Letter to the Editor

A B S T R A C T

This letter challenges the concept that the metallic iron (Fe^0) surface contributes directly to the process of micro-organism inactivation in aqueous solutions. It is shown that any antimicrobial properties of Fe^0 is related to the cycle of expansion/contraction accompanying aqueous iron corrosion. This demonstration corroborates the concept that aqueous contaminant removal in the presence of Fe^0 mostly occurs at the Fe-oxide/water interface or within the oxide-film on Fe^0.

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On the mechanism of microbe inactivation by metallic iron

1. Introduction

Following the successful use of micro-scale metallic iron (Fe^0) for groundwater remediation [1–4], micro- and nano-Fe^0 have shown promise as strong antimicrobial agents against a broad spectrum of bacteria and viruses [5–8]. While the efficiency of Fe^0 for micro-organism inactivation is certain, the reported inactivation mechanisms are not convincing. The antimicrobial effect of Fe^0 has been reported to involve the generation of intracellular oxidants (e.g. HO° and Fe^{VI}) produced by the reaction with hydrogen peroxide or other species, as well as a direct interaction of Fe^0 with cell membrane components [8]. However, it is clear that this elucidation has not properly considered three important facts: (i) at pH >5.0 the surface of Fe^0 is permanently covered by an oxide-film and is therefore not directly accessible to microbes [9], (ii) oxide-film components (Fe-oxides) are antimicrobial agents and might independently inactivate microbes [10,11], and more importantly (iii) Fe^0 oxidation coupled to Fe-oxide precipitation and oxide-film formation is a dynamic process [9]. Accordingly, Fe-oxides are continually produced for micro-organism inactivation, ideally until Fe^0 is totally depleted. Addition of Fe^0 as a remediation strategy is therefore appealing due to the progressive slow release of highly reactive Fe-oxides. In contrast, in systems using less sustainable synthetic Fe-oxides (also as coatings on granular surfaces) the initial inactivation capacity may be high but the retention capacity is limited and microbe inactivation is due to pure adsorption and/or mechanical trapping.

The inactivation of pathogens in filtration systems is known to occur through adsorption, mechanical trapping (size-exclusion or straining), natural death, and predation [12,13]. Pathogen predation is not addressed in this work. Natural death mostly results from transport retardation through straining or adsorption and died microbes may be transported across the filter. Adsorption results from electrostatic interactions between pathogens and involved solid phases. For example, in comparison to bacteria inactivation, slow sand filters have shown limited inactivation efficiency for viruses in natural waters ($6.0 \leq pH \leq 9.0$) [12]. This observation was attributed to the fact that, under these pH conditions, sand and most viruses are negatively charged, leading a net repulsion and thus relative less virus removal by sand filtration [12,14]. Fe-oxide

amended sand filters have shown improved pathogen inactivation [5,12,15] because the positively charged surface of oxide layer may electrostatically adsorb viruses [16]. Fe-oxides are either immobilized on granular media [15] or added as granular Fe^0 [12] or supported nano-Fe^0 [17].

Investigations regarding the addition of Fe^0 to slow sand filter for safe drinking water provision at household level have boomed in recent years [5,8,12]. The next section gives an overview of efforts to elucidate the mechanism of microbe inactivation.

1.1. Apparent quest for the mechanism of microbe inactivation

The presentation above has shown that the scientific community is still looking for plausible explication of the efficiency of Fe^0 for the inactivation of microbes [8,18–20]. For example, Kim et al. [8] reported on the elucidation of the removal mechanism of MS2 coliphage (a virus) by Fe^{II} and nano-Fe^0 and suggested the need of more research to characterize the impact of nano-Fe^0 on other microbes (e.g. bacterial species, viruses, protozoan cysts, and complex matrices). Clearly, the mechanism of micro-organism inactivation is considered species-dependant. This approach is the one that has been used for chemical contamination but has been proven superfluous because contaminant removal in Fe^0/H_2O systems is not primarily a characteristic of any contaminant, but a characteristic of aqueous iron oxidation at pH >5.0 [9,21,22]. Before recalling, the mechanism of contaminant removal by Fe^0, the following conclusion of Kim et al. [8] should be given: "*The applications of nano-Fe^0 to inactivate viruses could be broader than for bacteria because nano-Fe^0 maintains virucidal activity in both the presence and absence of oxygen, whereas aerobic conditions may limit the bactericidal activity of nano-Fe^0.*"

2. Mechanism of aqueous contaminant removal by Fe^0

The suitability of Fe^0 as a universal material for safe drinking water production has been theoretically discussed during the past three years [23–28]. The basic idea is that iron (hydr)oxides are good adsorbents of chemical and microbial contaminants. This idea has already led to the development of metal hydroxide-coated granular materials (e.g. gravel, sand) as an efficient adsorption medium in water treatment [11,29]. The approach of using Fe^0 as in situ iron oxide generator for contaminant removal was also

known but was tested on a case-by-case basis for selected contaminants: e.g. arsenic [30,31] and viruses [5,8]. However, filters designed for As removal [30] were able to remove more that 27 other species including heavy metals, organic compounds and pathogens [32–34]. This latter observation clearly exceeded design expectations and demand for accurate explanations.

The observed efficiency of Fe^0-based filters was explained by considering the dynamic nature of Fe^0 corrosion within the porous media (filters) [23,24,28]. In fact, iron corrosion is volumetric expansive in nature [35,36]. Depending on the oxygen availability, the volume of formed iron oxides may be up to 6.40 times larger that the volume of Fe^0 in the metal lattice [35]. However, formed oxides go through intermediate stages of more voluminous hydroxides which are colloidal in nature and very adsorptive for any dissolved species. Accordingly, the process of Fe^0 corrosion is a cycle of expansion and contraction events. Expansion corresponds to the transformation "$Fe^0 \Rightarrow$ voluminous hydroxides". Contraction corresponds to the transformation "voluminous hydroxides $\Rightarrow$ final oxides". During these events, contaminants are basically enmeshed in the mass of precipitating oxides (within the oxide-film). Additionally, contaminant adsorption onto the surface of resulted precipitates is also efficient (at the interface Fe-oxide/H_2O). The overall process in packed beds was termed as "reactive filtration" and convincingly explained the reported efficiency of Fe^0-based filters [24,28].

It should be explicitly stated that the extent and "apparent mechanism" of contaminant removal in laboratory experiments (including microbe inactivation) depend on the used experimental designs. This issue will not be further discussed here. However, it should be stated that to be relevant for practical situations, Fe^0 materials should be tested under conditions in which the formation of oxide-films at their surface is not disturbed. The initiation and growth of oxide-films are highly dependent on the Fe^0 intrinsic reactivity and availability of reactants [37,38]. It is well-documented that after the formation of the oxide-film on the Fe^0 surface, the Fe^0 oxidation progressed at a significantly reduced speed. This phase of reduced oxidation kinetics corresponds to real-world situations for Fe^0-based filters. Accordingly, long-term laboratory experiments are suitable for a better understanding of the operating mode of Fe^0 filters.

The use of Fe^0 for microbe inactivation was first tested on a pragmatic basis based on the success of Fe^0 in permeable reactive barriers [5]. A science-based introduction of elemental metal for microbe inactivation was reported earlier [39] as discussed in the next section.

2.1. Elemental metals for microbe inactivation

Irrespective from the author's previous works on the Fe^0/H_2O system summarized in Refs. [24,28], the mechanism of microbe removal by Fe^0 can be derived by analogy to the process of electro-coagulation (EC) using Al and Fe as sacrificial anodes. The effects of Al^0/Fe^0 are based on spontaneous dissolution in contact with water, with generation of Al^{III}/Fe^{III}-species and OH^- ions, and finally voluminous insoluble $Al(OH)_3$/$Fe(OH)_3$. If O_2 is absent or limited, less voluminous $Fe(OH)_2$ will be formed. That is the sole difference between oxic and anoxic conditions. Bearing in mind the great efficiency of Al^0 EC and Fe^0 EC for the aqueous removal of many chemical pollutants, efficient inactivation of microbiological water pollutant is expected too. This principle was used by Bojic et al. [39] to develop a very efficient micro-alloyed Al^0-based composite for water treatment. It should be recalled that conventional Al^0 is very low reactive as it is instantaneously covered by an impervious film Al_2O_3 film on Al^0 [40]. The same trend is observed for elemental zinc. From a pure thermodynamic perspective, however, Al and Zn are stronger reducing agents than Fe^0 [40]. The standard electrode

potentials for the redox couples of the three elements are: $-1.66\,V$ for Al^{III}/Al^0, $-0.763\,V$ for Zn^{II}/Zn^0, $-0.44\,V$ for Fe^{II}/Fe^0 and $0.77\,V$ for Fe^{III}/Fe^{II} [40,41].

Considering the thermodynamics of oxide-film formation on the three metals (Al, Fe and Zn), it appears that Fe^0 is the sole multivalent element (Fe^{II}, Fe^{III}) [41]. Because of differences in size and chemical properties of Fe^0, Fe^{II} and Fe^{III} species, the formation of an impervious oxide-film on Fe^0 is not likely, this is the rational for the better suitability of Fe^0 for environmental remediation. In other words, to render Al and Zn (and other aqueous reactive metals) suitable for environmental remediation, tools have to be found to avoid the formation of an impervious oxide-film on their surface. Despite this evidence, researchers are continuing to discuss the suitability of conventional Zn^0 for aqueous contaminant removal [42–48]. For Al^0, Bojic et al. [39,49–51] have presented an efficient micro-alloyed composite. The composite consists of micro-alloyed aluminium coated over a thin iron net.

This microalloyed Al^0-based composite has been successfully used for the aqueous removal of trihalomethanes, textile dyes, natural organic mater, pesticides, heavy metals and *Escherichia coli* [49–51]. The removal mechanisms had been reported in terms of flocks of aluminium hydroxide acting "as adsorbents and/or traps for ions, molecules or suspended particles thus removing them from the solution by sorption, co-precipitation or electro-static attraction followed by coagulation" [51]. This description corresponds to adsorption and co-precipitation as a fundamental mechanism of chemical contaminant removal and micro-organism inactivation [9,52]. It should be recalled that generated iron species will not segregate bacteria, chemical contaminants and viruses. All benign or pathogenic species are removed from the aqueous phase, provided that enough time is left for sufficient production of removing agents. Accordingly, all reports on the demonstration of microbe-specific interactions leading to other removal mechanisms (e.g. cytotoxic) were somehow faulty.

3. Concluding remarks

In a recent review on biological research, Brenner [53] stated that *the conversion of data into knowledge constitutes a great challenge for future research*. It is intuitive to conclude that this conversion will be very difficult when the data are produced on a pragmatic basis. This has been the case for the use of Fe^0 for water treatment [8,18,19]. Ideally concepts (e.g. theories of the system) should exist which are to be approved or disproved by experimental data. In the absence of any concept, there is no guide to constrain the choice of model. In addition, most of the observations (e.g. nature of corrosion products, percent removal) made by individual researchers are static snap-shots and their measurements could be experimentally impacted [53]. Therefore, it will be impossible to use available data to understand the dynamic processes of contaminant removal by aqueous iron corrosion. The situation is exacerbated by the huge difference of time scales between laboratory experiments (hours to days) and field application (years).

For a more effective development of the iron reactive wall technology, the state-of-the-art knowledge on the mechanism of contaminant removal should be considered by all investigators regardless the size of used materials (nm, μm and mm) and the nature of the contaminant (biological, chemical or physical). The sole impact of the particle size is on the kinetic aspects [2,54]. Factors introducing biases in the experimental protocols have been intensively discussed [55]. These factors included [55]: the available reactive sites (Fe^0 particle size, Fe^0 loading), the intrinsic reactivity of used Fe^0 [56], the volume of the solution, the contaminant concentration, the mixing type (shaking, stirring, vortex), the mixing intensity, and the Fe^0 pre-treatment for batch experiments.

For column experiments, factors influencing the treatment efficiency include: the reactivity of used Fe^0, the proportion of Fe^0 in the mixture, the nature of the admixing agent (e.g. gravel, perlite, pumice, sand), the water characteristics (dissolved O_2 level, pH value, nature of contaminants), and the hydraulic loads.

In conclusion, the long-lasting debate on the toxicity or the mode of toxicity of Fe^0 [3,57,58] should be re-oriented. Whether Fe^0 (nano-Fe^0), released Fe^{II}, generated HO° and Fe^{IV} are cytotoxic or not, quantitative microbe removal is likely. Nano-Fe^0 reacts and depletes rapidly [2,54], producing more Fe-oxides per time unit. Moreover, it is difficult to understand the relevance of Fe^0, Fe^{IV} and HO° as virucidal and bactericidal agents [8] when microbes are readily and irreversibly removed from the aqueous phase by the dynamic process of iron corrosion.

Acknowledgments

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