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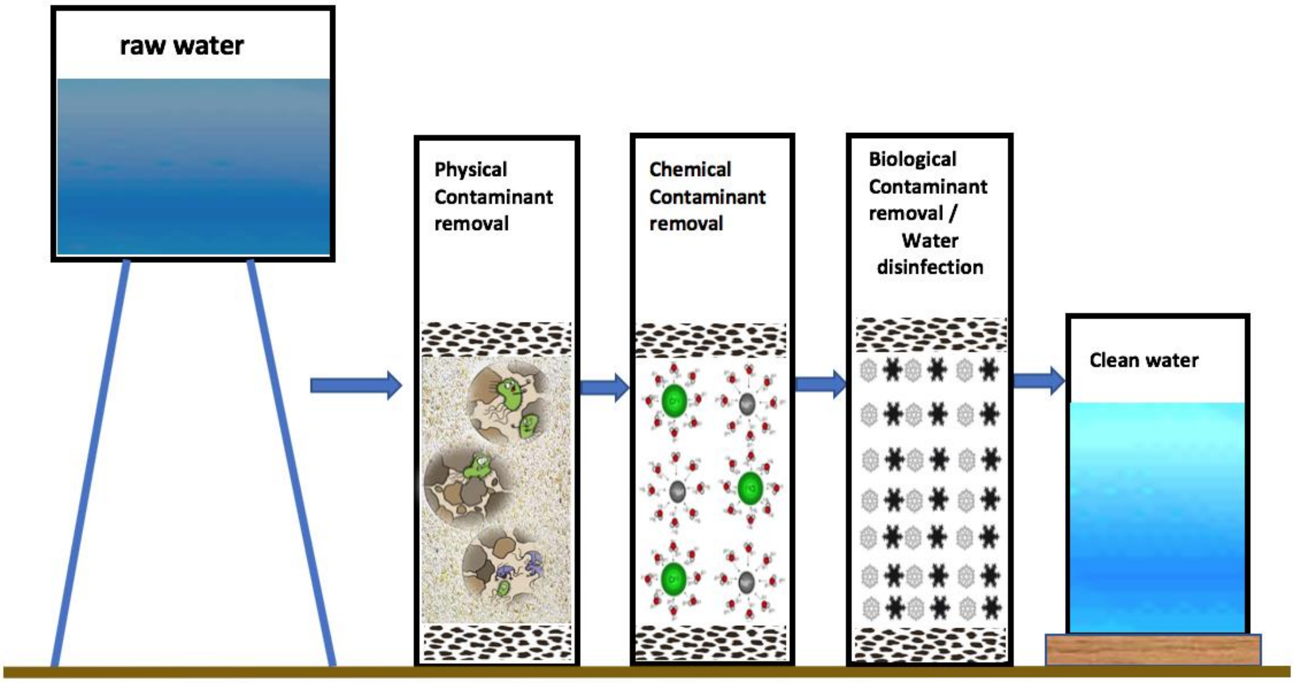

TEPONG TSINDE, RAOUL

Designing and Piloting a household filter for the peri-urban population of Douala (Cameroon)

91 pages, 09 figures, 05 tables, 253 references

"The scientific man does not aim at an immediate result. He does not expect his advanced ideas will be readily taken up. His work is like that of the planter ... for the future. His duty is to lay the foundation for those who are to come and to point the way. "

Nikola Tesla
“The Problem of Increasing Human Energy”
(The Century Magazine, June, 1900)

Preface

The present work was presented as a PhD Dissertation in Geoscience at the University of Göttingen (Germany). The Dissertation was accepted on December 04, 2020. The thesis designed and pilot tested a household filter in the coastal city of Douala (Cameroon). The general context of this work is achieving universal access to safe drinking water by 2030.

There are an uncountable number of people who supported me during this Ph.D. study.

First and the foremost I would like to express my sincere gratitude to my supervisor PD. Dr. Chicgoua Noubactep. Thank you very much for valuable advice, fruitful discussions, and constant guidance all along this research work. Also, I fully acknowledge him the great freedom, the unconditional support during my several stays abroad, and the opportunity he gave me to seek and define my own research interests and apply them in this thesis. I owe him very much and my greatest thanks go to him because of his substantial contribution to my personal and professional development during these years being a good teacher, inspirer, and friend.

Loads and loads of thanks to my co-supervisor Prof. Dr. Hans Ruppert, for providing me with the best time I have ever had at the University of Göttingen. Your opinion, view, comments, and thoughts have been truly considered and appreciated along this time as Ph.D. student. I really appreciate the high standards you have set for me, which I would never have reached without your help.

I am particularly grateful to Prof. Dr. Achille Nassi of the University of Douala, who gave me the chance to spend these fabulous times of my research in Cameroon, in the beautiful city of Douala.

In this research work several people were involved during the development of some of the chapters/papers in which is comprised. I would like to express my gratitude to all of them.

Many thanks to my wife Tsadjeu Tsamo Mirabelle L. for her deep love and having braved all the difficulties to supervise our two sons Tsadjeu Tsinde Raoul and Manko Tsinde Nils Meyer during my long stay in Cameroon.

Last but not least, I should say thanks from the bottom of my heart to my beloved mother Manko Catherine, to my Father Tsinde Maurice, and my brothers and sisters for their never-ending love, help, good food and unwavering support in so many ways through all this time.

Thank you so much.

Abstract:

In rural and peri-urban regions of the developing world, many tube wells used as drinking water sources are microbially and chemically polluted. Consequently, hundreds of millions of people lack access to “safe” drinking water worldwide. People drinking tube well water may suffer from preventable water-borne diseases including diarrhea, skin lesions, and cancer. To address this problem, the United Nations have launched the Sustainable Development Goals (UN SDGs) which are regarded as a global urgent call for action by all countries, in a global partnership. The UN SDGs for safe drinking water (Goal 6) aims to achieve universal water supply by 2030. This goal can only be achieved if affordable and efficient water treatment technologies are made available for households and small communities for simultaneous removal of chemicals and pathogens. Ideally, such systems should be constructed using locally available materials and labor. Filtration on metallic iron (Fe^0) based beds has been identified as such an appropriate technology and steel wool (SW) a universally available material. Moreover, Fe^0-based filters have been designed and disseminated in some parts of the world but have not yet reached global applicability.

A critical review on the abundant literature on using Fe^0-based filters for safe drinking water provision revealed that existing devices were not designed on the knowledge basis of the science of aqueous iron corrosion (corrosion science). Iron corrosion induces generation of solid iron corrosion products (FeCPs) which are well-documented contaminant scavengers. FeCPs consisting of Fe-oxide hydroxides are formed in the vicinity of the Fe^0 surface and act as a diffusion barrier for dissolved species. Iron corrosion is additionally a volumetric expansive process because the volume of each oxide or hydroxide is at least twice larger than that of iron metal (Fe^0). These two main characteristics imply that (i) the efficiency of each Fe^0-based filter depends on the kinetics of production of FeCPs (reactivity loss), and (ii) Fe^0-based filters will experience porosity loss with increasing service life (permeability loss). In other words, reactivity loss and permeability loss are inherent characteristics of Fe^0-based filters which should be addressed in the design stage. Moreover, designed systems should be tested for months or years, given the incertitude on the kinetics of iron corrosion.

The objective of the present work was to design a science-based household filter and to test it for one year in the coastal city of Douala (Cameroon). The work started with a systematic review of available designs and a presentation of two main potentially durable designs. The one with a Fe^0/sand filter sandwiched between two biological sand filters (BSFs) was tested with polluted well water from Logpom (Douala, Cameroon) using 300 g of a commercial SW (grade 000; d = 50 μm) as Fe^0 source. Previous works using Fe^0 SW in water filters revealed that grade

00 (d = 25 μm) was depleted after some 6 months. The used well water was slightly turbid, polluted with pathogens (total coliforms = 1950 UFC mL^{-1}), and contaminated with nitrate ([NO$_3^-$] = 24.0 mg L^{-1}). The following parameters were monitored twice per month for one year in the influent and effluent water of the filter unit: (i) nitrate concentration, (ii) coliform level, (iii) pH value, and (iv) turbidity. The iron concentration and the hydraulic conductivity (permeability) were also determined. Prior to pilot testing, the impact of chloride ions (Cl$^-$) on the efficiency of Fe^0 filters was characterized in laboratory column experiments, using the methylene blue discoloration method.

Results of laboratory column experiments revealed that the chloride concentrations expected in well waters in Douala would not negatively impact the efficiency of Fe^0 filters. The tested design could produce safe drinking water for at least one year. Coliforms (> 99% decrease), nitrate (> 99%) and turbidity (> 96%) were nearly quantitatively removed over the whole testing period and well below the recommended limits of the World Health Organization (WHO). The effluent pH increased continuously from 6.6 to 8.4. The effluent iron concentration was constantly lower than 0.2 mg L^{-1}. These values are within the WHO drinking water quality standards. The initial flow velocity of 20 L h^{-1} decreased to ~8.33 L h^{-1} after one year, corresponding to a permeability loss of nearly 41.5 %. At the end, the filter was still producing 200 L of drinking water

These results confirmed the suitability of commercial Fe^0 SW as efficient material to construct durable water filters for households. It appears that the success of the design relied on the low ratio of Fe^0 SW (10 vol %) dispersed in the matrix of sand (90 vol %). The tested design can be immediately be applied practically, provide that appropriate construction materials are found. Future research should include (i) testing lower Fe^0 SW ratios (same grade), (ii) testing other grades of Fe^0 SW in parallel experiments (1 year or more); (iii) testing the same systems for the removal of arsenic and uranium which are the most widespread natural pollutants. Fe^0 SW based water filters can be considered as one of the best tools for the achievement of Goal 6 of the United Nations sustainable development goals (SDGs), despite the threat of COVID-19.

Keywords: Fe^0-based filter; household filter; permeability loss, steel wool, zero-valent iron.

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List of Acronyms

Fe^0	Metallic iron
UN	United nations
SDG	Sustainable development goals
FeCP	Iron corrosion product
SW	Steel wool
BSF	Biological sand filters
Cl^-	chloride ions
WHO	World health organization
pH	Power of hydrogen
CFU/UFC	Colony forming units
NO_3^-	nitrate
PET	PolyethyleneTerephthalate
Fe^{II} /Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
μmol	micromole
$mg\ L^{-1}$	Milligrams per liter
NTU	Nephelometric turbidity units
H_2	Dihydrigen
HCO_3^-	Hydrogencarbonate/Bicarbonate ion
PO_4^{3-},	Phosphate ion
MDG	Millennium development goals
BSF	Biological sand filter
Fig.	Figure
RZ	Reactive zone
SO_4^{2-}	Sulfate ion
Co	Cobalt
Cu	Copper
Ni	Nickel
As	Arsenic
Cr	Chromium
PVC	Polyvinyl chloride
Sec.	Seconde
$\mu S.cm^{-1}$	Microsencond per centimenter
Tab.	Table
Cl^-	Chloride ion
MB	Methylene blue
MnO_2	Manganese dioxide
UV	Ultra violet
ZVI	Zero-valent iron

1.0 Introduction

1.1 Access to safe drinking water in the developing world

Potable water is the most essential commodity on the earth for survival of human beings (Gleick 2000, Ali 2014). The availability of fresh water is decreasing continuously due to world population growth, increased use in agriculture, increased industrialization, and increased urbanization. Environmental, geological, and global changes are also continuously contaminating natural water resources (Gleick 2000, Shannon et al. 2008). As a consequence, the quality of an ever-increasing number of natural waters sources are no more safe for drinking purposes (Hussam and Munir 2007, Shannon et al. 2008, Etmannski et al. 2014, Ndé-Tchoupé et al. 2015). Therefore, the world community (including scientists and academicians) are working on affordable, applicable and efficient technologies for water treatment (Howe et al. 2012, Etmannski et al. 2014, Hering et al. 2016, Naseri et al. 2017, Nanseu-Njiki et al. 2019, Ogata et al. 2020, Huang et al. 2021a, Huang et al. 2021b, Mueller 2021, Mueller et al. 2021, Nya et al. 2021). The most important technologies for the water treatment are adsorption, coagulation, crystallization, distillation, oxidation, filtration, reverse osmosis, sedimentation and screening (Howe et al. 2012, Ali 2014). From these technologies, adsorption on fixed beds has been proven an easy to handle and affordable technology for low-income communities, including remote and scattered villages in the developing world (Hussam and Munir 2007, Noubactep et al. 2009, Noubactep et al. 2012, Ali 2014, Banerji and Chaudhari 2017, Bretzler et al. 2020, Ogata et al. 2020, Huang et al. 2021b, Mueller et al. 2021, Nya et al. 2021). Adsorption is also considered as one of the best wastewater treatment technologies due to its wide range of applications and ease of operation. During the past three decades, the scientific community has rediscovered metallic iron (Fe^0 also called zero-valent iron) as a powerful reactive material for water treatment on decentralized manner (Henderson and Demond 2007, Guan et al. 2015, Antia 2020, Cao et al. 2020, Hu et al. 2020, Yang et al. 2020, Huang et al. 2021b, Nya et al. 2021).

1.2 The suitability of Fe^0 filters

Metallic iron (Fe^0) is a non-toxic and inexpensive reactive material that is readily available (Noubactep 2010, 2013a, 2013b, 2013c, 2014, Gatcha-Bandjun et al. 2017, Antia 2020). Research over the last three decades has demonstrated the effectiveness of Fe^0/sand filter for the treatment of water contaminated physically (color, turbidity) (Tomizawa et al. 2016, Naidu and Birke 2015, Xiao et al. 2020a, Xiao et al. 2020b), chemically (dyes, anionic and cationic metal and metalloid ions, nitrogen compounds, radionuclides) (Heimann et al. 2018, Guan et al. 2015, Noubactep 2015) and microbiologically (bacteria, viruses) (You et al. 2015, Ghauch 2015, Kim et al. 2021). The operating mode of Fe^0 bed filters is based on the interactions between Fe^0 in-situ generated corrosion products (example: Fe^{II}, H_2, iron oxides and hydroxides) and water pollutants (Noubactep 2013a, 2013b, 2013c, 2014, Ndé-Tchoupé et al. 2015, Noubactep 2015, 2018, Xiao et al. 2020a, Xiao et al. 2020b). This knowledge was already familiar to the first designers of Fe^0 filters about 150 years ago (Bischof 1873, 1877, 1878, Anderson 1883, 1884, 1885, Ogston 1885, Devonshire 1890, Mwakabona et al. 2017, Antia 2020, Noubactep 2020) but was little noticed since the 1990s (Guan et al. 2015, Naidu and Birke 2015). The application of the Fe^0 technology for safe drinking water provision nearly 150 years ago contradicts the perception that this technology is recent or innovative (Devonshire 1890, Mwakabona et al. 2017, Antia 2020, Noubactep 2022). Despite its old age, there are not yet clear scientific design principles, which engineers can use to construct sustainable Fe^0 filters on a site- and pollution-specific basis (Domga et al. 2015, Naseri et al. 2017, Noubactep 2018, Yang et al. 2020, Yang et al. 2021). Moreover, apart from sponge iron (Bischof 1873, Hussam and Munir 2007) no specific material for safe drinking water provision has been presented (Noubactep et al. 2005, Kim et al. 2014, Li et al. 2016, Hu et al. 2019, Li et al. 2019, Lufingo et al. 2019, Yang et al. 2020). The resolution of these two open issues would facilitate the conversion of existing knowledge of the science of aqueous corrosion of iron into an effectively practical solution for decentralized safe drinking water provision (Ndé-Tchoupé et al. 2015, Clasen et al. 2009, Noubactep et al. 2009, 2012, Tepong-Tsindé et al. 2015, Gatcha-Bandjun et al. 2017, Naseri et al. 2017, Noubactep 2018, Yang et al. 2020, Noubactep 2022). In other words, providing people with knowledge and tools to facilitate self-reliance in the supply of safe and healthy drinking water is an important goal (Shannon et al. 2008, Hering et al. 2016, Naseri et al. 2017, Noubactep 2018, Huang et al. 2021a, Nya et al. 2021).

1.3 Fe^0 materials for household filters

A wide array of Fe^0 materials have been tested and used as filters. Relevant materials include iron coils, iron composites (e.g. bimetallics), iron filings, iron nails, iron wire, scrap iron, nano-Fe^0, sponge iron, and steel wool (Bischof 1877, Anderson 1886, Landis et al. 2001, Westerhoff and James 2003, Btatkeu-K et al. 2013, Lufingo et al. 2019). The reactivity of all these materials is characterized by the electrode potential of the redox couple Fe^{II}/Fe^0 (E^0 = -0.44 V). This implies that reactivity differences amount various Fe^0 specimens are kinetic in nature. In fact, large differences in oxidation trends of Fe^0 materials have been documented, even for materials from the same class (Landis et al. 2001, Btatkeu-K et al. 2013, Stefanoni et al. 2018, Li et al.

2019, Lufingo et al. 2019, Yang et al. 2020, Yang et al. 2021). It has therefore been posited that difficulties in comparing available results to each other is mostly due to differences in intrinsic reactivity (Noubactep et al. 2005, Btatkeu-K et al. 2013, Li et al. 2019, Lufingo et al. 2019). As an affordable and widely available material, steel wool (Fe^0 SW) has been largely tested for safe drinking water provision (Lauderdale and Emmons 1951, Bradley et al. 2011, Lufingo et al. 2019, Hildebrant 2018, George and Ahammed 2019) and wastewater treatment (James et al. 1992, Erickson et al. 2007, Erickson et al. 2017, Li et al. 2017).

There are seven grades of Fe^0 SW with filament widths varying from 10 to 90 μm (Lufingo et al. 2019, Hildebrant et al. 2020). From these, only grade 000 (d = 25 μm) was tested in long-term experiments for water treatment and was depleted after 8 months. The present study tests grade 0 (d = 50 μm) to find out whether it will last for one year. One year is regarded as a reasonable duration to change filtration units and avoid the use of exhausted filters.

1.4 Current state in designing Fe^0 filtration systems

Fe^0 is an excellent material for water treatment in filtration systems (Gheju 2011, Ghauch 2015, Gheju 2018, Noubactep 2018). However, porosity decline due to the formation of expansive iron corrosion products and subsequent filter clogging is one of the major limitations to utilize such a system (Anderson 1886, Westerhoff and James 2003, Bartzas and Komnitsas 2010, Guan et al. 2015, Noubactep 2015, Yang et al. 2021). In order to prevent premature filter clogging (e.g. clogging occurs before Fe^0 is exhausted), hybrid reactive zones (e.g. Fe^0/FeS_2, Fe^0/MnO_2, Fe^0/sand) have been recommended (Noubactep 2010, Noubactep and Care 2010, Noubactep 2011, Miyajima 2012, Noubactep 2012, Caré et al. 2013, Miyajima and Noubactep 2013, Ndé-Tchoupé et al. 2018). Because of its low cost and high availability, sand is a commonly used additive for this purpose (Bi et al. 2009). Fe^0 SW/sand filters for households are a promising class of cost-effective Fe^0 amended sand filters which can be disseminated in remote communities (Bradley et al. 2011, George and Ahammed 2019, Hildebrant et al. 2020).

Despite almost seven decades of technical expertise on using Fe^0 SW in household water filters (Lauderdale and Emmons 1951, George and Ahammed 2019), available information is still weak for any rational design. The very first reason is that used materials were not characterized for their intrinsic reactivity (Noubactep et al, 2004, Noubactep et al, 2005, Li et al. 2019, Lufingo et al. 2019, Hu et al. 2021a). Some studies have not even specified the grade of used SW and the elemental composition is not specified as a rule (Nde-Tchoupe et al. 2015, Hildebrant et al. 2020). However, as demonstrated by Lufingo et al. (2019), differences in the initial kinetics of Fe^0 SW dissolution in 1,10-Phenanthroline can be as large as factor 20. The second reason for the lack of design information is that available works have not always specified the used Fe^0:sand ratios and the thickness of the reactive zone (Hildebrant et al. 2020). To these two reasons, the use of column of different sizes, differences in experimental duration and in feeding water quality are further aggravating factors (Yang et al. 2020, Huang et al. 2021b). In particular, while the long-term kinetics of Fe^0 SW corrosion is certainly nonlinear (Nesic 2007, Lazzari 2008) and is yet to characterize in the context of water treatment, experimental duration exceeding four months are rare.

The following example illustrates the incompleteness of information regarding the design Fe^0 SW/sand filters. Bradley et al. (2011) mixed 260 g of a Fe^0 SW (extra fine – Grade 000) with 1.563 g sieved sand (effective size 0.4 mm) to form a 20 cm-thick filter for virus removal over 300 days (10 months). The used Fe^0 SW (d_1 = 25 µm) was completely depleted after 170 days (8 months) but the system was still permeable. On the contrary, George and Ahammed (2019) tested a filter containing iron nails (d_2 = 2.0 mm) mixed with sand for just four months and did not consider the work of Bradley et al. (2011) in their discussion. Using larger particles (d_2/d_1 = 80) and testing them for a shorter experimental duration (t_1/t_2 = 2.5) is counter-productive, particularly in a context where long-term experiments are needed (Naseri et al. 2017, Hu et al. 2020, Yang et al. 2020, Huang et al. 2021b, Nya et al. 2021). There is a need to further investigate the relationship between SW proportion in a Fe^0 filter, its long-term permeability, and its efficiency for water treatment.

1.5 Access to safe drinking water in the peri-urban areas of Cameroon

Cameroon has failed to meet the MDGs. Ako at al. (2010) noted that Cameroon is not yet on track to meet the targets of the MDGs for water and sanitation, but it has made notable progress since 1990. And Since 2015 the research work is orienting to the SDGs.

Figure 1 shows the comparative evolution of the percentage of household with access to a safe drinking water in the economic city of Douala and in Cameroon from 1990 to 2015.

It was established that in general, access to safe drinking water in Cameron decreased with a coverage rate of about 58% in 1990 and a rate of about 48% in 2015. In Douala, the biggest and most populated city of Cameroon, there was a drop in its access rate from 45% in 1990 to about 22% in 2015.

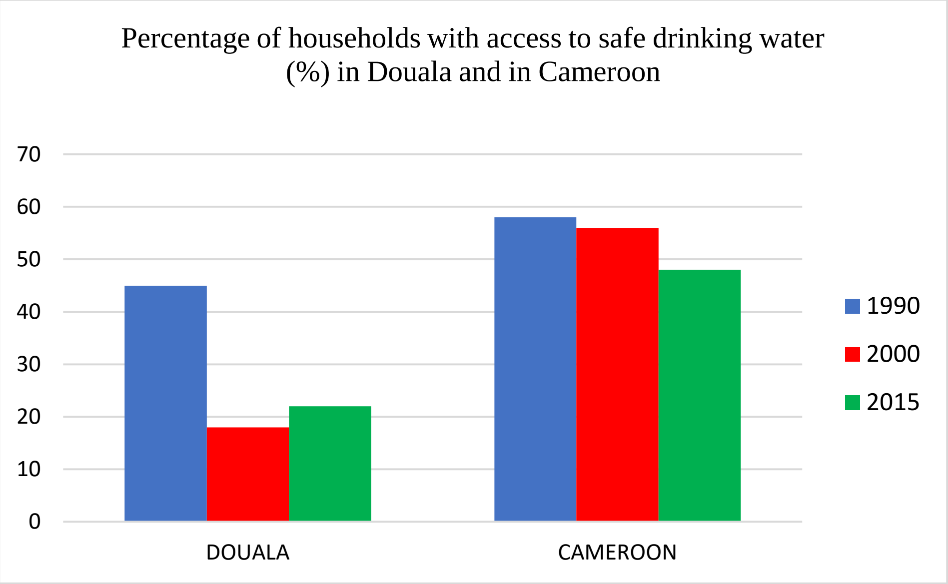


***Figure** 1:* Evolution of percentage of households with access to safe drinking water in Douala and in Cameroon during the MDG era. (Source: Ako et al. 2010, modified).

From 1990 to 2000, country-wide there was a significant drop in access to potable water. This was attributed to the economic crisis of 1986 –1993 in Cameroon which caused a significant reduction in public investments, therefore in the domain of water resources. For the Cameroon government to reach the 75 percent access rate it fixed by 2015, it had to increase access rate by 1.5 points per year (MINPLADAT, 2006). Instead from Figure 1, it is observed that the national access rate fell from about 58% in 1990 to 56% in 2000 and then to about 49% in 2015. Based on this, Ako et al (2010) concluded that Cameroon will fail to reach the safe drinking water MDG target.

Due to poor planning and uncontrolled urbanization, peri-urban areas in Cameroon emerge spontaneously (Nya 2020, Nya and Mougoué 2020). Most of the inhabitants of the peri-urban areas are urban poor who cannot afford the cost of living in the city or rural people who move to the city in search of greener pastures as well as a few middle-class people. The absence of roads, water, electricity, housing, schools, and other services makes living in the peri-urban areas challenging (Fonjong and Fokum, 2017, Hope and Ballon 2019, Hope et al. 2020).

CAMWATER, the national water utility oversees production and distribution of potable water in urban areas of Cameroon while the Ministry of Water and Energy and NGOs supply the rural population (Ako et al., 2009, Nya 2020). CAMWATER is present in only 35% of Cameroonian cities and towns (Tanawa et al., 2002, Nya 2020). According to WHO (2008b), 82% of the Cameroon’s urban population and 42% of the rural population are covered in terms of water supply with 23% of households having direct access to drinking water. Rapid urbanization in cities and towns has often rendered existing infrastructure inadequate, with frequent service interruptions and many peri-urban dwellers lacking access to safe drinking water. All this clearly indicates that the access to save drinking water in Cameroon for peri-urban population is difficult. This can be caused by the rural exodus, that can justify the proliferation of wells and rivers in peri-urban areas of the city of Douala.

1.6 The problem

Peri-urban area can be designed as a territory (or rather a set of territories) for which the inhabitants develop a feeling of identification or belonging, while maintaining links with the city, which provides them with jobs, goods and services. One of the main difficulties of these peri-urban areas is access to save drinking water. But these difficulties which hamper access to drinking water in homes are mainly linked to technical, social, legal, or governance resources (Hope and Ballon 2019, Nya 2020, Hope et al. 2020). So, the main problem is how to bring water to people in the peri-urban areas without need of electricity, without high maintenance and at a lower cost.

To solve this problem, a household Fe^0 SW water filter for the supply of people living in poor settlements in the developing world is designed and pilot tested. Natural well water from Logpom (Douala) was used for the experiments. The well water is polluted with coliforms, suspension, and contains up to 24 mg L^{-1} nitrate.

1.7 Research objectives

The goal of this thesis is to shape a practical application of Fe^0 SW/sand filter combination for household water purification. An important feature of the design is to treat contaminated water without any use of chemicals or electricity, but to provide a cheap, simple, and easily manageable device that brings clean drinking water into the reach of single dwellings in peri-urban and rural areas.

1.9 Outline of the thesis

In the chapter 1 (Introduction) of this thesis the theoretical background and application of existing Fe^0-based filters are summarized. Chapter 2 describes the designing of Fe filters for small communities: An overview corresponds to the literature review and has already been published. Chapter 3 investigates the impacts of chloride ions on the efficiency of Fe^0 filters. This Chapter corresponds to the literature review and has also been published. The insights gained from the previous Chapters made it possible to carry out the designing and pilot-testing a household Fe^0 SW filter in Douala (Cameroon). This is the subject of Chapter 4. The results of the experiment are presented and discussed. The Chapter has been published.

Chapter 5 deals with general discussion and limitations. Chapter 6 provides a general conclusion of this work and gives some suggestions for further research. The appendix includes a list of journal articles that were authored or co-authored by me and directly related to the presented work. References are provided at the end of all chapters.

2 Designing Fe0 filters for small communities: An overview

2.0 Preamble

During the past five years, some important innovations were made available which can be summarized in two key points: (i) the ancient technology of using metallic iron (Fe^0) for safe drinking water was rediscovered (Mwakabona et al. 2017, Antia 2020), and (ii) new articles validating the 2015 designs (Tepong-Tsindé et al. 2015) were published (Etmannski 2014, Etmannski and Darton 2014, Casentini et al. 2016, Smith et al. 2017, Ahmed et al. 2018, Abbas et al. 2018, Bretzler et al. 2020). The net result is that new Fe^0 filter designs co-exist with old ones, while a critical literature review consolidating available information is yet to be written (Yang et al. 2021). Therefore, this chapter is not only giving an overview of the appended Tepong-Tsindé et al. (2015), but rather a general overview of the 170 years of using metallic iron for safe drinking water provision. The presentation will start with the chemistry of the Fe^0/H_2O system.

2.1 The Fe^0/H_2O system

When a reactive piece of Fe^0 is immersed in water, its oxidative dissolution is spontaneous. This occurs because the electrode potential of the redox couple H_2O/H_2 or H^+/H_2 ($E^0 = 0.00$ V) is higher than that of Fe^{II}/Fe^0 ($E^0 = –0.44$ V) (Whitney 1903, Landolt 2007, Groysman 2010). The corresponding electrochemical reaction is given by Equation 2.1:

$$Fe^0 + 2\ H_2O \Rightarrow Fe^{2+} + 2\ OH^- + H_2 \qquad (2.1)$$

$$Fe^0 + 2\ H^+ \Rightarrow Fe^{2+} + H_2 \qquad (2.1a)$$

$$Fe^0 + 2\ H_2O \Rightarrow Fe(OH)_2 + H_2 \qquad (2.1b)$$

Equation 2.1a specifies that oxidizing protons (H^+) from water dissociation are the real oxidizing agents. Equation 2.1b recalls that one mole Fe^{2+} is combined with 2 moles of OH^- to form one mole of $Fe(OH)_2$ which polymerizes and precipitates in the vicinity of the Fe^0 surface (Nesic 2007, Lazzari 2008, Groysman 2010, Noubactep 2010a, Cao et al. 2020, Noubactep 2022).

As reaction after Equation 2.1b proceeds, $Fe(OH)_2$ may disproportionate to magnetite and H_2 according to the Schikorr reaction (Equation 2.2) (Beverskog and Puigdomenech 1996, Qin et al. 2018).

$$3\ Fe(OH)_2 \Rightarrow Fe_3O_4 + 2\ H_2O + H_2 \qquad (2.2)$$

Combining Equation 2.1b and Equation 2.2 yields to Equation 2.3:

$$3\ Fe^0 + 4\ H_2O \Rightarrow Fe_3O_4 + 4\ H_2 \qquad (2.3)$$

Equation 2.3 reveals that the oxidation of 3 moles of Fe^0 releases 4 moles of H_2. In other words, the overall stoichiometry of H_2 production from Fe^0 varies from 1:1 (Equation 2.1) to 4:3 (Equation 2.3) (Reardon 1995, Reardon 2005, Velimirovic et al. 2013, Qin et al. 2018). The reaction shown in Equation 2.1 is the stoichiometrically dominant reaction under anoxic conditions (O_2 free). However, even under oxic conditions, Equation 2.1 is the sole path for iron corrosion because the in-situ generated oxide film acts as a diffusion barrier for dissolved species (including O_2) (Whitney 1903, Stratmann and Müller 1994) and a conduction barrier for electrons from the metal body (Hu et al. 2019a, Noubactep 2022). In the recent remediation literature, it has been largely considered that reducible contaminants compete with water for Fe^0 oxidation (Liu et al. 2013, Qui et al. 2018, He et al. 2020, Hu et al. 2021b). The electron efficiency concept will not be discussed herein. Interested readers are referred to the excellent recent review article by He et al. (2020). For the presentation in this dissertation, it suffices to consider that each oxidized mole of Fe^0 potentially yields one mole of $Fe(OH)_2$ or other iron hydroxides (e.g. $Fe(OH)_3$) and oxides (e.g. Fe_2O_3, Fe_3O_4) that are all larger in volume than the parent iron (Fe^0): $V_{oxide} > V_{iron}$.

The expansive nature of metal corrosion was described in the 1920s (Pilling and Bedworth 1923, Caré et al. 2008) and first considered in the Fe^0 remediation literature only a decade ago (Noubactep 2011, Caré et al. 2013, Domga et al. 2015). The key issue of the volumetric expansion of iron corrosion is that the process which is put into use (iron corrosion) is the first cause of permeability loss of Fe^0-based filters. Accordingly, pure Fe^0 filters (100 % Fe^0) can be efficient but never sustainable. This pure physical consideration rationalizes the need of using hybrid systems (e.g. Fe^0/sand) to design sustainable systems (Noubactep et al. 2011, Nanseu-Njiki et al. 2019, Yang et al. 2020, Yang et al. 2021). During the past decade, Noubactep and colleagues have developed a facile method to characterize the reactivity of the Fe^0/H_2O system: The methylene blue method or MB method (Chapter 3). Using the MB method Miyajima (2012) and Btatkeu-K (2015) have demonstrated that sustainable filters should contain less than 50 % (vol/vol) Fe^0. These experiments have validated theoretical predictions by Togue-Kamga (2013) and rationalized observations by several authors, that some systems with less Fe^0 performed better than pure Fe^0 systems as summarized in Tepong-Tsindé et al. (2015).

For Fe^0 SW used in water treatment, there are investigations with 100 % Fe^0 (Lauderdale and Emmons 1951, Hildebrant 2018) and some few with up to 5 % (Wakatsuki et al. 1993, Erickson et al. 2007, 2017, Latrach et al. 2018). Only Bradley et al. (2011) have worked with 10 % Fe^0 SW. Accordingly, the range 5 to 50 % Fe^0 SW is largely unexplored. This work was also designed to contribute to fill this knowledge gap.

2.2 Contaminant removal in Fe^0/H_2O systems

The evidence that iron corrosion is volumetric expansive implies that in filtration beds, available pores are filled with in-situ generated solid corrosion products (FeCPs) (Yang et al. 2020, Yang et al. 2021). This also implies that contaminant removal by size-exclusion is improved with increasing service life, at least as long as the filter is still permeable. This predictable result has been observed in several systems (Westerhoff and James 2003, Hussam 2009, Tepong-Tsindé et al. 2015, Guan et al. 2015). Noubactep (2010, 2011) has demonstrated that the described volumetric expansion is factually a cycle of expansions and compressions going through the colloid phase and implying contaminant enmeshment (co-precipitation). In other words, a species entering a Fe^0/H_2O system can be (i) adsorbed onto aged FeCPs, (ii) co-precipitated by nascent FeCPs or (iii) be removed by pure size-exclusion.

Contaminant removal by adsorption and co-precipitation corresponds to the operating mode of coagulation/flocculation and was known by Gustav Bischof already (Bischof 1873, Anderson 1883). In the Bischof Process, Fe^0 (sponge iron) was used to remove pathogens and color from river waters (Antia 2020). In the design of Lauderdale and Emmons (1951), Fe^0 in the form of steel wool was also used to generate scavengers of radionuclides. After 1990 and the advent of Fe^0 permeable reactive barriers, Fe^0 was used for the first time to selectively remove contaminant by (i) a reductive mechanism (e.g. Cr, Cu), (ii) an adsorptive mechanism (e.g. As), (iii) by co-precipitation (e.g. As) or a synergy of several mechanisms. However, the abundance of water (the solvent) and the spontaneous nature of Equation 2.1 implies that Fe^0 oxidation by a contaminant is not likely to occur. Thus, Fe^0 should be regarded as a generator of contaminant scavengers, regardless from the redox properties of the contaminants (Gheju 2011, Ghauch 2015, Gheju 2018). It follows that, a key question to answer while designing Fe^0/H_2O systems is: What is the long-term kinetics of generation of contaminant scavengers? In other words, which parameters should be considered for the design of efficient and sustainable Fe^0 filters?

2.3 Testing Fe^0-based filters for safe water provision

Already during the 19th Century, it was acknowledged that designing a water filter is a complex issue that is possibly surrounded with “much ignorance and misapprehension” (Notter 1878). The reactive nature of Fe^0 and its nonlinear corrosion kinetics are further aggravating factors (Moraci et al. 2016, Noubactep 2016, Qin et al. 2018). The success of any filter depends on at least four groups of variables: (i) the quality of raw water (e.g. pH, salinity, extent of contamination), (ii) the quality and volume of water to produce by unit time (e.g. daily), (iii) the speciation of the contaminants of concern (e.g. As^{III} or As^{V}), (iv) the characteristics of used Fe^0 and admixing aggregates. Relevant characteristics of Fe^0 include its size, form, surface state, intrinsic reactivity and storing conditions or pre-treatment.

Rationally designing a water filter implies combining the named variables to determine the Fe^0 amount (mass), its proportion in the mixture (e.g. 10% vol/vol), the thickness of the reactive zone, and the service life of the filter in satisfactorily treating a given polluted water. Given that each water source, each Fe^0 and each Fe^0/aggregate combination are unique, there is an infinite number of possible filters capable at efficiently treating any polluted water. All is needed is a systematic testing program and the readiness for long term experiments (Naseri et al. 2017, Nanseu-Njiki et al. 2019, Yang et al. 2020).

2.3.1 State-of-the-art knowledge

The current state-of-the-art knowledge on designing Fe^0/H_2O systems is excellently summarized in a recent publication by Antia (2020). As far as drinking water is concerned, there is an expanded use of small-scale Fe^0 reactors for households and small communities (Hussam 2009, Banerji and Chaudhari 2017, Bretzler et al. 2020). Treated water sources are mostly wells and tube wells, mostly in regions without municipal water treatment infrastructures. The current production capacity for small communities is 150,000 to 250,000 $m^3\ d^{-1}$ (Antia 2020). Fe^0/H_2O systems have also been discussed for their suitability to produce potable water for emergency relief (Noubactep et al. 2009, Antia 2020). The potential global commercial market for Fe^0-based technologies is huge, but its current coverage is rather very small. If the technology can be downscaled to meet the needs of individual households, then its future global commercial market may exceed any actual predictions.

To meet the needs of households on a global level, the first issue is to find a suitable Fe^0 material (Btatkeu-K 2015, Ndé-Tchoupé 2019). Steel wool and iron nails are currently the most used (Nanseu-Njiki et al. 2019). However, their intrinsic reactivity has not been characterized (Hu et al. 2019b, Hu et al. 2019c, Lufingo et al. 2019, Hildebrant et al. 2020). Our research group has tested several classes of Fe^0 materials (Btatkeu-K 2015, Ndé-Tchoupé 2019) before opting for steel wool. The rationale for this choice is the tiny size of the filaments (< 100 μm) and the probability of their depletion under field applications. The hypothesis is supported by results from Bradley et al. (2011) reporting on the depletion of Fe^0 SW grad 000 (d = 25 μm) after 6 months in their experiments. Fe^0 SW grade 0 (d = 50 μm) was tested herein.

The most efficient Fe^0 materials for water treatment in filters over the decades are porous ones (Bischof 1873, Hussam 2009). Contrary to compact materials (e.g. iron filings, iron nails, scrap iron) they are likely to be extensively corroded under natural conditions. This is because the "extraction" of iron from deeper layers of compact materials is uncertain in the long term ('reactivity loss'). Once a Fe^0 material is selected for the construction of a filter, an appropriate arrangement of the materials should be sought (Tepong-Tsindé et al. 2015).

2.3.2 Research gap

The literature on Fe^0 household filters until 2014 (start of this work) was full of different designs of which only the SONO filters were sustainable (Neumann et al. 2013, Wenk et al. 2014). Devices for small communities were rare and long-term experience was similarly missing (Gottinger et al. 2013, Chaudhari et al. 2014, Kowalski and Søgaard 2014). Caré et al. (2013) justified the success of SONO filters by the porous nature of the used Fe^0-based composite. However, the system was patented and thus not universally accessible. The calculations of Caré et al. (2013) demonstrated that admixing Fe^0 and non-expansive aggregates would result in efficient and sustainable systems.

The science-based hypothesis of Caré et al. (2013) was in frontal contradiction with the then prevailing view that Fe^0/sand mixture are best used as O_2 scavenger pre-treatment layers to enable anoxic systems where contaminants are reduced by electrons from Fe^0, non-disturbed by dissolved O_2 (Mackenzie et al. 1999, Westerhoff and James 2003, Henderson and Demond 2007). Fortunately, some researchers had used Fe^0/sand column to treat water (Khan et al. 2000, Lackovic et al. 2000). In particular, Khan et al. (2000) used Fe^0 to in-situ increase aqueous iron concentration and induce As co-precipitation. In other words, a Fe^0/sand mixture cannot be regarded as a pre-treatment zone. The open question was how long such a mixture can efficiently treat water? One partial answer was that, under oxic conditions, filter clogging is more likely because larger corrosion products are generated (Domga et al. 2015). In other words, creating conditions of low O_2 concentrations is a tool to sustain the service life of Fe^0 filters.

The conventional water treatment system suggests that a low-cost way to consume dissolved O_2 from water is to let it flow through a slow sand filter (SSF) (Campos 2002, Haig et al. 2011), of which a miniature version is available and termed as biological sand filter (BSF) (Lea 2008). Accordingly, a BSF preceding a Fe^0/sand filter would result in a more sustainable system. Given that Fe^0 alone, sand alone and Fe^0/sand systems were already compared for water treatment efficiency and the superiority of Fe^0/sand systems demonstrated (Miyajima 2012, Phukan 2016) that the discussion was limited to the design of Fe^0/sand systems. The main operational variable is the Fe^0:sand ratio. Based on previous works in Cameroon, commercial steel wool (SW) was used as Fe^0 source. The rationale of using Fe^0 SW was that given their tiny diameters (μm) compared to granular materials (mm) there is a chance that they are exhausted in a test. Moreover, Bradley et al. (2011) had already experienced the depletion of extra-fine SW (d = 25 μm).

2.3.3 Research objective and research design

The objective of the paper was to make recommendations based on the current state of the science concerning (i) aqueous iron corrosion and (ii) contaminant removal by iron oxides/hydroxides in the environment. Tested SONO-like with grade 0 SW (d = 50 mm) using well water for one year in Douala is the specific objective of this work.

One objective of the research has been to design a long-lasting drinking water filter for coastal regions with fluctuating salt intrusion into the aquifer.

2.3.4 Methodology

The technical steps to realize a water purification unit are: (i) developing, as a prelude to the pragmatic laboratory tests, a concept for the dimensioning of such filters; (ii) characterize and rationalize the suitability of the Fe^0-material for the construction and the guideline of the Fe^0-Filter; (iii) solve the well-known clogging (loss of permeability) problem of Fe^0 bed filters; (iv) test the applicability and effectiveness of Fe^0 filters for domestic use.

In this thesis, the production of quality drinking water by removing dissolved iron, nitrate, turbidity, and pathogens from influent water could successfully be accomplished.

2.3.5 Performed investigations

In the framework of this dissertation, experimental research has been carried out in two domains: (i) characterizing the effects of chloride on the efficiency of Fe^0/H_2O systems (Chapter

3), and (ii) testing a steel wool-based household filter for safe drinking water provision in Douala, Cameroon (Chapter 4).

2.3.5 Experiment location

The field experiments were conducted in the peri-urban area of the city of Douala in Cameroon’s Littoral Region. Douala is located between 4°04′ Nord latitude and 9°45′ Est longitude, 13 m above sea level, it is directly at the estuary of Wouri River which discharges into the Atlantic (Direct in the Gulf of Guinea). The Wouri River is at least brackish. The city and its surrounding area had an estimated population of 3 638 237 in 2019. Douala is divided into five districts. The region has a humid equatorial climate which is characterized by a long rainy season from April to October and a short dry season from November to March (Suchel 1988). The peak rainfall occurs from July to September. The average annual rainfall is around 4.000 mm. The annual temperature is between 23°C and 33°C (average 27°C), January and February being the hottest months of the year. The ferralitic soils of the area vary from yellow through brown to black, freely drained and are sandy, while being sandier at the top and more sandy clayey in the subsoil (Asaah et al. 2006). The groundwater table is generally located less than 10 m below the surface (Mafany et al. 2006), the aquifer being continuously recharged by rainfalls. Wastewater from drainage channels also infiltrates into this aquifer. Several streams run in the area and may recharge the aquifer depending on season and water level. The fluctuations of the average groundwater levels range from 0.3 to 2.1 meter between the dry and wet seasons.

Given its coastal location, it seems theoretically possible, that upon excessive groundwater extraction, seawater intrusion may occur in the more coastal areas of Douala (Mafany et al. 2006). To account for slightly saltwater affected groundwaters, the influence of chloride (Cl^-) on the cleaning efficiency of the Fe^0/H_2O system is also characterized in this thesis (chapter 3).

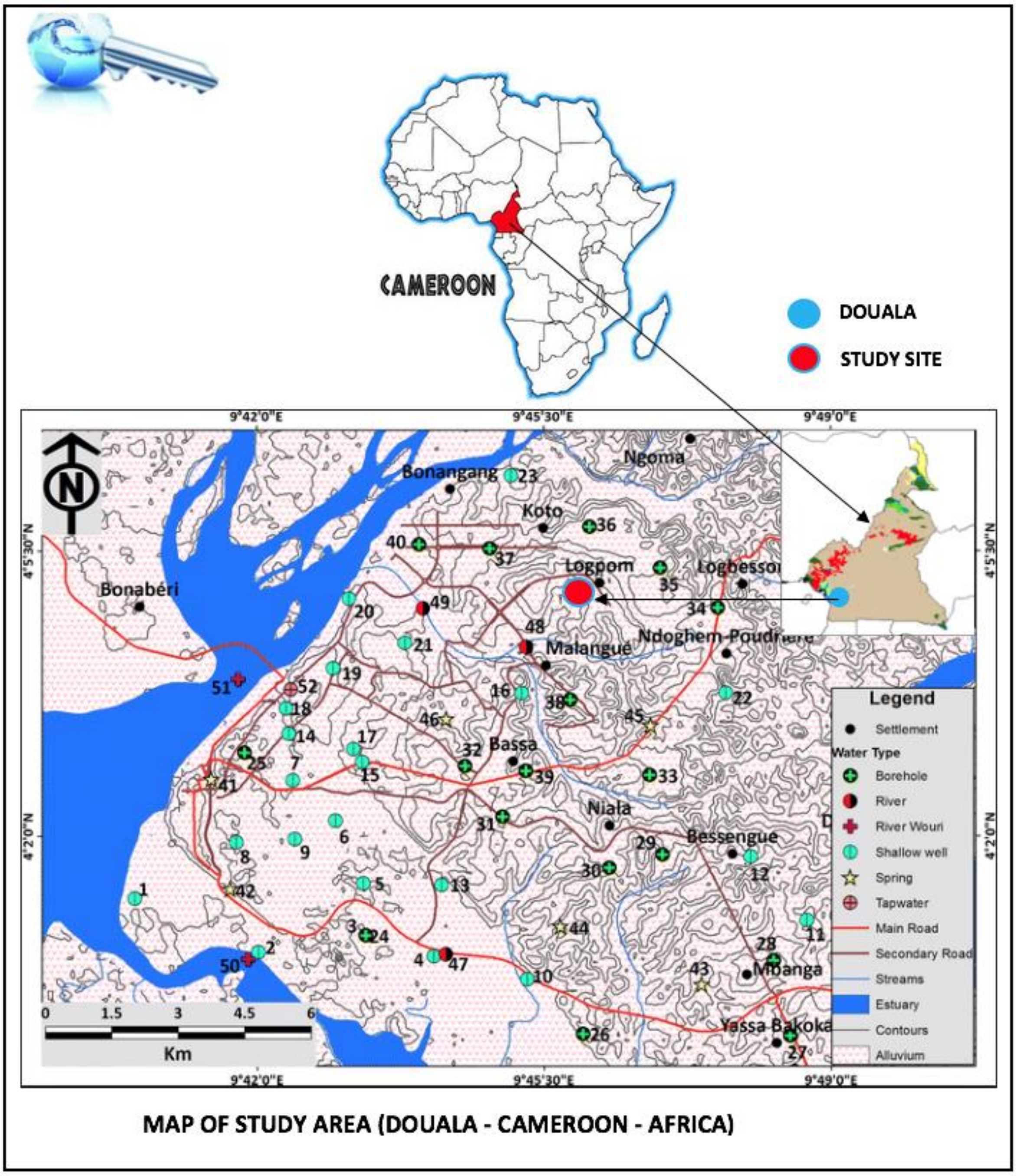


Figure 2: Location of water sources (well) in the study site (Douala Logpom).

3 Characterizing the impacts of chloride ions on the efficiency of Fe^0 filters

3.0 Preamble

This chapter evaluates the potential effects of salt intrusion (presence of NaCl) on the efficiency of Fe^0 filters. The evidence that chloride ions affect the extent of iron corrosion is given by the comparison of the chemical potential (Gibbs energy – G°_{T}) of iron corrosion by H_2O (Equation 3.1) and HCl (Equation 3.2). Changes in Gibbs energy of substances are used to judge whether a chemical process can occur spontaneously under specific conditions of temperature and pressure (Groysman 2010).

Like for any other chemical process, corrosion occurs only if $G^{\circ}_{T} < 0$.

$$Fe^0 + 2\,H_2O \Rightarrow Fe(OH)_2 + H_2 \qquad (3.1)$$

$$Fe^0 + 2\,HCl \Rightarrow FeCl_2 + H_2 \qquad (3.2)$$

The corresponding Gibbs energy changes at T = 25 °C are -15.7 and -84.9 kJ mol^{-1} respectively (Groysman 2010), showing that the presence of Cl^- significantly accelerates iron corrosion. Another comparative lecture of Equations 3.1 and 3.2 is that $FeCl_2$ is more stable than $Fe(OH)_2$. In other words, in the presence of NaCl, iron precipitation is delayed.

The current state-of-the-art knowledge on contaminant removal in Fe^0/H_2O systems is that it is the precipitation and further transformation of $Fe(OH)_2$ which implies contaminant removal, mainly by adsorption and co-precipitation (Miyajima 2012, Miyajima and Noubactep 2012, Miyajima and Noubactep 2013, Miyajima and Noubactep 2015, Btatkeu-K et al. 2016, Gatcha-Bandjun et al. 2017). By complexing Fe^{2+}, chloride ions avoid or delay the formation of contaminant scavengers. In this chapter, the impact of chloride ions on the efficiency of Fe^0/H_2O systems will be characterized using the methylene blue method (MB method) (Miyajima and Noubactep 2012, Btatkeu-K et al. 2016, Xiao et al. 2020b).

3.1 The dynamic of the Fe^0/H_2O system and the MB method

When a reactive piece of Fe^0 is immersed in water, its spontaneous oxidative dissolution occurs after Equation 3.3. Generated Fe^{2+} ions may form complexes with available ligands, including HO^- from water dissociation (Equation 3.4) and chloride from NaCl addition (Equation 3.5). Deriving from the solvent (water). HO^- is stoichiometrically very abundant, meaning that whatever the chloride concentration, there shall be $Fe(OH)_2$ precipitation if enough Fe^0 is available.

$$Fe^0 + 2\ H^+ \Rightarrow Fe^{2+} + H_2 \qquad (3.3)$$

$$Fe^{2+} + 2\ OH^- \Rightarrow Fe(OH)_2 \qquad (3.4)$$

$$Fe^{2+} + 2\ Cl^- \Rightarrow FeCl_2 \qquad (3.5)$$

The profound investigation of the Fe^0/H_2O system is complicated by the difficulty to perform Fe mass balance. Equation 3.3 implies that there are three ways to quantify the extent iron corrosion: (i) quantifying Fe^0 depletion (e.g. mass loss), (ii) quantifying H_2 evolution and (iii) quantifying soluble Fe^{2+} (Groysman 2010). At $pH > 4.5$ where iron precipitation is quantitative, this task is a very challenging because of the very low solubility of iron (Reardon 1995, Lewis 2010) and the interactions of H_2 with both, solid iron corrosion products and metallic iron (Reardon 1995, Reardon 2014). According to Lee et al. (2004), "no carbon balances between reactants and products have ever been successfully done for many chlorinated hydrocarbons, which indicates that reduction pathways of metal-mediated reactions are not fully understood yet". The situation is not better for other species, including inorganic ones. One thinking mistake in this endeavor has been that the fraction of reactants enmeshed in the matrix of FeCPs has been considered reductively transformed (Noubactep 2007, Noubactep 2008). The digestion of FeCPs is known to be challenging (Heron et al. 1994, Noubactep et al. 2006) but has not been considered in the discussion of mass balance within the Fe^0 research community (Noubactep 2007, Noubactep 2008).

3.1.1 The conventional approach to investigate the Fe^0/H_2O system

The use of Fe^0 in permeable reactive barriers (PRBs) has emerged in the 1990s (Gillham 2008, Guan et al. 2015, Chen et al. 2019, Li et al. 2021). Fe^0 PRBs are currently established as an effective and sustainable approach for the remediation of polluted groundwater. Several technical documents for the design and use of Fe^0 PRBs have been developed (ITRC 1999, Schirmer 2003, ITRC 2005, ITRC 2011, CRC CARE 2016). These documents are regarded as useful guidance for assessing the suitability of Fe^0 materials, designing Fe^0-based systems, as well as operating, monitoring, and decommissioning the same. Laboratory testing as described in CRC CARE (2016) will be presented herein. CRC CARE (2016) is one of the most recently developed documents and can be considered as the state-of-the-art knowledge.

Laboratory testing typically includes batch and column experiments. Where possible, testing should be performed by laboratories with proven expertise on individual aspects (CRC CARE 2016). Column experiments are designed from results of batch studies and should typically use site groundwater. Polluted water is pumped through the column at a velocity similar to field conditions. Concentrations of contaminants of concern, major ions, the pH value, and changes of the hydraulic conductivity are usually monitored to assess the efficiency of the design, including mineral precipitation (McGuire et al. 2003). The time-dependent changes of these parameters are plotted as a function of distance along the column. This experiment is replicated for each contaminant to determine the rate constant and calculate the half-life. Estimated half-lives for common contaminants using Fe^0 are tabulated (CRC CARE 2016). Even though such values are just indicative and should be confirmed using site-specific information, the usefulness of half-live values is questionable because the intrinsic reactivity of used Fe^0 materials also matters (McGeough et al. 2007, Li et al. 2019, Lufingo et al. 2019). On the other side, given the huge number of species that are potential pollutants at many sites, it would be difficult to determine their half-lives even under standardized conditions (Kim et al. 2014, Li et al. 2016, Li et al. 2019). The methylene blue method was introduced to consider the limitations of the half-life approach (Xiao et al. 2020b).

3.1.2 The MB method

Methylene blue (MB) adsorption on several minerals has been largely tested and used in environmental research (Mitchell et al. 1955, Barker and Linge 1981, Avom et al. 1997, Attia et al. 2008, Kurth 2008, Frost et al. 2010, Abdel Muslim et al. 2014, Btatkeu-K et al. 2016). Its applications include the measurement of specific surface areas (Barker and Linge 1981) and the characterization of the material's porosity (Attia et al. 2008). In investigating Fe^0/H_2O systems, MB is mostly considered as a model contaminant (Kurth 2008, Frost et al. 2010, Abdel Muslim et al. 2014). However, considering the evidence, that MB is a cationic dye (Mitchell et al. 1955) and that the Fe^0 surface is permanently shielded with a positively charged oxide scale, more attention should be paid to the real mechanism of MB discoloration in the presence of metallic iron. The historical work of Mitchell et al. (1955) has supported this reasoning.

In the neutral pH range, the surface of sand is negatively charged (Kosmulski 2016). This makes sand an excellent adsorbent for positively charged MB. When sand is coated with positively charged iron oxides, its affinity to MB automatically decreases. Mitchell et al. (1955) have excellently demonstrated this evidence using sixty-five (65) natural sand specimens. In fact, after freeing sand specimens from the inter-granular material (including iron oxides), their adsorption for MB considerably increased. In other words, if the same sand is coated with iron oxides (FeCPs) to several, then differential extents of MB discoloration will be achieved. The MB method is grounded on this premise (Miyajima 2012, Btatkeu-K et al. 2016). If the same Fe^0 mass is admixed to various masses of sand for the same duration, sand will be deferentially coated with FeCPs. For a given experimental design (pH value, shaking intensity, temperature, volume of solution), the relative mass of Fe^0 and sand to be used are to be determined in primarily experiments.

The MB method consists in following the time-dependent extent of MB discoloration in various Fe^0:sand mixtures (including pure sand). Observed changes correspond to the extent of sand coating by in-situ generated FeCPs. Thus, without any iron mass balance nor any identification or quantification of the generated FeCPs, their impact is characterized. For this reason, MB is an operational tracer of the reactivity in Fe^0/H_2O system (Xiao et al. 2020b).

3.1.3 Past achievements of the MB method

Noubactep and his collaborators have introduced the MB method around 2012 (Miyajima 2012, Miyajima and Noubactep 2012). Its first merit was to consolidate past results that co-precipitation is a stand-alone path in the process of contaminant removal in Fe^0/H_2O systems (Noubactep et al. 2005, 2006). In fact, because of electrostatic non-favorable conditions, MB adsorption by FeCPs is negligible. Thus, MB discoloration is due to its enmeshment in precipitating nascent FeCPs. Btatkeu-K et al. (2013, 2014a, 2014b) and explains that FeCPs for MB discoloration represent the excess after sand coating. Sand coating also competes with MB discoloration as both Fe^{2+} and Fe^{3+} are positively charged (like MB). However, MB adsorption onto sand is suppressed only after coating with FeCPs (Btatkeu-K et al. 2016). As a result, the MB method implicitly demonstrates the ion selective nature of the Fe^0/H_2O system (Sato 2001). Phukan (2015) has confirmed this selectivity in parallel experiments using MB and Orange II (Phukan et al. 2015, 2016).

The most important achievement of the MB method is that is has ended the discussion as whether admixing Fe^0 to sand (and other aggregates) is beneficial to Fe^0 filtration systems or not. Fe^0/sand mixtures were considered useful as O_2 scavengers designed to enable that pure Fe^0 systems operate under anoxic conditions (Westerhoff and James 2003). Admixing sand to Fe^0 was considered as “Fe^0 dilution” with the potential to negatively impact the efficiency of the systems. The MB method has clearly demonstrated that, due to the volumetric expansive nature of iron corrosion, admixing non-expensive aggregates with Fe^0 is even a prerequisite for sustainability (Btatkeu-K et al., 2014a, 2014b, 2016), validating the concept of Domga et al. (2015).

3.2 The impact of chloride on the Fe^0/H_2O system

One objective of the research has been to design a long-lasting drinking water filter for coastal regions with fluctuating salt intrusion into the aquifer.

The effect of the chloride ions (Cl^-) on the efficiency of Fe^0/sand systems was characterized in column studies for 4 months on basis of methylene blue (MB) discoloration. Tested systems were: pure sand (0 % Fe^0) as reference and a Fe^0/sand mixture (50 vol.% Fe^0 and 50 vol.% sand). Tested Cl^- concentrations were 0.0, 2.1, 21.1 and 42.2 mM. The used MB concentration was 16 μM (5 mg L^{-1}) and used Fe^0 mass was 100 g. Discoloration experiments lasted for 89 days and were followed by a 26 days desorption experiment. Each system was characterized by the time-dependent changes of the pH value, the iron breakthrough, the MB breakthrough, and the hydraulic conductivity (permeability). During the discoloration experiments, a total of 17.4 L (184 pore volumes) of the MB solution flowed through each column (279 μM dye or 87.2 mg). No significance changes in pH value and permeability were observed. Discoloration and desorption results confirmed that sand is an excellent MB adsorbent (only 11 % discoloration in the reference system). In the absence of Cl^-, 15 mg MB was discolored. Up to 18 mg of MB was discolored in the presence of Cl^-. A similar trend was observed for the iron release which was 7.3 mg at 0.0 mM Cl^- and 16.2 mg at 42.2 mM Cl^-. This confirms that chloride ions enhance the kinetics of Fe^0 corrosion and thus the production of contaminant collectors (for MB co-precipitation). Results confirmed the suitability of MB as a powerful operative indicator for the characterization of processes in the Fe^0/H_2O system.

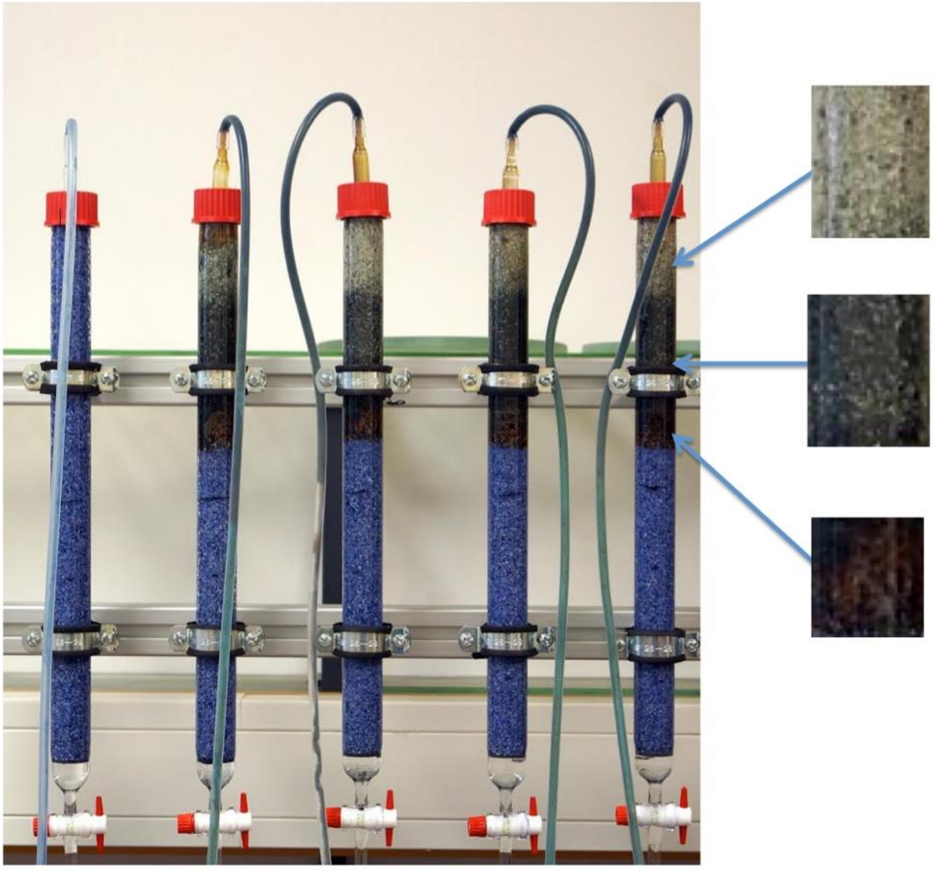


***Figure 3**:* Photograph of a column design depicting the typical sequence of coloration described by Westerhoff and James (2003). The picture shows that the entrance zone of the Fe^0/sand zone is colored brown while the upper section is black. The sand layer after the Fe^0/sand zone more or less maintains its "white" / brownish color by Fe^{III} iron oxide from the Fe^0/sand zone. Sand in the reference system (first column) and the sand layers preceding the Fe^0/sand zone are blue colored by methylene blue. (*Picture from Miyajima 2012)*

Five glass columns were used for the design. Four columns filled with sand and granular iron (sandwiched with sand in the column) and one reference column (sand alone). It is seen that the reference system (sand alone) and the sand layer preceding the reactive layer are uniformly blue-colored. A brownish coloration of the tubing material is also observed in all Fe^0-based systems (Figure 3).

These experiments have clearly demonstrated that seawater intrusion would enhance the concentration of dissolved iron in the effluent of any Fe^0-based filter that is initially designed for low saline or fresh water. For this reason, in case of a saltwater intrusion, new Fe^0 filters should be designed which incorporate for example a subsequent unit containing biochar for iron removal (Gwenzi et al. 2017). However, elevated concentration of dissolved iron is not the sole potential problem, because effluent iron concentration increases due to the higher solubility of

$FeCl_2$ and $FeCl_3$ relative to $Fe(OH)_2$ and $Fe(OH)_3$ (Gatcha-Bandjun et al. 2017). The hydroxides are the real contaminant scavengers, meaning that thicker Fe^0-based beds would be necessary to achieve the expected efficiency. Fe^0 systems have been reported to induce water desalination (Antia 2015a, 2015b, 2016, 2917), but this aspect is not presented herein. It is certain that water desalination is complex and expensive. It is better to avoid it, for example by increasing artificial groundwater recharge to balance extracted groundwater (Marwa et al. 2018, Qi et al. 2019, Pembe-Ali et al. 2020).

4 Designing and pilot-testing a household Fe^0 SW filter in Douala (Canmeroon)

4.0 Introduction

Lack of safe drinking water is one of the most characteristics and most serious health issues in the developing world (Ali 2014). All the 46 nations of Sub-Sahara Africa for example, currently have not achieved universal access to safe drinking water and most of them are not on track to meet the UN SDGs in 2030 (Hering et al. 2016, Nanseu-Njiki et al. 2019). This sad situation calls for the development of applicable and affordable tools to treat available water sources on a decentralized manner (Shannon et al. 2008). In the city of Douala, well water is by far the main source of drinking water (Ako et al. 2010), but its quality is largely unknown (Mafany et al. 2006). During the past two decades, intensive efforts have been made to establish metallic iron (Fe^0) based filtration systems as a universal tool for potable water production (Ngai et al. 2006, Hussam and Munir 2007, Banerji and Chaudhari 2017, Nanseu-Njiki et al. 2019, Yang et al. 2020).

Although Fe^0-based filters are the most extensively investigated approach in the last two decades, scientifically sound, economically viable, and sustainable strategies for their design remain elusive (Etmannski 2014, Banerji and Chaudhari 2017, Bretzler 2018, Bretzler et al. 2020, Ullah et al. 2020, Yang et al. 2020). To date, the design of sustainable Fe^0 filters is impaired by the evidence that the kinetics of iron corrosion under environmental conditions is rather slow and could continue for several years or even decades (Wilkin et al. 2014). While the kinetics of Fe^0 specimens typically used in water treatment is yet to be characterized, the greatest challenge will be to couple “residual corrosion” and contaminant removal. Given that each Fe^0 specimen and each water source are unique, it is rather difficult to generate transferable results. There have been little efforts in this sense as for example the seven or eight classes of iron steel wool (Fe^0 SW) have been mistakenly presented as Fe^0 SW, without even specifying the used grade (Lufingo et al. 2019). Additionally, the tested experimental duration has rarely accounted for the non-linear kinetics of Fe^0 corrosion (Cao et al. 2020, Xiao et al. 2020a, Xiao et al. 2020b, Yang et al. 2020).

Any sustainable Fe^0-based solution for decentralized safe drinking water provision should be presented with an appropriate business model. Such a model includes the price of the used Fe^0 specimen, the admixing material (e.g. sand), and the filter container. The business model also includes the service life of filters and how they will be decommissioned (Etmannski 2014). In the absence of reliable and accurate knowledge on the long-term reactivity of used Fe^0 serious business models are possible. The present work aims at contributing to fill this knowledge gap using Fe^0 SW as reactive material.

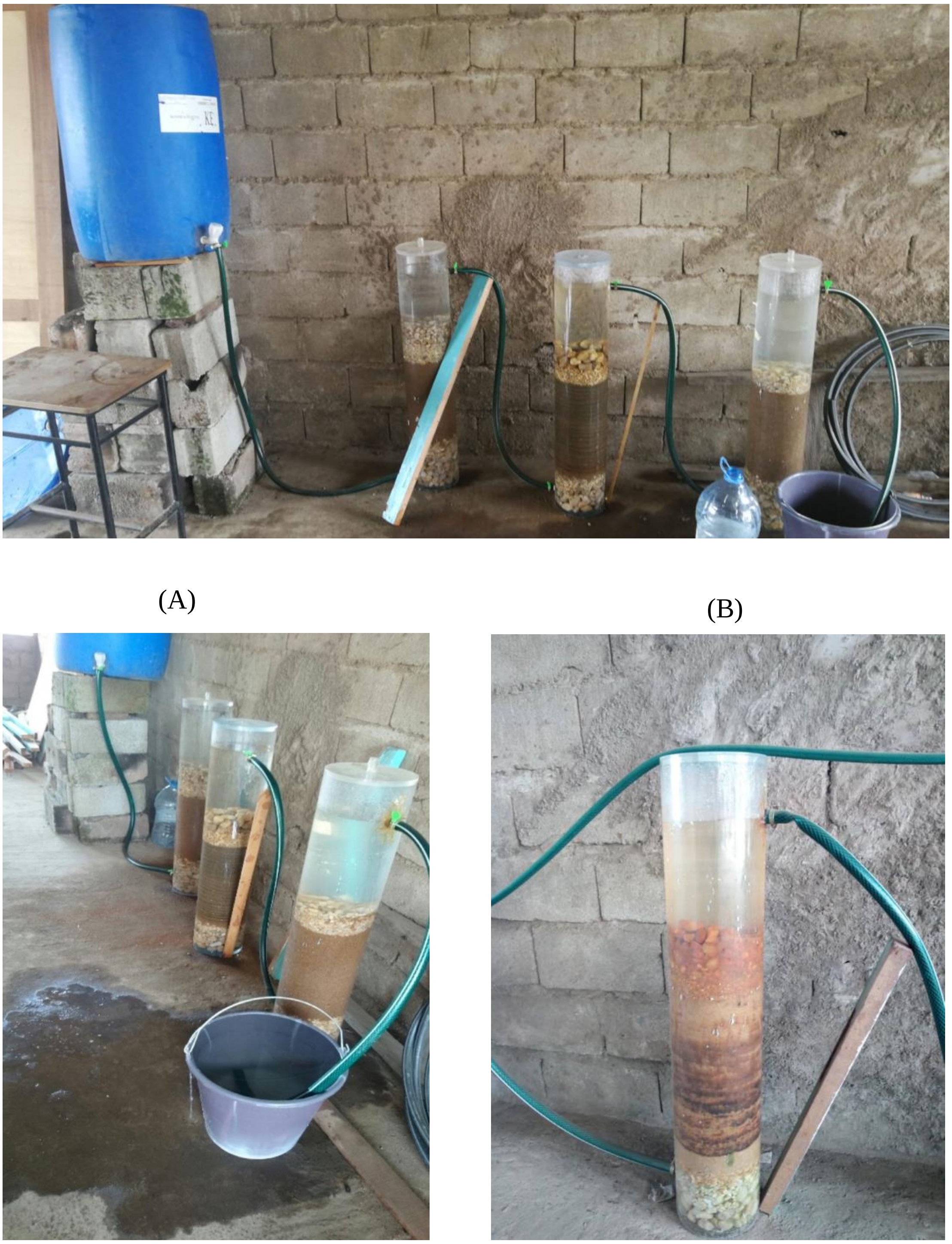
The used Fe^0 SW (d = 50 µm) corresponds to grade 0 which is twice larger in diameter than the one used by Bradley et al. (2011) in their experiments lasting for 1o months. Fe^0 SW (d = 25 µm) represented 10 % of the reactive mixture and was depleted after eight months. Herein, preliminary experiments were performed with 50 % (vol/vol) Fe^0 SW and the filters were clogged after six months. The main experiments were performed with 10 % (vol/vol) Fe^0 SW and lasted for one year. No material depletion was observed. The results are presented and discussed in this chapter.

4.1 Materials and Methods

The choice to experiment with this filter (BSF+Fe^0-Filter) was based on the following three criteria:

First, the Fe^0-SW is an excellent choice as a source of Fe^0 for the design of Fe^0- filters. The second hypothesis is that to properly size a Fe^0 bed filter, that will be efficient and durable, amounts to defining well the mixture of materials forming the heart of such a system (reactive zone - RZ). The last hypothesis is that to reiterate while also demonstrating that the Fe^0 bed filters are efficient and reliable systems, amounts to putting in advance its capacity, to chemically eliminate a pollutant that is difficult to extract in the like fluorine, and from a biological point of view, to eliminate pathogens.

Furthermore, the choice of SW as Fe^0 (materials for the construction of the RZ) for this study is due to the fact that the EDTA tests suggest that the SW are more reactive than most local materials (Ndé-Tchoupé 2019, Hildebrant et al. 2020).



(A) (B)

Figure 4: Picture of the designed filtration system: Well water was stored in blue 200 L tank. The first and the third columns are conventional bio sand filters (BSF). In the middle of column 2 is Fe^0 SW mixed with sand coarse (Picture B). The columns are connected to each other with a PET tube.

4.2 Filter construction and Design

The tested design is made up of three identical cylindrical Plexiglass columns with a length: of 100 cm and an inner diameter of 20.0 cm mounted in series: two conventional BSFs and one

Fe^0 SW unit in between. Upon successful testing, the unit was intended to be transferred for use in households, but with a proper housing (e.g. concrete material). The test device was constructed inside a room of the Institute of Applied Technology in Douala. The used room was not a conventional experimental laboratory but offers representative conditions for a household situation. The room temperature range was 26 ± 2 °C.

Schematic diagram of the designed filtration system is presented in Fig. 4. The columns were connected to each other by using a 1.5 m PET (polyethylene terephthalate) tube with an inner diameter of 2.4 cm. The columns were packed from the bottom to the top as follows (Table 2): 15.0 cm gravel ($H_{gravel,1}$) followed by 40.0 cm of a reactive layer, and topped by a 15.0 cm gravel layer ($H_{gravel, 2}$). For column 1 and 3, the reactive layer was a medium sand layer ($H_{sand, 1}$). In column 2, the 40 cm consist of a mixture of 30.0 cm Fe^0 SW and coarse sand (Fe^0/sand) (reactive zone RZ) sandwiched between two 5.0 cm medium sand layers ($H_{sand, 2}$).

The reactive zone layer was prepared by carefully introducing sand grains and chopped Fe^0 SW in small lofts into the column. The Fe^0/sand mixture (10 vol.% SW + 90 vol.% coarse sand) was previously mixed in a large beaker. Once in the column, water was added to the mixture and it was gently compacted by manual tapping using a 100 mL PET bottle filled with water. The 300 g of Fe^0 SW and 14,200 g of coarse sand mixed together, had a Fe^0 concentration of 2.07 weight %. The strong discrepancy between volume and weight percent is caused by the very low density of SW (low weight and large volume). To build a 20 cm reactive layer under their experimental conditions, Bradley et al. (2011) used 260 g of Fe^0 SW (extra fine) with 1,563 g sieved sand (effective size 0.4 mm).

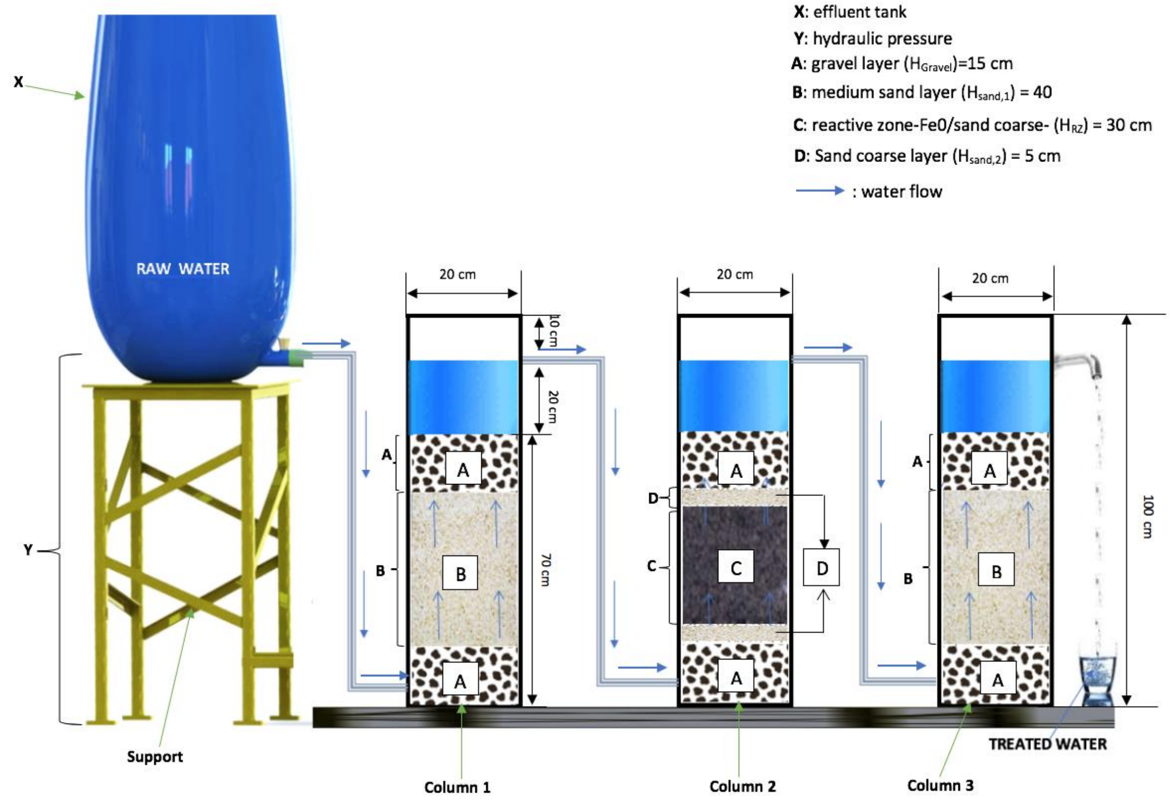


Figure 5: Schematic diagram of the designed filtration system: Well water was stored in 200 L tank. The first and the third columns are conventional bio sand filters (BSF). In the middle of column 2 is Fe^0 SW mixed with coarse sand. The columns are connected to each other with a PET tube.

Table 1: Summary of the used experimental set up. $H_{gravel1}$ and $H_{gravel2}$ are the heights of the underdrain and the upper layer respectively; H_{sand1} the heights of medium sand; H_{Sand1} is the medium sand layer (BSF) and H_{RZ} is the height of the reactive layer (Fe^0/sand) sandwiched by H_{sand2}.

Designation	**Height (cm)**		
	Column 1	**Column 2**	**Column 3**
Gravel ($H_{gravel\ 1}$)	15.0	15.0	15.0
Sand coarse (H_{Sand2})	-	5.0	-
medium sand (H_{Sand1})	40.0	-	40.0
RZ(Fe^0/ Sand coarse) (H_{RZ})	-	30.0	-
Sand coarse (H_{Sand2})	-	5.0	-
Gravel ($H_{gravel\ 2}$)	15.0	15.0	15.0

The total thickness of solid materials in each column was 70.0 cm, the free water column was 15 cm thick.

4.3 Solid materials

4.3.1 Metallic iron (Fe^0)

Fe^0 SW was used as a generator of iron hydroxides for contaminant scavenging (Noubactep et al. 2009, Jia et al. 2007, James et al. 1992). A fine-grade Fe^0 SW (grade 0) of 50 µm fiber thickness from “Grand Menage” trademark brand purchased in Douala (Cameroon) was used. Its average elemental composition was not determined as it was proven to be not a stand-alone determining reactivity parameter for Fe^0 in general. Recently, Lufingo et al. (2019) presented the first systematic study comparing the intrinsic reactivity of Fe^0 SW. The elemental composition (%) of the grade 0 (d = 50 µm) material they tested was: Fe: 99.08; Co: 0.05; Cu: 0.27; Ni: 0.11; and Cr: 0.49.

The Fe^0 SW used in this study was chopped in sections of 1.0 to 5.0 mm length.

4.3.2 Sand

The used sand was a natural material from the Mungo River (Cameroon). Mungo sand was selectively sieved, using a set of sieves to split the sand to gravel. The sieve A made with grain size of 2 mm in diameter (metal net) is used to select a more coarse sand. Sieve B made with mosquito net with grain size of 0.63 mm in diameter is used to obtain a medium sand. This medium sand is retained using a sieve with a size of 0.2 mm in diameter (Fig. 6).

The portion passing through 2 mm sieve and retained on 0.63 mm was mixed to Fe^0-SW to build the reactive zone and to sandwich these RZ layer. The medium sand retained with the sieve with a size of 0.2 mm is used as filter media in the BSFs (H_{sand1}). This step is also to eliminate all silt and clay contained in sand.

As received Mungo sand was washed several times using tap water until the wash water became clear. Retained fractions were separately warmed in boiling water for about 3.0 h. The sand was further dried at the sun for about 6.0 h. Sand was used because of its worldwide availability and its use as an admixing agent in Fe^0/H_2O systems (Ndé-Tchoupé 2019).

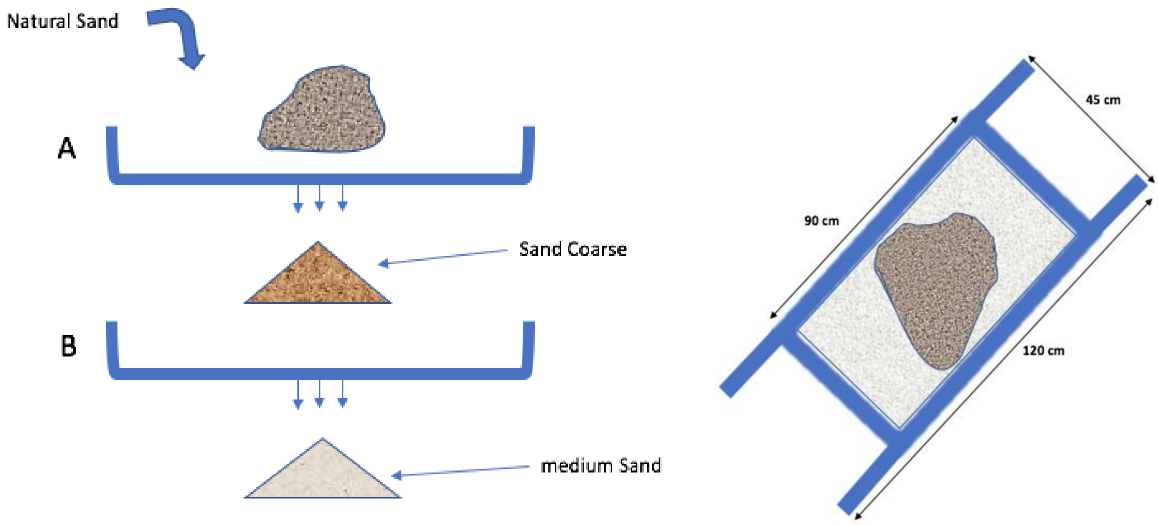


Figure** 6**: This step needed to sieve the grad of medium sand media. Sand coarse is maintained between A (2 mm in diameter) and B (0.63 mm in diameter). The sieve material for sieve A is a metal net and for the sieve B is the mosquito net. Each sieve is made with wooden frame.

4.3.3 Gravel

The Gravel was pre-treated like coarse sand. The particle size separated by two sieves ranged from (B') 4 mm to (A') 8 mm (Fig. 7). Gravel was used as lower supporting layer and as top layer in the individual columns. The bottom gravel layer partially removes solids from raw water entering the first column (Fig. 5). The gravel layer also prevents the entrance of sand particles into the inlet pipe and facilitates the water flow in the inlet of the column. Wegelin (1996) also recommended a gravel layer with grain sizes between 4 to 8 mm.

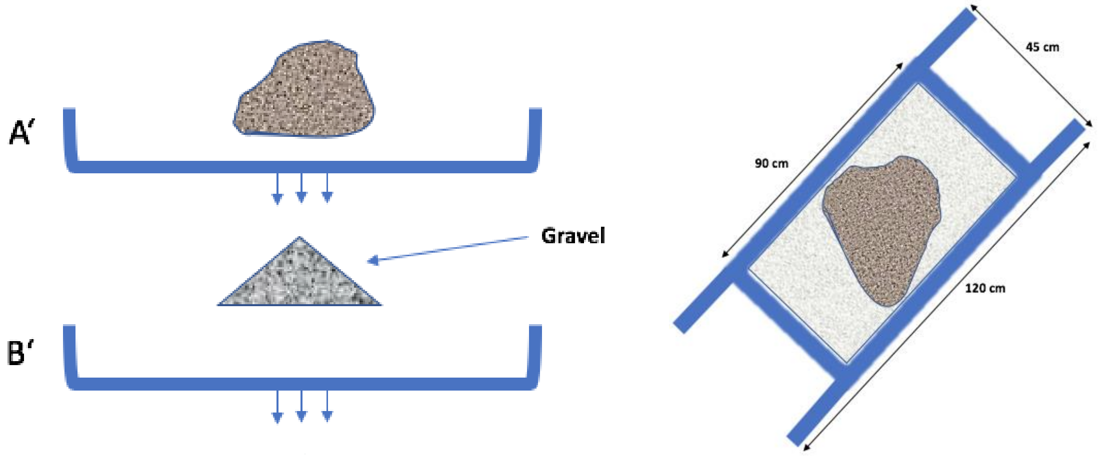


***Figure** 7:* Scheme of the steps to obtain gravel with 4 to 8 mm diameter. A' is the first step of sieve to obtain gravel but the step B' is to eliminate all sand size contain in gravel from A'. The sieve materials in sieves A' and B' consist of metal wire meshes fixed in a wooden frame.

4.4 Construction protocol and guideline for the Fe^0 based sand filter device

This protocol describes the steps in preparing solid media (medium sand, coarse sand, gravel and Fe^0-SW) for use in a Fe^0 based filter device.

(1) Prepare the sand and gravel for their use in the filter device

First, mixed sand and gravel must be separated into its different-sized grain sizes by passing through a series of sieves, because the filtration rate is strongly influenced by the grain size of media. Next, sand and gravel must be washed to remove finer particles such as silt, clay, and other impurities.

An important factor is the selecting of source of sand and gravel. Last, use natural water to wash the sand and gravel, and place the media in the sun to dry: the solar radiation will inactivate any possible attached pathogens. If this is not possible, remember that pathogens within the water or attached to sand grains will be consumed by the filter's normal biological processes or, when exposed to an anaerobic environment within the filter, will not survive.

(2) The following items are necessary:

one 200 liters (50 gallons) raw water tank,

one 50 liters (12,5 gallons) drinking water tank,

Column integrated Tubes (diameter of 2 cm, length = 3 cm) to connect the columns, PVC pipe (inner diameter of 2 cm, length = 150 cm) and ring to attach PVC pipe and Column integrated Tubes.

One tap for flow rate regularization.

One 100 mL PET bottle filled with water to compact media in the column by manual tapping.

Materials for testing filter flow rate including a measuring vessel (1-liter PET bottle is adequate) and one stopwatch.

(3) To place the media in the filter columns, certain procedures must be respected.

At first, place the empty filter units inside the house or in a corner of a yard. It must be an appropriate place because its location final. Secondly fill the column with media from the bottom to the top as follows: a) Gravel, sand, and gravel for the BSF filter column and b) Gravel, coarse sand, Fe^0 SW /coarse sand mixture (Fe^0/sand), coarse sand, and gravel for the Fe^0 SW based filter column. After filling, make sure that the drain hole, PVC connect pipe, and outlet pipe are unobstructed.

Following steps are necessary for mounting the filter:

a) Installing the raw water tank by the height greater than that of the columns (to generate a gravity pressure)
b) Place all the columns in order at the same horizontal level as follows: BSF1, Fe^0/Sand Filter, BSF2.
c) Connect the raw tank and the columns with PVC connecting pipes as follows: outlet of raw tank and inlet of the first column. Then outlet of the BSF1 column to inlet of Fe^0/Sand Filter column. At the end connect the outlet of this to the inlet of BSF2.

Ensure that the connecting pipes are securely attached to each column and to the raw water tank.

Water is required to be inside the filter before starting the filtration of the raw water. This prevents pockets of air from being trapped within the media. The presence of air pockets would slow down the flow rate. A reliable filling of media in the column is essential for a proper operation of the filter.

Fill natural raw water in 200 liters (50 gallons) and let it flow until all columns filling with water. After that, the level of water in all column is stable, let it flow through out of the outlet pipe of the last column for around 21 days. So that the filter should reach the maturation.

The circulation and pressure of the water in the filter is determined by the hydraulic pressure. Due to a siphoning effect, the water will stop coming out of the filter when the water is at the same level as the bottom of the column integrated tubes.

4.4.1 Testing filter flow rate

The amount of water that flows through the filter is controlled by the column diameter, the thickness and grain size distribution of sand media contained within the filter and the control tap place by outlet of the influent tank. If the rate is too fast, the efficiency of bacterial removal may be reduced by lowering the flow at the tap. If the flow rate is too slow, the amount of treated water is insufficient to meet the needs of the users and the flow should be increased at the tap.

The flow rates of a filter can be derived from the time it takes to fill up a container of a known volume with water. To test the flow rate, place a graduated 1-liter container under the outlet of the filter. The flow rate through the filter decreases as the height of the water in the influent reservoir drops. Measure with a stopwatch how long it takes to completely fill the 1-liter container with filtered water. For this study 0.34 liter has been obtained per min (that means 176.5 sec for one liter).

The filter is still functional, but it will require more maintenance than normally due to frequent clogging. Some experimentation will be necessary to achieve the desired flow rate. Since the flow rate is controlled at the tap and by the porosity of the sand, the tap should be adjusted and/or the sand should be washed more intensively (removal of finer particles) to achieve the desired flow rate.

4.4.2 Preparation of the material

Consumers are required to disinfect the gravel and coarse and medium-sized sand by boiling it in water for approx. 3 hours, before drying it in the sun for about 6 hours. Afterwards, the SW chopped in small particles was mixed with coarse sand to obtain the reaction layer of the second column.

4.5 Experimental procedure

An intermittent gravity-driven filtration was performed for one year with the device described above (Fig. 4). Each filtration event was initiated by opening the outlet-controlled tap connected to column 1 and allowing the stored well water from the reservoir to flow through the entire system. Experiments were conducted on a daily basis from Monday to Friday. Two hundred liters of water were filtered per filtration event. Raw water was collected from a well, used for drinking and other domestic purposes (Tab. 2). Since the well water was polluted with microorganisms; there was no need for artificially seeding it. The volume of effluent recorded during the first 10 min was used to calculate the flow velocity. At the end of the filtration event, the reservoir was immediately refilled with 200 L well water. The initial flow rate was 0.34 L min^{-1} (20.40 L h^{-1}) and was not further modified. This approach perfectly mimics pilot-scale intermittent filtration using household filters for daily water need in low-income communities. The pH value, the iron level, and the extent of water decontamination were monitored. Complete water analysis including search for pathogens was performed twice per month at the Centre Pasteur in Douala.

4.6 Sample collection and efficiency characterization

The 1 L sample bottles were provided by the Laboratory at the Centre Pasteur du Cameroon (Douala) and used to collect water samples from the filter unit twice per month for microbial analysis. These samples included the raw water from a private well (Tab. 2). The time from sample collection and transportation to the lab was less than 4 hours. It is considered that the effects of time and temperature on microbial survival is negligible.

***Table** 2:* Average composition of the used well water. The well is polluted with coliforms and depicts high levels of conductivity and turbidity compared to the WHO guidelines (2017). WHO stands for World Health Organization.

Parameter	**Unit**	**Well Water**	**WHO (guideline)**
Turbidity	(NTU)	35 ± 2	< 5
Conductivity	(μS.cm^{-1})	296 ± 7	250
Total iron	(mg L^{-1})	1.45 ± 0.25	< 0.2
Nitrate	(mg L^{-1})	23.5 ± 4.5	< 50
pH value (25 °C)	(-)	4.9 ± 0.2	6.5 – 8.5
Total coliform (TC)	(UFC mL^{-1})	1 949 ± 45	0.0
Faecal coliforms (FC)	(UFC mL^{-1})	1 495 ± 97	0.0

The efficacy of the designed filter to treat water was accessed by the extent of reducing the concentration of fecal coliform (FC) and total coliform (TC). In addition, turbidity, permeability loss, nitrate, and iron concentration were monitored.

4.7 Analytical methods

Iron concentrations were determined by using a UV–Vis spectrophotometer (Dr. Lange CADAS 200 LPG 392). The working wavelength was 510 nm. A cuvette with 1.0 cm light path was used. The iron determination followed the o-phenanthroline method (Saywell and Gunningham 1937, Fortune and Mellon 1937). The spectrophotometer was calibrated for iron concentrations $\leq$10.0 mg L^{-1}. The pH values were measured by a WTW pH meter. Conductivity was analyzed by the ISO 7888 method using a portable (WTW 340i) conductivity meter with automatic temperature compensation, so that all results refer to 20 °C. All other parameters including turbidity and biological analysis were performed at the laboratory of the Institute Louis Pasteur in Douala using following analytical method (Tab.3):

Table 3: Analytical method used in this study for physico-chemical and biological parameters

Physico-chemical parameters	**Abbreviation**	**Unit**	**Analytical method**	**Water fraction**	**Location of analysis**
Turbidity	Turb	NTU*	NF EN ISO 7027: nephelometry	Whole water	in situ
Conductivity	EC	µS cm^{-1}	ISO 7888	Whole water	in situ
Total Iron	Fe	mg L^{-1}	Validated in-house method: o-phenanthroline	Dissolved fraction (filtered at 0.45 µm)	Laboratory
Nitrates	NO3	mg L^{-1}	Validated in-house method: capillary electrophoresis	Dissolved fraction (filtered at 0.45 µm)	Laboratory
Power of hydrogen	pH (25 °/ 77 °F)	(-)	NF T90-008	Whole water	in situ
Total coliforms	TC	(UFC mL^{-1})	NF ISO 4832	Dissolved fraction (filtered at 0.45 µm)	Laboratory
Faecal coliforms	FC	(UFC mL^{-1})	NF ISO 4832	Dissolved fraction (filtered at 0.45 µm)	Laboratory
Temperature	T	°C	Integrated temperature probe of the combined pH electrode sensor	Whole water	in situ

*NTU = Nephelometric Turbidity Units

4.8 Expression of Experimental Results

4.8.1 Value of E

To characterize the extent of the decontamination for individual contaminants (e.g., coliform, nitrate, turbidity), the effectiveness of the treatment (E) or attenuation percentage was calculated as follows (Equation (1)):

$$E = [1 - (C/C_0)] \times 100\ [\%] \qquad (4.1)$$

where C is the concentration after the experiment in the effluent concentration, and C_0 the initial aqueous influent concentration. The effectiveness comprises adsorption in the filter and possible other reactions that may occur during water throughput.

4.8.2 Hydraulic Conductivity

Changes of the hydraulic conductivity (permeability) were characterized by calculating the percentage of the relative permeability φ at each filtration event relative to the initial value of the hydraulic conductivity φ_0 (Equation 2):

$$\varphi = 100 \times \varphi/\varphi_0 \text{ [vol.\%]} \qquad (4.2)$$

4.9 Results and Discussion

4.9.1 Results

4.9.1.1 Hydraulic conductivity

Figure 8 and Table 4 (row 3) summarize the changes of relative filtration rate (φ) in the investigated filter. The results of a previous experiment for 6 months with a 50:50 Fe^0/sand volumetric ratio (experiment 1) are also shown. It is seen that the filter in experiment 1with the same Fe^0-SW was not sustainable as an almost 90% permeability loss was observed. The present experiment with a 10% Fe^0 (vol/vol) was designed accordingly (experiment 2). The results of experiment 1 depict the typical profile of permeability loss in Fe^0-based filtration systems (Westerhoff and James (2003), Mackenzie et al. (1999) with the φ value dropping very abruptly. This behavior can be attributed to a local formation of a cake (more spongy, stratified form) within the filter (Santisukkasaem and Das 2019). Clearly most of the filter material stays still porous, but the inter-connectivity is suppressed in the domain where cake is formed. This is a testimony that the used Fe^0 ratio is too high (Domga et al. 2015).

The progressive decrease of the φ values observed in this work (41.5 % in 12 months) was mainly attributed to iron corrosion products. This assumption is supported by results of George and Ahammed (2019) who performed similar experiments but with three individual systems (BSF and Fe^0-amended BSF) for 4 months. The φ values were 50.0%, 42.9%, and 15.6% for the systems Fe^0-nails/sand, Fe^0- scrap/sand, and BSF respectively. While George and Ahammed (2019) are still speculating about the presence of Fe^0 as cause of decline in flow rate, the present study was designed to verify the textbook knowledge that iron corrosion is a volumetric expansive process (Landolt 2007), which implies that systems with lower Fe^0 ratios are more permeable (Tepong-Tsinde et al. 2015a, Domga et al. 2015, Caré et al. 2013).

The design tested in this work, a Fe^0 SW filter sandwiched between two BSF filters, was an attempt to prolong the service life of the filter by consuming dissolved O_2 in the first BSF, therefore operating under O_2 depleted conditions and avoiding rapid system clogging (Tepong-Tsinde et al. 2015a, Noubactep et al. 2012). The second BSF was used as Fe scavenger to fix iron escaping from the Fe^0 filter. The results of George and Ahammed (2019) confirmed the O_2

scavenging nature of both BSF and Fe^0 filters. Westerhoff and James (2003) also used hybrid Fe^0/sand layers as O_2 scavengers to sustain the efficiency of Fe^0/H_2O systems.

The qualitative similitude between this work and that of George and Ahammed (2019), Mackenzie et al. (1999) and Westerhoff and James (2003) should not be overemphasized. This study used 300 g of Fe^0 SW making up a volumetric ratio of 10% while George and Ahammed (2019) used 7.5 kg of mild steel nails and the same mass of iron filing scrap uniformly mixed with sand throughout the reactive layer (Tab. 4). Given differences in key characteristics including density, form, intrinsic reactivity, and size of the zerovalent iron used, a quantitative comparison is difficult or even impossible. Obviously, under the respective operative conditions, the permeability loss at the end was acceptable.

The results achieved herein are more comparable to those of Bradley et al. (2011). The authors used a different grade of steel wool (d = 25 µm vs. 50 µm herein) in the same volumetric percentage (10%) and reported a completed SW depletion after 170 days (almost 6 months). Upon Fe^0 depletion, the SW filter performed worse than the parallel operating BSF. This key observation was postulated by Noubactep et al. (2012) and considered while designing the system tested by Tepong-Tsindé et al. (2015a). In fact, O_2 depleted by Fe^0 is essential for the formation of the biofilm (Schmutzdecke), and pore filling by iron corrosion products have created preferential flow paths (Miyajim 2012).

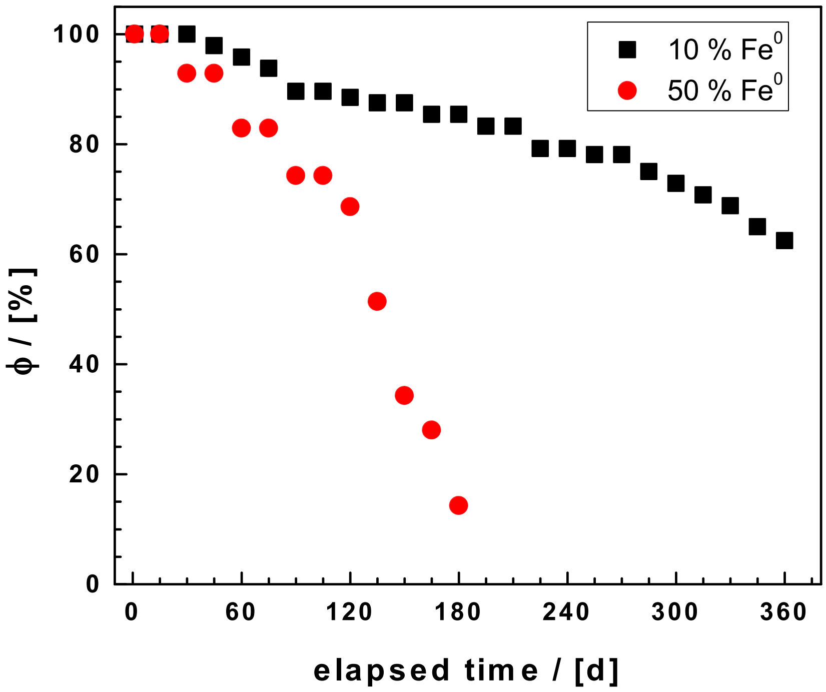


Figure 8: Flow rate variation over the length of filter runs for the Fe^0 SW ratios of 50 % and 10 vol.% respectively. Experimental conditions: 800 g SW for 50 % Fe^0 and 300 g SW for 10 % Fe^0 of Fe^0 SW (grade 0) of 35 µm fiber thickness from “Grand Menage”; filling material: sand. Column length 100 cm, column diameter 20 cm. The system was fed with natural well water polluted by fecal coliforms.

Lufingo (2019) recently presented the first systematic characterization of Fe^0 SW specimens using their own developed tool (the Phen test). His results confirm the observed trends that neither the elemental composition, the size, or the surface state alone determine the kinetics and the extent of Fe^0 dissolution in aqueous solution. However, because the pH value was still slightly increasing at the end of the experiment, it can be considered that SW was not depleted in his tests. Assuming that each natural water should be regarded as a unique system impacting the efficiency of Fe^0 filters (Naseri et al. 2017), the results achieved herein are not easily transferable to other locations with different water qualities. The authors suggest, however, that it is possible to design an efficient SW containing 10% Fe^0 (vol/vol) for use at household level. More systematic research is needed using, for example, the seven grades of Fe^0 SW characterized by Lufingo et al. (2019) in combination with typical model (examples of water) waters representing the most common water sources (surface water, less and more saline groundwater) [Luo et al. 2013].

***Table** 4:* Characteristics of the effluent water over the testing period. The effluent iron concentration was constantly lower than the detection limit of the UV–Vis spectrophotometer ([Fe] < 0.2 mg L^{-1}). φ is the water flow velocity in L h^{-1}.

t	**pH**	**Φ**	**Total coliform**	**Turbidity**	**Nitrate**
(days)		(L h^{-1})	(CFU/100 mL)	(NTU)	(mg L^{-1})
Raw water	4.9	-	1,950	35.0	23,5
1	6.6	20.0	0.11	1.09	0.21
15	6.7	20.0	0.11	1.07	0.19
30	6.6	20.0	0.11	1.00	0.20
45	6.8	20.0	0.10	1.00	0.20
60	6.8	19.6	0.10	1.01	0.15
75	6.9	19.6	0.10	1.00	0.15
90	6.7	18.8	0.10	0.99	0.12
105	6.6	18.8	0.08	0.80	< 0.1
120	6.8	17.9	0.08	0.90	< 0.1
135	7.0	17.5	0.08	0.90	< 0.1
150	7.1	17.5	0.08	0.80	< 0.1
165	7.3	17.1	0.08	0.80	< 0.1
180	7.4	17.1	0.08	0.80	< 0.1
195	7.5	16.7	0.02	0.90	< 0.1
210	7.5	16.7	< 0.02	0.90	< 0.1
225	7.5	15.8	< 0.02	0.80	< 0.1
240	7.6	15.8	< 0.02	0.90	< 0.1
255	7.6	15.6	< 0.02	0.90	< 0.1
270	7.7	15.6	< 0.02	0.80	< 0.1
285	7.5	15.0	< 0.02	0.80	< 0.1
300	7.6	15.8	< 0.02	0.70	< 0.1
315	7.9	15.2	< 0.02	0.80	< 0.1
330	8.1	13.8	< 0.02	0.70	< 0.1
345	8.3	13.0	< 0.02	0.80	< 0.1
360	8.6	12.5	< 0.02	0.70	< 0.1

4.9.1.2 Turbidity removal

Table 4 (row 5) summarizes the results of turbidity removal by listing the residual turbidity; the corresponding percent removal is depicted in Figure 9. The average influent turbidity was 35 NTU. The average effluent turbidity from the system was 0.7 NTU. The average turbidity removal efficiency from the influent was >98 % during the experiment. This corroborates the results of George and Ahammed (2019) and Bradley et al. (2011) reporting about quantitative turbidity removal in both BSF and Fe^0-amended BSF. George and Ahammed (2019) also reported that the amendment of Fe^0 filters does not improve their turbidity removal efficiency. The results presented herein seem to confirm this assertion. However, the removal efficiency depends on the design and the operational conditions. In essence, Fe^0 amendment should improve turbidity removal because of pore space reduction (expansive corrosion) [Domga et al. 2015].

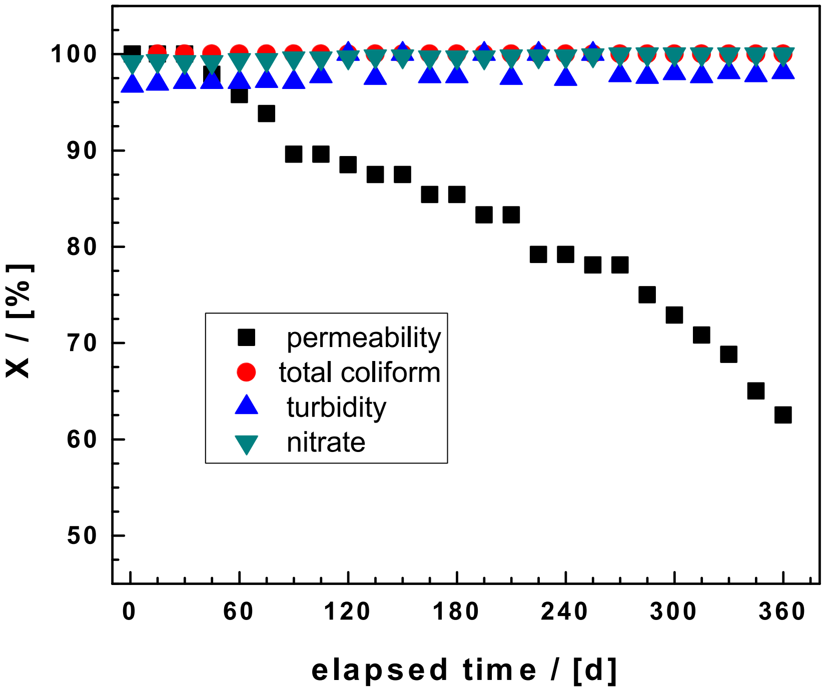


Figure 9: Permeability loss (percent) of the filter material and efficiencies of the removal of fecal coliform, turbidity, and nitrate (percent) in the effluent water over the length of filter run for the experiment with 10% Fe^0 SW (vol/vol). Experimental conditions: 300 g SW at 26 ± 2 °C; filling material: Sand; column length: 100 cm, column diameter: 20 cm. The system was fed by natural well water polluted by fecal coliform.

4.9.1.3 Nitrate removal

Table 4 (row 6) lists the results of NO_3^- concentration in the outlet water over time. The corresponding percent removal is presented in Figure 9. The average influent NO_3^- concentration was 23.5 mg L^{-1}. Compared to the results of George and Ahammed (2019), it is clear that NO_3^- removal mainly occurs in the Fe^0 SW column. In fact, the authors spiked their influent solution with 26.0 mg L^{-1} NO_3^- and observed NO_3^- removal in all the three systems. The conventional BSF showed the lowest NO_3^- removal. The NO_3^- removal in BSF is well-documented, but the removal is never quantitative (Nakhla and Faroow 2003, Murphy et al.

2010). Thus, although the influent water used herein was not additionally spiked by NO_3^- (Table 2), its removal was quantitative and occurred presumably in the Fe^0 SW column (Westerhoff and James 2003).

The mechanism of NO_3^- removal is complex and implies microbiological process in the BSF units (George and Ahammed 2019, Murphy et al. 2010) and both abiotic and biotic processes in the Fe^0 SW unit (Westerhoff and James 2003, George and Ahammed 2019).

4.9.1.4 pH value and iron breakthrough

Table 4 lists the pH values (row 2) in the system's effluent. No iron breakthrough was observed. The iron concentration was constant below the detection limit of 0.2 mg L^{-1}. The pH value progressively increased within the operational time and reached 8.5 at the end of the experiments. The iron concentration was monitored to check whether any breakthrough occurred. The results showed that the second BSF quantitatively fixed iron for the whole duration of the experiment. Systems without scavenging BSF contain higher iron concentrations (Westerhoff and James 2003, Heimann et al. 2018). For example, Westerhoff and James (2003) reported on up to 6 mg L^{-1} Fe in their effluent solutions. The very low iron concentration recorded herein is also in agreement with the pH dependent solubility of Fe hydroxides (Liu and Millero 1999) as discussed for the "Fe^0 remediation" literature by Ghauch (2015). The fact that no iron breakthrough is observed herein suggests that the amount of iron (mainly Fe^{2+}) escaping column 2 could not saturate the amount of sand in the second BSF. Fe^{2+} is adsorbed onto sand by pure electrostatic interactions (Btatkeu-K et al. (2014a and 2014b)).

4.9.1.5 Removal of coliforms

Table 4 (row 4) and Figure 9 show a very pronounced reduction in total coliform concentration over the whole operation time: There was a quantitative coliform removal already at the beginning of the experiment (E > 99.99%), and this trend kept through to the end (one year). This is due to three synergy processes: (i) formation of the biofilm in BSF, (ii) in situ generation of iron corrosion products (FeCPs), and (iii) reduction of the flow rate. As discussed in Section 4.9.1.1, accumulation of FeCPs reduces the porosity and the permeability, what improves coliform removal through adsorption (Bradley et al. 2011, Noubactep et al. 2012). It is essential to recall that the intrinsic bacterial inactivation capacity of Fe^0 was already reported in the 19th century (Bischof (1873,1877,1878), Notter (1878), Hatton (1881), Bache (1891), Tweeddale (1898), Baker (1934), and Leffmann(1991)) and has been independently demonstrated in the recent "Fe^0 remediation" research (Bojic et al. 2001, Lee et al. 2008, Diao and Yao (2009), Crampon et al. 2019, Hu et al. 2019, Sun et al. 2019). In the 19th century, quantitative pathogen removal in Fe^0 filters was demonstrated before the nature of individual bacteria was established. On the contrary, current research efforts are trying to demonstrate the efficiency of Fe^0 filters for pathogen removal on a case-by-case basis (You et al. 2005, Ingram et al. 2011, Shi et al. 2012, Marik et al. 2019).

4.9.2 Discussion

Previous studies testing contaminant removal from water by using Fe^0-based column household water filters are numerous (Naseri et al. 2017). They were mostly designed to test diverse Fe^0 specimens for the removal of selected contaminants (George and Ahammed 2019) and/or to compare the efficiency of Fe^0 filters to that of other systems, including BSFs (Noubactep et al. 2012). In a recent review, Hu and Noubactep (2019c) compiled available results to demonstrate the suitability of Fe^0 filters for water treatment. However, results from independent research are difficult to compare to each other. This section illustrates this difficulty based on selected references on the removal of pathogens from water. The six selected publications (Table 6) were not only focused on pathogen removal, they were selected to reflect the large diversity of experimental designs. The focus is not on achieved results but on operational conditions. They determine the results, but are rarely considered while discussing achieved results (Naseri et al. 2017).

Six operational parameters were selected for this discussion: (i) the column dimensions (D and L), (ii) the Fe^0/sand ratio, (iii) the initial flow velocity (F_0), (iv) the experimental duration (t), (v) the Fe^0 type, and (vi) the used Fe^0 mass. Only Fe^0/sand ratio and the Fe^0 type were specified by all six publications. The used volumetric Fe^0 ratio varied between 10% and 50%, while Fe^0 SW and granular materials were used. Concerning the column dimensions, small-scale columns and columns pertinent to pilot-scale tests were used while the flow velocities differed by more than three orders of magnitude. Lastly, 0.15 to 23 kg of Fe^0 materials were used for operational duration varying from 10 to 365 days. There is no scientific basis to compare results from such experiments, particularly because the kinetics of iron corrosion are never linear, and the systems are dynamic in nature (Hu and Noubactep 2019c).

Table 5 compiles some results of six selected peer- reviewed articles with column experiments for the removal of biological contamination including column dimension (length and diameter), the Fe^0 to sand ratio, the initial flow velocity (φ_0), the experimental duration (t), Fe^0 type, and the used Fe^0 mass it is seen that one paper has not explicitly given the experimental duration. Shi et al. (2012) used the number of pore volumes in their discussion. Two papers tested periods exceeding four months (120 days). In general, there is a large variability of the considered operational parameters. * is given in weight/weight; ‘n.s.’ stands for not specified and ‘non SI’ for units given in a not known system, for example ‘2″ x 2′ PVC plain-end-pipe’.

Table 5: Summary of parameters of column experiments for the removal of biological contamination compared with data from six selected peer-reviewed articles.

L	**D**	**Fe^0 to sand**	**Φ_0**	**t**	**Fe^0 type**	**m_{iron}**	**Reference**
(cm)	(cm)	(vol/vol)	(L h^{-1})	(days)		(kg)	
10	3.8	50/50	0.06	10	granular	0.15	You et al. 2005
20	n.s.	10/90	0.03	300	SW	0.26	Bradley et al. 2011
0.77	0.14	50/50*	n.s.	15	granular	23.0	Ingram et al. 2011
10	3.8	50/50	4.38	n.s.	granular	n.s.	Shi et al. 2012
non SI	non SI	35/65	222	154	granular	n.s.	Marik et al. 2019
n.s.	n.s.	n.s.	n.s.	120	granular	7.5	George et al. 2019
100	20	10/90	20.4	365	SW	0.30	This study

* is given in weight/weight; ”n.s.” stands for not specified and ”non SI” for units given in a not known system, for example “2″ × 2 PVC plain-end pipe”.

Table 5 additionally shows a general weakness of the research projects undertaken to date: the long-term efficiency of Fe^0 systems for water treatment has not been investigated. Experiments designed for more than three months are rare. The time span of most tests is rather counter-intuitive in a context where long-term monitoring data is urgently needed (Hu and Noubactep 2019c, Hu et al. 2019).

4.9.3 Significance of the Results

Fe^0 materials have demonstrated their suitability for the design and dissemination of affordable, efficient, and sustainable safe drinking water provision systems over the past 170 years (Devonshire 1890, Tucker 1892, Lauderdale and Emmons 1951, Hussam 2009, Banerji and Chaudhari 2017). For the most recent success stories in decentralized systems, Hussam (2009) used a proprietary material and Banerji and Chaudhari (2017) used affordable iron nails. Progress in the large-scale realization of these and similar devices has been highly impeded by the lack of easy transferable designs. Using universally available steel wool (Fe^0 SW) in this study was a step toward achieving a universal access to safe drinking water (Noubactep et al. 2009, Ndé-Tchoupé et al. 2015, Tepong-Tsindé et al. 2015a, Nanseu-Njiki et al. 2019, Ndé-Tchoupé 2019, Yang et al. 2020).

Based on a concept presented by Noubactep et al. (2009) and a mathematical model reasonably predicting optimal Fe^0/sand ratio for a sustainable filter (Caré et al. 2013, Domga et al. 2015), the present work has tested a volumetric Fe^0/sand ratio of 10:90 (300 g Fe^0 SW plus 14,200 g coarse sand) and obtained a filter that is able to treat well water polluted with pathogens for one year while depicting a permeability loss of only 41.5 %. After one year the system was still capable of producing 200 L water per day, with an acceptable flow velocity (8.33 L h^{-1}). This amount is far above the water needs of an average family. Assuming that each person needs 8 L water per day for drinking and cooking, the designed filter can supply 25 people with safe drinking water, whether they are living in a small village, an urban slum, or a modern city. The filter is relatively easy in design. The most challenging task is to homogeneously build up the reactive zone consisting of Fe^0 SW and sand. A dry packing approach in small lots was adopted. For future works, however, a wet packing approach as suggested by Sleiman et al. (2016) should be tested. These authors pre-wetted the Fe^0/sand mixture to facilitate homogeneous Fe^0 distribution in the column material.

The most important result here is that a column containing 10% vol.% of Fe^0 SW and 90 vol.% of sand corresponding to just 2 wt.% of Fe^0 and fed with a turbid natural water was still permeable after one year of operation. This result might not be reproduced by another Fe^0 SW or a different water source, but the Fe^0 /sand ratio can be further decreased (and the column length increased) until a satisfactory balance is identified for each specific case. Sleiman et al. (2016) used just 1% of Fe^0 in their systems while Erickson et al. (2017) hardly used more than 5% (w/w). Clearly, there is room for adjusting the operational conditions to any site-specific situation. Where necessary, additional units made of affordable materials should be added to remove contaminants that are not well addressed by Fe^0/H_2O systems such as some radioactive substances or fluoride (Lauderdale and Emmons 1951, Gwenzi et al. 2017).

5 General discussion

5.1 Significance of the results

The present work is a continuation of an effort started some twelve years ago with the aim to make Fe^0 filters a universal solution for safe drinking water provision (Noubactep and Woafo 2008, Noubactep et al. 2009, Noubactep and Schöner 2010a). One initial goal was to design a household filter which can operate for at least six months without any maintenance (Noubactep et al. 2009). The concept was rooted on experimental evidence achieved in the framework of the development of Fe^0-based permeable reactive barriers for ground water remediation (O´Hannesin and Gillham 1998, Richardson and Nicklow 2002, Henderson and Demond 2007) where Fe^0 used as filter material can quantitatively remove biological and chemical contaminants from polluted waters.

An initial survey of the literature revealed that Fe^0 household filters have been often tested for arsenic removal (Khan et al. 2000, Ngai et al. 2006, Hussam and Munir 2007, Ngai et al. 2007). Reviewing the existing literature, it was observed that Fe^0 filters designed for As removal eliminate beside arsenic up to 24 other contaminants including inorganic and organic components as well as pathogens (Tuladhar and Smith 2009). This observation was in tune with several previous works which have tested Fe^0 for water treatment on a contaminant by contaminant basis (Bojic et al. 2001, Richardson and Nicklow 2002, Bojic et al. 2004, Purenovic et al. 2004, Bojic et al. 2007, Bojic et al. 2009). In particular, Bojic et al. (2001, 2004, 2007, 2009) clearly demonstrated that heavy metals, halogenated carbons and pathogens are removed by flocculation or coagulation in the vicinity of the Fe^0 surface. This view is indeed known to scientists since the 1850s (Bischof 1873, Tucker 1892, Baker 1934, van Craenenbroeck 1998, Mwakabona et al. 2017, Antia 2020, Cao et al. 2020). Clearly, the corrosion products of Fe^0 are contaminant scavengers but the kinetics of iron corrosion is not a linear function of time, but rather depends on a myriad of operational parameters including the Fe^0 intrinsic reactivity, temperature, and water chemistry (Cao et al. 2020, Ogata et al. 2020, Müller et al. 2020, Yang et al. 2020, Lanet et al. 2021, Yang et al. 2021). Moreover, iron corrosion is a volumetric expansive process (Whitney 1903, Pilling and Bedworth 1923).

The next question to answer was which species shall be used to test Fe^0 filters? An operational indicator was one needed. Methylene blue (MB) was identified as a tracer to characterize the reactivity of Fe^0/H_2O systems (Miyajima 2012, Miyajima and Noubactep 2013). Mitchell et al. (1955) in their historical work already demonstrated the suitability of MB for this aim by showing that sand is an excellent adsorbent for MB but iron oxide-coated sand has practically no adsorptive affinity to MB. In order words, by rationally selecting the amount of Fe^0 and sand in a system, it is possible to reconstruct the extent of sand coating by in-situ generated iron corrosion products (Xiao et al. 2020, Yang et al. 2021). The extent of porosity loss and the related permeability loss can also be evaluated (Njaramba et al. 2021, Yang et al. 2021). Permeability loss is due to initial pore space saturation as a result of the expansion of in-situ generated iron corrosion products which rapidly occurs under conditions accelerating the corrosion process (e.g. presence of chloride ions) (Zhao et al. 2011, Stefanoni et al. 2018).

5.1.1 The validation of the MB discoloration method

This thesis has particularly validated the suitability of MB to characterize the effects of chloride ions on the efficiency of Fe^0/H_2O systems for contaminant removal. In presence of chloride ions, aqueous iron corrosion is accelerated rendering Fe corrosion products abundantly available in the system. MB was observed to be weakly adsorbed onto the positively charged in-situ generated iron oxides (partly in-situ coated on sand). This confirms the ion-selective nature of Fe^0/H_2O systems reported by Phukan et al. (2015). Previous studies tested Fe^0 as removing agent for dyes mostly in wastewater treatment (Miyajima and Noubactep 2013 and ref. cited therein). In successfully testing dyes in general and MB in particular as operative indicators for the characterization of Fe^0-based systems, the practicability and cost-efficiency of experimental device using dyes in general (Noubactep 2009, Phukan et al. 2015) is made available for the investigation of various aspects relevant for the design of Fe^0 filters. This aspect is important for scientific research under financially less favorable conditions (e.g. developing countries) (Cao et al. 2021a, 2021b, 2021c).

The MB method has for instance already been used to investigate the impact of the Fe^0/sand ratio on the durability of Fe^0 filters (Miyajima 2012, Miyajima and Noubactep 2013). Results confirmed theoretical predictions that no pure Fe^0 filter is sustainable and that the volumetric Fe^0 proportion should not exceed 51 %. Many field applications have fortuitously used similar Fe^0 ratios. However, the objective in using sand as admixing agent was to save iron costs (Mackenzie et al. 1999, Westerhoff and James 2003, Kaplan and Gilmore 2004, Bi et al. 2009). In other words, the MB method has demonstrated that admixing Fe^0 with inert (e.g. pumice, sand) or reactive materials (e.g. MnO_2) is a prerequisite for durable systems (Ullah et al. 2020, Njaramba et al. 2021). The next question to answer is: Why are sustainable household filters not been yet designed?

5.1.2 Reasons for existing designs failure

The reasons for the failure of existing designs are numerous as summarized by Noubactep et al. (2012). Beside inappropriate Fe^0/sand ratios, the use of very different types of Fe^0 materials was regarded as the main cause of lack of transferable results. This situation is exacerbated by experiments lasting for just some few weeks or months while there is a large uncertainty on the long-term corrosion rate (Moraci et al. 2016, Noubactep 2016, Naseri et al. 2017, Yang et al. 2020, Yang et al. 2021). The present work has successfully tested steel wool, a readily available Fe^0 material for an experimental duration of 12 months. There are seven (7) grad of steel wool (Lufingo et al. 2019, Hildebrant et al. 2020) of which grade 000 (extra fine - d1 = 25 μm) was successfully tested for pathogen removal until material depletion after some 8 months (Bradley et al. 2011). The grade of Fe^0 SW (fine) tested herein corresponds to twice larger filaments (fine - d_2 = 50 μm) than those tested by Bradley et al. (2011) and could clean polluted water for one year without material exhaustion.

5.2 Improving household Fe^0-based filters design

The results of this study suggest that an effective and sustainable household Fe^0-based filter for a large family (e.g. ≥ 10 people) in the developing world should comprise: (i) at least one polyethylene tank (≥ 1 000 L) installed beside the water treatment plant for raw water storage; (ii) a slow sand filter (SSF) for pre-filtration (e.g. for the removal solid matters); (iii) a Fe^0/sand filter (which is the unit in which the reactive filtration effectively takes place), eventually (iv) SSF for the removal of Fe escaping from the Fe^0/sand filter; and finally (vi) a polyethylene tank to collect and store the produced drinking water. The number of filters in series depends on the extent of the raw water contamination and the required quality of potable water (Notter 1878, Naseri et al. 2017, Yang et el. 2020. Huang et al. 2021b, Nya et al. 2021).

5.2.1 Considerations for efficient household Fe^0-based on-site filters

A minimum of six variables including Fe^0 intrinsic reactivity, Fe^0 shape and size, Fe^0 content (amount and proportion), solution pH, and the redox potential have been demonstrated to have an important impact on the decontamination efficiency of Fe^0/sand filters (Tepong-Tsindé et al. 2015, Ndé-Tchoupé et al. 2015, Naseri et al. 2017, Huang et al. 2021b, Nya et al. 2021). This makes comparisons and correlation of available data difficult. However, a profound analysis of the fundamental reactions involved in the present work, together with some recently obtained design criteria (Noubactep 2012, Nde-Tchoupé et al. 2015, Naseri et al. 2017), have brought out a number of important considerations which may simplify design efforts. They can be summarized as (i) use only volumetric Fe^0 ratios ≤ 50%; (ii) characterize the intrinsic reactivity of used Fe^0; (iii) use as little Fe^0 as necessary for reliable observations; and (iv) avoid too short experimental times. Testing Fe^0 materials at pilot scale can be summarized in the following: (i) test several well-characterized Fe^0 materials; (ii) test several Fe^0/sand ratios ($Fe^0 < 50\%$), for a given Fe^0 material and a Fe^0/sand ratio; (iii) test the number of each unit for satisfactory water treatment; (iv) insert wood charcoal units before Fe^0/sand units; (v) partly or totally replace sand by porous materials including: anthracite, gravel, MnO2 and pumice.

5.2.2 Containment

The household Fe^0-based filter designed and presented herein is an open architecture which could be constructed, modified, adapted, and improved on a site-specific basis. Filters containers can be locally built, for example from stackable prefabricated concrete rings commonly used for tank construction. Commercially available plastic tanks can be also modified and used. Appropriately skilled masons can construct custom ferro-cement tanks. In this case the dimensions should enable facile filling of filter media and routine maintenance including the removal/replacement of all materials. Some cover material (lid) should be used to exclude sunlight and inhibit the growth of photosynthetic microorganisms (algae, cyanobacteria) in the system. Tank tops should be wrapped in fine mesh screening to prevent entrance of insects, bird droppings, leaves, and bits of debris, etc. into the system.

5.3 Designing functioning Fe^0-based filters

This thesis, was initiated to enable the design of Fe^0 filters able at operating for 12 months without clogging nor material depletion. This objective was largely achieved: (i) a filter with a 1:1 volumetric Fe^0:sand ratio clogged after six months, while (ii) a second filter with a 1:9 volumetric Fe^0:sand ratio was still permeable after 12 months. To the best of the author’s knowledge, this is the first study based on the science (Hu et al. 2019) of the system that has lasted for 12 months. Comparable studies have just lasted for some few months (George and Ahammed 2019, Njaramba et al. 2021) and are certainly of low operational value as clogging is very rapid once it starts (Westerhoff and James 2003). In other words, this work presents a prototype for a functioning household filter, provided the raw water is of comparable quality (e.g. E coli level, NO_3^- level, pH value). This prototype can be adapted to the treatment of more or less contaminated waters. A viable prototype for Fe^0 filters using steel wool is presented.

The tested 1:9 volumetric Fe^0:sand ratio can be also optimized for wastewater treatment and community-scale drinking water systems. Erickson et al. (2012) and Wakatsuki et al. (1993) used far lower Fe^0:sand ratios (< 5 %) in this Fe^0-based filters for wastewater treatment.

The other issue successfully addressed in this thesis is the mechanism of NO_3^- removal by Fe^0. While active researchers are still reporting on "NO_3^- removal by reducing Fe^0" (Khalil et al. 2018, Liu and Wang 2019. Kodikara et al. 2020, Villen-Guzman et al. 2020), the results of this work clearly demonstrate that the amount of removed NO_3^- is far larger than the Fe^0 amount initially available in the system. In fact, during the 12 months 204 g of NO_3^- were removed, which would have necessitated 1102 g of Fe^0. However, the total amount of Fe available was 300 g.

In fact, NO_3^- is reduced by Fe^{2+} from Fe^0 oxidative dissolution. The oxidation of Fe^{2+} to Fe^{3+} releases one mole of electrons (Eq. 5.3-1) while the oxidation of one mole of N_2 to NO_3^- releases 10 electrons (Eq. 5.3-2). Eq. 5.3-3 gives the balance for the reduction of NO_3^- by Fe^{2+} (from Fe^0).

$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^- \qquad (5.3\text{-}1)$$

$$2\ NO_3^- + 10\ e^- + 12\ H^+ \Leftrightarrow N_2 + 6\ H_2O \qquad (5.3\text{-}2)$$

$$10\ Fe^{2+} + 2NO_3^- + 12\ H^+ \Rightarrow 10\ Fe^{3+} + N_2 + 6\ H_2O \qquad (5.3\text{-}3)$$

In this study, N_2 was not quantified; it is just assumed that the reduction of NO_3^- (to N_2) is quantitative. From a pure kinetic perspective, it is even not likely that this reaction can be quantitative but discussing this issue is over the scope of this work. It suffices to elegantly exclude abiotic reduction by Fe^0 as relevant reaction mechanism. These results clearly showed that NO_3^- microbial degradation occurred in the system and was event very significant. The importance of microbial activity in Fe^0 filters corroborates the view that the long-term permeability is the main issue of Fe^0-based filters (Naseri et al. 2017, Noubactep 2021a, Njaramba et al. 2021, Huang et al. 2021b, Yang et al. 2021, Noubactep 2022).

The results achieved in this work (Tepong-Tsindé et al. 2019) have inspired the further development of the concept that Fe^0 can be the cornerstone in global efforts for universal access to safe drinking water (Noubactep 2010, 2011). On the one hand, it is confirmed that a key issue to design functioning Fe^0 filters is to spatially disperse reactive Fe^0 materials in a matrix of a non-expansive aggregate (e.g. sand) (Caré et al. 2013, Domga et al. 2015). In this this regard, this work and related ones have recalled that steel wool is not an homogeny class of Fe^0 materials (Lufingo et al. 2019). On the other hand, taking advantage of the modular multi-stage system for safe drinking water supply presented by Dr. Kearns (Kearns 2016, Huang et al. 2021b, Nya et al. 2021), Fe^0 units can be simply replaced upon material depletion or bed clogging. In other words, despite the absence of reliable data on the long-term corrosion kinetics, functioning Fe^0 filters can be designed and used. All is needed is to train user for maintenance, including the frequency of replacement. Clearly, unlike for subsurface permeable reactive barriers which need Fe^0 materials able at reacting for the long term (decades) without maintenance, Fe^0 based water filters can be designed to operate even for three months. In this regard, for the same polluted water, it can be expected that units with the material used herein are replaced twice less frequently than units using the Fe^0 SW from Bradley et al. (2011). This simple idea makes Fe^0 filters probably the best design capable at enabling universal access to safe drinking water by 2030 (Naseri et al. 2017, Noubactep 2018, Yang et al. 2020, Huang et al. 2021b, Nya et al. 2021). In fact, the technical expertise is available since 1881 (140 years). All what is needed are systematic, and well monitored pilot-scale investigations with well-characterized Fe^0-materials.

6 General conclusions

This dissertation provides novel insights into the dynamics of metallic iron (Fe^0) depletion in filtration systems. There is a 160-years-old technical expertise on using Fe^0 water filters for households (Antia 2020, Cao et al. 2020, Cao et al. 2021d). Fe^0 water filters are affordable and easy to implement. However, designing new filters is fraught by the evidence that past research has not properly considered the sustainability as resulting from the intrinsic characteristics of Fe^0 materials, in particular, the time-dependent and non-linear decrease of the corrosion kinetics. Taking steel wool (Fe^0 SW) as an example, several dozens of articles have presented Fe^0 SW as a good reactive material for water treatment without even specifying the used grade (Ndé-Tchoupé et al. 2015, Lufingo et al. 2019, Ndé-Tchoupé et al. 2019). In other words, the Fe^0 filtration technology has been developed with little attention to its sustainability, which is indeed a pivotal factor in the implementation of any real applications. Clearly, despite plentiful availability of data, the emerging technology of Fe^0 filters cannot be quantitatively assessed due to inhomogeneity of operational conditions, including the used Fe^0/sand ratio and the experimental duration. As far as the experimental duration is concerned, only Bradley et al. (2011) have tested a Fe^0 SW ($d = 25$ µm) for ten months and realized a material depletion after eight months. A coarser Fe^0 SW ($d = 50$ µm) is tested herein for 12 months.

This work describes conditions for a water filter design and includes the results from a pilot study of a household filter in Douala (Cameroon). The presented Fe^0-based filter is an innovation that combines two proven water treatment techniques: (i) removal of microbes by biological sand filtration (BSF) process and (ii) contaminant adsorption and co-precipitation with iron oxide-hydroxides. The BSF, preceding the Fe^0/sand layer, additionally contributed to lower the O_2 level, thus sustaining the functionality of the filter overall. The designed Fe^0 SW filter containing 10 vol.% of Fe^0 is affordable and applicable for the water conditions generally encountered in scattered villages and pre-urban areas in developing countries. This technology is easily adaptable to many kinds of off-site treatment situations, including farms, health centers, hotels, restaurants, and rural schools. Beside Fe^0, no chemicals must be used, therefore maintenance is easy.

The results indicate a clear advancement in designing Fe^0-based household water units by rationally combining BSF and Fe^0/sand filters (Ullah et al. 2020, Yang et al. 2020). By using a comparable volumetric Fe^0/SW ratio but a different Fe^0 SW grade than Bradley et al. (2011), a system still depicting acceptable permeability after one year was obtained. The designed system was able to convert polluted well water containing nitrate, particles, and microbes into clean drinking water according to WHO standards. The results of this study suggest that Fe^0 SW filters are very affordable as only small amount of affordable SW (300 g) is required to provide each day 200 L of clean water over one year.

Considering that the duration of effective decontamination of Fe^0-based systems depends on both, the water composition and the nature of used Fe^0, the achieved results are only qualitative. The presented results call for further systematic research, which can start by duplicating the experiments reported herein with the seven grades of Fe^0 SW from the same supplier. Another field for future research is the characterization of the effects of typical water constituents on the efficiency of Fe^0 SW filters to eliminate pollutants. Relevant parameters include the presence of Cl^-, HCO_3^-, humic substances, PO_4^{3-}, and SO_4^{2-}. Filter containers can be locally designed and constructed.

Providing a chemistry- and electricity-free filter barrier against waterborne diseases by contaminants based on SW filtration appears possible for hundreds of millions of people. Up scaling the presented design for larger communities is one of the next steps. There is a real chance to achieve the US SDGs by implementing Fe^0 filters everywhere (Nanseu-Njiki et al. 2019, Yang et al. 2020, Huang et al. 2021b). Strategies for the rapid dissemination of such household and small community Fe^0-based filter designs have already been developed and presented in the literature (Ngai et al. 2007; Banerji and Chaudhari 2017).

7. Epilogue

The presented work corresponds to the original manuscript evaluated by two referees. Minor revisions were performed, strictly limited at improving Chapter 5 and actualizing bibliographic references. The major concern raised by the referees and during the defense was the lack of mass balance to support the mechanistic discussion. This concern is addressed in the revised version where it is demonstrated, that on a pure chemical perspective, at least 1000 g of Fe^0 is needed to achieve the reduction of the 204 g of nitrate observed in this work. Another concern, not addressed here, was the lack of duplicates (triplicates) for statistical considerations. The reason why this was not done is that the main operational parameter tested herein was the experimental duration. In fact, current and past experiments testing household filters have lasted just for some few weeks (Bradley et al. 2011, George and Ahammed 2019, Njaramba et al. 2021). Only Bradley et al. (2011) tested their filters for up to 10 months. Herein, two sets of conclusive experiments were performed for 6 and 12 months. Performing them in duplicates or triplicates would be better, however, there was also lack of funding for material and analysis. Having used steel wool like Bradley et al. (2011), this thesis is regarded as starting point for the design of Fe^0-based filters for decentralized safe drinking water provision.

The results of this work have inspired the actualization of the concept orginally presented in 2009 (Noubactep et al. 2009). This has let to a Special Issue at the MDPI-Journal Processes (www.mdpi.com/journal/processes) with 13 articles (Noubactep 2021). This special issue elucidates the applicability, benefits, constraints, effectiveness, and limitations of Fe^0 filters for safe drinking water provision. Tools to make rainwater a primary water source were also presented (Hussain et al. 2019, Guan et al. 2020) together with ways to transform existing centralized water management systems into decentralized ones (sectorization) (Vegas Niño et al. 2021).

Beside safe drinking water provision, research on Fe^0/sand filters for the treatment of agricultural drainage water and domestic and industrial wastewater will benefit from the results of this thesis (Chen et al, 2019, Konadu-Amoah et al. 2021, Li et al. 2021). In fact, in the past few years, a great body of results on testing Fe^0/aggregate filters have been published (Shearer et al. 2018, Kulkarni et al. 2019, Marik et al. 2019, Chopyk et al. 2019, Kim et al. 2020, Kim et al. 2021, Njaramba et al. 2021). Tested aggregates include pumice and sand. However, available results are not based on a holistic approach in investigating the complex Fe^0/sand systems (Hu et al. 2021b, Konadu-Amoah et al. 2021, Yang et al. 2021, Noubactep 2022). In particular, little attention has been paid to the Fe^0/aggregate ratio and the experimental duration (Konadu-Amoah et al. 2021, Yang et al. 2021, Noubactep 2022). For this reason, even the excellent work of Njaramba et al. (2021) is limited for the too short experimental duration (90 days or three months). The paramount importance of the experimental duration arises from the evidence, that the long-term kinetics of iron corrosion is not known (Stefanoni et al. 2018, Stefanoni et al. 2019, Yang et al. 2021, Noubactep 2022). It is hoped that science-based design of Fe^0-based filters presented herein will accelerated the design of efficient and sustainable systems for decentralized safe drinking water provision and wastewater treatment worldwide.

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Practical example of calculation and ideas concerning porosity loss and clogging by using steel wool filters.

Assumption, calculations, and results in this part of work imply that per volume of sand it takes such a maximum quantity of iron to avoid clogging.

Assumption:

100g Fe^0/sand mixture with 10 vol.% steel wool + 90 vol.% coarse sand

Fe concentration in the mixture: 2.07 wt.% = 2.07 g per 100g mixture

Calculations:

Full transformation of 2.07 g Fe^0 into ferrihydrite (assumed formula $Fe(OH)_3$): 2.07 * 1.9136 = 3.96 wt.%

This corresponds to 3.96 g ferrihydrite in 100 + (3.96 - 2.07) g = 101,89 g mixture

Density of ferrihydrite: 3.8 g/cm^3; 3.96 g ferrihydrite per 101,89 g mixture correspond to 3.96 / 3.8 = 1.042 cm^3

Density of Fe^0 (not as steel wool): 7.87 g/cm3; 2.07 g Fe^0 per 100 g mixture correspond to 2.07 / 7.87 = 0.263 cm^3

Result:

The volume of Fe^0 of 0.263 cm^3 increased to 1.042 cm^3 through complete oxidation into ferrihydrite. At the same time, the 10 vol.% of the steel wool space are vacated. This means, that altogether the pore space increased through the oxidation by nearly 9 vol.% (rough calculation with rounded numbers). In addition, we have a huge pore space between the sand grains of at maximum 26 % (value for closest packing of spheres/round grains with equal diameter).

Consequence:

Through the application of voluminous steel wool, as used in the manuscript, a clogging of the filters through oxidation of Fe^0 can never happen, even at very high steel wool concentrations. On the contrary, steel wool amended filters should get an increased porosity in the iron-containing section. Fig.10 illustrate a cake formed in the filter during the elapsed time of 1 year.

Picture of cake formed in the filter during the elapsed time of 1 year.

However, clogging could occur, if the formed ferrihydrite gels/nanoparticles would move up in the column and would accumulate in certain layers. Another explanation: under sub/anoxic conditions Fe^{2+} may migrate and accumulate in more oxidizing layers. The understanding of formation and transport behavior of the formed oxidized iron phase(s) is the key for understanding an eventual clogging.

Related articles:

This doctoral thesis is based on three appended papers. These papers are equally referred below by their Roman numerals and DOI. In general, six papers were published during this thesis in which I was either main author or co-author (not included in the online version):

1. **Tepong-Tsindé R.,** Ndé-Tchoupé A.I., Noubactep C., Nassi A., Ruppert H. (**2019**): Characterizing a newly designed steel-wool-based household filter for safe drinking water provision: Hydraulic conductivity and efficiency for pathogen removal. Processes 7, 966. DOI: 10.3390/pr7120966
2. **Tepong-Tsindé R.**, Phukan M., Nassi A., Noubactep C., Ruppert H. (**2015**): Validating the efficiency of the MB discoloration method for the characterization of Fe^0/H_2O systems using accelerated corrosion by chloride ions. Chemical Engineering Journal 279, 353–362. DOI: 10.1016/j.cej.2015.04.129
3. **Tepong-Tsindé R.**, Crane R., Noubactep C., Nassi A., Ruppert H. (**2015**): Fundamentals for designing sustainable metallic iron-based filters for water treatment. Water 7, 868–897. DOI: 10.3390/w7030868
4. Ebelle T.C., Makota S., **Tepong-Tsindé R.,** Nassi A., Noubactep C. (**2016**): Metallic iron and the dialogue of the deaf. Fresenius Environmental Bulletin 28(11A):8331-8340.
5. Makota S., Ndé-Tchoupé A.I., Mwakabona H.T., **Tepong-Tsindé R.,** Noubactep C., Nassi A., Njau K.N. (**2017**): Metallic iron for water treatment: leaving the valley of confusion. Appl Water Sci., DOI 10.1007/s13201-017-0601-x.
6. Arnaud Igor Ndé-Tchoupé*, **Raoul Tepong-Tsindé**, Mesia Lufingo, Zuleikha Pembe-Ali, Innocent Lugodisha, Risala Iddi Mureth, Mihayo Nkinda, Janeth Marwa, Willis Gwenzi*, Tulinave Burton Mwamila, Mohammad Azizur Rahman, Chicgoua Noubactep, Karoli N. Njau. (**2018**): White teeth and healthy skeletons for all: The path to universal fluoride-free drinking water in Tanzania. Water 2018, 10, x; DOI: 10.3390/w11010131 www.mdpi.com/journal/water