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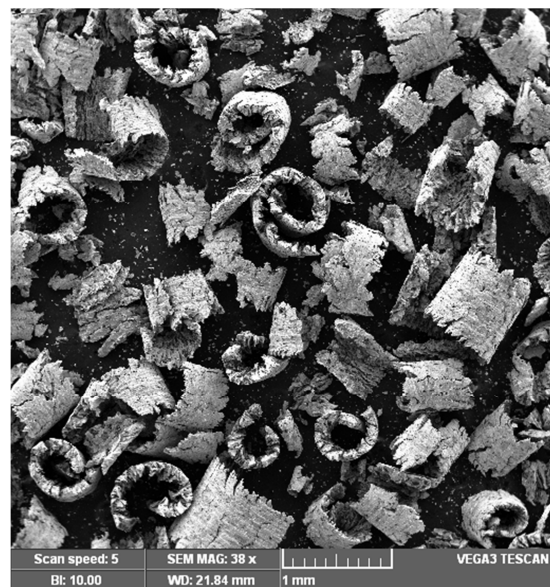
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Iron-based metallic systems: an excellent choice for sustainable water treatment

80 pages, 4 figures, 1 table, 328 references



This work is dedicated to
my parents Angele and Cmdt Rajaa,
my brothers Marwan and Joseph,
my lovely wife Alice,
my beloved children Anthony and Marc
for their endless love

Preface

The present work was presented as thesis for the Habilitation degree in Chemistry at Joseph Fourier University of Grenoble 1 (France) under “Chimie et Sciences du Vivant” Doctoral School and was accepted on December 13, 2013.

This thesis investigates the important role that metallic iron (Fe^0) or Fe^0 -based systems (including bimetallics, trimetallics and nano- Fe^0) can play in sustaining the efficiency of physical-chemical treatment systems for water decontamination. Relevant water treatment technologies include:

- $\text{Fe}^0/\text{H}_2\text{O}$ systems using mm, μm and nm particles
- $\text{Fe}^0/\text{Me}^0/\text{H}_2\text{O}$ systems where Me^0 is a transition metal e.g. Pd, Cu, Co, Ni, etc.
- $\text{Fe}^0/\text{H}_2\text{O}_2$ systems known by the Fenton and Fenton-like reactions (silent system)
- $\text{Fe}^0/\text{US}/\text{H}_2\text{O}_2$ systems (sonicated system at low frequency)
- $\text{Fe}^0/\text{Persulfate}$ and $\text{Fe}^0/\text{Me}^0/\text{Persulfate}$ systems in addition to persulfate heated systems.

Cleaning water from common and emergent contaminants becomes a priority since provision in drinking water of an increasing worldwide population continue to grow in a complicated and uncertain future in terms of global warming and environmental challenges. Directions toward cost effective, affordable and sustainable technologies for water treatment could be achieved by using cost-effective materials like Fe^0 -based alloys in combination with adequate harmless reagents.

Chapter 1 presents the scientific basis of iron corrosion and filtration on iron filters. It also addresses some unanswered questions regarding the removal mechanism of organic contaminants in $\text{Fe}^0/\text{H}_2\text{O}$ systems. Chapter 2 presents the attached articles in relation to their contribution in order to better understand the removal mechanism of organic contaminants in Fe^0 systems (micrometric and nanometric scale) with application to antibiotics and emphasis on permeability loss. Chapter 3 presents the appended articles in the perspective of using Fe^0 amended systems (e.g. bimetallics and trimetallics) in addition to technical issues relative to experimental design with application to emergent contaminants (Pharmaceuticals and Personal Care Products, PPCPs). Chapter 4 investigates the role that nanometric and micrometric Fe^0 can play in improving the Fenton process in terms of sustainability in

sonicated and silent systems. Chapter 5 shows that Fe^0 and Fe^0 -based systems (bimetallics and trimetallics) could be considered as reliable catalysts for persulfate activation yielding complete degradation of PPCPs toward full mineralization. Thermal activation of persulfate is considered as well showing the possibility of application of such advanced oxidation process to hot spot effluents. An outlook is given in form of specific recommendations for future works. This acclaims the use of natural iron-based minerals (lemonite, ferrihydrite, etc.) as durable catalysts or recycled iron based material (e.g. brake rotor) and sunlight energy as renewable heating source for a sustainable water treatment process. Chapter 6 suggests a common basis for future scientific research on Fe^0 remediation (as a whole). Chapter 7 lists cited references. The sixteen (16) peer-reviewed original research papers on which this thesis is formulated are included in appendix.

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Abstract

The permanent quest for affordable, applicable and efficient technologies for water treatment has culminated in the use of metallic elements as universal remediation materials. Contaminants of concern are biological (e.g. bacteria, viruses), chemical (organic and inorganic compounds) and physical (e.g. color, turbidity) in nature. The current classification of chemical contaminants is confusing as it accounts for (i) their origin/use (e.g. dyes, pesticides), (ii) the time scale at which their relevance was realized (e.g. emergent contaminants including pharmaceutical and personal care products) or simply the organic or inorganic nature. However, the physico-chemical nature of individual contaminants should be considered. Relevant intrinsic characteristics include: (i) charge, (ii) chemical reactivity, (iii) polarity, (iv) size and (v) structure. Intrinsic characteristics determine the interactions of each species with the environment. These interactions comprise the decontamination process. Relevant decontamination processes include adsorption, co-precipitation, oxidation, precipitation, reduction, and size-exclusion. From these processes, oxidation and reduction are not removal processes at $\mu\text{g/L}$ -level. In other words, whenever oxidation and reduction are involved, contaminant removal must be guaranteed by one or a combination of the five other processes.

The universal character of metallic elements for water treatment arises from the fact that all interactions described above are likely to occur in a metal/water system. In particular, (i) native metal hydroxides are progressively generated and co-exist with primary iron corrosion products (e.g. Fe^{2+} and H_2/H), (ii) in the presence of native metal hydroxides, metal ions (e.g. Fe^{2+}) and adsorbed hydrogen are powerful reducing agents, and (iii) metal hydroxide precipitation and crystallization occurs in the presence of contaminants that are simply enmeshed, even though their adsorptive affinity to metal hydroxides might be weak. Clearly, the metal/water system is a dynamic system which huge potential for environmental remediation is yet to be exploited. The present work is focused on metallic iron (Fe^0) as a universal material showing successful use in water filtration systems and in advanced oxidation processes (AOPs), e.g. Fenton and persulfate. The elucidation of the chemical reactivity of the $\text{Fe}^0/\text{H}_2\text{O}$ system is crucial for the understanding of the interactions of contaminants therein.

Based on the above assertion and the experimental evidence that Fe^0 and Fe^0 -based systems can be used as adsorbents generators and peroxide/persulfate activators to enhance the longevity of AOPs toward sustainable water treatment technologies, the objectives of the present work are: (i) to show why discrepancies exist among published data regarding Fe^0 technologies and its application to a wide range of contaminants; (ii) to demonstrate that Fe^0 and Fe^0 -based bimetallic (multimetallic) systems are operating in aqueous solutions on a basis of adsorption of contaminants after the formation of a porous nascent oxide scale of volumetric expansion/regression properties rather than pure reduction; (iii) to confirm the beneficial properties of Fe^0 particles, bimetallic and trimetallic Fe^0 -based systems of different sizes (nm, μm and mm) in order to activate hydrogen peroxide and persulfate into powerful radical oxidants for micro-contaminants degradation and (iv) to demonstrate that thermally and chemically activated persulfate is a successful technology that can be used for long term applications to overcome pollution of aquifers in organic contaminants toward more sustainable solutions.

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1. Overview on water remediation techniques

1.1. Introduction

1.1.1. Worldwide water situation: an overview

Save drinking water and sanitation are the primary source of human health, prosperity, and security. The provision of clean water to population is a global challenge for which scientific efforts should constantly support political decision making. The world's population is expected to reach about nine billion by around 2050. If the living standards continue to rise, the requirement of potable water for human consumption will amount to the resources of about three planet Earths (Dyson 1996, Daigger 2003, Hussam 2013). Water bodies are actually receiving from point and non-point sources per day an estimated amount of 2 million tons of anthropogenic waste including industrial waste (e.g. dyes, heavy metals, pharmaceuticals), human waste (e.g. faeces, urine) and agriculture waste (e.g. pesticides). Natural contamination is also an issue of concern. Relevant natural contaminants include arsenic, fluoride, pathogens (e.g. bacteria and viruses) and uranium (You et al. 2005, Shannon et al. 2008, Diao and Yao 2009, Momba et al. 2009, Litter et al. 2010, Giles et al. 2011, Noubactep 2011a, Shafiquzzaman et al. 2011, Ali 2012, Michen et al. 2012, Shi et al. 2012, Chiu 2013, Neumann et al. 2013). Accordingly, there is an increasing challenge to improve and preserve the quality of available water resources in order to prevent fresh water scarcity (Droste 1997, Franklin 1991).

In tune with scientific progress, including in chemical analytic, the focus of the water remediation industry constantly changes. For example, for some two decades, pesticides and other agricultural products were regarded as 'emergent contaminants'. However, their concern for water quality has decreased in recent years thanks to strict science-based regulations (Daughton 2002). Specific attention has been given to Pharmaceutical and Personal Care Products (PPCPs). The relevance of PPCPs as 'emergent contaminants' of worldwide concern relies on their worldwide spreading and their still unknown environmental fate. Moreover, because of their beneficial effects on human health, it is not likely that PPCPs will be successfully restricted in the same way as pesticides (Daughton 2007). Also, their consumption has an increasing trend with the increasing average age of the population (Daughton and Ternes 1999). The present work is mostly focused on the removal of PPCPs from water.

Residues of PPCPs were detected in a multiplicity of matrices using advanced analytical techniques (Petrovic et al. 2005, Hao et al. 2007, Klosterhaus et al. 2013) constituting

therefore a potential risk for aquatic and terrestrial organisms (Ternes 1998, Hirsch et al. 1999, Brown et al. 2006, Feitosa-Felizzola and Chiron 2009, Klosterhaus et al. 2013). Some of them, especially antibiotics, can also cause resistance in bacterial population, making them inefficient in the treatment of many diseases (Schwartz et al. 2003, Martinez 2009, Rosenblatt-Farrel 2009).

1.2. Existing decontamination processes

To prevent contamination of water matrices, researchers have developed different processes able to remove/degrade aqueous contaminants. Among those techniques one can enumerate conventional treatments including (i) biological processes via waste water treatment plants (WWTPs) including filtration and coagulation/flocculation/sedimentation (Adams et al. 2002, Arikan 2008), (ii) oxidation and advanced oxidation processes (AOPs) including chlorination (Sharma 2008, Acero et al. 2010), ozonation (Andreozzi et al. 2005, Cokgor et al. 2004), Fenton (Andreozzi et al. 1999] and photo-Fenton (Arslan-Alaton and Gurses 2004, Gonzalez et al. 2007, Bautitz and Noguerira 2010), photolysis (Boreen et al. 2004, Jiao et al. 2008) and semiconductor photocatalysis (Calza et al. 2004, Klauson et al. 2010), electrochemical processes (Hiorse et al. 2005, Jara et al. 2007), adsorption (Crisafully et al. 2008, Putra et al. 2009, Kim et al. 2010), reverse osmosis (Li et al. 2004, Radjenovic et al. 2008), nano and ultrafiltration (Kosutic et al. 2007, Koyuncu et al. 2008), ion exchange (Choi et al. 2007, Ustun et al. 2007) and some combined processes (Klavarioti et al. 2009, Augugliaro et al. 2005).

Of the enumerated processes, the present work will focus on such involving the $\text{Fe}^0/\text{H}_2\text{O}$ systems. Those are systems in which elemental iron (Fe^0) is used either as stand-alone remediation agent or as agent to enable or sustain remediation by other processes. A brief description of individual processes will be given below.

1.3. $\text{Fe}^0/\text{H}_2\text{O}$ as stand-alone remediation systems

Elemental iron (Fe^0) has been introduced in the remediation as a reactive filler in subsurface permeable reactive barriers (PRBs). The initial goal was to reductively transform chemical species to less harmful, less mobile/soluble and/or more biodegradable species. For example, reduction of the chlorinated solvent trichloroethene (TCE) by Fe^0 is reported as an abiotic process that mainly follows a beta-elimination mechanism with acetylene as an intermediate and ethene as the final product (Bigg and Judd 2000, ITRC 2011, Chen et al. 2012a, Chen et al. 2013). Accordingly, the reductive process, mostly randomly interchanged with the elimination process, is considered a reductive transformation resulting in

dechlorination/hydroxylation (Gillham and O'Hannesin, 1994, Matheson and Tratneyk, 1994). This chemical reaction has been reported to occur at the Fe^0 surface and Fe^0 considered the electron donor (direct reduction) (Weber 1996, Arnold and Roberts 1998, Arnold and Roberts 2000a, Arnold and Roberts 2000b).

The elimination of species without redox properties in $\text{Fe}^0/\text{H}_2\text{O}$ systems (Jia et al. 2007, Noubactep 2009a, Noubactep 2011b, Noubactep 2011c, Scott et al. 2011, Miyajima 2012, Miyajima and Noubactep 2015) has challenged the view that contaminant elimination/removal in PRBs is a reductive process. New paths toward the elucidation of the fundamental mechanisms of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems have been paved (Noubactep 2009b, 2010a, 2011b, 2011c, 2012, 2014a, 2014b, 2015). In this effort several branches of science involving aqueous iron corrosion were considered. These included electrocoagulation (Li et al. 2012, Moreno et al. 2009, Noubactep and Schöner 2010), corrosion science (Wilson 1923, Vernon 1945, Caule and Cohen 1959, Sato 2000, Sato 2001, Nestic 2007, Odziemkowski 2009, Schindelholz and Kelly 2012), synthetic organic chemistry (Werner 1951, Werner 1961, Noubactep 2012) and hydrometallurgy (Noubactep 2009c, Noubactep 2010c, Crane and Noubactep 2012). The process of iron corrosion and its volumetric expansive nature has been considered as well (Noubactep 2010c, Caré et al. 2013, Domga et al. 2015). In particular, the proper consideration of the expansion/compression cycles accompanying the well-documented volumetric expansion has enabled the description of Fe^0 PRBs as filtration systems in which contaminant removal is improved by adsorptive size-exclusion (Miyajima 2012, Bilardi et al. 2013a, Bilardi et al. 2013b). The net result is that the mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems is fundamentally revisited. Relevant removal mechanisms included adsorption onto iron corrosion products, co-precipitation (enmeshment, entrapment or sequestration) of contaminants into precipitating corrosion products and adsorptive size exclusion (Noubactep 2007, 2008, 2009a, 2010a, 2010b, 2011a, 2011b, 2011c, 2012, 2013a, 2013b, 2013c, 2014a, 2014b, 2015).

The presentation in this section clearly shows that immersed reactive Fe^0 creates a dynamic cumulating in contaminant removal. The prevailing view is still the one that Fe^0 acts as a reducing agent for oxidized contaminants (Henderson and Demond 2007, Painter and Milke 2007, Tanboonchuy et al. 2012, Cai et al. 2013, Correia de Velosa and Pupo Nogueira 2013, Henderson and Demond 2013, Yu et al. 2013, Tepong-Tsindé et al. 2015a, Tepong-Tsindé et al. 2015b). This initial discrepancy on the nature of the processes yielding contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems hinders progress in research as it has a direct impact on all operational parameters that influence contaminant removal (Noubactep 2013c). Relevant

operational parameters include: (i) the intrinsic reactivity of Fe^0 , (ii) the availability of dissolved oxygen (e.g. oxic/anoxic systems), (iii) the availability of humic substances, inorganic species, manganese oxide, carbonates and phosphates.

The author has tested several PPCPs (e.g. Flutriafol, clofibrac acid, diclofenac, dichlorophen, β -lactam antibiotics) to demonstrate the validity of the adsorption/co-precipitation model for the process of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems (Noubactep 2007, 2008). Tested systems include Fe^0 , bimetallic and trimetallic Fe^0 -based combinations. The availability of iron corrosion products were controlled in some key experiments by using controlled amounts of MnO_2 .

1.4. Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are common techniques used for the degradation of organic contaminants. AOPs are usually a pre-treatment in efforts of pollution abatement and rarely stand-alone remediation options. Several methods have been explored based on the provision of the medium with an oxidant that might work alone or with the help of a catalyst. The latter allows the production of powerful free radicals (e.g. Hydroxyl, Sulfate, Peroxyl, etc.) more or less selective with different rate constants that depend on the targeted contaminant (Andreozzi et al. 1999). Hydroxyl and sulphate radicals will be considered through this work upon investigation into (i) Fenton's reagent and Fenton-like reaction using $\text{Fe}^0/\text{H}_2\text{O}_2$ systems under sonicated and silent operational conditions and (ii) persulfate oxidation upon thermal and chemical activation. Pharmaceuticals (e.g. bisoprolol, ibuprofen, sulfamethoxazole) and dyes (e.g. Methylene blue) usually found in water ways and drinking water (Ternes 1998, Hernando et al. 2006) will be considered as selected probes for this investigation.

1.4.1. Fenton's reagent and Fenton like US assisted processes

Known by the iron-catalyzed hydrogen peroxide system, the Fenton's reagent is an experimental device releasing very strong but non-specific hydroxyl radicals oxidants into the aqueous phase. Those can be produced through two ways: (i) by Fenton oxidation using soluble iron such as dissolved ferrous iron (Fe^{2+}) or (ii) by Fenton-like process using iron oxyhydroxide such as goethite or even magnetite (Fe_3O_4) magnetic nanoparticles (MNPs) (Dhakshinamoorthy et al. 2012). The iron-based catalyst is here playing a key role in activating hydrogen peroxide into hydroxyl radicals. Such activation can be done homogeneously or heterogeneously. The former is based on dissolved Fe^{2+} while the latter of greater importance can be based on the use of iron particles (Fe^0) or iron-derived particles of

micrometric and/or nanometric scale allowing easier separation from the effluent and, eventually, reuse (Corma and Garcia 2003). Optimization of the oxidation process should take into account agglomeration of the heterogeneous catalyst so as low frequency US (40 kHz) is used to assume (i) homogeneous distribution of the solid catalyst into the reactive medium and (ii) non accumulation of an oxide scale inhibiting therefore corrosion products to be released into the bulk solution such as Fe^{2+} . Additional factors including pH, ionic strength and ions identity are also of main importance for the optimization of the heterogeneous catalytic oxidation. Carbamazepine has been used as pharmaceutical probe as well as sulfamethoxazole.

1.4.2. Persulfate oxidation through thermal and/or chemical activation

Recently introduced for application to effluents and soils contaminated with organic compounds, persulfate (PS) use becomes of universal interest (Huang et al. 2005). PS can be used to degrade organic contaminants however after being activated into sulfate radicals (Liang et al. 2004). Those are powerful oxidants more selective than hydroxyl radicals and work by electron abstraction instead of hydrogen abstraction as it is the case of hydroxyl radicals (Minisci and Citterio 1983). Activation can take place thermally by simple heat of the solution (Liang et al. 2003), photo-chemically through UV irradiation (Lin et al. 2011a) or chemically after adding appropriate amount of a specific transition metal such as cobalt, silver or iron (Anipsitakis and Dionysiou 2004). Being very selective, sulfate radicals can even degrade the transformation products toward full mineralization that is the conversion of the original compounds into CO_2 and H_2O . However, this AOP has also some limitations especially related to the experimental conditions in terms of pH, ionic strength, radical quenching related to an excess of catalytic cations (Fe^{2+} , Co^{2+} , Ag^+). Accordingly, optimization of this process will be presented through the selection of different pharmaceutical probes (Bisoprolol, Ibuprofen, Sulfamethoxazole) and a universal dye (Methylene Blue) in addition to iron-based catalysts including monometallic (Fe^0), bimetallic (Fe^0Ag^0 , Fe^0Co^0) and trimetallic systems ($\text{Fe}^0\text{Ag}^0\text{Co}^0$, $\text{Fe}^0\text{Co}^0\text{Ag}^0$). These systems are presented as an alternative to the use of dissolved catalysts where PS activation is extremely rapid resulting in cannibalization of radicals and very low reaction stoichiometric efficiency (RSE) defined as the number of molecules of probe degraded over the number of molecule of PS consumed ($\Delta[\text{Probe}]/\Delta[\text{PS}]$).

2. Iron corrosion for environmental remediation

2.0 Preamble

A survey of the sixteen papers on which this work is based reveals that a very recent article (P12 – Caré et al. 2013) deals with fundamental theoretical considerations of processes of iron corrosion. It may be surprising that for a 30-years-old technology, basic aspects of involved processes are still discussed. The situation is even worse as P12 (Caré et al. 2013) was written as collective response of five of the six authors to numerous colleagues acting as peer-reviewers at several high impact scientific journals to which articles post P3 (Ghauch 2008) were submitted. The expertise of the sixth author (Dr. Caré) is “iron corrosion in steel rebar” with particular emphasis on concrete cracking caused by expansive iron corrosion (Caré et al. 2008, 2010).

The views presented in P12 (Caré et al. 2013) are controversially discussed in the literature although they are based on the first principle of chemical thermodynamics (iron mass balance). The still prevailing view, that metallic iron is an environmental reducing agent, is based on the thermodynamic valid argument, that the redox potential of the electrode reaction $\text{Fe}^{\text{II}}/\text{Fe}^0$ ($E^0 = -0.44$ V) is lower than that of dissolved oxygen ($E^0 = 0.81$ V) and several oxidized species available as contaminants. However, water (H_2O or H^+) is also an oxidant for Fe^0 ($E^0 = 0.00$ V). Because water is the solvent, its stoichiometric abundance makes Fe^0 oxidative dissolution by H_2O the most favourable reaction in the $\text{Fe}^0/\text{H}_2\text{O}$ system. The consequence is that the Fe^0 surface is constantly covered by iron oxides and Fe^0 is not (readily) available for electron transfer to the contaminant (direct reduction, electrons from the metal body).

It is important to notice that the view that Fe^0 is an environmental reducing agent has: neither properly considered (i) the thermodynamics of iron oxide precipitation nor (ii) the thermodynamics of processes occurring within the oxide scale at the vicinity of Fe^0 . Although these aspects have been presented in the scientific literature six years ago (Noubactep 2007, 2008), there is evidence that this alternative view is not really understood by the majority of active researchers on “ Fe^0 for environmental remediation”. Therefore, the present chapter aims at reviewing the essential features of aqueous iron corrosion and outlining their significance for processes yielding contaminant removal or contaminant oxidation in $\text{Fe}^0/\text{H}_2\text{O}$ systems. Moreover, the key features will be contrasted by the state-of-the-art knowledge on the operating mode of $\text{Fe}^0/\text{H}_2\text{O}$ systems.

2.1 State-of-the-art knowledge on Fe⁰/H₂O systems

2.1.1 Remediation Fe⁰/H₂O systems

Permeable reactive barriers (PRBs) containing granular metallic iron (Fe⁰) are regarded as an accepted technology for the remediation of contaminated groundwater. Fe⁰ PRBs operate with natural groundwater gradients driving flow to treat large volumes of water with low concentrations of contaminants (Bigg and Jugg 2000, O'Hannesin and Gillham 1998, Scherer et al. 2000, Jambor et al. 2005, Painter and Milke 2007, Henderson and Demond 2013). The most commonly used Fe⁰ is of mm or μm size and represents a standard material (conventional Fe⁰) against which alternatives are compared. Alternative materials included nano-sized Fe⁰ (nano-Fe⁰) and multi-metallic systems (including nano-sized). Other reactive metals (e.g. Al⁰, Cu⁰, Mg⁰, Mn⁰, Ni⁰ and Zn⁰) have been also tested at all particle sizes (nm, μm and mm) (Bokare et al. 2013, Du et al. 2013, O'Carroll et al. 2013). A general trend is that nano-Fe⁰ are more efficient than Fe⁰, bimetallic more efficient than Fe⁰, and Zn⁰ is more efficient than Fe⁰ (Grittini et al. 1995, Liang et al. 1997, Elliot and Zhang 2001, Lien and Zhang 2002, Begum and Gautam 2011, Salter-Blanc and Tratnyek 2011, Bokare et al. 2013, Cai et al. 2013, Liu et al. 2013).

Fe⁰ is considered a (strong) reducing agent which induces the reductive transformation of organic species or promote the reductive precipitation of oxidized metals (Henderson and Demond 2013). It is acknowledged that water and other species like nitrate or oxygen will quantitatively oxidize Fe⁰. The net result may be the production of gases (H₂, N₂). In addition, the pH increase inherent to iron corrosion has been reported to result in the precipitation of non-contaminant phases (e.g. CaCO₃, FeCO₃). Because species like calcium and carbonate are typically present at concentrations several orders of magnitude higher than that of target contaminants, it is commonly reported that non-contaminant phases dominate the precipitates that are formed in field Fe⁰/H₂O systems (Westerhoff and James 2003, Huang and Zhang 2005, Henderson and Demond 2013).

The drawbacks of Fe⁰ PRBs have been identified. They include (i) lack of opportunities for external reactivity manipulation (**drawback 1**), as the efficiency of the system is mostly determined by the reactivity of used Fe⁰, (ii) progressive Fe⁰ passivation by precipitation of minerals at the surface (reactivity loss) (**drawback 2**), and (iii) gradual decrease of the porosity and permeability of the system (permeability loss) (**drawback 3**) yielding at the term to system clogging (Morrison et al. 2006, Noubactep et al. 2010, Caré et al. 2013). To

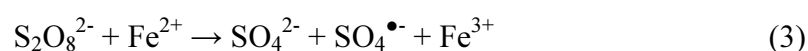
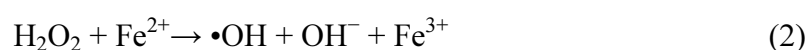
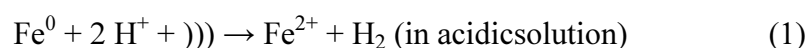
properly address these drawbacks (drawback 1 through 3), the fundamental understanding of the mechanisms of the dynamic processes occurring in Fe⁰/H₂O system must be realized.

Summarized, Fe⁰ is considered a reducing agent for the reductive transformation of oxidized contaminants. Fe⁰ is also oxidized by water and elevated pH values induce the precipitation of non-contaminant phases and the production of gases (H₂, N₂). At the term, non-contaminant phases and produced gases (H₂, N₂) significantly reduce the porosity, and thus, the permeability of Fe⁰ PRBs. It is essential to notice that this prevailing approach has never been univocally accepted (Lipczynska-Kochany et al. 1994, Bonin et al. 1998, Lavine et al. 2001, Furukawa et al. 2002, Jiao et al. 2009, Odziemkowski 2009, Liu et al. 2013). For example, using differential pulse polarography to simultaneously monitor the disappearance of nitrobenzene and the appearance of Fe^{II}, Lavine et al. (2001) could not clarify mechanistic details of processes yielding to the chemical reduction of “organic compounds at the Fe⁰ surface”. Moreover, the reductive transformation model cannot explain why inorganic and organic species without redox properties are quantitatively removed in Fe⁰/H₂O systems (Noubactep 2007, 2008). On the other hand, the whole discussion on the process of permeability loss has not properly considered the iron mass balance (Caré et al. 2013).

2.1.2 AOP Fe⁰/H₂O systems

Metallic iron (Fe⁰) has been shown an effective material for the improvement of advanced oxidation processes (AOPs). The idea behind using Fe⁰ for oxidant generation is that Fe^{II}, Fe^{III} and Fe^{II}/Fe^{III}-based minerals are known for their ability to serve as catalyst for the oxidative degradation of recalcitrant contaminants (Lipczynska-Kochany et al. 1995, Pham et al. 2009). Fe⁰ can induce a prolong activation of specific reactants like hydrogen peroxide (HP) or persulfate (PS) into powerful oxidative radicals e.g. Hydroxyl Radicals (HRs) and Sulfate Radicals (SRs).

Fenton (Segura et al. 2013, Cao et al. 2013), Fenton-like assisted sonication (Ziylan et al. 2013, Lai et al. 2013) and Persulfate (Hussein et al. 2012, Oh and Shin 2013) technologies are AOPs primarily using catalytic materials (e.g. Fe⁰ - Eq. 1) to produce HRs (Eq. 2) and SRs (Eq. 3) from hydrogen peroxide and persulfate, respectively.



Fe^0 aqueous oxidative dissolution (Eq. 1) in-situ generates iron corrosion products with well-documented catalytic properties. Relevant catalytic species include Fe^{2+} , Fe^{3+} , iron oxides, iron hydroxides, iron oxo-hydroxides.

Most of these iron corrosion products are reactive (Sikora and McDonald 2000), allowing additional useful catalytic properties that are yet to be characterized under well-controlled experimental/operational conditions. It is essential to notice that Fe^0 is irreversibly consumed in AOP $\text{Fe}^0/\text{H}_2\text{O}$ systems. However, Fe^0 consumption produce useful species (Fe^{2+} , Fe^{3+} , Fe oxides and hydroxides) that might be regenerated upon redox reactions. Furthermore, Fe^0 mass loading can be optimized to avoid that the maximum contaminant level (MCL) for dissolved iron ($0.3 \text{ mg}\cdot\text{L}^{-1}$) is not reached. This precaution avoids sludge generation through iron oxide precipitation.

Summarized, Fe^0 can induce an optimal promotion of the degradation of recalcitrant organic contaminants. Fe^0 improves the efficiency and longevity of AOPs once coupled to HP or PS in aqueous media. The key feature of using Fe^0 in AOPs is the chemical reactivity of Fe^0 that should be sustained to enable continue and progressive release of Fe-based activators of HP and PS.

2.2 Aqueous iron corrosion

Wealth of information is available on aqueous iron corrosion under natural conditions. They can be found in academic thesis, encyclopaedias, peer-reviewed scientific literature, technical reports and textbooks. Information on aqueous iron corrosion originates from various research branches including pipe corrosion in the oil and gas industry, waste repository industry and water supply industry (Snoeyink and Jenkins 1980, van Orden 1989, Brondel et al. 1994, Stratmann and Müller 1994, Antonio et al. 2000, Sikora and Macdonald 2000, Sarin et al. 2001, Sarin et al. 2004a, Sarin et al. 2004b, Nalli 2010, Obanijesu et al. 2010). However, profound understanding of the corrosion mechanism under remediation conditions is very important for material selection and design of sustainable systems (Gheju and Balcu 2011, Miyajima 2012, Bilardi et al. 2013a, Bilardi et al. 2013b, Btatkeu et al. 2013). In particular, the specificities of Fe^0 as used in environmental remediation have to be considered in its totality before a decision is made on the proper materials (Reardon 1995, Noubactep et al. 2005a, Reardon 2005, Noubactep et al. 2009, Btatkeu et al. 2013). The present section is a consolidated information pooled from various sources for the benefit of properly designing 'Fe⁰ remediation' systems.

2.2.0 Fe⁰ materials for environmental remediation

The Fe⁰ remediation industry would like to design Fe⁰/H₂O systems able at uninterrupted treat groundwater for some decades (up to four). During this long service life, used Fe⁰ materials would undergo corrosion under varying environmental conditions due to seasonally changes in water compositions and temperatures. The key feature of Fe⁰ materials for environmental remediation is that mechanical properties (e.g. ductility, elongation, hardness, impact strength, proof stress, tensile strength) are not of any important significance (**Feature 1**). Only the chemical reactivity is important. This key feature suggests that purposeful materials for environmental remediation should be characterized for their intrinsic chemical reactivity (Btatkeu et al. 2013). The second important feature of remediation Fe⁰ is their availability as chips, fillings and granules whose thickness (< 4 mm) is hardly larger than the wall thickness of industrial iron pipes (**Feature 2**). **Feature 1** suggests that available Fe⁰ materials are not optimised for environmental remediation as care was taken for optimal mechanical properties during their manufacture. On the other hand, **Feature 2** suggests remediation Fe⁰ particles are considerably most reactive than Fe⁰ pipes because of their smaller particle size (larger surface area). However, a smaller particle size also means shorter distance for electrons transfer and higher passivation probability in comparison to (thicker and longer) Fe⁰ pipes for which anodic and cathodic regions for a galvanic cell may be some km distant (Snoeyink and Jenkins 1980).

Taken together, **Feature 1 and 2** clearly demonstrate that despite the abundance of literature on aqueous iron corrosion, remediation Fe⁰/H₂O systems is a stand-alone research area which can only intelligently use impetius from the broad corrosion knowlegde. It has already been discussed, that this task was not properly done (Noubactep 2007, Ghauch et al. 2011a, Gheju and Balcu 2011, Togue-Kamga et al. 2012, Caré et al. 2013, Noubactep 2013c). Hence it is imperative for Fe⁰ remediation research community to be familiar to basic aspects of iron corrosion concerning the systems they are striving to design (Noubactep 2013c). Such a generalized “Corrosion Awareness” would ensure a scientific basis for sustainable Fe⁰/H₂O systems. The chapter is an attempt in this direction.

2.2.1 Electrochemical corrosion: Galvanic cells

Electrochemical corrosion of Fe⁰ materials involves a flow of electrons between cathodic and anodic areas on a piece of Fe⁰ metal or several pieces of Fe⁰ joined together by an electronic conductor (e.g. metal, metal oxide, activated carbon). A galvanic cell is created when two different metals (areas of the same alloys) develop a potential difference between them in a

conducting electrolyte. The metal with the lower positive electrochemical potential (E^0 value) acts as an anode and corrodes metal ions away to balance the electron flow. The second metal with higher positive E^0 value acts as a cathode and is protected from corrosion.

The kinetics (and probably the extent) of corrosion in a galvanic cell depends primarily upon the difference in potentials of involved alloys/metals, their surface areas and the solution chemistry (conductivity, pH, temperature). The difference in potentials created between two metals depends on their relative ranking in the electrochemical series. Whenever two metallic materials are in contact and are exposed to an ionic conductive environment, the metal with most negative potential becomes anode and starts corroding. In other words, when Fe^0 ($E^0 = -0.44$ V) is alloyed with other metals with more positive potential ($E^0 > -0.44$ V), iron corrodes. Relevant metals include: Ag^0 , Cd^0 , Co^0 , Cu^0 , Ni^0 , Sn^0 , Pd^0 , Pt^0 . In other words, alloying or plating Fe^0 with one or more elements with $E^0 > -0.44$ V solely accelerates the kinetics of Fe^0 corrosion. This evidence demonstrates that bimetallic and multi-metallic systems used in environmental remediation accelerate Fe^0 corrosion by increasing the number of galvanic cells. Clearly, any increased chemical process (e.g. reduction) in a multi-metallic system relative to a mono-metallic system is only indirectly coupled to iron corrosion (**statement 1**). Statement 1 suggests that although accelerated iron corrosion (anodic reaction) of a multi-metallic system is an electrochemical process, observed contaminant reduction is not a simultaneous reaction (the corresponding cathodic reaction). Statement 1 also suggests/confirms that observed contaminant reduction by conventional Fe^0 is not necessarily the cathodic reaction corresponding to anodic iron dissolution (Noubactep 2009d).

2.2.2 Interactions within a Fe^0/H_2O system

This section describes Fe^0 corrosion under anoxic conditions and discusses the significance of iron corrosion for environmental remediation. Fe^0 oxidation by water is described by Eq. 4:

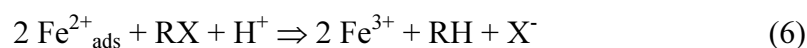
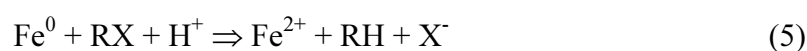


A key feature of Eq. 4 is that both Fe^{2+} and H_2 are reducing agents. In other words if a species is chemically reduced in a Fe^0/H_2O system, it is difficult to segregate whether involved electrons are from Fe^0 , Fe^{2+} or H_2 . This fact was already acknowledged by Matheson and Tratnyek (1994) but further investigations have culminated in direct reduction (electrons from Fe^0) being favoured as major mechanism of contaminant reduction in Fe^0/H_2O systems (Ghauch et al. 2011, Gheju and Balcu 2011, Noubactep 2011b, Noubactep 2011c, Caré et al.

2013, Noubactep 2013a, Noubactep 2013b, Noubactep 2011d). In Eq. 4 water (H₂O or 2 H⁺) is the cathodic reaction coupled to anodic Fe⁰ dissolution.

After Le Chatelier principle, Eq. 4 is shifted to the right (accelerated Fe⁰ dissolution) if: (i) H⁺ is abundantly available (acidic conditions), (ii) Fe⁰ is more reactive (e.g. bimetallic and trimetallic systems – Section 2.1) or (iii) Fe²⁺ and H₂ are consumed. Fe²⁺ can be consumed by relevant oxidizing species (E⁰ > 0.77 V) and the system will be enriched in Fe^{III} species including oxides and hydroxides. Fe^{II} and Fe^{II}/Fe^{III} oxides and hydroxides are porous precipitates with documented adsorptive affinity to both Fe²⁺ and H/H₂ (Charlet et al. 1998, Jiao et al. 2009). In particular, adsorbed Fe^{II} (or structural Fe^{II}) is a more powerful reducing agent than dissolved Fe^{II} (White and Paterson 1996, Charlet et al. 1998). The fact that reducing species are abundantly produced in Fe⁰/H₂O systems complicates mechanistic discussion and severely questions the prevailing view that Fe⁰ reduces organic species (reductive degradation) and sequesters inorganic species (reductive precipitation) (Lackovic et al. 2000, Lavine et al. 2001). This assertion alone makes clear that it is yet not clear how organic species are removed as their quantitative removal was largely documented, even for species that are not reducible (Lai et al. 2006, Jia et al. 2007, Miyajima 2012). On the other hand, adsorption and co-precipitation of organics species by iron oxide is well-documented (Gu et al. 1994, Bojic et al. 2009, Noubactep and Schöner 2010, Eusterhues et al. 2011).

The presentation above suggests that chemical reactions responsible for contaminant reduction are the following (RX stands for a halogenated organic compound):



While Eq. 5 is still conventionally used to rationalize contaminant reduction in Fe⁰/H₂O systems (Liu et al. 2013), the occurrence of reactions according to Eq. 6 and 7 have been traceably demonstrated (Gould 1982, Charlet 1998, Jiao et al. 2009). Moreover, the occurrence of individual reactions depends on the accessibility of the reaction site. Fe⁰ is constantly covered by an oxide scale such that a contaminant (RX) must migrate through the oxide scale to reach the reactive site on Fe⁰ (Noubactep 2007, 2008). It is not likely, that contaminants will quantitatively migrate to the Fe⁰ surface. This assertion is supported by the results of Strathmann and Müller (1994) who demonstrated that even molecular oxygen cannot diffuse to the Fe⁰ surface. Thus, Fe⁰ is oxidized by water (Eq. 4) and oxygen is reduced by Fe^{II} (Eq. 6-like). In other words, even if the oxide scale is electronic conductive

(e.g. Fe_3O_4), the chemical reduction by Fe^{II} species is kinetically more favourable than the electrochemical reduction by Fe^0 (statement 1 – section 2.1).

2.2.3 Contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems

The presentation above has recalled that Fe^0 is mainly oxidized by the solvent (H_2O). Thus iron corrosion products are abundant in the system. Any contaminant entering in such an ‘ocean’ of iron oxides and hydroxides (Noubactep 2009a) could be adsorbed by already precipitated species or enmeshed in the matrix of precipitating hydroxides (co-precipitation). Thus, adsorption and co-precipitation are the fundamental mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems (Noubactep 2010a). In a column system, size-exclusion is the third removal mechanism. Adsorptive size exclusion, coupled to adsorption and co-precipitation explain why all classes of contaminants could be quantitatively removed in $\text{Fe}^0/\text{H}_2\text{O}$ systems. Recent experimental works have confirmed theoretical predictions, that the primary selectivity criterion is the contaminant affinity to iron corrosion products (Gheju and Balcu 2011, Scott et al. 2011, Miyajima 2012, Miyajima and Noubactep 2012, Bilardi et al. 2013a, Bilardi et al. 2013b, Btatkeu et al. 2013, Miyajima and Noubactep 2013). Clearly, Fe^0 -based filtration systems are more suitable for contaminants with high affinity to iron hydroxides/oxides. This conclusion does not consider the chemical reducing power of Fe^0 and confirm the view that Fe^0 is a generator of removing agents.

Regarding Fe^0 as a generator of removing agents has rationalized the operating mode of remediation $\text{Fe}^0/\text{H}_2\text{O}$ systems. It explains why all classes of contaminants are removed and intuitively dictates that more material amounts are used for species with less affinity to iron oxides. Moreover, it eases the design of filtration systems, as main and side reactions are no more significant. The major task is to sustain iron corrosion and by ricochet contaminant removal. Now how to sustain iron corrosion?

While focussing the attention of contaminant reduction, researchers have forgotten to chemically induce reductive dissolution of iron corrosion products to complete mass balance (Kishimoto et al. 2011). On the other hand, iron balance has not considered the volumetric expansive nature of iron corrosion (Pilling and Bedworth 1923). The volume of each corrosion product is 2.1 to 6.4 times larger than the volume of Fe^0 in the metal body (Caré et al. 2008). This volumetric expansion is the major cause of permeability loss (Bilardi et al. 2013a, Bilardi et al. 2013b, Caré et al. 2013) and not the accumulation of non-contaminant phases (CaCO_3 , FeCO_3) and/or the accumulation of gas (H_2 , N_2) (Henderson and Demond 2011).

The proper consideration of the volumetric expansive nature of iron corrosion has opened an avenue for sustainable Fe⁰-based filtration systems. It has confirmed that a 100 % Fe⁰ system may be efficient but not sustainable (Hussam and Munir 2007, Hussam 2009). Moreover, the reproducible observation of Hussam and Munir (2007) is rationalized. In a pure Fe⁰ system, all particles are volumetric expansive and no place “is left” for expansive iron corrosion. Calculations showed that such a 100 % Fe⁰ system is clogged before one half of Fe⁰ is consumed. Accordingly, besides being a non-sustainable system, a 100 % Fe⁰ system is a pure material wastage. These theoretical considerations have demonstrated unambiguously that admixing Fe⁰ to non-expansive (inert or reactive) materials is a prerequisite for sustainable filtration systems (Caré et al. 2013). First experimental results have shown that the optimal Fe⁰:additive volumetric ratio is 25:75 (Bilardi et al. 2013a, Miyajima and Noubactep 2013). This low Fe⁰ ratio makes the resulting system a Fe⁰-amended system in which Fe⁰ is the additive (e.g. Fe⁰-amended sand filter).

2.3 Questioning the prevailing premise

2.3.1 Fe⁰ as reactive material

The presentation above has severely questioned the validity of the prevailing paradigm that Fe⁰ is an environmental reducing agent. Moreover, the prevailing paradigm should be abandoned to booster advance in research and thus, acceptance of the Fe⁰ remediation technology (Noubactep 2011b, Noubactep 2011c, Noubactep 2011d, Noubactep 2013c, 2014a, 2014b). The major curse of the prevailing paradigm is that it has created and maintained confusion on the true mechanism of “contaminant reduction” and “contaminant removal” in Fe⁰/H₂O systems (Noubactep 2015). Acknowledging that Fe⁰ is a generator of removing agents has re-directed efforts to overcome or at least limit the identified drawbacks of the Fe⁰ remediation technology (drawback 1 through 3 – Section 2.1.1).

It is certain that external reactivity manipulation (**drawback 1**) is not possible but materials should be selected to be long-term reactive in the subsurface. Tasks to this end include plating, admixing Fe⁰ with reactive oxides or granular activated carbon (Noubactep et al. 2012a). The reactivity loss (**drawback 2**) is unavoidable but material selection and system design should occur such that the residual Fe⁰ reactivity and the thickness of the system will guarantee long term efficiency. Finally, permeability loss (**drawback 3**) is solved by saving Fe⁰ material costs as the volume of Fe⁰ corresponding to a pure Fe⁰ system should be reduced at least to one half. However, admixing Fe⁰ with non-expansive materials suggests that

thicker filters should be built. This will be coupled to higher installation costs. Accordingly, even the installation costs of permeable reactive barriers could be revised.

2.3.2 Alternative materials

The search for alternatives to Fe^0 was based on the premise that Fe^0 ($E^0 = -0.44 \text{ V}$) is an environmental reducing agent. Accordingly, mostly tested alternatives are two metallic elements with more negative E^0 values: Al^0 ($E^0 = -1.66 \text{ V}$) and Zn^0 ($E^0 = -0.76 \text{ V}$). However, these efforts have ignored the fact that iron hydroxides are the sole low soluble hydroxides in the whole pH range of natural waters (Lewis and Swartbooi 2006, Lewis and van Hille 2006, Lewis 2010, Noubactep 2013a, Noubactep 2013b) (Fig. 1). Figure 1 suggests that $\text{Fe}(\text{OH})_2$ is more soluble than $\text{Zn}(\text{OH})_2$, however, because of the very strong hydrolysis and polymerisation of Fe^{2+} species, the concentration of dissolved Fe^{II} is always comparable to that of Fe^{III} . In other words, testing Al^0 and Zn^0 has not properly considered the thermodynamics of involved species. On the other hand, it has been traceably demonstrated that, despite more positive E^0 values, iron corrodes under environmental conditions because oxide scales on Fe^0 are neither adherent nor impermeable (Dickerson et al. 1979, Sato 2001, Noubactep 2010b). The fact that Al^0 and Zn^0 are likely to be passivated in the middle term questions the significance of results from short term batch and column laboratory experiments for field situations.

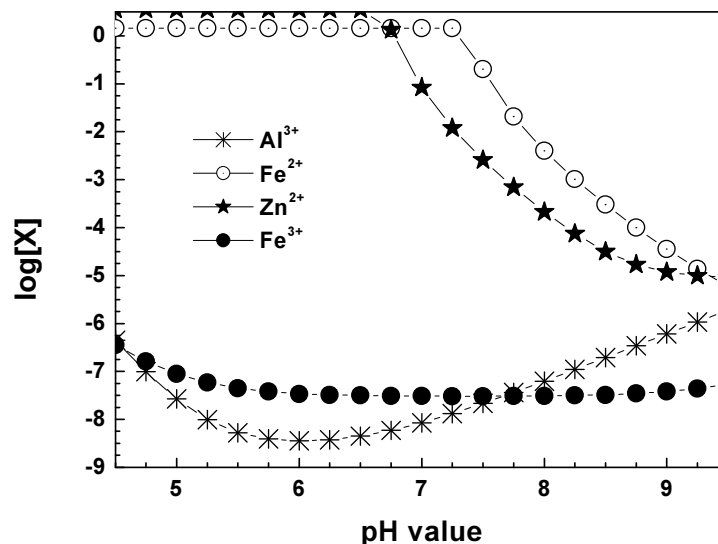


Figure 1. pH dependence of metal hydroxide solubility. The presentation is limited to the range of natural waters ($4.5 \leq \text{pH} \leq 9.5$). A clear pH dependence of hydroxide solubility can be observed. Considered minerals are $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$. (Data from Lewis 2010).

2.4 Conclusions

This chapter has clearly shown that the description of processes leading to contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems are currently very empirically based. There is an urgent need to improve the scientific understanding of these processes for control, optimisation, scale-up and at term proper design of efficient and sustainable Fe^0 remediation systems. The coming chapters will summarize the contribution of the author to the still widely ignored state-of-the-art knowledge on the processes governing contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems (Comba et al. 2011, Gheju and Balcu 2011, Scott et al. 2011, Caré et al. 2013, Noubactep 2013a, 2013, 2013c). It is clearly demonstrated that the suitability of Fe^0 for contaminant removal and oxidation process results from the long term production of reactive species. Thus, in both cases, Fe^0 is an in place (in-situ) generator of remediation agents.

3. Overview on the appended articles on Fe⁰ remediation

3.1 Introduction

2007 was a crucial year for the development of the Fe⁰ remediation technology. Two complementary peer-reviewed critical review articles were published during this year. The first article by Henderson and Demond was published in the established journal “Environmental Engineering Science” (Vol. 24). The second article by Noubactep was published in the first issue of “The Open Environmental Journal”.

Contrarily to previous overview articles/reports analysing individual case studies (e.g. Scherer et al. 2000, Richardson and Nicklow 2002, Tratnyek et al. 2003, Warner and Sorel 2003), Henderson and Demond (2007) rather considered broad performance issues. Accordingly, they analysed available data from field Fe⁰ PRBs and determined parameters contributing to system failure. Their analysis supported the view that Fe⁰ reactivity loss, rather than a decrease of the system’s hydraulic conductivity (permeability loss), is more likely to limit PRBs sustainability (long-term efficiency). They concluded that, because of the sparseness of field monitoring of relevant parameters (including Eh), their results needed to be corroborated by future data. It is essential to state that the review of Henderson and Demond (2007) (105 independent citations at Scopus on 2013/07/01) was based on the unrestricted view that Fe⁰ is a reducing agent. Moreover, as shown in Chap 2, the volumetric expansive nature of iron corrosion was not properly considered in discussing permeability loss.

Noubactep (2007) (Scopus not indexed) came along with a different view stating that the well-documented contaminant reductive transformation results from indirect reduction by primary iron corrosion products (e.g. Fe^{II} and H/H₂). Accordingly, iron is corroded by water and contaminant reductive transformation occurs within the oxide scale on Fe⁰. This oxide scale is regarded by the reductive transformation model as a curse (reactivity loss). The model introduced by Noubactep (2007, 2008) belittled the importance of contaminant reductive transformation and revealed the essential role of adsorption and co-precipitation in the process of contaminant removal. Adsorption and co-precipitation were mostly considered as side processes in a reductive system (Mantha et al. 2001, Furukawa et al. 2002). It is essential to notice that Noubactep used a system-based approach (which is contrary to the still common approach) to determine the suitability of Fe⁰ for individual contaminants in treatability tests (Richardson and Nicklow 2002, Oh 2009, Huang et al. 2013a).

The present work is a contribution to the global effort to optimise the efficiency of Fe⁰ remediation systems (including Fe⁰ PRBs). This chapter will summarize the author’s

achievements, which are presented in details in the appended original articles P1 through P10. Results were all obtained in batch experiments but their contribution to properly design Fe^0 filtration systems (Chap. 2) is obvious.

The presentation will follow a chronological perspective to clarify how the author has liberated himself from the still prevailing model that Fe^0 is an environmental reducing agent to one of the main co-developers of the alternative model regarding Fe^0 as generator of removing (and reducing) agents. The state-of-the-art knowledge on the treatment of PPCPs will first be presented.

3.2 Removal of PPCPs in $\text{Fe}^0/\text{H}_2\text{O}$ systems: The state-of-the-art

During the past 14 years, an increasing awareness of the health impacts of pharmacological pollution has been observed (Daughton and Ternes 1999, Ternes and Hirsch 2000, Heberer 2002, Ternes et al. 2004, Westerhoff et al. 2005, Pauwels and Verstraete 2006, Stieber et al. 2008, Kümmerer 2009, Stieber et al. 2011, Kaplan 2013, Zhang et al. 2013). Conventional (waste)water treatment technologies are not able to efficiently address pharmacological pollution, which is collectively termed pharmaceuticals and personal care products (“PPCPs”) (Daughton and Ternes 1999). A specific treatment of hospital wastewater should minimise the emission of PPCPs. Various strategies have been introduced to mitigate the extent of contamination due to PPCPs. One approach is to incorporate a Fe^0 remediation unit.

The idea of using Fe^0 for PPCPs mitigation relies on the premise, that PPCPs chemical reduction ideally leads to non-bioactive and readily biodegradable transformation products, which can then be treated in conventional wastewater treatment plants. The same idea has been followed to demonstrate the suitability of Fe^0 for individual biological and chemical contaminants (Richardson and Nicklow 2002). However, given the huge number of PPCPs (more than 30,000) that are additionally present as mixtures in hospital wastewaters, it is questionable whether all PPCPs could be individually tested according to the present approach (Hendriks 2013). Admittedly, some published works have tested the suitability of Fe^0 for several PPCPs. For example, Stieber et al. (2011) tested the suitability of a granular commercial Fe^0 material (Gotthard Mayer Metallpulver GmbH, Rheinfelden/Germany) for the treatment of 7 PPCPs. However, the selection of the tested PPCPs was not based on their affinity to iron corrosion products. In fact, to be quantitatively transformed in a $\text{Fe}^0/\text{H}_2\text{O}$ system, any reducible contaminant must not be repulsed by iron oxides (covering the Fe^0 surface). In other words, the adsorptive affinity to iron oxides should be the paramount

criterion to segregate species treatable in $\text{Fe}^0/\text{H}_2\text{O}$ systems (Scott et al. 2011, Miyajima 2012).

The evidence that hydrophilic and poorly degradable organics survive wastewater treatment corroborates the importance of electrostatic interactions in the process of contaminant removal. This evidence has been known for decades (Mitchell et al. 1955) although its proper consideration in several aspects of environmental science is still poor (Nödler et al. 2010, Schaffer et al. 2012a, Schaffer et al. 2012b, Hendriks 2013, Hillebrand et al. 2013, Niedbala et al. 2013, Miyajima 2012). As an example, despite the report of Mitchell et al. (1955) that the cationic dye methylene blue (MB) is poorly adsorbed onto iron-oxide-coated sand (thus, on iron oxides), Fe^0 has been repeatedly reported to efficiently treat aqueous solutions containing MB (Ma et al. 2004, Frost et al. 2010). Actually this experimental observation cannot be refuted. However, it should be recognized that despite low affinity to iron oxides, enough adsorbents have been generated under experimental conditions to induce quantitative removal. This is exactly the principle of electro-coagulation (Bojic et al. 2009, Noubactep and Schöner 2010).

Another shortcoming of current procedures is the lack of characterization of used materials (Btatkeu et al. 2013 and ref. cited therein). For example, considering the work of Stieber et al. (2011), one should ask about the intrinsic reactivity of the commercial Fe^0 material (from G. Maier GmbH). If the intrinsic reactivity of this material is not known, what is the basis to compare the results to that obtained by other commercial materials (e.g. from Connelly-GPM, iPutec GmbH or Peerless Metals)? Moreover, other results are likely obtained only largely under different operational conditions (e.g. Fe^0 mass loading, mixing regime, volume of reaction vessels, pH value) (Miehr et al. 2004, Noubactep et al. 2009).

Another important feature from the Fe^0/PPCPs literature is that conventional Fe^0 (μm , mm) has been first tested. For reducible PPCPs exhibiting low level of degradation by conventional Fe^0 , multi-metallic systems and nano Fe^0 have been tested. However, as theoretically discussed (Noubactep 2009, Noubactep and Caré 2010a, Noubactep and Caré 2010b, Noubactep and Caré 2011, Noubactep et al. 2012b, Noubactep et al. 2012c) and experimentally demonstrated (Ghauch et al. 2011a, Gheju and Balcu 2011) the crucial factor is not primarily the higher reactivity of alternative materials but the (time-dependent) density of reducing agents within the system (Fe^{II} , H/H_2). This view has been recently independently confirmed by Liu et al. (2013) who introduced the concept of electron efficiency. Liu et al. (2013) have clearly criticized the current approach of material selection as a race to the most reactive material. The sole exception the author could identify is the work of Li et al. (2010),

purposefully alloying Fe⁰ to decrease the kinetics of iron corrosion. Liu et al. (2013) introduced an economy-based factor of electron efficiency defined as the percentage of electrons utilized in a target reduction over an entire consumption at a given time interval. The concept of electron efficiency demonstrates that not the most reactive but rather the most appropriate material should be sought (Btatkeu et al. 2013).

The presentation above has clearly demonstrated that the research community on Fe⁰ remediation has been working on a false premise for more than two decades. To the best of the author's knowledge, only five active research groups have realized and addressed the original mistake: (i) the group of Dr. Gheju at the university of Bucarest (Romania), (ii) the group of Dr. Moraci at the university of "Reggio Calabria" (Italy), (iii) the group of Dr. Noubactep at the university of Göttingen (Germany), (iv) the group of Dr. Scott at the university of Bristol (United Kingdom), and (v) the author's group at the American University of Beirut (Lebanon). In essence, these five research groups are far from the still active 'circle of founding fathers' (Canada/USA) (Painter 2004, 2005). Over the years, several researchers have challenged the current premise (e.g. Lipczynska-Kochany et al. 1994, Odziemkowski et al. 1998, Lackovic et al. 2000, Lavine et al. 2001, Mantha et al. 2001, Furukawa et al. 2002, Jiao et al. 2009). However, their contributions were mostly limited to 'gently' or 'collegially' criticizing the validity of some aspects of the still prevailing reductive transformation paradigm. On the contrary, Noubactep (2006a, 2006b, 2007, 2008) clearly challenged the concept as a whole and suggested a paradigm shift (Noubactep 2011b, 2011c, 2013a, 2013b, 2013c). This has been accomplished with more than 70 peer-reviewed articles including (<http://www.uni-goettingen.de/de/8681.html> - access 2013/07/04): (i) 23 short communications, 18 comments on research articles, (iii) 12 review articles and (iv) a thesis (habilitation degree). It is important to notice that the replies to Noubactep's comments were mostly severe, but not objective (Elsner et al. 2007, Tratnyek and Salter 2010, Nagpal et al. 2010). The next section will summarize the contribution of the author's group to the establishment of the state-of-the-art knowledge on processes yielding contaminant removal in Fe⁰/H₂O systems.

3.3 Removal of PPCPs in Fe⁰/H₂O systems: Beyond the state-of-the-art

As previously stated, the author contribution can be divided into two groups: (i) papers before P3 in which the experimental design and results interpretation followed the still prevailing reductive transformation paradigm ('dancing in the round'). P4 belongs to this group although

it was published later (2009), and (ii) papers after P3 which should be regarded as the major contribution to the validity of the alternative adsorption/co-precipitation paradigm.

3.3.1 Dancing in the round

The titles of the three papers from this group reveal that the presentation followed the reductive transformation concept (Ghauch 2008a, Ghauch 2008b, Ghauch and Tuqan 2008, Ghauch and Tuqan 2009): “*Rapid removal of flutriafol from water by zero valent iron powder*”, “*Catalytic degradation of chlorothalonil in water using bimetallic iron-based systems*”, and “*Reductive destruction and decontamination of aqueous solutions of chlorinated antimicrobial agent using bimetallic systems*”. The critics made to the still prevailing paradigm are guilty for these three papers. However, the good documentation of reaction products was an excellent aspect in all three articles and are still valuable for the discussion of the efficiency of processes occurring in $\text{Fe}^0/\text{H}_2\text{O}$ systems.

The major corrections made for further works included: (i) the use of lower Fe^0 mass loadings, (ii) the use of various mixing devices and mixing intensities (including undisturbed systems), (iii) the use of MnO_2 to control the availability of corrosion products, (iv) the record of the pH value and the iron concentration during the experiments, and testing trimetallic systems.

It is worth noting that the author was initially sceptic about some aspects of Noubactep’s model as can be read in the discussion of P3. For example the following paragraph is very illustrative:

“Dr. Noubactep has demonstrated that “contaminant coprecipitation through corrosion products has been shown to be primary removal mechanism in $\text{Fe}^0\text{-H}_2\text{O}$ systems”. This assumption could be true for a significant number of contaminants especially those without any halogens (X) on their structure. Because R–X bonds are sensitive to ET (electron transfer), this will lead to a breakdown of halogen bond and the halogens remain free into the solution unless they are adsorbed onto iron oxidation products.”

This text passage illustrates the fact that the well-documented reductive transformation of contaminant could be the reason for the rejection of the co-precipitation concept. In fact adsorption and co-precipitation as fundamental removal mechanisms may be misinterpreted as negation of chemical reduction. Instead of simply refuting Noubactep’s concept like other working research groups (Elsner et al. 2007, Tratnyek and Salter 2010, Nagpal et al. 2010), the author has poised to test its validity as it will be shown in the next section.

3.3.2 In tune with the mainstream science

To test the validity of the concept that contaminants are fundamentally removed from the aqueous phase by adsorption and co-precipitation (Noubactep 2007, 2008, 2010, 2011b), whether they are reduced or not, amoxicillin, ampicillin, β -lactam antibiotics, clofibric acid and diclofenac were used as probe PPCPs (Ghauch et al. 2009, Ghauch 2010, Ghauch et al. 2010a, Ghauch et al. 2010b, Ghauch et al. 2011a, Ghauch et al. 2011b). Used Fe^0 materials included mm, μm and nm Fe^0 , bimetallic and trimetallic systems.

Results generally confirmed and completed the state-of-the-art knowledge on the effect of various experimental parameters. In particular: (i) the positive effect of controlled plating to form mono-, bi- and trimetallic systems, (ii) increased reduction under anoxic conditions coupled to a slower reaction kinetics, (iii) accelerated contaminant removal under oxic conditions. These well-documented aspects will not be addressed here, interested readers are referred to individual papers and works of Jiao et al. (2009), Gheju and Balcu I. (2011), Scott et al. (2011) or Btatkeu et al. (2013). The present overview will be limited to the major innovative contributions of the appended papers for the area of ' Fe^0 remediation'.

3.3.2.1 The $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$ system

A major innovation of the experimental design was the parallel investigation of $\text{Fe}^0/\text{H}_2\text{O}$ and $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$ systems. These systems were reported in the literature for the investigation of radium, uranium and methylene blue removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems (Burghardt and Kassahun 2005, Noubactep et al. 2005, Noubactep et al. 2006, Noubactep 2009). Published results were not univocal as the reported delay of contaminant removal was seemingly in contradiction with the claims that MnO_2 sustains systems efficiency. Using more reactive bimetallic and trimetallic systems has resolved this issue (Ghauch et al. 2011a). In fact, MnO_2 delays the availability of corrosion products but definitively sustains iron corrosion, which guarantees contaminant removal as reduction is just a side aspect. In particular, in column studies iron corrosion products improve adsorptive size-exclusion (Caré et al. 2013).

3.3.2.2 Oxic vs. anoxic conditions

Oxic vs. anoxic experiments for bi- and trimetallic systems have demonstrated the importance of material intrinsic reactivity and operational conditions for the extent of reduction, the nature of reaction products, and the detection of both educts and products (Ghauch et al. 2011a). In fact, for the same experimental duration, using the same mass loading has resulted in various extent of (i) contaminant reductive transformation, (ii) species co-precipitation, and

(iii) various intermediate reaction products. These results suggest that without an unified protocol for the investigation of processes in $\text{Fe}^0/\text{H}_2\text{O}$ systems, produced data will keep a qualitative nature. For a proper design however, reliable quantitative data are needed.

3.3.2.3 Passivation of Fe^0 materials

For the first time within the Fe^0 remediation, experimental evidence is given demonstrating the importance of the kinetics of Fe^0 corrosion for the passivation of its surface. As summarized by Nesic (2007), the protectiveness of an oxide scale on Fe^0 depend primarily on the precipitation rate: *“As the Fe^0 surface corrodes under the scale, corrosion continuously undermines the scale. As voids are created, they are filled up by the ongoing precipitation, etc. When the rate of precipitation at the Fe^0 surface exceeds the rate of corrosion (scale undermining) dense protective scales form.. Vice versa, when the corrosion process undermines the newly formed scale faster than precipitation can fill in the voids, a porous and unprotective scale forms”*.

Working with trimetallic systems under oxic and anoxic conditions has corroborated this model. In fact the most reactive trimetallic system was the one who lost more rapidly his reactivity under oxic conditions suggesting that it was rapidly covered with an impervious layer of oxides. This result clearly shows that appropriate Fe^0 materials for site specific use should be identified/developed. A Fe^0 material which is very reactive will be rapidly passivated under more aggressive conditions. Here a less reactive material will be suitable. Therefore, a unified protocole for material testing is urgently needed.

3.4 Significance for future research

The observed reduction of oxidized contaminants and the oxidation of Fe^0 is not a simultaneously coupled-redox reaction. Clearly, contaminant reductive transformation is not the cathodic reaction coupled to anodic Fe^0 oxidative dissolution. In other words, although Fe^0 oxidative dissolution is an electrochemical reaction, contaminant reductive transformation is mostly a chemical reaction (electrons from Fe^{II} and/or H/H_2). However, as a rule the remediation industry is interested in removing contaminant and reduction of organics is mostly a mean to facilitate biodegradability. Whether the goal is reduction or elimination, the contaminant of concern has to reach the reaction site, the surface or the vicinity of Fe^0 .

The remediation industry has to deal with more than 100,000 substances at numerous sites with countless specificities (Hendriks 2013). Threatening more than 100,000 species requires an intelligent approach. A relevant strategy for the Fe^0 remediation industry could consist in assessing the affinity of relevant substances for iron corrosion products in laboratory

experiments. Later field studies could include multi-species settings. It is certain that this approach could be limited by financial constraints. However, primary target working with some relevant groups of species (e.g. anionic, cationic, neutral dyes) (Saha et al. 2011) would set the basis for a systematic research which can be first based on documented properties of individual species. In this approach lab and field experiments will be designed to fine tune design tools (thickness of the reactive bed, number of beds, mass of Fe⁰/bed).

4. Nanoscale and microscale iron particles for the improvement of the Fenton process under sonicated and silent systems

4.1. Introduction

Fenton's reagent is one of the oldest advanced oxidation technologies able to oxidize and destroy organic molecules under acidic conditions. The reaction products in most of the cases are benign (Diya'uddeen et al. 2012). The effectiveness of this technology toward water micro-contaminants has been demonstrated in a myriad of scientific publications and field applications during the last decades. In the conventional process, contaminated aqueous solutions are supplied with hydrogen peroxide (H_2O_2) and dissolved Fe^{II} species (from Fe salts). The whole process occurs in the aqueous phase (homogeneous reactions). The present work advocates for an alternative heterogeneous system (Segura et al. 2013). The Fenton process is coupled to low frequency ultra-sonication in an heterogeneous system in which dissolved Fe^{II} species are produced in-situ from the oxidative dissolution of micrometric or nanometric iron particles (Fe^0 or nano- Fe^0). For this purpose, the fundamentals of Fenton's reaction (advantages and limitations) will be presented first, then an overview on sonication at low frequency will be given, finally a summary of the results of carbamazepine and sulfamethoxazole degradation by Fenton/sonicated systems will be discussed.

4.2. Fundamentals of Fenton chemistry

Invented in 1890s by Henry John Horstman Fenton, the Fenton's reagent is developed in an aqueous solution containing H_2O_2 and Fe^{2+} species (Fenton, 1894). H_2O_2 is a weak acid ($\text{pK}_a = 11.65$) not able to oxidize directly, at a moderate load, high concentrations of organic compounds with aromatic moiety. However, if mixed with transition metals like Fe^{2+} , the mixture becomes extremely high oxidative due to the formation of hydroxyl radicals OH^\bullet (HR, redox potential of about 2.80 V) upon H_2O_2 activation and this in a stoichiometric manner. In such systems, HRs are the primarily reactive species that harshly oxidize organic molecules classified as persistent organic pollutants (POPs) (Gan et al. 2009). HRs are known for their potential to add hydroxyl substituents to aromatic rings yielding therefore ring opening and, under optimum condition, full mineralization by converting POPs to carbon dioxide and water (Rogers and Bunce, 2001).

4.2.1. Mechanisms

Originally applied to homogeneous media, Fenton's reaction showed also its performance in heterogeneous systems where solid additives like iron oxides were able to catalyze the scission of H_2O_2 followed by the production of HRs. Figure 2 shows the schematic of organic compound oxidation by Fenton reaction. Many side reactions are involved in this process as widely reported in the literature and include: radical initiation, radical propagation and termination, reaction with intermediates, carbonate species and natural organic matter (NOM) (Eq. 8 to 27) (Kang and Hua 2005, De Laat and Lee 2005, Venny and Gan 2012).

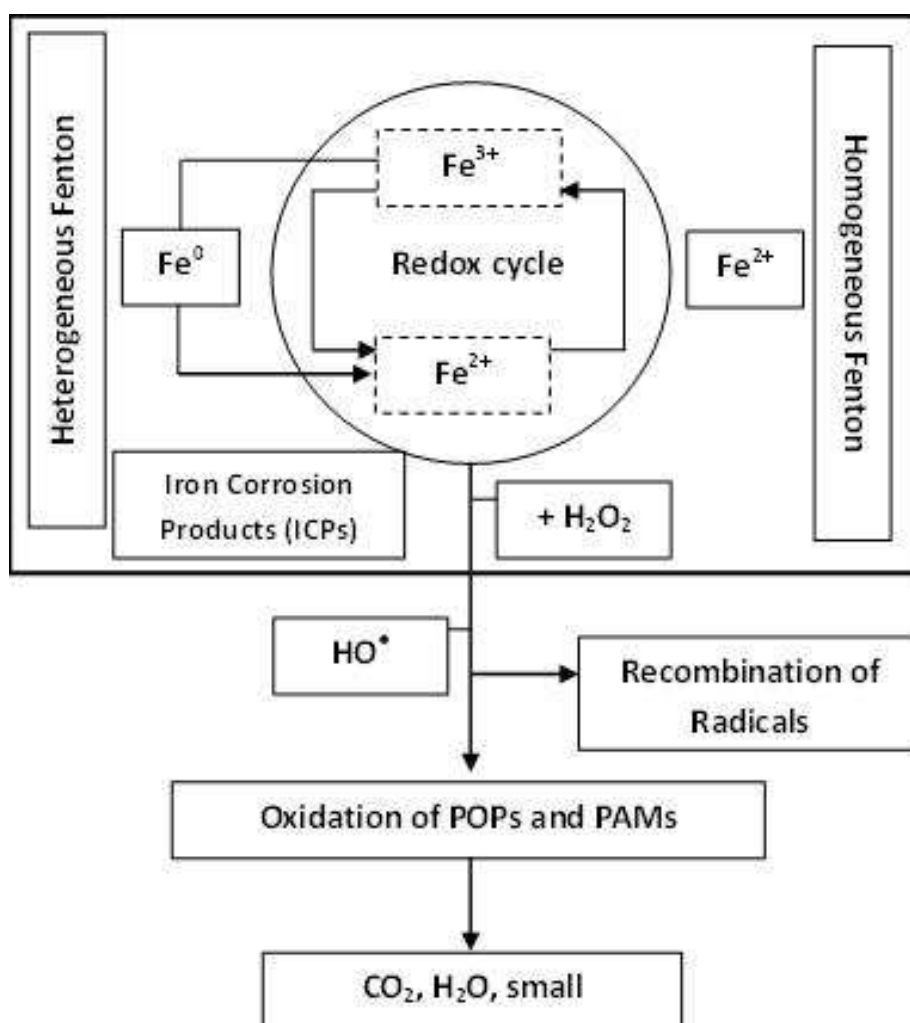
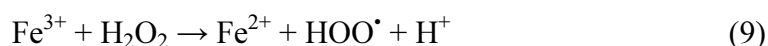
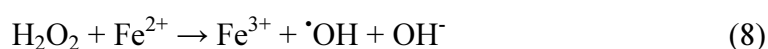
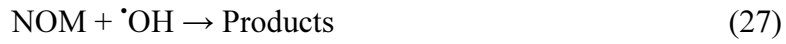
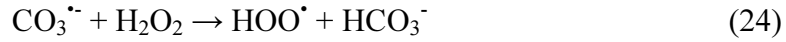
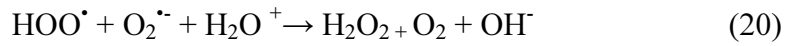
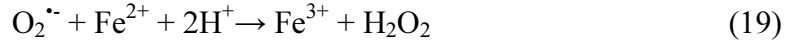
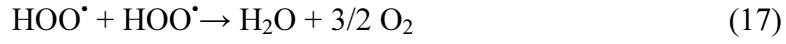
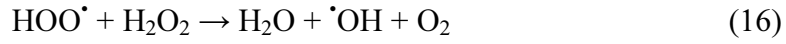
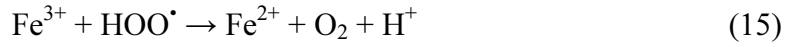
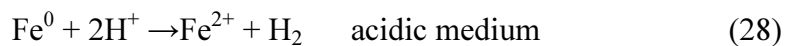


Figure 2: Schematic of organic compound oxidation by Fenton reaction.





The above equations are relative to reactions mainly occurring in homogeneous systems. However, in heterogeneous media using iron particles for example as H_2O_2 activators, additional reactions dealing with iron corrosion should also be considered. Reactive metallic iron (Fe^0) for example produces, upon immersion, iron corrosion products (ICPs) including nascent oxides and Fe^{2+} that might play a crucial role in H_2O_2 activation (Eq. 28). The kinetics of iron corrosion certainly varies depending on the intrinsic reactivity of used Fe^0 and the solution chemistry (O_2 level, pH value) (Fig. 3a). Concerning the variation as function of the acidity, the corrosion rate decreases with increasing pH till pH 4.0, becomes almost stable at $4.0 < \text{pH} < 10.0$ and decreases slightly above pH 10.0 (Fig. 3a). Within a medium rich in ICPs, Fe^{2+} recycling might also occur in the presence of Fe^{3+} species (Eq. 29). However, since the solubility of Fe^{3+} is very limited in aqueous solutions of $\text{pH} > 5$ (Fig. 3b), this phenomenon is not really favored. Instead, Fe^{2+} might be regenerated after reaction of radical species with soluble Fe^{3+} (Eq. 30).



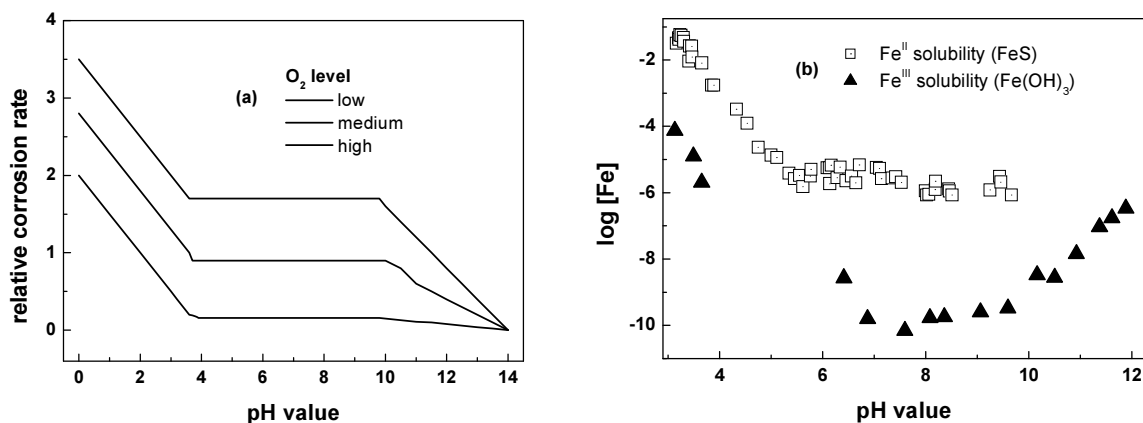


Figure 3. (a) Relative corrosion rate of iron as a function of pH (Wilson, 1923). It is arbitrarily assumed that at pH 4 iron corrodes with 12% of its rate at pH 0. (b) Solubility data of Fe^{II} in 0.1 M NaCl (25 C) and Fe^{III} in 0.01 M NaCl (25°C) as a function of pH (Noubactep and Schöner, 2010).

4.2.2. Types of Fenton's reaction

Three kinds of Fenton reactions have been described and tested for micro-pollutants: the Classical Fenton (CF), the Fenton-Like (FL) and the Amended Fenton (AM). To these three Fenton processes, one should add an improved Fenton-like oxidation process (IFOP) based on the use of low frequency ultra-sonication in heterogeneous solutions fed by H₂O₂ and micrometric or nanometric iron particles to form US/Fe⁰/H₂O₂ systems. The major challenge in improving Fenton process is the possibility to work at circumneutral pH instead of an acidic pH and to avoid the continuous feeding in H₂O₂ activators. CF is only based on dissolved Fe²⁺ however FL uses Fe³⁺, native or synthesized iron oxides or certain transition metals. Examples of iron oxides include: goethite (α -FeOOH), hematite (α -Fe₂O₃), magnetite (Fe₃O₄) and ferrihydrite (α -Fe₁₀O₁₅•9H₂O). The AM, however, is based on the addition of some chelating agents preventing thereby iron precipitation even at neutral pH operating conditions. If very abundant in solution, H₂O₂ activators might alter the Reaction Stoichiometric Efficiency (RSE) of the reaction where huge amount of HRs is activated while few moles of contaminants are degraded. The catalytic conversion of H₂O₂ into HRs is so rapid that radical-radical quenching might occur.

In order to overcome such situation, an AM system called IFOP is proposed in which iron particles are the promoters of Fe²⁺, Fe³⁺ and iron corrosion products (ICPs) into the solution that might be used for the production of HRs upon reaction with H₂O₂. The system became more efficient once coupled to low frequency US as it has been proposed for some permeable

reactive barriers for field application. This was helpful in cleaning iron particles surface making them more accessible by organic contaminants increasing thereby the longevity of the PRBs and keeping good efficiency in removing contaminants.

4.2. Fundamentals of ultra-sonication chemistry

Ultra sonication occurs at any wave frequency greater than 20 kHz. The ultrasonic wave includes compression and expansion cycles called rarefaction (Thompson and Doraiswamy 1999, Adewuyi 2001) during which dissolved molecules are entrapped by micro-bubbles that grow and expand under acoustic cycles. Upon adiabatic collapse, implosion of micro-bubbles occurs (Fig. 4). This will result in the release of high temperatures and high pressures yielding in some cases thermal dissociation of water molecules into H^\bullet and OH^\bullet . This phenomenon is known by the sonochemistry of water involving several chemical reactions (Eqs. 31-35).



HRs produced during the cavitation process can diffuse to the interfacial regions and bulk solution encountering specifically hydrophilic and non-volatile compounds for further oxidation reaction yielding hydroxylation, ring opening, etc. until partial or complete mineralization of the organic target (David 2009).

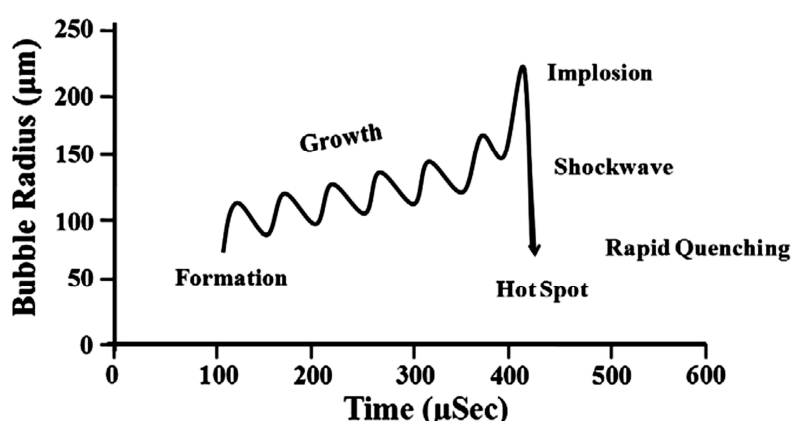


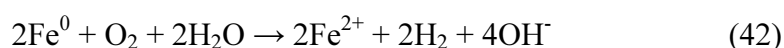
Figure 4. Growth and implosion of cavitation bubble in aqueous solution with ultrasonic irradiation (Suslick 1989).

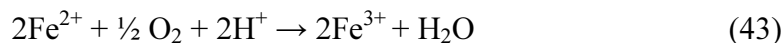
4.3. Coupling sonochemistry with Fenton using Fe⁰ (IFOP)

The developed IFOP is based on coupling of ultrasonication with Fenton reagent, however, using iron particles instead of dissolved iron species. The advantage of such system remains in the possibility of releasing smoothly ICPs responsible of the activation of H₂O₂ at low frequency sonication e.g. 20, 40 kHz. The latter is able to split H₂O₂ added into two HRs under the hot spot conditions in ultrasonic cavitation as the dissociation energy for the O—O bond in H₂O₂ is only 213 kJ/mol compared to 418 kJ/mol, the dissociation energy of O—H bond in H₂O (Eq. 36). In addition, US can improve iron corrosion by avoiding the formation of iron oxides able to stick at the surface of iron particles and consequently rendering passive the oxide scale at the surface of iron particles. At low frequency sonication, the amount of H₂O₂ produced is not at all significant to induce degradation of micro contaminants. Accordingly, the addition of H₂O₂ as external oxidant can greatly accelerate the degradation process especially if H₂O₂ is not in excess (Goel et al. 2004). Otherwise H₂O₂ can play a scavenger role after reaction with HRs producing [•]OOH (weaker oxidant and much less reactive) (Eqs. 36-40) (Ku et al. 2005; Nam et al. 2003).



Sonication of aqueous solutions containing H₂O₂ at 20 kHz and slightly acidic pH is not capable of producing HRs. However, this becomes possible at basic pH (10-12) because H₂O₂ is a very weak acid (Svitelska et al. 2004). These conditions are not relevant to natural waters and effluents making the process not applicable. Instead, feeding the solution with iron particles under low frequency sonication can easily induce the diffusion of Fe²⁺, Fe³⁺ and ICPs into the bulk solution through the interface iron particles/solution. It can also favor the dissociation of H₂O₂ at the surface of iron particles upon the presence of some catalytic sites. Such process can be considered as an improved Fenton system because CF, FL and AM can take place at the same time into the solution in parallel to iron surface cleaning from oxides and ICPs under US effect. Basically, iron particles corrode in aqueous solution and are converted into Fe²⁺ (Eqs. 41, 42) (Merouani et al. 2010) and even Fe³⁺ after further oxidation (Eq. 43).





Fe^{2+} and Fe^{3+} react separately with H_2O_2 as previously reported to form $\cdot\text{OH}$ and $\cdot\text{OOH}$, respectively (Eqs. 8, 9). However, $\cdot\text{OOH}$ resulting from the dissociation of the complex $\text{Fe}-\text{O}_2\text{H}^{2+}$ at a very slow rate can be greatly enhanced upon US effect (Eq. 44). The latter can also dissociate iron(III) complex to produce HRs as it is has been reported in our work on carbamazepine in the case of IFOP (Eqs. 45, 46). A cycle mechanism can then be established after the isolated Fe^{2+} further reacts with H_2O_2 to generate HRs (Eq. 8).



Finally, one of the advantages of using iron particles in such oxidation processes is the increase in the nucleation sites at the proximity of iron particle surface favoring the process of cavitation inception increasing thereby the probability of formation of hydroxyl radicals.

The IFOP developed in our study was tested on solutions containing carbamazepine (CBZ) and sulfamethoxazole (SMX). CBZ was tested with only micrometric iron particles while SMX was degraded using nanometric as well as micrometric iron particles (Ghauch et al. 2011c).

4.4. Degradation of PAMs by IFOP

4.4.1. Case of CBZ

The study on carbamazepine investigated the suitability of the improved Fenton oxidation process in rapidly degrading one of the non-chlorinated PAMs that has been recently detected in water resources in France used to produce water for human consumption. Experiments were performed at room temperature (21 ± 2 °C) and different pHs (3, 5, 7 and 9). Powerful oxidative hydroxyl radicals for CBZ oxidation were produced by H_2O_2 (12.5-100 mM) and Fe^0 (0.44-3.57 mM) additives under low frequency ultrasonication (40 kHz). Results showed no CBZ oxidation in the presence of an $\cdot\text{OH}$ scavenger (MeOH), confirming the Fenton's nature of the process. Acid-washed Fe^0 feeding showed increased CBZ oxidative degradation up to 85%. Recycling experiments demonstrated also the ability of Fe^0 to maintain its capability of releasing Fe^{2+} into the media to promote $\cdot\text{OH}$ generation for CBZ degradation (> 80% after 4 cycles). This was ascribed to the cracking effect on the surface of iron particles preventing thereby the formation of passive oxide. The process was also efficient in natural waters containing different species (e.g. Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , etc).

The OH radicals were shown as the primary oxidative species after being generated by H₂O₂ additives in the presence of small amounts of Fe⁰ acting as pseudo catalyst under low US frequency (40 kHz). Complete degradation of CBZ (42 μM, 20 mL) occurred at pH 3 after less than 30 min of reaction while almost 90% CBZ disappearance was reached at pH 5 after 1h of reaction with 100 μL of H₂O₂ additives and 200 mg of Fe⁰ load.

Comparison between one and multiple steps H₂O₂ addition did not show any significant difference after 1h of reaction. Recycling experiments showed clearly the ability of the US/Fe⁰/H₂O₂ system to be effective even after 4 successive cycles. However, the efficiency of the system vanished if non acid-washed Fe⁰ is used.

Intermediate oxidation products (by-products) were identified by LC/MS. Most of them are unstable hydroxylated-CBZ that disappeared at longer treatment durations after being attacked by hydroxyl radicals, a sign toward full CBZ mineralization.

Finally, the results on CBZ demonstrated that IFOP (US/Fe⁰/H₂O₂) is a promising technique for oxidative removal of non-halogenated pharmaceuticals under mild conditions. It allowed successful removal of CBZ dissolved in natural water, by its conversion into biodegradable transformation products which could be degraded later within a biological step.

4.4.2. Case of SMX¹

Sulfamethoxazole (SMX) solution was subjected to low frequency ultrasonication (US) at 20°C and pH 5 in US/nanoFe⁰/H₂O₂ and US/microFe⁰/H₂O₂ systems. Removal rates of SMX were compared under different reagents loads. Results showed that (i) SMX degradation depends on water matrix and (ii) is positively affected by the presence of carbonate species favoring iron corrosion that enhances H₂O₂ activation. Experiments showed also that nanoFe⁰ were not efficient in activating H₂O₂ in silent systems while microFe⁰ showed better efficiency. This was ascribed to the increase in the nucleation sites at the proximity of microFe⁰ surface favoring the process of cavitation/inception increasing thereby the probability of formation of hydroxyl radicals. The developed system showed clearly that advanced oxidation processes work better in a Fenton-like process by heterogeneous catalysis in US/microFe⁰/H₂O₂ system instead of nanometric iron slurry solution e.g. US/nanoFe⁰/H₂O₂ system.

A comparative study undertaken in silent and sonicated systems using μFe⁰ or nFe⁰ is presented below.

¹ Results on SMX were presented at the 245th ACS national meeting at New Orleans on April 9, 2013.

4.4.2.1. $\mu\text{Fe}^0/\text{H}_2\text{O}_2$ systems (Silent vs US)

In the absence of H_2O_2 μFe^0 does not seem to show an appreciable difference in the degradation efficiency of SMX between silent and US systems. However in the presence of H_2O_2 it has been found that sonication actually inhibited the degradation of SMX when compared to similar experiments operating under silent conditions. A further advantage that the silent system has over the US system is that it shows a slower rate of consumption of H_2O_2 especially at the lower iron concentrations. This discrepancy between the two systems may be ascribed to the increased iron(II) production under US conditions which acts as a quenching agent for hydroxyl radicals.

4.4.2.2. $\text{nFe}^0/\text{H}_2\text{O}_2$ systems (Silent vs US)

In the absence of H_2O_2 nFe^0 seems to lose its efficiency and reaches a steady state within 30 min of reaction. Furthermore there is no observable difference between the US and silent systems. However in the presence of H_2O_2 an increase in the degradation efficiency of $\sim 10\%$ was observed for the silent system; and a substantial increase in the degradation efficiency especially for high iron loads under US conditions. This seems to suggest that sonication has the ability to make nFe^0 more accessible by avoiding its agglomeration into the solution increasing thereby its corrosion rate which favors the activation of H_2O_2 in a moderate way. Finally one can notice the change in color of the nFe^0 solution from gray to yellow in the presence of H_2O_2 indicating that the nFe^0 particles are more oxidized only in the presence of H_2O_2 .

4.4.2.3. Identification of the transformation product

The improved advanced oxidation process of SMX showed the presence of one transformation product analyzed by HPLC-MS (Fig. 5). The study of the mass spectrum of this product analyzed in positive ESI mode depicted ring opening of the isoxazole moiety followed by hydroxylation of the open ring. The resulting transformation product ($[\text{M}+\text{H}]^+$ at 272.2 m/z) got disappeared at longer treatment time suggesting mineralization of SMX into more harmless products.

4.5. Conclusion: nFe^0 vs μFe^0 in Fenton-like oxidation

Presented results clearly demonstrated the importance of systematic investigations for the establishment of the science of ' Fe^0 remediation'. Considering the particle size alone, nFe^0 systems have a clear advantage over μFe^0 systems in terms of its consumption of H_2O_2 . This result is in tune with increased reactivity of nano-particles (Comba et al. 2011, Crane and

Scott 2012, Noubactep et al. 2012c). However, $n\text{Fe}^0$ systems do not exhibit excellent reusability results as is evidenced by the pronounced change in the color of the solution in the presence of H_2O_2 . This result suggests rapid and full oxidation of iron nano-particles within the experimental duration. It is clearly demonstrated that μFe^0 is advantageous in the sense that it is not completely exhausted for the experimental duration. μFe^0 can be reused for numerous cycles of reaction, as well as the fact that it does not need sonication to be activated which is a good advantage in terms of energy consumption. This observation is the essence of using $n\text{Fe}^0$ systems for rapid degradation but their long-term reactivity under environmental conditions has not been properly addressed (Noubactep and Caré 2010b, Crane and Scott 2012, Noubactep et al. 2012b). These fundamental aspects of iron corrosion should be routinely considered in all systems involving Fe^0 . Reproducible and comparable results will only be obtained when Fe^0 reactivity and all other operational parameters are properly considered.

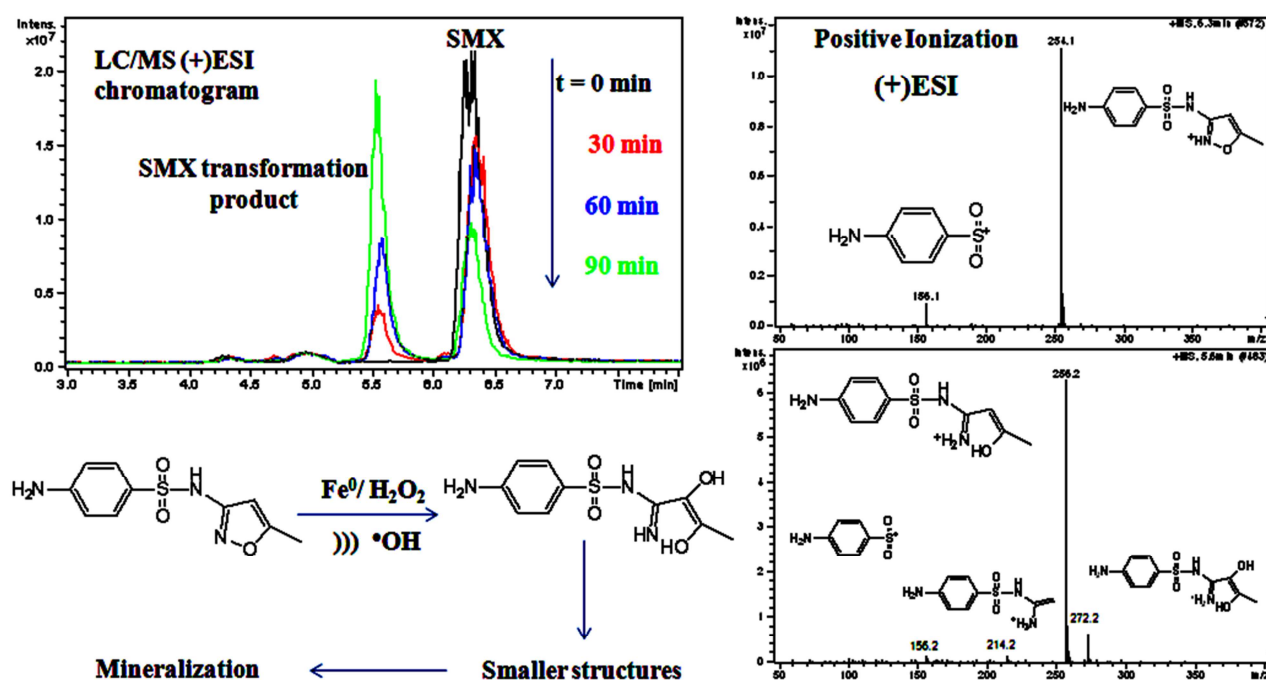


Figure 5: (a) HPLC/MS chromatogram of SMX during Fenton process. (b) MS spectra of SMX and its transformation product.

5. Persulfate for the degradation of organic contaminants: Activation through thermal and chemical ways using zero-valent iron particles

5.1. Introduction

Persulfate is considered the newest oxidant being used for the decontamination of soil and groundwater (Tsitonak et al. 2010). A search in Scopus database (23/06/2013) using the keywords: 'oxidation', 'persulfate', and 'pollutants' revealed a total of 141 articles published during the last 3 decades. From the 141 articles, 90 (64 %) have been published since 2009. In other words, only 51 articles have been published in almost 25 years. These statistics clearly show increasing interest of the scientific community in persulfate based degradation processes. Further systematic investigations are needed in order to (i) elucidate the degradation mechanisms of relevant organic compounds and (ii) optimize system design relevant to field operations.

Initially used for organic synthesis (Austin 1911), polymerization (Dyer et al. 1956) and as digester in the total organic carbon (TOC) analyzers (Walker and Clifford 2002) for the determination of TOC in water samples and effluents (Sharp 1973), persulfate (PS) becomes in recent years one of the most used oxidants for environmental applications. A survey of the three named original applications reveals that these are technical operations performed under controlled conditions (by skilled personnel). In particular, PS needs an initial (or a primary) activation to be efficient. Accordingly, to be successfully used in environmental applications, intelligent systems for PS activation must be developed.

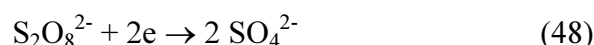
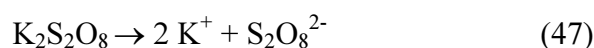
Activated PS generates sulfate radicals (SRs) of high redox potential ($E^0(\text{SO}_4^{2-}/\text{SO}_4^{\cdot-}) = 2.40 \text{ V}$) (Huie et al. 1991). This E^0 value is comparable to that of hydroxyl radicals (HR) ($E^0(\text{HO}^{\cdot}/\text{HO}^{\cdot-}) = 2.7 \text{ V}$) (Buxton et al. 1988). HRs have been widely used in environmental applications (see Chapter 4). However, those radicals are not very efficient in terms of selectivity and reaction stoichiometric efficiency (RSE). Therefore, catalysts capable of increasing lifetime of HRs precursors (e.g. H_2O_2) have been developed/synthesized in order to optimize the oxidation process in terms of longevity (Pham et al. 2009, Huang et al. 2013). In contrast, SRs are more selective and can be generated in a more controlled fashion from many PS salts precursors (e.g. Na^+ , K^+ , NH_4^+) for field applications over longer period resulting in sustainable decontamination solutions (Anipsitakis and Dionysiou 2004, Waldemer et al. 2007, Liang et al. 2008, Antoniou et al. 2010, Vicente et al. 2011, Rodriguez et al. 2012, Fang et al. 2013a, Fang et al. 2013b).

This chapter briefly gives an overview on the state-of-the-art of activation methods for PS with emphasis on (i) thermal activation upon heating and (ii) chemical activation using micrometric iron particles (MIPs) and iron corrosion products (ICPs). Own results gained with several probe species are summarized to substantiate that the efficiency of the PS/Fe⁰ system is primary a function of the reactivity (e.g. the intrinsic properties) of the organic molecules of concern. Optimum conditions for degradation reactions are determined based on a maximum of RSE. As for the elucidation of the degradation mechanisms of each probe, different schemes are available based on the identified intermediates. Sulfonated intermediates were identified for the first time during PS thermal oxidation of methylene blue as a dye probe.

5.2. Fundamentals of Persulfate Chemistry

5.2.1. Non activated persulfate

Highly soluble in water, persulfate salts (Na₂S₂O₈, K₂S₂O₈ and (NH₄)₂S₂O₈) dissolve yielding strong however relatively stable PS anions according to the following equations:



A review by House (1962) compiled the major PS oxidation reactions with inorganic species as well as organic molecules. It also described the mechanism of PS oxidation reactions as well as some kinetics study relative to the rate of oxidation of some compounds by PS. His review stills providing basic information on PS oxidation reactions with almost 607 citations in web of science (July 2013). It serves as a support for the application of PS oxidation to an important number of organic molecules of environmental concern.

5.2.2. Activated persulfate

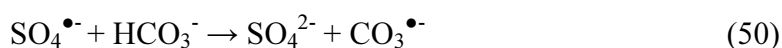
Several ways have been considered for the activation of PS into SRs. All of them are based on the breakdown of the O-O bond. The corresponding uncatalyzed reaction requires activation energy of about 33.5 kcal per mole (Kolthoff and Miller, 1951, Kolthoff et al. 1951). Accordingly, a raise in the temperature of the solution allows such energy to be reached (Waldemer et al. 2007) or the use of a metal ion (Anipsitakis and Dionysiou 2004) can easily catalyze the breakdown of the O-O bond. Also, photolysis (Lin et al. 2011) and microwaves (Yang et al. 2009) showed potential activation of PS into SRs however under specific conditions.

The produced SRs are species known by their very high reactivity and short lifespan able to oxidize with different extent most of the organic compounds much like HRs however under different mechanism. SRs remove electrons from an organic molecule to produce an organic radical cation, such as Eq. (49) (Forsey, 2004), while HRs abstract hydrogen from the C-H bond (Neta et al., 1977) or add to C=C bonds.



SRs are electrophilic reagents favoring high oxidation rates of aromatic organic molecules containing electron donating groups such as $-\text{(NH}_2\text{)}$, $-\text{(OH)}$, or $-\text{(OR)}$. However, if electron-withdrawing groups ($-\text{NO}_2$, $\text{C}=\text{O}$) are present on an aromatic cycle, the oxidation rate of the reaction decreases (Neta et al. 1977). On the other hand, substituents as Cl atoms are also expected to slow oxidation rates. For example, reaction rates for halogenated benzoic acids were 10 times lower than those for benzoic acids (Neta et al. 1997) and the presence of halogens in organic compounds (Sedlak and Andren 1991, Haag and Yao 1992, Tang and Huang 1995) has been shown to slow down reactions with HRs, and it is possible that the same applies for SRs.

Furthermore, solution additives (matrix effect) might also have negative effect on the oxidation rates by SRs. In fact, some of the inorganic species omnipresent in water (e.g. CO_3^{2-} , HCO_3^- , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , PO_4^{3-} , H_2PO_4^- , etc) react with SRs decreasing therefore the efficiency of the degradation reaction of organic contaminants. For example, the very well-known case is the one of carbonate species. Depending on the pH of the solution, these species might largely affect the degradation rate because of the reaction of SRs with carbonate species as supported by Eq. 50.



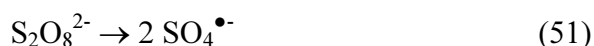
Finally, a decrease in the degradation rate of contaminants might take place in solutions of high ionic strength I that can be explained by a synergetic effect of all ions together into the solution yielding quenching phenomena of SRs. Accordingly, a case-by-case study could not reveal or reflect correctly and accurately the effect of separated ions into the solutions on the degradation rate of organic micro-contaminants. Instead, a comprehensive study should take into account all species in a mixture mimicking natural conditions.

Some of the useful methods for persulfate activation are summarized below.

5.2.2.1. Thermal activation

Upon heating (40-99°C), PS can be easily converted into SRs having one unpaired electron. Sulfate free radical is formed by thermal decomposition of the persulfate anion in an

aqueous solution as shown in Eq. 51. The reaction kinetics follows first order and is better catalyzed in solutions of acidic pH (House 1962).



Thermal activation is the simplest way to activate persulfate into SRs intermediates avoiding thereby any additives to the solution. It can be considered a green chemistry process because no chemicals are needed to achieve activation. However, thermal activation is an energy demanding process and its application to relatively high effluent volumes cannot be considered as cost effective by industrials. Accordingly, if applied, this should only be done on small effluents' volume like for example hot spot hospital effluents, pharmaceutical industries, PAH charged effluents (Zhao et al. 2013, Tan et al. 2012, Deng and Ezyske 2011, Huling et al. 2011, Antoniou et al. 2010, Gosetti et al. 2004). Another feature of using thermal activation is the possibility of its application to already heated effluent which is the case of some dyeing industries producing effluents at temperatures up to 50°C where no additional heat is needed. Recall that textile dyeing industries need huge quantity of water for textile dyeing, which they normally pump out repeatedly from the ground or natural water sources resulting in depletion of ground water level.

In this sense, using solar energy to heat normal effluents from room temperature to 40-50°C can be a good alternative in order to minimize the decontamination process cost. Such possibility is applicable in countries where abundance of sun is usually present e.g. (MENA, Gulf).

Appended articles P13 and P14 are some of the rare papers recently published (Nfodzo and Choi, 2011) and dealing with the degradation of pharmaceutical compounds using PS thermal oxidation. However, appended article P15 shows our contribution in the elimination of MB for it, sulfonated intermediates were identified to clearly demonstrate the direct implication of SRs in the oxidation process.

5.2.2.2. Chemical activation

In the presence of electron donor metals (e.g. Fe, Co, Ag, Mn, Cu, etc.) (Liu et al. 2012), PS can be chemically activated to produce sulfate free radicals at even room temperature (Eq. 52). The reaction is so rapid that excess of activators might allow SRs quenching by favoring radical-radical reactions (Eq. 53) instead of radical-organic molecule reactions.



Accordingly, the reaction should be well controlled in terms of additives so as to optimize the oxidation process. Furthermore, the concentration of metallic species should be maintained below the MCL defined by regulator's bodies in order to comply with recommended standards values.

Chemical activation has also been tested using metallic oxides (synthetic and natural) at the micrometric and nanometric scale (Zhu et al. 2013), citrate chelated iron, alkaline solution, hydrogen peroxide (H₂O₂) (Zhao et al. 2013), quinones and humic acids (Fang et al. 2013), minerals e.g. siderite (Huang et al. 2013), ferrous hydroxide colloids (Yan et al. 2013), granular activated carbon (Huling et al. 2011), etc. However, there is no published data on the longevity of the oxidation process once iron particles are used to activate PS and the role that can play in-situ generated iron corrosion products (ICPs) in sustaining the oxidation process over longer periods.

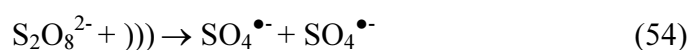
In this sense, the last appended article (P16) shows our contribution in understanding PS chemical oxidation of sulfamethoxazole (SMX) that has been improved in heterogeneous medium. This improvement is due to the adsorption of SMX on the surface of nascent iron oxide whose chemical properties are much elaborated than commercial iron oxides.

5.2.2.3. UV light and sun light activation

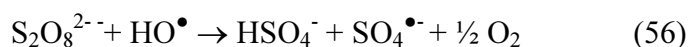
Upon irradiation with UV light, PS can be converted into SRs without any specific additive making easier kinetics studies in such medium. Several papers appeared recently on UV activated PS. Applications to a wide range of pollutants was successful as for example the mineralization of 2,2,3,3-tetrafluoro-1-propanol (Shih et al. 2013), the destruction of cyanobacterial toxin cylindrospermopsin (He et al. 2013), the degradation of rhodamine B (Chen et al. 2012), the oxidation of sulfamethazine (Gao et al. 2012) and bisphenol A (Yoon et al. 2012), etc. According to these authors, UV PS activation is a promising advanced oxidation technology for the degradation of organic contaminants. Its application can be extended to solar activation reducing thereby the operational cost.

5.2.2.4. Ultrasonic (US) PS activation

It has been demonstrated that a PS solution can produce under low frequency US SRs to carry out, in aqueous solutions, oxidation reactions yielding degradation and mineralization of organic contaminants. Under acoustic cavitation, PS is able to split into 2 SRs as reported in Eq. 54.



Those radicals can undergo additional reactions (Eqs. 55, 56) to produce hydroxyl radicals as secondary oxidation source of organic compounds.



However, if high frequency US is used, additional species can add to the oxidative medium enhancing thereby its efficiency in terms of chemical oxidation (Eqs. 57, 58).



This can also be accompanied by pyrolysis of PS upon raise of the temperature of the solution under sonication (Eq. 59).



5.2.2.5. Other PS activation methods

5.2.2.5.1. Microwave (MW)

In this case, microwaves are only used to heat the solution and therefore the result is similar to thermolysis where PS is converted to SRs by the mean of temperature. Some applications using MW-AOP are known as for example the discoloration of acid Orange 7 (Yang et al. 2009), the removal of 1,1,1-trichloroethane (Li et al. 2009) and oxidation of As(III) into As(V) in an aqueous environment (Neppolian et al. 2010).

5.2.2.5.2. Electron beam (EB)

Electron beam technology has also been tested on PS solutions in order to investigate PS activation into SRs. For example investigations into this direction included the irradiation of PS solution in the presence of different ions (Criquet et al. 2011), the oxidation of benzotriazole and humic acid (Roshani et al. 2011), and the influence of persulfate ions on the removal of phenol in aqueous solution (Boukari et al. 2011).

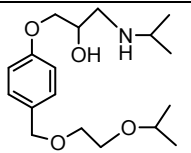
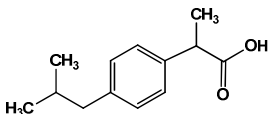
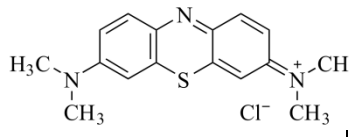
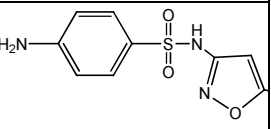
In all the above mentioned activation techniques, recently appeared the problem of secondary products formed upon oxidation as for example bromate in solutions containing bromide ions. This issue is seriously considered by the scientists and several studies with regard to this topic are under progress (Fang and Shang, 2012).

5.3. Application to PPCPs

Table 1 summarizes the most important physical properties of the different PPCPs investigated by PS oxidation through thermal (TA-PS) and chemical activation (CA-PS)

techniques. As it can be seen, these molecules have different properties giving them different affinities vis-à-vis of the advanced oxidation treatment in terms of degradation mechanism and resistance to mineralization. Only after proper consideration of these intrinsic properties of individual PPCP could the impact of additional parameters be traceably investigated. A paramount importance should be reserved to matrix composition of the contaminated water (pH, ionic strength). In fact, the presence of dissolved inorganic species might significantly affect the oxidation process. A general overview of these impacts have been investigated and presented in the appended articles P13-P16 (Ghauch and Tuqan 2012, Ghauch et al. 2012a, Ghauch et al. 2012b, Ghauch et al. 2013).

Table 1: Selected physical properties of pharmaceutical and personal care products (PPCPs) tested in this work.

	Bisoprolol (BIS)	Ibuprofen (IBU)	Methylene Blue (MB)	Sulfamethoxazole (SMX)
Medicinal property	β -blocker Hypertension	Non-steroidal Anti-inflammatory	Dye, monoamine oxidase inhibitor	Bacteriostatic Antibiotic
CAS Number	66722-44-9	15687-27-1	7220-79-3	723-46-6
Chemical Formula	C ₁₈ H ₃₁ NO ₄	C ₁₃ H ₁₈ O ₂	C ₁₆ H ₁₈ N ₃ SCl	C ₁₀ H ₁₁ N ₃ O ₃ S
Molecular weight (g/mol)	325.44	206.29	319.85	253.279
Chemical structure				
Solubility (mg/L)	2240	21	43,600	610
pKa	9.5	4.91	3.8	6.16
LogP (lipophilicity)	1.87	3.97	0.9	0.89
Density g/mL	1.033	1.029	1.0	1.462
mp °C	100	75-78	100-110 °C	166-169

5.3.1. Case of Bisoprolol (TA-PS)

Experiments undertaken on BIS solutions showed successful degradation over 1 h in aqueous solutions under thermal persulfate activation (40-70°C) through oxidation reactions

involving different radicals e.g. $SO_4^{\bullet-}$ and HO^{\bullet} . The calculated reaction stoichiometric (RSE) efficiency was very satisfying at 50°C (RSE = 1.0) and 60°C (RSE > 0.8). The reaction kinetics was attributed pseudo-first order rate with respect to BIS. Results showed that high temperatures and neutral pH values e.g. 7.0 were more favorable than acidic solutions and low temperatures for complete BIS degradation. Alcohol additives demonstrated the responsibility of hydroxyl radicals HO^{\bullet} as well as sulfate radicals $SO_4^{\bullet-}$ in oxidizing BIS. Among all inorganic additives, only HCO_3^- slightly influenced the observed degradation rates of BIS. Tests done on spiked BIS drinking water showed almost complete BIS degradation over 1 h of reaction regardless of a slight decrease in the observed degradation rate. The study of the total ion chromatograms obtained showed explicitly the formation of intermediate BIS oxidation products through hydroxylation and/or peroxydation. Oxidation reactions extended over 2 h confirmed the total disappearance of all byproducts. However, in order to confirm full mineralization, additional work should be undertaken using appropriate analytical techniques. The efficient oxidation of BIS can be considered as good indicator in order to extend this AOP to additional pharmaceutical persistent molecules dissolved in water or adsorbed on soils.

5.3.2. Case of Ibuprofen (TA-PS)

This work demonstrated that thermally activated persulfate can also effectively oxidize recalcitrant pharmaceuticals like IBU over a reasonable period of time (e.g. min to hours) at pH 7.0 with high RSE of about 0.65 compared to that of pHs 4.0 and 9.0. The oxidation reaction showed excellent Arrhenius behavior with activation energy of about 168 (± 9.5) kJ mol⁻¹ higher than the one previously obtained with BIS e.g. 119 (± 10.8) kJ mol⁻¹ which confirm the more recalcitrant character of IBU compared to that of BIS. Reactions in the presence of radical quenchers (EtOH and TBA) showed the implication of both radicals HO^{\bullet} and $SO_4^{\bullet-}$ in oxidizing IBU. Results showed also that IBU degradation can be explained by pseudo-first order model as for BIS however a deep investigation into the reaction order yielded a more accurate kinetics rate equation that can be described by the following

equation:
$$-\frac{d[IBU]}{dt} = (2.71 \times 10^{-4} \text{ mM}^{1-(a+b)} \text{ min}^{-1}) \times [IBU]^{0.25} [SPS]^1$$

. The oxidation reaction exhibited a fractional order 0.25 with respect to IBU demonstrating that a change in $[IBU]_0$ at a fixed $[SPS]_0$ would result in different IBU degradation rates. Furthermore, the elaborated kinetics model showed that the reaction is first order with respect to SPS therefore an increase

in $[\text{SPS}]_0$ for a fixed $[\text{IBU}]_0$ will result in a faster IBU degradation rate. Future attempts are planned in order to check the validity of this kinetics model to similar pharmaceutical molecules serving as acting ingredient in drug formulation. This could be considered as additional evidence of the feasibility of the thermal activation PS process that can be used in order to establish a kinetics model widely applied for waste water treatment charged in pharmaceuticals.

5.3.3. Case of Methylene Blue (TA-PS)

Experiments carried out on MB solutions showed clearly full discoloration and important degradation of the dye by thermally activated SPS at different temperatures (30-70°C). Results showed that discoloration kinetics depend on the initial concentrations of MB and SPS, the pH and the activation temperature as well. The reaction kinetics fits well with the pseudo-first order model ($R^2 > 0.99$), however, under specific conditions where the molar ratio $[\text{SPS}]_0/[\text{MB}]_0 > 32$. Under non-moderate conditions (50-70°C), full MB discoloration occurred quickly. This was totally achieved in less than 20 min for $[\text{SPS}]_0/[\text{MB}]_0 \geq 640$. However, under moderate conditions (30-40°C) running over two weeks, complete discoloration is reached in less than one day for $[\text{SPS}]_0/[\text{MB}]_0 \sim 160$ -1,600 and in 4-10 days for $[\text{SPS}]_0/[\text{MB}]_0 \sim 16$ -64. On the other hand, MB discoloration showed an Arrhenius behavior with greater activation energy for solutions of $[\text{SPS}]_0/[\text{MB}]_0 < 32$ than for solutions of $[\text{SPS}]_0/[\text{MB}]_0 > 32$ (e.g. $E_A = 145.3 (\pm 27.5) \text{ kJ mol}^{-1}$ and $107.4 (\pm 24.4) \text{ kJ mol}^{-1}$, respectively). This correlates with the principle of the pseudo-first order kinetics where the concentration of the oxidant should remain in large excess compared to that of the treated molecule. MB degradation by thermally activated SPS showed also an advantage of being successful for the dissolution and the degradation of MB-derivative precipitate formed after the addition of SPS to MB solutions at moderate temperatures. Both sulfate and hydroxyl radicals are responsible for the oxidation of MB into colorless derivatives. The LC-APPI-MS analysis showed the ephemeral character of those MB sulfonate derivatives. In fact, after 20 min of reaction, complete disappearance of all intermediates was noticed. This can strongly be considered as a possible route to full mineralization making from thermally activated SPS an advanced oxidation process that can be successfully used for the treatment of industrial effluents contaminated with dyes. Heating effluents to above 40°C is a costly process that is hardly affordable by industrials. However, this could be minimized if solar stills are used to increase the temperature of those effluents to more than 40°C accelerating therefore the discoloration process. Research in this direction is currently in progress.

5.3.4. Case of Sulfamethoxazole (CA-PS)

This work demonstrated that PS chemical activation is a reliable method for the treatment of water contaminated with recalcitrant SMX (39.5 μM) in less than 2 h. $\text{Fe}^0/\text{H}_2\text{O}$ systems were efficient in activating PS progressively minimizing therefore under optimized conditions SRs quenching. A small load of commercial micrometric iron particles (MIPs) (e.g. 2.23 mM) was sufficient to completely degrade SMX over a 60 min reaction time. The application of PS in different water-based matrices revealed that initial pH is important to consider, especially in the context of initiating iron corrosion responsible for the release of Fe^{2+} species for PS activation. Results using deionized (DI), tap and underground (UG) water revealed similarities between the last two water types where SMX degradation efficiency was directly affected by bicarbonate content. In contrast, after its elimination through acidification, all solutions showed similar behavior toward SMX degradation over 3 cycles of 1 h until complete MIPs depletion. SMX degradation in $\text{Fe}^0/\text{H}_2\text{O}$ systems showed the presence of a stable transformation product. However, in $\text{Fe}^0/\text{H}_2\text{O}$ PS-spiked systems, complete disappearance of SMX and its transformation product occurred; the mineralization extent reached 37% under smooth conditions making PS oxidation technology an excellent method for the treatment of organic micro-contaminants. Additional investigations into the long-term use of PS activators like bimetallics, trimetallics and natural iron oxide-based systems (e.g. ferrihydrite, lemonite, etc.) might be useful in order to improve the RSE that reached a maximum of 5.2% in the current work (Ayoub and Ghauch, 2014). Compared to thermal activation, PS chemical activation could present an economical advantage in terms of energy consumption and long term application if natural minerals could demonstrate their effectiveness for sustainable solution toward PS activation. Research in this direction is in progress in our laboratory for a comprehensive optimization of PS/Activators in aqueous systems using natural minerals.

5.4. Conclusions

The use of PS as oxidant has proved its effectiveness in degrading PPCPs under very moderate conditions that can be encountered in real case effluents. For example, the pH, ionic strength, ions content, concentration of PS, temperature and activator loads are parameters that can affect the efficiency of the oxidation process.

Iron particles demonstrated high potential of PS activation especially for long term applications because of their smooth oxidation in the medium. Iron corrosion products (ICPs)

generated include dissolved Fe(II) and nascent iron oxides capable of sustaining the oxidation process due to the intrinsic properties of those ICPs known by their high reactivity.

Optimization of operational parameters has been established. For example the RSE reached in TA can lead to 100% efficiency increasing thereby the longevity of the process. Also, a kinetics model has been developed with possible implementation to specific effluents of small volumes e.g. hospital effluents.

The results showed also for some species the implication of both SRs and HRs in the oxidation process. The identification of sulfonated transformation products can be considered as an evidence of the direct implication of SRs in the oxidation process and their reactivity toward aromatic cycles. However, hydroxylated intermediates demonstrated in the majority of the cases the implication of HRs in the oxidation process.

The mineralization extent was acceptable (e.g. 37%) considering the small concentration of PS used (1 mM). This could be much higher if greater PS amount has been used e.g. 20-100 mM. However, this should also be well controlled in order to avoid radical quenching and therefore a decrease in the RSE of the reaction.

5.5. Future developments

In view of the obtained results, several recommendations can be addressed in order to better improve the use of PS for the degradation of recalcitrant organic molecules especially PPCPs.

For example, more emphasis should be given to natural activators usually abundant without any prior treatment minimizing therefore the operational cost. Some of these activators are iron-based systems in the form of oxides or silicates to be collected in zones that was under volcanic activities.

Another source of PS activators can be found in several industrial wastes as for example the iron collected upon cleaning of the surface of rotor disk before the installation of new pad breakers. Preliminary results (not yet published) indicate clearly the potential of this iron waste in activating smoothly PS in aqueous solutions of circumneutral pH.

Coupling CA with TA might increase the mineralization yield of organic contaminants because of the high density of SRs that will be produced in the medium. Despite the fact of being expensive if classical energy is used to heat solutions for PS oxidation, renewable energy can be used for this goal. Existing or new engineered solar stills can help in this direction because temperatures of 50°C can be easily reached.

Finally, it also might be interesting to do column experiments in which a reactive zone of a mixture of sand and iron (to define the % of each) is used for an influent gradually spiked by PS. In such a case, permanent oxidation can be reached accompanied by water filtration on sand/iron oxides bed.

6. Concluding remarks

Remediation with elemental iron (Fe^0 or ZVI) is overviewed in this thesis. Issues and limitations of experimental designs aiming at optimising the Fe^0 technology were identified and avenues for further improvements suggested. At the term the huge potential of this excellent water treatment material could be fully exploited in appropriate designs.

Remediation with Fe^0 is a rapidly growing sector of environmental science. A search at Scopus (23/06/2013) with ‘zerovalent iron’ and ‘remediation’ revealed that 2,029 scientific articles may have been published on this sector since 1994. In particular, a growing body of evidence has proven Fe^0 as highly efficient and affordable remediation material. In recent years, the focus was mainly directed on nano-scale Fe^0 and various Fe^0 -based systems (including bimetallic and persulfate heated systems). However, the general competitiveness of Fe^0 against conventional treatment systems (e.g. adsorption on granular activated carbon, chemical oxidation) is still widely disputed. It is even not yet established, whether Fe^0 plays any significant role in the process of contaminant chemical reduction. To sum up, the available literature on remediation with Fe^0 is a confusing array of independent data (Henderson and Demond 2007, Comba et al. 2011, Ghauch et al. 2011, Gheju 2011, Crane and Scott 2012, Noubactep 2012, Noubactep et al. 2012b, Btatkeu et al. 2013, Tepong-Tsindé et al. 2015a, Tepong-Tsindé et al. 2015b). Consequently, in order for different Fe^0 -based systems to be effectively contrasted with each other and to other conventional remediation technologies, a universal empirical testing framework is required. In particular, the term ‘reactivity’ should be carefully used and its relationship to ‘efficiency’ well-defined (Miyajima 2012, Btatkeu et al. 2013, Miyajima and Noubactep 2015).

The reactivity of Fe^0 material is commonly characterized in short term (lab or field) experiments. The initial reactivity is typically high as aqueous iron corrosion is a self-inhibitive process. Therefore, the efficiency of a Fe^0 system should be designed based on the ‘residual’ material reactivity: that is the Fe^0 reactivity beyond the formation of an oxide scale. Fig. 6 illustrates the evolution of the treatment efficiency of two different Fe^0 systems as compared to a reference (non-reactive system). It is seen that the reference system is not reactive at all. Here, the breakthrough occurs after 10 % of the treatment duration (arbitrary relative value). Such a system can be sand or pumice filter (media filtration). The two other systems could be differentiated by the nature of used Fe^0 (nm, μm or mm) or their amounts. Fig. 6 reveals that for up to 22 % of the treatment time both systems are very efficient at treating the water of concern. An initial breakthrough is observed in system ZVIa after some

22 days and pseudo-equilibrium after some 30 days. This pseudo-equilibrium corresponds to a relative removal efficiency of about 50 %. In other words, system ZVIa is suitable for water for which 50 % removal of the initial amount of contaminant is satisfactorily. If the extent of contaminant removal should reach 70 to 80 %, then system ZVIb is the suitable material to be used. It should be pointed out that ZVIa can still be used to achieve 70 to 80 % contaminant removal, but in a different design (e.g. two columns in series, a low flow rate).

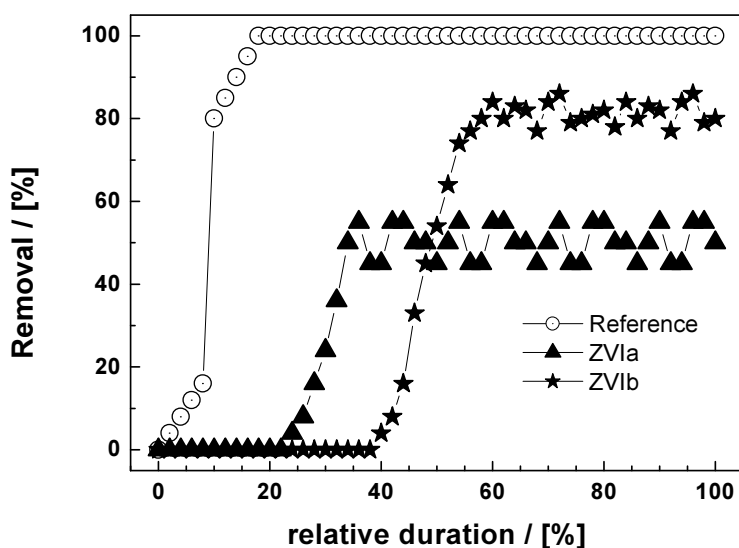


Figure 6: Schematic representation of the time-dependant evolution of the efficiency of three filtration systems: a non-reactive system (reference) and two Fe⁰-based systems.

The discussion in Fig. 6 is based on a conventional granular Fe⁰ material for reactive filtration. However, the resulting rule of thumb can be extended to all other Fe⁰-based systems. Thereby, the main question is ‘how long should the used material be efficient?’ For nano-Fe⁰ for example, the total reaction time could be some few days/weeks, while the duration for micro-Fe⁰ could reach some years/decades. Similarly, for wastewater treatment a micro-Fe⁰ can be recommended for use in some treatment cycles before recycling. Here, recycling could just mean ‘allow the surface layers to be corroded by air O₂’ (‘initiation/regeneration by aeration’). It is essential to recall that the kinetics of Fe⁰ corrosion is a paramount design parameter as water is treated by corrosion products (not by the parent Fe⁰). The validity of this assertion is more evident for other Fe⁰-based systems (e.g. Fe⁰/H₂O₂, Fe⁰/US/H₂O₂, Fe⁰/Persulfate) than for reactive filtration (Fe⁰/H₂O system).

The universal acceptance of Fe⁰ remediation systems will not occur until a fundamental understanding of involved processes, interactions and impact has been traceably

demonstrated. Therefore, future research must seek to establish a sound body of evidence upon which predictions of Fe^0 service life may be accurately made. For reactive filtration systems, such evidence has already allowed cost reductions of more than 50 % because the volumetric ratio of Fe^0 should not exceed 50 %. The establishment of Fe^0 -based technologies can be regarded as the scientific challenge of the next years. In particular, this is because of the appropriateness of Fe^0 -based systems for decentralized water treatment.

7. Epilogue

The presented work corresponds to the original manuscript evaluated by three anonymous referees. Minor revisions were performed, strictly limited at actualising bibliographic references. One significant concern was raised by one referee: a small summary section supported by a table comparing the costs of the presented Fe⁰-based treatment systems would have enabled sound scientific conclusions. This concern is not addressed here for one major reason: the subject of the thesis is that past Fe⁰-based experiments cannot be compared because of the different set ups used and because of intrinsic differences between used Fe⁰ materials used. The fundamental point that tested and used Fe⁰ materials are not comparable in their intrinsic reactivity makes any cost comparison non-reliable. The view that used Fe⁰ materials are not comparable in their intrinsic reactivity was discussed in this thesis (Section 2.2) using references from Reardon (1995, 2005), Noubactep et al. (2005a, 2009) and Btatkeu et al. (2013). This view is largely confirmed by a recent overview article by (Birke et al. 2015).

Beside intrinsic differences related to the material reactivity, many researchers have tested Fe⁰-based systems as ‘treatment units’ in a chain (Gottinger et al. 2010, Gottinger et al. 2013, Kowalski 2014, Kowalski and Søgaard 2014). For example, Kowalski and Søgaard (2014) used Fe⁰-units to generate iron oxide for As co-precipitation in a separate sand filter. The approach presented herein is that of Fe⁰ being a stand-alone treatment unit possibly coupled to other units in a treatment train (Rahman et al. 2013, Tepong-Tsindé et al. 2015a).

Recent publications have demonstrated that the lack of a holistic approach in investigating complex systems is a general concern for environmental remediation (Westholm et al. 2014, Zafarani et al. 2014, Domga et al. 2015, Tepong-Tsindé et al. 2015a). Coming back to Fe⁰ based systems, it is hoped that science-based designed system will soon accelerated the design of efficient systems for environmental remediation, safe drinking water provision and wastewater treatment worldwide.

8. References

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9. Appended articles

The present work is based on the following papers (not included in the online version):

- P1. Ghauch, A. (2008) Rapid Removal of Flutriafol from water by zero valent iron powder. **Chemosphere 71, 816-826.**
- P2. Ghauch, A., Tuqan A. (2008) Catalytic Degradation of Chlorothalonil in water using Bimetallic Iron-Based Systems. **Chemosphere 73, 751-759.**
- P3. Ghauch, A. (2008) Discussion of Chicgoua Noubactep on "Removal of thiobencarb in aqueous solution by zero valent iron" by Md. Nurul Amin et al. [Chemosphere 70 (2008) 511-515]. **Chemosphere 72, 328-331.**
- P4. Ghauch, A., Tuqan, A. (2009) Reductive destruction and decontamination of aqueous solutions of chlorinated antimicrobial agent using bimetallic systems. **J. Hazard. Mater. 169, 665-674.**
- P5. Ghauch, A., Tuqan, A., Abou Assi, H. (2009) Antibiotic removal from water: Elimination of amoxicillin and ampicillin by microscale and nanoscale iron particles. **Environ. Pollut. 157, 1626-1635.**
- P6. Ghauch, A. (2010) Response to Dr. Frańska's comments on the paper "Antibiotic removal from water: Elimination of amoxicillin and ampicillin by microscale and nanoscale iron particles." Ghauch et al. (2009) Environ. Pollut. 157, 1626-1635. **Environ. Pollut. 158, 3030-3031.**
- P7. Ghauch, A., Abou Assi, H., Tuqan, A. (2010) Investigating the mechanism of clofibrac acid removal in Fe⁰/H₂O systems. **J. Hazard. Mater. 176, 48-55.**
- P8. Ghauch, A., Abou Assi, H., Bdeir, S. (2010) Aqueous removal of diclofenac by plated elemental iron: bimetallic systems, **J. Hazard. Mater. 182, 64-74.**
- P9. Ghauch, A., Abou Assi, H., Baydoun, H., Tuqan, A., Bejjani, A. (2011) Fe⁰-based trimetallic systems for the removal of aqueous diclofenac: mechanism and kinetics, **Chem. Eng. J. 172, 1033-1044.**

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- P11. ²Ghauch, A., Baydoun, H., Dermesropian, P. (2011) Degradation of aqueous carbamazepine in ultrasonic/ $\text{Fe}^0/\text{H}_2\text{O}_2$ systems, **Chem. Eng. J.** **172**, 18-27.
- P12. Caré, S. Crane, R., Calabro, P.S. Ghauch, A., Temgoua, E., Noubactep, C. (2013) Modeling the permeability loss of metallic iron water filtration systems, **Clean-Soil, Air, Water** **41**, 275–282.
- P13. Ghauch, A., Tuqan, A.M. (2012) Oxidation of bisoprolol in heated persulfate/ H_2O systems: kinetics and products, **Chem. Eng. J.** **183**, 162-171.
- P14. Ghauch, A., Tuqan, A.M., Kibbi, N. (2012) Ibuprofen removal by heated persulfate in aqueous solution: a kinetics study. **Chem. Eng. J.** **197**, 483-492.
- P15. Ghauch, A., Tuqan, A.M., Kibbi, N. Geryes, S. (2012) Methylene Blue discoloration by heated persulfate in aqueous solution. **Chem. Eng. J.** **213**, 259-271.
- P16. ³Ghauch, A., Ayoub, G. Naim, S. (2013) Degradation of sulfamethoxazole by persulfate assisted micrometric Fe^0 in aqueous solution. **Chem. Eng. J.** **228**, 1168-1181.

² This paper was elected featured article and selected for the cover page of Volume 172 (Issue of August 2011).

³ This paper was elected featured article and selected for the cover page of Volume 228 (Issue of July 2013).