A 'Smart' Approach on Fluoride Removal: Detection in Water Sources and Removal with Biomass

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Preface

Modern research on water defluoridation place more emphasis on the search of the best defluoridation materials. As such, challenges delaying the field application of the studied materials (some of which are low-cost and renewable) are often forgotten. In the world of limited resources this is of vital importance. This thesis presents the challenges related to application of plant biomass and iron-based materials for water defluoridation. It also covers the special chemical interactions between iron and fluoride materials with the aim of exploiting such interactions for fluoride detection. Defluoridation efficiency/capacity of the studied materials at non-optimised condition are also presented.

Presenting the challenges delaying application of the different plant- and iron-based materials may instil the desire (in researchers and water practitioners) to look back into the abandoned materials that showed best properties but presented serious challenges. This may in turn make the dream to provide low-cost fluoride remediation technologies for rural and resource deprived communities realisable. Additionally, the new properties of the materials revealed in this thesis may open doors to new research orientations.

The presentation of the text in this thesis is kept simple and direct. Where the methods are used, low-tech methods are preferred. Thence, the presented technologies/methods are expected to be practical to researchers in water defluoridation from a diverse audience. Therefore, this work may be consumable by both seasoned and beginner researchers in the field.

Abstract

Fluoride is one of the common minerals found in natural water, ingestion of which, at moderate concentration, is linked to good dental health. However, ingestion of higher concentrations of this mineral over a period is responsible for fluorosis, a disorder characterised by mottling of teeth and skeletal deformations. Therefore, the WHO sets the highest permissible level of this mineral in drinking water at 1.5 mg/L to limit its effect on public health. Consequently, a water source with fluoride concentration above this highest permissible level is regarded as unfit for human consumption, hence, requiring a treatment before consumption. As such, several studies have explored different low-cost methods to detect and remove this contaminant from drinking water. These include defluoridation and detection of fluoride by plant biomass and iron-based materials, respectively. These materials are attractive because they have a potential for providing efficacious and cost-effective methods to deal with this water contaminant. In this thesis, the challenges delaying their field application (in detection and removal) of fluoride are identified and suitable solutions are presented. Furthermore, the properties of iron that make it suitable for fluoride detection and removal enhancement in aqueous media are presented.

A critical review of the studies published over the past three decades on water defluoridation by non-activated biomass reveals that, most studies explore extensively only the defluoridation efficiency/capacity of these materials. This bias in studied properties is shown to be due to inadequacy in selection of study parameters, where, the defluoridation mechanisms are poorly studied. This could have resulted in the current poor understanding of their defluoridation mechanisms. Therefore, lessons from these studies were used to identify and propose the "must include" parameters to direct the future studies for better understanding of their defluoridation properties, especially, the defluoridation mechanisms. These are: effect of solution pH, point of zero charge and surface functional groups characterisation before and after material use.

For plant biomass ash, the major challenge associated with its application in water defluoridation was found to be related to media-induced contamination of the treated water, notorious being the elevation of the pH of the treated water. This challenge could have repelled many possible applications of this material in water treatment besides its great potentials as water treatment material. In this study, the *Cyperus* plants were successfully

used in adjusting the elevated pH of the ash-treated water, lowering and maintaining it at around 7.3.

For the Fe(III)-loaded biomass materials, the discrepancy in their defluoridation properties in aqueous media was found to be related to the differences in their respective preparation pathways. The inclusion or exclusion of the post-alkalisation procedure was found to influence both the defluoridation efficiency and mechanisms. The post-alkalised material was found to have higher fluoride removal in acidic conditions, mainly by electrostatic interactions. The higher fluoride removal efficiency of the non-alkalised material was found to be in neutral conditions, with ligand exchange as the main removal mechanism.

A study of the ancient application of metallic iron in water treatment show that Fe(III) ions and their hydr(oxides) are the predominant end products in aqueous media. The major contaminant removal processes by this material were found to be redox, coagulation and adsorption reactions. More laboratory experiments, revealed that, at low pH, these end products interact in a special way to enhance the fluoride removal efficiency of the Fe^0 and Fe(III)-loaded materials. This implies that application of metallic iron for water defluoridation could be greatly enhanced by spiking the water to be treated by Fe(III) ions.

The interactions between Fe^{3+} and F^- were found to be strong at low solution pH, at which a visible-to-eye discolouration of the $FeCl_3$ solution was observed. At this pH, the effect of the water molecules is likely suppressed by their protonation, hence, allowing discoloration to occur at an unusually low Fe:F mole ratio of 1:0.7. The higher detection limit of F^- (130 mg/L) by Fe(III) was shown to be due to poor spectrophotometric detection of $FeCl_3$ in aqueous media, where, the minimum detectable concentration was 250 mg/L of Fe^{3+}. Therefore, lowering the detectable concentration of Fe^{3+} was achieved by addition of excess ammonium thiocyanate solution. Ammonium thiocyanate was found to be capable of improving this detectability of $FeCl_3$ salt solution in aqueous media from 250 to 1 mg/L Fe^{3+}.

An Fe-F-SCN system was established as capable of detecting F^- at low levels in synthetic water. Since the performance of this system is greatly affected by co-ions, this study recommends that the F^- in natural water be pre-concentrated and extracted before analysis by this method. For this purpose, bone char and Fe(III)-loaded biomass were found to be unfit for the pre-concentration of fluoride, because of their richness in phosphate and Fe(III) ions, respectively, that caused unexpected discolouration and no discolouration of the extracted fluoride, respectively. This study recommends further that the mechanisms by which *Cyperus* plants buffer the pH of the ash-treated water, and Fe^{3+} enhances the fluoride removal efficiency of the Fe(III)-loaded materials be further studied and that suitable fluoride adsorbents for preconcentration of fluoride be sought for application with the Fe-F-SCN system.

LIST OF ABBREVIATIONS AND SYMBOLS

AP	Anderson's process
BP	Bischof's process
BSIF	Bischof's sponge iron filter
CW	Constructed wetland
F	Fluorine atom
F^-	Fluoride ion
Fe(II)	Iron in the oxidation state of 2
Fe(III)	Iron in the oxidation state of 3
Fe(III)-ASF	Fe(III)-Activated Sisal Fibres
Fe/H_2O system	Iron/water system
Fe^0	Zero valent iron
Fe^{2+}	An ion of iron in the oxidation state of 2
Fe^{3+}	An ion of iron in the oxidation state of 3
Fe-F-SCN system	Iron-fluoride-thiocyanate system
FT-IR Spectrometer	Fourier Transform Infrared Spectrometer
PA-Fe(III)-ASF	Post Alkalised-Fe(III)-Activated Sisal Fibres
POU treatment	Point of Use treatment
PZC	Point of Zero Charge
SCN^-	Thiocyanate ion
SF	Sand filters
SIF	Sponde iron filter
VFCW	Vertial flow constructed wetland
ZVI	Zero Valent Iron

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closely located water sources could have fluoride levels remarkably dissimilar. This phenomenon, together with the saturation limitations of the adsorption technologies, necessitates a "smart" approach on water defluoridation advocated by this project. In this approach, the fluoride levels in the water sources are monitored at the point of use for "smart" interventions. The ideal methods for fluoride monitoring and remediation in rural African settings, where point of use treatment is recommended would be low cost ones. In fact, the technology affordability stands as a major hindrance towards field deployment of the invented technologies in rural settings typical for the developing world. In this context, affordability is obviously related to the cost and availability of the adsorbent and detection materials used, respectively.

Interestingly, efforts of the fluoride research community have recently been directed towards exploring, developing and testing fluoride removal properties of the low cost materials (Manna et al., 2018a; Yadav et al., 2018). One orientation has been investigating the water defluoridation properties of the plant biomass materials (Nath and Dutta, 2015; Darchen et al., 2016; Yadav et al., 2018). These materials are preferable due to their ubiquitous availability, biodegradability and renewability. Thus, their fluoride removal properties are widely studied with the aim of providing low cost materials for water defluoridation in rural (resource-limited) communities.

In the past three decades, researchers have explored the defluoridation properties of the plant biomass materials in their activated and non-activated forms. However, their defluoridation properties are yet to be fully understood. For instance, Srimurali et al. (1998) studied the effect of contact time, solution pH and particle size on the fluoride removal properties of the nirmali seeds biomass. The fluoride removal efficiency of the non-activated biomass was found to be so low that it was not studied further, and the removal mechanism was not proposed.

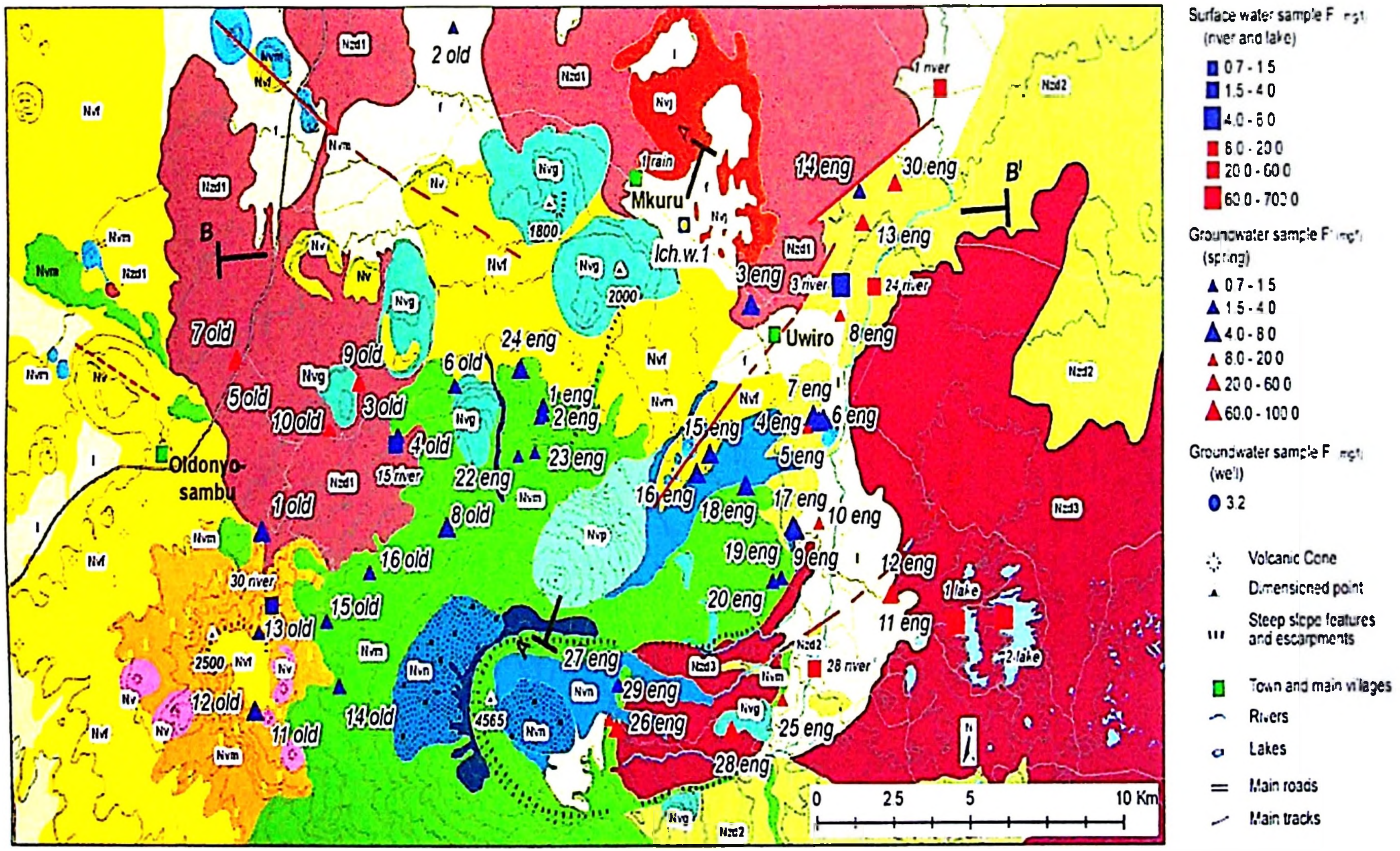

Fig. 1. 3. Map showing variation of fluoride concentrations in surface and groundwater in Northen Tanzania (Ghiglieri et al., 2010)

CHAPTER 1: General Introduction

Fluoride contamination in water sources is a global problem with over 200 million people vulnerable globally (Brunt et al., 2004; Fawell et al., 2006; Dahi, 2016). Almost all continents are affected with fluoride in some of their states at different levels. The most affected parts of the globe include South America, Africa and Asia (Fig. 1.1). In Africa, the problem is worse in the northern and eastern parts and along the rift valley.

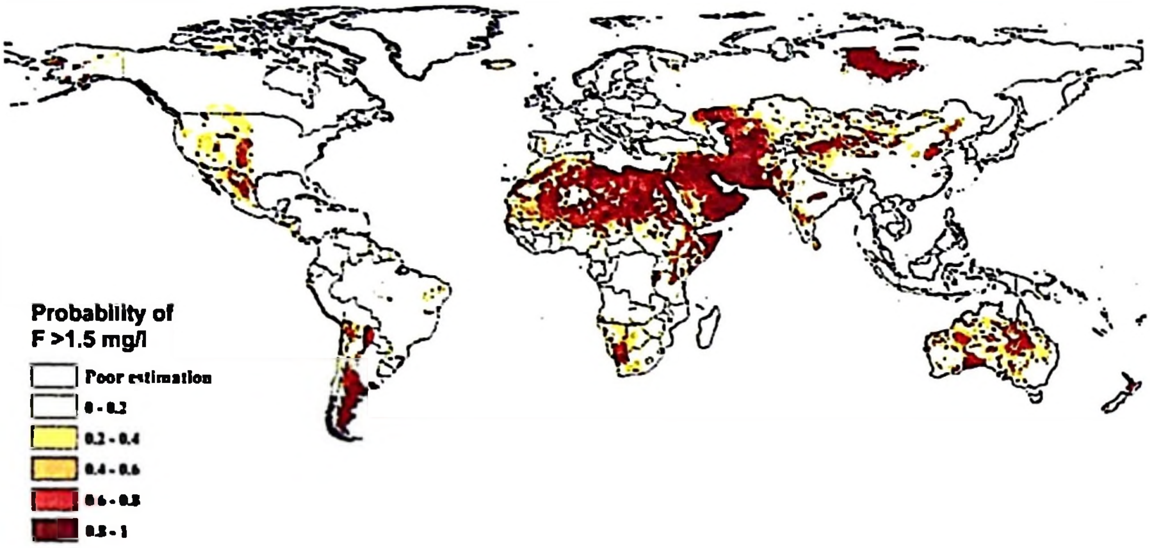

Fig. 1. 1. Map showing the global fluoride distribution in groundwater, coloured are areas rich in fluoride-containing minerals (taken from Brunt et al., 2004)

Although anthropogenic activities contribute to fluoride contamination of water sources, natural geological activities play a major role (Vengosh and Pankratov, 1998; Queste et al., 2001; Farooqi et al., 2007; Armienta and Segovia, 2008; Edmunds and Smedley, 2013). Thus, the presence of fluoride in natural water is mainly due to dissolution of fluoride ion from fluoride rich minerals such as granitic rocks (Saxena and Ahmed, 2001; Kim and Jeong, 2005). The anthropogenic sources, however, include domestic and industrial wastes and wastewater and fertilisers application (Vengosh and Pankratov, 1998; Farooqi et al., 2007).

Because of its chemistry, fluoride ion can react with bone materials and compounds of such metals as aluminium, magnesium, calcium, iron, lanthanum, zirconium and cerium. These properties render fluoride toxic when present in drinking water with its effect in the skeletal material (Fig. 1.2) and physiological processes in the body (Aasenden and Peebles, 1974; Grynpas, 1990; Vani and Reddy, 2000). These disorders are referred to as fluorosis and are common among the inhabitants in fluoride rich areas.

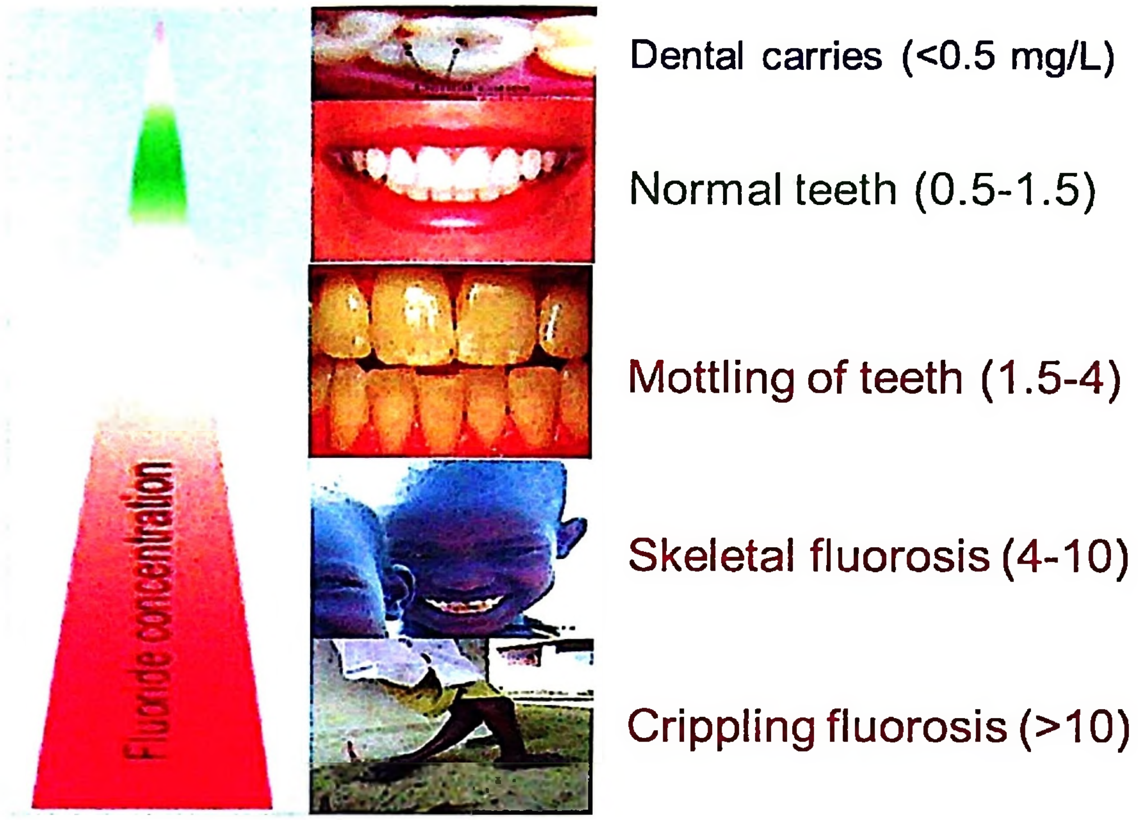

Fig. 1. 2. A schema showing the effects of different concentrations of fluoride in the dental and skeletal system. (modified extract from Mjengera and Mkongo (2003))

The wide natural spatial distributions of fluoride rich rocks in fluoride affected areas make alternative clean water sources a rare commodity (Brunt et al., 2004; Dahi, 2016) and the problem is expected to expand with population growth and increased demand for clean water. As such, water defluoridation (the process of adjusting fluoride concentration in the drinking water to acceptable levels) remains the only option for the affected communities to access fluoride free water in such areas (Fawell et al., 2006). This, therefore, has called for the unceasing search for defluoridation methods by researchers and water practitioners all over the world. These defluoridation methods can be broadly categorized as membrane technologies, adsorption and coagulation technologies (Jagtap et al., 2012). Of these, adsorption technologies have gained popularity especially in the developing world because of their easy operation and cost effectiveness (Bhatinagar et al., 2011; Habuda-Stanic et al., 2014; Yadav et al., 2018). Moreover, in the volcanic fluoride rich areas, such as along the east African rift valley, the fluoride rich rocks are unevenly distributed and the surface and groundwater fluoride concentrations variable across the area (Fig. 1.3). This implies that, two closely located water sources could have fluoride levels remarkably dissimilar. This phenomenon, together with the saturation limitations of the adsorption technologies, necessitates a "smart" approach on water defluoridation advocated by this project. In this approach, the fluoride levels in the water sources are monitored at the point of use for "smart" interventions. The ideal methods for fluoride monitoring and remediation in rural African settings, where point of use treatment is recommended would be low cost ones. In fact, the technology affordability stands as a major hindrance towards field deployment of the invented technologies in rural settings typical for the developing world. In this context, affordability is obviously related to the cost and availability of the adsorbent and detection materials used, respectively.

Interestingly, efforts of the fluoride research community have recently been directed towards exploring, developing and testing fluoride removal properties of the low cost materials (Manna et al., 2018a; Yadav et al., 2018). One orientation has been investigating the water defluoridation properties of the plant biomass materials (Nath and Dutta, 2015; Darchen et al., 2016; Yadav et al., 2018). These materials are preferable due to their ubiquitous availability, biodegradability and renewability. Thus, their fluoride removal properties are widely studied with the aim of providing low cost materials for water defluoridation in rural (resource-limited) communities.

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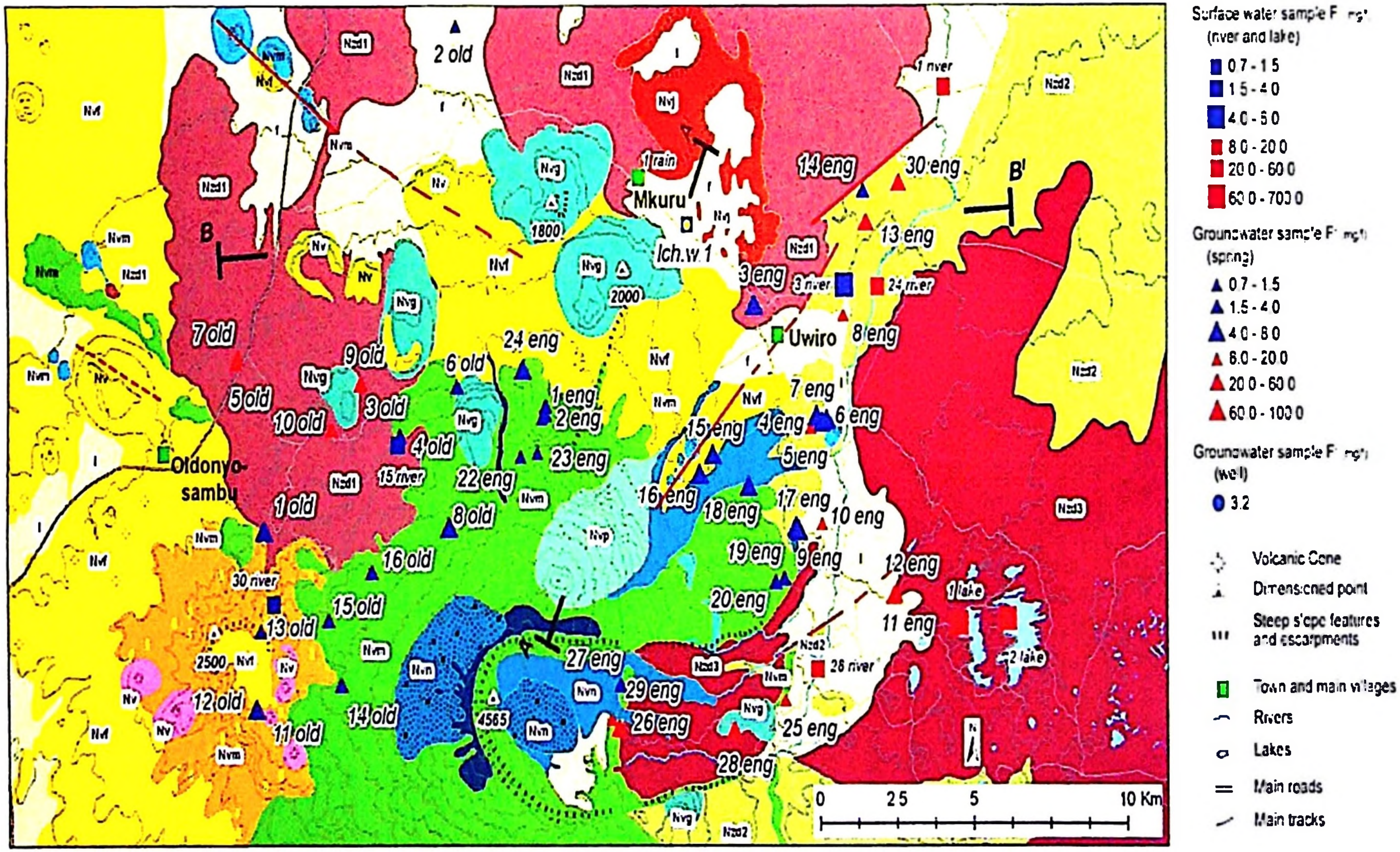

Fig. 1. 3. Map showing variation of fluoride concentrations in surface and groundwater in Northen Tanzania (Ghiglieri et al., 2010)

Murugan and Subramainan (2002, 2006) expanded these parameters to include particle size, surface characteristics, temperature, contact time, initial fluoride concentration, adsorbent dose, solution pH and point of zero charge when studying the water defluoridation properties of the Indian *Aloe vera* and Tamarind seed biomass materials. The fluoride removal mechanisms of both Aloe vera and Tamarind seed biomass in these studies were proposed based on the observations in the effect of solution pH on the fluoride removal efficiency and the point of zero charge values. The point of zero charge value was useful in predicting the surface charge of the biomass materials, hence, the possible interaction between the negatively charged fluoride ion and the charged biomass surface at a given solution pH.

Nevertheless, a later study by Kumar et al. (2012), which explored the effect of the solution pH, adsorbent dose, porosity, and initial fluoride concentration on the fluoride removal properties of Tamarind fruit cover proposed the fluoride removal mechanism of this biomass material using only the results from the effect of solution pH on the fluoride removal efficiency. This is flawed as the surface charge of the adsorbent and the possibility of electrostatic interactions between the charged ions in solution and the adsorbent surface can only be predicted when the point of zero charge of the adsorbent is determined. Further in time in a comparative study of the fluoride sorption properties of vetiver, tamarind seed, clove, neem, acacia, nutmeg and coffee husk biomass materials, the fluoride removal mechanisms were proposed on the basis of the effect of pH on the fluoride removal efficiency alone after studying the effect of solution pH, adsorbent dose, contact time, initial fluoride concentration, adsorbent particle size and surface characteristics (Harikumar et al., 2012), thence the flaw repeated.

Moreover, comparison of the defluoridation efficiency of the selected biomass materials was conducted at a solution pH 6 which was the optimal solution pH of only one of the selected biomass materials. Although some of the plant biomass materials are reported to have high fluoride removal efficiency at neutral conditions (Murugan and Subramanian, 2002; Murugan and Subramanian, 2006; Kumar et al., 2012) others have such low fluoride removal efficiency at neutral conditions that only their activated forms were further studied (Srimurali et al. 1998; Sinha et al., 2003; Parmar et al., 2006; Lakshminarayan et al., 2011). Interestingly, fluoride removal properties of the plant biomass materials are highly affected by solution pH (Murugan and Subramanian, 2006; Yadav et al., 2013; Patil et al., 2013; Khound and Bharali, 2018). Therefore, as revealed by distinct effects of the solution pH on the fluoride removal properties of the plant biomass materials, a comprehensive comparison of the defluoridation efficiencies of plant biomass materials would be pH sensitive (Murugan and Subramanian, 2006; Yadav et al., 2013; Patil et al., 2013; Khound and Bharali, 2018).

Studying the fluoride sorption properties of the Indian rosewood saw dust and wheat straw biomasses, Yadav et al. (2013) included solution pH, surface characteristics, adsorbent particle size, adsorbent dose, contact time, and initial fluoride concentration. The fluoride removal mechanism was proposed based on kinetic model studies. Sumalatha et al. (2014) studied the defluoridation properties of *Citrus limonium* fruit biomass by studying the effect of contact time, adsorbent dose, particle size and initial fluoride concentration parameters. The fluoride removal mechanism was not proposed. Mwakabona et al. (2014) investigated the effect of the contact time, adsorbent dose, initial fluoride concentration and solution pH to study the fluoride removal properties of the sisal pith, Aloe leaf, sisal fibre, banana pseudo-stem, goose grass and maize leaf biomass. The fluoride removal mechanism was proposed based on the effect of solution pH on the fluoride removal efficiency. This comparison of the fluoride removal efficiency at a single solution pH could be biased as different materials have different optimal solution pH and respond differently to variation in solution pH (Fig. 1.4). This contrasting trend could be observed in several other studies as further explained in Chapter 2.

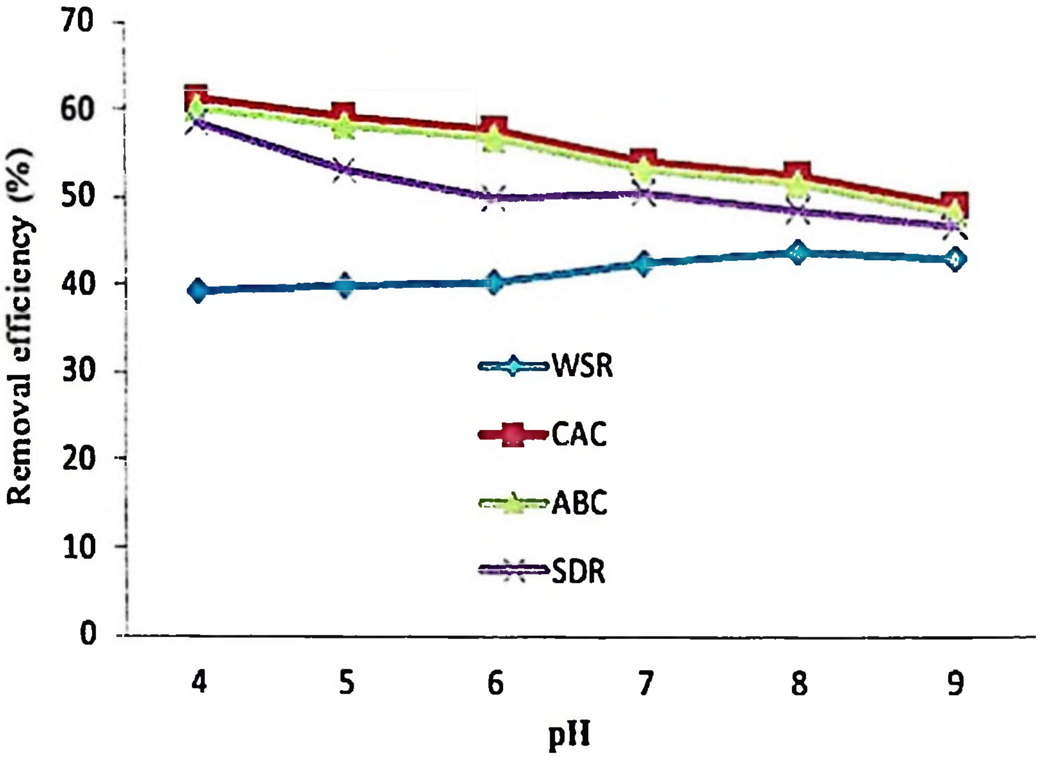

Fig. 1. 4. The effect of pH on fluoride removal efficiency of wheat straw (WSR), saw dust (SDR), bagasse activated carbon (ABC) and commercial activated carbon (CAC) biomasses (taken from Yadav et al., 2013)

Similarly, proposing the fluoride removal mechanism based on the effect of solution pH on the fluoride removal efficiency of the biomass alone could be misleading, thence, a flaw perpetuated. Interestingly, studying the water defluoridation properties of banana peel biomass, Mondal (2017) included point of zero charge (pzc) (the pH at which the charge at the adsorbent surface is zero), adsorbent pH, solution pH, initial fluoride concentration, contact time, adsorbent dose, co-ions, temperature, surface characteristics and FT-IR spectral shift. The fluoride removal mechanism was proposed on the basis of the effect of solution pH on the fluoride removal efficiency in light of the point of zero charge value and the FT-IR spectral shift readings. The added FT-IR spectral shift readings provided information on the possible active sites involved in fluoride adsorption, on the biomass surface. Similarly, Romar-Gasalla et al. (2017) included the point of zero charge, initial fluoride concentration, solution pH, dissolved organic carbon and co-ions in studying the water defluoridation properties of the wheat straw biomass. The fluoride removal mechanism was implied by relating the point of zero charge value of the adsorbent and the effect of solution pH on the fluoride removal efficiency. However, Keshtkar et al. (2019) included adsorbent point of zero charge, surface morphology, contact time, initial fluoride concentration and adsorbent dose to compare the fluoride removal properties of *Syzygium cumini* and *Prosopis cineraria* leaf biomass. The effect of varying solution pH was not studied. Therefore, the optimal solution pH for the two biomass materials was not studied thus, the grounds for selection of the comparison pH could be biased. The fluoride sorption mechanism was proposed on the basis of kinetics model studies and point of zero charge.

A careful scrutiny of these few selected studies reveals that most of them focus on fluoride removal efficiencies than mechanisms. The bias may have led to wrong conclusions drawn from incomplete information and comparisons. This in turn may have led to obscured focus in subsequent studies involving these materials and consequently poor understanding of their defluoridation properties, thence delayed actualisation of the technology. Therefore, a systematic presentation of defluoridation properties of different non-activated plant biomass materials studied in different conditions is needed. It is envisaged that this will help in identifying the key parameters for expanding our understanding on the fluoride removal mechanisms of the non-activated plant biomass materials and arrive at meaningful and correct conclusions.

In the activated forms, plant biomass materials are reported to have relatively higher fluoride removal efficiencies than in their non-activated forms (Bhatnagar et al., 2011; Manna et al., 2018b; Yadav et al., 2018). The common plant biomass activation methods (methods of improving the fluoride removal efficiency of the adsorbent/material) are heat and chemical activation (Darchen et al., 2016; John et al., 2018; Manna et al., 2018b). When plant biomass materials are heated in presence of limited supply of air/oxygen, activated carbon is produced. These materials' defluoridation properties are widely studied and presented in literature (Fawell et al., 2006; Yadav et al., 2013). Differently, in the presence of air/oxygen, heat produces biomass ash from plant biomass. From the cost point of view, biomass ash could be desirable for water defluoridation in rural areas of the developing countries, where cost stands as the major obstacle towards field application of most studied defluoridation technologies.

Therefore, efforts to study the suitability of this waste biomass ash are worthwhile for providing low cost fluoride adsorbent materials for rural Africa. The high defluoridation efficiency of the biomass ash material is attributable to its modified chemical composition where the concentration of chemical species such as Ca and Mg, which have affinity for fluoride ions, is higher in the ash than in the precursor biomass (Nath and Dutta, 2015; Darchen et al., 2016). This concept has been studied and established over a long period (Chaturvedi *et al.*, 1990; Mondal et al., 2012; Vassilev et al., 2013; Darchen et al., 2016; Bibi et al., 2017a; Bibi et al., 2017b; Mondal et al., 2017). The studied ash materials include fly ash (Chaturvedi et al., 1990) from coal-based power plants, and plant biomass ash (Mondal et al., 2012; Nath and Dutta, 2015; Bibi et al., 2017b; Mondal, 2017). While fly ash from coal seems to have much more of the toxic contaminants, ash from plant materials appears to be promising (Dhadse et al., 2008; Vassilev et al., 2013; Nath and Dutta, 2015; Mondal, 2017). Findings from diverse studies on water defluoridation by plant biomass ash from different plant materials, prepared in controlled conditions have revealed their higher fluoride removal capabilities in aqueous media (Nath and Dutta, 2015; Darchen et al., 2016; Manna et al., 2018).

However, controlled conditions involved in preparation of heat activated biomass will likely affect the cost of the resulting units, thence decreased affordability. Interestingly, the chemical composition found in waste wood ash (Table 1.1) (Vassilev et al., 2013), which is produced from fireplaces in most households in rural areas of most African countries reveals a great potential for their application in water defluoridation. This is remarkable, but unexplored. This is likely due to the chemistry of this material in aqueous media, where it is expected to release its water soluble components into the treated water (Vassilev et al., 2013) and elevate the pH of the treated water (Nath and Dutta, 2015; Darchen et al., 2016). Thus, biomass ash from fireplaces in fluoride affected rural Africa is currently treated as a waste besides its great potential of being applied as fluoride adsorbent material. Therefore, a study is needed to elucidate the properties of plant biomass ash in aqueous media and capability of constructed wetland in adjusting the elevated pH in the treated water. It is envisaged that the constructed wetland will be capable of adjusting the elevated pH of the ash treated water by using its plant exudates.

Table 1. 1. The chemical composition of plant biomass ash from different plant materials extracted from Vassilev et al. (2013)

Ash source	% CaO	% MgO	% SiO_2	% K_2O	% Na_2O	% Al_2O_3	% P_2O_5	% Fe_2O_3	% SO_3
Woody biomass	43.03	6.07	22.2	10.75	2.85	5.09	3.48	3.44	2.78
Grasses	11.23	4.02	46.18	24.59	1.25	1.39	6.62	0.98	3.66
Agricultural waste	14.86	5.62	33.39	26.65	2.29	3.66	6.48	3.26	3.61
Animal biomass	49.04	2.75	2.90	7.67	3.50	1.69	28.17	0.35	3.91
Coal	6.57	1.83	54.06	1.60	0.82	23.18	0.50	6.85	3.54

Chemical activation of the plant biomass comprises the impregnation of the biomass surface with chemical species that have higher and or selective affinity for fluoride (Paudyal et al., 2011; Singh et al., 2013; Manna et al., 2018a; Manna et al., 2018b; Yadav et al., 2018). Some of these metallic species employed for fluoride removal enhancement of the biomass materials are Ca, Al, La, Cr, Zr, Fe and Ce (Kamble et al., 2007; Wang et al., 2007; Paudyal et al., 2011; Darchen et al., 2016; Manna et al., 2018a; Yadav et al., 2018). Of these, Al, Fe and Ca are low cost materials. When used in activating the plant biomass, these materials modify the chemistry of the biomass surface, increasing its affinity and selectivity for fluoride ion to different extents. Since the field application of the chemically activated biomass materials will also be controlled by both the versatility and cost of the prepared adsorbent materials, it follows that these chemical species are promising low-cost activating materials with higher fluoride removal enhancement of the plant biomass materials at neutral conditions (Zhao et al., 2008; Paudyal et al., 2011; Cai et al., 2015; Zhang et al., 2015). The low toxicity and solubility in aqueous media of the Fe present it as a widely acceptable material for water treatment with its application dating back to the 19th century.

However, different Fe-loaded materials reported by defferent studies have contrasting defluoridation properties under varying solution pH conditions as shown in Fig. 1.5 and 1.6

(Zhao et al., 2008; Paudyal et al., 2011; Cai et al., 2015; Zhang et al., 2015). This could suggest that the method employed in loading the iron on the biomass surface has an influence on the resulting defluoridation properties. Since solution pH is one of the key parameters in adsorption processes, a study to understand the underlying causes for such contrasting defluoridation properties is important. Therefore, addressing this challenge will help in selection of efficient preparation methods and best defluoridation conditions for best results.

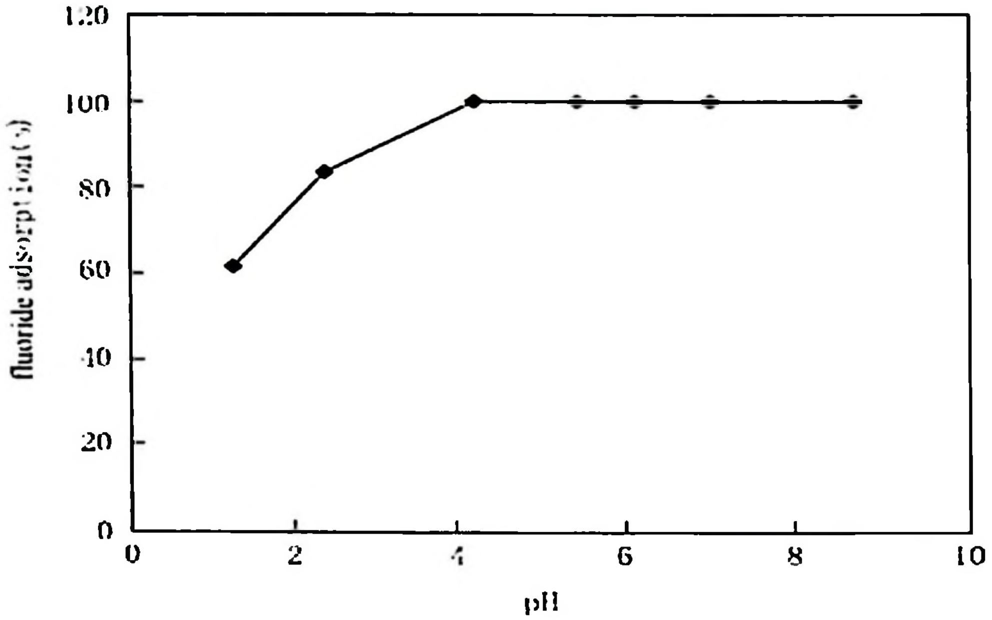

Fig. 1. 5. The fluoride removal efficiency of the Fe-loaded cotton cellulose in varying solution pH (taken from Zhao et al., 2008)

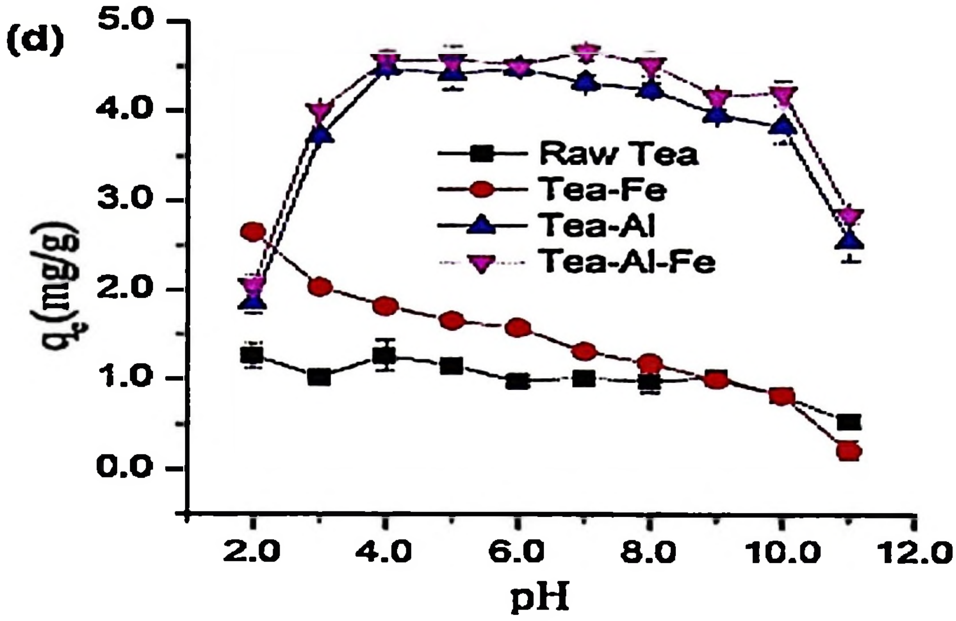

Fig. 1. 6. The fluoride removal capacities of Fe-loaded tea waste (Tea-Fe) in varying solution pH (taken from Cai et al., 2015)

As mentioned earlier, the application of iron in water treatment dates to the 19th century (Anonymous, 1867). A study on the evolution of the historical application of iron for water treatment will shed important light on the properties of iron in aqueous media, generation and interaction of its end products, and potentials for exploiting these interactions in water defluoridation by iron and iron-based materials. Fortunately, the ancient application of iron in water treatment provides a rich resource for understanding the properties of iron in aqueous media (Anonymous, 1867; Devenshire, 1890; Tucker, 1892; van Muyden, 1894; Baker, 1934; van Craenenbroeck, 1998). Initially, iron salts were used in central Europe for removing suspended matter from the contaminated water (Anonymous, 1867). This application exploited the ability of the iron in the oxidation state of three (III) to form precipitates of iron hydr(oxides) in aqueous media laying the basis for the modern-day application of iron salts as coagulants in water treatment (Kerslake et al., 1946). Later applications involved the use of metallic iron and iron oxides as filter media. These filters were efficient in removing both the suspended matter and the microbial contamination from the treated water (Devenshire, 1890). The high redox power of iron was exploited in this application. A large-scale application of metallic iron for water treatment was successfully deployed in the late 19th century in Antwerp, Belgium (Anonymous, 1881; Anderson, 1883; Devonshire, 1890; Swete, 1892).

This large-scale application was a result of successful application of this material in household scale water treatment filters (Bischof, 1873). This was successfully used because of the easy preparation and handling of metallic iron (spongy iron) material, consequently low-cost water treatment units. Although this ancient application of iron for water treatment was primarily designed for removing suspended matter and microbial contaminants it showed significant ability in removing chemical contaminants from treated water (Devenshire, 1890). Therefore, re-introduction of iron in water treatment in the late 20th and early 21st centuries largely investigated the ability of iron in immobilising both microbial and chemical contaminants (Wegelin et al., 1991; Gillham and O'Hannessin, 1994; O'Hannessin and Gillham, 1998; Ngai et al., 2006; Sarkar et al., 2015) which later included fluoride contaminant with observable diverse removal capacities (Zhao et al., 2008; Jahin, 2014; Cai et al., 2015; Zhang et al., 2015). Therefore, review of the previuos application of iron in water treatment may shed an important light on the reactivity and end products of iron.

These end products of iron which accumulates to different levels are the ones shown to have high fluoride affinity by recent studies on water defluoridation by iron and iron-based materials (Zhao et al., 2008; Jahin, 2014; Cai et al., 2015; Nde-Tchoupe et al., 2015; Zhang et al., 2015; Bischof, 1873; Devonshire, 1890; Wegelin et al., 1991; Ngai et al., 2006; Zhao et al., 2008; Ghauch, 2015). Interestingly, different iron-based materials with different abilities to release iron in the treated solution have reported different fluoride removal properties (Zhao et al., 2008; Cai et al., 2015). Furthermore, increasing acidity in the treated water leads to increase in dissolution of iron and enhanced fluoride removal efficiency. This may suggest a relationship between the fluoride removal properties of the iron based materials and the presence of Fe^{3+} in aqueous media. Since these are common final products in the application of iron in water treatment, a purposive study to determine the effect of their interaction in relation to the fluoride removal efficiency of the iron-based material is needed. This will shed important light on the effect of the Fe^{3+} on the fluoride removal properties of iron-based materials. It is expected that addition of Fe^{3+} will change the defluoridation properties of the iron-based materials. Furthermore, investigating the interactions between iron and fluoride ions in different chemical backgrounds is expected to reveal the potential of Fe as fluoride detector in aqueous media.

The efforts to study the defluoridation properties and possible field application of the plant biomass materials are retarded by challenges related to their inherent and induced defluoridation properties. Therefore, efforts to address some of these challenges may enhance our understanding and accelerate realisation of their field application. In Fe-activated materials, this understanding may reveal their inherent interactions with fluoride and other ions, hence, show possible ways of exploiting such interactions in developing low cost fluoride detectors and efficacious iron-based defluoridation materials. Therefore, in addressing part of this problem, this thesis presents the challenges related to the water defluoridation properties of the selected plant biomass materials (non-activated plant biomass, plant biomass ash and Fe(III)-activated biomass materials) and solutions to address such challenges. It further identifies the properties of iron and their common end products in aqueous media and investigates their potential for fluoride detection and removal enhancement in aqueous media.

In studying the lessons from the application of plant biomass materials for water defluoridation, only studies involving the non-activated plant biomass materials were included as these studies are key in determining the suitability of these materials in water defluoridation and the need for their activation. Therefore, most studies investigating plant biomass for water defluoridation included experimentations on the non-activated plant biomass materials. Furthermore, for convenient comparison of findings (of this and related studies, the selected fluoride concentration in the synthetic water was 10 mg/L except when natural water was used.

Therefore, the following questions will be answered:

i. What are the challenges and potential solutions related to the water defluoridation by non-activated plant biomass?
ii. What are the challenges and possible solutions related to application of biomass ash for water defluoridation?
iii. What is the effect of the preparation methods on the defluoridation properties of the iron-activated biomass materials?
iv. What the properties of iron materials in aqueous media are as observed from previous application of iron in water treatment?
v. What is the effect of Fe^{3+} ion on the fluoride removal properties of the iron and iron coated materials?
vi. Can interactions between fluoride and Fe^{3+} be exploited in developing the low-cost fluoride detectors for use in rural Africa?

Answers to these questions are important in furthering our understanding of the defluoridation properties of plant biomass materials and their activated forms.

In answering these questions, Chapter 2 of this thesis presents lessons from the previous studies of the non-activated plant biomass materials in water defluoridation with the aim of highlighting the inadequacy in study parameters' selection and identifying key parameters for understanding the fluoride removal mechanisms involved. Chapter 3 presents the defluoridation properties of the fireplace waste biomass ash and methods to control media-induced contamination in the treated water. Chapter 4 discusses the effect of activation methods on the defluoridation properties of the iron-activated biomass materials. Chapter 5 revisits the historical application of iron in water treatment with the aim of understanding the properties of iron materials in aqueous media. Since different iron-based materials have a different dissolution tendency to form ions of iron in water, Chapter 6 discusses the effect of Fe^{3+} ion on the fluoride removal properties of the iron loaded materials. Finally, Chapter 7 presents the interactions of Fe^{3+} with fluoride and thiocyanate ions and the potential for exploiting such interactions in developing a low-cost fluoride detector.

CHAPTER 2: Fluoride removal properties of plant biomass: Lessons from studies published in the past three decades

2.1. Introduction

The low cost and renewability of the plant biomass materials substantiate their potential for wide application in water defluoridation, especially in the developing world where point of use application is recommended. Field application of any material is possible when their defluoridation properties such as defluoridation capacities/efficiencies and mechanisms are well understood. Since activation has an implication on the cost of plant biomass materials, non-activated (plant biomass) materials are more likely to attract the attention of researchers. Furthermore, most studies exploring the defluoridation properties of these materials start with the non-activated materials. Therefore, lessons derived from defluoridation studies on non-activated plant biomass materials may shed an important light and direct future studies.

The trend in the three decades of studying defluoridation properties of the non-activated plant biomass materials reveals the continued inadequacy and or bias in selection of the parameters to be studied leading to bias in the studied properties. For instance, in one of the early studies on water defluoridation by plant biomass, the three parameters (solution pH, contact time and particle size) included in studying the defluoridation properties of the nirmali seeds biomass materials (Srimurali et al., 1998) were efficiency/condition based. From these parameters, the fluoride removal efficiency could be deduced, but, the fluoride removal mechanisms could not. More parameters were added when studying the water defluoridation properties of Aloe and Tamarind seed biomass to include the particle size, surface characteristics, solution temperature, contact time, initial fluoride concentration, adsorbent dose, solution pH and point of zero charge (Murugan and Subramanian, 2002; Murugan and Subramanian, 2006)

These parameters were useful in deducing the fluoride removal efficiency and or capacity of these materials as well as the fluoride removal mechanisms. The proposed fluoride removal mechanism in this case was electrostatic interactions between the negatively charged fluoride ion and the positively charged biomass surface. This proposal was based on the effect of solution pH on the fluoride removal efficiency and the point of zero charge values studied. Since the increase in solution pH resulted into decrease of the fluoride removal efficiency and the highest removal was observed at a pH value below the point of zero charge of the materials, it follows that, electrostatic forces play an important role in the fluoride removal mechanism.

Moreover, in the subsequent studies, Yadav et al. (2013) studied the effect of solution pH, adsorbent dose, contact time, and initial fluoride concentration when comparing the defluoridation properties of the selected biomass materials. The type of interaction between the fluoride ion and the biomass surface was suggested to be chemical interaction from the study of the kinetic models. The decreasing fluoride removal efficiency of the saw dust and the contrary increasing fluoride removal efficiency of the wheat straw biomass with increasing solution pH suggested that, the biomass surface charge had a significant but distinct effect on the fluoride removal process of different biomass materials. However, the point of zero charge and the surface functional groups (the groups of atoms (in a molecule/compound that reoresent the reactivity of a givent molecule/compound), which could help in understanding the effect of solution pH on the biomass surface charge, were not determined, thus, the fluoride removal mechanisms could not be better explained. This means that, the studied parameters could be used to explain the fluoride removal efficiency/capacity but not the mechanisms.

Paradelo et al. (2017) selected four parameters, namely, adsorbent pH, solution pH, initial fluoride concentration and contact time in in studying the water defluoridation properties of pine bark biomass. The fluoride removal mechanism was suggested based on the effect of solution pH on the defluoridation efficiency of the materials. However, the charge of the biomass surface at a given pH could be better predicted when the point of zero charge value and the changes in the functional groups are determined. Furthermore, in exploring the defluoridation properties of the *Syzygium cumini* and *Prosopis cineraria* leaf biomass, Keshtkar et al. (2019) studied the point of zero charge of the adsorbent, surface morphology, contact time and initial fluoride concentration. The interaction of fluoride ion with the biomass materials was proposed based on the kinetic models that were studied. The effect of solution pH and surface functional groups which could be important in predicting the surface charge, hence, the fluoride sorption mechanisms were not studied.

These examples reveal that most studies were skewed by focussing mainly on the defluoridation efficiency/capacity of the materials than their removal mechanisms. This is understandable in the first early studies, however, its continuation in the later studies may be an indication of the imbalance in parameter selection. This continued inadequacy in selection of the parameters to be studied may have in part contributed to the fluoride removal mechanisms proposed based on wrong or insufficient information, thence, delayed field application of the materials. Therefore, this chapter critically reviews the reported studies on water defluoridation by plant biomass with the aim to reveal the perpetuated inadequacy and or skewedness in selection of the key parameters to be included in studying the fluoride removal properties of the plant biomass materials and identify the key parameters for better understanding the responsible fluoride removal mechanisms. It is envisaged that this will shape and direct future studies and contribute to the realisation of the field application of these materials for water defluoridation in the near future.

2.2. Materials and methods

Papers presenting the use of plant biomass materials for water defluoridation were retrieved through different search engines from the World Wide Web (www) including Google scholar, Scopus and Web of Science by using the following search terms: "plant biomass for fluoride removal", "fluoride removal by plant biomass", "water defluoridation by plant biomass" and "fluoride removal by low cost biosorbents". Many retrievable studies on water defluoridation by plant biomass could be found dating from early 21st century. Therefore, the search for relevant literature was extended to 1990s during which two studies could be retrieved one in 1991 and the other in 1998. This makes the 28 publications used in this study cover the period from 1991 to 2019. Although greater than this number of publications could be retrieved, the focus was on articles that presented the defluoridation properties of non-activated plant biomass materials. Thus, when a retrieved publication included both the non-activated and activated plant biomass materials, only results from the non-activated plant biomass materials were included.

In the review process, the history of and trends in the water defluoridation by non-activated plant biomass were summarised and the general motivation for selection of such materials identified. Using the effect of solution pH on fluoride removal efficiency, different plant biomass materials were divided into two categories based on their response to variation of solution pH. The variation in the studied parameters in the different studies throughout history was critically studied. The relationship between the studied parameters and the information that can be deduced from each were established and lessons drawn. The lessons drawn from the studied parameters related to the proposed mechanisms were used to propose the "must include" parameters in the future studies for better understanding the plausible fluoride removal mechanisms of these materials.

2.3. Results and Discussion

2.3.1. The history of water defluoridation by non-activated plant biomass

Published studies on water defluoridation by plant biomass started to appear in the late 20th century (Shirke and Chandra, 1991; Srimurali et al., 1998). The motivation was to provide low-cost and biodegradable materials for water defluoridation (Table 2.1). The defluoridation capacities of the two early studied plant biomasses, duckweed (*Spirodela polyrrhiza*) and nirmali (*Strychnos potatorium*) seeds were found to be 0.91 and 0.15 mg/g (dry weight) respectively. This difference in sorption capacities revealed that different plant biomass materials may have different water defluoridation properties. This triggered expanded studies on both the non-activated and activated plant biomass materials in the early 21st century which demonstrated further from varied individual studies that different plant biomass materials have different defluoridation properties (Murugan and Subramanian, 2002; Sinha et al., 2003; Jamode et al., 2004; Murugan and Subramanian, 2006; Parmar et al., 2006). Therefore, further studies in the second decade of the 21st century on fluoride removal properties of plant biomasses involved a comparison of defluoridation properties of different plant biomass materials under similar conditions (Vardhan and Karthikeyan, 2011; Harikumar et al., 2012; Yadav et al., 2013; Patil et al., 2013; Mwakabona et al., 2014; Keshtkar et al., 2019).

From these studies, it could be confirmed that different biomass materials have different fluoride removal properties. From early 21st century, efforts to understand the fluoride removal mechanism by plant biomass materials were made (Murugan and Subramanian, 2002; Murugan and Subramanian, 2006) and biomass material properties such as point of zero charge and effect of pH of the treated water were related to the fluoride removal efficiencies. However, throughout history, most studies on water defluoridation by plant biomass have not included a complete set of important parameters for understanding the fluoride ion-biomass surface interaction. This occurs while such key parameters were already explored by the preceding studies, thence, a perpetuated inadequacy in selection of the parameters to be included in the studies to enhance understanding of the fluoride sorption mechanisms. In the next section, the widely studied parameters are identified and their relations to the most important defluoridation properties highlighted.

2.3.2. The widely studied parameters (over the past three decades) that affect fluoride sorption of different plant biomass materials

Adsorbent dose. Studying this parameter provides information on the materials' sorption capacity and or efficiency. It is one of the widely studied parameters which are commonly used to determine the effect of adsorbent amount and or compare the sorption capacities of the different biomass materials (Jamode et al., 2004; Lakshminarayan et al., 2011; Vardhan and Karthikeyan, 2012; Yadav et al., 2013; Mwakabona et al., 2014). It is interesting that this parameter was included in the early exploratory studies (Shirke and Chandra, 1991, Srimurali et al., 1998) and is still an important parameter in recent studies (George and Tembhukar, 2018; Sunitha and Reddy, 2018; Gandhi and Sirisha, 2019; Keshtikar et al., 2019). In these studies, increasing adsorbent dose is linked to increased and decreased sorption efficiencies and capacities, respectively, from which an optimal dose is established.

Adsorbent particle size. Decreasing adsorbent particle size is shown to have effect on the on the surface area of the adsorbent particles. This in turn increases the possibilities of interaction between the fluoride ions and the adsorbent particles, thence, increasing the fluoride sorption efficiencies and capacities (Jamode et al., 2004; Harikumar et al., 2012; Patil et al., 2013; Sumalatha et al., 2014; Sunitha and Reddy, 2018). Therefore, the optimal particle size which may influence the size of the resulting defluoridation units can be established when this parameter is studied.

Contact time. This is the time allowed for the fluoride ion to interact with the adsorbent active site. Generally, increasing contact time results into increase in fluoride removal efficiency prior to the equilibrium point (Murugan and Subramanian, 2002; Sinha et al., 2003; Jamode et al., 2004; Murugan and Subramanian, 2006; Parmar et al., 2006; Vardhan and Karthikeyan, 2011; Yadav et al., 2013; Mwakabona et al., 2014; Mondal, 2017; Saikia et al., 2017; Khound and Bharali, 2018). For some plant biomass materials, further increase in contact time past the equilibrium point results in decreased fluoride removal efficiency (Mwakabona et al., 2014). Therefore, from the effect of contact time, optimal time required for effective interaction between fluoride ions and the adsorbent materials when designing the defluoridation units can be established.

Initial fluoride concentration. In defluoridation studies, initial fluoride concentration is correlated with the fluoride removal efficiency (Murugan and Subramanian,2002; Jamode et al., 2004; Pandey et al., 2012; Patil et al., 2013; Sumalatha et al., 2014; Bharali and Battacharyya, 2015; Paradelo et al., 2017; Romar-Gasalla, 2017). Before equilibrium point, increasing initial fluoride concentration results into increasing fluoride removal efficiency and past the equilibrium point, the effect is reversed (Mwakabona et al., 2014). By determining the effect of initial fluoride concentration, the fluoride removal efficiency and capacity can be deduced. Furthermore, the suitable fluoride concentration in the water to be treated can be identified.

Solution temperature. Determination of the effect of solution temperature is helpful in determining the type of the reaction involved between fluoride ions and biomass surfaces. From the effect of defluoridation on solution temperature, the type of the fluoride-biomass reaction can be categorised as either exothermic or endothermic (Murugan and Subramainan, 2006; Bharali and Battacharyya, 2015; Mondal, 2017; Khound and Bharali, 2018). Furthermore, the temperature condition of the water to be treated for maximum fluoride removal efficiency can identified by determining this parameter.

Co-and counter ions. By determining the effect of co- and counter-ions, the efficiency of the biomass material in the different types of water is identified. Findings from this parameter may further give a clue on the nature and or chemistry of the biomass material's active sites. This is possible when a combination of other related parameters are determined. In most studies, however, this parameter has been used to identify co- and counter-ions that have negative effect on the fluoride removal efficiency of a given biomass materials (Vardhan and Karthikeyan, 2011; Pandey et al., 2012; Kumar et al., 2012; Mondal, 2017).

Solution pH. By determining the effect of solution pH, the optimal pH at which the fluoride removal is maximum can be identified (Jamode et al., 2004; Vardhan and Karthikeyan, 2011; Bharali and Battacharya, 2015). Furthermore, correlating the variation in solution pH to the fluoride removal efficiency may provide a clue on the fluoride removal processes involved (Patil et al., 2013; Saikia et al., 2017; Khound and Bharali, 2018). Many studies have proposed the possible fluoride removal mechanisms of the plant biomass materials based on this correlation (Kumar et al., 2012; Yadav et al., 2013; Mwakabona et al., 2014). However, as further discussed in the next section, information obtainable from this correlation is insufficient in explaining the fluoride removal mechanisms involved, therefore, other relevant parameters need to be determined.

Surface functional groups (FT-IR spectral shift). Determination of the surface functional groups and the corresponding change (spectral shift) after use provides useful information about the responsible active sites (Pandey et al., 2012; Saikia et al., 2017; Khound and

Bharali, 2018; Keshtkar et al., 2019). These studies have used this FT-IR spectral shift to identify the responsible functional groups in fluoride sorption. The observed variation in fluoride removal efficiency with changes in solution pH may useful in explaining the nature of the interaction between fluoride and the biomass surfaces (Kumar et al., 2012; Yadav et al., 2013; Mwakabona et al., 2014).

Table 2. 1. A summary of the selected plant biomass materials used for water defluoridation and motivation(s) for their selection

Biomass type(s)	Motivation(s)	References
Duck weed (*Spirodela polyrrhiza*)	Low cost materials	Shirke and Chandra, 1991
Nirmali seeds	Other application/low cost materials	Srimurali et al., 1998
Water hyacinth (*Eichhornia crassipe*)	Low cost materials	Sinha et al., 2003
Neem (*Azadirachta indica*) leaves	Low cost materials	Jamode et al., 2004; Lakshminarayan et al., 2011
Pipal (*Ficus religiosa*) leaves		
Khair (*Acacia catechu wild*)		
Tamarind seed	Waste re-use/low cost materials	Murugan and Subramanian, 2006; Harikumar et al., 2012
Indian rosewood (*Dalbergia sissoo*) saw dust	Low cost materials	Yadav et al., 2013; Romar-Gasalla et al., 2017
Wheat straw (*Triticum spp*)		
Banana peel (*Musa acuminate*)	Low cost/eco-friendly materials	Mondal, 2017
Pine bark	Availability/Low cost materials	Paradelo et al., 2017
Possotia leaf (*Vitex negundo*)	Other applications/low cost materials	Saikia et al., 2017
Indian sandalwood (*Santalum album*)	Low cost materials	Khound and Bharali, 2018
Ficus glomerata	Low cost materials	George and Tembhukar, 2018
Syzygium cumini leaf	Low cost materials/wide availability	Keshtkar et al., 2019
Prosopis cineraria leaf		

Point of zero charge. This parameter provides information on the surface charge of the biomass (adsorbent) material in relation to the solution pH. The pH at which the charge of the adsorbent material is zero is the point of zero charge. Many studies have used the point of zero charge to predict the surface charge at optimal pH and understand the effect of solution pH on the fluoride removal efficiency and nature of interaction between fluoride ion and charged biomass surfaces (Murugan and Subramanian, 2002; Balouch et al., 2013; Mondal, 2017; Romar-Gasalla et al., 2017; Kestkar et al., 2019).

These widely studied parameters reveal an imbalance in their selection and or combination (Table 2.2). Most of the parameters studied are on the fluoride removal efficiencies or capacities and the conditions for optimizing them while a few studies have included those parameters that can be used to propose the fluoride removal mechanisms. Although an increase in number of parameters that can be used to understand the fluoride removal mechanisms is observable overtime, the combination of these parameters is incomplete such that the proposed fluoride removal mechanisms are based on incomplete information (Table 2.3) as further explained in the next sections.

Table 2. 2. Widely studied parameters in water defluoridation by plant biomass

Period	Propert(y)ies	Parameter(s)	Number of studies	Reference(s)
1990-2000	F removal efficiency/capacity	dose, time, initial F,	2	Shirke and Chandra, 1991; Srimurali et al., 1998
	F removal mechanism	NIL	NIL	NIL
2001-2010	F removal efficiency/capacity	Dose, Time Initial F Temperature Particle size	5	Murugan and Subramanian, 2002; Sinha et al., 2003; Jamode et al., 2004; Murugan and Subramanian, 2006; Parmar et al., 2006
	F removal mechanism	Temperature pH pzc,	2	Murugan and Subramanian, 2002; Murugan and Subramanian, 2006
2011-2019	F removal efficiency/capacity	Time Dose Initial F Solution pH Co- and counter ions Agitation speed Temperature Particle size	19	Lakshminarayan et al., 2011; Vardhan and Karthikeyan, 2011; Harikumar et al., 2012; Kumar et al., 2012; Pandey et al., 2012; Balouch et al., 2013; Patil et al., 2013; Yadav et al., 2013; Mwakabona et al., 2014; Bharali and Bhattacharyya, 2015; Paradelo et al., 2017; Mondal, 2017; Romar-Gasalla et al., 2017; Saikia et al., 2017; Khound and Bharali, 2018; George and Tembhukar, 2018; Sunitha and Reddy, 2018; Gandhi and Sirisha, 2019; Keshtkar et al., 2019
	F removal mechanism	Surface morphology (SEM) Surface functional groups pH pzc temperatre	9	Pandey et al., 2012; Patil et al., 2013; Balouch et al., 2013; Mwakabona et al., 2014; Bharali and Bhattacharyya, 2015; Mondal, 2017; Khound and Bharali, 2018; Sunitha and Reddy, 2018; Keshtkar et al., 2019

Table 2. 3. A summary of scientific bases for proposed fluoride removal mechanisms of the selected plant biomass materials in relation to the studied parameters and their deficiencies

Biomass	F removal mechanism(s)	Bases for the mechanisms	Studied parameters	Deficiency	References
Aloe vera	Chemical forces	Effect of solution pH on the fluoride removal efficiency and the point of zero charge value of the biomass	Effect of (pH, initial F, dose and time), point of zero charge	Possible active sites not identified (FT-IR spectral shifts not determined)	Murugan and Subramanian, 2002
Tamarind seed	Electrostatic forces	Optimal pH and point of zero charge value of the biomass	Effect of (pH, initial F, dose and time), point of zero charge	Possible active sites not identified (FT-IR spectral shifts not determined)	Murugan and Subramanian, 2006
Dalbergia sissoo	adsorption	Effect of solution pH on the fluoride removal efficiency	Effect of (pH, time, dose and initial F)	Possible active sites & effect of surface charge not identified (FT-IR spectral shifts & point of zero charge not determined)	Yadav et al., 2013
Musa acuminate	physisorption (electrostatic forces)	Effect of solution pH and point of zero charge value of the biomass	Effect of (pH, initial F, dose, co-ions, temperature and time), point of zero charge, SEM and FT-IR spectral shift	Nil	Mondal, 2017
Santalum album	Ionic interactions	Types of functional groups present	Effect of (pH, initial F, dose, co-ions, temperature and time), SEM and FT-IR before use	Possible effect of surface charge not substantiated (point of zero charge not determined) Involved active sites not confirmable (FT-IR analysis after use not included)	Khound and Bharali, 2018
Prosopis cineraria Syzygium cumini	Coulombic forces	Point of zero charge values and types of surface functional groups	Effect of (dose, time, initial F), XRD, FT-IR, SEM and point of zero charge values	Presence of coulombic forces not confirmable (effect of pH /optimal pH not determined) Involved active sites not predicted (FT-IR analysis after use not determined)	Keshtkar et al., 2019

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Period	Propert(y)ies	Parameter(s)	Number of studies	Reference(s)
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	F removal mechanism	NIL	NIL	NIL
2001-2010	F removal efficiency/capacity	Dose, Time Initial F Temperature Particle size	5	Murugan and Subramanian, 2002; Sinha et al., 2003; Jamode et al., 2004; Murugan and Subramanian, 2006; Parmar et al., 2006
	F removal mechanism	Temperature pH pzc,	2	Murugan and Subramanian, 2002; Murugan and Subramanian, 2006
2011-2019	F removal efficiency/capacity	Time Dose Initial F Solution pH Co- and counter ions Agitation speed Temperature Particle size	19	Lakshminarayan et al., 2011; Vardhan and Karthikeyan, 2011; Harikumar et al., 2012; Kumar et al., 2012; Pandey et al., 2012; Balouch et al., 2013; Patil et al., 2013; Yadav et al., 2013; Mwakabona et al., 2014; Bharali and Bhattacharyya, 2015; Paradelo et al., 2017; Mondal, 2017; Romar-Gasalla et al., 2017; Saikia et al., 2017; Khound and Bharali, 2018; George and Tembhukar, 2018; Sunitha and Reddy, 2018; Gandhi and Sirisha, 2019; Keshtkar et al., 2019
	F removal mechanism	Surface morphology (SEM) Surface functional groups pH pzc temperatre	9	Pandey et al., 2012; Patil et al., 2013; Balouch et al., 2013; Mwakabona et al., 2014; Bharali and Bhattacharyya, 2015; Mondal, 2017; Khound and Bharali, 2018; Sunitha and Reddy, 2018; Keshtkar et al., 2019

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Biomass	F removal mechanism(s)	Bases for the mechanisms	Studied parameters	Deficiency	References
Aloe vera	Chemical forces	Effect of solution pH on the fluoride removal efficiency and the point of zero charge value of the biomass	Effect of (pH, initial F, dose and time), point of zero charge	Possible active sites not identified (FT-IR spectral shifts not determined)	Murugan and Subramanian, 2002
Tamarind seed	Electrostatic forces	Optimal pH and point of zero charge value of the biomass	Effect of (pH, initial F, dose and time), point of zero charge	Possible active sites not identified (FT-IR spectral shifts not determined)	Murugan and Subramanian, 2006
Dalbergia sissoo	adsorption	Effect of solution pH on the fluoride removal efficiency	Effect of (pH, time, dose and initial F)	Possible active sites & effect of surface charge not identified (FT-IR spectral shifts & point of zero charge not determined)	Yadav et al., 2013
Musa acuminate	physisorption (electrostatic forces)	Effect of solution pH and point of zero charge value of the biomass	Effect of (pH, initial F, dose, co-ions, temperature and time), point of zero charge, SEM and FT-IR spectral shift	Nil	Mondal, 2017
Santalum album	Ionic interactions	Types of functional groups present	Effect of (pH, initial F, dose, co-ions, temperature and time), SEM and FT-IR before use	Possible effect of surface charge not substantiated (point of zero charge not determined) Involved active sites not confirmable (FT-IR analysis after use not included)	Khound and Bharali, 2018
Prosopis cineraria Syzygium cumini	Coulombic forces	Point of zero charge values and types of surface functional groups	Effect of (dose, time, initial F), XRD, FT-IR, SEM and point of zero charge values	Presence of coulombic forces not confirmable (effect of pH /optimal pH not determined) Involved active sites not predicted (FT-IR analysis after use not determined)	Keshtkar et al., 2019

2.3.3. Lesson from the effect of varying solution pH

From the previous sections, it is evident that solution pH is an important parameter when studying the sorption properties of the plant biomass materials. It provides information on the optimal pH condition for highest fluoride removal efficiency and the adsorbent surface charge, consequently, its interaction with charged ions, hence, usable in explaining the fluoride removal mechanisms. Interestingly, many studies have included the effect of pH in studying water defluoridation properties of the plant biomass materials (Murugan and Subramanian, 2002; Jamode et al., 2004; Murugan and Subramanian, 2006; Vardhan and Karthikeyan, 2011; Kumar et al., 2012; Harikumar et al., 2012; Yadav et al., 2013; Mwakabona et al., 2014; Sumalatha et al., 2014; Bharali and Battacharyya, 2015; Mondal 2017; Saikia et al., 2017; Khound and Bharali, 2018) and characteristic patterns are observable. However, there are several flawed generalisations that have led to misuse of this parameter in explainng the fluoride removal mechanisms of plant biomass materials (Jamode et al., 2004; Vardhan and Karthikeyan, 2011; Kumar et al., 2012; Harikumar et al., 2012; Yadav et al., 2013; Mwakabona et al., 2014). The flaw could be due to the tendency of many studies to ignore the diverse response in fluoride removal efficiency of these materials in varying pH conditions. In the pH range between 2 and 11, the studied biomass materials can be categorized into two major groups (Table 2.4) based on their response to the effect of variation of the solution pH on the fluoride removal efficiency. The first group constitutes plant biomass materials with their fluoride removal efficiency declining steadily with increased solution pH. In the list are Neem leaves, Rice husks and Indian rosewood saw dust (Jamode et al., 2004; Vardhan and Karthikeyan, 2011; Balouch et al., 2013; Yadav et al., 2013). The point of zero charge values of rice husk and neem leaves biomasses are 6.45 and 4 respectively, as reported in other related studies (Arshad et al., 2008; Vieira et al., 2012). This could suggest that the electrostatic forces play a major role in the interaction between the fluoride ion and the biomass materials because the highest removal efficiency is at the solution pH below the point of zero charge values and increase in solution pH past the pzc results in decreased pH-induced surface positive charge on the biomass surface, consequently, decreased fluoride removal efficiency. Therefore, in absence of the point of zero charge values, the solution pH cannot be used to predict the type of charge on the biomass surface, making this parameter inadequate to explain the fluoride removal mechanism unless combined with other relevant parameters.

Another group constitutes the plant biomass materials with fluoride removal efficiency increasing with increasing pH to the optimal pH after which it declines with further increase in solution pH. Some examples in the list are wheat straw, banana peel, *Aloe vera*, *Tinospora cordifolia* leaves, Tamarind seed, *Azadirachta indica* leaves, possotia leaves, Indian sandalwood leaves, saw dust and *Passiflora foetida* fruits (Murugan and Subramanian, 2002; Murugan and Subramanian, 2006; Pandey et al., 2012; Harikumar et al., 2012; Balouch et al., 2013; Yadav et al., 2013; Mondal, 2017; Romar-Gasalla et al., 2017). While some of these biomass materials have a higher fluoride removal efficiency at solution pH below the point of zero charge values (Murugan and Subramanian, 2002, 2006; Mondal, 2017), others show higher fluoride removal at solution pH above the point of zero charge values (Balouch et al., 2013; Romar-Gasalla et al., 2017).

Furthermore, increasing solution pH which is supposed to decrease positive charge on the biomass surface results into increase in fluoride removal efficiency. This would imply that some other forces than the electrostatic forces play a role in the fluoride-biomass interactions. This fact can be explained by the influence of the solution pH on the biomass surface charge as follows; increasing the solution pH decreases the pH induced positive charge on the surface of the biomass materials, thence, decreased positive charge-dependent interactions between the negatively charged fluoride ion and the positively charged biomass surface. The parallel increase of the fluoride removal efficiency with increase in solution pH could be explained by the instability of the biomass active sites in acidic conditions.

These observations establish that a fair comparison of the defluoridation capacities of the plant biomass should be done when the optimal solution pH of all the materials are determined, because, different materials show best fluoride removal efficiency at different solution pH (although the biomass materials that work best in the neutral condition are more likely to find way to field application in the treatment of the naturally contaminated fluoride water). Considering the condition of the targeted fluoride contaminated water, either group one or group two biomass materials could be selected (Table 2.4). Thus, the effect of solution pH may be one of the key parameters which when determined, both the optimal pH condition and the possible interactions between the biomass surface and fluoride ion can be identified.

It is further established that the effect of solution pH could be used to predict the type of interaction between the fluoride ions and biomass surface when the biomass surface charge is predictable. The latter is possible only when the point of zero charge value of the biomass material is known. Therefore, determination of the effect of solution pH alone can only be used to determine the optimal pH for higher fluoride removal efficiency or capacity. For predicting the surface charge of the biomass materials, other parameters such as the point of zero charge values need to be determined as further explained in the next section.

Table 2. 4. Categorisation of plant biomass materials based on their fluoride removal efficiency in response to change in solution pH

Material(s)	Category	Characteristics	Examples	References
Plant biomass	Group 1	F removal decreases with increasing solution pH	Saw dust, rice husks, Indian rosewood and Neem leaves.	Jamode et al., 2004; Vardhan and Karthikeyan, 2011; Balouch et al., 2013; Yadav et al., 2013
	Group 2	F removal increases with increasing solution pH	Tamarind seed, *Aloe vera*, Wheat straw, *Tinospora cordifolia* and Banana peel.	Murugan and Subramanian, 2002; Murugan and Subramanian, 2006; Pandey et al., 2012; Harikumar et al., 2012; Balouch et al., 2013; Yadav et al., 2013; Mondal, 2017; Romar-Gasalla et al., 2017

2.3.4. Lesson from the point of zero charge values

Since the effect of the solution pH is one of the important parameters in understanding the fluoride removal properties of the biomass materials, it follows that, the point of zero charge value of the adsorbent material is an equally important parameter to understand the effect of solution pH on the surface charge of the biomass materials (Parks, 1967; Lyklema, 1984; Nasiruddin Khan et al., 2007) (Table 2.5). A reflection on the reviewed studies reveals that only a small fraction of studies (Murugan and Subramanian, 2002; Murugan and Subramanian, 2006; Balouch et al., 2013; Mondal, 2017; Romar-Gasalla et al., 2017) included determination of both the point of zero charge and the effect of solution pH in explaining the fluoride removal mechanisms of their selected biomass materials. As a result, for most studies, defluoridation mechanisms are proposed based on incomplete information.

However, determination of the effect of solution pH and material's point of zero charge values is not without limitations. As pointed earlier, variation in solution pH does not always result in the same effect in defluoridation efficiency of all plant biomass materials. For group one materials, defluoridation efficiency decreases steadily with increasing solution pH (Jamode et al., 2004; Vardhan and Karthikeyan, 2011; Yadav et al., 2013). As the solution pH is increased, the biomass surface positive charge is likely decreased. Thus, the corresponding stead decrease in fluoride removal efficiency may imply that the pH induced charge is directly proportional to the fluoride sorption efficiency.

For the second group of plant biomass materials, the increase in solution pH results in the increase of the fluoride removal efficiency. The fluoride removal efficiency appears to increase with decreasing pH-induced positive charge on the biomass surface and the pH with highest fluoride removal efficiency is above the point of zero charge value (Balouch et al., 2013; Romar-Gasalla et al., 2017). Therefore, these opposing trends show that neither the point of zero charge values nor the effect of solution pH can be used alone to sufficiently explain the interaction between the fluoride ions and the biomass surfaces.

Moreover, for some plant biomass materials, the point of zero charge value has a positive correlation with their fluoride removal efficiencies suggesting that the point of zero charge value could be used in predicting the fluoride removal efficiencies. For instance, in their study involving comparison of fluoride removal efficiencies of rice husk and Moringa seed biomass, Vardhan and Karthikeyan (2011) found that at fixed pH (pH 6), the fluoride sorption efficiency of Moringa seed biomass was greater (87%) in the biomass materials with higher pzc (7.0) than that of that of rice husk biomass (84%) with relatively lower pzc (6.45). Similarly, at fixed neutral pH, findings by Keshtikar et al. (2019) show a positive correlation between the point of zero charge and fluoride sorption capacity of the two biomass materials. *Syzygium cumini* biomass with pzc value of 5.2 had higher fluoride sorption capacity of 11.52 mg/g than *Prosopis cineraria* biomass with pzc of 4.4 and fluoride sorption capacity of 7.407 mg/g. Likewise, *Aloe vera*, sisal fibre, banana pseudo-stem and maize leaf biomass materials were found to have the fluoride sorption efficiency of 29.4, 26.6, 7.1, and 4.1 % respectively at pH 6 (Mwakabona et al., 2014). The point of zero charge values reported by related studies for these biomass materials are 7.43, 6, 5.5 and 5.1 for *Aloe vera*, sisal fibre, banana pseudo-stem and maize leaf biomass materials respectively (Murugan and Subramanian, 2002; El-Sayed et al., 2015; Bagali et al., 2017; Vargas et al., 2019).

In the other biomass materials, however, the correlation between the point of zero charge values and defluoridation efficiency is unpredictable. For instance, tamarind seed, neem leaves, and coffee husk biomass materials studied by Harikumar et al. (2012) had the fluoride sorption efficiency of 75, 52, and 38%, respectively, at pH 6. The point of zero charge values reported in the related studies are 7.44, 4, and 4.3-4.5 for tamarind seed, neem and coffee husk biomasses, respectively (Murugan and Subramanian, 2006; Arshad et al., 2008; Oliveira et al., 2008).

Table 2. 5. Summary of the relationship between the point of zero charge values, optimal solution pH and F removal mechanisms of different plant biomass materials

Biomass	**Point of zero charge**	**Optimal pH**	**F removal mechanism**	**References**
Aloe vera	7.43	7 (below pzc)	Chemical forces	Murugan and Subramanian, 2002
Tamarind seed	7.44	7 (below pzc)	Electrostatic forces	Murugan and Subramanian, 2006
Saw dust	4.9	6 (above pzc)	-	Balouch et al., 2013
Banana peel	5.63	4 (below pzc)	Electrostatic forces	Mondal, 2017
Wheat straw	6.8	8 (above pzc)	Van der Waals forces	Romar-Gasalla et al., 2017
Syzygium cumini	5.2	-	Electrostatic forces	Keshtkar et al., 2019
Prosopis cineraria	4.4	-	Electrostatic forces	Keshtkar et al., 2019

These opposing properties of plant biomass materials show that the defluoridation mechanisms of these materials cannot be sufficiently explained by the determination of the effect of pH and point of zero charge values alone. Therefore, determination of the functional groups on the biomass surface that are involved in the fluoride adsorption is important as further explained in the next section.

2.3.5. Lesson from the change in surface functional groups (FT-IR spectral shift)

Determination of the surface functional groups helps in identifying the possible reaction of the materials in different conditions. The FT-IR spectral reading before and after biomass use, may show the functional groups that take part in fluoride sorption (Pandey et al., 2012; Bharali and Battacharyya, 2015; Mondal, 2017). The spectral shift shows the changes in the bond vibrations in the functional groups at the active sites. However, it tells less on the type of interaction between the fluoride ions and the functional groups. Therefore, highlighting the relationship between the change in the FT-IR spectral shifts, point of zero charge values and the effect of solution pH on the fluoride removal efficiency may be help in understanding type of interaction between the fluoride ions and the biomass active sites, hence, the fluoride removal mechanisms involved (Murugan and Subramanian, 2002; Murugan and Subramanian, 2006; Yadav et al., 2013; Harikumar et al., 2012; Kumar et al., 2012; Mwakabona et al., 2014; Sumalatha et al., 2014; Bharali and Bhattacharyya, 2015; Mondal, 2017; Paradelo et al., 2017; Khound and Bharali, 2018; Gandhi and Sirisha, 2019; Keshtkar et al., 2019). The FT-IR spectral shift reading has been used by some authors to propose the fluoride sorption mechanisms (Pandey et al., 2012; Bharali and Battacharyya, 2015; Mondal, 2017). Since, many functional groups assume different charges in different solution pH, failure to combine the three parameters may limit understanding of the fluoride sorption processes involved.

Therefore, the adsorbent point of zero charge, effect of solution pH and biomass surface functional group before and after sorption are three key parameters to be included for understanding the fluoride removal mechanisms involved when non-activated plant biomass materials are used for water defluoridation. While determination of the FT-IR spectral shift may help in identifying the functional groups with which fluoride ion interacts, the effect of solution pH and adsorbent point of zero charge values considered together may help in predicting the biomass surface charge at the optimal pH which in turn may be useful in predicting the type of interaction between the fluoride ion and the functional groups identified. Hence, inclusion of these parameters in future studies will help to furnish the missing information required to correctly propose the fluoride removal mechanisms of the studied non-activated plant biomass materials.

2.4. Conclusion

In this chapter, the challenges related to selection of study parameters in studying the water defluoridation properties of the non-activated plant biomass materials are identified and discussed. The parameters widely studied in the investigation of the defluoridation properties of the non-activated plant biomass include, adsorbent particle size and adsorbate dose, contact time, solution pH and temperature. Most of these parameters provide more information on the defluoridation efficiency than mechanisms. Solution pH is found to have a strong relation to the biomass surface charge and fluoride removal efficiencies of the biomass materials. But when used alone, it cannot be used to adequately explain the fluoride removal mechanisms. Therefore, a combination of the point of zero charge values coupled with the effect of solution pH and biomass functional groups could enhance our understanding of the fluoride ion-biomass interaction when studying the defluoridation properties of the plant biomass materials. That is, when the point of zero charge is determined, it makes interpretation of the effect of solution pH possible, thence, the interaction between the fluoride ion and the adsorbent surface predictable. When the biomass surface functional groups are determined (before and after biomass use), the chemical nature of the active sites and the type of the interaction and the fluoride removal mechanisms can be better understood. This is true when the material used removes fluoride by adsorption. The story is different when other forms of biomass, such as plant biomass ash are used. In this form the media-induced contamination is expected. In the next chapter, possible solutions to the challenges associated with application of plant biomass ash in the water treatment are presented and discussed.

CHAPTER 3: Biomass ash-Cyperus plants coupling: A novel low-cost technology for fluoride and pH remediation

3.1. Introduction

Generally, the plant biomass ash consists of (hydr)oxides, carbonates and hydrogencarbonates of such elements as, Ca, Si, K, P, Al, Mg, S, Fe and Na (Ward and French, 2006; Sakthivel et al., 2012; Vassilev et al., 2013; Nath and Dutta, 2015; Darchen et al., 2016) and residues of partially burnt biomass. While some of these chemical compounds are partially soluble, others are highly soluble in aqueous media. As a result, when used in water defluoridation, there is great chance of causing media induced contamination by leaching their water-soluble compounds and elevating the pH of the treated water. To solve this problem (of media-induced contamination), post-treatment remediation is required. Considering the great potential of this material in water defluoridation and its ever-increasing abundance as a fireplace waste, these interventions are worthwhile. Since water defluoridation by plant biomass ash is linked to the presence of the partially soluble (hydr)oxides of Ca and Mg, contamination by the highly soluble compounds can be addressed by throwing a few first aliquots of the treated water. However, extracting the water-soluble contaminants may result into reduced defluoridation efficiency of the corresponding biomass ash materials (Nath and Dutta, Darchen et al., 2016; John et al., 2018), thence, a need to understand their contaminant leaching in relation to their defluoridation properties.

Furthermore, the ash-induced elevated pH of the treated water can conventionally be addressed by post-treatment addition of acids to neutralise the treated water. This, however, will require predetermination of the levels of contamination in the treated water, to establish the required concentrations of acids, every time neutralisation is required. Moreover, addition of mineral acids into the treated water may be another source of contamination and added cost. This, therefore, implies that a better method to address the elevated pH challenge of the ash treated water is needed.

To this end, this chapter, therefore, presents the defluoridation properties of the wood biomass ash produced from the kitchen fireplaces both in batch and column experiments. The contaminant leaching and pH elevation challenges are identified and ways to control presented. The design in the column experiments is made to mimic the constructed wetland with plants used in adjusting the pH of the treated water. While the constructed wetland is a well-studied technology for treatment of wastewaters from various sources (Kadlec and Wallace, 2008; Vyamazal, 2010), its application for fluoride treatment is however, scantly studied with a few studies pointing to a combination of plants and adsorbents for enhancing fluoride adsorption on the substrate (adsorbent) (Li *et al.*, 2014). No studies have explored the capabilities of plants to adjust the water pH in the constructed wetland. Therefore, in this study the capabilities of waste wood ash produced in kitchens and *Cyperus* plants on water defluoridation and pH adjustment respectively, are studied and findings presented. These capabilities are further combined in a special way in the constructed wetland for provision of a novel and low-cost technology for fluoride remediation.

3.2. Methodology

3.2.1. Materials and materials preparation

The ash used was collected from fireplaces in kitchens of selected households in Morogoro, Tanzania. It was then mixed and sieved through 0.1 mm sieve to remove unburnt and other dirty particles and characterised to obtain its chemical composition as further explained in the next section. The plant used for constructed wetland was *Cyperus esculentus* locally found in swampy areas and riverbanks. This plant was selected because of its ability to survive in water logging conditions and richness in natural flavonoids presented in literature. The plants were immediately washed in fluoride free tap water to remove soil particles from both the roots and the leaves. Washed plants were immediately stored in a solution prepared from mixing the prepared ash and fluoride free tap water for future use. Natural water with fluoride concentration of around 20.8 mg/L measured using ion selective electrode (HI 98402 supplied by Hanna Instruments Company) was obtained from a natural spring in the Usa river area in Arusha, Tanzania.

3.2.2. Material and water characterization

The elemental analysis of the ash (solid sample) used was done using X-ray Fluorescence spectrometer (S8 Tiger, Bruker AXS GmbH, Germany) to establish the chemical composition of the ash used and its water extract. The levels of Ca and K in the water before and after treatment with ash and plants (in the batch and continuous flow experiments) were determined by Atomic Absorption Spectrometer (919 SOLAAR, UNICAM, UK) and Digital Flame Analyzer (2655-00 Cole-Parmer Instrument Company, Chicagi, IL), respectively. The carbonates and hydrogencarbonates of the untreated and treated water in the batch experiments were determined by a standard titrimetric method and the pH was estimated using a pHep pH tester (HI 98128, Hanna Instruments, USA).

In order to establish the chemistry of the ash in aqueous media, 3 kg of the sieved ash was added into 6 L of distilled water in the 10 L plastic bucket, stirred for 30 minutes and left to settle for another 30 minutes. The supernatant solution was siphoned into a 1 L Pyrex beaker and boiled to obtain the solid ash extract. The residue ash (partially leached ash) was sun dried and used in defluoridation experiments as partially leached ash. The fluoride removal efficiency from this ash was compared with that from the original ash to explain the fluoride removal processes.

The XRF analysis results of this ash extract was used to approximate the leaching property of the different compounds in the used ash. The compound with highest concentrations in the extract was considered to have highest tendency of leaching, thus, selected to indicate the contaminant leaching behaviour of the used ash. In the alkaline condition of the ash treated water (in which most heavy metals would form precipitates), the concentration of the component with highest leaching tendency could fairly be assumed to represent the levels of the media-introduced contaminants in the treated water. This assumption, however, has limitations as different ash materials may have different chemical compositions.

In the continuous flow, 1 kg of ash was packed in a 5 L capacity column and distilled water was allowed to flow in the downwards flow through the ash and the flow control valve by gravity at the rate of 0.18 L/h for a total of 24 hours. The concentration of component with highest leaching tendency (identified from the previous experiment) was monitored at regular intervals (as explained above) to establish the effect of time on the contaminant leaching in the treated water. This was expected to shed light on the quality of the treated water in the continuous flow design when the ash with similar properties is used.

3.2.3. Fluoride removal experiments

First, 10 g of sieved ash was equilibrated in 250 ml of the 20.8 mg/L natural fluoride water in a 1 L plastic bottle for a total of 24 hours, as follows: the mixture was shaken vigorously for the first five minutes and left to settle for the rest of the time. The residual fluoride concentration was determined after 0.5, 1, 4, 8, 12 and 24 hours. Different selected physico-chemical parameters (turbidity, total dissolved solids (TDS) and solution pH of the untreated and treated water were established. Then, the effect of solution pH was determined by adjusting the pH of the natural water with fluoride concentration of 20.8 mg/L using the 0.1 M HCl and NaOH solution to obtain the pH of 2,4,6,8, and 10. The effect of initial fluoride concentration was determined by standard dilution of the natural 20.8 mg/L fluoride water using distilled water to obtain the fluoride concentration of 5,10,15, and 20.8 mg/L. These experiments were equilibrated for two (2) hours in replicates, and averages used to plot graphs.

3.2.4. The pH adjustment experiments

Exactly 1 L of the treated water from the batch reactors was transferred into two separate 1.5 L plastic vessels where 350 g (35) of the live *Cyperus esculentus* plants were immersed with half of the plant height in water (like in the modified hydroponics). To further understand the neutralisation mechanism, parallel experiments were conducted using the natural water with HCl induced pH of 3.5 (adjusted using 0.1 M HCl and NaOH). All the vessels were left undisturbed throughout the experiment. About 10 ml of the treated water was drawn from each vessel with the aid of the 10 ml plastic syringe (fitted with a long needle) after 0.5, 1, 2, 3, 4 and 5 hours and their pH estimated using portable pH meter. The fitted long needle helped to minimise the water disturbance in the reactors so that the pH of the samples drawn from different heights in the vessels was compared to trace the source of the natural buffer secretion (roots or leaves). The effect of the number of plants on the neutralization of the ash-water was determined as in modified hydroponic by immersing (to half their height) 7, 14, 21, 28, 35 and 42 plants in the prepared ash solution for a total of 2 hours and pH of the water determined by the pH meter.

3.2.5. Column experiments

To determine the performance of the continuous flow system, two columns with diameter of 9 cm and height of 40 cm were packed with coarse sand 6 cm in the lower section, ash (7 cm) in the middle section and fine sand (10 cm) in the upper section and *Cyperus* plants in the upper most section (15 cm) as shown in Fig. 3.1. The column was set such that water driven by gravity flowed vertically upwards through coarse sand, ash, fine sand and plants in that order with influent water flowrate maintained at 0.18 L/h throughout the experiment. The lower coarse sand and the upper fine sand zones were meant to facilitate water flow and settling of the adsorbent/CaF_2 and MgF_2 particles from ash zone sandwiched between them. The actual fluoride removal and pH adjustment were meant to take place in the ash zone and plant zone, respectively. Another set of two columns packed with sand and plants without ash were used as control. The levels of fluoride, potassium and pH in the effluent water were monitored for 14 days with measurements taken every after 12 and 24 hours and every after 0.5 L of water flow.

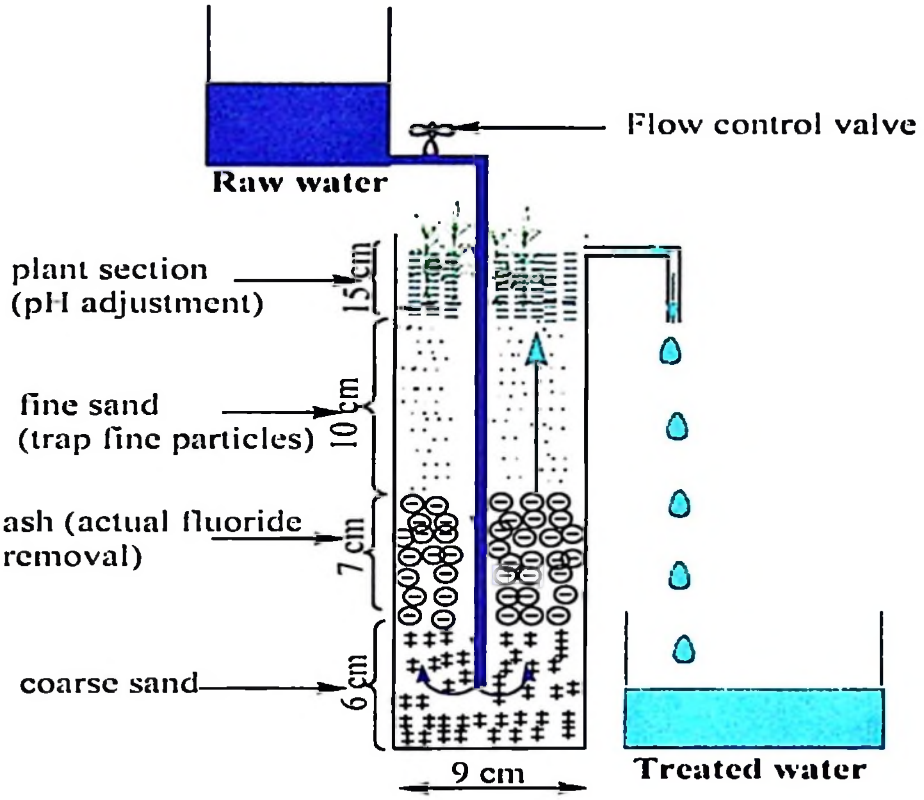

Fig. 3. 1. A vertical flow design of the constructed wetland for fluoride and pH adjustment (drawn not to scale)

3.3. Results and discussion

3.3.1. Characterisation of the ash and ash extract

XRF analysis of the raw ash used revealed that it was rich in Ca, O, Mg, K and Si with concentrations of 537.9, 301.9, 39.1, and 12.8 g/kg, respectively, as shown in Fig. 3.2a. In comparison to other reported wood ashes (Vassilev *et al.*, 2013), this ash is evidently very rich in oxides of calcium. Its Ca concentration is nearly two times higher than the average concentration of Ca in most reported wood ashes (Sakthivel *et al.*, 2012; Vassilev *et al.*, 2013). Although calcium rich wood ashes have been reported for soil fertilisation and liming (Knapp and Insam, 2011), this abundance in oxides of Ca and Mg is an advantage in its application for water defluoridation as it may be regenerated through many cycles without significantly losing its defluoridation capacity.

In the ash extract, the concentrations of K, S, Si, Na and Cl were found to be higher than in the original ash (Fig 3.2a & b). This may suggest high leaching tendency of these components when ash is placed in aqueous media. The concentrations of Ca, Al, Fe, and Mg were found to be less in the ash extract than in the original ash (Fig. 3.2a & b). This could be due to the low solubility of the oxides and carbonates (which the ash extract is rich in) of these metals in aqueous media (Knapp and Insam, 2011). For similar reasons, the concentrations of Ba, Mn and Ti was found to be zero in the ash extract (Fig 3.2b). These observations show that, when the ash with these properties is used in a proper design (and water with similar properties) there is a reduced chance of the heavy metals to leach into the treated water (Ouhadi et al., 2010; Knapp and Insam, 2011).

The presence of oxygen in the raw ash confirms that the metals in this material occur in their oxide forms, which could account for the low solubility of Ca and Mg (Knapp and Insam, 2011). Furthermore, the loss on ignition values obtained (38.81-40.12 %) suggest the presence of carbonates and hydrogencarbonates. This imply that the used ash was rich in the oxides, carbonates and hydrogencarbonates of K, Ca and Mg. It can thus be asserted that the fluoride removal process in this ash is largely by precipitation of the CaF_2 and MgF_2 salts (Piekos and Paslawska, 1999; Nath and Dutta, 2015; Darchen *et al.*, 2016) and that the presence of the carbonates could be affecting this process. This is further explained in section 3.3.2.

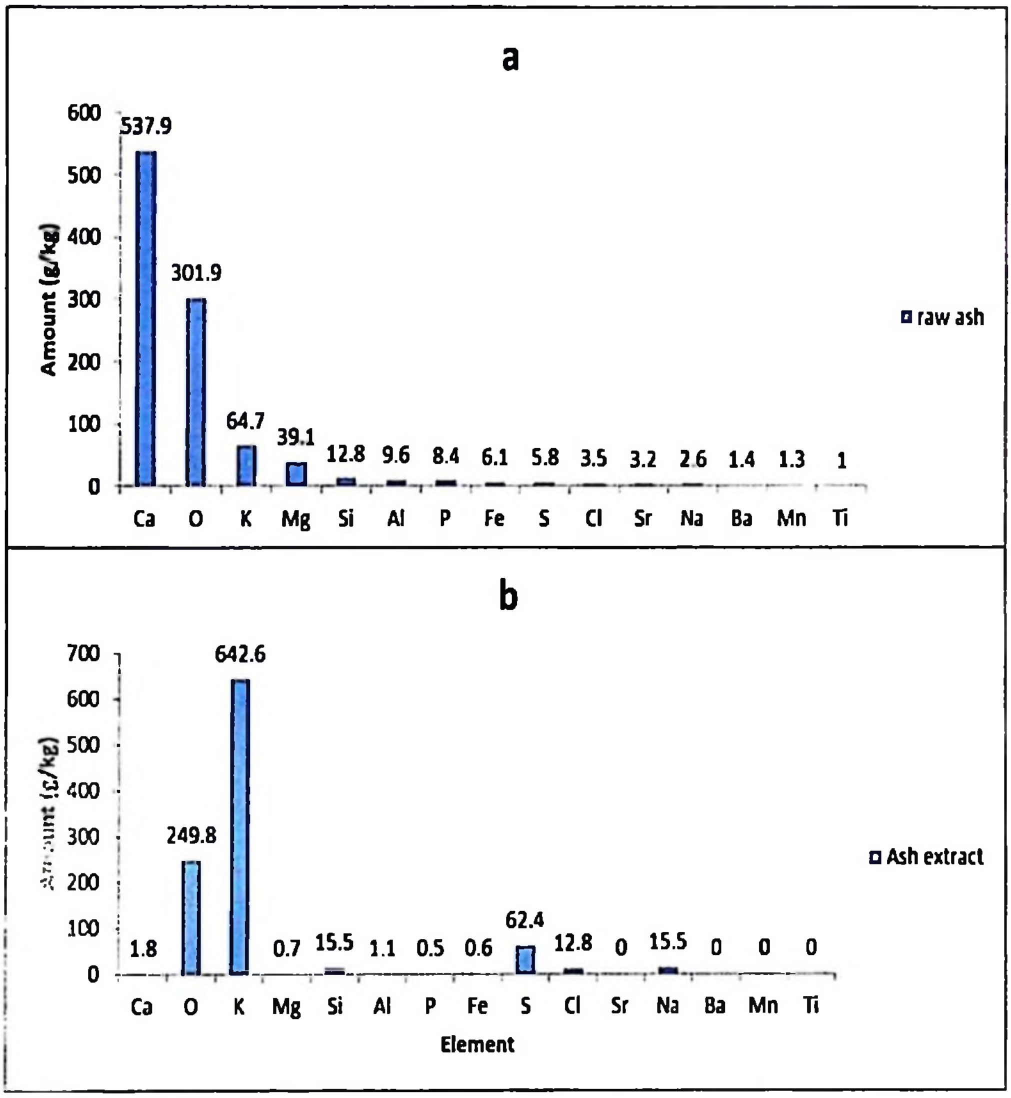

Fig. 3. 2. The chemical composition of the waste wood ash and ash-extract in batch experiments

In the continuous flow experiment, findings reveal that the concentration of the media-introduced contaminants in the treated water declines steadily with time. In the first three hours the concentration of the K was found to increase sharply from 2,578 to 5,612 mg/L as shown in Fig. 3.3. This increase could indicate that the material had not reached its maximal dissolution. A further increase of time resulted in the continuous decline in the concentration of K down to below 500 mg/L after 24 hours (Fig. 3.3). Since K ion was the most soluble component of the material, it can reasonably be used to indicate the quality of the treated water with respect to the ash-introduced contaminants. It therefore implied that the treated water will be suitable for consumption after discarding a few first aliquots. However, this makes sense if and only if its defluoridation capacity is sustained beyond this contaminant leaching time. This is further explained in the subsequent sections when the ash is used in the modified constructed wetland for water defluoridation.

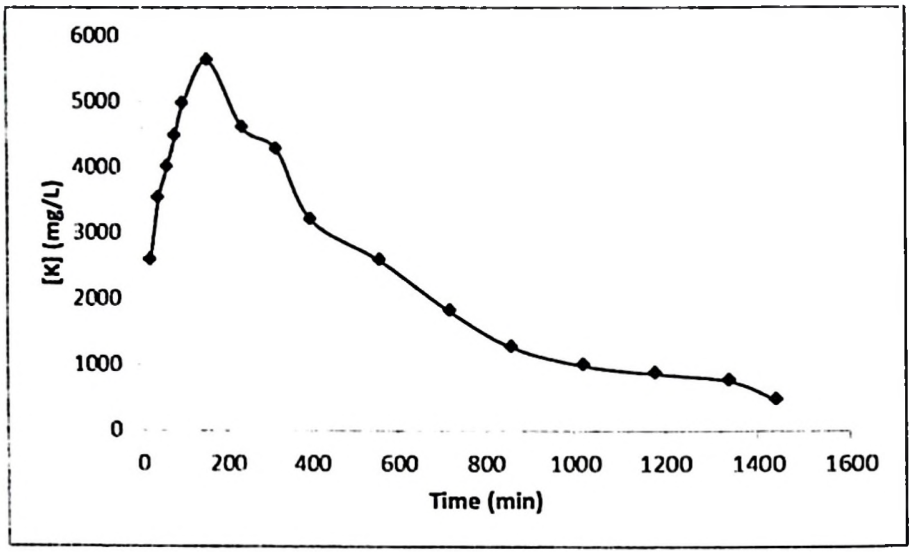

Fig. 3. 3. The effect of time on the concentration of K in the treated water at flowrate = 0.18 L/h

3.3.2. Fluoride removal efficiency in the batch experiments

Vigorous shaking of 10 g of ash and 250 mL of fluoride water for 5 minutes and allowing 30 minutes for settling, resulted in a reduction of fluoride concentration from 20.8 to 4.5 mg/L. This suggests that a large proportion of fluoride is removed when the ash particles settle down, thence, suggesting removal co-precipitation (Darchen et al., 2016). A further increase in settling time resulted in an increase of the fluoride removal efficiency from 80% at 0.5 hours to 97% after 24 hours (Fig. 3.4a), when the residual fluoride was below 0.5 mg/L.

In the partially leached ash, the fluoride removal efficiency was significantly reduced (Fig. 3.4b). After 0.5 hours, there was only 37 % fluoride removal in the partially leached ash against 80 % fluoride removal in the original ash. Since the water used for leaching was distilled water, the reduction in fluoride removal efficiency could be attributed solely to the decreased leaching tendency of Ca and Mg with time implied by the declining leaching tendency of the ash omponents explained in section 3.3.1.

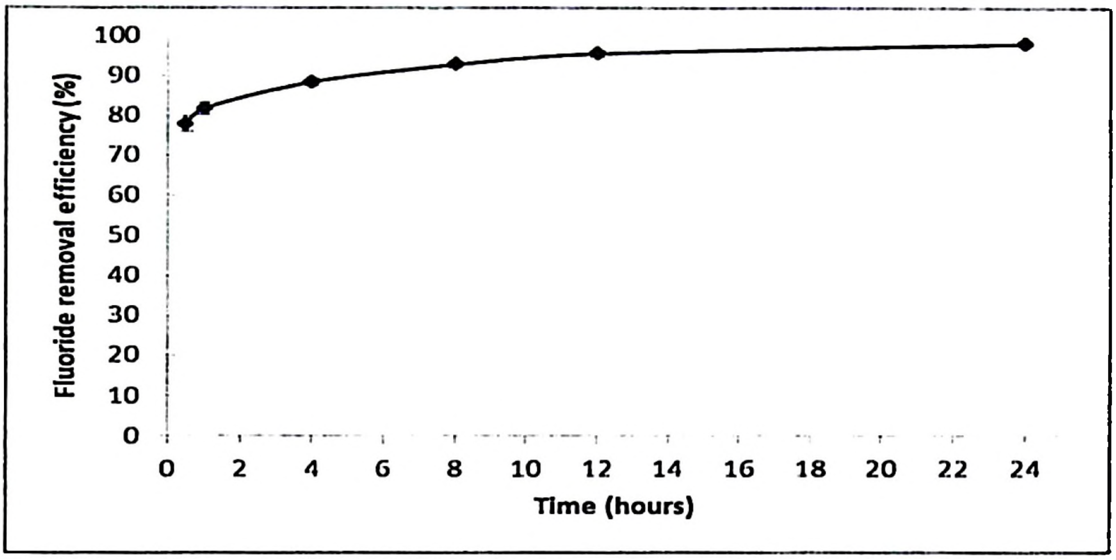

Fig. 3. 4a. The effect of time on the fluoride removal efficiency of the original wood ash at dose = 10 g/250 mL, F = 20.08 mg/L, pH = 8.3

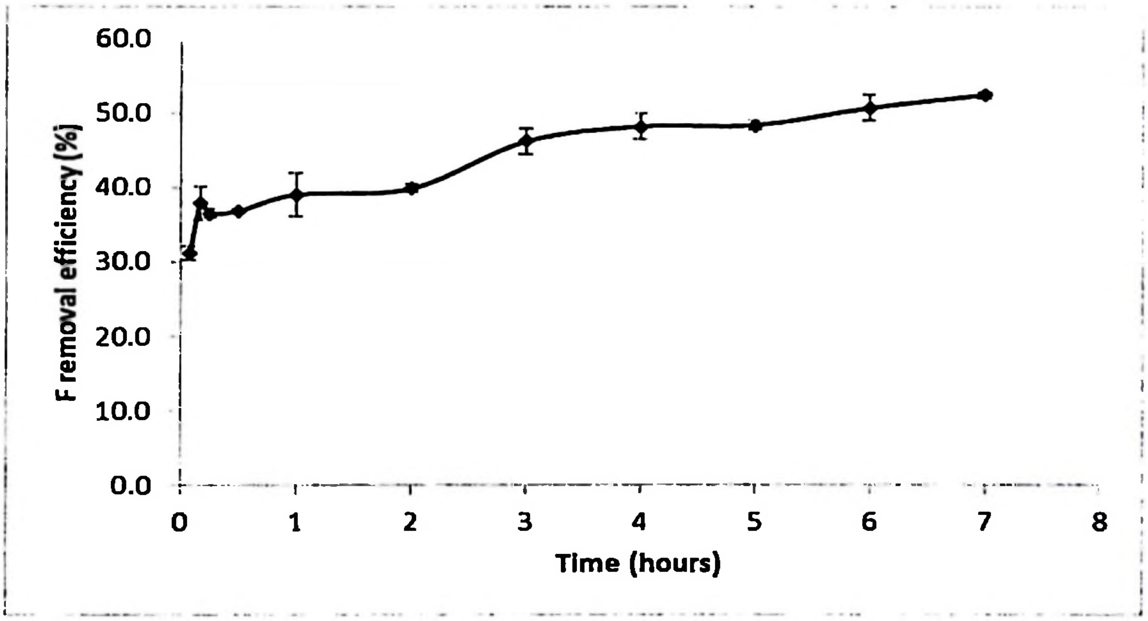

Figure 3.4b. The effect of time on the fluoride removal efficiency of the partially leached wood ash at dose = 10 g/250 mL, F=20.08 mg/L, pH = 8.3

This increasing removal with settling time could be due to co-precipiation of the ash particles with the formed fluoride salts of Ca and Mg (Nath and Dutta, 2015; Darchen *et al.*, 2016) as indicated by the high positive correlation (Table 3.1) between the decline in turbidity and the residual fluoride of the supernatant water. These results reveal that the reaction between fluoride ion and adsorbent is complete within the first 30 minutes (Bibi et al., 2017b) and that further time is required to effect settling of the ash particles and fluoride precipitates of Ca and Mg.

Therefore, a low flowrate is necessary in the column design to ensure that the fluoride precipitates do not escape to the treated water (Piekos and Paslawska, 1999). The pH of the treated water was elevated from 8.3 to an average of 12.9 in the treated water. The observed increase of the pH of the treated water can be attributed to the dissolution of oxides and carbonates of metals present in the raw ash.

Table 3. 1. The effect of time (h) on the total dissolved solid and turbidity of the ash treated water

S/N	Parameter	Before treatment	t_4	t_8	t_{12}	t_{24}
1	Turbidity (NTU)	0	79	16	2	0
2	TDS (ppm)	130	6860	7105	7230	7920
3	pH	8.3-8.5	12.1	12.4	12.9	12.9

3.3.3. The effect of solution pH on fluoride removal efficiency

Increasing the solution pH resulted in a decrease of the fluoride removal efficiency of the biomass ash, as shown in Fig. 3.5. The higher fluoride removal efficiency of the biomass ash at acidic conditions could be attributed to increased dissolution of Ca and Mg from the ash matrix and reduced competition from the carbonates. A similar trend was observed when fly ash, potato peel and rice husk ash were used in water defluoridation (Chaturved et al., 1990; Bibi et al., 2017). The dissolved Ca and Mg ions in acidic media could be responsible for increased co-precipitation of the fluorides of Ca and Mg ion (Darchen et al., 2016). The plateau between pH 5-8 could be due to the neutralising effect of the carbonates in ash material to the solution pH. This may imply that there is a pH limit above which the effect of acidity is counteracted by the present carbonates.

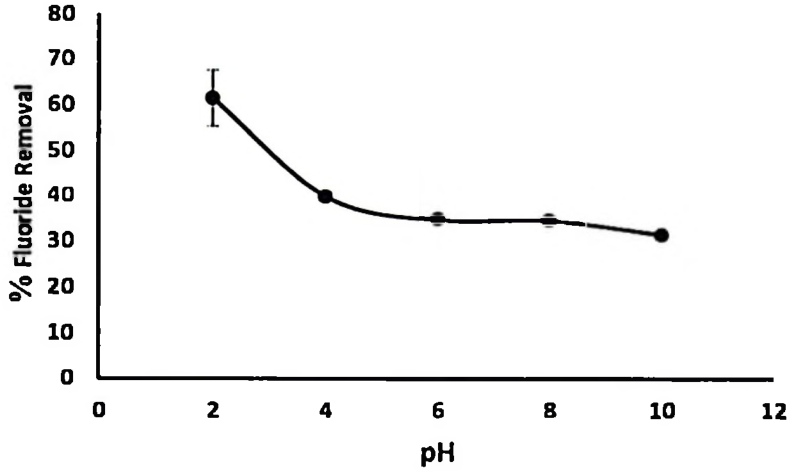

Fig. 3. 5. The effect of pH on the fluoride removal efficiency of the partially leached wood ash at F = 20.8 mg/L, dose = 10 g/250 mL, time = 2 h

3.3.4. The effect of initial fluoride concentration on fluoride removal efficiency

An increase in the initial fluoride concentration resulted in an increase in the fluoride removal efficiency by biomass ash as shown in Fig. 3.6. This increase in fluoride removal efficiency from the initial fluoride concentration of 5 to 15 mg/L could be the result of an increased probability of reaction between fluoride ion and the active site or the precipitating ions (Ca^{2+} and Mg^{2+}) before the saturation point is reached. A similar trend was observed when fly ash was used for water defluoridation (Piekos and Paslawska, 1999). This suggests that biomass ash is a potential material for fluoride removal in water with high concentrations of fluoride.

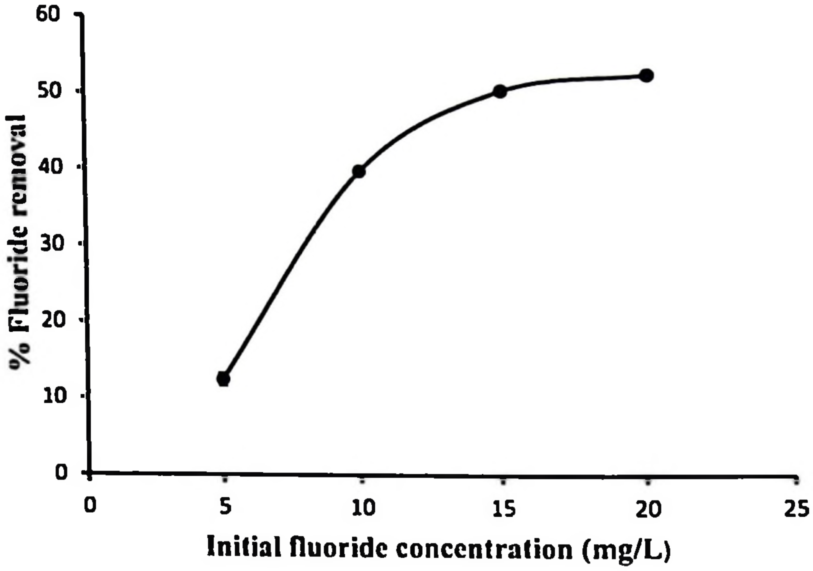

Fig. 3. 6. The effect of the initial fluoride concentration on the fluoride removal efficiency of the partially leached wood ash at dose = 10 g/250 mL, time = 2 h, pH = 8.3

3.3.5. Plant-assisted pH adjustment efficiency in the batch experiments

When ash treated water was added in a container with 35 plants (@10.0g), such that half of the plant height was immersed in water, its pH declined steadily with time from pH 12.2 to pH 7.3, at which no further decrease was observed with further increase of time. This is shown in Fig. 3.7. Interestingly, plants left in this solution for extended times, started to produce new outgrowths indicating its capability to live longer in this kind of environment. A parallel experiment using HCl treated water with pH 3.5, in place of ash-treated water showed a steady increase of pH with time from 3.5-6.8 (Fig. 3.7). This effect was found to depend on the number of plants used, where the greater the number of plants the faster the pH change.

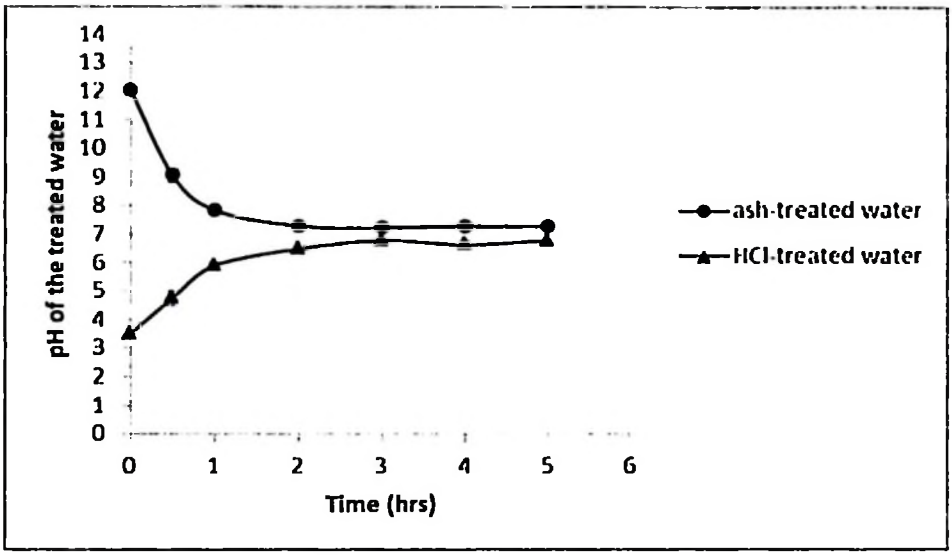

Fig. 3. 7. The effect of Cyperus plants on the pH of the treated water at dose = 350 g/L (35 plants per litre of water)

The neutralising effect of the *Cyperus* plants increased with increasing the number of plants up to the maximum dose, as shown in Fig. 3.8. This increase in the neutralising power of the *Cyperus* plant with increasing number of plants is attributable to the increasing concentration of the secreted natural exudates resulting from the increased number of plants. The attainment of a constant pH from both pH extremes (acidic and alkaline) in the pH scale suggests that, the pH adjustment mechanism involved the secretion of some form of the natural buffer by *Cyperus* plants. These natural buffers are likely the natural exudates, which these plants are rich in (El-Habashy et al., 1989; Van de Staaij et al., 2002). Samples collected from different height in the vessel revealed no significant difference in rate of neutralisation in the roots and leaves.

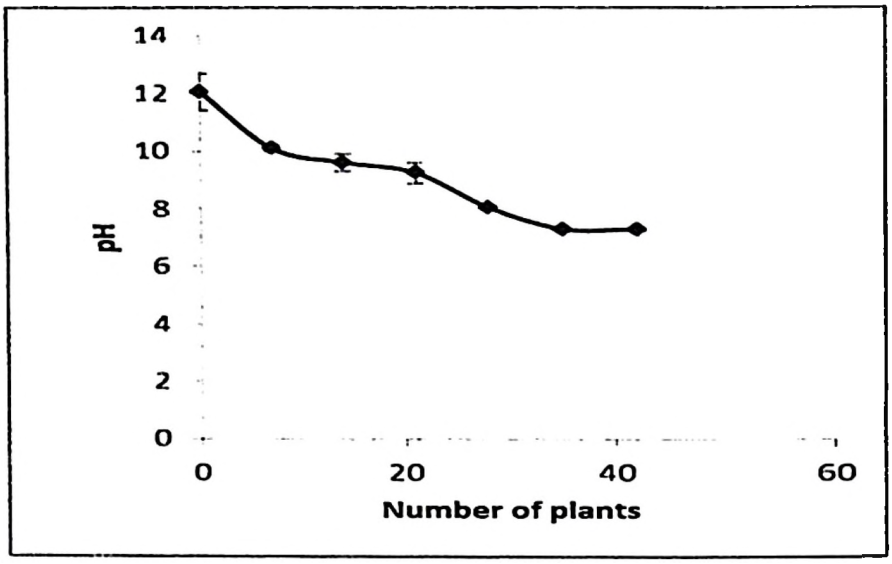

Fig. 3. 8. The effect of the plant dose on the pH of the treated water at initial pH = 12, time = 2 h

This observation indicated that the *Cyperus* exudates or their metabolites furnish H^+ to the aqueous solution, which combines with the carbonates and the hydroxyl ions as shown in equation 3.1 and 3.2. This is likely due to the instability of the natural exudates in the varying solution pH (Friedman and Jürgens, 2000). This is a novel invention, which presents a new function of these plants in the field of water treatment. It highlights the potential application of these plants in soil treatment and natural products and phytochemistry.

$CO_3^{2-} + FLV\text{-}H \rightarrow HCO_3^- + FLV^-$ (3.1)

$OH^- + FLV\text{-}H \rightarrow H\text{-}OH + FLV^-$ (3.2)

3.3.6. Performance of the constructed wetland

When coarse sand, ash and fine sand were packed in a vertical flow constructed wetland (Fig. 3.1) design, 120 g of ash was able to produce up to 10 L of the treated water, with a fluoride concentration below the WHO guideline of 1.5 mg/L at a flowrate of 0.18 L/h, as shown in Fig. 3.9. The lower flowrate was important to ensure maximum precipitation of the fluoride (CaF_2/MgF_2) salts (Piekos and Paslawska, 1999; Nath and Dutta, 2015; Darchen et al., 2016) and neutralisation of the treated water in the plant zone. A comparison of the experimental and control columns reveals that, fluoride remediation in this system is generally insignificant outside the ash zone and takes only a short time. Equally, the pH of the treated water was adjusted in the plant zone. A decline in pH of the treated water from 7.9 - 7.35 (Fig. 3.10) may be ascribed to the decline in the concentration of hydroxides in the water as more and more water washes through the ash zone.

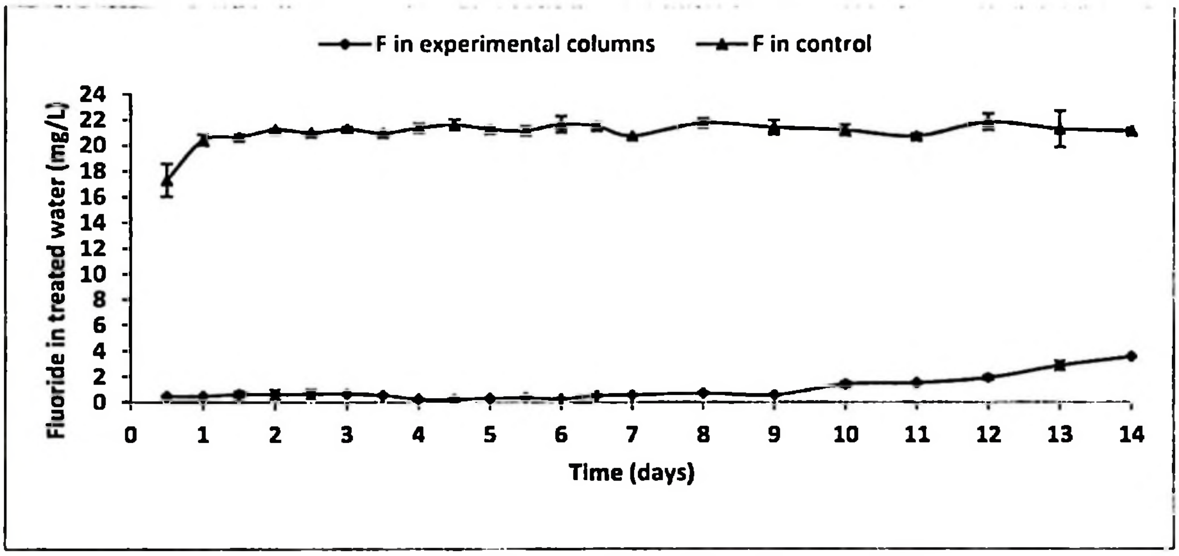

Fig. 3.9. The variation of the residual fluoride concentration in the effluent water from the designed construdted wetland at flowrate = 0.018 L/h

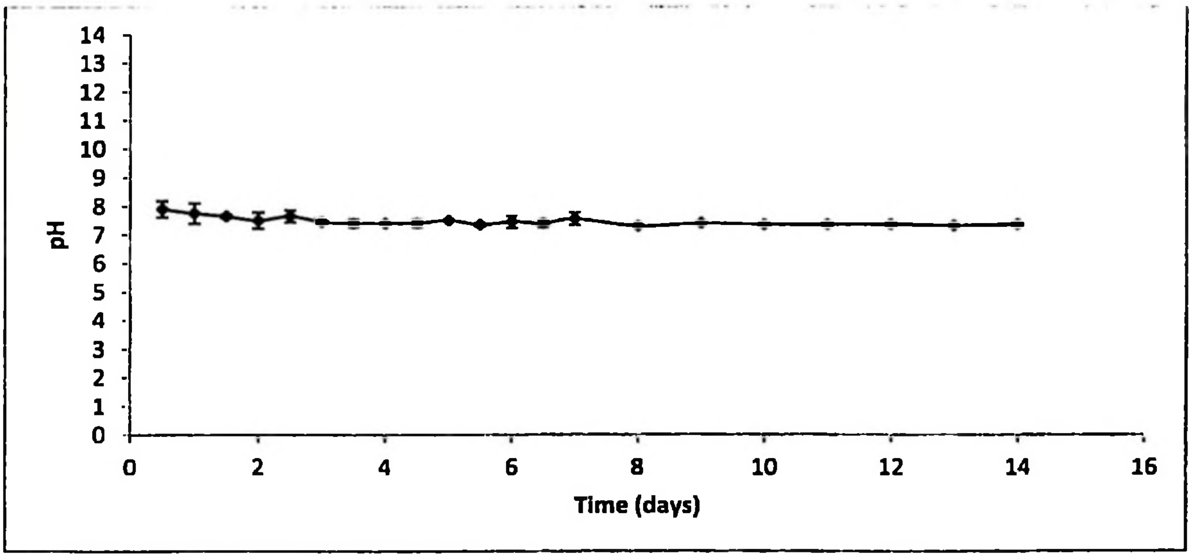

Fig. 3. 10. The variation of the pH of the effluent water from the designed constructed wetland at flowrate = 0.18 L/h

The concentration of potassium as the highly soluble component in the ash used was found to decrease steadily with time from 1653 in day 1 to below 50 mg/L in day 14. This indicates that the concentration of potassium falls steadily with time as the water washes through the ash as shown in Fig. 3.11. When this is observed in the background of the defluoridation efficiency as presented in Fig. 3.9, three litres on average need to be discarded, after which the average concentration of the K was well below 100 mg/L. Considering the total amount of defluoridated water produced, and the low toxicity of the K in concentrations below 100 mg/L (WHO, 2009), this material can be reckoned as one of the most inexpensive materials tested for water defluoridation. It is imaginable that application of biomass ash (bottom ash) for water treatment was not seriously pursued due to its property of releasing its water-soluble components into the treated water thence elevating the its pH. This study, therefore, affirms that the studied biomass ash retains its water defluoridation efficiency even after it has leached its contaminating components to acceptable levels.

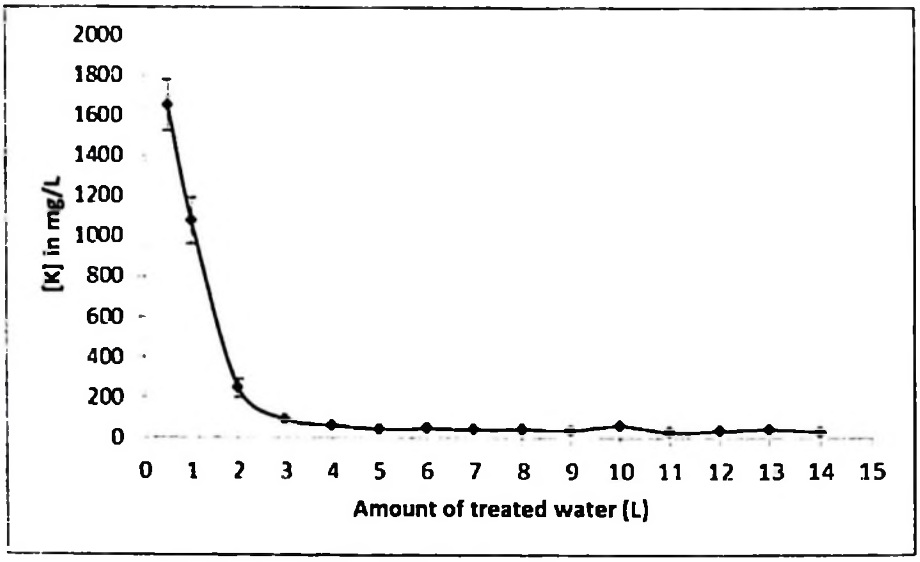

Fig. 3. 11. The variation of the concentration of K in the effluent water from the designed constructed wetland

Although waste biomass ash is well known for its application as soil liming and fertilizer material for long, its application in water treatment is not widely reported (Darchen *et al* 2016; Manna *et al.*, 2018a). Its application for water defluoridation as presented in this paper, represent a realizable and explicitly low-cost material in the water treatment arena. Therefore, this combination of the powers of the wood ash and *Cyperus* plants constitutes a facile and explicitly low-cost fluoride remediation technology in the modified constructed wetland for use among rural communities.

However, this is possible for the ash with low solubility of the toxic compounds like the one shown in Fig. 3.2. It may not be suitable for ash materials with high solubility of the toxic compounds like fly ash from coal power plants. Since the chemical composition of the ash is dependent on the type of plant and soil where the plant grows, it follows that the ash must be characterised before use to establish its chemical composition. This is important because some fuel sources (woods/charcoal) are from hard wood which may contain toxic copounds which are harmful at very low concentrations. The fluoride in the used ash could be immobilised by using this fluoride loaded ash in making bricks.

3.4. Conclusion

In this chapter it is shown that waste biomass ash (wood ash) produced from kitchens in rural Africa can be used for water defluoridation. However, the application of biomass ash in water defluoridation presents a pH alteration challenge, which can be addressed naturally and inventively by *Cyperus esculentus* plants in a constructed wetland. Interestingly, these plants keep the pH of the treated water at near neutral condition, thus reducing the need for pre-calculations to determine the required dose. The pH adjustment by this plant is likely by natural buffers (exudates) secreted by these plants in ash solutions. The applicability of this material however, is dependent on the characteristics of the ash used. The preferable ash is one that has low solubility of the toxic components. To minimize the threat of unknown toxic contaminats in the materials, efforts to activate plant biomass by known less toxic compounds are made. The defluoridation properties of these materials differ significantly even when the same activating compounds are used. In the next chapter the effect of preparation methods on the defluoridation properties is discussed.

CHAPTER 4: Water defluoridation by Fe(III)-loaded sisal fibre: Understanding the influence of the preparation pathways on biosorbents' defluoridation properties

Based on:

Mwakabona, H. T., Mlay, H. R., Van der Bruggen, B., & Njau, K. N. (2019). Water defluoridation by Fe (III)-loaded sisal fibre: Understanding the influence of the preparation pathways on biosorbents' defluoridation properties. *Journal of Hazardous Materials, 362*, 99-106.

In which the PhD researcher conducted research and wrote the first draft of the paper.

4.1. Introduction

Chemical activation of the plant biomass to enhance their fluoride removal efficiency involves the loading of the biomass materials with the chemical species that have a higher affinity for fluoride (Zhao et al., 2008; Bhatnagar et al., 2011; Cai et al., 2015; Yadav et al., 2018; Manna et al., 2018a). Some of these chemical species are Ca, Al, Fe, Zr, La, Ce and Cr (Kamble et al., 2007; Wang et al., 2007; Paudyal et al., 2011; Darchen et al., 2016; Manna et al., 2018a; Yadav et al., 2018). These chemical species enhance the fluoride removal properties of the selected biomass materials to different extents depending on the chemical properties of the materials.

In practice, different researchers have used different materials and or methods in activating plant biomass materials with the aim of developing efficacious fluoride adsorbent materials, cost-effective adsorbents or both. Interestingly, different methods used in activation biomass materials using the same chemical species showed contrasting defluoridation properties (Zhao et al., 2008; Cai et al., 2015). Therefore, a comparative study to determine the influence of the activation methods on the defluoridation properties of the resulting activated biomass is important to address this challenge. This will help in identifying appropriate methods for production of best activated materials which are efficient and low cost.

This chapter therefore, compares the fluoride removal properties of the two Fe-activated biomass materials (sisal fibres); the non-alkalised and post-alkalised Fe(III)-activated sisal fibres. The differences in defluoridation properties are highlighted and the underlying causes identified. It is expected that varying the preparation pathways of the Fe-loaded materials will help in understanding the reasons for the differences in their defluoridation properties.

4.2. Methodology

4.2.1. Materials

Sisal fibre used for this study was obtained from a sisal processing factory in Morogoro, Tanzania. This biomass was selected due to its plentiful availability as short fibres which are regarded as reject in these factories, and thus, available freely as waste. It was then washed with distilled water to remove dust and water-soluble impurities, dried and used in its original texture and size. All chemicals (Anhydrous $FeCl_3$, KNO_3 and NaOH) were reagent grade supplied by Loba Chemie (Loba Chemie and Ranken Companies, Mumbai, India). Standard stock (1000 mg/L) fluoride solutions were obtained from Hanna Instruments Company. All vessels used were strictly plastic. The fluoride levels were measured by an ion selective electrode (ISE Fluoride meter, HI 98402, Hanna Instruments Company, Romania).

4.2.2. Reagents preparation

All standard solutions (0.03 M KNO_3, 0.5 M $FeCl_3$, 0.1 M NaOH and HCl) were prepared by standard dilutions in distilled water of the corresponding pure/concentrated reagents and left overnight. Commonly studied concentrations of fluoride (5, 10, and 15 mg/L) were prepared by standard dilutions of a stock of fluoride solution (1000 mg/L) in distilled water. For synthetic fluoride water, these concentrations are widely studied by related studies. Therefore, by using these concentrations, findings from this study can be conveniently compared with findings from related studies.

4.2.3. Biosorbents preparation and characterisation

To understand the cause for the discrepancy in both performance and response to pH of the two reported Fe(III) loaded biosorbents (Fe (III)-loaded cellulose and Fe(III)-loaded tea waste) (Zhao et al., 2008; Cai et al., 2015) the two biosorbents (Fe(III)-ASF and PA-Fe(III)-ASF) were prepared by modification of the steps followed by Zhao et al. (2008) and Cai et al. (2015) in preparation of their biosorbents while mimicking the principles in their final steps. The (Fe (III)-ASF) was prepared by soaking 200 g of clean and dry sisal fibre in 1 L of a 0.5M Fe(III) chloride solution and left undisturbed for 24 h after which it was removed from the solution and washed with distilled water until colourless wash water was obtained. This action allowed impregnation of Fe(III) on the surface of biomass largely by coordination bonds facilitated by electrostatic forces between the biomass surface and the Fe(III) complex in solution (Zhao et al., 2008).

The washed Fe(III)-ASF was dried under shade until complete dryness (48 h). Half of the obtained portion of Fe(III)-ASF was soaked in sodium hydroxide solution with pH of 12 for 1 min (post-alkalization), washed with distilled water until colourless wash water was obtained and dried under shade (2 days) to prepare PA-Fe(III)-ASF. The alkalization was done to effect coprecipitation of the Fe(III) forming Fe(III) (hydr)oxide coated surfaces. The different surface characteristics of the two biosorbents were expected to result into different defluoridation properties.

The chemistry of the two biosorbents was determined in two steps: (i) establish elemental composition of the two biosorbents in comparison to the unmodified sisal fibre by XRF analysis (Spectro xepos edxrf) (ii) determine the type of interaction between Fe(III) and the biomass surface by assessing the stability of the biosorbent in aqueous media as indicated by the concentration of desorbed Fe(III) in fluoride solution. It was envisaged that biosorbents with higher concentration of desorbed Fe(III) indicate the presence of coordination bonds between loaded iron and biomass surface functional groups and the reverse indicate precipitation of insoluble Fe(III) (hydr)oxides on the surface of the biomass. Levels of Fe and Cl were compared in the two biosorbents and correlated to their defluoridation properties. The surface chemistry was established indirectly by relating the Fe(III) de-sorption tendency (stability), elemental composition and fluoride removal properties observed in different pH.

4.2.4. Adsorption experiments

All the adsorption experiments were performed as described in the methodology in Chapter 3 with slight modifications as described below.

4.2.5. Determination of the influence of post-alkalization on the biosorbents stability and defluoridation properties

The effect of each biosorbent on the pH of the treated water was estimated before and at different time intervals after treatment by a portable pH meter (PHep supplied by Hanna Instruments). Parallel measurements of the concentration of desorbed Fe(III) were taken in the treated water in both Fe(III)-ASF and PA-Fe(III)-ASF batch reactors by the method proposed by (Gojmerac Ivšić and Tamhina, 2003) by using the Multiparameter photometer (HI 83300, Hanna Instruments, Australia) at the wavelength of 466 λ.

These Fe(III) concentration values of the two biosorbents were correlated with variations in the pH of the treated water to understand the cause for the decline in pH of the treated water. To determine the role of post-alkalization on the fluoride sorption mechanism, the reactivity of the Fe (III)-ASF and PA-Fe(III)-ASF in aqueous media was compared in graphs with focus on the effect of time on the pH of the treated water and desorbed Fe(III). This was important to understand chemical stability of the two biosorbents which in turn would provide information on their different defluoridation properties. The effect of pH on the fluoride removal efficiencies of the two biosorbents was correlated with Fe(III) speciation charge in different pH using method proposed reported by (Katsoyiannis and Zouboulis, 2002) in light of their point zero charge (pzc), which was determined by the immersion technique described by (Fiol and Villaescusa, 2009). Results from this would provide useful insights on the fluoride removal mechanisms involved in the two biosorbents. The type of interaction between the metal and the biomass surface was thus deduced with reference to the established stability and elemental composition of the biosorbents obtained.

4.2.6. Defluoridation capacities and fluoride adsorption isotherms

The adsorbed fluoride was calculated by using a standard equation as follows:

$$q_e = \frac{(C_i - C_f)}{[X_{ads}]} \tag{4.1}$$

where q_e in mg/g is defluoridation capacity at equilibrium, C_i and C_f are initial and final fluoride concentrations in mg/L, respectively, and $[X_{ads}]$ is the dose of adsorbent in g/L. The data from the two biosorbents were determined by employing a data fitting method for the Langmuir and Freundlich models (Freundlich, 1906; Langmuir, 1918) and interpreted according to the following equations:

$$\frac{1}{q_e} = \frac{1}{q_{max}K_l}\frac{1}{C_i} + \frac{1}{q_{max}} \tag{4.2}$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_i \tag{4.3}$$

respectively, where q_{max}, K_l and K_f are maximum defluoridation capacity, Langmuir constant and Freundlich constant.

4.3. Results and discussion

4.3.1. Biosorbent characterisation

XRF analysis reveals that sisal fibre activation which involved loading of Fe(III) by soaking the biomass in 0.5M $FeCl_3$ solution, on average, increased levels of Fe and Cl in biomass sample from 97 and 102 to 11695 and 618 mg/kg respectively. An equivalent amount of PAFe(III)-ASF showed levels of Fe and Cl of 11172.3 and 136.2 mg/kg respectively as shown in Fig. 4.1. A decline of the concentration of Cl in the PA-Fe(III)-ASF relative to

Fe(III)-ASF, may imply that alkalization leads to substitution of Cl^- by OH^-. It is obvious from this result that; post-alkalization does not significantly reduce the amount of loaded Fe as it does to the amount of Cl. It is thus clear that discrepancy in defluoridation properties between Fe(III)-ASF and PA-Fe(III)-ASF is better accounted by a change in biosorbents' surface chemistry (from Fe(III)- chloro to Fe(III)-(hydr)oxo compounds) than by reduction in amount of Fe as is further explained in the next sections.

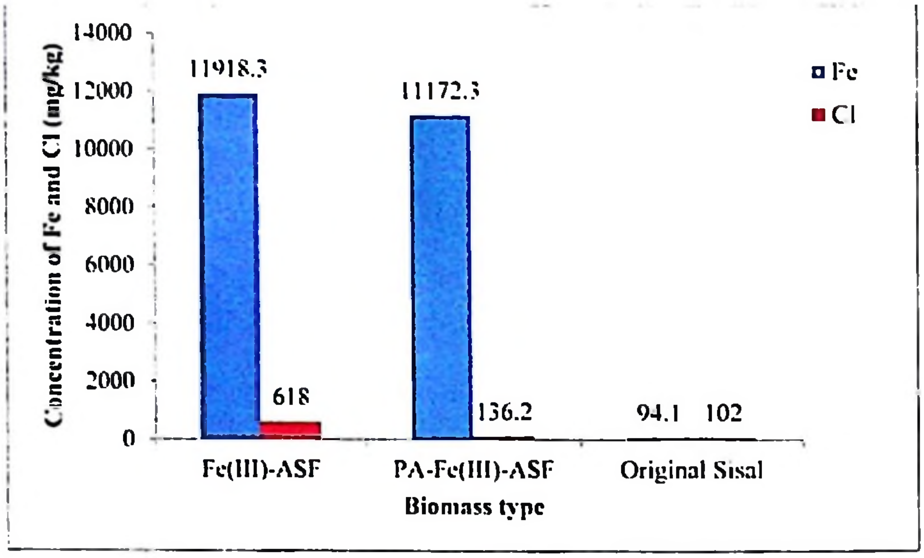

Fig. 4. 1. The concentration of Fe and Cl in the Fe(III)-ASF, PA-Fe(III)-ASF and original sisal fibres

4.3.2. The effect of contact time

When equal amounts of virgin sisal fibre, Fe(III)-ASF and PA-Fe(III)- ASF were equilibrated in 10.2 mg/L fluoride solution and samples drawn at intervals of 5, 15, 30, 60 min and every after two hours for 24 h, the fluoride removal efficiency was found to increase rapidly in the first few minutes and reach equilibrium with efficiency of 81% (Fe (III)-ASF), 37% (PA-Fe(III)-ASF) and 22% (virgin sisal fibre) in neutral aqueous media as shown in Fig. 4.2. While the removal remained constant after equilibrium for Fe(III)-ASF and PA-Fe(III)-ASF, it declined for virgin biomass to<10% in the same period of time. It is clear from the Fig. 4.2 that a higher removal occurs in the first 60 min. thence, one hour was taken as the optimal time for further experiments.

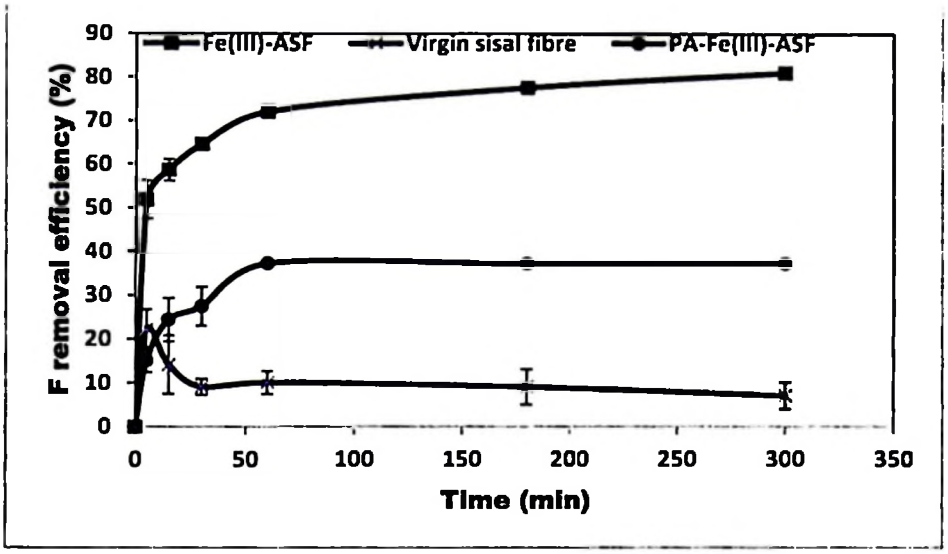

Fig. 4. 2. The effect of time on the fluoride removal efficiency at pH = 7.2, dose = 0.02 kg/L and F = 10.2 mg/L

The higher increase of defluoridation efficiency in the first 60 min indicates that these materials have a higher affinity for fluoride ion in aqueous media. Similar trends were reported by other related studies (Zhao et al., 2008; Cai et al., 2015; Zhang et al., 2015). As the number of active sites decreased (with increase of time), the increase of fluoride removal efficiency (from 60 to 300 min) was small for Fe(III)-ASF and PA-Fe(III)-ASF. The levelling of the efficiency curve with further increase of time could imply that the interaction between the fluoride ion and the active site is permanent as opposed to temporary in the virgin sisal fibre and that the equilibrium state was already attained. The difference in removal efficiencies between Fe(III)-ASF and PA-Fe(III)-ASF is attributable to both the chemistry of the surface of the biosorbent as explained in Section 4.3.1 and the type of interaction between the active site and the fluoride ion, as will be explained in the following sections.

4.3.3. The effect of dose

The progressive increase of Fe(III)-ASF and PA-Fe(III)-ASF biosorbent dose from 0.1 to 1 g resulted in the increase of the fluoride removal efficiency from 20 to 77 and 10-34 % respectively when equilibrated for 1 h. The fluoride removal efficiency was found to be rapidly increasing up to the dose of 0.02 and 0.015 g/mL (=kg/L) for Fe(III)-ASF and PA-Fe(III)-ASF respectively, as shown in Fig. 4.3. A further increase did not result into any significant increase in the removal efficiency. The difference in the optimal dose between the two biosorbents could be indicating the difference in the number of active sites in the studied biosorbents. It could also imply the decline in the number of active sites as a result of post-alkalization in this experiment. The increase of fluoride removal efficiency with an increase of dose could be attributed to an increase in the number of active sites (Zhao et al., 2008; Cai et al., 2015; Manna et al., 2018b; Yadav et al., 2018). As the dose is increased beyond optimal (0.02 and 0.015 kg/L for Fe(III)- ASF and PA-Fe(III)-ASF respectively), the compaction of the sisal fibre due to its low density (Bisanda and Ansell, 1991) in the small solution volume could be suppressing the effect of increasing active sites by active sites overlapping at higher dosage.

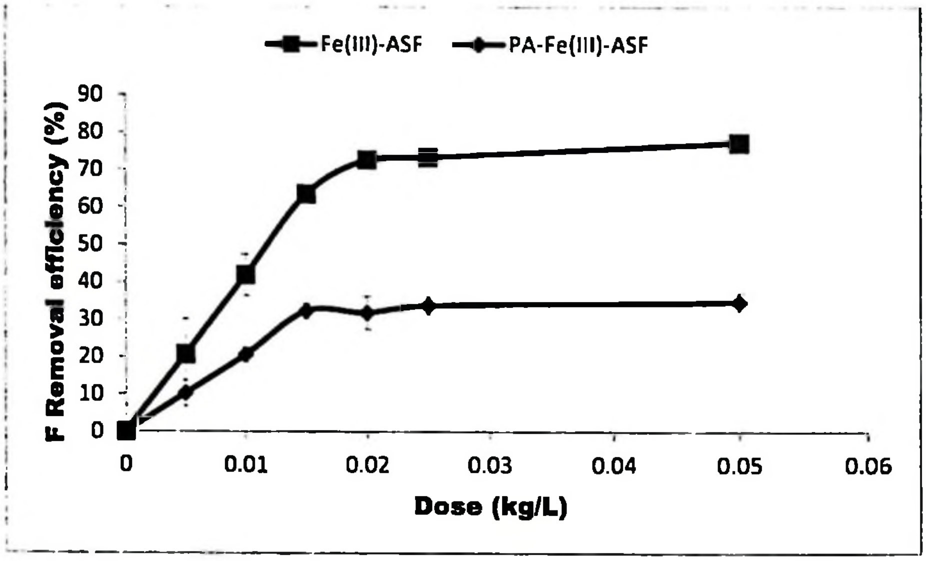

Fig. 4. 3. The effect of dose on the defluoridation efficiency of the Fe(III)-ASF and PA-Fe(III)-ASF at time = 60 min, F = 10.2 mg/L, pH = 7.2

4.3.4. The effect of initial fluoride concentration

The effect of variation of fluoride concentrations at 5, 10 and 15 mg/L on the Fe(III)-ASF and PA-Fe(III)-ASF resulted in a removal efficiency of 54, 73 and 68 and 28, 31 and 43% after 60 min equilibration for Fe(III)-ASF and PA-Fe(III)-ASF, respectively, as shown in Fig. 4.4. The increase of fluoride removal efficiency from 57 to 73% when the fluoride concentration is increased from 5 to 10 mg/L (in Fe(III)-ASF) could suggest the involvement of the coagulation/precipitation reactions between Fe^{3+} and F^- in fluoride removal along with adsorption. The slight decrease at 15 mg/L might be due to an increased effect of formation of soluble fluoro-complexes of Fe(III), which might take part in desorbing the loosely held Fe(III) ions from the surface of the adsorbent (Nordstrom and Jenne, 1977; Krishnamurti and Huang, 1990; Gendel and Lohav, 2008), reducing the number of active sites. This is confirmed by the decrease of the spectrophotometrically detectable concentration of Fe(III) with time when the fluoride solution is equilibrated with Fe(III)-ASF for extended periods. This phenomenon is not observed in the PA-Fe(III)-ASF where the removal efficiency appears to increase with increasing initial fluoride concentrations, likely because of the nature of interaction between F ion and the surface of this biosorbent (Cai et al., 2015).

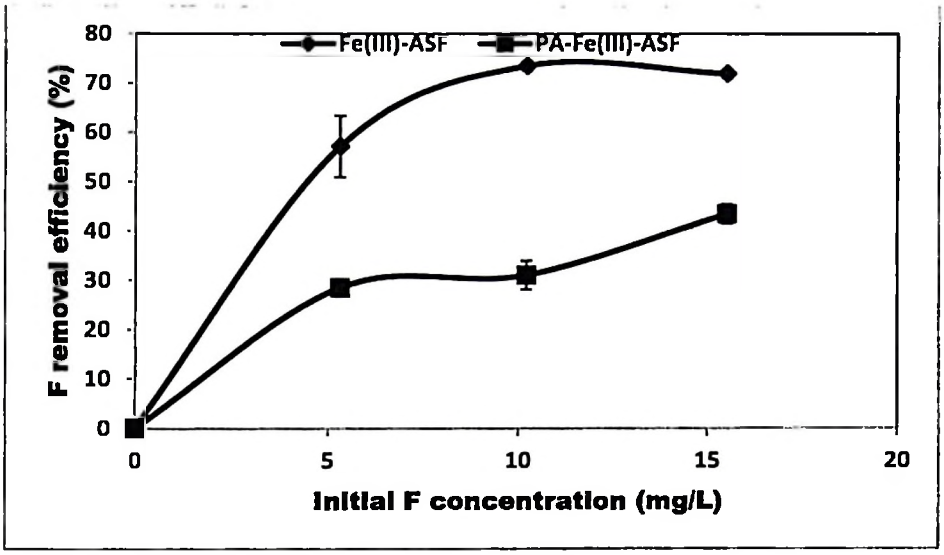

Fig. 4. 4. The effect of initial fluoride concentration on the fluoride removal efficiency at pH = 7.2, time = 60 min, dose 0.02 kg/L

4.3.5. The effect of pH

By increasing the pH from 2 to 4, an increased fluoride removal efficiency from 44% at pH 2 to 59% at pH 4 was observed. A further increase in pH resulted in a small increase in efficiency up to 66% at pH 8 when Fe(III)-ASF was used. To understand the effect of the biosorbent preparation pathway on the initial pH of the fluoride water, the PA-Fe (III)-ASF biosorbent, for which the preparation involved post-alkalization, was used in the same condition. The efficiency decreased steadily from 53-16% with an increase in pH from pH 2-10. Fig. 4.5 shows the contrasting trends in response to the effect of changing pH of the two biosorbents (Fe(III)-ASF and PA-Fe(III)-ASF). Moreover, Fe(III)-ASF showed a higher fluoride removal efficiency in a wide pH range. The increase of fluoride removal efficiency with increasing pH when Fe(III)-ASF is used can be attributed to the increasing stability of the biosorbent (Zhao et al., 2008) as observed in decreasing tendency of desorption of Fe (III) (Table 1). At low pH, some actives sites on the surface of the biosorbent are destroyed by desorption of the Fe(III). This was confirmed by the higher concentration of desorbed Fe(III) observed at lower pH, and is in line with Fe(III) speciation in different pH conditions (Katsoyiannis and Zouboulis, 2002). From pH 4-8 the removal efficiency was maintained high for the Fe(III)-ASF biosorbent. This suggests that the removal efficiency is less affected by pH as implied by low pzc (3.5) and is high in a wider pH range. This finding thus supports that the plausible mechanism of fluoride removal when Fe(III)-ASF is used is ligand exchange reaction than electrostatic interactions (Zhao et al., 2008). Conversely, in PA-Fe(III)-ASF, the decrease in removal efficiency with increasing pH can be attributed to the decreasing charges on the surface of the adsorbent with increase in pH. This is confirmed by strong negative correlation (−0.98) between pH change and charge variation. Similar findings were reported by Cai et al. (2015) when they used tea waste loaded with Fe(III) in which surface charges increase with decreasing pH (Katsoyiannis and Zouboulis, 2002; Kumar et al., 2014; Sujana and Anand, 2014). A close look at the pathway followed in loading Fe(III) in both cotton cellulose (Zhao et al., 2008) and tea waste (Cai et al., 2015) reveals that while the preparation of the former did not involve alkalization in the final stage, that of the latter did. Thus, although OH ion exchange with fluoride ion as proposed by Cai et al. (2015) is still a valid mechanism at nearly neutral conditions, electrostatic interaction appear to have a significant influence in the removal efficiency of the PA-Fe(III)- ASF in acidic media. It can thus be asserted that post-alkalization in preparation of Fe(III) loaded biosorbent diminishes the chance of ligand exchange reaction on the adsorbent surface in acidic media, as it leads to the formation of ferric (hydr)oxides interaction of which is by electrostatic forces (Kumar et al., 2014; Cai et al., 2015). This is supported by other findings on defluoridation by Fe(III) (hydr)oxides materials, where all showed higher fluoride removal in acidic pH (Kumar et al., 2014; Sujana and Anand, 2014; Ndc-Tchoupe et al., 2015). The pzc of 8 of the PA-Fe(III)-ASF confirms the similarity of the surface chemistry of PA-Fe(III)-ASF and the Fe(III) (hydr)oxides (Kumar et al., 2014; Mwakabona et al., 2017; Yadav et al., 2018).

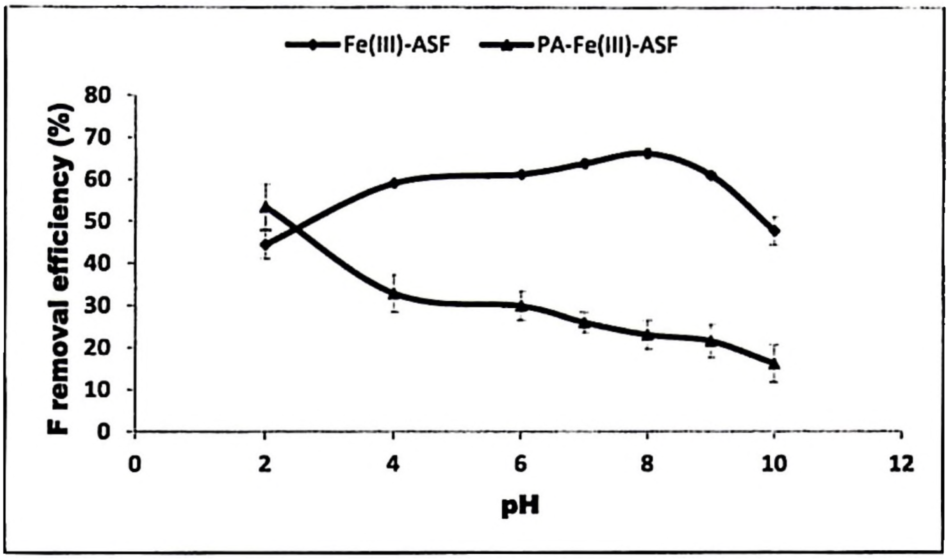

Fig. 4. 5. The effect of pH on the fluoride removal efficiencies of Fe(III)-ASF and PA-Fe(III)-ASF at dose = 0.02 kg/L, F concentration = 10.2 mg/L, time = 60 min.

4.3.6. The influence of post-alkalization on biosorbent stability and defluoridation properties

The pH of the untreated water was found to range between 7-7.2, while the pH of the treated water by Fe(III)-ASF decreased steadily from 7 to 3.0 in the first few hours (Fig. 4.6). For this biosorbent, the concentration of desorbed Fe(III) increased with time from 13 mg/L to 22 mg/L between 5 min and 60 min. For the PA-Fe(III)-ASF, the pH of the treated water increased from 7.2 to 8 while the concentration of desorbed Fe(III) remained very low (< 0.2 mg/L) throughout the time (Fig. 4.6) at neutral conditions. The comparison of the variation of concentration of desorbed Fe(III) with time reveals that Fe(III)-ASF is chemically less stable than PA-Fe (III)-ASF. This phenomenon is accentuated when the pH is varied, as shown in Table 4.1. This in turn would suggest the existence of coordination bonds between the Fe(III) ions and the functional groups on the biomass surfaces in Fe(III)-ASF (Zhao et al., 2008; Xu et al., 2016), and the existence of ferric (hydr)oxides surfaces in PA-Fe(III)-ASF. The pzc of these biosorbents (Fe(III)-ASF and PA-Fe(III)-ASF) and that reported in the literature for Fe (III) loaded biosorbents and ferric (hydr)oxides confirm this assertion (Chesworth, 2007; Zhao et al., 2008; Kumar et al., 2014; Sujana and Anand, 2014; Cai et al., 2015; Nde-Tchoupe et al., 2015; Mwakabona et al., 2017). The decrease of pH with time in Fe(III)-ASF can be attributed to the presence of desorbed Fe(III) in treated water, due to the low stability of the adsorbent. This is confirmed by the positive correlation between the pH change in the treated water and the concentration of desorbed Fe (III) (Fig. 4.7). The increasing pH of the treated water by PA-Fe(III)-ASF could be due to the exchange reaction between fluoride in water and hydroxyl ions on the adsorbent surface (Krishnamurti and Huang, 1991; Katsoyiannis and Zouboulis, 2002; Cai et al., 2015). The relatively low concentration of the desorbed Fe(III) in solution when PA-Fe(III)-ASF was used could imply that inclusion of post-alkalization in biosorbent preparation pathway results in precipitation of the Fe(III) (hydr)oxides on the biomass surface rather than coordination bonds between the metal and the biomass functional groups. Conversely, the pathway followed in the preparation of Fe(III)-ASF, produced biosorbents for which the interaction between metal ions and the biomass surface is through coordination bonds (Zhao et al., 2008; Xu et al., 2016; Manna et al., 2018b). This is understandable since the postactivation alkalization should have precipitated all the loosely bonded Fe(III) into iron(III) hydroxides (Vance, 1994) as confirmed by the different stabilities of the studied biosorbents. When the surface charge/speciation of Fe(III) was correlated with the fluoride removal efficiencies of the two biosorbents, a positive (0.98) and negative (0.19) correlation was observed for PA-Fe(III)-ASF and Fe(III)-ASF, respectively. This is shown in Fig. 4.7. In the Fe(III)-ASF, the increase in fluoride removal efficiency with increase of pH paralleled the decrease of desorbed Fe(III) (Table 1), which was in line with the Fe(III) speciation in varying pH (Vance, 1994; Katsoyiannis and Zouboulis, 2002). The fact that the removal efficiency trend in Fe(III)-ASF is opposite to the trends of both the Fe(III) speciation/charge and desorbed Fe(III) confirms that the removal mechanism is not principally influenced by the adsorbent surface charge and that desorption of Fe(III) affects the number of active sites, thus lowering the removal efficiency. Therefore, the removal mechanism in this biosorbent is mainly by ligand exchange between the Cl- on the biosorbent and the F- ion in the aqueous media, as proposed by Zhao et al. (2008). A small change of removal efficiency between pH 4-8 above its pzc (3.5) confirms also that the surface charge has less influence on the fluoride uptake. For PA-Fe(III)ASF, the decrease in removal efficiency with increase of pH (2-10) parallels the change of charge/speciation of Fe(III) and the concentration of residue Fe(III) in the studied pH range (Figs. 4.6 & 4.7). Therefore, the decrease in removal efficiency with increase of pH is attributable to the decrease of electrostatic forces caused by the decrease in surface charges. This is confirmed by the higher pzc (8.0) and the speciation of the Fe(III) in changing pH environments. This trend was also reported by Cai et al. (2015) and is common when the adsorbents have ferric (hydr)oxides surfaces (Chesworth, 2007; Avilés et al., 2013; Jahin, 2014; Kumar et al., 2014; Sujana and Anand, 2014). It can thus be asserted that the fluoride removal mechanism in ferric (hydr)oxide surfaces is principally by electrostatic forces between the adsorbent surface and the fluoride ion in aqueous media. This is confirmed by the strong positive correlation (0.98) between the removal efficiency and the surface charge and the residual Fe(III) observed (Fig. 4.7). Although ion exchange reactions remain a plausible mechanism at ca. neutral conditions, it is less likely to have a significant contribution in acidic media. This is due to the action of acid on the ferric (hydr)oxide surfaces forming positively charged surfaces (Manna et al., 2018b; Yadav et al., 2018). Findings from this study and similar findings reported elsewhere when biomass loaded with Fe(III) was used for water defluoridation reveal that surfaces with -Fe-Cl functional groups perform well in a wide pH range and are less stable in acidic environments while when hydrous ferric hydroxide coated biomass/sorbents are used for water defluoridation, a higher fluoride removal is observed in acidic media, and they are more stable in acidic environments (Zhao et al., 2008; Kumar et al., 2014; Sujana and Anand, 2014; Cai et al., 2015; Manna et al., 2018b; Yadav et al., 2018). These results may also help to understand reported low fluoride removal efficiencies at nearly neutral conditions of the of the ferric (hydr)oxides based adsorbents (Avilés et al., 2013; Jahin, 2014; Nitzsche et al., 2015) besides the presence of ferric (hydr)oxide rich surfaces in the systems. It can also be asserted from these findings that NaOH based regeneration in non-alkalized Fe(III)-activated biomass may lead to a change of the chemistry of the original Fe(III)-loaded biosorbents leading to changes in defluoridation efficiency. These findings indicate that NaOH regeneration of the non-alkalized Fe(III)-loaded biosorbents may introduce new functional groups (ferric (hydr)oxides) (Zhao et al., 2008) that may alter their defluoridation properties, thence, calling for regeneration by Fe(III) salt solutions than NaOH solutions (Zhang et al., 2015).

Table 4. 1. The effect of pH on the desorption of Fe and F removal efficiency of the Fe(III)-ASF and PA-Fe(III)-ASF

pH	Fe(III)-ASF		PA-Fe(III)-ASF	
	[Fe(III)] desorbed	F removal efficiency (%)	[Fe(III)] desorbed	F removal efficiency (%)
2	51.8	44.4	1.4	53.4
4	22.5	59.0	0.5	32.8
7	13.2	63.8	0.19	26.0
8	9.1	66.3	0.19	23.0
9	6.1	61.0	0.17	21.6
10	3.0	47.7	0.20	16.2

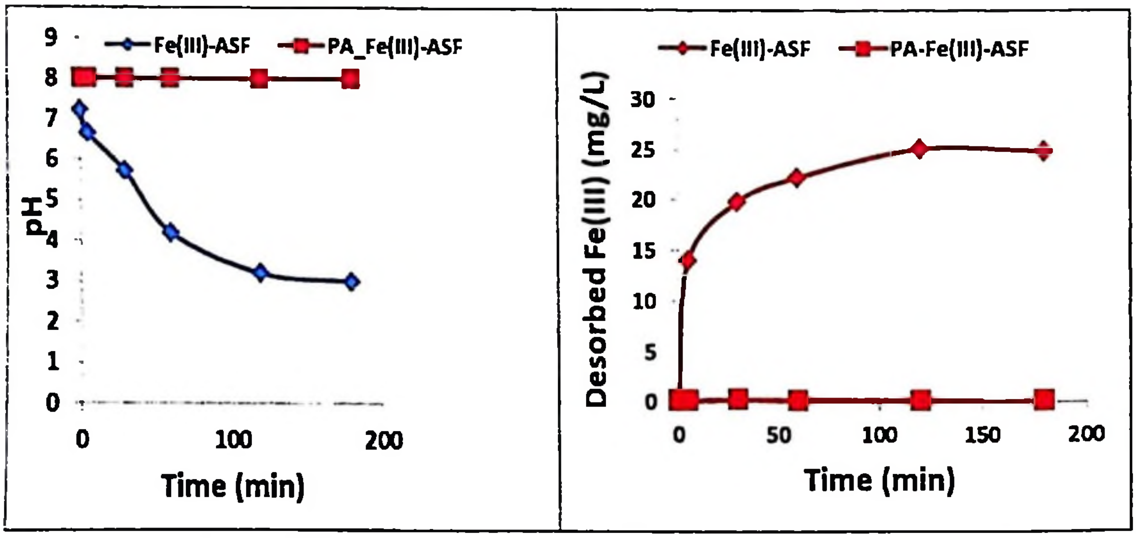

Fig. 4. 6. The effect of time on the pH and concentration of desorbed Fe in the treated water

4.3.7. Defluoridation capacity and fluoride adsorption isotherms

The defluoridation capacity (DC) of Fe(III)-ASF and that of PA-Fe(III)-ASF as determined by Langmuir model is found to be 0.4 and 0.2 mg/g, respectively, around neutral conditions. The R^2 values from the Langmuir and Freundlich isotherms reveal that both biosorbents fit well in the Langmuir and Freundlich model with R^2 values of 0.99 versus 0.99 and 0.99

versus 0.98 for Fe(III)-ASF and PA-Fe(III)-ASF in the Langmuir and Freundlich models, respectively. This is shown in Fig. 4.8. The RL factor for both biosorbents in the studied initial concentrations showed that adsorption is close to linear; R_L=0.89 at lower initial fluoride concentrations and 0.70 at higher concentrations. This is indicative that for these adsorbents, high fluoride removal is favourable at higher concentration. The defluoridation capacity of the Fe(III)-ASF is twice as high as that of PA-Fe(III)-ASF in neutral aqueous media. This can be attributed to the type of interaction between the F- ion in water and the active sites. Since the ligand exchange reaction leads to coordination bonds between the metal on the active site and the F- ion (Zhao et al., 2008; Xu et al., 2016) and that Fe (III) can form a maximum of six coordination bonds, it follows that more than one F- ion can coordinate to Fe(III) in active site. This is difficult for the PA-Fe(III)-ASF due to factors such as the type of interaction between the biomass and the Fe(III) which is coating of the (hydr)oxides of Fe(III) on the biomass surface, and the type of interaction between active site and F-, which plays an important role, namely electrostatic interactions. The defluoridation capacity of PA-Fe (III)-ASF close to that of Fe(III)-ASF in acidic media, where the PA-Fe (III)-ASF is highly charged as explained above.

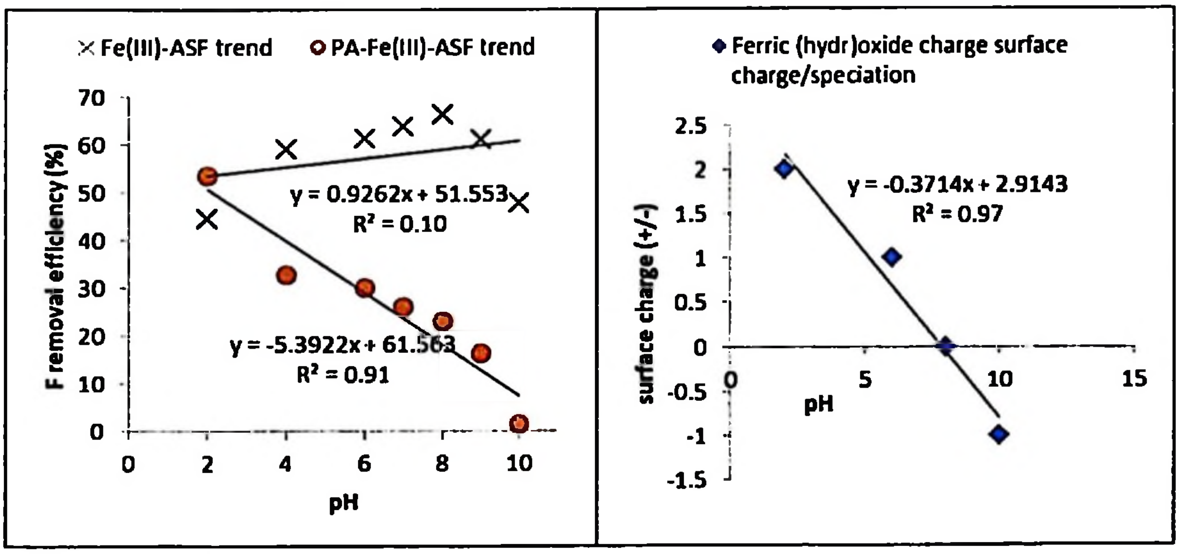

Fig. 4. 7. The relationship between removal efficiency and charge/speciation of Fe(III) in varying pH

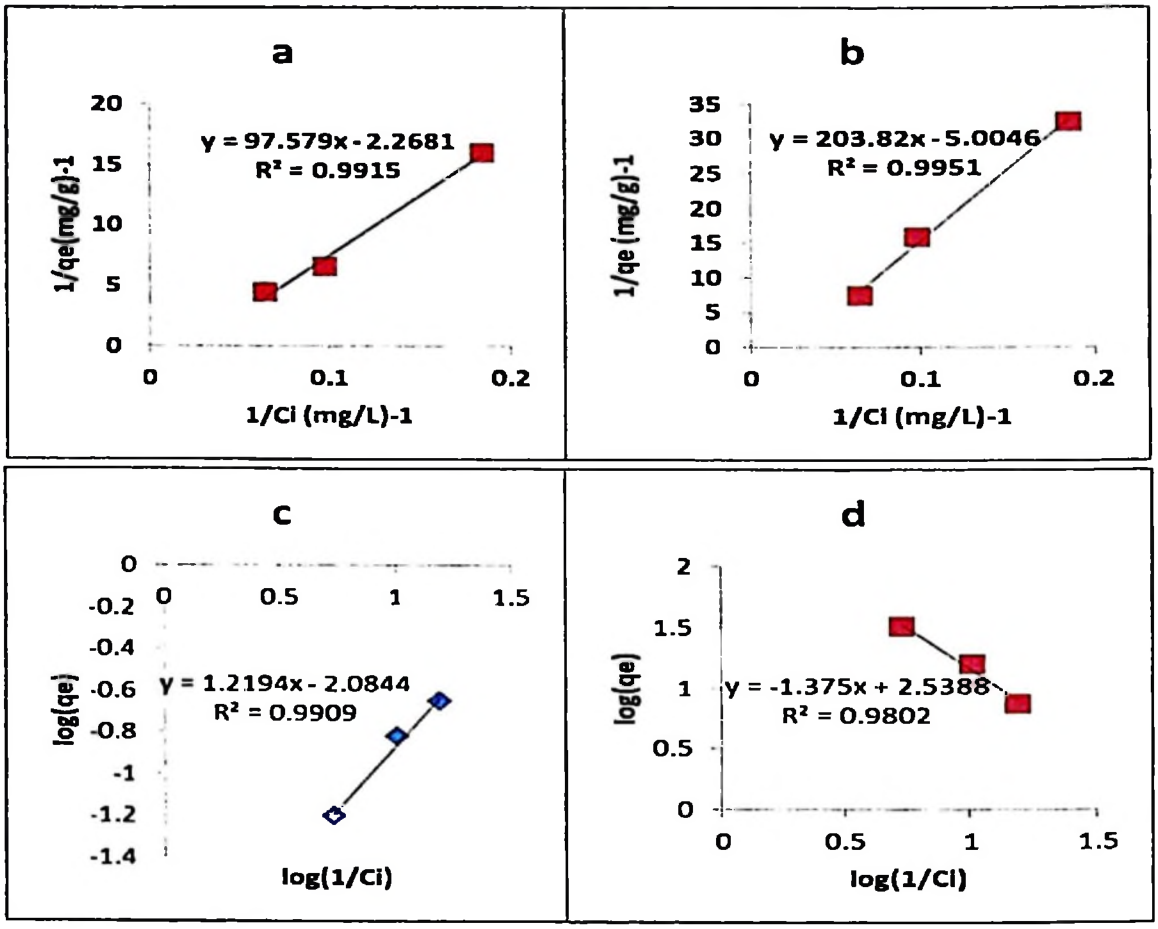

Fig. 4. 8. The Langmuir (a and b) and Freundlich (c and d) adsorption isotherms plots for Fe(III)-ASF and PA-Fe(III)-ASF biosorbents

The isorthem studies presented in Fig. 4.8 are not comprehensive as only a few data points were used. These findings cannot be used to represent the maximum defluoridation capacities of the materials prepared by these methods. As explained in the previous sections the major aim of the chapter was to present the possible causes for the observed difference in defluoridation properties of the iron-loaded plant biomass materials. Therefore, the isotherm results presented here can be regarded as the capacities at the studied conditions.

4.4. Conclusion

Disparities in Fe(III)-loaded biosorbents preparation pathways appear to alter the defluoridation properties of the resulting activated materials. Findings from this study reveal that inclusion of post-alkalization of the Fe(III)-loaded biosorbent alters their defluoridation properties by increasing their chemical stability while restricting higher removal efficiencies in acidic pH. Therefore, exclusion of this procedure in the final preparation steps will enable the biosorbent to be effective in a wide pH range, at the cost of its chemical stability. The strong positive correlation between the Fe (III) speciation charge at variable pH of the post-alkalized biosorbent (PA-Fe(III)-ASF) suggests that the principal fluoride removal mechanism is by electrostatic interactions between F^- in aqueous media and biosorbent surface and ligand exchange between F^- in aqueous media and Cl on biosorbent surface in the Fe(III)-ASF. The non-alkalised Fe(III)-activated biomass is highly unstable in aqueous media and has higher fluoride removal efficiency at neutral conditions. This suggests that understanding the properties of iron materials in aqueous media may improve our knowledge and help in finding other forms of iron that can best be used for water defluoridation. The next chapter presents the historical application of iron for water treatment highlighting their forms and properties while drawing important lessons on properties of iron in aqueous media. This lost knowledge will shed more light on the contemporary controversies in the properties of iron in aqueous media.

CHAPTER 5: Metallic iron for safe drinking water provision: Considering a lost knowledge

Based on:

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In which the PhD researcher conducted literature research and wrote the first draft of the paper.

5.1. Introduction

Metallic iron (Fe^0) is about to be established as an excellent filling material for decentralized safe drinking water filtration systems (Fe^0 filters) (Ngai et al., 2006; Hussam and Munir, 2007; Noubactep et al., 2009; Antia, 2010, 2011; Giles et al., 2011; Noubactep et al., 2012; Gottinger et al., 2013; Antia, 2014; Chaudhari et al., 2014; Kowalski and Sogard, 2014; Wenk et al., 2014; Antia, 2016; Noubactep, 2016a; Smith et al., 2017). The path to achieved prominence was rocky as design issues challenged Fe^0 filter's researchers (Noubactep et al., 2012; Car_e et al., 2013; Noubactep, 2013, 2014; Domga et al., 2015; Noubactep, 2015; Noubactep, 2016b, 2016c). For example, the embodiment mistake impairing the sustainability of the Kanchan Arsenic Filter (KAF) (Ngai et al., 2006, 2007) as demonstrated by Noubactep et al. (2012) has not yet been considered by active researchers (O_2 scavenging impairs BSF operation). On the contrary, investigators are still using the criticized original KAF. Two recent examples are (i) Wenk et al. (2014) redemonstrating the inefficacy of the original KAF and (ii) Smith et al. (2017) comparing the original KAF to a SONO-like filter, without considering the evidence that all tested Fe^0-based filters impair the functionality of the biosand filter (BSF). In essence, a BSF is a stand-alone efficient filter to reduce the concentration of pathogens (Wegelin et al., 1991; Sarkar et al., 2015). An efficient BSF uses dissolved O_2 to build and maintain a biofilm (e.g. Schmutzdecke) some 10 cm below the resting water (Lea, 2008). Accordingly, any O_2 scavenger (here Fe^0) placed before a BSF impairs its functionality (Noubactep et al., 2012). The Fe^0 filter technology as investigated for water treatment during the past 17 years (Khan et al., 2000; Leupin et al., 2005; Ngai et al., 2007; Hussam, 2009; Gottinger et al., 2013; Chaudhari et al., 2014; Kowalski and Sogard, 2014) is considered an adaptation of the Fe0-based permeable reactive barriers (PRBs) for groundwater remediation (Gillham and O'Hannesin, 1994; O'Hannessin and Gillham, 1998; Henderson and Demond, 2007; Comba et al., 2011; Gheju, 2011; Obiri-Nyarko et al., 2014). In the 1990s, Fe^0 was 'discovered' as a reducing agent for environmental remediation (Reynolds et al., 1990; Lee et al., 2004; Gillham, 2010). The view that Fe^0 is an environmental reducing agent has been severely challenged (Noubactep, 2007, 2009, 2008; Jiao et al., 2009, 2010, 2011; Gheju, 2011; Gheju and Balcu, 2011; Noubactep, 2013, 2015; Ghauch, 2015; Gheju et al., 2016) but is still prevailing (Fu et al., 2014; Guan et al., 2015; Guo et al., 2016; Sun et al., 2016). In fact, regarding Fe^0 as a reducing agent implies that contaminant reduction is the cathodic reaction of aqueous iron corrosion in an electrochemical process (Ghauch, 2015; Gheju et al., 2016; Noubactep et al., 2016; Noubactep, 2016b). This is not possible because iron corrosion by water is a universal process that has been studied for centuries (Nesic, 2007; Noubactep, 2016c). The evidence that more species are chemically reduced under conditions favouring iron corrosion, for instance in the presence of organic ligands (Song et al., 2017) is by no means a proof of any dominant reductive mechanism. In most of the cases, involved experiments lasted for some hours or days, while filters are designed for months and years. The Fe^0 filtration technology as a whole is currently facing a controversy. Controversy is well-known as a barrier or at least brake to new technologies. In other words, ways and means should be sought to help the Fe^0 remediation research community out of the valley of confusion. The history of centralized safe drinking water provision reveals that the Fe^0 filters are not a new technology but rather an outdated one (Devonshire, 1890; Swete, 1892; Tucker, 1892; van Muyden, 1894; Burton, 1898a, 1898b; Hill, 1898; Konig, 1899a,b; Don and Chilson, 1911; Baker, 1934; van Craenenbroeck, 1998). In particular the large scale use of Fe0 materials for safe drinking water provisionwas successfully pioneered in Antwerp (Belgium) in 1881 (Anonymous, 1881; Anderson, 1883; Devonshire, 1890; Swete, 1892; Burton, 1898b) and applied in several other towns until 1930 (van Muyden, 1894; van Craenenbroeck, 1998). The basis for the deployment of Fe^0 at large scale is accredited to its success as filter material at household scale (Bischof, 1873). In those days, the river Nethe was both the source for drinking water and the destination for wastewater in Antwerp. As a rule, industrial wastewaters were not treated before disposal. It appears that the Fe^0-based technology was outdated not because of any fundamental inadequacy, but rather because of increasing pollution of the Nethe (Devonshire, 1890; van Craenenbroeck, 1998). This chapter presents and discusses the ancient Fe^0-based technology for safe drinking water as implemented in Antwerp. It then explores the lessons that could be learned in the perspective of solving controversies within the current Fe^0 research community.

5.2. Research Approach

To address the objectives, the method described in Chapter 2 was modified and used where published literature from the world wide web (www) including Google Scholar®, Scopus® and Web of Science® on water 'purification' by metallic iron were retrieved using the following search terms: 'Anderson process', 'metallic iron', 'water purification', and 'revolving purifier'. Most of the 19th century literature which form the foundation for this chapter can be termed as 'fragmented' as articles were not referenced like today. This explains why it was necessary to use a variety of search terms in different databases to retrieve enough relevant literature. Scopus gave the best results with 15 relevant publications, most of which are from The Journal of the Franklin Institute. From the 15 articles, 09 were proceedings of the meetings. References from the 15 articles and further searches at google with several keywords gave other interesting references, most of which could be found at www.books.google.com. The whole search was motivated by an article by Easton Devonshire (1890) titled "The purification of water by means of metallic iron". This article was uploaded at http://www.sciencedirect.com/ in 2016. A total of 25 publications focusing on using metallic iron for water treatment at large scale were retrieved. These papers covered the period from 1864 to 1998 and included two overview articles (1892 and 1934) and a couple of standard textbooks (e.g. Davis, 1891; Tudsbery and Brightmore, 1893; Burton, 1898a, 1898b; Hill, 1898; Konig, 1899a, 1899b; Fischer, 1902; Don and Chilson, 1911).

To ensure the knowledge is well presented, a brief history of water treatment and water quality is first given. Then both the design and operation parameters of the iron materials are fairly discussed highlighting the pertinent aspects that can help to shed light to the present day iron and iron loaded materials investigations. The presentation of the design is not a complete one; it is rather the description of the way the materials were packed and the effects originating from such arrangements. In so doing the strengths and weaknesses of the systems under consideration are exposed and causes thereof highlighted. Finally, the lessons that could be learnt are summarized before the conclusion is reached.

5.3. Results and discussion

5.3.1. The history of water treatment

In the early 19th century, most societies obtained their water for domestic purposes from wells, springs and rivers (van Muyden, 1894; Johnson, 1914; Baker, 1934; Kroehler, 2014). Population growth and industrialisation presented the then new challenge, namely, disposal of both domestic and industrial wastes (Anderson, 1883; Conder, 1885; Swete, 1892). In most cases, these sources of water were the sinks for the industrial and or domestic wastewaters or received infusion from proximally located wastewater sinks. In Antwerp for instance, the water in the wells that served as the water source for domestic use was polluted by seepage from proximally located cesspits as the sandy soil could not form the effective barrier for the percolating contaminants from the cesspits (Anderson, 1883). The increased occurrence of cases of diseases which were later related to water pollution signalled the need to act on the problem (Anonymous, 1891; Smee, 1899; Baker, 1934). The options to get rid of this problem were either find new uncontaminated water sources or purify the contaminated water. Although finding new uncontaminated water sources was attractive, it was not always possible due to infrastructural and financial constraints (Anonymous, 1888, 1891; Swete, 1892; Mckee, 1934). Sand filtration availed the first widely applied filtration remedy for contaminated water challenge in the mid-19th century (Johnson, 1914; Baker, 1934; Kroehler, 2014). Initially, it was thought that the removal mechanism of sand was only mechanical by size exclusion through the inter-particle interstices. Studies later revealed that slow sand filters (SSF) develop an active biofilm (termed as Schmutzdecke) around the sand grain that was rich in bacterial populations which improved the filtration power of the media (Bamber et al., 1886; Gill, 1895; Johnson, 1914). This technology found its way into many European and American cities until the first quarter of the 20th century (Johnson, 1914; Baker, 1934; Kroehler, 2014). The notable challenge with the application of SSF was its inefficiency in removing chemical contaminants and its failure to completely remove germs besides vulnerability to accidents and change in flow rate (Bamber et al., 1886; Gill, 1895; Swinburne et al., 1903; Johnson, 1914). Attempts to address these challenges lead to the testing of other materials as 'purifiers' such as animal and plant charcoal, coke, cinders and Fe^0 in filtration, which was already then established as the best water purification process (Anonymous, 1867; Hering, 1895). The former was not widely applied at treatment plants likely due to their inability to completely and permanently inactivate microbes and the fact that they required frequent replacement (De Chaumont, 1880; Ogston, 1883; Frankland, 1884; Anonymous, 1888). During the 19th century there was already an increasing interest in testing new technologies for safe drinking water provision. Table 5.1 gives a summary of treatment processes then tested and applied. It appears that the technologies currently used at large scale mostly originated from that period. The following section will discuss the history of water quality.

5.3.2. Context of the first use of Fe^0-based materials

The historical development of safe drinking water supply from the early 19th century is given in this section to outline lessons from the past Fe^0 use that could sustain its contemporary application. It is during this period of the human history that people had to live for the first time in so densely populated agglomerations (cities, towns), that drinking water was often exposed to significant contamination from animal and human faeces. This was evidenced by the frequency of epidemics of water-borne diseases including cholera, dysentery and typhoid fever. The first solution was to perform sanitation by using water to transport human wastes to the nearest watercourse (mostly rivers). In other words, human wastes were transported to rivers that were in many cases the source of drinking water (Bostock, 1829; Devonshire, 1890; Tweeddale, 1898; Cooke, 1914; Johnson, 1914). The realisation, that bringing human wastes to the drinking water source was not really a solution, had initially prompted engineers and scientists to two key actions (Burton, 1898b; Don and Chilson, 1911; Kroehler, 2014): (i) find a source of water that has never been exposed to human waste (and eventually protect it from contamination) and (ii) use continuously pressurized water systems (less widely appreciated). Simultaneous compliance with these two principles (actions) is sufficient to end classical waterborne diseases. However, many other cities did not have access to a protected clean water source. This evidence had prompted to a third universal action explained in section 5.3.1: The development of water treatment technology as a way to restore the drinking quality of polluted waters. Endeavouring to mimic nature based on the evidence that safer water was supplied from deep wells (no outbreaks of water borne diseases), filtration was favoured (Burton, 1898b; Don and Chilson, 1911). Early technologies (around 1850) were river-bank filtration, dune filtration and slow sand filtration (SSF) (Johnson, 1914). However, filtration was not always reliable as bacteria were found in some filtered waters. On the other hand, heavily polluted waters required multi-barrier filtrations (Baker, 1934). Later, a treatment chain comprising coagulation (using aluminium or iron salts), sedimentation and rapid sand filtration was largely adopted (Swinburne et al., 1903; Baker, 1934). The former use of Fe^0 material was within this trend (Burton, 1898b;

Don and Chilson, 1911). Fe^0 was either used to improve SSF/BSF (Spencer process, Bischof process - section 5.3.4) or to generate iron hydroxides acting as coagulant preceding sedimentation and sand filtration (Anderson process - section 5.3.6). It is important to check which contamination was addressed by ancient Fe^0-based processes as indicated in Table 5.2. By year 1950 the developed world had defeated classical waterborne disease of the human-to-human fecal-oral route (Bache, 1891; van Muyden, 1894; Hoover et al., 1915; Ellms, 1920; Streeter and Raneri, 1944; Straub, 1955; Colten, 1988; Kroehler, 2014). To date, the developing world is still facing the overcome of endemic, classical water-borne diseases to the extent that it can be said that the major distinguishing characteristic between the developed and the developing worlds is the general availability of safe drinking water (Nde-Tchoupe et al., 2015; Lilje and Mosler, 2016; Oladoja, 2016). As will be seen in section 5.3.11, the application of Fe^0 materials for safe drinking water provision was abandoned around 1930. Accordingly, Fe^0-based systems have helped the developed world to defeat water-borne diseases and would solve the safe drinking water problem in the developing world in the near future. The next section presents chlorination as disinfection tool to make clear that it should not be universally regarded as stand-alone technology for safe drinking water provision (as often recommended).

Table 5. 1. The different filters used in the 19th century, their active media/material and contaminant removal processes

Filter	Active media/material	Main removal process	References
Sand filter	Zoogene/biofilm (Schmutzdecke)	Biological action	Bamber et al., 1886; Gill, 1895
Cistern filter	Animal charcoal	Adsorption	Anonymous, 1867; Notter 1878
Silicated filter	Animal charcoal/coke	Adsorption	Anonymous, 1867; Notter, 1878
Magnetic carbide	carburetted oxide of iron	Coagulation/Adsorption	Burton, 1898b
Polarite filters	Iron oxide	Coagulation/adsorption	Burton, 1898b
Sponge iron filter	Metallic iron	Coagulation/adsorption	Anderson, 1883; Ogston, 1883, Bischof, 1878a,b; Anonymous, 1888
Anderson revolving purifier	Metallic iron	Coagulation	Anderson, 1884; Devonshire, 1890; Scowden, 1896
Mechanical filters/rapid filters	Coagulant(alum)/sand	Coagulation prior to filtration and size exclusion in the sand filter	Swinburne et al., 1903

5.3.3. Chlorination

Another key feature of water supply is the distribution of treated water. Safe drinking water leaving a treatment plant must remain safe until it is consumed in households. In rural areas where safe drinking water supply is rare, water disinfection has been proven an efficient way to prevent waterborne diseases and to fight water microbial contamination (Bache, 1891; Ellms, 1920). Water disinfection by chlorination is among the early water treatment methods (Bache, 1891; Traube, 1895). Around the beginning of the 20th century, disinfectants, particularly chlorine, began to be increasingly adopted for water treatment and became nearly universal by 1940 (Savage, 1916; Streeter and Raneri, 1944). Water treatment by chlorination can considerably address some microbiological contaminations, but is inefficient at both physical and chemical decontamination. This explains, why in most of the conventional treatment plants, the process is combined to other processes (e.g. filtration) and justifies why the use of this unique process cannot be adopted as a stand-alone water treatment method for physical and chemical decontamination. Coagulation/ flocculation þ sedimentation, filtration and disinfection remain the core of the modern water treatment today. For the developing world, chlorination systems are developed as stand-alone water treatment. The other argument against chlorination by a non-skilled personal is the well-documented harmful nature of its by-products (Rook, 1974a; 1974b, 1975; 1977; Gallard and von Gunten, 2002).

5.3.4. Nature of water contaminants

Until 1930 microbial and physical contamination was the major issue, even though the nature of pathogens was not always analytically addressed. The development of water treatment after the Second World War (WWII) was mostly centred on understanding the nature of contamination. For physical contaminants, the number of particles per volume is characterized; a turbidity unit (light scattering) is introduced, as well a particle size analysis. For organic chemical contamination, the following classes are distinguished: (i) disinfection byproducts (1974), (ii) volatile organic chemicals (around 1980), (iii) herbicides and pesticides (1980s), and (iv) pharmaceuticals and personal care products (1990s).

Table 5. 2. Historical application of iron in water purification

Age/Time	Material	Usage	Destined impurities	Application	Reference
Pre-1850	Iron salts	Shaken with impure water then left to settle	Suspended matter	Proposed, but not widely used	Anonymous, 1867; Baker, 1934
	Old iron nails	Shaken with impure water then left to settle	Suspended matter	Used in West England	Swete, 1892
1850-1900	Iron plates/wires (1857)	Suspended in flowing impure water	Suspended matter	Tested but not widely applied	Devonshire, 1890
	Magnetic carbide/Iron oxide	Filter media	Suspended matter/microbes	Widely applied household scale filters	Devonshire,1890
	Polarite	Filter media	Suspended matter/colour/microbes	Household filters	Bischof, 1877; Burton 1898b
	Spongy iron	Filter media	Suspended matter/ colour /microbes/chemical contaminants	Household and large scale filters	Anderson, 1883
	Iron fillings	Agitated in the revolving purifier	Suspended matter/ colour /microbes	Large scale in treatment plants	Anderson, 1989
1900-1950	Iron fillings	Agitated in the revolving purifier	Suspended matter/ colour /microbes/chemical contaminants	Large scale in treatment plants	Anderson, 1989, Van Craenenbroeck, 1998
	Iron salts with lime		Microbes	Large scale in treatment plants	Tyler, 1931; Kerslake, 1946
Post 1990s	Metallic iron	Reactive media in PRBs	Chemical contaminants	Controversial	(Fu et al., 2014; Colombo et al., 2015

For biological contamination, the following classes are distinguished: (i) pathogens, (ii) enteric bacteria (*Campylobacter jejuni, E. coli, Helicoobacter pylori, Legionella pneumophila, Streptococcus pneumoniae*), (iii) enteric viruses (Hepatitis, norovirus, Polio, rotavirus) and (iv) protozoa (*Cryptosporidium parvum, Giardia Lamblia* - zoonotic).

Summarized, Fe^0 occupies an important place in the development of effective water remediation technologies even before knowledge of contaminants' nature was well understood. There is significant improvement in water quality laws that presently, micro-pollution is addressed with very stringent guidelines at international level. The present work aims at discussing knowledge from water filtration through Fe^0 filters during two very distinct periods (namely late 19th century and late 20th century) with regards to water quality. The following sections present and discuss the ancient application of Fe^0 in water treatment.

5.3.5. The ancient Fe^0 application for water treatment

The first engineered process of water treatment based upon the use of Fe^0 (e.g. plates, wires), was described by Medlock in 1857 (Devonshire, 1890; Ogston, 1885). However, even before 1857, a crude application of FeO materials (e.g. iron nails) in water purification was a popular knowledge, at least in Western England (Swete, 1892). In the Medlock's design Fe^0 particles were suspended in water tanks through which water was allowed to pass. According to Ogston (1885), the low reactivity of used plates and wires hindered the widespread application of Medlock Process. In 1867, Spencer described magnetic carbide as a more efficient reactive material (Anonymous, 1867; Devonshire, 1890; Konig, 1899a). Spencer's magnetic filters, which were efficient at producing wholesome water at household scale, hinge on the characteristics of Fe^0 to generate Fe oxides in aqueous solution (rusting or iron corrosion). In particular, the Spencer filters were relatively more efficient than animal charcoal based filters in removing toxic aqueous species (Anonymous, 1867, 1888). Around 1864 a form of porous iron (termed as spongy iron or simply sponge iron) was invented by Bischof and first used in cementation process and then in the synthesis of aniline (Anonymous, 1864). About seven years later, this material was discovered to have 'energetic action' on organic matter in water (Anonymous, 1871). This water purifying properties of spongy iron was subsequently put to application for that purpose a few years later (Bischof, 1877, 1878a,b). Sponge iron was mixed with fine gravel and successfully used as filter bed in household filters, outperforming the Spencer's filter (Anderson, 1883, 1884; Ogston, 1885; Anderson, 1885). Sponge iron was obtained by the reduction of hematite ore at an incipient fusion. It was proved that sponge iron could treat even the sewage effluent besides water contaminated with it by completely inactivating the microorganisms (Bischof, 1877, 1878a,b; Frankland, 1884; Conder, 1885). Besides completely removing putrefying bacteria, spongy iron, which was found to reduce temporary hardness to some significant extent while maintaining its power for a long time (Wigner, 1878; Anonymous, 1888), was successfully tested for reduction of nitrates and found to be effective (Hatton, 1881). However, other experiments revealed that sponge iron based household filters produced water with earthy taste (Wigner, 1878; Anonymous, 1888).

Fig. 5.1 shows the design of the household Bischof filter (Bischof, 1877, 1878a,b). Polluted water first interacts with a layer of sponge iron, then pyrolusite, sand and finally gravel. Even though neither dimensions of the vessel in which the filtering materials were packed nor the amount of materials were routinely stated, it is clear that in this design the active layer was the spongy iron layer and the lower layers served the purpose of supporting the reactive layer and removing coagulated iron salts (hydrated ferric oxides) (Notter, 1878). Contaminant removal mechanisms are mainly physical: straining (size-exclusion) and enmeshment (co-precipitation) in the insoluble matrix of hydrated ferric oxides. It appears that the earthy taste originated from 'excess' iron hydroxides in filtered water. This is understandable, as aeration (after contact with spongy iron) which was important for development of precipitates (ferric hydr(oxides)) (Don and Chilson, 1911) was not a prominent feature in the design. For contemporary application, insertion of the BSF above the household Bischof's filter (Fig. 5.2) can improve its sustainability and performance. In the optimisation studies, the quantity of reactive and inert materials (labelled A-D) may be varied to establish optimal combination. The optimized Bischof's filter may present a robust household filter especially in developing countries where point of use (POU) treatment is recommended (Shannon et al., 2008). The time line of improving 'Fe^0 for safe drinking water' in the 19th century is summarized in Table 5.3.

Table 5. 3. Summary of the historical evolution of the early application of Fe0 for water treatment until the Anderson's revolving purifier adoption at Antwerp

Event	**Date**	**Fe^0 type**	**Reference**
Medlock's process	1857	Plates and wires	Ogston, 1885; Tucker, 1892
Spencer's process	1867	Magnetic carbide	Devonshire, 1890; König, 1899a
Discovery of spongy iron (Bischof)	1864	Spongy iron	Anonymous, 1864
Testing Bischof's process	1871	Spongy iron	Anonymous, 1871; Tucker, 1892
Testing the Bischof's process at large scale (Antwerp)	1879	Spongy iron	Anderson, 1883
Application of Bischof's process at Antwerp	1881	Spongy iron	Anderson, 1883; Ogston, 1883; Devonshire, 1890
Testing Anderson's process at Antwerp	1884	Granular iron	Anderson, 1885
Application of the Anderson process at Antwerp	1885	Granular iron	Anderson, 1885

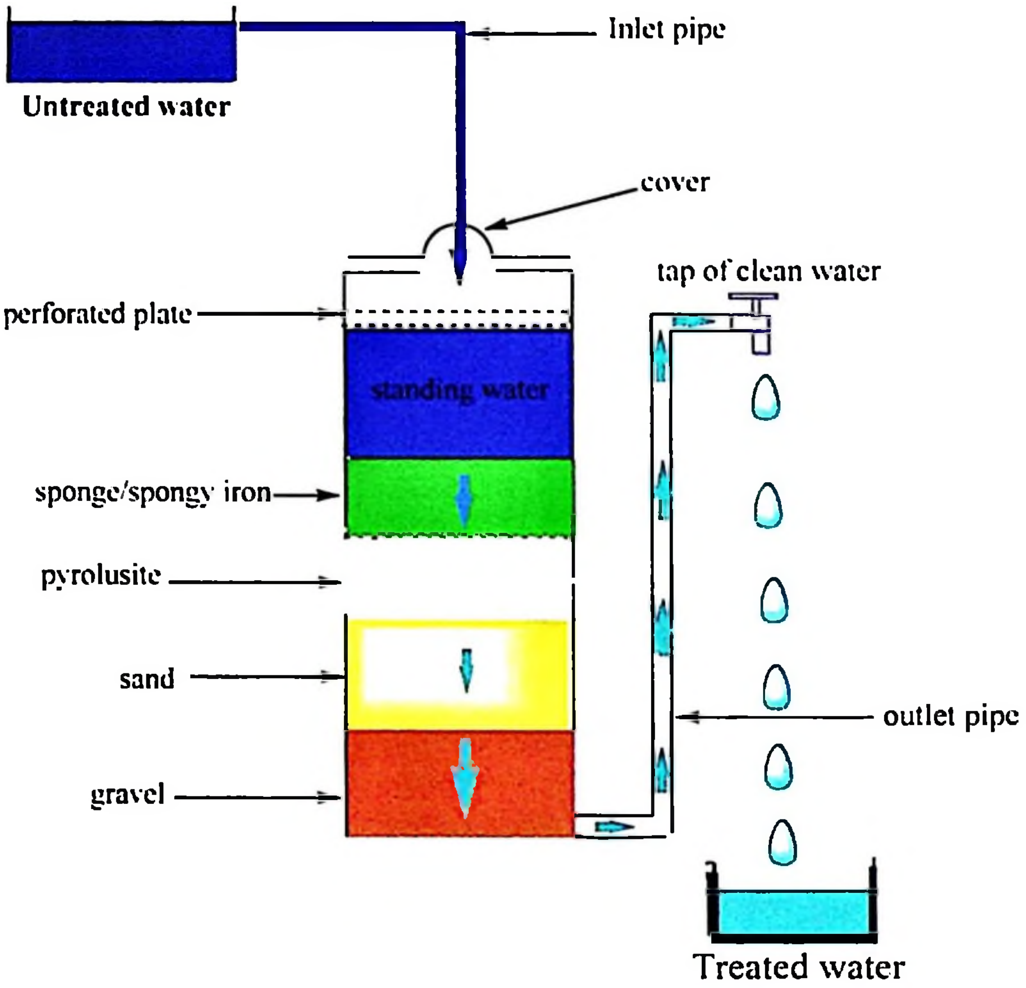

Fig. 5. 1. A schematic representation of the Bischof's spongy iron filter (Bischof, 1877, 1878)

5.3.6. Bischof process at Antwerp water works

General aspects

The river Nethe water which was yellow in colour and rich in dissolved and finely divided suspended matter presented a challenge to water treatment engineers. This river was then also highly contaminated with wastewater from domestic and industrial sources. Experiments had revealed that ordinary sand filters could not convert this water to potable and acceptable water (Anderson, 1883; Ogston, 1883; Devonshire, 1890). The demonstrated power of sponge iron as efficient filter material to free polluted water from biological, chemical and physical contamination has prompted the first large scale testing to treat river Nethe water (from 1879) and supply to the town of Antwerp from 1881 to 1883 (Anderson, 1883; Ogston, 1885). As stated earlier (section 5.4), spongy iron was invented for other purposes and then successfully tested and applied for water treatment (Anonymous, 1864, 1871; Bischof, 1877; Anderson, 1883).

Design specifications

The large scale application of the Bischof Process at Antwerp consisted of two filters arranged in series, namely, the sponge iron filter (SIF) and the sand filter. The SIF was raised above ground to maintain the head of about 0.7 m between it and the lower sand filter to allow water to flow by gravity as depicted in Fig. 5.3 (Anderson, 1883, 1884; Devonshire, 1890; Tucker, 1892; Konig, 1899a). In the experimental design (as described by Anderson, 1883), the SIF consisted of a cast-iron tank, 18 feet 6 inches square, and 11 feet deep, raised 3 feet 21/2 inches (1.167 m) above the ground. The filtering materials in the SIF were arranged as follows: (i) the top 2 feet (0.6 m) were occupied by coarse sand, (ii) this was followed by 3 inch (0.0762 m) layer of fine sand, (iii) the next layer was a mixture of iron and gravel in the ratio of 1:3 and the last component was (iv) a layer of bricks. This description implies that sponge iron occupied about one third of the reactive layer which is equivalent to 1 foot (0.3 m) thickness. Between the SIF and the ordinary sand filter was a cast iron trough which water would flow in a thin sheet for fast aeration (Anderson, 1883). The first filter was related to the second filter by a 3-inch pipe, with a regulating cock, fixed from the middle of the bottom of the tank and through which could pass the partially-filtered water from the first filter. The second filter or lower sand filter was also a cast-iron tank of 18 feet 6 inches square, but only 7 feet 6 inches deep, and with the bottom raised 1 foot 6 inches (0.45 m) above the ground. The depth of the water over the upper surface of the sand in both filters was to reach a maximum of 4 feet, the lower filter being placed at such a level that the surface of its sand was 4 feet (1.2 m) below that of the upper filter. Finally, the filtered water was drawn off by a 3-inch pipe. The arrangement of the materials in the ordinary sand filter was as follows; at the top there was 2 feet 2 inch (0.65 m) of fine sand followed downwards by a 3 inch (0.0762 m) layer of fine gravel below which there was a 12 inch (0.3048 m) layer of coarse gravel (Anderson, 1883). Before the SIF, there was the settling tank/pond to facilitate the deposition of coarse suspended particles (subsidence) and after the ordinary filter there was the supply reservoir.

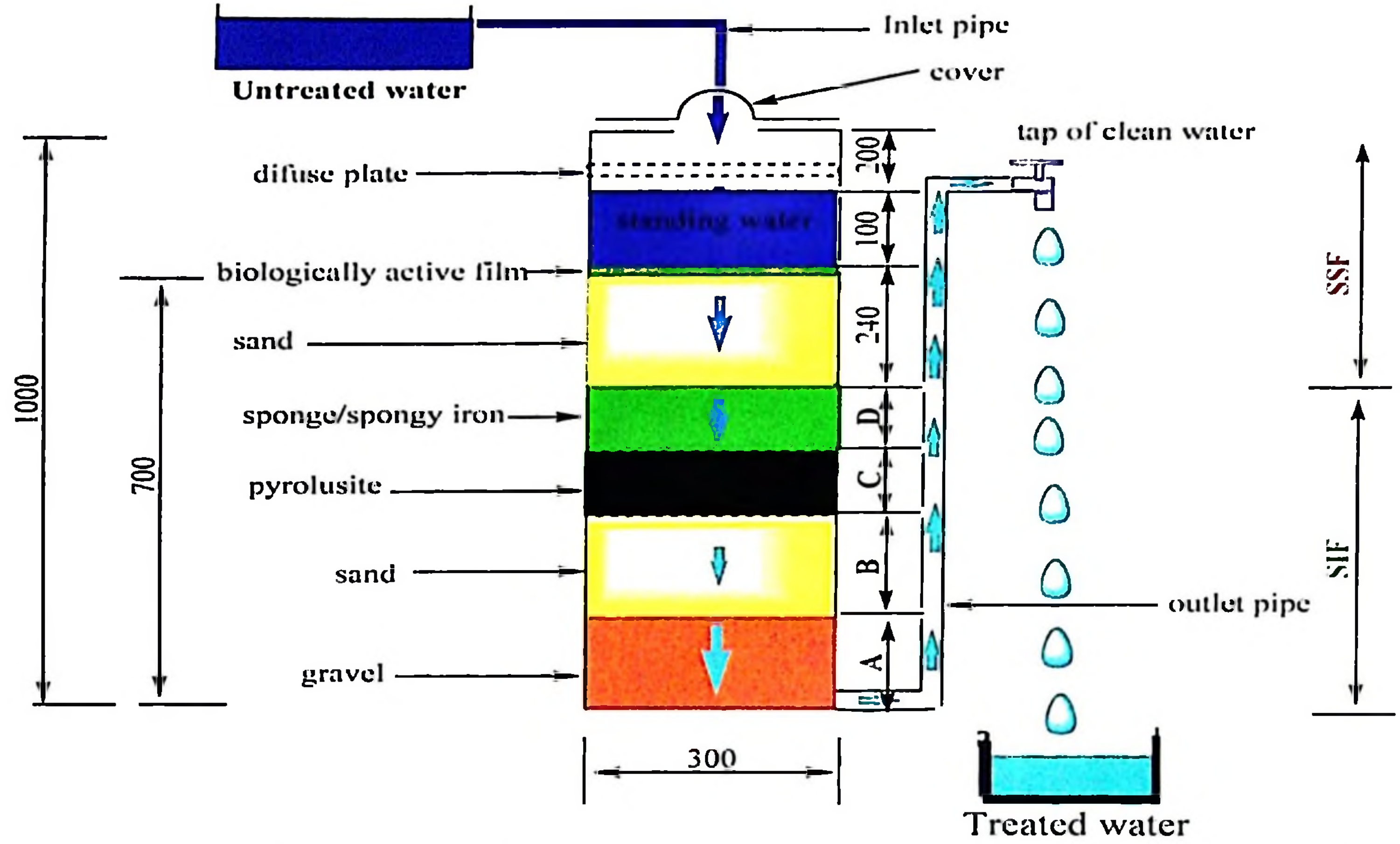

Fig. 5. 2. A schematic representation of the modified household spongy iron filter (SIF) with SSF inserted above for experimentation. (All dimensions in mm drawn not to scale)

5.3.7. Operational aspects

The Nethe water was allowed to first flow through the coarse sand layer where remaining suspended particles were removed by mechanical straining. The physically clean water then flowed through to fine sand and iron/gravel layers. The design allowed a contact time of about 45 min between water and the reactive media in which water flow was gravity-driven sustained by different elevations of the filters. During this time, sponge iron (the reactive material in the system) generated ferrous salts which were known to be coagulating agents (Anderson, 1883, 1884; Ogston, 1883; Devonshire, 1890). Then, water was allowed to overflow in thin sheet in the hole that was located between the two filters. In this structure water was retained for 6-8 h to ensure enough aeration of the water before entering the second filter (Anderson, 1883; Ogston, 1883). It was clear to the designers, that this aeration structure was important to enhance precipitation of the ferric oxide compounds and in doing so encasing other contaminants including finely divided suspended matter and dissolved organic matter (Anderson, 1883, 1884; Devonshire, 1890; Tucker, 1892). When compared to the household Bischof's filters, this design had an additional aeration structure that enhanced the oxidation of the ferric hydr(oxides) and eventually facilitated their removal by mechanical straining. This ensured that much of the iron are precipitated or flocculated and subsequently removed from the treated water. This structure, therefore, may explain why the water treated by this process in large scale filters was actually said to have a fresh and agreeable taste (Devonshire, 1890), thus, would not be expected to taste earthy, the challenge that was associated with household filters as explained in section 5.3.4.

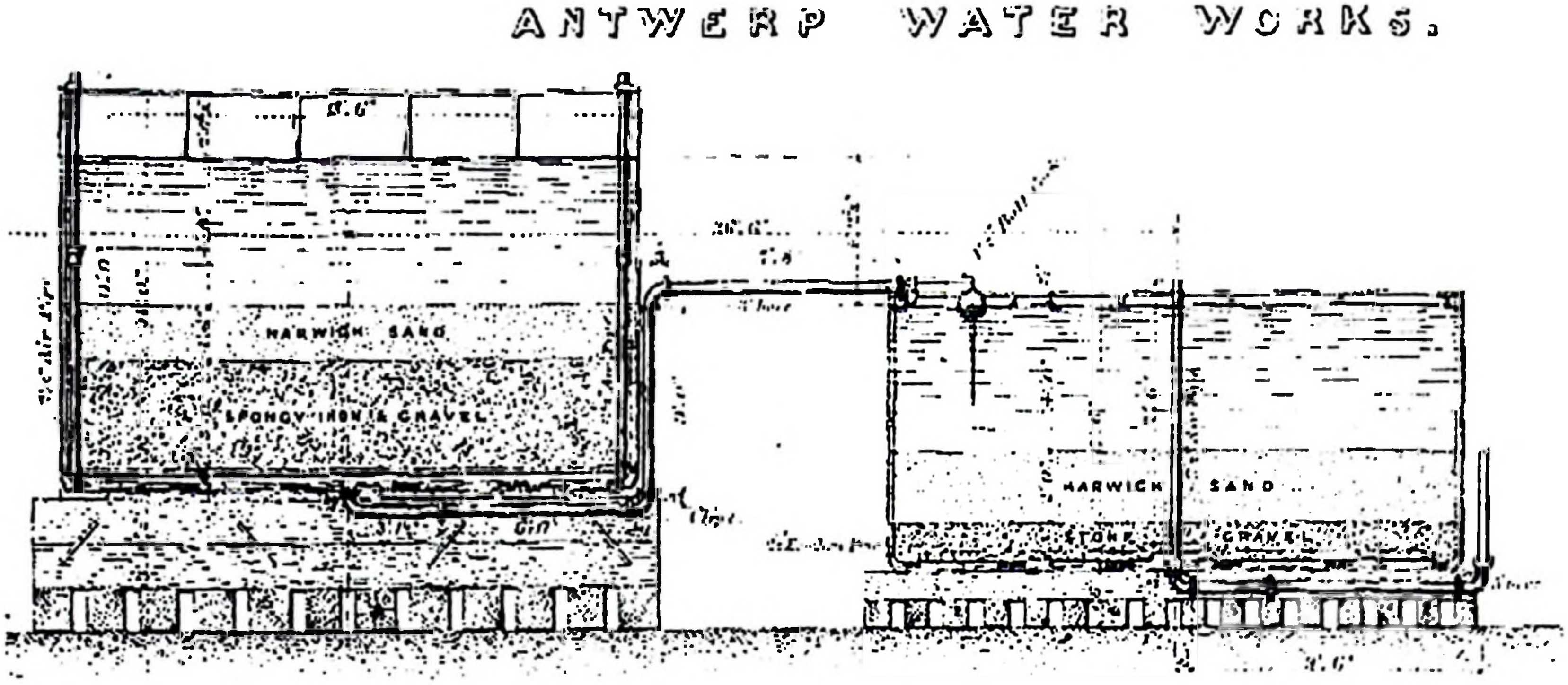

Fig. 5. 3. A side view of the experimental spongy iron filter. The bottom of the SIF is 0.7 m higher than that of sand filter (Anderson, 1883)

The second filter was basically the ordinary sand filter, which served the purpose of mechanically straining the formed precipitate from the aerated water, which formed a felt at the top of the sand layer (Devonshire, 1890; Don and Chilson, 1911; vanCranenbroeck, 1998). The top sand layers in both filters (spongy iron and sand) required regular stripping off of deposits from the passing water.

5.3.8. Efficiency aspects

During the first 1.5 years of operation at Antwerp, the Bischof process worked perfectly (Devonshire, 1890; Anderson, 1891; Don and Chilson, 1911). During this time, the spongy iron filter was producing nearly half of its full capacity and loosened once every six (6) months (Anderson, 1889). The increase in water demand necessitated increase in flow rate which then exposed the unbearable challenge, namely 'too soon clogging' (Anderson, 1884, 1885; Devonshire, 1890). This increased the operation cost too much, such that the whole business was considered unprofitable. The clogging deposits consisted of salts of lime (calcium) and magnesia and organic matter made insoluble by the action of iron (Anderson, 1885). It is worth noting here, that these deposits and consequential clogging occurred before the spongy iron was depleted and were not observable in ordinary sand filters. These challenges of the design made the system work fairly well, when it was used to treat only a half of the quantity of water it was designed for (Anderson, 1884, 1885; Devonshire, 1890). These challenges, thus, mark the discontinuation of the design and introduction of the Anderson revolving purifier. The Bischof's process was subsequently replaced at Antwerp by the Anderson's revolving purifier (Anderson, 1885; Ogston, 1885; Tucker, 1892).

Table 5. 4. The Summary of the Antwerp waterworks analysis results from both the Bischof's and Anderson's processes. Results obtained for water treated using the Anderson's "revolving purifier" in some few others European cities are also included. X stands for the followed effluent contaminant and [X] for its concentration ($[x]_0$ before treatment and $[x]_i$ after treatment).

Ref.	Process	Iron type	Water from	x	[x] (mg/L)		[x] (%)	Fe0 (mg/L)	pH value	Capacity (m3/day)
					[x]0	[x]i				
Ogston, 1883	Bischof	Spongy iron	Antwerp	Albumenoid ammonia	0.10	0.04	60.00	n.s.	n.s.	> 9000
			Antwerp	Chlorides	5.50	5.20	5.45	-	-	-
			Antwerp	Nitrates	9.10	7.30	19.78	-	-	-
			Antwerp	Free ammonia	0.03	0.01	66.66	-	-	-
			Antwerp	Organic matter	n.s.		-	-	-	-
			Antwerp	Micro-organisms	n.s.		-	-	-	-
			Antwerp	Total solids	119.00	76.00	36.13	-	-	-
Ogston, 1885	Anderson	Iron fillings	Antwerp	Albumenoid ammonia	0.20	0.08	60.00	n.s.	n.s.	9100
			Antwerp	Chlorides	n.s.		-	-	-	-
			Antwerp	Nitrates	n.s.		-	-	-	-
			Antwerp	Free ammonia	n.s.		-	-	-	-
			Antwerp	Organic matter	n.s.		-	-	-	-
			Antwerp	Micro-organisms	n.s.		-	-	-	-
			Antwerp	Total solids	n.s.		-	-	-	-
			Zurich	Albumenoid ammonia	0.02	0.01	50.00	n.s.	n.s.	-
			Ostend	Albumenoid ammonia	0.14	0.08	42.86	n.s.	n.s.	-
			Laeken	Albumenoid ammonia	0.185	0.06	67.57	n.s.	n.s.	-
			Thames	Albumenoid ammonia	0.15	0.06	60.00	n.s.	n.s.	-
			Malines	Albumenoid ammonia	0.26	0.06	76.92	n.s.	n.s.	-

5.3.9. The Anderson process

General aspects

The caking and clogging challenges of the Bischof's spongy iron filters was successfully addressed by the introduction of the Anderson revolving purifier apparatus (Anderson, 1883, 1884; Ogston, 1885; Devonshire, 1890; Davis, 1891). The logic behind this intervention was to ensure that, the formed precipitate in the iron mass, which caused hardening and clogging of the filter bed in the Bischof's spongy iron application, is constantly washed away and the surfaces of the active media are always clean and active (Anderson, 1883, 1884; Ogston, 1883; Devonshire, 1890; van Muyden, 1894). This idea which was suggested by Frederick Abel was not put to application immediately because of the belief (by Bischof) that a contact time of about 45 min was necessary to bring about the desired contaminant removal (Devonshire, 1890), so that the Abel's suggested modifications were only considered after the total failure of the SIF design. The revolver occupied a relatively smaller space than the SIF and could produce enough amount of desired quality of water in a short time. Even though the Anderson's revolving apparatus, which replaced the SIF, has succeeded in overcoming most of the SIF design challenges, and subsequently adopted in various European cities (Anderson, 1883, 1884; Ogston, 1885), it is Bischof who has the chief credit of introducing the use of Fe^0 for water treatment at large scale (Ogston, 1885; Tucker, 1892).

Design specifications

The revolving purifier consisted of the wrought iron cylinders or "revolving purifiers" (as they were then called) which were 5 feet (1.5 m) in diameter by 15 feet (4.5 m) maximum length. The revolver (Fig. 5.4) charged with a mixture of fine and coarse Fe^0 particles is longitudinally supported on the 10 inches internal diameter hollow trunnions and fitted with stuffing boxes, through which the inlet and outlet pipes pass. A hole fitted with a cover is made available in the centre of the revolver through which addition of Fe^0 mass could be made. The arrangement is made by placing blades askew in such a way, that if the current of water passing through the revolver should leach the iron towards the outlet, it would rather be thrown back towards the inlet and showered down to the bottom. In the process, every portion of the water is necessarily brought into contact with the Fe^0 particles in the revolver turning at a rate of 0.33 revolution/min. At this rate, the in-situ formed iron corrosion products are constantly washed out, and the Fe^0 particles' surfaces in the revolver maintained bright and active. Next to the revolver followed the aeration structure and the ordinary sand filter. When the design allowed a contact time of 45 min, the treated water was concentrated with iron. The step by step reduction in contact time revealed that a contact time of 3.5 min, in the apparatus as described herein was enough to produce water of the desired quality per day (Anderson, 1885; Ogston, 1885; Tucker, 1892).

5.3.10. Operational aspects

In a revolving purifier, Fe^0 is allowed to contact raw water for 3.5 min. During this time, a fraction of Fe^0 particles dissolves and forms iron hydroxides and oxides (iron corrosion products or FeCPs) (Anderson, 1883; Ogston, 1883; Devonshire, 1890). Enough FeCPs is generated to quantitatively enmesh available dissolved contaminants. Ideally, the liquid phase leaving the purifier is a suspension containing a large proportion of colloidal ferrous iron(Fe^{2+}). From the revolver water mixed with corrosion products flowed into the aeration unit where oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) is induced and sustained by air O_2. Fe^{3+} species are known to be less soluble than Fe^{2+} ones. Ferric hydroxides coagulate and in so doing entangle contaminants and precipitate down (Anderson, 1884, 1885; Devonshire, 1890; Swete, 1892).

The precipitates from the aeration unit are mechanically removed by straining in the ordinary sand filter. Some iron oxides that could not be trapped formed an iron oxide film around sand grain (in-situ coating), making it a better adsorbent for negatively charged contaminants including As(III), F^- and U(VI). From the ordinary sand filter water flowed into the supply reservoir tank. The mechanism, by which this oxide film trapped impurities, was not well established. For instance, it was theorised by Swete (1892), that the oxygen trapped in this film reduced the size of the interstices, thus isolating impurities by size-exclusion. This corresponds to the volumetric expansive nature of iron corrosion as later demonstrated (Care et al., 2013; Domga et al., 2015). Today it is understood that the film is positively charged and by that can trap charged impurities.

Table 5. 5. The Summary of optimisation processes of iron(metallic/salts) and their effect on performance

Material(s)	**Application**		**Remarks /Outcomes**	**References**
	Previous	**Modified**		
Iron salts	Applied alone	Applied with lime	Lime provide alkaline pH conducive for coagulation of iron oxides	Anonymous, 1867;Tyler 1931; Kerslake et al., 1946
Metallic /Spongy iron	Without aeration at household scale application	Aerated for 6-8 hours at large scale spongy iron application	Aeration enhanced coagulation of ferric hydr(oxides)	Bischof, 1877; Bischof, 1878; Anderson, 1884, Ogston, 1885 Devonshire, 1890
	Without agitation in filters	Agitated in the revolving purifiers	Agitation kept the Fe^0 surfaces active while increasing and sustaining the production of FeCPs (contaminant collectors)	

Two notable observations were obvious in the design during its operation; (i) the mossy growth was common in the inlet and not outlet valve/pipe of the revolver (ii) the O_2 deprived gas was collected above the water level in the revolving purifier that extinguished fire (Anderson, 1889; Devonshire, 1890; Hill, 1898). It is claimed that with this process both micro-organisms and chemical pollutants (e.g. albuminiod ammonia) are totally removed (Anderson, 1885; Ogston, 1885; Tucker, 1892). However, because real and reliable chemical analyses were then not done on filtrates, but rather its quality and safety been appreciated on the basis of absence of bad taste and its physical cleanness, the previous assertion can be questioned (Ogston, 1885; Devonshire, 1890). However, it was obvious, that the contaminant removal was significantly enhanced by the revolver over the SIF (Anderson, 1884; Hill, 1898) as revealed by the results of some physicochemical analyses made on filtrates obtained from both filtering apparatus which are summarized in Table 5.4. Further experiments with the revolving purifier revealed that cast iron borings/turnings outperformed the spongy iron in the revolver (Anderson, 1885; Ogston, 1885). This was believed to be due to the fact that the cracked and rough surfaces of the sponge iron particles dictates that only prominences are brightened by the agitation, thus, only prominences remain active during the operation, hence, a reduced active surface area. This is supported by the observation by Ogston (1885), that oxidation of the iron surface lowers their functionality. While this argument is valid, the relative density of porous sponge iron (<4.0 g/cm^3) and compact dense Fe^0 (7.8 g/cm^3) is another possible explanation (Westerhoff and James, 2003; Zafarani et al., 2014). Heavier particles are prone to more intensive attrition than lighter, inducing more FeCPs for contaminant removal.

5.3.11. Optimizing revolving purifier

The success of the Anderson revolving purifier soon publicised the technology all around Europe and beyond. For example the technology found application in other cities like Ostend/Belgium (Tucker, 1892), Vienna/Austria (Tucker, 1892) Dordrecht/Holland (Devonshire, 1890), Strahlsun/Germany (Bamber et al., 1886), Worcester and Stamford both in England (Booth et al., 1883; Ogston, 1883; Baker, 1934), Paris/France (Tucker, 1892; Hill, 1898). The revolving purifier was also applied in some non-Western countries including Egypt, India and Turkey (Anonymous, 1896). It was also experimented or proposed in Ohio and Brooklyn in the USA, Berlin/Germany, London/England and Florence/Italy (Anderson, 1889; Anonymous, 1891; Hill, 1898; Baker, 1934). Some cities have adopted Antwerp revolving purifier without modification but others have modified it (Baker, 1934). The original revolving purifier was also sized down (downscaled) to meet the requirements of small communities (Konig, 1899a). This aspect is perhaps the most important innovation with regard to the current trend for decentralized solutions for safe drinking water provision. A survey of some of the named modifications will help to enhance understanding of the Anderson water purification process.

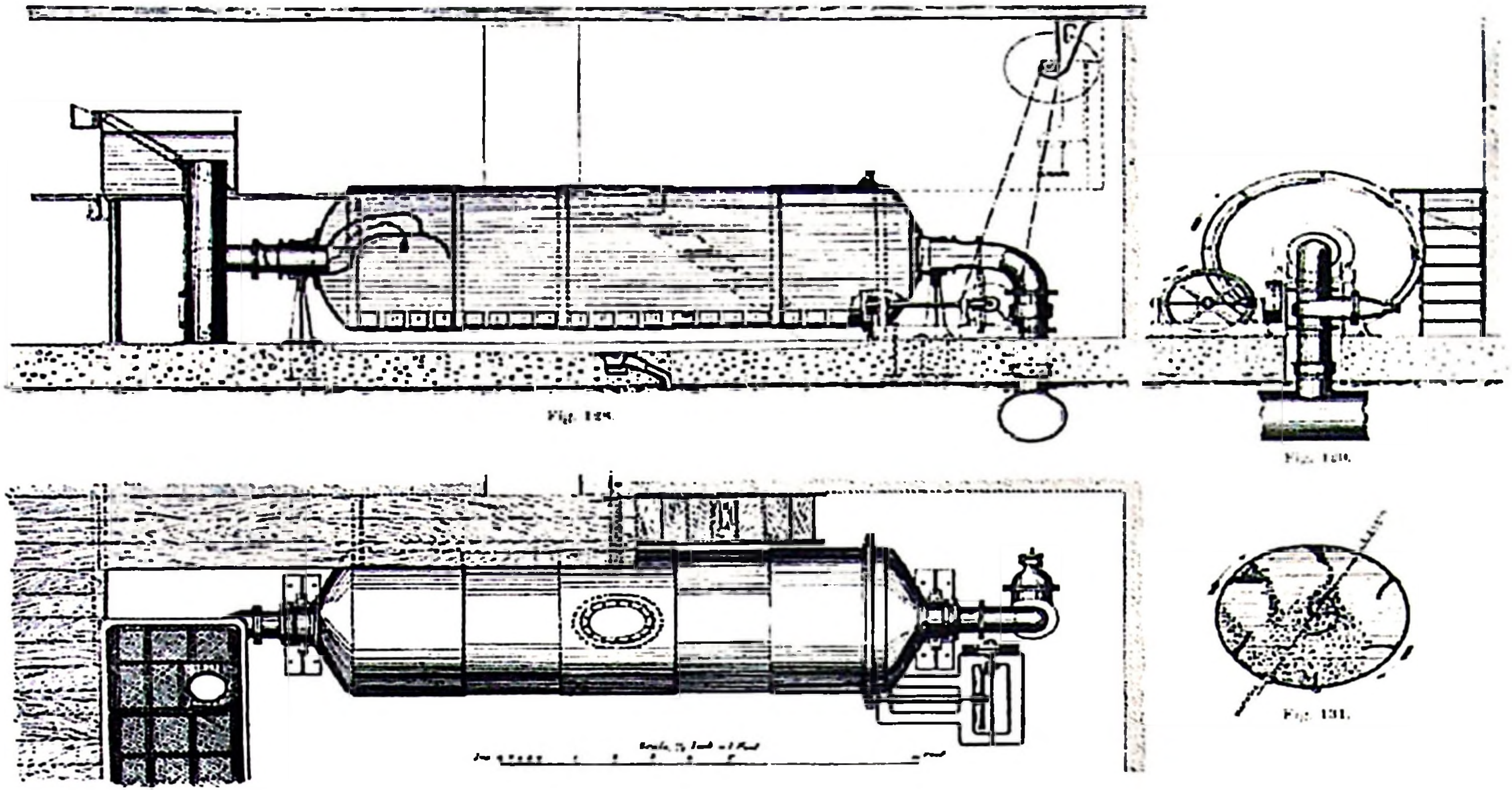

Fig. 5. 4. A side view of the Andersons's revolving purifier (5 feet in diammeter and 15 feet in length) (Anderson, 1885)

Operation of the revolving purifier pinpointed the significance of aeration in the process (Table 5.5). This is vivid in the modification done to the revolver by Devonshire's patent (1890), Anderson (1891) and Scowden (1896). These patents mainly modified the aeration process, by introducing air (O_2 for Fe(II) oxidation) right in the cylinder. Agitation coupled with this modification significantly enhanced efficiency of the revolver by increasing formation of FeCPs and subsequent contaminant co-precipitation.

The other important modification is that of introducing artificial aeration structures in the aeration hole and reservoirs between the revolver and the sand filter. In Dordrecht/Holland, for example, the modification involved the introduction of baffles along the aeration orifice (Devonshire, 1890). These baffles could increase aeration at the same time enhancing settling of the precipitate of iron. The result being that the sand filter needed cleaning only once in three months (Devonshire, 1890). In other places this entailed artificial aeration of the water or cascading the aeration for increased aeration (Devonshire, 1890; Don and Chilson, 1911). Even though this primarily aimed at lowering the operation cost as it reduced the number of times the sand filter was to be cleaned (Devonshire, 1890), its advantages point to the importance of aeration in the mechanism by which contaminants were removed (Devonshire, 1890; Tucker, 1892). For instance, while the sand filter was to be cleaned twice every fortnight, it could work for six weeks without cleaning after introducing the reservoir, therefore, facilitating the oxidation of the iron compounds into ferric hydrates and their subsequent flocculation after which they were easily precipitated and or removed by mechanical straining in the ordinary sand filter.

Summarized, (improved) aeration constituted the most important modification of the original revolving purifier. It should be anticipated, that this old knowledge requiring two or three steps for improved water treatment using Fe^0 has only been rediscovered around 2010 (Gottinger et al., 2013; Neumann et al., 2013; Kowalski and Sogaard, 2014; Casentini et al., 2016; Yang et al., 2016, 2017; Smith et al., 2017). In the contemporary context, however, not mechanical agitation, but the use of strong oxidants (e.g. H_2O_2 and O_3) induces increased generation of FeCPs (Yang et al., 2016, 2017). For water treatment in the developing world, the use of chemicals should be avoided if the technology should be sustainable and frugal. In essence, the failure of the Kanchan filter (Ngai et al., 2006, 2007) is due to lack of increased generation of FeCPs. These two aspects made it abundantly clear, that considering the lost knowledge would have sped the establishment of the Fe^0 technology as a whole.

5.3.12. Rediscovery of Fe^0 for water treatment (1990s)

The efficiency of Fe0 filters to treat chemical and microbiologically contaminated water have been well proven in practice and established during the past two decades (Guan et al., 2015; Noubactep, 2015; Sun et al., 2016). However, related works show, that the sustainability of Fe^0 beds is still severely confined by (i) reactivity loss and (ii) permeability loss (Henderson and Demond, 2007; Noubactep, 2011; Car_e et al., 2013; Domga et al., 2015; Ghauch, 2015; Guan et al., 2015). The first is due to the formation of an oxide scale on Fe0 and the second to pore filling by in-situ generated FeCPs. It appears that these two key issues are necessarily linked to iron corrosion and common during the lifespan of a Fe^0 bed mainly at pH 4.5. Enhancing the sustainability can impair the system efficiency, thus current efforts in properly designing Fe^0 filters seek to find a compromise between enhanced sustainability and long-term efficiency (Miyajima and Noubactep, 2013; Btatkeu-K et al., 2014). It is important to underline that, contrary to the operating mode of 'revolving purifiers', current Fe^0 filters are designed based on results fromwell-mixed batch experiments. This approach criticized in the peer-reviewed literature in 2007 (Noubactep, 2007, 2008) is still commonplace (Ghauch, 2015; Noubactep, 2015). In retrospective, it is as if the continuous generation of FeCPs in the vicinity of Fe^0 particles (Bischof Process) is optimized separately like in the Anderson process (remark 1).

During the last decade, it has been extensively demonstrated that the most important challenge faced by the Fe^0 technology derives from the evidence that (i) water is not properly regarded as the most important corroding agent, yielding abundant FeCPs, and (ii) the volumetric expansive nature of iron corrosion (Pilling and Bedworth, 1923; Care et al., 2008; Zhao et al., 2011) was not properly considered. In fact, the volume of any oxide is larger than that of the parent Fe^0 (Pilling and Bedworth, 1923). The larger the availability of dissolved O_2, the larger the amount of the FeCPs. This knowledge implies three tools to sustain the efficiency of Fe^0 filters: (i) decreasing the proportion of Fe^0 in the filter (Care et al., 2013; Domga et al., 2015), (ii) limiting the level of dissolved O_2 (Mackenzie et al., 1999) and/or (iii) using the porous Fe^0 materials (Hussam and Munir, 2007; Rahman et al., 2013). In essence, the Sono Arsenic filter of Hussam and Munir (2007) corresponds to the Bischof filter (1877). With the subtle but important difference, that they were designed to address different contaminants.

This volumetric expansive nature of iron corrosion implies, that contaminants' elimination by both (i) physical sequestration (as a result of contaminants enmeshment during the precipitation of oxides) (Crawford et al., 1993) and (ii) improving size exclusion (Duff et al., 2002) do occur independent of any adsorptive affinity between the contaminants and the formed iron hydr(oxides). On the other hand, as the Fe^0 surface is continuously shielded with porous positively charged hydr(oxides), both negatively and positively charged contaminants can be removed by adsorption during the filter service life (Phukan, 2015; Kumar and Sinha, 2017). Beside this, adsorbed intermediate species (including Fe^{2+} and H^+/H_2) onto oxides also increasingly participate to contaminants removal by chemical transformation (e.g. reduction) (Charlet et al., 1998). This contradicts the concept that iron is a lone reducing agent, and justifies, why filtration on Fe^0 beds is admittedly a reactive filtration with adsorption, co-precipitation and adsorptive size-exclusion as the main mechanisms yielding contaminants removal (Noubactep, 2007; London et al., 2013; Ghauch, 2015). It should be recalled that any reductive transformation observed in Fe^0/H_2O systems is a chemical reaction (electrons from Fe(II) and H species, not from Fe^0) (Ghauch, 2015; Noubactep, 2015; Gheju et al., 2016).

5.3.13. Designing Fe^0 filters for water treatment

A well-designed Fe^0 filter can free polluted water from physical (taste, odours, and suspended solids), micro-biological (bacteria, viruses) and chemical (inorganic and organic) contaminants (Ngai et al., 2007; Noubactep et al., 2012; Gottinger et al., 2013). Some particularities of Fe^0 filters are that they operate without chemicals and electricity. As a result, the efficiency of a Fe^0 filter depends on the used Fe^0 size, intrinsic reactivity and the thickness of the reactive zone. The effluent physicochemical properties (e.g. pH and competing species) and its resident time in the filter are also considered. Truly, there is a high degree of diversity among operational factors that makes it difficult to easily identify real conditions for optimal operation (Domga et al., 2015; Tepong-Tsinde et al., 2015). In conventional application, sand (coarse or fine) is used in a pre-filtration (Fig. 5.3) to remove suspended matters. This operation, analogue to that of a BSF, encourages the development of a microbiological community consequently forming a biofilm (Haig, 2014), which, through respiration reduces the dissolved O_2 concentration, and thus enhances the sustainability of the Fe^0 filter. In fact, in the presence of high oxygen levels or under oxic conditions, the service life of Fe^0 filters are considerably shortened by the formation of more voluminous corrosion products (Care et al., 2013; Noubactep, 2014; Domga et al., 2015). Besides reducing the O_2 concentration, Fe^0 is often mixed with inert additive materials (e.g. sand, pumice), and hence the filter initial porosity is increased. Pure Fe^0 filters (100% Fe^0 beds) have been proven efficient, but not sustainable. Increasing the initial porosity improves the sustainability but can impair the efficiency. Thus, properly designing Fe^0 filters should therefore be finding a compromise between enhanced sustainability and long-term efficiency. In other words, successfully combining the BSF O^{2-} removing capacity and the aqueous contaminant-scavenging ability of the used Fe^0 material may present a powerful and long-lasting contaminant remediation system.

5.3.14. Controversies among the Fe^0 research community

The controversy among Fe^0 researchers is mainly in the mechanism by which the media remove contaminants from water (Nkundimana et al., 2015). While one 'school of thoughts' advocates reduction as the main contaminant removal mechanism (Henderson and Demond, 2007; Fu et al., 2014; Colombo et al., 2015), the other advocates co-precipitation, adsorption and size exclusion as the main removal mechanisms (Ghauch, 2008; Gheju, 2011; Gheju and Balcu, 2011; Ghauch et al., 2011; Ghauch, 2015; Noubactep, 2015; Gheju et al., 2016). This controversy is already lasting for a decade and it seems there is no way out of the valley of confusion. While all arguments supporting the reductive transformation, view have been ruled out (Noubactep, 2015; Ebelle et al., 2017), active researchers are still ignoring the made amendments (Noubactep, 2011; Song et al., 2017). The next section will point to some of the lessons which ancient application of Fe^0 in water treatment provides for Fe^0 research community today. Considering these lessons may in part help to re-direct and settle the controversy amongst Fe^0 researchers.

5.3.15. Lessons from ancient Antwerp waterworks

Lesson from the Bischof process

The design of the SIF (Bischof process) involved a reactive bed of three feet thickness with a mixture of spongy iron and gravel in the ratio 1:3 (Anderson,1883; Devonshire,1890). This 1:3 material ratio corresponds to the one recently theoretically established (Domga et al., 2015) and experimentally validated (Btatkeu-K et al., 2014). This result suggests that the design of Bischof resulted from preliminary systematic investigations that may have even been published, but the publication style of those days could not ease a definitive answer to this concern (see section 5.2). Accordingly, the first lesson from the ancient Fe^0 technology can be formulated as: "Never use a pure Fe^0 filter for a sustainable filter" (Lesson 1). Bischof gave the Fe0/additive ratio in volumetric proportions. This approach is very practical and has been independently rationalized both on a scientific (Care et al., 2013; Domga et al., 2015) and a frugal perspective (Btatkeu-K et al., 2016). The scientific rationalization is that, it is the time-dependent change of initial porosity of the filter which is to be followed. The frugal rationalization is that balance may not be available in some locations to weight the required mass of Fe^0 and sand. As pointed out recently, a critical review of published data on Fe^0 technology is impaired by the evidence, that the operational conditions including the Fe^0/ additive ratio are not properly documented. In addition, giving the mass of used Fe^0 or the proportion in the mixture without details on the size of the reaction vessels could be regarded as incomplete. The second lesson from the ancient Fe^0 technology can be formulated as "record details on the operational conditions" (Lesson 2). The evidence that despite a good Fe^0/sand ratio, the SIF filters at Antwerp clogged completely after 18 months making the filter useless despite Fe^0 not being exhausted demonstrated, that a design challenge was still available. Bischof was convinced that a contact time of 45 min was necessary to induce complete contaminant removal. This assumption evidently neglected the evidence that the kinetics of iron corrosion is neither constant nor a linear function of the time (Noubactep, 2016b). It is worth noting that Fe^0 clogging intensified, when the filter operated to produce large volumes of water within a short time (Anderson, 1889). The Fe^0 amount (e.g. mass or volume), the Fe^0/aggregate ratio and the dimension of the Fe^0 bed should be brought into relation with the kinetics of iron corrosion and the contaminant flux. This evidence implies that reactivity loss and permeability loss are not independent processes. Most importantly, only experience (pilot test for long time) can enable the design of efficient Fe^0 filters. This was excellently demonstrated at Antwerp, as the system excellently worked for 18 months, but the efficiency deteriorated within 6 months and made the system no more affordable. Despite this negative aspect, the Lesson 3 is a positive one: "A properly designed Fe^0 filter can be operated optimally for up to two years". This has been the goal of recent efforts to design Fe^0 filters for decentralized safe drinking water provision (Nde-Tchoupe et al., 2015 Tepong-Tsinde et al., 2015).

Lesson from the Anderson Process

The revolving purifier was aimed at agitating Fe^0 to prevent what is commonly termed 'reactivity loss' (Henderson and Demond, 2007) by keeping its surface clean all the time (Anderson, 1884, 1885; Ogston, 1885; Devonshire, 1890). This agitation enabled progressive generation of FeCPs for aqueous contaminant removal (Anderson, 1889; Devonshire, 1890; Swete, 1892; Don and Chilson, 1911; van Craenenbroeck, 1998). This made the revolver a better approach (than the SIF filter; Bischof process) to use Fe^0 for the production of large amount of safe drinking water during a relative short time. The evidence that the Bischof process was proven inefficient in satisfying the needs of the city of Antwerp beyond 1883 (Anderson, 1884, 1885; Ogston, 1885; Devonshire, 1890; Swete, 1892; Don and Chilson, 1911; van Craenenbroeck, 1998) does not mean, that SIF is not an efficient process for safe drinking water provision. It should be recalled that SIF filters were efficient at large scale for the first 18 months. Accordingly, Lesson 4 can be formulated as: "The Fe^0 technology is an appropriate one as it can be designed to meet the needs of the community".

Another key issue from testing the Anderson process at Antwerp was the observation, that the revolver performed better with iron boring/turnings than with sponge iron (Anderson, 1885; Ogston, 1885). As discussed in section 3.6.3, the given rationale for this was not convincing. However, the fact that the best material for the Bischof process was the worse in the Anderson process demonstrates that there is no universal Fe^0 material that could be regarded as good for all the situations (Doula, 2009). Given that each water source is unique, even the same material would not give the same results at two distinct sites. The next lesson (Lesson 5) from the ancient use of Fe^0 for safe drinking water provision is formulated as: "Fe^0 materials should be systematically characterized for their intrinsic reactivity". There is evidence that such a systematic material characterization is yet to be started (Btatkeu-K et al., 2013; Birke et al., 2015; Li et al., 2016; Sun et al., 2016). This makes available results collectively qualitative as independent results cannot be really compared to each other.

The major modification of the original Anderson process involved the introduction of artificial aeration, settling reservoir between the revolver and the sand filter (Devonshire, 1890; Swete, 1892; Scowden, 1896). The main feature of aeration is Fe(II) oxidation to less soluble FeIII species (Liu and Millero, 1999). The subsequent precipitation induced co-precipitation of species available in trace amounts (Crawford et al., 1993; Duff et al., 2002). This is the removal mechanism for chemicals, colour, pathogens and suspended solids as explained then (Devonshire, 1890; Swete, 1892; Don and Chilson, 1911). This explanation corresponds to the idea which has recently led the suggestion of Fe^0 as universal material for safe drinking water production (Noubactep et al., 2009; Noubactep, 2010, 2011; Noubactep et al., 2012). Thus, Lesson 6 can be formulated as: "Fe^0 is a universal material for safe drinking water provision". The open question is to identify which levels of which contaminant impair the process of iron corrosion and to which extent. This research question is valid for Fe^0 filters (Bischof or Spencer process) and for methods similar to the Anderson process

(Gottinger et al., 2013; Chaudhari et al., 2014; Kolwalski and Sogaard, 2014; Casentini et al., 2016).

5.3.16. The decline of the Anderson process

The literature found and considered for this work has not given a clear reason, why the Anderson Process was outdated. It is certain that the occupation of Belgium during World War I (WWI) has impaired the further development of the revolving purifier (Anonymous, 1919). WWI has also possibly 'catalysed' the insolvency of Easton and Anderson, the company which has introduced Fe^0 in safe drinking water provision at large scale in Antwerp (Belgium). Easton and Anderson supplied Antwerp with safe drinking water until 1930 (van Craenenbroeck, 1998). According to van Craenenbroeck (1998), the underperformance of revolving purifiers at Antwerp was coupled to the increasing deterioration of the quality of the water from the river Nethe. The same source indicated that worsened raw water quality prompted to put off revolvers around 1908 in several plants. Analysis of water around 1914, when the remaining revolvers were already reckoned unsuitable for water treatment, showed that the water contained higher concentrations of humic acids which were also condemned for imparting yellow colour. These were known to form soluble complexes with iron which in turn limited the precipitation of ferric oxide (van Craenenbroeck, 1998). The view of van Craenenbroeck (1998) that the Fe^0 technology for safe water provision was outdated before 1914 is contradicted with reports on the impact of WWI on the development of revolving purifiers (Anonymous, 1919; van der Taelen, 1919). Davis (1891) argued that both the Bischof and the Anderson processes were abandoned because they were not cost-effective. It is not the objective of this study to bring clarity in the actual decline cause or the exact reason for this. It is sufficient to state that a knowledge loss has occurred as a consequence.

5.4. Discussion

Metallic iron (Fe0) has been successfully used for safe drinking water provision during the 19th century (Baker, 1934; van Craenenbroeck, 1998). Prior to the invention of household Fe0- based filters (1856), rusty Fe^0 materials (e.g. iron nails) were used to treat water before consumption (Konig, 1899a). Between 1856 and 1877 several different Fe0 materials were tested or developed as filter materials. The sponge iron (a porous material) of Prof. Bischof showed the best performance (Bischof process) (Hill, 1898; Konig, 1899a). The success of Bischof process at household level prompted the testing and application at large scale in Antwerp (Belgium) between 1881 and 1883. The first 18 months of operation were very satisfactory. However, the Bischof process was proven unable to cope with increasing water demand. But the history of water supply in Antwerp teaches that properly designed Fe^0-based filters can supply relatively large communities with safe drinking water (Devonshire, 1890). The failure of the Bischof process was mainly due to permeability loss (filter clogging), because Fe^0 and gravel particles were cemented into a cake. In the absence of permeability, the required 45 min contact time was impossible to observe (section 5.3.5).

The Bischof process (one step filtration) was replaced by a twostep process consisting in shaking finely divided Fe^0 particles in a 'revolving purifier' and subsequently aerate the solution from the purifier to enable oxidation of Fe(II) species to less soluble Fe(III) ones (Hill, 1898). The solution from the aeration unit is filtered through a conventional sand filter, where iron precipitates (enmeshing the contaminants) are captured. This three-step-system was termed Anderson process (Devonshire, 1890). The success of the Anderson process prompted its application in several other countries including Egypt, England, France, Germany, India, Italy and the USA (Baker, 1934; van Craenenbroeck, 1998). At Antwerp, the Anderson process operated until at least 1908. The exploited literature has demonstrated that both the Bischof process and the Anderson process were mainly outdated because of worsened raw water quality. However, the water quality then and now is not really comparable. In addition, used materials were (and are currently) not characterized for their intrinsic reactivity (Hill, 1898; Noubactep et al., 2005; Btatkeu-K et al., 2013; Li et al., 2016). A critical study on the chemical processes involved in ancient Fe^0 application reveals, that they were not different from ones observable in the recent Fe^0 studies and applications. The main contaminant removal mechanism then established was basically co-precipitation, with Fe^0 being a generator of the co-precipitants (Bischoff Process, Anderson Process). The late 20th century literature on the application of Fe^0 for environmental remediation seems to have completely ignored this ancient knowledge (Gillham, 2010; Guan et al., 2015; Song et al., 2017).

5.5. Conclusion

This chapter capitalized on the availability of a large number of field scale uses of Fe^0 for safe drinking water provision performed mainly in Europe during last and first quarter of the 19th and 20th century respectively. The results are collectively regarded as an independent validation of the concept that Fe^0 is a universal generator of adsorbing (contaminant collectors) and reducing agents. The knowledge indicates that the final product in all the iron based treatment units is Fe(III) ions and hydr(oxides) and that it is a cost-effective universal material for safe drinking water provision both at household and community level. These products are common in the modern-day application of iron materials for water defluoridation. Therefore, determination of the effect of Fe(III) ions on the fluoride removal properties of the iron-based materials is important. Knowledge from this will help in improving the iron-based activation methods of the plant biomass materials and possible application of metallic iron for water defluoridation as presented in Chapter 6.

CHAPTER 6: The effect of Fe^{3+} on the fluoride removal properties of the iron-based materials

6.1. Introduction

In the ancient large-scale application of iron for water treatment presented in Chapter 5, the treatment plant design involved the structures for aeration of the treated water (Anderson, 1883; Devonshire, 1890). These structures were meant to accelerate the oxidation of Fe to Fe(III) and consequential coagulation of the Fe(III) hydr(oxides). In the household scale units in which the aeration structures could not be installed, the treated water tested rusty (Wigner, 1878; Devonshire, 1890). This implied that the treated water contained residues of Fe(III) hydr(oxides). In the modern day studies involving investigation of iron-activated materials for water defluoridation iron Fe(III) is loaded on the surface of the materials (Zhao et al., 2008; Cai et al., 2015). These Fe(III)-loaded materials have shown different stabilities in aqueous media. Where some have insignificant desorption of Fe(III) ion, others release a quantifiable amount of Fe(III) into the treated water (Zhao et al., 2008; Cai et al., 2015; Xu et al., 2015). For instance, the post-alkalised Fe(III)-loaded biomass was found to be stable in aqueous media with insignificant desorption of Fe(III) ions into the treated water (Cai et al., 2015) but this increased in acidic condition where the biomass performed best. When the loading of the biomass materials with Fe(III) did not involve post-procedure alkalisation, the resulting activated biomass released a significant amount of Fe(III) (Zhao et al., 2008) into the treated water. Since the iron can be easily oxidised in the presence of air to Fe(III), it follows that the a mixture Fe(III) ions and hydr(oxides) is predictable in most systems that use iron or iron-loaded materials for water treatment. For this reason, a study is needed to understand the effect of this co-existence on their defluoridation properties.

This is because, Fe(III) hydr(oxides) are shown to have a special affinity for fluoride ions and most of the modern day studies have explored the defluoridation properties of such compounds (Cai et al., 2015; Xu et al., 2015). On the other hand, for a long time, Fe(III) ions have been reported to have affinity for fluoride ions (Foster, 1933; Ingols et al., 1950; Baily, 1957; Krishnamurti et al., 1990) and that this affinity is affected by solution pH. Therefore, co-existence of Fe(III) ions and their hydr(oxides) could predictably have an influence on their defluoridation properties. Since both in the ancient and modern application of iron for water treatment Fe(III) ions are shown to commonly exist with their hydr(oxides), the effect of these ions on the fluoride removal properties of the Fe(III)-loaded biomass materials is a worthwhile pursuit.

In this chapter, the effect of the Fe^{3+} ions on the fluoride adsorption properties of the Fe(III)-loaded sisal fibre and zero valent iron is presented. This is important to improve our understanding on the fluoride removal mechanism of the metallic iron and iron-loaded materials and therefore shed light on the appropriate designs for field application of the materials in water defluoridation. This knowledge may be useful in directing future studies in exploring possible application of other forms of iron for water defluoridation.

6.2. Materials and methods

6.2.1. Materials and materials preparation

The Fe(III)-loaded materials (non-alkalised and post-alkalised Fe(III)-activated sisal fibres) for this study were prepared according to methods described in Chapter 4 of this thesis. The 0.1 M solution of $FeCl_3$ solutions were prepared by appropriate dilution of the stock solutions (0.5 M) prepared from the pure reagents as described in Chapter 4. The zero valent iron (fine steel wool) was supplied by Lakairo steel wool (Lakairo Industries, Mwanza, Tanzania) and used in its original condition.

Methods

6.2.2. Determination of the influence of Fe^{3+} ion on the fluoride adsorption efficiency of the Fe(III)-loaded biomass

To determine the influence of the Fe^{3+} ion on fluoride adsorption efficiency of the non-alkalized and post-alkalized Fe(III)-loaded biomass, 1 g of each of the non-alkalized and post alkalized Fe(III)-loaded sisal fibres was added into 40 mL of the 10 mg/L of fluoride solution in the separate 50 mL plastic falcon tubes in in the control experiment. The 10 mg/L concentration of fluoride is widely used in related studies; hence, it was (in this study) selected for comparison purposes as stated in Chapter 4. In the experimental set, the 40 mL of 10 mg/L fluoride solution was spiked with 3 drops of the prepared 0.1 M $FeCl_3$ solution. The pH of the fluoride solution before and after addition of drops of the $FeCl_3$ solution and the fluoride concentrations were determined as described in the methodology in Chapter 3 of this thesis. All experiments were triplicated, and average values used in plotting graphs.

6.2.3. Determination of the difference between the influence of the Fe^{3+}- and HCl-induced acidity in enhancing the fluoride removal efficiency of Fe(III)-loaded biomass

To determine the difference between the HCl-induced acidity and Fe^{3+} induced acidity, two sets of experiments were conducted. In the first set the pH of the 40 mL of 10 mg/L fluoride solution was adjusted to 4 in in two separate 50 mL plastic falcon tubes by using 0.1 M HCl solution. Then 1 g of the non-alkalized and post-alkalized Fe(III)-loaded biomass was added into each of the HCl-acidified 40 mL of 10 mg/L fluoride solution and shaken at regular intervals for a total of one hour after which the concentrations of fluoride ions were determined by ion selective electrode. In the second set, the 40 mL of the 10 mg/L fluoride solution was acidified by adding Fe^{3+} solution dropwise to prepare solutions with pH 4 for adding 1 g of the post-alkalised and non-alkalised Fe(III)-activated sisal fibres. The mixtures were shaken at regular intervals as above for one hour and fluoride levels estimated. The effect of HCl-induced acidity on desorption of the Fe^{3+} from the biomass was determined by estimating the concentration of Fe^{3+} ions in the HCl-spiked reactors by Atomic Absorption Spectrometer (919 SOLAAR, UNICAM, UK).

6.2.4. Determination of the detectability of fluoride in presence of the Fe^{3+} ions

To determine whether the difference in the measured fluoride concentration in the Fe^{3+}-spiked solution was not due to the presence of fluoro-complexes of Fe^{3+} ions, the effect of time on the fluoride concentration in the Fe^{3+} solution was investigated as follows; equal volumes of the 10 mg/L of the fluoride solution and 324 mg/L of $FeCl_3$ solution were mixed in three different 1 L plastic vessels and shaken vigorously for e few seconds. Then the pH and fluoride concentration of the mixtures were determined at regular intervals for a total of 24 hours. Average values were used to show the trend in graphs.

6.2.5. Determination of the effect of Fe^{3+} on the fluoride removal efficiency of the metallic iron

To determine the effect of Fe^{3+} on the fluoride removal efficiency of the metallic iron, 9 g of the fine steel wool was added into 300 mL of 10 mg/L fluoride solution in a 500 mL plastic bottle. Another 9 g of steel wool was added into 300 mL of the 10 mg/L fluoride solution spiked with $FeCl_3$ solution as explained in the previous sections. The mixtures were shaken at regular intervals for a total of four days after which the samples taken from each bottle for fluoride analysis. The fluoride concentration and initial and final pH values in the samples were estimated by the method described in Chapter 3. These experiments were duplicated and averages used in plotting graphs.

6.2.6. Determination of the effect of time on the fluoride removal efficiency of the $FeCl_3$-spiked and non-spiked fluoride solution

In determination of the effect of time on the fluoride removal efficiency of the $FeCl_3$-spiked and non-spike fluoride solutions, 300 mL of the 10 mg/L fluoride solution spiked with $FeCl_3$ was equilibrated with 9 g of metallic iron for a total of 14 days with vigorous shaking at regular intervals. Exactly 5 mL was withdrawn from the reactor after day one, day three, day six, day nine, day twelve and day fourteen. A similar control treatment involved non-spiked fluoride solutions. Fluoride levels in the withdrawn samples were estimated by ion selective electrode as described above.

6.2.7. Determination of the effect of Fe^{3+} concentration on the fluoride removal by metallic iron

The fluoride solution with the concentration of 20 mg/L was prepared by appropriate dilution of the fluoride stock solution (F = 1000 mg/L). This was used in preparation of the 10 mg/L fluoride solution with Fe^{3+} concentrations of 0.001, 0.005, 0.01, 0.05, 0.1 M by mixing equal volumes of the 20 mg/L of fluoride solution with the appropriate (with a concentration twice of the required) $FeCl_3$ solution prepared by dilution of the 0.5 M $FeCl_3$ solution to make 300 mL of the fluoride solutions spiked with Fe^{3+}. The mixtures were shaken vigorously and 9g of the steel wool (Fe^0) was added. Shaking was continued at regular intervals for a total of 4 days after which the concentration of fluoride was estimated as described in Chapter 3.

6.3. Results and discussion

6.3.1. The influence of Fe^{3+} ion on fluoride adsorption by Fe(III)-loaded biomass materials

Addition of three drops of 0.1 M $FeCl_3$ solution in the fluoride solution resulted in the increase of the fluoride removal efficiency of both the non-alkalized and post-alkalized Fe(III)-loaded biomass materials from 32 to 54 and 10.6 to 23 % respectively as shown in Fig. 6.1. This addition of Fe^{3+} solution lowered the pH of the fluoride solution to between 3.5 and 4.5. Similar findings were reported when the stability of the non-alkalised and post-alkalised Fe(III)-activated biomass materials were compared in relation to their defluoridation capacities where the non-alkalized which showed higher Fe^{3+} desorption had higher fluoride removal efficiency than the post-alkalized one which was more stable in fluoride solution as discussed in Chapter 4. This suggests that the presence of Fe^{3+} in the water to be treated may increase interactions between fluoride and the Fe(III)-loaded biomass materials. This enhanced interaction between fluoride ion and Fe(III)-loaded materials proposed here could aid in the explanation of the low fluoride removal efficiency and consequential sorption mechanism when iron salts are used for coagulation of fluoride (Boruff, 1934). This is because in alkaline media, the affinity of hydroxyl ions to the Fe^{3+} is greater than that of the fluoride ion (Kerslake et al., 1946; Baily, 1957; Gregory and Duan, 2001) as shown on Chapter 5. Since the presence of Fe^{3+} ion in water results in lowering of its pH, the enhanced fluoride removal property of the Fe(III)-loaded materials in the presence of Fe^{3+} may partly be due to lowered solution pH (Cai et al., 2015). Therefore, the next section presents the differences between the acid- and Fe^{3+}-induced acidity on the fluoride removal efficiencies of the studied Fe(III)-activated biomass materials.

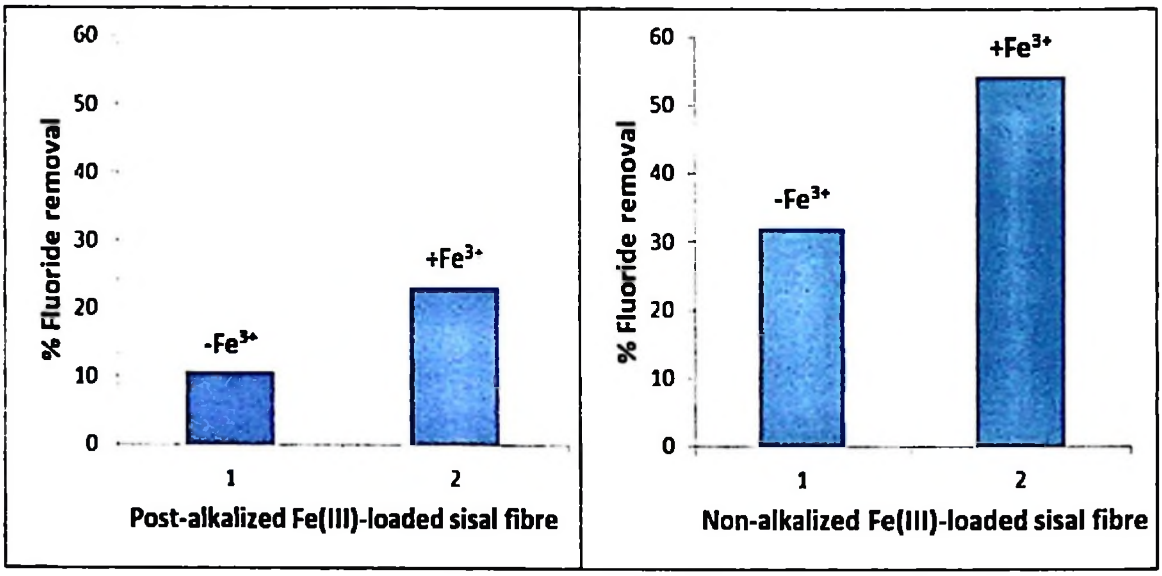

Fig. 6. 1. The effect of Fe(III) ion on the fluoride removal efficiency of Fe(III)-loaded biomass at dose = 1 g/40 mL, pH = 7, F concentration = 10 mg/L

6.3.2. The difference between Fe^{3+}- and HCl-induced acidity in enhancing the fluoride removal efficiency of Fe(III)-loaded biomass.

The fluoride removal efficiency of HCl-induced (pH=4) acidity in the post-alkalized Fe(III)-loaded sisal fibre was found to be 16.3 % while that in the non-alkalized biomass was 26.8 %. For the corresponding Fe^{3+}-induced acidity the fluoride removal efficiency of the post-alkalized and the non-alkalized Fe(III)-loaded biomass were found to be 22.5 and 45.1 % respectively. This is shown in Fig. 6.2. These findings show that the presence of Fe^{3+} in the fluoride solution enhances fluoride removal properties of the Fe(III)-loaded biomass by additional processes than the induced acidity. This suggests that, the higher fluoride removal efficiency of the non-alkalized Fe(III)-loaded sisal fibre than the post-alkalized one (Chapter 4) could be explained in part by the tendency of the former to undergo desorption of the Fe^{3+}

into the treated solution, allowing the co-existence of the Fe^{3+} and its hydr(oxides) in aqueous media. It is thus envisaged that in a solution with excess Fe^{3+}, fluoride removal by coagulation of fluoride will be higher than in the solution with limited supply of Fe^{3+}.

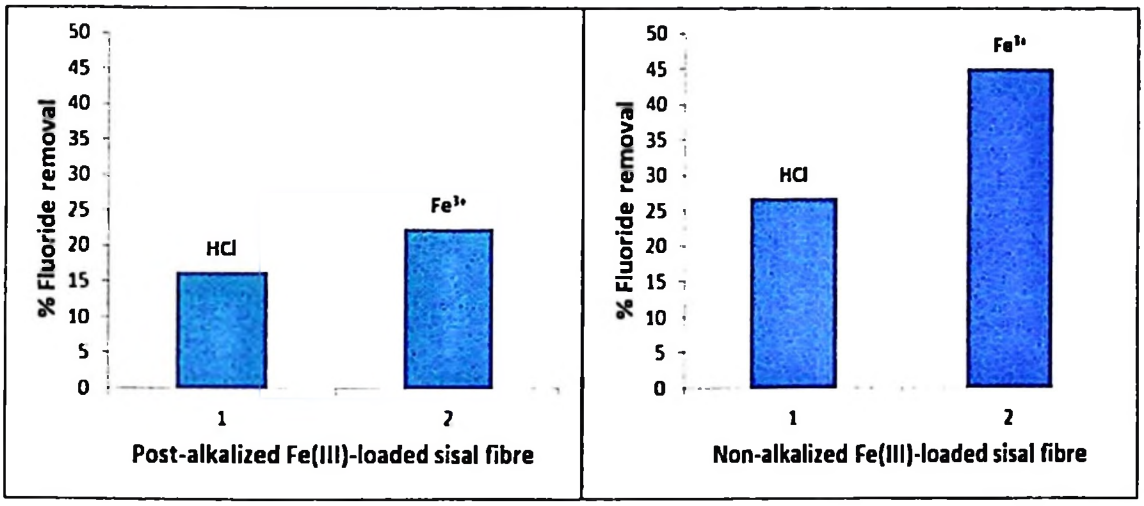

Fig. 6. 2. Comparison of the HCl-induced and Fe(III)-induced acidity on the fluoride removal efficiency of the Fe(III)-loaded materials at dose = 1 g/40 mL, F concentration =10 mg/L

6.3.3. The effect of the HCl-induced acidity on the desorption of Fe^{3+} from the Fe(III)-loaded biomass materials

When the HCl was added into the mixture of Fe(III)-loaded biomass and fluoride solution incubated for one hour, the concentration of desorbed Fe^{3+} ion increased from 0.8 to 66 mg/L and 183 to 254 mg/L (Fig. 6.3a & b) in the post-alkalized and non-alkalized Fe(III)-loaded biomass reactors respectively. This indicates that the HCl-induced acidity also increases the Fe^{3+} desorption of the Fe(III)-activated biomass materials as discussed in Chapters 4 and 5. Therefore, while increased surface charges and consequential electrostatic forces due to increased acidity may play an important role in increasing the fluoride removal efficiency by Fe(III)-loaded biomass (Cai et al., 2015), parallel increase of the Fe^{3+} may be playing and in important role in increasing the fluoride removal efficiency of these materials. This could likely be due to the enhanced surface charging of the Fe(III)-activated materials when Fe^{3+} is present (forming the coordinate bonds between the biomass surface and the fluoride ion) in the fluoride solution or the interaction between the fluoro-complexes of Fe(III) formed preferentially at low pH (Krishnamurti et al., 1990). However, this is a subject of further study.

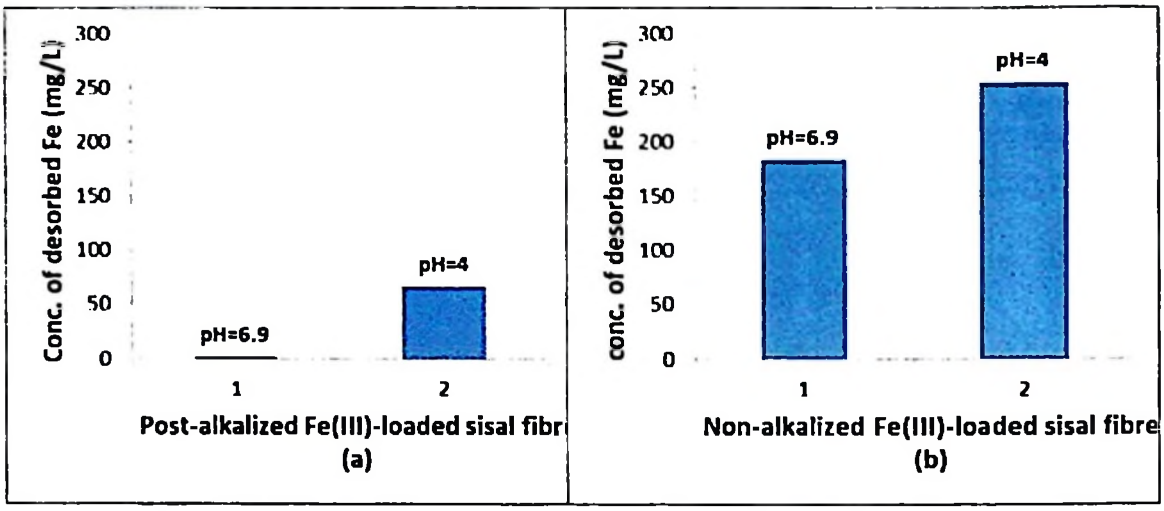

Fig. 6. 3. The effect of HCl-induced pH on the desorption of Fe(III) ion from the Fe(III)-loaded biomass at F concentration = 10 mg/L, pH = 4

6.3.4. Detectability of fluoride ion in presence of Fe^{3+}

The concentration of fluoride detectable in the $FeCl_3$ solution was generally over 97 % as shown in Fig. 6.4. The pH of the resulting solution ranged between 3.1 and 3.2. This indicated that there was greater chance of formation of fluoro-complex of Fe(III) at this pH (Tamura et al., 1974; Krishnamurti et al., 1990; Gendel and Lahav, 2008). This may serve as a proof that the differences in fluoride levels observed when Fe(III)-loaded biomass was used in the fluoride solution spiked with Fe^{3+} ion was not due to the fluoro-complex of iron limiting the detectability of fluoride ions. It may also suggest that Fe^{3+} ions need the Fe(III)-loaded surfaces to enhance their fluoride removal efficiency. Therefore, lowering the pH of the solution by HCl acid in the non-alkalized Fe(III)-loaded biomass resulted in lowering of the fluoride removal efficiency likely due to increased desorption of Fe^{3+} which in turn reduced the Fe(III)-loaded surface needed by the Fe^{3+} ions to enhance fluoride removal and that the concentration of Fe^{3+} was already in excess. However, this needs further study to reveal the actual interaction between the Fe(III)-loaded biomass and the fluoride ions when Fe^{3+} is present.

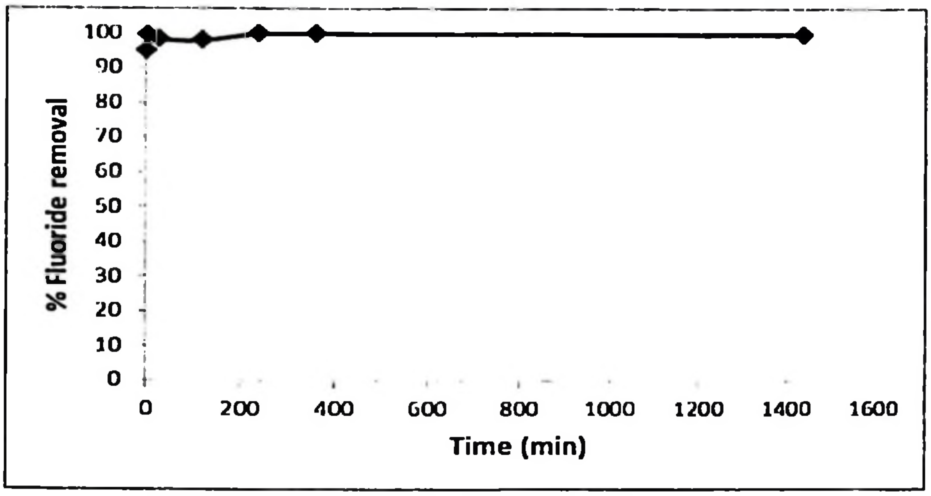

Fig. 6. 4. The effect of time on the fluoride detectability in Fe(III) spiked solutions at F concentration = 5 mg/L, Fe(III) concentration = 162 mg/L

6.3.5. The effect of Fe^{3+} on the fluoride removal efficiency of the metallic iron

The fluoride removal efficiency of the metallic iron in the fluoride solution spiked with $FeCl_3$ solution was found to be 35.9 % while that in the non-spike fluoride solution was 5.3 %. This is shown in Fig. 6.5. The pH of the solution in the $FeCl_3$-spiked sample was elevated from 3.9 before addition of the steel wool to 4.8 after addition and equilibration for four days. The corresponding change in the non-spiked solutions was from pH 6.9 to 7.5 before and after equilibration respectively. The precipitate formed in the $FeCl_3$-spiked bottles was brown to red brown likely due to co-existence of Fe^{3+} and their hydr(oxides) in solution, while, in the non-spiked bottle was dark brown to black in colour, likely due to the presence of the hydr(oxides) of Fe(II) (Chesworth, 2008). The difference in the colour of the formed precipitates could indicate the difference in the chemistry of the precipitates formed. The red-brown precipitates in the $FeCl_3$-spiked bottles could indicate that the added Fe^{3+} ions are interacting with the precipitated Fe(III) hydr(oxides) such that the higher fluoride removal efficiency observed in these bottles are the results of these interactions. When studying the effect of pH on the fluoride removal efficiency of nanoscale Fe^0, Jahin (2014) found that the maximum fluoride removal was at the pH of 4. At this pH there is a mixture of Fe^{3+} and Fe(III) hydr(oxides) in the solution (Chesworth, 2008; Kumar et al., 2014), thence, possible interaction between them. Therefore it can be asserted here that interaction between Fe^{3+} and Fe(III) hydr(oxides) coupled with the lowered pH, alters the surface characteristics of the hydr(oxides) and consequently improves their fluoride removal efficiency.

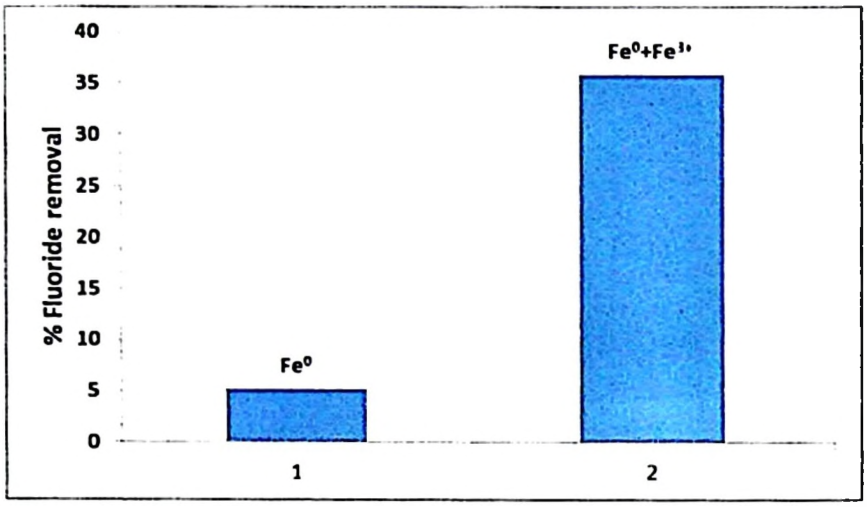

Fig. 6. 5. The effect of Fe(III) ion on the fluoride removal efficiency of Fe^0 at dose = 0.03 kg/L, F concentration = 10 mg/L, time = 4 days

6.3.6. The effect of time on the fluoride removal efficiency of the FeCl$_3$-spiked and non-spiked metallic iron

The fluoride removal efficiency of the Fe^0 increased with increasing contact time in both the FeCl$_3$-spiked and non-spiked fluoride solutions (Fig. 6.6) until after day 9 and 12 respectively. This increase in removal efficiency occurred in parallel with the increase in formation of Fe(III) hydr(oxides) precipitates formed in the solutions which could imply that the fluoride removal is effected by the Fe(III) hydr(oxides) and not the Fe^0. The colour of the precipitate in the spiked solution maintained the red-brown colour while in the non-spiked solution it turned from brown to brownish black colour. The plateau in fluoride removal efficiency of the FeCl$_3$-spiked solution after day 9 could indicate that the equilibrium state is attained, and that the fluoride removal is mainly by adsorption process. The decline in fluoride removal efficiency after day 12 in the non-spiked solution could indicate the formation of the Fe(II) hydr(oxides) with low fluoride affinity which were associated with the formation of the brownish-black precipitates (Chesworth, 2008) in the reducing Fe^0 environment. The sustained red-brown colour of the precipitate in the FeCl$_3$-spiked fluoride solution could suggest that the presence of the Fe^{3+} ions in the solution inhibit the formation of the Fe(II) hydr(oxides) with low fluoride affinity. Therefore, and addition of FeCl$_3$ solution is important in enhancing the fluoride removal efficiencies of the Fe^0 materials.

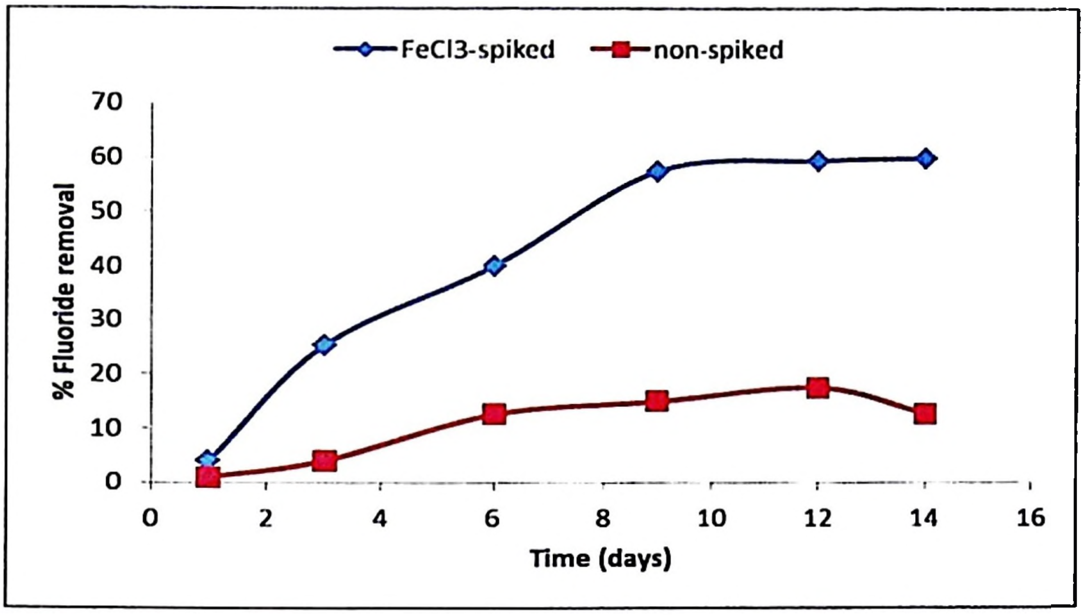

Fig. 6. 6. The effect of time on the fluoride removal efficiency of Fe^0 in the Fe(III)-spiked solution at dose = 0.03 kg/L, F concentration = 10 mg/L

From these observations it is clear that in acidic conditions the Fe(III) ions and hydr(oxides) co-exist in solutions containing iron or iron coated materials. This co-existence of the Fe(III) ions and their hydr(oxides) tend to modify the charges of the Fe(III) hydr(oxides) likely by olation of the Fe(III) ions forming the highly charged precipitates. Therefore the fluoride removal in the $FeCl_3$ spiked fluoride solution is likely due to the adsorption of the fluoride ions onto the highly charged polymeric Fe(III) hydr(oxides) precipitate.

6.3.7. The effect of Fe^{3+} concentration on the fluoride removal by metallic iron

Increasing the concentration of $FeCl_3$ from 0.001 to 0.1 M resulted in corresponding increase in the fluoride removal efficiency of the Fe^0 from 22 to 79.7 % in the $FeCl_3$-spiked fluoride solution (Fig. 6.7). This increase in concentration of the $FeCl_3$ was associated with increase in the observable amount of precipitate of Fe(III) hydr(oxides). Therefore, the increase in fluoride removal efficiency observed is attributable to the increase in amount of the Fe(III) hydr(oxides) which could imply an increase in the number of active sites.

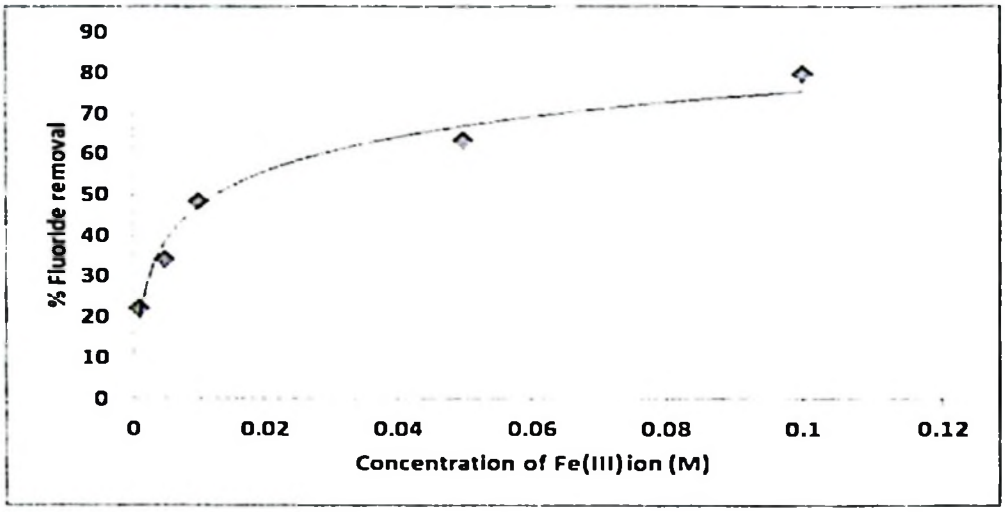

Fig. 6. 7. The effect of concentration of Fe(III) ion on the fluoride removal efficiency of Fe^0 in the Fe(III)-spiked solutions at Fe^0 dose = 0.03 kg/L, time = 4 days

These results show that the best way to use Fe^0 to remove fluoride from water is by spiking the fluoride water with Fe^{3+} salts. This Fe(III)-spiking enhances the fluoride removal efficiency of the Fe^0 materials significantly. However, for this technique to be applicable, additional action to lower the concentration of both the Fe^{3+} and neutralise the treated water will be required. As presented in Chapter 5, this can be effected by imrptoved aeration which will accelerate the formation of solid hydr(oxides) of iron.

6.4. Conclusion

The co-existence of Fe^{3+} ions and Fe(III) hydr(oxides) materials tend to enhance the fluoride removal efficiency of the Fe(III) hydr(oxides). This may likely be due to the modified surface charges of the Fe(III) hydr(oxides) which is favourable in acidic media. This could suggest that in acidic conditions the co-existence of the Fe^{3+} and the Fe(III) hydr(oxides) tend to enhance the olation of the Fe^{3+} ions in acidic media implying that the fluoride removal by these materials may be complex. This understanding sheds an important light on the fluoride removal properties of the low-cost metallic iron and iron loaded materials. It may open a new door to effective application of iron materials in water defluoridation. This special affinity of Fe^{3+} to F^- could further be exploited in efforts to develop low-cost fluoride detectors, a requirement for applicability of a smart approach in water defluoridation in rural African settings. The next chapter presents findings revealing the potential of Fe^{3+} for fluoride deection.

CHAPTER 7: Iron based detection of fluoride in aqueous media

7.1. Introduction

In a 'smart' approach for water defluoridation in rural Affrican settings explained in Chapter 1, the fluoride removal and detection materials are are to be low-cost ones. The properties of iron and Fe(III)-loaded materials in aqueous media along with the special affinity of F^- to Fe^{3+} in aqueous media, discussed in the Chapters 4, 5 and 6 are an important component in addressing the cost of the defluoridation materials. The interactions between the ions of fluoride and iron discussed in Chapters 4 and 6 may be useful in developing the low-cost fluoride detectors applicable in rural African settings, where, water defluoridation is to be done at the point of use rather than at the centralised treatment plants. This enables that; only the water for drinking and cooking is defluoridated, thence, lowering the cost of treatment. In Tanzania, for instance, the largest bone char-based treatment plants are those installed in schools for provision of clean water for school children (Fig 7.1) (Mjengera and Mkongo, 2003; Dahi, 2016). The rest are household scale units designed for medium sized families. Since these treatment units are used continually, usually not in supervision of the suppliers or by experts from the suppliers, it is obvious that they may reach saturation points without users' awareness. Furthermore, the distribution of fluoride ion in ground and surface water in this area is not predictable (Ghiglieri et al., 2010). As such, it is essential to develop and equip these communities with low cost means to detect and decontaminate their water (a smart approach) as advocated by this thesis. The methods to detect fluoride in water will enable these communities to test the saturation points of their used filters and determine time for their replacement. Alternatively, this may enable rural communities to determine the level of fluoride in the newly found water sources. While much is done to supply water treatment units for rural communities (Zevenbergen et al., 1996; Mjengera and Mkongo, 2003; Hussain et al., 2012), little is done to equip these communities with affordable technologies to determine the presence of fluoride contaminant in their water sources. This could possibly be due to the high cost and operational fragility associated with the application of the conventional fluoride analysis methods. Therefore, several studies have explored and tested the usability of different materials for detection of fluoride in aqueous media (Willard and Winter, 1933; Willard and Horton, 1950; Banerjee, 1950; Bertolacini and Barney, 1958; Belcher et al., 1959; Gaál et al., 1978; Cho et al., 2003; Zhou et al., 2014; Das et al., 2019). However, most of these methods rely on expensive rare earth metals and synthetic organic compounds, hence, the foreseeable unaffordability to poor rural communities. Therefore, the focus should be directed to low cost materials that can be used for fluoride analysis.

Therefore, the special affinity between F^- and Fe^{3+} ions in aqueous media discussed in the previous chapters provides an attractive option that could be further explored with the aim of developing low cost fluoride detectors. Interestingly, efforts to use Fe^{3+} for fluoride detection have a long history. For instance, the thiocyanato-complex of iron(III) was tested for use in calorimetric determination of fluoride (Foster, 1933) in which the presence of fluoride ions was associated with the fading of the colour of the thiocyanato-complex of iron(III). Further study by Ingols et al. (1950) revealed that the colour of the thiocyanato-complex of iron(III) is destroyed in the presence of light and that low pH intensifies the effect. However, low pH minimizes the effect of co-ions on the colour of the complex (Baily, 1957; Below et al., 1958) and enhances the affinity of F^- to Fe^{3+}. These findings, therefore, suggest that Fe-F-SCN system could be developed to a low-cost fluoride detection method for use in rural Africa. To this end, an understanding of the interactions between fluoride and thiocyanate ions with Fe^{3+} is vital.

In this chapter, the reactivity of fluoride and thiocyanate ions with Fe^{3+} and their corresponding effects on the colour of the resulting complexes in aqueous media conditions are investigated. Findings are discussed and possibilities for field application of the materials highlighted.

Fig. 7. 1. A community-scale defluoridation plant at a village school (Dahi, 2016)

7.2. Materials and methods

7.2.1. Materials and materials preparation

Analytical grade ammonium thiocyanate used in this experiment was supplied along with other chemicals by Loba Chemie Company (Loba Chemie and Ranken Companies, India) as explained in chapter three of this thesis. A 1 M NH_4SCN solution was prepared by dissolving 76.2 g of analytical grade NH_4SCN into 500 mL of distilled water and then after complete dissolution diluting to 1000 mL in a glass 1 L volumetric flask. The acidified 0.5 M $FeCl_3$ solution was prepared by modifying the methods described in Chapter 4 of this thesis for preparation of the 0.5 M $FeCl_3$ by using 1M HCl solution instead of the distilled water. The concentration and colour of Fe(III) ion was estimated by a Multiparameter photometer (HI 83300, Hanna Instruments, Rumania) according to the method described in Chapter 4 of this thesis. Different concentrations of F solution were prepared by standard dilution of 1000 mg/L F solution as described in Chapter 4 of this thesis.

Methods

7.2.2. Determination of the effect of fluoride concentration on the colour of the acidified FeCl₃ solution

Four drops of the acidified 0.5 M $FeCl_3$ solution were added into 10 mL of 2, 5, 10, 20, 40, 80, 120 and 130 mg/L of fluoride solution in separate 20 mL plastic beakers. The mixture was stirred thoroughly for a few seconds before being transferred into the 10 mL special glass vial for measuring absorbance in the multiparameter photometer for determination of the effect of fluoride concentration on the colour of the fluoro-complex of Fe(III). The experiments were replicated, and average values used in plotting graphs. The concentration of iron in the beaker that gave zero absorbance was measured by Atomic Absorption Spectrometer (SOLAAR 919, UNICAM, Cambridge, UK) according to the methods described in Chapter 6 to determine the Fe:F mole ratio at zero absorbance concentrations.

7.2.3. Determination of the effect of pH on the colour of the fluoro-complex of Fe(III)

To determine the effect of pH on the colour of the fluoro-complex of Fe(III), a 10 mL of 130 mg/L fluoride solutions with pH 1, 3, 5, 7, 9 and 11 were prepared in separate 20 mL plastic beakers by adjusting the pH of the fluoride solution according to the method described in Chapter 3. Four drops of the acidified 0.5 M $FeCl_3$ solution were added to each of the solutions and the mixture stirred thoroughly for a few seconds after which each solution was transferred to the 10 mL glass vial for measuring absorbance in the multiparameter photometer as described above. The experiments were replicated, and average values used in plotting graphs.

7.2.4. Determination of the effect of the concentration of Fe(III) on the absorbance of the $FeCl_3$ solution

In determination of the effect of concentration of Fe(III) on the colour of the $FeCl_3$ solution, different (20, 50, 100, 250, 500, 1000, 1500 mg/L) concentrations of $FeCl_3$ solutions were prepared by standard dilution of the 2000 mg/L $FeCl_3$ solution in distilled water. A 10 mL of each solution was transferred into the special glass vial and absorbance measured by the multiparameter photometer to determine the minimum detectable concentration of Fe(III) in the $FeCl_3$ solution. These experiments were conducted in duplicate. The average absorbance values were used for plotting the graphs.

7.2.5. Determination of effect of Fe^{3+} concentration on the colour of the thiocyanato-complex of Fe(III)

For determination of the effect of ammonium thiocyanate on the colouration of the $FeCl_3$ solution, the following procedures were employed: Firstly, 1, 2, 4, 10 and 20 mg/L of $FeCl_3$ solution were prepared in separate containers. Secondly, a 10 mL of each solution was transferred separately to a 20 mL plastic beaker to which two drops of 1M NH_4SCN solution were added and the mixture shaken for a few seconds. Then the absorbance of each solution was determined by the multiparameter photometer according to the methods described above to determine the minimum detectable concentration of Fe(III). The experiment was replicated, and average values used in plotting graphs.

7.2.6. Determination of the effect of fluoride concentration on the colour of the 5 mg/L thiocyanato-complex of iron

A total of seven different concentrations (0.5, 1, 2, 3, 4, 5 and 10 mg/L) of fluoride solutions were prepared by standard dilution of a 1000 mg/L F solution in 5 mg/L $FeCl_3$ solution (instead of distilled water) to make dilute fluoro-complexes of Fe(III). A 10 mL of each solution was transferred to a 20 mL plastic beaker to which two drops of 1 M NH_4SCN solution were added and shaken vigorously for a few second to allow the formation of the dilute thiocyanato-complex of Fe(III). Then the absorbance of each solution was estimated by the multiparameter photometer according to the method described above to determine the effect increasing fluoride concentration on the colour of the dilute thiocyanato-complex of Fe(III).

7.2.7. Determination of the chemical stability of thiocyanato-complex of Fe(III)

To determine the stability of the thiocyanato-complex of Fe(III), two drops of 1 M NH_4SCN solution were added into a 10 mL of 20 mg/L $FeCl_3$ solution in 10 mL glass vials in duplicate. The vials were then caped and shaken vigorously for a few seconds and left in the laboratory room light for a total of 60 minutes. During this time, absorbance of each solution was estimated after 5, 10, 20, 30, 40, 50 and 60 minutes by a multiparameter photometer to determine the effect of time on the stability of thiocyanato-complex of Fe(III).

7.3. Results and discussion

7.3.1. The effect of F^- ions concentration on the colour of the acidified $FeCl_3$ solution

When the concentration of fluoride was varied from 2 to 130 mg/L the colour of the resulting acidified solution of iron(III) chloride changed from orange to colourless, as indicated by decreasing solution absorbance in Fig. 7.3. At the zero absorbance the concentration of fluoride and ferric ions were found to be 130 mg/L and 1650 mg/L, respectively, equivalent to 0.0068 and 0.0102 moles of F^- and Fe^{3+}, respectively. At zero absorbance, the calculated Fe^{3+}:F^- mole ratio, therefore, was found to be 1:0.7. This is different from the predictable (1:6) mole ratio of Fe to F in a standard colourless fluoro-complex of Fe(III), indicating that in acidic conditions, Fe^{3+} has a higher affinity for fluoride ion than the hydroxyl and water molecules (Krishnamurti and Huang, 1990) as discussed in Chapter 6. Since the colour of the $FeCl_3$ solution is established to be due to the presence of the hydroxo- or aquo-complexes of iron(III), it can be asserted here that at low pH, the formation of the aquo-complexes of Fe(III) is suppressed, while that of the fluoro-complex of Fe(III) is enhanced. This tendency could be due to the effect of protonation of the water molecules in acidic condition, which in turn lowers the ability of the water molecules to form coordinate bonds with the Fe(III) ion. This property could be exploited in developing the iron-based fluoride detector, as further explained in the following sections. Since these solutions are acidic, the effect of pH to the affinity of the F^- to Fe^{3+} should be further investigated. This is presented and discussed further in the next section.

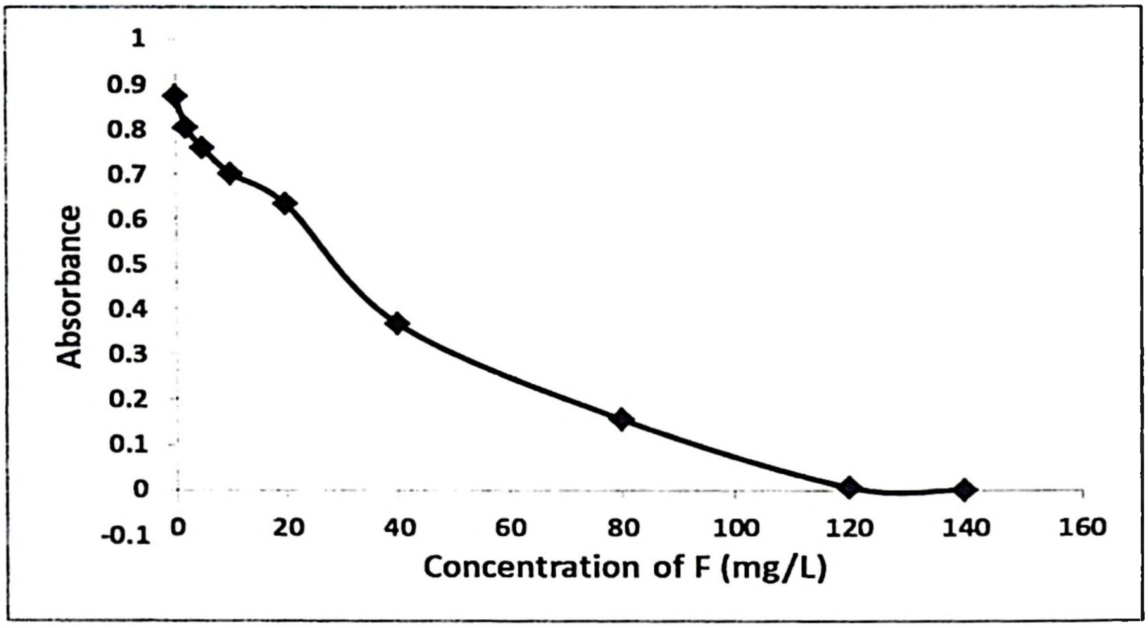

Fig. 7. 2. The effect of F concentration of the absorbance of the acidified $FeCl_3$ solution

7.3.2. The effect of pH on the absorbance of the Fe^{3+}-fluoride solution

Increasing the pH from 1-11 in the solution containing the fluoro-complex of Fe(III) resulted in the increased absorbance of the prepared solution from 0-2.3, as indicated in Fig. 7.3. The solution is colourless at low pH and develops colour as the pH is increased. This colour could be due to the formation of the aquo-complexes of Fe(III). At a pH above 7, visible red-brown precipitate of Fe(III) are formed. These precipitates are likely the solid $Fe(OH)_3$ formed as a result of increased hydroxyl ions in the solution. This indicates that, increasing the solution pH is associated with an enhanced affinity between water molecules and Fe^{3+}. This could be due to the deprotonation effect of the water molecules and the introduction of hydroxyl ions into the solution. This, therefore, implies that, at neutral and alkaline pH conditions, Fe^{3+} has a higher affinity for water molecules and hydroxyl ions than for fluoride ions as explained in Chapter 6. Thus, pH is an important parameter if iron is to be used for fluoride detection in aqueous media. It therefore, follows that, to exploit the Fe(III)-fluoride interactions in developing the Fe-F-SCN system for fluoride detection, a low pH should be ideal. To be able to use lower concentrations of fluoride, the lowest detectable concentrations of Fe in acidic media should be established. The next section is dedicated for that.

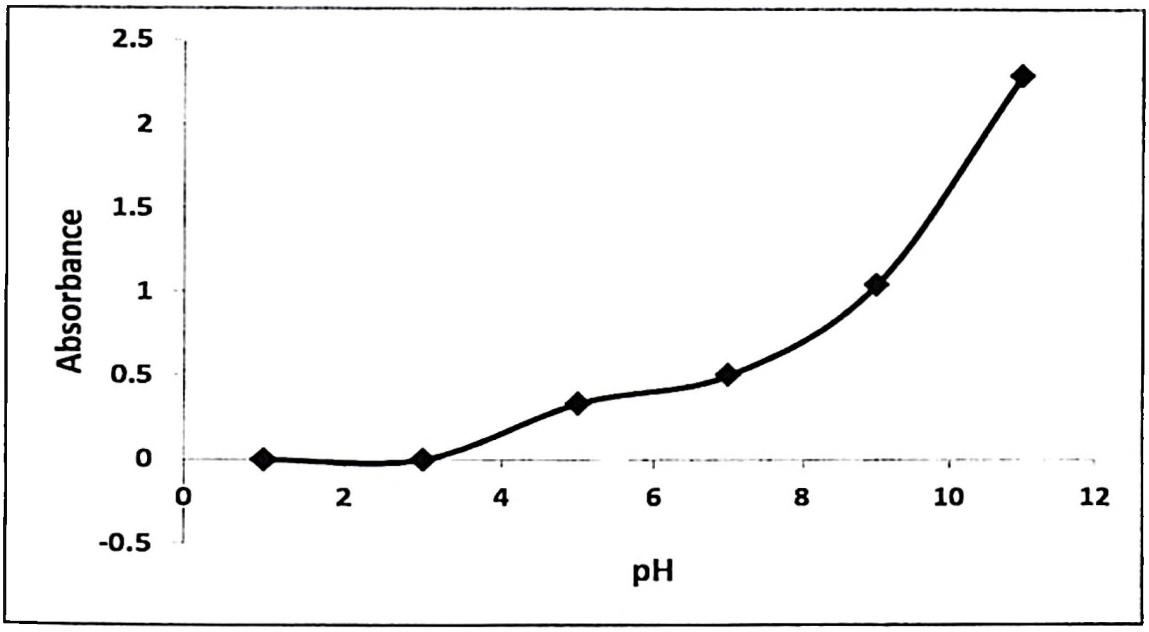

Fig. 7. 3. The effect of pH on the absorbance of the fluoro-complex of Fe(III)

7.3.3. The effect of concentration of Fe(III) on the absorbance of the $FeCl_3$ solution

At concentrations below 250 mg/L, $FeCl_3$ solutions gave zero absorbance values as indicated in Fig. 7.3. The absorbance values were observed to increase from 250 to 1500 mg/L concentration of $FeCl_3$ solutions. This increase is obviously due to increased concentrations of Fe(III) in the measured solutions. This, therefore implies that, for use in the naked eye fluoride sensors, and in the absence of strong colouring ligands, Fe(III) should be used in higher concentrations. These required higher concentrations of Fe(III) will require corresponding higher concentrations of F as indicated by the Fe:F mole ratio of 1:0.7 discussed in the previous sections. Therefore, the observed higher detection limits of $FeCl_3$ solutions in aqueous media could explain the higher fluoride detection limit (F=130 mg/L) explained in the previous sections. These observations further imply that, water molecules form a weakly coloured complexes of Fe(III). However, since the discolouration of $FeCl_3$ solution in fluoride occurred at a low Fe:F mole ratio of 1:0.7 as explained above, it follows that a strong coloured complex of Fe(III) that will allow detection of iron in low concentrations, such as thiocyanato-complex of Fe(III), could give better detection results at lower concentrations of F ions.

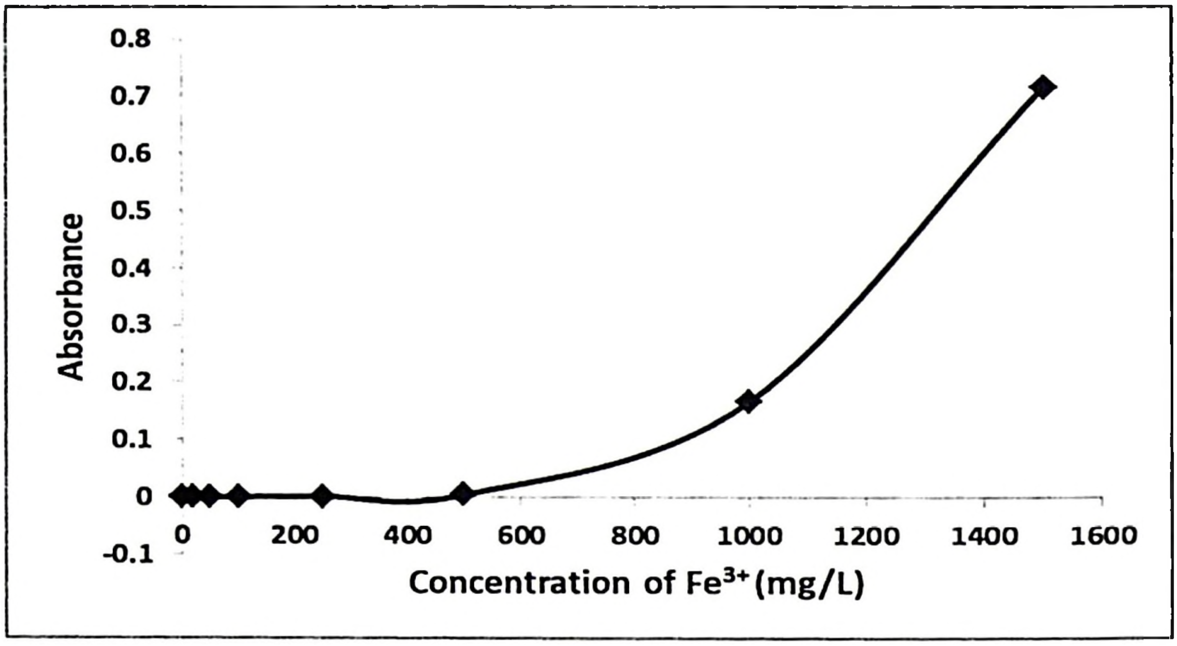

Fig. 7. 4. The effect of Fe(III) concentration on the absorbance of the acidified $FeCl_3$ solution

7.3.4. The effect of ammonium thiocyanate solution on the absorbance of the $FeCl_3$ solution

The addition of ammonium thiocyanate solution was observed to significantly enhance the detectability of Fe(III) in the $FeCl_3$ solution by forming strong blood red colour. As indicated in Fig. 7.4, the detection of Fe(III) was lowered from 250 mg/L in the aquo-complex to 1 mg/L in the presence of thiocyanate ions. This is obviously a result of the strong colour formed between the thiocyanate and the Fe(III) ions. In a different experiment elevated pH conditions were shown to be unsuitable for formation of a strong coloured thiocyanato-complex of Fe(III). From these observations, it is clear that thiocyanato-complexes of Fe(III) could form sharp colour changes at low concentrations of Fe(III) and F ions in acidic conditions. Similar findings indicated that, solution pH is an important factor in the application of thiocyanate ions for detection of iron in aqueous media (Woods and Melon, 1941; Hayashi et al., 1978). This is interesting because the same condition is important for stronger interactions between iron and fluoride ions as discussed in the previous sections. Therefore, colour changes of the thiocyanato-complex of Fe(III) at a low concentrations of fluoride need to be understood and this is presented in the next sections.

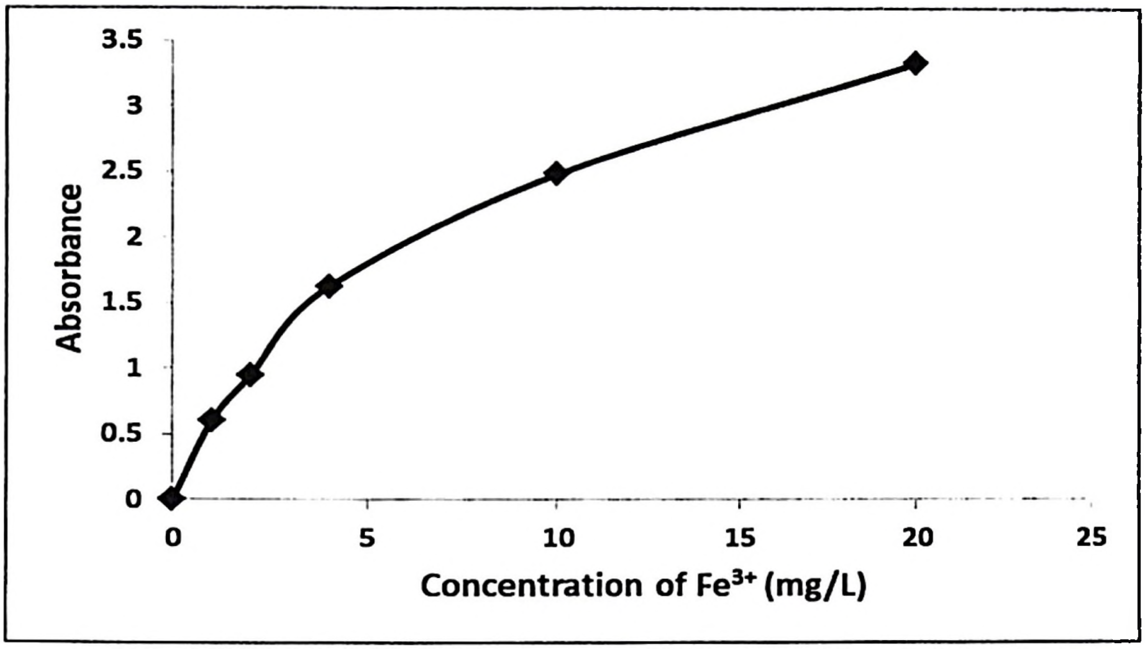

Fig. 7. 5. The effect concentration of Fe(III) on the absorbance of the Fe(III) thiocyanate solution

7.3.5. The effect of fluoride concentration on the absorbance of the iron(III) thiocyanate complex

Increasing the concentration of fluoride in the background of 5 mg/L $FeCl_3$ resulted in a decreased absorbance of the mixture solution, as shown in Fig. 7. 5. This fading of the formed thiocyanato-complex of Fe(III) can be related to the formation of the fluoro-complex of Fe(III) by substitution of SCN^- by F^- in the thiocyanato-complex (Woods and Melon, 1941; Hayashi et al., 1978). This observation shows that, the detection limit of fluoride was lowered significantly by introducing thiocyanate ion. It further indicates that, the fluoride ion has higher affinity for Fe^{3+} than thiocyanate ion and that at this substitution occurs at low pH conditions. Therefore, the Fe-F-SCN system could be further explored for developing the low-cost fluoride detection method for use in rural Africa. However, the thiocyanato-complex of Fe(III) is known to be chemically unstable in aqueous media. Therefore, the rate of destruction of its colour is presented and discussed in the next section.

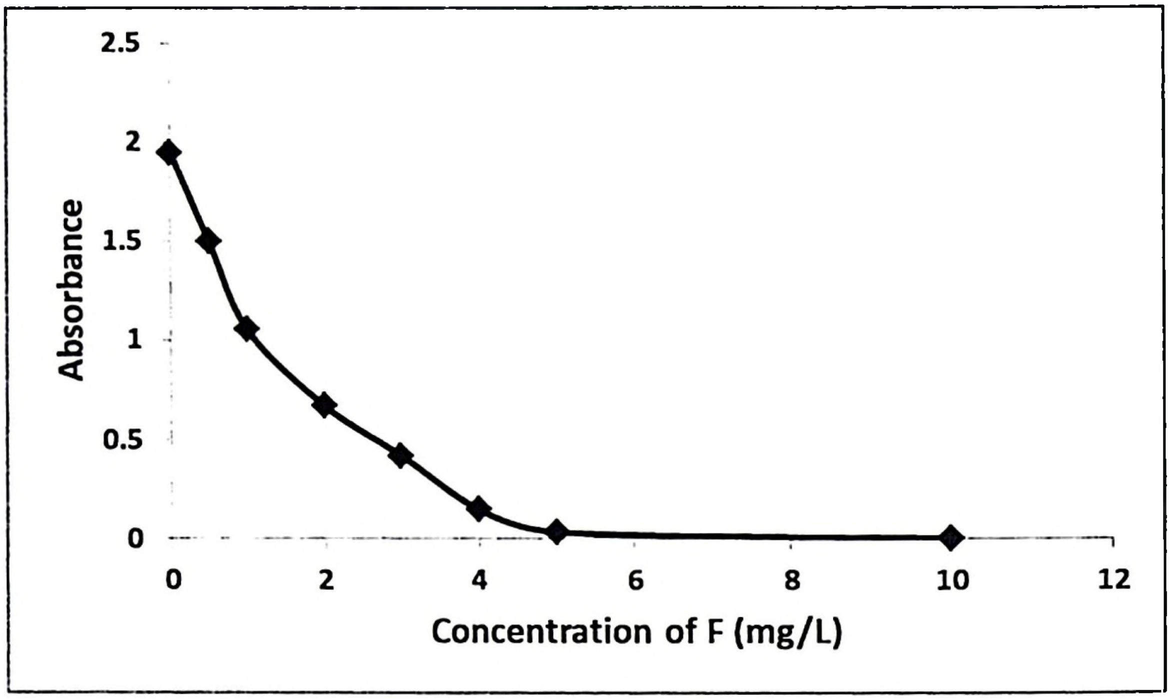

Fig. 7. 6. The effect of fluoride concentration of the absorbance of the thiocyanato-complex of Fe(III)

7.3.6. The stability of thiocyanato-complex of iron(III) in aqueous media

The absorbance of the thiocyanato-complex of iron, in presence of light, was observed to decrease with time, as shown in Fig. 7.6. This observation implies that, the thiocyanato-complex of Fe(III) is chemically unstable in presence of light. This decrease in absorbance could be due to the reduction of iron from Fe^{3+} to Fe^{2+}, which is a common reaction in acidified thiocyanato-complexes of iron(III) (Hayashi et al., 1978; Pouli and Smith, 1960). However, the observed discolouration of the thiocyanato-complex is generally slow and can allow its use in the naked eye fluoride detection in aqueous media (Baily, 1957; Below et al., 1958; Pouli and Smith, 1960).

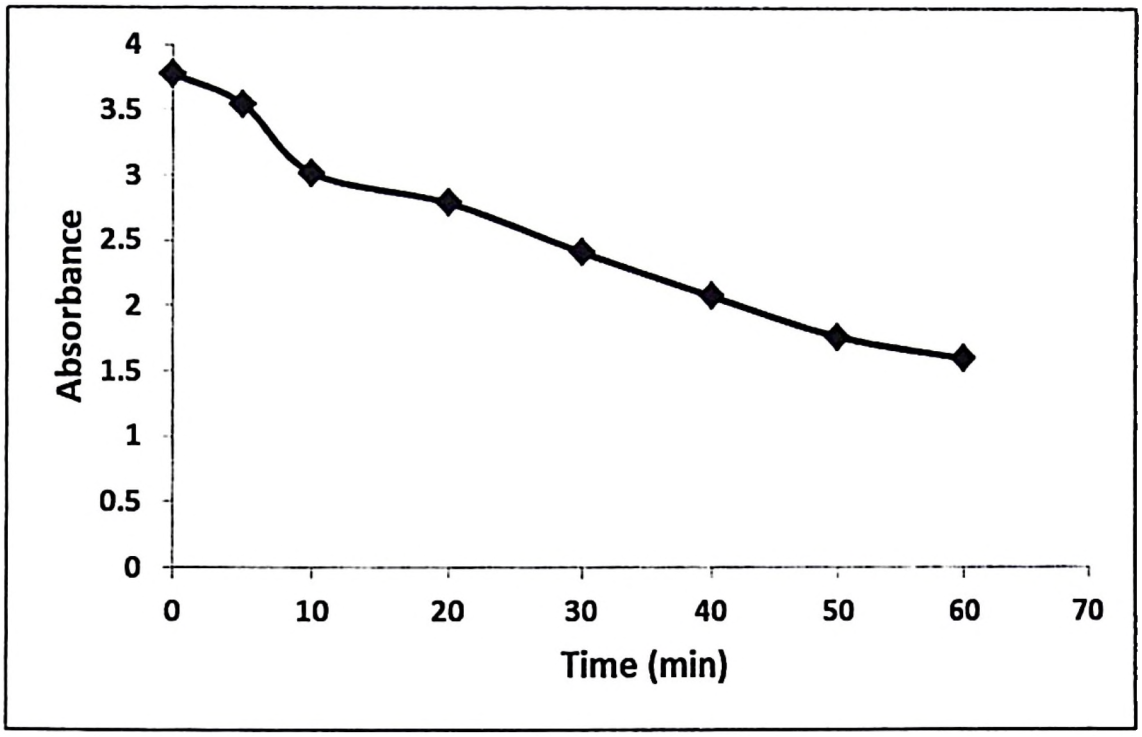

Fig. 7. 7. The effect of time on the chemical stability of the thiocyanato-complex of Fe(III)

7.3.7. Suitability of Fe(III)-loaded biomass and bone char for preconcentration of F in fluoride detection by Fe-F-SCN system

Since the colour of the thiocyanato-complex of Fe(III) is affected by co-ions (Ingols et al., 1950), the Fe-F-SCN system cannot used directly in the natural water. It requires that, the fluoride ions are pre-concentrated and extracted by the suitable fluoride adsorbents. Testing bone char and Fe(III)-loaded biomass for this purpose showed that these fluoride adsorbents are unsuitable for pre-concentrating the fluoride ions to be detected by the Fe-F-SCN system. In the bone char experiment, both the control and the experimental set resulted in the discolouration of the thiocyanato-complex. This could be due to the desorbed phosphate ions from the bone char which have a strong decolourising effect to the complex than fluoride ions (Baily, 1957). In the Fe(III)-loaded biomass experiment, both the control and the experimental sets could not be discoloured. This is likely due to presence of excess Fe(III) ions desorbed from the adsorbent along with F^-.

7.4. Conclusion

In this chapter it is shown that at low pH, the fluoride ion has a special affinity for Fe(III) ion. At this pH, the formation of the hydroxo- or aquo-complex of Fe(III) is suppressed, likely by the protonation of the water molecules enabling the discolouration of the aquo-complex of Fe(III) at a low Fe:F mole ratio of 1:0.7. The higher concentrations of F^- required to effect discolouration of $FeCl_3$ can be addressed by using the thiocyanate solution to form the strong coloured complex with Fe(III) ions. To eliminate the effect of co-ions in natural water, F- should be pre-concentrated and then extracted by the suitable adsorbents. Bone char and Fe(III)-loaded biomass are shown to be unsuitable for the purpose. Therefore, other fluoride adsorbents need to be tested.

CHAPTER 8: General conclusion

The presence of fluoride ion (in water sources) above permissible levels in fluoride affected areas has made fluorosis a common endemic disorder among the inhabitants in fluoride affected areas. In the developing world, where the population growth is alarming, and the effects of climate change more pronounced, the demand for natural resources such as water is immense. These exacerbate the effect of shortage of water for domestic consuption, thus, increasing the exploitation of the groundwater. With point of use treatment (recommended in the developing world) and unpredictable concentration of fluoride in groundwater a "smart approach" is required (to address the fluoride problem), where, communities are equipped with means to detect and treat the fluoride water. This way, only the water with fluoride concentrations above permissible levels is treated, thence, prudent use of limited resources.

The existing technologies for fluoride removal and detection present several challenges including the unaffordable cost and unacceptability. As such, efforts to develop widely acceptable and low-cost technologies for both fluoride removal and detection in water sources are worthwhile. These efforts, however, are challenged by poor understanding of the reactivity (with fluoride) of these materials. In this thesis, some of the challenges delaying the application of the selected low cost materials (plant biomass and iron based materials) are explored and possible solutions presented. To that end, the inadequacy in the study processes and reactivity of selected materials are presented. The reactivity of metallic iron is further explored and special interactions of Fe(III) with F^- are extensively studied to understand possible ways to exploit such interactions for enhancing the fluoride removal properties of the iron-based materials and fluoride detection (by Fe(III)).

The inadequacy in the study process is revealed when the studies on water defluoridation by non-activated plant biomass reported over the past three decades are reviewed. Results show that most of these studies are biased in the properties they explore. Typically, most studies have explored the fluoride removal efficiency/capacity of these materials. This is partly caused by inadequacy in selection of study parameters. As such, the fluoride removal mechanisms of these materials remain poorly understood hitherto and realisation of their field application delayed. To address this, in this thesis, the key parameters that when studied enhance understanding of the defluoridation mechanisms of the plant biomass materials are identified and proposed. These include the effect of solution pH on the defluoridation efficiency of the material, the point of zero charge of the biomass materials and the surface functional groups of the biomass materials before and after use.

From studies that explored these three key parameters over the past three decades, it is revealed that the defluoridation mechanisms of the non-activated plant biomass materials are complex. Whereas in some biomass materials fluoride removal is dependent on surface charges on the biomass, it follows a contrary course in others. As such, two groups of biomass materials are identifiable: those with decreasing fluoride removal efficiency in response to increasing solution pH in which electrostatic forces better describe their fluoride removal mechanism and those with increasing fluoride removal efficiency in response to increasing solution pH in which chemisorption or ion exchange better describe the fluoride removal mechanisms. While the former may be appropriate for defluoridation of the acidic industrial wastewater, the latter are recommendable for natural water with the pH ranging around neutral.

In studying the reactivity of the wood biomass ash produced at fireplaces and normally considered as waste in rural Africa, its great potential as a defluoridation material is shown. The higher concentrations of Ca and Mg in this material may suggest that the main fluoride removal mechanism is likely by co-precipitation of fluoride salts of Ca and Mg. This implies that the efficacious column designs by this material should be those that have small flowrate or relatively large sized columns. A major challenge for this material is related to media-induced contaminants that alter the pH of the treated water. Results from batch reactions show that many toxic metals from this ash have low solubility in aqueous media, likely due to their low solubility in the basic condition of the ash treated water (although this cannot be extended to other types of ash). Thus, the components with higher concentrations in the ash treated water are the highly soluble species, such as K. For these, throwing a few first aliquots of the treated water is enough to control its concentration in the treated water. However, additional measures are needed to lower the pH of the treated water. In this thesis a novel and natural way of controlling the pH of the treated water is presented. The technique employs a species of Cyperus plants called *Cyperus esculentus* to naturally lower the pH of the alkaline ash-treated water to around neutral. The combination of the waste biomass ash and the *Cyperus* plants in a column design (constructed wetland) present an attractive option for water defluoridation and pH adjustment in resource deprived communities in rural Africa. More studies are needed to understand the chemistry of the exudates of these plants.

Comparison of the Fe(III)-activated sisal fibre and post-alkalised Fe(III)-activated sisal fibre reveals that preparation pathways of these materials significantly affect their defluoridation properties. While the post-alkalised biomass had its fluoride removal efficiency decreasing with increasing solution pH, it increased with increasing solution pH for the non-alkalised biomass. This indicates that the variation in the preparation pathways may alter the optimal defluoridation conditions, efficiency and fluoride removal mechanisms. The optimal pH is in the acid range for the post-alkalised biomass and in the neutral range for the non-alkalised biomass and the fluoride removal mechanisms are Coulombic and ligand exchange interactions respectively. Moreover, variation in the preparation pathways significantly affects the defluoridation capacities and stability of the materials in aqueous media with the less stable material having higher fluoride removal properties in neutral aqueous media.

A review of the historical application and studies of iron in water treatment reveal that the redox and coagulative properties of iron are widely exploited in both studies and field application of iron for water treatment. A close look at these studies and applications unveils many lessons for the modern-day studies and application of iron in the water treatment field. Initially iron salts were used for removing suspended matter from water. This application exploited the coagulative power of Fe(III) which is formed when iron salts are mixed with water in aerated condition. Therefore, the end product in such applications were Fe(III) ions and their hydr(oxides). Later application which basically targeted microbial contamination used metallic iron for water decontamination. This exploited the redox properties of this form of iron and the end products were again Fe(III) ions and their hydr(oxides). To minimise the concentration of Fe(III) ions in the treated water, structures to effect aeration of the treated water were designed and installed. This redox power of iron has made iron a robust and versatile material for both chemical and biological contaminants remediation. These findings show that in water treatment systems where iron in different forms is employed to treat water, Fe(III) ions and their hydr(oxides) co-exist at some point. Therefore, exploring the effect of this co-existence in the water defluoridation properties of iron activated materials is expected to shed important light on the possible application of the metallic iron or iron-loaded materials for water treatment.

Further investigation of the interaction of these end products in relation to their effect on the fluoride removal properties of the Fe(III)-loaded material is presented. Addition of small amounts of Fe^{3+} salts to the water to be treated was found to lower the pH of the water and enhance the fluoride removal efficiency of both the non-alkalised and the post-alkalised Fe(III)-activated biomass materials. This means that when the defluoridation efficiency of the iron-loaded materials on fluoride solution with and without Fe^{3+} ions were compared, the Fe(III)-spiked solution exhibitd higher removal efficiency. This increase in fluoride removal efficiency in presence of Fe^{3+} ions was not due to the induced acidity alone. Comparison of the Fe^{3+}- and HCl-induced acidity showed that the former had higher fluoride removal efficiency than the latter with the post-alkalised and non-alkalised Fe(III)-activated biomass material.

Therefore, although accompanying decrease in solution pH upon addition of the Fe^{3+} ions may be contributing to the observed enhanced fluoride removal efficiency, Fe^{3+} itself plays certain roles in such fluoride removal enhancement. In view of the reported low fluoride removal efficiency of the Fe(III) salts in alkaline media, it is clear that pH is an important aspect if Fe^{3+} ions have to enhance the fluoride removal efficiency of the Fe(III)-loaded biomass materials significantly. The $FeCl_3$ solution equally increased the fluoride removal efficiency of the Fe^0. The observed enhanced fluoride removal efficiency of the Fe^0 in $FeCl_3$-spiked fluoride solution was accompanied with the formation of the red-brown precipitate against the brown to brownish-black precipitate in the non-spiked solutions. This may suggest that the Fe^{3+} ion modifies the charge of the Fe(III) hydr(oxides) and hinders the formation of the Fe(II) hydr(oxides). This charge modification may likely be due to olation of the Fe(III) ions on the surface of the Fe(III) hydr(oxides) in acidic media. This observation, therefore, improves our understanding of reactivity of the iron-based materials with fluoride and can be exploited in developing efficacious iron-based defluoridation systems and fluoride detectors.

To deliver the low-cost water defluoridation materials, this thesis has identified and discussed the challenges and solutions related to the defluoridation properties of the selected plant biomass materials. For the non-activated plant biomass materials, these are related to the selection of the key parameters that make the understanding of the fluoride removal mechanisms of the reported materials better and guide future studies for better understanding of their defluoridation properties. Challenges associated with the application of the plant biomass ash are identified and methods to address them discussed. The effect of the pathways followed in preparing the iron-activated biomass materials are presented with the aim of identifying the source of the discrepancy in their defluoridation properties. The properties of iron in aqueous media are explored from the rich historical application of this material in water treatment and findings presented. The common end products in such systems are identified and their effect on water defluoridation properties of such materials showed. Further investigation has shown that these interactions (of end products) have a potential to be applied in enhancing the fluoride removal properties of the iron-based materials and iron-based detection of fluoride ion in aqueous media.

The knowledge on the selection of key parameters may help to direct future studies and consequently remove the observed inadequacy in selection of study parameters when studying the water defluoridation properties of the plant biomass materials. This may accelerate researchers' efforts towards understanding the defluoridation properties of non-activated plant biomass materials. The defluoridation properties of the waste wood ash presented add value to the on-going efforts of exploring the usability of the vast resources currently considered as waste. The novel and natural method of lowering the elevated pH of the ash treated water is expected to open a new research orientation of using plant and constructed wetlands in buffering the pH of the alkaline contaminated water. The presented influence of the preparation pathways of the Fe(III)-activated materials has added in a body of knowledge that not only the type of activating reagent that affects the defluoridation properties of the chemically activated materials, the methods also do. This will enable researchers and water practitioners to make informed choices of the activation methods to suit their materials research and or application purposes. The historical application of iron in water treatment presented in this thesis will serve a broad purpose of directing the future studies on application of iron for water treatment. The effect of co-existence of the Fe^{3+} ions and the Fe(III) hydr(oxides) in acidic media on the defluoridation properties of iron and iron-loaded materials presented in this thesis, reveals that, attempts to use iron salts for water defluoridation by coagulation in alkaline media will likely have low fluoride removal efficiency. It further reveals that fluoride removal by zero valent iron is effected by both adsorption and coagulation processes due to the resulting Fe(III) ions and hydr(oxides) in acidic media. This Knowledge is important in furthering our understanding on the defluoridation properties of the iron and iron-activated materials. It therefore, implies that, the Fe(III) salts may be used to enhance the fluoride removal efficiency of the Fe^0 and that best removal of fluoride by metallic iron is achieved when Fe^0 is added into the Fe^{3+} -spiked fluoride water. The interactives reactions of the Fe(III), F and thiocyanate ions presented here provide the possibility of using the Fe-F-SCN system for developing a low cost fluoride detector applicable in rural African settings. It further establishes that when the preconcentration of fluoride is needed, the adsorbent for pre-concentration of fluoride need to be carefully selected so that it does not interfere the interaction of the F^- and SCN^- with the

Fe(III) ions. Iron rich and phosphate rich adsorbents such as Fe(III) loaded materials and bone char may be unsuitable for the purpose.

The water defluoridation unit involving coupling of the biomass ash and *Cyperus* plants presented in this thesis may represent a low-cost and efficacious defluoridation unit that may find application in rural Africa. The ash to be used, however, needs to be characterised prior to its application to establish its chemical composition. As the fluoride removal mechanism is mainly by co-precipitation, the low flowrates are recommendable in the design to ensure enough time for fluoride immobilisation and pH adjustment. The mechanism by which pH of the treated water is adjusted is not fully understood because the chemical structures of the exudates of the *Cyperus* plants that perform the pH adjustment are not known. On the other hand, the findings on the ability of the Fe^{3+} to detect the presence of fluoride and enhance its removal from water by the zero valent iron and Fe(III)-loaded biomass materials represent only a few first stairs in a multi-storey spectrum of research needed to realise their field application. A full-scale study on the interactions of the F^- and Fe^{3+} in presence of the hydr(oxides) of Fe(III) need to be conducted. Methods to regulate the Fe^{3+}-induced acidity in the Fe^0-Fe(III) system were also not studied. Furthermore, the suitable fluoride adsorbents for pre-concentration of fluoride to be detected by the Fe-F-SCN system were not identified. From this, the following procedural recommendations can be made:

1) When studying the defluoridation properties of the non-activated plant biomass materials the effect of the solution pH on the fluoride removal efficiency, the point of zero charge and the surface functional groups before and after use are included as key parameters in the study in order to better understand the nature of the fluoride-biomass interactions.
2) The *Cyperus esculentus* plants can be used for adjusting the pH of the treated water when the biomass ash is used for water treatment.
3) Procedures involved in preparation of the Fe(III)-loaded biomass materials purposively considered to prepare the biosorbents with desirable properties.
4) When Fe(III) salts are used in water defluoridation by coagulation, the pH of the system should be kept low and coagulants generated by addition of Fe^0.

Furthermore, the following recommendations for further study can be made:

1) The mechanism by which *Cyperus* plants adjust the pH of the ash treated water need to be further studied. In this, the chemical composition of the exudates and their reactivity with alkaline solutions needs to be understood.
2) The mechanism by which Fe(III) enhances the fluoride removal efficiency of the Fe0 and Fe(III)-loaded biomass need to be further understood by determining the possible interaction between the F and the Fe(III) ions.
3) The suitable adsorbent for pre-concentrating F for possible detection by the Fe-F-SCN system needs to be sought by determining the effect of different adsorbents on the properties of the used fluoride extracting solutions.

References:

Aasenden, R., & Peebles, T. C. (1974). Effects of fluoride supplementation from birth on human deciduous and permanent teeth. *Archives of Oral Biology, 19*(4), 321-326.

Anderson, A. (1891). On the Revolving Purifier for the Treatment of Water by Metallic Iron. Paper read before the Mechanical Section of the British Association, on August 21st, 1891. *Sandwell Community History & Archives Service*, Ref No: BSW/5/1/6.

Anderson, W. (1883). The Antwerp waterworks. *Minutes Proceeding of the Institute of Civil Engineering, 72*, 24-44.

Anderson, W. (1884). The purification of water by means of iron on the large scale. *Journal of the Society of Arts 32*, 963-964.

Anderson, W. (1885). The purification of water by means of iron on the large scale. *Minutes Proceeding of the Institute of Civil Engineering, 81*, 279-284.

Anderson, W. (1889). The revolving purifier: an apparatus which effects purification of river water and sewage effluent. In: *The 1885 Anderson Patent.*

Anonymous, (1864). Finely divided iron and its application for the precipitation of copper from solutions and other purposes. *Chemical News, 205*, 239-240.

Anonymous, (1867). The lancet sanitary commission: report on filters, and other water-purifying agents. *The Lancet, 89* (2273), 371-374.

Anonymous, (1871). Items and novelties. *Journal of the Franklin Institute, 92*, 217-232.

Anonymous, (1881). Filtration by spongy iron. *Journal of the Franklin Institute, 111*, 312.

Anonymous, (1888). Report of the lancet analytical sanitary commission on house filters. *The Lancet, 131* (3358), 37-38.

Anonymous, (1919). The Antwerp waterworks during the war period. *Journal of the American Water Works Association, 6*, 486-489.

Anonymous, 22 August (1891). The drinking-water of Florence. *The Lancet, 138* (3547)

Anonymous, September 12, 1896. Water Purified with Iron. *The New York Times.*

Antia, D.D.J. (2010). Sustainable zero-valent metal (ZVM) water treatment associated with diffusion, infiltration, abstraction and recirculation. *Sustainability*, *2*, 2988-3073.

Antia, D.D.J. (2011). Modification of aquifer pore-water by static diffusion using nanozero- valent metals. *Water*, *3*, 79-112.

Antia, D.D.J. (2014). Groundwater water remediation by static diffusion using nanozero valent metals (Fe^0, Cu^0, Al^0), n-FeHnO, n-Fe(OH)x, n-FeOOH, n-Fe- [OxHy](n/-). In: Kharisov, B.I., Kharissova, O.V., Rasika Dias, H.V. (Eds.), *Nanomaterials for Environmental Protection*, pp. 1-25. http://dx.doi.org/10.1002/ 9781118845530.ch1.

Antia, D.D.J. (2016). ZVI (Fe^0) desalination: stability of product. *Water Resources*, *5*, 15. http://dx.doi.org/10.3390/resources5010015.

Antunes, M. C. G., Pinto, S., Braga, F. G., & Esteves Silva, J. C. (2012). Optimisation of bisphenol A removal from water using chemically modified pine bark and almond shell. *Chemistry and Ecology*. *28*(2), 141-152.

Armienta, M. A., & Segovia, N. (2008). Arsenic and fluoride in the groundwater of Mexico. *Environmental Geochemistry and Health*, *30*(4), 345-353.

Arshad, M., Zafar, M. N., Younis, S., & Nadeem, R. (2008). The use of Neem biomass for the biosorption of zinc from aqueous solutions. *Journal of Hazardous Materials*, *157*(2-3), 534-540.

Avilés, M., Garrido, S. E., Esteller, M. V., De La Paz, J. S., Najera, C., & Cortés, J. (2013). Removal of groundwater arsenic using a household filter with iron spikes and stainless steel. *Journal of Environmental Management*, *131*, 103-109.

Bache, R.M., (1891). Possible sterilization of city water. *Proceeding of the American Philosophical Society*, *29*, 26-39.

Bagali, S. S., Gowrishankar, B. S., & Roy, A. S. (2017). Optimization, Kinetics, and Equilibrium Studies on the Removal of Lead (II) from an Aqueous Solution Using Banana Pseudostem as an Adsorbent. *Engineering*, *3*(3), 409-415.

Baily, P. (1957). Stabilization of ferric thiocyanate color in aqueous solution. *Analytical Chemistry*, *29*(10), 1534-1536.

Baker, M.N., (1934). Sketch of the history of water treatment. *Journal of the American Water Works Association, 26*, 902-938.

Balouch, A., Kolachi, M., Talpur, F. N., Khan, H., & Bhanger, M. I. (2013). Sorption kinetics, isotherm and thermodynamic modeling of defluoridation of ground water using natural adsorbents. *American Journal of Analytical Chemistry, 4*(5), 221.

Bamber, H.K., Gill, M., Higgin, G., & Irving, A., (1886). Water purification. *Minutes Proceeding of the Institute of Civil Engineering, 85*, 247-263.

Banerjee, G. (1955). Rapid titrimetric determination of microgram amounts of fluoride ion with spadns-thorium lake. *Analytica Chimica Acta, 13*, 409-414.

Belcher, R., Leonard, M. A., & West, T. S. (1959). 717. Submicro-methods for the analysis of organic compounds. Part X. Determination of fluorine. *J. chem. Soc.*, 3577-3579.

Below Jr, J. F., Connick, R. E., & Coppel, C. P. (1958). Kinetics of the formation of the ferric thiocyanate complex. *Journal of the American Chemical Society, 80*(12), 2961-2967.

Bharali, R. K., & Bhattacharyya, K. G. (2015). Biosorption of fluoride on Neem (Azadirachta indica) leaf powder. *Journal of Environmental Chemical Engineering, 3*(2), 662-669.

Bhatnagar, A., Kumar, E. and Sillanpaa, M. (2011). Fluoride removal from water by adsorption: A Review. *Chemical Engineering Journal. 171*: 811-840.

Bibi, S., Farooqi, A., Yasmin, A., Kamran, M. A., & Niazi, N. K. (2017)b. Arsenic and fluoride removal by potato peel and rice husk (PPRH) ash in aqueous environments. *InternationalJjournal of Phytoremediation, 19*(11), 1029-1036.

Bibi, S., Kamran, M. A., Sultana, J., & Farooqi, A. (2017)a. Occurrence and methods to remove arsenic and fluoride contamination in water. *Environmental Chemistry Letters, 15*(1), 125-149.

Birke, V., Schuett, C., Burmeier, H., & Friedrich, H.J. (2015). Impact of trace elementsand impurities in technical zero-valent iron brands on reductive dechlorination of chlorinated ethenes in groundwater. In: Naidu, R., Birke, V. (Eds.), *Permeable Reactive*

Barrier Sustainable Groundwater Remediation. CRC Press, ISBN 978-1- 4822-2447-4, pp. 87-98.

Bisanda, E. T. N., & Ansell, M. P. (1991). The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites. *Composites Science and Technology*, *41*(2), 165-178.

Bischof, G. (1873). Über das Reinigen des Wassers und über die Wirkung des Eisenschwammes auf unreines Wasser. *Polytechnic Journal, 210 (VII)*, 40e59. http:// dingler.culture.hu-berlin.de/article/pj210/ar210007.

Bischof, G. (1877). On putrescent organic matter in potable water. *Proceeding of the Royal Society of London, 26*, 258-261.

Bischof, G. (1878)a. On putrescent organic matter in potable water II. *Proceeding of the Royal Society of London, 27*, 152-156.

Bischof, J. (1878)b. Thorne R. Thorne on filtration of water 'letter'. *RSA Journal, 27*, 691.

Booth, T. Mcculloch, A., Ogston, G.H., (1883). Antwerp waterworks. *Minutes of the Proceeding of the Institute of Civil Engineering, 72*, 78-83.

Boruff, C. S. (1934). Removal of fluorides from drinking waters. *Industrial & Engineering Chemistry, 26*(1), 69-71.

Bostock, J. (1829). On the spontaneous purification of Thames water. *Philosophical Transactions of the Royal Society of London, 119*, 287-290.

Brunt, R., Vasak, L., and Griffioen, J. (2004). Fluoride in groundwater: Probability of occurrence of excessive concentration on global scale. *International Groundwater Resource Assessment Centre Report*.

Btatkeu-K, B.D., Olvera-Vargas, H., Tchatchueng, J.B., Noubactep, C., Care, S. (2014). Determining the optimum Fe^0 ratio for sustainable granular Fe^0/sand water filters. *Chemical Engineering Journal, 247*, 265-274.

Btatkeu-K, B.D., Tchatchueng, J.B., Noubactep, C., Care, S. (2016). Designing metallic iron based water filters: Light from methylene blue discoloration. *Journal of Environmental Management 166*, 567-573.

Burton, C.E. (1898)a. Purification of water by action of iron - softening of water by action of lime - natural filtration (Chapter XIII). In: *The Water Supply of Towns and the Construction of Waterworks*. Crosby Lockwood, London, pp. 116-126. http://dx.doi.org/10.1680/twsotatcow.52635.0013.

Burton, C.E. (1898)b. *The Water Supply of Towns and the Construction of Waterworks: a Practical Treatise for the Use of Engineers and Students of Engineering*. Crosby Lockwood, London, p. 486. http://dx.doi.org/10.1680/ twsotatcow.52635.0013.

Cai, H. M., Chen, G. J., Peng, C. Y., Zhang, Z. Z., Dong, Y. Y., Shang, G. Z., Zhu, X., Gao, H., & Wan, X. C. (2015). Removal of fluoride from drinking water using tea waste loaded with Al/Fe oxides: A novel, safe and efficient biosorbent. *Applied Surface Science, 328*, 34-44.

Care, S., Crane, R., Calabro, P.S., Ghauch, A., Temgoua, E., Noubactep, C. (2013). Modelling the permeability loss of metallic iron filtration systems for water treatment. *Clean Soil, Air, Water, 41*, 275-282.

Care, S., Nguyen, Q.T., L'Hostis, V., Berthaud, Y. (2008). Mechanical properties of the rust layer induced by impressed current method in reinforced mortar. *Cement and Concrete Research, 38*, 1079-1091.

Casentini, B., Falcione, F.T., Amalfitano, S., Fazi, S., Rossetti, S. (2016). Arsenic removal by discontinuous ZVI two steps system for drinking water production at household scale. *Water Research, 106*, 135-145.

Charlet, L., Liger, E., Gerasimo, P. (1998). Decontamination of TCE- and U-rich waters by granular iron: role of sorbed Fe (II). *Journal of Environmental Engineering, 124*, 25-30.

Chaturvedi, A. K., Yadava, K. P., Pathak, K. C., & Singh, V. N. (1990). Defluoridation of water by adsorption on fly ash. *Water, Air, and Soil Pollution, 49*(1-2), 51-61.

Chaudhari, S., Banerji, T., Kumar, P.R. (2014). Domestic- and Community-scale Arsenic Removal Technologies Suitable for Developing Countries, A2-ahuja, Satinder. In: *Water Reclamation and Sustainability*. Elsevier, Boston, pp. 155-182.

Chesworth, W. (Ed.). (2008). *Encyclopedia of soil science*. Springer Science & Business Media. pp 365-369.

Cho, E. J., Moon, J. W., Ko, S. W., Lee, J. Y., Kim, S. K., Yoon, J., & Nam, K. C. (2003). A new fluoride selective fluorescent as well as chromogenic chemosensor containing a naphthalene urea derivative. *Journal of the American Chemical Society*, *125*(41), 12376-12377.

Colombo, A., Dragonetti, C., Magni, M., Roberto, D. (2015). Degradation of toxic halogenated organic compounds by iron-containing mono-, bi-and tri-metallic particles in water. *Inorganica Chimica Acta 431*, 48-60.

Colten, C.E. (1988). Historical questions in hazardous waste management. *Public Hist. 10*, 6-20.

Comba, S., Di Molfetta, A., Sethi, R. (2011). A Comparison between field applications of nano-, micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers. *Water Air and Soil Pollution, 215*, 595-607.

Conder, F.R. (1885). Dangers of the London water supply. *The Lancet, 126* (3240), 644.

Cooke, K. (1914). Our water supply. *American Journal of Nursing, 14*, 524-526.

Crawford, R.J., Harding, I.H., Mainwaring, D.E. (1993). Adsorption and coprecipitation of single heavy metal ions onto the hydrated oxides of iron and chromium. *Langmuir, 9*, 3050-3056.

Dahi, E. (2015). A simple procedure for the routine determination of the standard defluoridation capacity of media. *Fluoride*, *48*(1), 22.

Dahi, E. (2016). Africa's U-Turn in defluoridation policy: From the Nalgonda technique to bone char. *Fluoride*, *49*(4), 401.

Darchen, A., Sivasankar, V., Chaabane, T., & Prabhakaran, M. (2016). Methods of Defluoridation: Adsorption and Regeneration of Adsorbents. In: *Surface Modified*

Carbons as Scavengers for Fluoride from Water (pp. 63-92). Springer International Publishing.

Das, A., Dighe, S. U., Das, N., Batra, S., & Sen, P. (2019). β-carboline-based turn-on fluorescence chemosensor for quantitative detection of fluoride at PPB level. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *220*, 117099.

Davis, F. (1891). *An Elementary Handbook on Potable Water*. Silver, Burdett & Co., Boston, p. 131.

De Chaumont, F. (1880). Filtering materials. *The Lancet 115* (2963), 934.

Devonshire, E. (1890). The purification of water by means of metallic iron. *Journal of the Franklin Institute*, *129*, 449-461.

Dhadse, S., Kumari, P., & Bhagia, L. J. (2008). Fly ash characterization, utilization and Government initiatives in India. A review.

Domga, R., Togue-Kamga, F., Noubactep, C., Tchatchueng, J.B. (2015). Discussing porosity loss of Fe^0 packed water filters at ground level. *Chemical Engineering Journal 263*, 127-134.

Don, J., Chilson, J. (1911). *Modern Methods of Water Purification*. Edward Arnold, London. Available at: https://ia600303.us.archive.org/31/items/ modernmethodswa01chisgoog/modernmethodswa01chisgoog.pdf.

Doula, M.K. (2009). Simultaneous removal of Cu, Mn and Zn from drinking water with the use of clinoptilolite and its Fe-modified form. *Water Research*.*43*, 3659-3672.

Duff, M.C., Coughlin, J.U., Hunter, B.D. (2002). Uranium co-precipitation with iron oxide minerals. *Geochimica Cosmochimica Acta 66*, 3533-3547.

Ebelle, T. C., Makota, S., Tepong-Tsindé, R., Nassi, A., & Noubactep, C. (2019). Metallic iron and the dialogue of the deaf. *Fresenius Environmental Bulletin*

Edmunds, W.M., & Smedley, P.L. (2013). Fluoride in natural waters, In: O. Selinus (Ed.), *Essentials of Medical Geology*, Springer, Dordrecht, pp. 311–336.

El-Habashy, I., Mansour, R. M. A., Zahran, M. A., El-Hadidi, M. N., & Saleh, N. A. M. (1989). Leaf flavonoids of Cyperus species in Egypt. *Biochemical Systematics and Ecology*, *17*(3), 191-195.

Ellms, J.W. (1920). Ozone as a disinfectant in water purification. *Journal of the American Water Works Association*, *7*, 60-64.

El-Sayed, G. O., El-Sheikh, R., & Farag, N. H. (2015). Maize Stalks as a Cheap Biosorbent for Removal of Fe (II) from Aqueous Solution. *International Research Journal of Pure and Applied Chemistry*, *6*(2), 66.

Farooqi, A., Masuda, H., & Firdous, N. (2007). Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. *Environmental Pollution*, *145*(3), 839-849.

Fawell, J., Bailey, K., Chilton, J., Dahi, E., & Magara, Y. (2006). *Fluoride in drinking-water*. IWA publishing, pp 5-116.

Fiol, N., & Villaescusa, I. (2009). Determination of sorbent point zero charge: usefulness in sorption studies. *Environmental Chemistry Letters*, *7*(1), 79-84.

Fischer, F. (1902). *Das Wasser: seine Verwendung, Reinigung und Beurtheilung*. J. Springer, Berlin, p. 502.

Foster, M. D. (1933). Colorimetric Determination of Fluoride in Water Using Ferric Chloride. *Industrial & Engineering Chemistry Analytical Edition*, *5*(4), 234-236.

Frankland, P.F. (1884). The removal of microorganisms from water. *Proceeding of the Royal Society of London*, *38*, 379-373.

Freundlich, H. M. F. (1906). Over the adsorption in solution. *Journal Physical Chemistry*, *57*(385471), 1100-1107.

Friedman, M., & Jürgens, H. S. (2000). Effect of pH on the stability of plant phenolic compounds. *Journal of Agricultural and Food Chemistry*, *48*(6), 2101-2110.

Fu, F., Dionysiou, D.D., Liu, H. (2014). The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *Journal of Hazardous Materials*, *267*, 194-205.

Gaál, F. F., Abramović, B. F., & Canić, V. D. (1978). Determination of fluoride with thorium nitrate by catalytic titration. *Talanta*, 25(2), 113-116.

Gallard, H., von Gunten, U. (2002). Chlorination of natural organic matter: kinetics of chlorination and of THM formation. *Water Research, 36*, 65-74.

Gandhi, N., & Sirisha, D. (2019). Removal of Fluoride by using Passiflora Foetida. Fruits as Natural Coagulant. *Discovery Nature, 13*, 44-61.

Gendel, Y., & Lahav, O. (2008). Accurate determination of Fe (II) concentrations in the presence of a very high soluble Fe (III) background. *Applied Geochemistry*, *23*(8), 2123-2129.

George, A. M., & Tembhurkar, A. R. (2018). Deflouridation of Water Using a New Biosorbent Developed from Ficus Glomerata Roxb. Bark. In: *Proceedings of the Institution of Civil Engineers–Water Management* (pp. 1-43). Thomas Telford Ltd.

Ghauch, A. (2008). Discussion of Chicgoua Noubactep on "Removal of thiobencarb in aqueous solution by zero valent iron" by Md. Nurul Amin et al. [Chemosphere 70(3) (2008) 511-515]. *Chemosphere, 72*, 328-331.

Ghauch, A. (2015). Iron-based metallic systems: an excellent choice for sustainable water treatment. *Freiberg Online Geoscience, 38*, 1-80.

Ghauch, A., Abou Assi, H., Baydoun, H., Tuqan, A.M., Bejjani, A. (2011). Fe^0-based trimetallic systems for the removal of aqueous diclofenac: mechanism and kinetics. *Chemical Engineering Journal, 172*, 1033-1044.

Gheju, M. (2011). Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems. *Water, Air and Soil Pollution, 222*, 103-148.

Gheju, M., Balcu, I. (2011). Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations. *Journal of Hazardous Materials, 196*, 131-138.

Gheju, M., Balcu, I., Vancea, C. (2016). An investigation of Cr(VI) removal with metallic iron in the co-presence of sand and/or MnO2. *Journal of Environmental Management, 170*, 145-151.

Giles, D.E., Mohapatra, M., Issa, T.B., Anand, S., Singh, P. (2011). Iron and aluminium based adsorption strategies for removing arsenic from water. *Journal of Environmental Management, 92*, 3011-3022.

Gill, H. (1895). The filtration of the Müggel Lake water-supply, Berlin. *Minutes of the Proceeding of the Institute of Civil Engineering, 119*, 236-263.

Gillham, R.W. (2010). Development of the granular iron permeable reactive barrier technology (good science or good fortune). In: Chen, Y., Tang, X., Zhan, L. (Eds.), *Advances in Environmental Geotechnics : Proceedings of the International Symposium on Geoenvironmental Engineering in Hangzhou*, China, September 8-10, 2009. Springer, Berlin/London, pp. 5-15.

Gillham, R.W., O'Hannesin, S.F. (1994). Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water, 32*, 958-967.

Gojmerac Ivšić, A., & Tamhina, B. (2003). Extraction and formation of iron (III) thiocyanate complexes: application for spectrophotometric determination of Iron. *Croatica Chemica Acta, 76*(4), 323-328.

Gottinger, A.M., McMartin, D.W., Wild, D.J., Moldovan, B. (2013). Integration of zero valent iron sand beds into biological treatment systems for uranium removal from drinking water wells in rural Canada. *Canadian Journal of Civil Engineering, 40*, 945-950.

Gregory, J., & Duan, J. (2001). Hydrolyzing metal salts as coagulants. *Pure and Applied Chemistry, 73*(12), 2017-2026.

Grynpas, M. D. (1990). Fluoride effects on bone crystals. *Journal of Bone and Mineral Research, 5*(S1), S169-S175.

Guan, X., Sun, Y., Qin, H., Li, J., Lo, I.M.C., He, D., Dong, H. (2015). The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: the development in zero-valent iron technology in the last two decades (1994-2014). *Water Research, 75*, 224-248.

Guo, X., Yang, Z., Dong, H., Guan, X., Ren, Q., Lv, X., Jin, X. (2016). Simple combination of oxidants with zero-valent-iron (ZVI) achieved very rapid and highly efficient removal of heavy metals from water. *Water Research, 88*, 671-680.

Habuda-Stanić, M., Ravančić, M. E., & Flanagan, A. (2014). A Review on Adsorption of Fluoride from Aqueous Solution. *Materials, 7*(9), 6317-6366.

Haig, S.-J., (2014). *Characterising the Functional Ecology of Slow sand Filters through Environmental Genomics*. Ph.D. Thesis. School of Engineering, University of Glasgow, Glasgow, UK.

Haj-Hussein, A. T., & Al-Momani, I. F. (1989). Indirect spectrophotometric determination of fluoride in water with zirconium-SPADNS by flow injection analysis. *Analytical Letters, 22*(6), 1581-1599.

Harikumar, P. S. P., Jaseela, C., & Megha, T. (2012). Defluoridation of water using biosorbents. *Natural Science, 4*(4), 245.

Harwood, J. E. (1969). The use of an ion-selective electrode for routine fluoride analyses on water samples. *Water Research, 3*(4), 273-280.

Hatton, F. (1881). XLI.—On the oxidation of organic matter in water by filtration through various media; and on the reduction of nitrates by sewage, spongy iron, and other agents. *Journal of the Chemical Society, Transactions, 39*, 258-276.

Hayashi, K., Sasaki, Y., Tagashira, S., Harada, K., & Okamura, K. (1978). Spectrophotometric determination of iron (III) with thiocyanate and non-ionic surfactant. *Bunseki Kagaku, 27*(6), 338-343.

Henderson, A. D., & Demond, A. H. (2007). Long-term performance of zero-valent iron permeable reactive barriers: a critical review. *Environmental Engineering Science, 24*(4), 401-423.

Hering, R. (1895). Water purification. *Journal of Franklin Institute. 139*, 213-224.

Hill, J.W. (1898). *The Purification of the Public Water Supplies*. Van Nostrand Company, New York, pp. 40-58.

Hoover, C.P., Diven, J.M., Caird, J.M., Hawkes, A.W., Caird, J.M., Burgess, P. (1915). The manufacture of sulphate of alumina at the Columbus water softening and purification works. *Journal of American Water Works Association, 2*, 693-702.

Hussain, I., Arif, M., & Hussain, J. (2012). Fluoride contamination in drinking water in rural habitations of Central Rajasthan, India. *Environmental Monitoring and Assessment, 184*(8), 5151-5158.

Hussam, A. (2009). Contending with a development disaster: SONO filters remove arsenic from well water in Bangladesh. *Innovations 4*, 89-102.

Hussam, A., Munir, A.K.M. (2007). A simple and effective arsenic filter based on composite iron matrix: development and deployment studies for groundwater of Bangladesh. *Journal of Environmental Science & Health A 42*, 1869-1878.

Ingols, R. S., Shaw, E. H., Eberhardt, W. H., & Hildebrand, J. C. (1950). Determination of Fluoride Ion with Ferric Thiocyanate. *Analytical Chemistry*, *22*(6), 799-803.

Jagtap, S., Yenkie, M. K., Labhsetwar, N., & Rayalu, S. (2012). Fluoride in drinking water and defluoridation of water. *Chemical Reviews*, 112(4), 2454-2466.

Jahin, H. S. (2014). Fluoride removal from water using nanoscale zero-valent iron (NZVI). *Inernational Water Technology Journal 4*, 173-182.

Jamode, A. V., Sapkal, V. S., & Jamode, V. S. (2013). Defluoridation of water using inexpensive adsorbents. *Journal of the Indian Institute of Science, 84*(5), 163.

Jiao, Y., Qiu, C., Huang, L., Wu, K., Ma, H., Chen, S., Ma, L., Wu, L., (2009). Reductive dechlorination of carbon tetrachloride by zero-valent iron and related iron corrosion. *Applied Catalysis B: Environmental*, 91, 434-440.

John, Y., David, V. E., & Mmereki, D. (2018). A Comparative Study on Removal of Hazardous Anions from Water by Adsorption: A Review. *International Journal of Chemical Engineering, 2018*.

Johnson, G.A. (1914). Present day water filtration practice. *Journal of American Water Works Association, 1*, 31-80.

Kadlec, R. H., & Wallace, S. (2008). *Treatment wetlands*. CRC press.

Kamble, S. P., Jagtap, S., Labhsetwar, N. K., Thakare, D., Godfrey, S., Devotta, S., & Rayalu, S. S. (2007). Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan. *Chemical Engineering Journal, 129*(1-3), 173-180.

Katsoyiannis, I. A., & Zouboulis, A. I. (2002). Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. *Water Research, 36*(20), 5141-5155.

Kerslake, J.E., Schmitt, H.C., Thomas, N.A. (1946). Iron salts as coagulants. *Journal of the American Water Works Association, 38*, 1161-1169.

Keshtkar, M., Dobaradaran, S., Keshmiri, S., Ramavandi, B., Arfaeinia, H., & Ghaedi, H. (2019). Effective Parameters, Equilibrium, and Kinetics of Fluoride Adsorption on Prosopis cineraria and Syzygium cumini Leaves. *Environmental Progress & Sustainable Energy, 38*(s1), S429-S440.

Khan, A.H., Rasul, S.B., Munir, A.K.M., Habibuddowla, M., Alauddin, M., Newaz, S.S., Hussam, A. (2000). Appraisal of a simple arsenic removal method for groundwater of bangladesh. *Journal of Environmental Science & Health A*, 35, 1021-1041.

Khound, N. J., & Bharali, R. K. (2018). Biosorption of fluoride from aqueous medium by Indian sandalwood (Santalum Album) leaf powder. *Journal of Environmental Chemical Engineering, 6*(2), 1726-1735.

Kim, K., & Jeong, G. Y. (2005). Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. *Chemosphere, 58*(10), 1399-1408.

Knapp, B. A., & Insam, H. (2011). Recycling of biomass ashes: current technologies and future research needs. In *Recycling of biomass ashes* (pp. 1-16). Springer, Berlin, Heidelberg.

Konig, J. (1899)a. *Die Verunreinigung der Gewasser deren Schadliche Folgen, sowie die Reinigung von Trink- und Schmutzwasser.* Erster Band. Springer-Verlag, Berlin Heidelberg, p. 454. http://dx.doi.org/10.1007/978-3-642-91823-0.

Konig, J., (1899)b. *Die Verunreinigung der Gewasser deren Schadliche Folgen, sowie die Reinigung von Trink- und Schmutzwasser*. Zweiter Band. Springer-Verlag, Berlin Heidelberg, p. 514. http://dx.doi.org/10.1007/978-3-642-91824-7.

Kowalski, K.P., Sogaard, E.G., (2014). Implementation of zero-valent iron (ZVI) into drinking water supply e role of the ZVI and biological processes. *Chemosphere, 117*, 108-114.

Krishnamurti, G. S. R., & Huang, P. M. (1990). Spectrophotometric determination of Fe (II) with 2, 4, 6-tri (2'-pyridyl)-1, 3, 5-triazine in the presence of large quantities of Fe (III) and complexing ions. *Talanta, 37*(7), 745-748.

Kroehler, C.J., (2014). Potable Water Quality Standards and Regulations: a Historical and World Overview. In *The Handbook of Environmental Chemistry*. Springer International Publishing, Switzerland.

Kumar, E., Bhatnagar, A., Hogland, W., Marques, M., & Sillanpää, M. (2014). Interaction of inorganic anions with iron-mineral adsorbents in aqueous media—a review. *Advances in Colloid and Interface Science, 203*, 11-21.

Kumar, N. P., Kumar, N. S., & Krishnaiah, A. (2012). Defluoridation of water using Tamarind (Tamarindus indica) fruit cover: Kinetics and equilibrium studies. *Journal of the Chilean Chemical Society, 57*(3), 1224-1231.

Kumar, R., Sinha, A. (2017). Biphasic reduction model for predicting the impacts of dye-bath constituents on the reduction of tris-azo dye Direct Green-1 by zero valent iron (Fe^0). *Journal of Environmental Science, 52*, 160-169.

Lakshminarayan, N., Giriraju, A., & Karnataka, D. (2011). Evaluation of the water defluoridating potential of Brushite-Calcite and two indigenous bioadsorbent materials. *Fluoride, 44*(1), 27.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society, 40*(9), 1361-1403.

Lea, M. (2008). Biological Sand Filters: Low-Cost Bioremediation Technique for Production of Clean Drinking Water. *Current Protocols in Microbiology, 9*(1), 1G-1.

Lee, G., Rho, S., Jahng, D. (2004). Design considerations for groundwater remediation using reduced metals. *Korean Journal of Chemical Engineering, 21*, 621-628.

Leupin, O. X., Hug, S. J., & Badruzzaman, A. B. M. (2005). Arsenic removal from Bangladesh tube well water with filter columns containing zerovalent iron filings and sand. *Environmental Science & Technology, 39*(20), 8032-8037.

Li, J., Liu, X., Yu, Z., Yi, X., Ju, Y., Huang, J., & Liu, R. (2014). Removal of fluoride and arsenic by pilot vertical-flow constructed wetlands using soil and coal cinder as substrate. *Water Science and Technology, 70*(4), 620-626.

Li, S., Ding, Y., Wang, W., & Lei, H. (2016). A facile method for determining the Fe (0) content and reactivity of zero valent iron. *Analytical Methods, 8*(6), 1239-1248.

Lilje, J., & Mosler, H. J. (2016). Continuation of health behaviors: Psychosocial factors sustaining drinking water chlorination in a longitudinal study from Chad. *Sustainability, 8*(11), 1149.

Liu, X., Millero, F.J. (1999). The solubility of iron hydroxide in sodium chloride solutions. *Geochimica et Cosmochimica Acta, 63*, 3487-3497.

Loganathan, P., Vigneswaran, S., Kandasamy, J., & Naidu, R. (2013). Defluoridation of drinking water using adsorption processes. *Journal of Hazardous Materials, 248*, 1-19.

London, M.R., Wahman, D.G., Katz, L.E., Speitel Jr., G.E., (2013). Zero-valent iron/biotic treatment system for perchlorate-contaminated water: Lab-scale performance, modeling, and full-scale implications. *Journal of Environmental Engineering, 139*, 1361-1367.

Lyklema, J. (1984). Points of zero charge in the presence of specific adsorption. *Journal of Colloid and Interface Science, 99*(1), 109-117.

Ma, Y., Wang, S. G., Fan, M., Gong, W. X., & Gao, B. Y. (2009). Characteristics and defluoridation performance of granular activated carbons coated with manganese oxides. *Journal of hazardous materials, 168*(2-3), 1140-1146.

Mackenzie, P.D., Horney, D.P., Sivavec, T.M. (1999). Mineral precipitation and porosity losses in granular iron columns. *Journal of Hazardous Materials, 68*, 1-17.

Mandal, S., Muralidharan, C., & Mandal, A. B. (2019). Water Pollution Remediation Techniques with Special Focus on Adsorption. In *Advanced Research in Nanosciences for Water Technology* (pp. 39-68). Springer, Cham.

Manna, S., Roy, D., Adhikari, B., Thomas, S., & Das, P. (2018)b. Biomass for water defluoridation and current understanding on biosorption mechanisms: A review. *Environmental Progress & Sustainable Energy*, *37*(5), 1560-1572.

Manna, S., Saha, P., Roy, D., Adhikari, B., & Das, P. (2018)a. Fixed bed column study for water defluoridation using neem oil-phenolic resin treated plant bio-sorbent. *Journal of Environmental Management*, *212*, 424-432.

Marier, J. R., & Rose, D. (1966). The Fluoride Content of Some Foods and Beverages–a Brief Survey Using a Modified Zr^{4+} SPADNS Method. *Journal of Food Science*, *31*(6), 941-946.

Mckee, R.H., (1934). Removal of fluorides from drinking water. *Industrial & Engineering Chemistry*, *26*, 849-851.

Miyajima, K., Noubactep, C., & Caré, S. (2013). Testing the suitability of metallic iron for environmental remediation: Discoloration of methylene blue in column studies. *Chemical Engineering Journal*, *215*, 959-968.

Miyajima, K., Noubactep, C., (2013). Impact of Fe^0 amendment on methylene blue discoloration by sand columns. *Chemical Engineering Journal*, *217*, 310-319.

Mohapatra, M., Anand, S., Mishra, B. K., Giles, D. E., & Singh, P. (2009). Review of fluoride removal from drinking water. *Journal of Environmental Management*, *91*(1), 67-77.

Mondal, N. K. (2017). Natural banana (Musa acuminate) peel: an unconventional adsorbent for removal of fluoride from aqueous solution through batch study. *Water Conservation Science and Engineering*, *1*(4), 223-232.

Mondal, N. K., Bhaumik, R., Baur, T., Das, B., ROY, P., & DATTA, J. K. (2012). Studies on defluoridation of water by tea ash: an unconventional biosorbent. *Chemical Science Transactions*, *1*(2), 239-256.

Murugan, M. (2002). Application of Aloe vera (Indian Aloe) a plant material for defluoridation. *Indian Journal of Environmental Protection, 22*(9), 1034-1049.

Murugan, M., & Subramanian, E. (2006). Studies on defluoridation of water by Tamarind seed, an unconventional biosorbent. *Journal of Water and Health, 4*(4), 453-461.

Mwakabona, H. T., Machunda, R. L., & Njau, K. N. (2014)a. The influence of stereochemistry of the active compounds on fluoride adsorption efficiency of the plant biomass. *American Journal of Chemical Engineering, 2*, 42-47.

Mwakabona, H. T., Said, M., Machunda, R. L., & Njau, K. N. (2014)b. Plant biomasses for defluoridation appropriateness: Unlocking their potentials. *Research Journal of Engineering and Applied Science, 3*, 167-174.

Nasiruddin Khan, M., & Sarwar, A. (2007). Determination of points of zero charge of natural and treated adsorbents. *Surface Review and Letters, 14*(03), 461-469.

Nath, S. K., & Dutta, R. K. (2015). Significance of calcium containing materials for defluoridation of water: a review. *Desalination and Water Treatment, 53*(8), 2070-2085.

Ndé-Tchoupé, A., Crane, R., Mwakabona, H., Noubactep, C., & Njau, K. (2015). Technologies for decentralized fluoride removal: Testing metallic iron-based filters. *Water, 7*(12), 6750-6774.

Nesic, S., (2007). Key issues related to modelling of internal corrosion of oil and gas pipelines e a review. *Corrosion Science 49*, 4308-4338.

Neumann, A., Kaegi, R., Voegelin, A., Hussam, A., Munir, A.K.M., & Hug, S.J., (2013). Arsenic removal with composite iron matrix filters in Bangladesh: a field and laboratory study. *Environmental Science & Technology 47*, 4544-4554.

Ngai, T.K.K., Murcott, S., Shrestha, R.R., Dangol, B., & Maharjan, M., (2006). Development and dissemination of Kanchan™arsenic filter in rural Nepal.Water Sci. Technol. *Water Supply 6*, 137-146.

Ngai, T.K.K., Shrestha, R.R., Dangol, B., Maharjan, M., & Murcott, S.E., (2007). Design for sustainable development e household drinking water filter for arsenic and pathogen treatment in Nepal. *Journal of Environmental Science & Health A 42*, 1879-1888.

Nitzsche, K. S., Lan, V. M., Trang, P. T. K., Viet, P. H., Berg, M., Voegelin, A., & Schröder, C. (2015). Arsenic removal from drinking water by a household sand filter in Vietnam—Effect of filter usage practices on arsenic removal efficiency and microbiological water quality. *Science of the Total Environment*, *502*, 526-536.

Nkundimana, E., Noubactep, C., & Uwamariya, V. (2015). Metallic iron for water treatment and environmental remediation: a handout to young researchers. *Fresenius Environmental Bulletin*, *24* (12c), 4842-4846.

Nordstrom, D. K., & Jenne, E. A. (1977). Fluorite solubility equilibria in selected geothermal waters. *Geochimica et Cosmochimica Acta*, *41*(2), 175-188.

Notter, J.L., (1878). The purification of water by filtration. *British Medical Journal*. *2* (928), 556.

Noubactep, C. (2010). The fundamental mechanism of aqueous contaminant removal by metallic iron. *Water Sanitation*, *36*(5).

Noubactep, C. (2011). Review Aqueous contaminant removal by metallic iron: Is the paradigm shifting? *Water SA*, *37*(3).

Noubactep, C. (2013). Relevant reducing agents in remediation Fe^0/H_2O systems. *Clean-Soil, Air, Water*, *41*(5), 493-502.

Noubactep, C. (2016)a. Designing metallic iron packed-beds for water treatment: a critical review. *Clean- Soil, Air, Water 44*, 411-421.

Noubactep, C. (2016)b. Predicting the hydraulic conductivity of metallic iron filters: Modeling gone astray. *Water*, *8*(4), 162.

Noubactep, C., (2007). Processes of contaminant removal in "Fe^0-H_2O" systems revisited. The importance of co-precipitation. *Open Environmental Journal*, *1*, 9-13.

Noubactep, C. (2008). A critical review on the mechanism of contaminant removal in Fe^0-H_2O systems. *Environmental Technology*, *29*, 909-920.

Noubactep, C. (2009). An analysis of the evolution of reactive species in Fe^0/H_2O systems. *Journal of Hazardous Materials*, *168*, 1626-1631.

Murugan, M. (2002). Application of Aloe vera (Indian Aloe) a plant material for defluoridation. *Indian Journal of Environmental Protection, 22*(9), 1034-1049.

Murugan, M., & Subramanian, E. (2006). Studies on defluoridation of water by Tamarind seed, an unconventional biosorbent. *Journal of Water and Health, 4*(4), 453-461.

Mwakabona, H. T., Machunda, R. L., & Njau, K. N. (2014)a. The influence of stereochemistry of the active compounds on fluoride adsorption efficiency of the plant biomass. *American Journal of Chemical Engineering, 2*, 42-47.

Mwakabona, H. T., Said, M., Machunda, R. L., & Njau, K. N. (2014)b. Plant biomasses for defluoridation appropriateness: Unlocking their potentials. *Research Journal of Engineering and Applied Science, 3*, 167-174.

Nasiruddin Khan, M., & Sarwar, A. (2007). Determination of points of zero charge of natural and treated adsorbents. *Surface Review and Letters, 14*(03), 461-469.

Nath, S. K., & Dutta, R. K. (2015). Significance of calcium containing materials for defluoridation of water: a review. *Desalination and Water Treatment, 53*(8), 2070-2085.

Ndé-Tchoupé, A., Crane, R., Mwakabona, H., Noubactep, C., & Njau, K. (2015). Technologies for decentralized fluoride removal: Testing metallic iron-based filters. *Water, 7*(12), 6750-6774.

Nesic, S., (2007). Key issues related to modelling of internal corrosion of oil and gas pipelines e a review. *Corrosion Science 49*, 4308-4338.

Neumann, A., Kaegi, R., Voegelin, A., Hussam, A., Munir, A.K.M., & Hug, S.J., (2013). Arsenic removal with composite iron matrix filters in Bangladesh: a field and laboratory study. *Environmental Science & Technology 47*, 4544-4554.

Ngai, T.K.K., Murcott, S., Shrestha, R.R., Dangol, B., & Maharjan, M., (2006). Development and dissemination of Kanchan™arsenic filter in rural Nepal.Water Sci. Technol. *Water Supply 6*, 137-146.

Ngai, T.K.K., Shrestha, R.R., Dangol, B., Maharjan, M., & Murcott, S.E., (2007). Design for sustainable development e household drinking water filter for arsenic and pathogen treatment in Nepal. *Journal of Environmental Science & Health A 42*, 1879-1888.

Nitzsche, K. S., Lan, V. M., Trang, P. T. K., Viet, P. H., Berg, M., Voegelin, A., & Schröder, C. (2015). Arsenic removal from drinking water by a household sand filter in Vietnam—Effect of filter usage practices on arsenic removal efficiency and microbiological water quality. *Science of the Total Environment*, *502*, 526-536.

Nkundimana, E., Noubactep, C., & Uwamariya, V. (2015). Metallic iron for water treatment and environmental remediation: a handout to young researchers. *Fresenius Environmental Bulletin*, *24* (12c), 4842-4846.

Nordstrom, D. K., & Jenne, E. A. (1977). Fluorite solubility equilibria in selected geothermal waters. *Geochimica et Cosmochimica Acta*, *41*(2), 175-188.

Notter, J.L., (1878). The purification of water by filtration. *British Medical Journal*, *2* (928), 556.

Noubactep, C. (2010). The fundamental mechanism of aqueous contaminant removal by metallic iron. *Water Sanitation*, *36*(5).

Noubactep, C. (2011). Review Aqueous contaminant removal by metallic iron: Is the paradigm shifting? *Water SA*, *37*(3).

Noubactep, C. (2013). Relevant reducing agents in remediation Fe^0/H_2O systems. *Clean-Soil, Air, Water*, *41*(5), 493-502.

Noubactep, C. (2016)a. Designing metallic iron packed-beds for water treatment: a critical review. *Clean- Soil, Air, Water* *44*, 411-421.

Noubactep, C. (2016)b. Predicting the hydraulic conductivity of metallic iron filters: Modeling gone astray. *Water*, *8*(4), 162.

Noubactep, C., (2007). Processes of contaminant removal in "Fe^0-H_2O" systems revisited. The importance of co-precipitation. *Open Environmental Journal*, *1*, 9-13.

Noubactep, C. (2008). A critical review on the mechanism of contaminant removal in Fe^0-H_2O systems. *Environmental Technology*, *29*, 909-920.

Noubactep, C. (2009). An analysis of the evolution of reactive species in Fe^0/H_2O systems. *Journal of Hazardous Materials*, *168*, 1626-1631.

Noubactep, C. (2014). Flaws in the design of Fe^0-based filtration systems? *Chemosphere, 117*, 104-107.

Noubactep, C. (2015). Metallic iron for environmental remediation: a review of reviews. *Water Research, 85*, 114-123.

Noubactep, C. (2016)c. Research on metallic iron for environmental remediation: stopping growing sloppy science. *Chemosphere, 153*, 528-530.

Noubactep, C., Meinrath, G., Dietrich, P., Sauter, M., & Merkel, B. (2005). Testing the suitability of zerovalent iron materials for reactive walls. *Environmental Chemistry, 2*, 71-76.

Noubactep, C., Schoner, A., Woafo, P. (2009). Metallic iron filters for universal access to safe drinking water. *Clean-Soil, Air, Water 37*, 930-937.

Noubactep, C., Tchatchueng, J.-B., & Woafo, P. (2016). Traitement decentralise de l'eau sur filtres a fer metallique: Le sentier africain. In: Noubactep, C. (Ed.), *Approvisionnement en eau potable en Afrique*. Afrique & Science (ISSN: 1862-6793), 57-73.

Noubactep, C., Temgoua, E., & Rahman, M.A. (2012). Designing iron-amended biosand filters for decentralized safe drinking water provision. *Clean-Soil, Air, Water 40*, 798-807.

Obiri-Nyarko, F., Grajales-Mesa, S.J., & Malina, G., (2014). An overview of permeable reactive barriers for in situ sustainable groundwater remediation. *Chemosphere, 111*, 243-259.

Ogston, F.H., (1885). The purification of water by metallic iron in Mr Anderson's revolving purifiers. *Minutes Proceeding of the Institute of Civil Engineering, 81*, 285-294.

Ogston, G.H., (1883). Correspondence on the Antwerp waterworks. *Minutes Proceeding*, 78-84.

O'Hannesin, S.F., & Gillham, R.W., (1998). Long-term performance of an in situ "iron wall" for remediation of VOCs. *Ground Water, 36*, 164-170.

Oladoja, N.A., 2016. Appropriate technology for domestic wastewater management in under-resourced regions of the world. *Applied Water Science*. http://dx.doi.org/10.1007/s13201-016-0495-z.

Oliveira, W. E., Franca, A. S., Oliveira, L. S., & Rocha, S. D. (2008). Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions. *Journal of Hazardous Materials, 152*(3), 1073-1081.

Ouhadi, V. R., Yong, R. N., Shariatmadari, N., Saeidijam, S., Goodarzi, A. R., & Safari-Zanjani, M. (2010). Impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by the electrokinetic soil remediation method. *Journal of Hazardous Materials, 173*(1-3), 87-94.

Pandey, P. K., Pandey, M., & Sharma, R. (2012). Defluoridation of water by a biomass: Tinospora cordifolia. *Journal of Environmental Protection, 3*(07), 610.

Paradelo, R., Conde-Cid, M., Arias-Estévez, M., Nóvoa-Muñoz, J. C., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M. J., & Núñez-Delgado, A. (2017). Removal of anionic pollutants by pine bark is influenced by the mechanism of retention. *Chemosphere, 167*, 139-145.

Parks, G. A. (1967). Aqueous surface chemistry of oxides and complex oxide minerals. Isoelectric point and zero point of charge. *Equilibrium Concepts in Natural Water Systems*, 67, 121-160.

Parmar, H. S., Patel, J. B., Sudhakar, P. A. D. M. A. J. A., & Koshy, V. J. (2006). Removal of fluoride from water with powdered corn cobs. *Journal of Environmental Science & Engineering, 48*(2), 135-138.

Patil, S., Renukdas, S., & Patel, N. (2013). Defluoridation of water using biosorbents: kinetic and thermodynamic study. *International Journal of Research in Chemistry and Environment, 3*(1), 125-135.

Paudyal, H., Pangeni, B., Inoue, K., Kawakita, H., Ohto, K., Harada, H., & Alam, S. (2011). Adsorptive removal of fluoride from aqueous solution using orange waste loaded with multi-valent metal ions. *Journal of Hazardous Materials, 192*(2), 676-682.

Phukan, M. (2015). Characterizing the Fe0/sand system by the extent of dye discoloration. *Freiberg Online Geosci. 40*, 70.

Piekos, R., & Paslawska, S. (1999). Fluoride uptake characteristics of fly ash. *Fluoride, 32*, 14-19.

Pilling, N.B., & Bedworth, R.E. (1923). The oxidation of metals at high temperatures. *Journal of the Institute of Metals*, 29, 529-591.

Pouli, D., & Smith, W. M. (1960). The kinetics of the formation of the mono–fluoro complex of iron (III) in aqueous solution. *Canadian Journal of Chemistry, 38*(4), 567-575.

Queste, A., Lacombe, M., Hellmeier, W., Hillermann, F., Bortulussi, B., Kaup, M., Ott, K., & Mathys, W. (2001). High concentrations of fluoride and boron in drinking water wells in the Muenster region-results of a preliminary investigation. *International Journal of Hygiene and Environmental Health, 203*(3), 221-224.

Rahman, M.A., Karmakar, S., Salama, H., Gactha-Bandjun, N., Btatkeu-K, B.D., & Noubactep, C., (2013). Optimising the design of Fe^0-based filtration systems for water treatment: the suitability of porous iron composites. *Journal of Applied Solution Chemistry and Modelling, 2*, 165-177.

Rajan, M., & Alagumuthu, G. (2012). Study of fluoride affinity by zirconium impregnated walnut shell carbon in aqueous phase: kinetic and isotherm evaluation. *Journal of Chemistry, 2013.*

Rajković, M. B., & Novaković, I. D. (2007). Determination of fluoride content in drinking water and tea infusions using fluoride ion selective electrode. *Journal of Agricultural Sciences, 52*(2), 155-168.

Reynolds, G.W., Hoff, J.T., & Gillham, R.W. (1990). Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environmental Science and Technology, 24*, 135-142.

Romar-Gasalla, A., Coelho, G., Nóvoa-Muñoz, J., Arias-Estévez, M., Fernández-Sanjurjo, M., Álvarez-Rodríguez, E., & Núñez-Delgado, A. (2017). Wheat Straw as a Bio-Sorbent for Arsenate, Chromate, Fluoride, and Nickel. *Water, 9*(9), 690.

Rook, J.J., (1974)a. Letters. Drinking biorefractories. *Environmental Science and Technology, 8*, 778.

Rook, J.J., (1974)b. Formation of haloforms during chlorination of natural waters. *Water Treatment & Examination, 23*, 234-243.

Rook, J.J., (1975). Letters. Uproar about chlorine. *Environmental Science & Technology 9*, 92-93.

Rook, J.J., (1977). Chlorination reactions of fulvic acids in natural waters. *Environmental Science & Technology, 11*, 478-482.

Saikia, P., Bharali, R. K., & Baruah, H. K. (2017). Kinetic and thermodynamic studies for fluoride removal using a novel bio-adsorbent from possotia (*Vitex negundo*) leaf. *Journal of Analytical Science and Technology, 8*(1), 23.

Sakthivel, S. R., Tilley, E., & Udert, K. M. (2012). Wood ash as a magnesium source for phosphorus recovery from source-separated urine. *Science of the Total Environment, 419*, 68-75.

Sarkar, L., Biswal, S. K., Panigrahi, R. K., & Sarkar, B. (2015). Estimation of filtration potential of an effective biosand filter for removal of iron, turbidity from various sources of water. *Current World Environment, 10*(2), 656.

Savage, W.G. (1916). Reviews of public health problems from the bacteriological point of view: IV. The emergency purification of drinking water supplies. *Public Health 30*, 235-239.

Saxena, V., & Ahmed, S. (2001). Dissolution of fluoride in groundwater: a water-rock interaction study. *Environmental geology, 40*(9), 1084-1087.

Schwertmann, U., & Fechter, H. (1982). The point of zero charge of natural and synthetic ferrihydrites and its relation to adsorbed silicate. *Clay Minerals, 17*(4), 471-476.

Scowden, R. T., (1896). Apparatus for purifying water. U.S. Patent No. 563811.

Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Marinas, B.J., & Mayes, A.M., (2008). Science and technology for water purification in the coming decades. *Nature 452*, 301-310.

Shirke, P. A., & Chandra, P. (1991). Fluoride uptake by duck weed *Spirodela polyrrhiza*. *Fluoride, 24*(3), 109-112.

Singh, G., Kumari, B., Sinam, G., Kumar, N., & Mallick, S. (2018). Fluoride distribution and contamination in the water, soil and plants continuum and its remedial technologies, an Indian perspective-a review. *Environmental Pollution*, 239, 95-108.

Singh, K., Lataye, D. H., Wasewar, K. L., & Yoo, C. K. (2013). Removal of fluoride from aqueous solution: status and techniques. *Desalination and Water Treatment, 51*(16-18), 3233-3247.

Sinha, S., Pandey, K., Mohan, D., & Singh, K. P. (2003). Removal of fluoride from aqueous solutions by Eichhornia crassipes biomass and its carbonized form. *Industrial & Engineering Chemistry Research, 42*(26), 6911-6918.

Smee, A.H. (1899). The death rate and the water supply. *Lancet, 153* (3936), 334-335.

Smith, K., Li, Z., Chen, B., Liang, H., Zhang, X., Xu, R., Li, Z., Dai, H., Wei, C., & Liu, S. (2017). Comparison of sand-based water filters for point-of-use arsenic removal in China. *Chemosphere, 168*, 155-162.

Song, X., Chen, Z., Wang, X., Zhang, S., (2017). Ligand effects on nitrate reduction by zero-valent iron: role of surface complexation. *Water Research, 114*, 218-227.

Srimurali, M., Pragathi, A., & Karthikeyan, J. (1998). A study on removal of fluorides from drinking water by adsorption onto low-cost materials. *Environmental Pollution, 99*(2), 285-289.

Straub, C.P., (1955). Limitations of water treatment methods for removing radioactive contaminants. *Public Health Report*. (1896-1970) 70, 897-904.

Streeter, H.W., & Raneri, R., (1944). National inventory of needs for sanitation facilities: I. Public water supply. *Public Health Report*. (1896-1970) 59, 1-20.

Sujana, M. G., & Anand, S. (2014). Ferric hydroxide: preparation, characterisation and fluoride removal studies from water. *Desalination and Water Treatment, 52*(34-36), 6453-6463.

Sumalatha, B., Narayana, A. V., Kumar, K. K., Kumar, Y. P., Babu, D. J., & Leela, M. V. (2014). Biosorption of Fluoride from Aqueous Solution on Citrus limonium. *Research Journal of Pharmacy and Technology*, *7*(5), 554.

Sun, Y., Li, J., Huang, T., & Guan, X. (2016). The influences of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero-valent iron: a review. *Water Research*, *100*, 277-295.

Sunitha, V., & Reddy, B. M. (2018). Defluoridation of water using Mentha longifolia (Mint) as Bioadsorbent. *Journal of the Indian Geophysical Union*, *22*(2), 207-211.

Swete, H. (1892). The purification of river water by agitation and metallic iron, as conducted with the water of the river Severn at Worcester. *Journal of the Royal Society for the Promotion of Health*, *13*, 309-315. http://dx.doi.org/10.1177/146642409201300314.

Swinburne, G., Whitehead, C.A., & Anderson, J.T.N. (1903). Note on Mechanical Filtration and Gravitation Filtration (Paper & Discussion).

Tamura, H., Goto, K., Yotsuyanagi, T., & Nagayama, M. (1974). Spectrophotometric determination of iron (II) with 1, 10-phenanthroline in the presence of large amounts of iron (III). *Talanta*, *21*(4), 314-318.

Tepong-Tsind_e, R., Crane, R., Noubactep, C., Nassi, A., & Ruppert, H., (2015). Testing metallic iron filtration systems for decentralized water treatment at pilot scale. *Water*, *7*, 868-897.

Traube, M., (1895). Purification of water. *American Journal of Medical Science*, *109*, 107.

Tucker, W.G., (1892). The purification of water by chemical treatment. *Science*, *20* (493), 34-38.

Tudsbery, T.J.H., & Brightmore, W.A. (1893). *The Principles of Waterworks Engineering*. Spon, London, p. 465.

Tweeddale, W. (1898). Water purification. Trans. Annu. Meet. *Kansas Academy of Science*, *16*, 48-52.

Tyler, R.G. (1931). Purification of water supplies. *American Water Works Association, 23*, 2113-2119.

Van Craenenbroeck, W., (1998). Easton & Anderson and the water supply of Antwerp (Belgium). *Industrial Archaeology Review, 20*, 105-116.

Van de Staaij, J., De Bakker, N. V. J., Oosthoek, A., Broekman, R., Van Beem, A., Stroetenga, M., & Rozema, J. (2002). Flavonoid concentrations in three grass species and a sedge grown in the field and under controlled environment conditions in response to enhanced UV-B radiation. *Journal of Photochemistry and Photobiology B: Biology, 66*(1), 21-29.

van der Taelen, (1919). The Antwerp water works during the war period. *Journal of the American Water Works Association, 6*, 486-489.

Van Muyden, A., (1894). La distribution d'eau de Lausanne et la purification des eaux alimentaires. *Bull.Soc. vaud. Ing. Archit. 20*, 1e3. http://dx.doi.org/10.5169/ seals-18221.

Vance, D. (1994). Iron: The environmental impact of a universal element. *National Environmental Journal, 4*(3), 24-25.

Vani, M. L., & Reddy, K. P. (2000). Effects of fluoride accumulation on some enzymes of brain and gastrocnemius muscle of mice. *Fluoride, 33*(1), 17-26.

Vardhan, C. V., & Karthikeyan, J. (2011, September). Removal of fluoride from water using low-cost materials. In *Fifteenth International Water Technology Conference, IWTC-15* (pp. 1-14).

Vargas, V. H., Paveglio, R. R., Pauletto, P. D. S., Salau, N. P. G., & Dotto, L. G. (2019). Sisal fiber as an alternative and cost-effective adsorbent for the removal of methylene blue and reactive black 5 dyes from aqueous solutions. *Chemical Engineering Communications*, 1-14. doi: 10.1080/00986445.2019.1605362

Vassilev, S. V., Baxter, D., Andersen, L. K., & Vassileva, C. G. (2013). An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. *Fuel, 105*, 40-76.

Vengosh, A., & Pankratov, I. (1998). Chloride/bromide and chloride/fluoride ratios of domestic sewage effluents and associated contaminated ground water. *Groundwater, 36*(5), 815-824.

Vieira, M. G. A., de Almeida Neto, A. F., Silva, M. G., Nóbrega, C. C., & Melo Filho, A. A. (2012). Characterization and use of in natural and calcined rice husks for biosorption of heavy metals ions from aqueous effluents. *Brazilian Journal of Chemical Engineering, 29*(3), 619-634.

Vymazal, J. (2010). Constructed wetlands for wastewater treatment. *Water, 2*(3), 530-549.

Wang, H., Chen, J., Cai, Y., Ji, J., Liu, L., & Teng, H. H. (2007). Defluoridation of drinking water by Mg/Al hydrotalcite-like compounds and their calcined products. *Applied Clay Science, 35*(1-2), 59-66.

Ward, C. R., & French, D. (2006). Determination of glass content and estimation of glass composition in fly ash using quantitative X-ray diffractometry. *Fuel, 85*(16), 2268-2277.

Wegelin, M., Schertenlei, R., & Boller, M. (1991). The decade of roughing filters: development of a rural water-treatment process for developing countries. *Journal of Water SRT - Aqua. 40*, 304-316.

Wenk, C.B., Kaegi, R., Hug, S.J. (2014). Factors affecting arsenic and uranium removal with zero-valent iron: laboratory tests with Kanchan-type iron nail filter columns with different groundwaters. *Environmental Chemistry, 11*, 547-557.

Westerhoff, P., & James, J. (2003). Nitrate removal in zero-valent iron packed columns. *Water Research, 37*, 1818-1830.

WHO (2006). Fluorides in drinkingwater. In: Bailey K, Chilton J, Dahi E, Lennon M, Jackson P, Fawell J, editors. *WHO drinking-water quality series*. London, UK: IWA Publishing.

WHO (2009). Potassium in drinking water: Background document for development of WHO Guidelines for Drinking-water Quality. Retrieved from: http://www.who.int/water_sanitation_health/waterquality/guidelines/chemicals/potassium-background.pdf on 2nd January 2018

WHO (2017). Guidelines for drinking-water quality: Fourth edition incorporating the first addendum. Geneva:World Health Organization. Licence: CC BY-NC-SA3.0IGO.

Wigner, G.W., (1878). On some experiments with silicated carbon and spongy iron filters. *The Analyst 3*, 338-341.

Willard, H. H., & Horton, C. A. (1950). Indicators for titration of fluoride with thorium. *Analytical Chemistry*, *22*(9), 1190-1194.

Willard, H. H., & Winter, O. B. (1933). Volumetric method for determination of fluorine. *Industrial & Engineering Chemistry Analytical Edition*, 5(1), 7-10.

Woods, J., & Mellon, M. (1941). Thiocyanate method for iron: a spectrophotometric study. *Industrial & Engineering Chemistry Analytical Edition*, *13*(8), 551-554.

Wu, D., Sedgwick, A. C., Gunnlaugsson, T., Akkaya, E. U., Yoon, J., & James, T. D. (2017). Fluorescent chemosensors: the past, present and future. *Chemical Society Reviews*, *46*(23), 7105-7123.

Xu, X., Gao, B., Jin, B., & Yue, Q. (2016). Removal of anionic pollutants from liquids by biomass materials: a review. *Journal of Molecular Liquids*, *215*, 565-595.

Yadav, A. K., Abbassi, R., Gupta, A., & Dadashzadeh, M. (2013). Removal of fluoride from aqueous solution and groundwater by wheat straw, sawdust and activated bagasse carbon of sugarcane. *Ecological Engineering*, *52*, 211-218.

Yadav, K. K., Gupta, N., Kumar, V., Khan, S. A., & Kumar, A. (2018). A review of emerging adsorbents and current demand for defluoridation of water: bright future in water sustainability. *Environment International*, *111*, 80-108.

Yang, Z., Shan, C., Zhang, W., Jiang, Z., Guan, X., & Pan, B. (2016). Temporospatial evolution and removal mechanisms of As(V) and Se(VI) in ZVI column with H_2O_2 as corrosion accelerator. *Water Research*, *106*, 461-469.

Yang, Z., Xu, H., Shan, C., Jiang, Z., & Pan, B. (2017). Effects of brining on the corrosion of ZVI and its subsequent As (III/V) and Se (IV/VI) removal from water. *Chemosphere*, *170*, 251-259.

Yu, Y., Yu, L., & Chen, J. P. (2015). Adsorption of fluoride by Fe–Mg–La triple-metal composite: adsorbent preparation, illustration of performance and study of mechanisms. *Chemical Engineering Journal, 262*, 839-846.

Zafarani, H. R., Bahrololoom, M. E., Javidi, M., Shariat, M. H., & Tashkhourian, J. (2014). Removal of chromate ion from aqueous solutions by sponge iron. *Desalination and Water Treatment, 52*(37-39), 7154-7162.

Zevenbergen, C., Van Reeuwijk, L. P., Frapporti, G., Louws, R. J., & Schuiling, R. D. (1996). A simple method for defluoridation of drinking water at village level by adsorption on Ando soil in Kenya. *Science of the Total Environment, 188*(2-3), 225-232.

Zhang, J., Chen, N., Tang, Z., Yu, Y., Hu, Q., & Feng, C. (2015). A study of the mechanism of fluoride adsorption from aqueous solutions onto Fe-impregnated chitosan. *Physical Chemistry Chemical Physics, 17*(18), 12041-12050.

Zhao, Y., Li, X., Liu, L., & Chen, F. (2008). Fluoride removal by Fe (III)-loaded ligand exchange cotton cellulose adsorbent from drinking water. *Carbohydrate Polymers, 72*(1), 144-150.

Zhao, Y., Ren, H., Dai, H., & Jin,W. (2011). Composition and expansion coefficient of rust based on X-ray diffraction and thermal analysis. *Corrosion Science. 53*, 1646-1658.

Zhou, Y., Zhang, J. F., & Yoon, J. (2014). Fluorescence and colorimetric chemosensors for fluoride-ion detection. *Chemical Reviews, 114*(10), 5511-5571.

Appendix

Curriculum Vitae:

Hezron Mwakabona

PUBLICATIONS

1. Journal Articles

Mwakabona, H. T., Mlay, H. R., Van der Bruggen, B., & Njau, K. N. (2019). Water defluoridation by Fe (III)-loaded sisal fibre: Understanding the influence of the preparation pathways on biosorbents' defluoridation properties. *Journal of Hazardous Materials, 362*, 99-106.

Makota, S., Nde-Tchoupe, 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. *Applied Water Science*, 1-20.

Naseri, E., Nde-Tchoupe, A., Mwakabona, H.T., Nanseu-Njiki, C.P., Noubactep, C., Njau, K.N., Wydra, K.D. (2017). Making Fe0-based filters a universal solution for safe drinking water provision. *Sustainability, 9*(1224), 1-31.

Kapenja, A. J., Msigala, L. C., & Mwakabona, H. T. (2017). The effect of *Amaranthus hybridus* on fluoride removal by iron (III) salts as fluoride coagulants. *African Journal of Environmental Science and Technology, 11*(4), 207-212.

Mwakabona, H. T., Ndé-Tchoupé, A. I., Njau, K. N., Noubactep, C., & Wydra, K. D. (2017). Metallic iron for safe drinking water provision: Considering a lost knowledge. *Water Research, 117*, 127-142.

Ndé-Tchoupé, A. I., Crane, R. A., Mwakabona, H. T., Noubactep, C., & Njau, K. N. (2015). Technologies for Decentralized Fluoride Removal: Testing Metallic Iron-based Filters. *Water, 7*(12), 6750-6774.

Mwakabona, H. T., Said, M., Machunda, R. L., & Njau, K. N. (2014). Plant biomasses for defluoridation appropriateness: unlocking their potentials. *Research Journal in Engineering and Applied Sciences 3* (3) 167, 174.

Mwakabona, H. T., Machunda, R. L., & Njau, K. N. (2014). The influence of stereochemistry of the active compounds on fluoride adsorption efficiency of the plant biomass. *American Journal of Chemical Engineering, 2*, 42-47.

2. Patents

Mwakabona H. T., Njau, K. N., Machunda, R. L. (2014). "A novel technique involving digestive enzymes and microbes in activation of plant for fluoride adsorption enhancement". Patent number : TZ/P/14/00388, Certification date: 18th January 2016

CONFERENCES:

Biomass ash-Cyperus plants coupling: A novel low-cost technology for fluor and pH contamination remediation in drinking water. *4th Green and Sustainable Chemistry 5-8 May 2019*. Dresden, Germany.

Fluoride problem in drinking water- *An International forum for technology exploration, 4-5 February, 2015*. NM-AIST, Arusha, Tanzania.

Plant biomass for defluoridation appropriateness: addressing the bone char limitations in Tanzania, *The 7th International Conference of the Africa Materials Research Society. December 8-13, 2013*. Addis Ababa, Ethiopia.

Fluoride removal from drinking water: health and technology implications: *An Interdisciplinary research workshop, 12-13 September 2013* NM-AIST, Arusha, Tanzania.