion is sufficient for
278 quantitative contaminant removal. To produce water in small municipal drinking water
279 utilities, it will be necessary that water flows at an increased velocity. Therefore, several beds
280 of more reactive materials could be necessary. Known tools for more reactive materials
281 should be tested. These tools include using smaller Fe^0 particles (small granules and powders)
282 [48], using bimetallic systems (e.g. Fe^0/Cu^0) [10,13,14], and mixing Fe^0 with a reactive oxide
283 as MnO_2 [16,17].

284 Intensive research is needed at several fronts to transform the concept of Fe^0 beds into a
285 viable technology for safe drinking production in water works. The research could/should

286 start by numerical modelling followed by laboratory studies and pilot scale installations to
287 determine the practicality of several designs from numerical modelling. It is emphasized that
288 Fe^0 intrinsic reactivity, and water flow velocity will be the most important design parameters
289 determining for example the thickness of the filter (or the number of beds). In particular Fe^0
290 materials of different size [42] could be used in individual beds or Fe^0 -based composites
291 could be developed. In this regard the porous composite iron matrix which has been
292 successfully used in SONO arsenic filters [17] could be used or at least serves as model.
293 Fe^0 beds could be a very efficient technology at several stages: from small communities up to
294 mega cities. This affordable technology further fulfils the key requirements of (i) minimum
295 electricity needs, and (ii) environmental friendliness [14]. It could be a precious instrument to
296 help to achieve the water Millennium Development Goal of “halving by 2015, the proportion
297 of people without sustainable access to safe drinking water”. Although cost issues are not
298 discussed here, it is expected that the Fe^0 bed technology will be affordable. Material
299 recycling is a point that should be considered from the beginning on. Several technologies are
300 available to transform iron oxides to Fe^0 at several scales [54,55]. Researchers are encouraged
301 to perform target experimental work to confirm the efficiency of this affordable technology
302 and identify its possible limits. In this effort characterizing the removal of molybdenum which
303 is known for its low adsorption efficiency onto iron oxides [56] will be a good (negative)
304 reference.

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309 **References**

310 [1] H. Zhou, D.W. Smith, Advanced technologies in water and wastewater treatment, J.
311 Environ. Eng. Sci. 1 (2002), 247–264.

- 312 [2] S. Li, S.G.J. Heijman, J.Q.J.C. Verberk, J.C. van Dijk, An innovative treatment concept
313 for future drinking water production: fluidized ion exchange – ultrafiltration –
314 nanofiltration – granular activated carbon filtration, *Drink. Water Eng. Sci.* 2 (2009), 41–
315 47.
- 316 [3] R. Srinivasan, G.A. Sorial, Treatment of perchlorate in drinking water: A critical review,
317 *Sep. Purif. Technol.* 69 (2009), 7–21.
- 318 [4] T.A. Ternes, M. Bonerz, N. Herrmann, B. Teiser, H.R. Andersen, Irrigation of treated
319 wastewater in Braunschweig, Germany: An option to remove pharmaceuticals and musk
320 fragrances, *Chemosphere* 66 (2007), 894–904.
- 321 [5] T. Heberer, G. Massmann, B. Fanck, T. Taute, U. Dünnbier, Behaviour and redox
322 sensitivity of antimicrobial residues during bank filtration, *Chemosphere* 73 (2008), 451–
323 460.
- 324 [6] B. Tansel, New technologies for water and wastewater treatment: A survey of recent
325 patents, *Recent Pat. Chem. Eng.* 1 (2008), 17–26.
- 326 [7] K. Kümmerer, The presence of pharmaceuticals in the environment due to human use –
327 present knowledge and future challenges, *J. Environ. Manag.* 90 (2009), 2354–2366.
- 328 [8] S.F. O’Hannesin, R.W. Gillham, Long-term performance of an in situ "iron wall" for
329 remediation of VOCs, *Ground Water* 36 (1998), 164–170.
- 330 [9] M.M. Scherer, S. Richter, R.L. Valentine, P.J.J. Alvarez, Chemistry and microbiology of
331 permeable reactive barriers for in situ groundwater clean up, *Rev. Environ. Sci. Technol.*,
332 30 (2000), 363–411.
- 333 [10] A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable
334 reactive barriers: a critical review, *Environ. Eng. Sci.* 24 (2007), 401–423.
- 335 [11] Y.W. You, J. Han, P.C. Chiu, Y. Jin, Removal and inactivation of waterborne viruses
336 using zerovalent iron, *Environ. Sci. Technol.* 39 (2005), 9263–9269.

- 337 [12] C. Noubactep, Processes of contaminant removal in “Fe⁰-H₂O” systems revisited. The
338 importance of co-precipitation, *Open Environ. J.* 1 (2007), 9–13.
- 339 [13] M. Diao, M. Yao, Use of zero-valent iron nanoparticles in inactivating microbes, *Water*
340 *Res.* 43 (2009), 5243–5251.
- 341 [14] T. Pradeep, Anshup, Noble metal nanoparticles for water purification: A critical review,
342 *Thin Solid Films* 517 (2009), 6441–6478.
- 343 [15] C. Noubactep, A critical review on the mechanism of contaminant removal in Fe⁰-H₂O
344 systems, *Environ. Technol.* 29 (2008), 909–920.
- 345 [16] A. Ghauch, H. Abou Assi, A. Tuqan, Investigating the mechanism of clofibric acid
346 removal in Fe⁰/H₂O systems, *J. Hazard. Mater.* 176 (2010), 48–55.
- 347 [17] A. Hussam, A.K.M. Munir, A simple and effective arsenic filter based on composite iron
348 matrix: Development and deployment studies for groundwater of Bangladesh, *J. Environ.*
349 *Sci. Health A* 42 (2007), 1869–1878.
- 350 [18] S. Ahamed, A.K.M. Munir, A. Hussam, Groundwater arsenic removal technologies
351 based on sorbents: Field applications and sustainability, in *Handbook of Water Quality*
352 *and Water Purity*, Elsevier Inc., Chapter 16 (2009), 379–417.
- 353 [19] S. Tuladhar, L.S. Smith, SONO filter: An excellent technology for save water in Nepal,
354 *SOPHEN* 7 (2009), 18–24.
- 355 [20] S. Choe, Y.Y. Chang, K.Y. Hwang, J. Khim, Kinetics of reductive denitrification by
356 nanoscale zero-valent iron, *Chemosphere* 41 (2000), 1307–1311.
- 357 [21] R. Miehr, P.G. Tratnyek, Z.J. Bandstra, M.M. Scherer, J.M. Alowitz, J.E. Bylaska,
358 Diversity of contaminant reduction reactions by zerovalent iron: Role of the reductate,
359 *Environ. Sci. Technol.* 38 (2004), 139–147.
- 360 [22] C. Noubactep, Characterizing the discoloration of methylene blue in Fe⁰/H₂O systems, *J.*
361 *Hazard. Mater.* 166 (2009), 79–87.

- 362 [23] C. Noubactep, Characterizing the effects of shaking intensity on the kinetics of metallic
363 iron dissolution in EDTA, *J. Hazard. Mater.* 170 (2009), 1149–1155.
- 364 [24] C. Noubactep, A.-M.F. Kurth, M. Sauter, Evaluation of the effects of shaking intensity
365 on the process of methylene blue discoloration by metallic iron. *J. Hazard. Mater.* 169
366 (2009), 1005–1011.
- 367 [25] C. Noubactep, T. Licha, T.B. Scott, M. Fall, M. Sauter, Exploring the influence of
368 operational parameters on the reactivity of elemental iron materials, *J. Hazard. Mater.* 172
369 (2009), (2-3), 943–951.
- 370 [26] K.C.K. Lai, I.M.C. Lo, V. Birkelund, P. Kjeldsen, Field monitoring of a permeable
371 reactive barrier for removal of chlorinated organics, *J. Environ. Eng.* 132 (2006), 199–
372 209.
- 373 [27] C. Noubactep, The suitability of metallic iron for environmental remediation, *Environ.*
374 *Progr.* (2009), doi:10.1002/ep.10406.
- 375 [28] P.G. Tratnyek, A.J. Salter, Response to Comment on “Degradation of 1,2,3-
376 Trichloropropane (TCP): Hydrolysis, Elimination, and Reduction by Iron and Zinc”,
377 *Environ. Sci. Technol.* (2010), DOI: 10.1021/es100490e.
- 378 [29] N. Zhu, H. Luan, S. Yuan, J. Chen, X. Wu, L. Wang, Effective dechlorination of HCB by
379 nanoscale Cu/Fe particles, *J. Hazard. Mater.* 176 (2010), 1101–1105.
- 380 [30] C. Noubactep, Investigations for the passive in-situ Immobilization of Uranium (VI)
381 from Water (in German), Dissertation, TU Bergakademie Freiberg, *Wiss. Mitt. Institut für*
382 *Geologie der TU Bergakademie Freiberg*, Band 21 (2003), 140 pp, ISSN1433-1284.
- 383 [31] C. Noubactep, A. Schöner, G. Meinrath, Mechanism of uranium (VI) fixation by
384 elemental iron, *J. Hazard Mater.* 132 (2006), 202–212.
- 385 [32] C. Noubactep, An analysis of the evolution of reactive species in Fe⁰/H₂O systems, *J.*
386 *Hazard. Mater.* 168 (2009), 1626–1631.

- 387 [33] C. Noubactep, A. Schöner, M. Sauter, Significance of oxide-film in discussing the
388 mechanism of contaminant removal by elemental iron materials, In "Photo-
389 Electrochemistry & Photo-Biology for the Sustainability"; S. Kaneco, B. Viswanathan, H.
390 Katsumata (Eds.), Bentham Science Publishers, 1 (2010), 34–55.
- 391 [34] A. van Wezel, M. Mons, W. van Delft, New methods to monitor emerging chemicals in
392 the drinking water production chain, *J. Environ. Monit.* 12 (2010), 80–89.
- 393 [35] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron
394 metal, *Environ. Sci. Technol.* 28 (1994), 2045–2053.
- 395 [36] Z. Wang, W. Huang, P. Peng, D.E. Fennell, Rapid transformation of 1,2,3,4-TCDD by
396 Pd/Fe catalysts, *Chemosphere* 78 (2010), 147–151.
- 397 [37] K.L. McGeough, R.M. Kalin, P. Myles, Carbon disulfide removal by zero valent iron,
398 *Environ. Sci. Technol.* 41 (2007), 4607–4612.
- 399 [38] S. Nam, P.G. Tratnyek, Reduction of azo dyes with zero-valent iron, *Wat. Res.* 34
400 (2000), 1837–1845.
- 401 [39] A. Ghauch, A. Tuqan, H. Abou Assi, Antibiotic removal from water: Elimination of
402 amoxicillin and ampicillin by microscale and nanoscale iron particles. *Environ. Pollut.*
403 157 (2009), 1626–1635.
- 404 [40] K.J. Cantrell, D.I. Kaplan, T.W. Wietsma, Zero-valent iron for the in situ remediation of
405 selected metals in groundwater, *J. Hazard. Mater.* 42 (1995), 201–212.
- 406 [41] J.T. Olegario, N. Yee, M. Miller, J. Sczepaniak, B. Manning, Reduction of Se(VI) to Se(-
407 II) by zerovalent iron nanoparticle suspensions, *J. Nanopart. Res.* (2009),
408 doi:10.1007/s11051-009-9764-1.
- 409 [42] N. Groza, R. Radulescu, E. Panturu, A. Filcenco-Olteanu, R.I. Panturu, Zero-valent iron
410 used for radioactive waste water treatment, *Chem. Bull. "POLITEHNICA" Univ.*
411 (Timisoara) 54 (2009), 21 –25

- 412 [43] C. Noubactep, A. Schöner, P. Woafu, Metallic iron filters for universal access to safe
413 drinking water, *Clean* 37 (2009), 930–937.
- 414 [44] S. Caré, Q.T. Nguyen, V. L'Hostis, Y. Berthaud, Mechanical properties of the rust layer
415 induced by impressed current method in reinforced mortar, *Cement Concrete Res.* 38
416 (2008), 1079–1091.
- 417 [45] K. Hanna, Sorption of two aromatic acids onto iron oxides: Experimental study and
418 modeling. *J. Colloid Interf. Sci.* 309 (2007), 419–428.
- 419 [46] M.N.B. Momba, C.L. Obi, P. Thompson, Survey of disinfection efficiency of small
420 drinking water treatment plants: Challenges facing small water treatment plants in South
421 Africa, *Water SA* 35 (2009), 485–494.
- 422 [47] A.M. Gottinger, Chemical-free arsenic removal from potable water with a ZVI-amended
423 biofilter. Master thesis, University of Regina (Saskatchewan, Canada) (2010) 90 pp.
- 424 [48] E.T. Shokes, G. Möller, Removal of dissolved heavy metals from acid rock drainage
425 using iron metal, *Environ. Sci. Technol.* 33 (1999), 282–287.
- 426 [49] E. Bi, J.F. Devlin, B. Huang, Effects of mixing granular iron with sand on the kinetics of
427 trichloroethylene reduction, *Ground Water Monit. Remed.* 29 (2009), 56–62.
- 428 [50] X. Meng, G.P. Korfiatis, Iron powder and sand filtration process for treatment of water
429 contaminated with heavy metals and organic compounds, (2005) US Patent 6,942,807.
- 430 [51] P. Westerhoff, J. James, Nitrate removal in zero-valent iron packed columns, *Water Res.*
431 37 (2003) 1818–1830.
- 432 [52] O.X. Leupin, S.J. Hug, Oxidation and removal of arsenic (III) from aerated groundwater
433 by filtration through sand and zero-valent iron, *Wat. Res.* 39 (2005) 1729–740.
- 434 [53] O.X. Leupin, S.J. Hug, A.B.M. Badruzzaman, Arsenic removal from Bangladesh tube
435 well water with filter columns containing zerovalent iron filings and sand, *Environ. Sci.*
436 *Technol.* 39 (2005) 8032–8037.

- 437 [54] S.J. Street, G.A. Brooks, H.K. Worner, Recent developments in the environment process,
438 Can. Metal. Quart. 36 (1997), 333–340.
- 439 [55] J. de Beer, E. Worrell, K. Blok, Future technologies for energy-efficient iron and steel
440 making. Ann. Rev. En. Environ. 23 (1998), 123–205.
- 441 [56] L. Brinza, L.G. Benning, P.J. Statham, Adsorption studies of Mo and V onto ferrihydrite.
442 Miner. Mag. 72 (2008), 385–388.
- 443

443 **Table 1:** Aqueous iron corrosion and associate reactions. All these reactions (Eq. 1-10) are
 444 considered side reactions in discussing the reductive contaminant transformation.
 445 The whole process of Fe⁰ oxidative dissolution, Fe^{II}/Fe^{III} nucleation, precipitation
 446 and recrystallization is responsible for contaminant removal in the presence of Fe⁰.
 447

Reaction	Eq.
$\text{Fe}^0 \Rightarrow \text{Fe}^{2+} + 2 \text{e}^-$	(0)
$2 \text{Fe}^0 + 2 \text{Fe}^{3+} \Rightarrow 2 \text{Fe}^{2+}$	(1)
$\text{Fe}^0 + 2 \text{H}^+ \Rightarrow \text{Fe}^{2+} + \text{H}_2$	(2)
$2 \text{Fe}^0 + \text{O}_2 + 4 \text{H}^+ \Rightarrow 2 \text{Fe}^{2+} + 2 \text{H}_2\text{O}$	(3)
$2 \text{Fe}^0 + 6 \text{H}^+ \Rightarrow 2 \text{Fe}^{3+} + 3 \text{H}_2$	(4)
$4 \text{Fe}^0 + 3 \text{O}_2 + 12 \text{H}^+ \Rightarrow 4 \text{Fe}^{3+} + 6 \text{H}_2\text{O}$	(5)
$2 \text{Fe}^{2+} + 2 \text{H}^+ \Rightarrow 2 \text{Fe}^{3+} + \text{H}_2$	(6)
$4 \text{Fe}^{2+} + 4 \text{H}^+ + \text{O}_2 \Rightarrow 4 \text{Fe}^{3+} + 6 \text{H}_2\text{O}$	(7)
$\text{Fe}^{2+} + 2 \text{OH}^- \Rightarrow \text{Fe}(\text{OH})_2$	(8)
$\text{Fe}^{3+} + 3 \text{OH}^- \Rightarrow \text{Fe}(\text{OH})_3$	(9)
$\text{Fe}(\text{OH})_2, \text{Fe}(\text{OH})_3 \Rightarrow \text{FeOOH}, \text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4$	(10)

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450 **Table 2:** Selected references supporting the suitability of metallic iron beds for safe drinking
 451 water production. Emerging chemicals are chemicals which are not covered by existing water
 452 quality legislation. Relatively little information is available on their environmental behavior
 453 and toxicological properties [34].
 454

Contaminant group	Examples	References
Chlorinated solvents	chlorinated hydrocarbons	[35], [36]
DNAPL	carbon disulfide (CS ₂)	[37]
Dyes	methylene blue, azo dyes	[38]
Emerging chemicals	pharmaceuticals, personal care products, drugs-of-abuse, endocrine disruptors, nanochemicals	[16], [39]
Inorganic ions	ammonium, nitrate, nitrite perchlorates	[3]
Metals and metalloids	copper, chromium, arsenic, selenium	[40], [41]
Pathogens	viruses, bacteria	[11], [13], [17], [18]
Radionuclides	technetium, uranium.	[30], [31], [42]

455

456

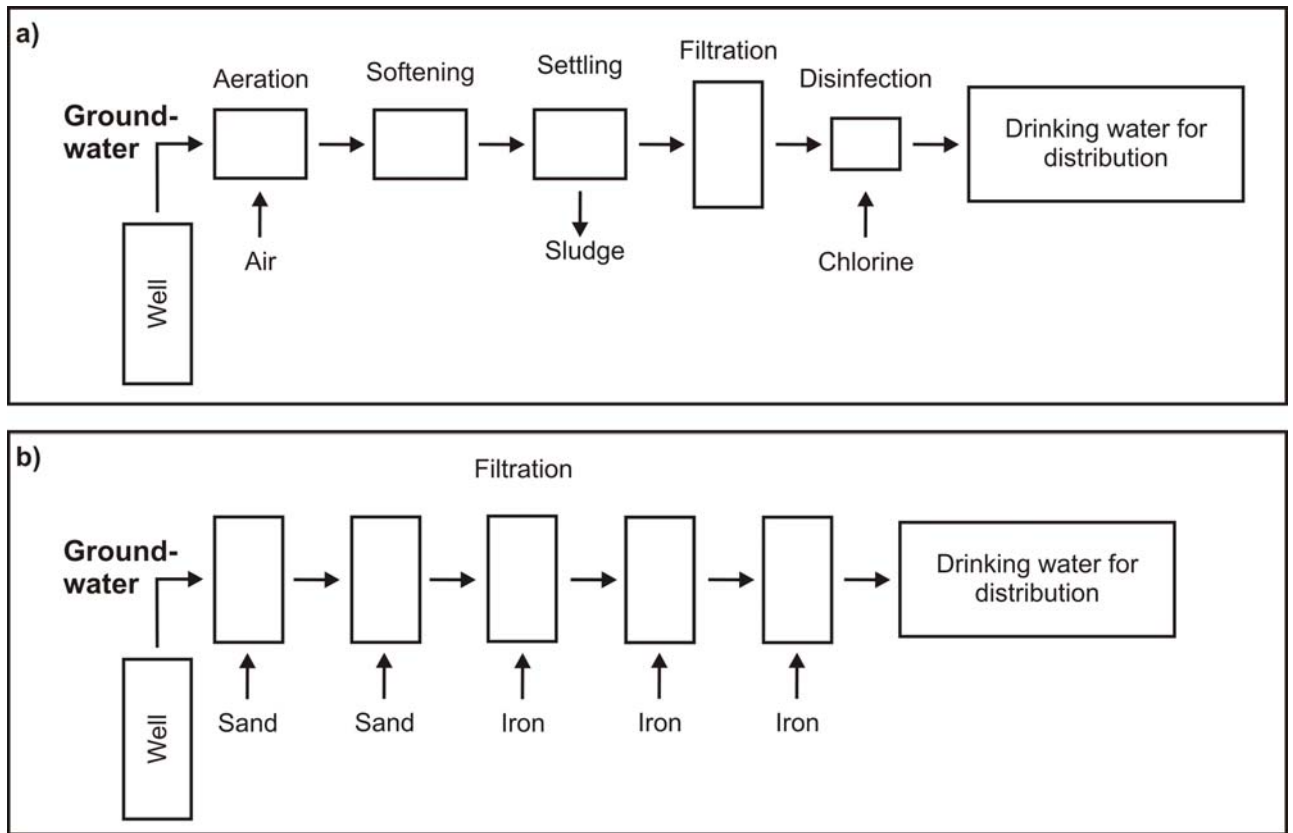
456 **Table 3:** Overview on the processes required for the removal of suspended solids and
 457 dissolved contaminants from raw waters to produce safe drinking water in a conventional
 458 water plant and by the innovative treatment concept. It is evident that no chemicals are needed
 459 in the new treatment concept.
 460

Contaminant	Conventional water plant	New concept
Colloidal solids	flocculation, sedimentation, media filtration	sand beds
Suspended solids	flocculation, sedimentation, media filtration	sand beds
Dissolved species	air stripping, carbon adsorption, ion exchange, membrane filtration, reverse osmosis	iron beds
Pathogens	disinfection (chlorination, ozonation, UV)	iron beds

461
 462
 463
 464

464 **Figure 1**

465



466

467

468 **Figure 1:** Comparison of the processes of groundwater treatment in a conventional treatment

469 plant and by metallic iron (Fe⁰) beds. Modified after ref. [6].