DEVELOPMENT OF A SMALL SCALE WATER TREATMENT SYSTEM FOR FLUORIDE REMOVAL FOR RURAL AREAS

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Engineering in Chemical Engineering in the Faculty of Engineering and the Built

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Declaration

I hereby declare that this dissertation is my own work unless stated to the contrary in the text, and that it has not been submitted for a degree to any other University or Institution.

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Abstract

Several areas in the world such as the United States of America, Sri Lanka, China, Argentina, Canada, Tanzania, Kenya, South Africa and many others have a problem of high fluoride content in drinking water. Generally fluoride levels above 1.5 ppm in water may result in dental and skeletal fluorosis in humans depending on quantity consumed (Fan *et al.*, 2003; Meenakshi, 2004). Remote rural areas where there are no water treatment facilities are more vulnerable to this problem.

Adsorbents such as activated alumina and FR-10 resin seem to have a potential for successful application in rural areas. These methods however require pre-treatment if the feed has high turbidity. A membrane based system called woven fabric microfiltration gravity filter (WFMFGF) developed by Durban University of Technology proved to be suitable for turbidity removal.

The main objective of this research was to develop a small water treatment system for fluoride removal. The small water treatment system developed in this study consists of WFMFGF for pre-treatment and an adsorption column. The WFMFGF is made up of a 40 L container packed with 15 immersed flat sheet membrane elements. The operation of the WFMFGF is in batch mode, driven by varying static head. The static head variation results in flow rate variation through the system. This in turn result in variation of contact time, velocity as well as pressure drop in the fluoride removal unit.

Specific objectives of the study were: (1) to establish the maximum and minimum flow rates through the WFMFGF system, the total run time before cleaning is required and the best cleaning method for this particular membrane system. (2) to evaluate and compare the performance of activated alumina and FR-10 resin on varying contact time, velocity and pressure drop on the fluoride removal unit. The adsorbents were also compared on adsorption capacity, cost and ease of operation.

The minimum and maximum flow rates through the WFMFGF were found to be 5 l/hr and 100 l/hr respectively. It was found that the system can be run for more than a month before requiring cleaning. The suitable cleaning method was found to be soaking the membranes in 0.0225 percent sodium hypochlorite solution overnight and brushing them using a plastic brush.

The comparison of the performance of FR-10 resin to activated alumina found that the adsorbents gave equal performance based on the given criteria. FR-10 resin had higher adsorption capacity, gave good quality treated water even with shorter contact time and operated at wider velocity range.

Activated alumina on the other hand had an advantage of lower costs, lower pressure drop and ease of use. According to Pontius (1990), the performance of activated alumina can be improved by intermittent operation. Point of use (POU) systems are generally operated intermittently. This improves the fluoride removal efficiency of activated alumina giving it more advantage over FR-10 resin. Based on this activated alumina was selected as the best adsorbent for the system.

After the adsorbent was selected, the adsorption column was designed. The column operation regime was 3.5 minutes minimum contact time and 1.17 to 7.8 m/hr velocity range. The activated alumina adsorption capacity was 1.53mg/g. The column had an inside diameter of 70 mm. It was packed with activated alumina to a bed height of 400 mm. The column inlet and outlet pipes were made of PVC with a standard pipe size of 20 mm outside diameter. A valve at the column inlet pipe allowed water to flow through the system.

Key words: membranes, WFMGF, adsorption, activated alumina, FR-10 resin, contact time, velocity, pressure drop, adsorption capacity.

Declaration

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Thulani Dlamini

Dedication

This dissertation is dedicated to my family.

Acknowledgements

First I would like to acknowledge the hand of God the Almighty in my life as a whole. It is through His doing that I am where I am. I will forever be grateful for His love and mercy.

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Symbols

M	Mass of adsorbent (g)
C_o	Feed concentration (mg/l)
C	Treated water concentration (mg/l)
V	Volume of treated water (l)
q	Adsorption capacity (mg/g)
q_e	Equilibrium capacity (mg/l)
C_e	Liquid phase equilibrium concentration (mg/l)
q_{max}	Maximum capacity obtained using Langmuir model (mg/g)
b	Langmuir equilibrium constant expressed as the ratio of adsorption to desorption rate constant (l/mg)
K_f	Freundlich adsorption capacity (mg/g)
n	Adsorption intensity (dimensionless)
R^2	Coefficient of regression (dimensionless)
u	Fluid velocity (m/hr)
V_B	Volume of bed in the adsorption column (l)
T_c	Contact time (min)
A_c	Column cross sectional area (m^2)
g	Gravitational constant (m/s^2)
z	Static head (m)
Q	Flow rate (l/hr)
d_c	Column diameter (mm)
H_B	Bed height (m)
ΔP	Pressure drop (Pa)
L	Length (m)
d_p	Particle diameter (m)
Mg/l	Milligram per litre
m/S^2	Meters per second square
m^2	Meter square
m/hr	Meter per hour
mg/g	Milligram per gram
°C	Degrees Celsius
NTU	Nephelometric turbidity units
ppm	Parts per million

ml	millilitre
mm	Millimetre
ml/min	Millilitre per minute
K_F	Mass transfer coefficient
Sc	Schmidt number
Re	Reynolds number
δ	Liquid film thickness
Dl	Liquid diffusivity
a_p	Adsorbent particle radius
ρ	Fluid density
ε	Void fraction
d_p	particle diameter
A	Blake-Kozeny-Carman constant
B	Burke-Plummer constant

Abbreviations

AA	Activated alumina
WFMFGF	Woven fabric Microfiltration Gravity Filter
BSF	Bio-Sand Filter
NOM	Natural Organic Material
PVDF	Polyvinylidene Difluoride
NAOCL	Sodium Hypochlorite
HOCL	Hypochlorous Acid
NAF	Sodium Fluoride
KF	Potassium Fluoride
USPHS	United State Public Health Service
UNICEF	United Nations Children's Fund
MSP	Dihydrogen Phosphate
RO	Reverse Osmosis
EBCT	Empty Bed Contact Time
MWCO	Molecular Weight Cut Off
WHO	World Health Organization
POU	Point of Use
PVC	Polyvinyl chloride
NGO	Non-Governmental Organisation
$CaCO_3$	Calcium carbonate
$CaSO_4$	Calcium sulfate
$CaPO_4$	Calcium phosphate
H_2O_2	Hydrogen peroxide
NaOCl	Sodium hypochlorite
$Al_2(SO_4)_3$	Aluminium sulfate
H_2O	Water
OH^-	Hydroxide
$Ca(PO_4)_2.CaCO_3$	Apatite
$Ca_{10}(PO_4)_6.(OH)_2$	hydroxyapatite

Chapter 1. Introduction

1.1 Background

Fluoride is one of the most abundant elements in rocks (Patil and Ingole, 2012). It gets dissolved into ground water through weathering of rocks (Loganathan *et al.*, 2013). Industrial as well as agricultural activities may also increase fluoride levels in water sources (Ayoob and Gupta, 2008; Goswami and Purkait, 2012).

Fluoride enters human bodies mainly through drinking water (Meenakshi and Maheshwari, 2006). The consumption of fluoride has beneficial and detrimental effects. It strengthens teeth and bones at low concentration below 1 mg/L (Fan *et al.*, 2003). At concentrations above 1.5 mg/L it causes illnesses such as dental and skeletal fluorosis (Fan *et al.*, 2003). The maximum fluoride concentration in drinking water permitted by the World Health Organisation (WHO) is 1.5 mg/L. However, the maximum allowable fluoride concentration can vary depending on air temperature. The maximum concentration is lower in areas with high temperature because of higher consumptions of water (Meenakshi, 2004).

The problem of fluorosis is a local and an international problem (Meenakshi and Maheshwari, 2006). Internationally, it have been reported in countries like United states of America, Sri Lanka, India, Argentina, China, Canada, Algeria, Libya, Tanzania and Kenya (Meenakshi and Maheshwari, 2006). In South Africa, it has been reported in North West Province, Limpopo, Northern Cape and KwaZulu Natal (Schoeman, 2009; Odiyo and Makungo, 2012).

There are different Point of Use (POU) water treatment methods available for removing fluoride in water. One of the methods is precipitation with alum and lime followed by coagulation (Meenakshi and Maheshwari, 2006; Srimurali and Karthikeyan, 2008). This method is suitable for water that has very high levels of fluoride. It however fails to produce treated water with fluoride concentration below 1.5 mg/l as specified in the WHO guideline.

Another available method that can be used for fluoride removal is membrane technology. The suitable membrane for dissolved substances like fluoride is reverse osmosis. However reverse osmosis membranes cannot be used in some rural areas because of high membrane cost and the unavailability of electrical power in some areas. The electrical power is required to pump the water through the membrane (Meenakshi and Maheshwari, 2006).

Adsorption is one other method that can be used for fluoride removal. There are different adsorbents that have been applied for fluoride removal. These include activated alumina, activated carbon, activated saw dust, activated coconut shell carbon, activated fly ash, ground nut shell, coffee husk, rice husk bone char coal, etc (Meenakshi and Maheshwari, 2006; Chauhan *et al.*, 2007). The main problem with most adsorbents is that they are not selective towards fluoride and other substances may occupy the adsorption site, reducing the efficiency of the adsorbent (Pontius, 1990).

Adsorbents such as activated alumina and FR-10 resin have been shown to be suitable adsorbents for fluoride removal as they are highly selective towards fluoride (Meenakshi and Viswanathan, 2007; Lorenzen *et al.*, 2009). The suitability of activated alumina for fluoride removal is well established (Chauhan *et al.*, 2007). FR-10 resin on the other hand is not yet well established but seem to be another good media for fluoride removal due to its high affinity towards fluoride (Meenakshi and Viswanathan, 2007).

If the feed water has high turbidity, pre-treatment is required to prevent clogging of the adsorption media. There is currently unavailable literature showing suitable pre-treatment systems for fluoride removal by adsorption in household systems.

The Durban University of Technology, Chemical Engineering, water research group, has been developing a water treatment system that has a potential for being used for pre-treatment on the fluoride removal system. The system is membrane based and developed using locally available materials. It is called the Woven Fabric Microfiltration Gravity Filter (WFMFGF) (Mecha and Pillay, 2014).

The WFMFGF is characterised by being robust, capable of producing enough volumes of treated water to be used by a family for cooking and drinking. It provide treated water with acceptable quality irrespective of feed concentration or operator skills, it is easy to use requiring no chemical addition during water treatment and is operated at low pressure (gravity).

Even though a lot of work had been done in developing the WFMFGF, there had been some work that had to be covered by this study. The work that had been covered on developing the system prior to this study include the design of the membrane element, the setup of the water treatment system, establishing the ability of the system to produce 20 l of water per hour enough to be used by one family per day for cooking and drinking. Also established is the ability of the system to remove impurities (Pikwa *et al.*, 2010).

This study had to establish the best cleaning method for the WFMFGF. Pikwa *et al.* (2010) proposed cleaning the system using a bottle brush once it fouls, however, the effectiveness of this method alone in bringing the membrane to initial condition had not been well investigated. According to Pearce (2007b) there are different substances that fouls the membrane. These substances can be removed using different techniques (Madaeni and Samieirad, 2010; Shi *et al.*, 2014). This study had to establish the effectiveness of cleaning the system with brushing only as proposed by (Pikwa *et al.*, 2010). The study also had find a cleaning method that will bring the membranes to initial condition.

Since the WFMFGF is gravity driven, the static head that drives water through the system decrease during treatment. This results in a decrease in the flow rate of permeate coming out of the system during treatment. The maximum and minimum flow rate through the system had to be established by this study. The total run time before cleaning is required was also not established by the previous researchers. This had to be established by this study. This information was critical in the design of the adsorption column.

The variation of flow rate from the WFMFGF means that fluid flow rate through the adsorption unit also varies. This causes a variation in contact time, pressure drop and fluid velocity in the adsorption column. Variation on contact time, velocity and pressure drop may affect the performance and operation of the adsorption column. Information regarding the effect of these variations on the performance of an adsorption column has not been available. As such it was not known if these parameters have operational limits in terms of minimum and maximum values. This study had to establish if these limits exist.

1.2 Main objective

The main objective of this research project was to develop a POU water treatment system for fluoride removal.

1.3 Specific objective

Specific objectives were as follows;

To characterise the WFMFGF based on the following:

- The total run time before cleaning is required.
- Best cleaning method for the system.
- Maximum and minimum flow rate through the system.

To compare the performance of activated alumina and FR-10 resin on the following:

- Adsorption capacity.
- Effect of contact time on fluoride removal.
- Effect of velocity on fluoride removal.
- Effect of pressure drop on column operation.
- Ease of use
- Cost

1.4 Approach

A literature survey was carried out to evaluate and compare the WFMFGF to other existing small water treatment system that can be used as pre-treatment for the fluoride removal system. Experimental work was then conducted to characterise the WFMFGF. River water was used for all the investigations. The maximum and minimum flow rates were determined by filling the WFMFGF with raw water and opening the tap to draw treated water. The maximum flow rate was measured at the beginning of a run when the static head was high, while the minimum flow rate was measured at the end of a run when the static head was at its lowest.

The best cleaning method was determined through running the WFMFGF first with pure water to observe the performance of a clean membrane. It was then run with raw water repeatedly until it fouled. Once fouled, it was cleaned with each of the cleaning methods. The cleaning method that matched the performance of a clean membrane was selected as the best method for the system.

The run time for the WFMFGF was determined by running the system repeatedly with raw water until the volume of permeate collected was reduced to half of the volume collected on the first run. The total volume of permeate collected from the first to the last run was then determined. This volume was divided by the volume of treated water required per day. This gave the number of days the system will be run before cleaning is required.

Experimental work on fluoride removal was then conducted to compare the performance of the selected fluoride removal methods. The aim was to select a process that will be sustainable in rural areas. The adsorbent capacities were determined through running batch experiments and development of adsorption isotherms. The effect of contact time was investigated at fixed flow rates and fixed amount of adsorbent by varying the column cross sectional area.

The effect of velocity was investigated at fixed flow rate and contact time by varying the column cross sectional area. The effect of pressure drop was investigated by varying flow rate through the column. The ease of use was assessed based on operational procedures as well as adsorption media characteristics. The cost of obtaining the adsorption media was the criteria used to compare the methods on costs.

1.5 Dissertation outline

Chapter 1

This chapter gives a brief background to the research project. It also presents the research problem and objectives.

Chapter 2

This chapter presents a review of literature relevant to the study. A comparison of WFMFGF to other available house hold water treatment systems was carried out. The membrane treatment is then discussed in detail including fouling and available cleaning methods. Fluoride is also discussed in detail including available household methods of removing fluoride from water. The best methods of fluoride removal suitable for POU systems were found from the literature review to be adsorption and ion exchange. Description of adsorption and ion exchange processes rounded up this section.

Chapter 3

This chapter presents the methods followed in conducting all the experiments

Chapter 4

This chapter presents and discusses the research findings. Results of investigation on WFMFGF are discussed first followed by results of comparison of activated alumina to FR-10 resin with the aim of selecting the best adsorbent for the POU system.

Chapter 5

This chapter provides the conclusion and recommendations.

Chapter 2. Literature survey

2.1 Water scarcity

There is an ongoing global concern about the growing fresh water scarcity (Gain and Giupponi, 2015). Water scarcity means that the available fresh water is battling to meet the water demand (Gain and Giupponi, 2015). A rule of thumb devised by hydrologist Falkenmark *et al.* (1989) is that countries with fresh water supply that is less than 1000 m^3 per person per year are regarded as water scarce. Those that have supply that is between 1000 to 1700 m^3 per person per year are water stressed and those that have supply that is above 1700 m^3 per person per year are water sufficient.

According to Stikker (1998) countries that were experiencing water scarcity were Saudi Arabia, Qatar, United Arab Emirates, Israel, Yemen, Cape Vade, Tunisia, Algeria, Burundi, Kenya, Malawi, Somalia and Rwanda. In 2001, there were 18 countries classified as water scarce (Bremere *et al.*, 2001). It was estimated that the number is expected to increase to 29 countries by 2025 (Bremere *et al.*, 2001).

The unfavourable trends in the water supply and demand are a result of rapid population growth, climate change as well as industrialization (Peter-Varbanets *et al.*, 2009). From 2000 to 2025 the population in regions where there is water scarcity is expected to be double and a large part of the population will have moved to urban areas increasing the withdrawal of water for municipal and agricultural use (Bremere *et al.*, 2001).

Climate change results in extreme conditions of drought and floods, which results in further contamination of water sources. Industrialisation requires that more water is drawn from the fresh water sources. The effluent water released back to the water source is contaminated. This further contaminates the already shrinking fresh water sources (Bremere *et al.*, 2001).

2.2 Condition in rural areas

Poor communities are most affected by the safe water shortage (Rijsberman, 2006). The poor availability of fresh water and sanitation combined with poor hygiene practices results in the outbreak of waterborne diseases such as cholera, typhoid, bacillary dysentery, infectious hepatitis, leptospirosis, giardiasis, gastroenteritis and many more (Pruss *et al.*, 2002; Peter-Varbanets *et al.*, 2009). To ensure that safe water is available for consumption, some intervention is required. The treatment of water is one of the available interventions.

2.3 Available treatment methods

2.3.1 Conventional water treatment system

Conventional water treatment systems are used to supply bulk water mainly to urban areas. A schematic representation of such a system is shown in

Figure 2.1. This process mainly depends on chemical addition for coagulation. This is followed by flocculation, clarification, filtration and disinfection. This system mainly

removes particulate matter as well as microbiological contaminants (Pearce *et al.*, 1998).

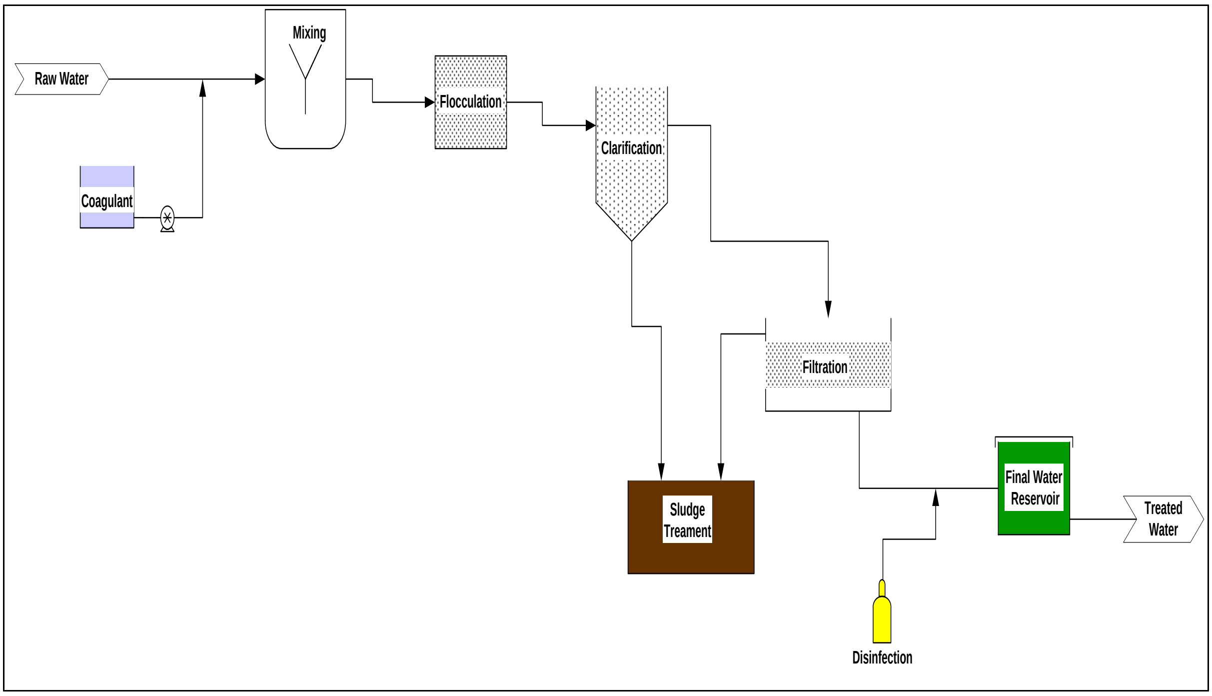


Figure 2.1: Schematic diagram of conventional water treatment system (adapted from (Pontius, 1990)

Rural areas are mostly located far from towns and normally do not have the conventional treatment methods to provide clean drinking water (Lenton and Wright, 2004). The scattered homesteads in rural areas greatly increase the cost of putting in place piping infrastructure that will distribute water to the homesteads. In some cases where the systems are installed, they normally fail due to shortage of skill, finance and spare parts to operate and maintain them (Lenton and Wright, 2004).

2.3.2 Household water treatment systems

While the bulk water supply infrastructure is still not available in most rural areas, an interim solution would be the use of household or point of use water treatment systems. The household water treatment technologies available for turbidity and microbiological contaminant removal were evaluated by Sobsey *et al.* (2008)

Technologies evaluated include chlorination and safe storage, combined coagulation and chlorination, solar disinfection (SODIS), ceramic filters as well as bio-sand household water treatment filters (Sobsey *et al.*, 2008).

The chlorine and safe storage involves addition of chlorine in the form of liquid or tablet into the water. This method is widely used and has been promoted by the United State Centers for Disease Control (Sobsey *et al.*, 2008). A randomised controlled trial indicated a diarrheal diseases reduction of 29 percent in communities using the method (Sobsey *et al.*, 2008). Other observations were that large volume of water could be treated by a single dose of chemical and the method is inexpensive (Sobsey *et al.*, 2008). The major disadvantages of this method are that if the water has organics, objectionable taste and odour can be produced (Sobsey *et al.*, 2008). Some carcinogenic substances can also be produced by the reaction of chlorine and organic substances (Perez Pavon *et al.*, 2008).

Combined coagulation and chlorination involves addition of coagulant for turbidity removal and chlorine for disinfection (Sobsey *et al.*, 2008). Major advantages with this method are that a large amount of treated water is produced from a single dose of chemicals and a better quality of treated water is produced as a result of combination of coagulation and chlorination (Sobsey *et al.*, 2008). Cases of diarrheal diseases were also reported to have been reduced by 26 to 37 percent in children in India and Africa. (Reller *et al.*, 2003). A disadvantage of this method is that chemical sachets are only produced in few countries and accessibility might be a challenge in some areas (Sobsey *et al.*, 2008).

SODIS involves putting aerated water in transparent polyethylene terephthalate bottles and exposing them to direct sunlight for disinfection. Percent reduction in diarrheal disease has been reported to be 19 to 59 in countries using this method. Other advantages are that the process is not complex and is less costly. The drawbacks of the method are that small amount of treated water is produced and too much work has to be done filling the bottles in order to get enough water. The system is also less effective if the water has high turbidity because the microorganisms are shielded from the sunlight (Sobsey *et al.*, 2008).

In the study by Sobsey *et al.* (2008) ceramic filters as well as bio-sand household water treatment filters were identified as methods that have potential for sustainable application in rural areas. A detailed description and comparison of ceramic and bio-sand water treatment to WFMFGF is presented in the next section.

2.4 Detailed comparison of WFMGF system against ceramic and household bio-sand filtration system

This section provides the bases on which Woven fabric microfiltration gravity filter was selected as the best treatment method that can be used as pre-treatment to the adsorption process. The WFMFGF was compared to a ceramic filter and bio-sand household water treatment system which were identified by Sobsey *et al.* (2008) as the best technologies among the technologies available in rural areas. The WFMGF was not among the technologies in the study by Sobsey *et al.* (2008) since this is a new technology.

2.4.1 Assessment criteria

According to Baker (2006), for a household water treatment system to be sustainable in rural areas, it must meet the criteria of the poor. The criteria on which the WFMFGF was developed which is the same criteria used by Sobsey *et al.* (2008) to evaluate available POU systems is summed up as follows (Baker, 2006; Kubare and Haarhoff, 2010):

- The system must produce enough quantity of water for a household
- It must improve the quality of treated water
- It must be easy to maintain and operate
- It must be affordable to obtain and to use, with zero or minimal maintenance costs
- It must be constructed using local material for easy maintenance
- It must require no chemicals or energy to use
- It must be robust enough to operate under different conditions

2.4.1.1 Production of enough quantity of water for a household

A technology must produce sufficient amount of water at a reasonable amount of time. This is to prevent the user from reverting back to using untreated water. According to

Sobsey *et al.* (2008) a household water treatment system must be able to provide 20L of treated water in 4 hours (5L/hr).

2.4.1.2 Improvement in the quality of treated water

A technology suitable for rural application must be able to produce good quality treated water in terms of appearance, smell and taste. The technology must also be applicable to a wide range of raw water quality. The raw water quality can be varied by seasonal fluctuation as well as new impurities entering the water sources. Key parameters for monitoring include turbidity and microbial contamination. The best technology is one that maintains good contaminant removal irrespective of water source and seasonal fluctuations (Baker, 2006).

2.4.1.3 Ease of maintenance and operation

Easy adoption and consistent use of a technology depends on how easy it is to use the technology. A technology that is straight forward to operate and maintain has more chances of success in rural areas. This is mainly because some people in rural areas are not educated. They would therefore battle with technologies that have complex procedures (Baker, 2006).

2.4.1.4 Affordability

The purchasing and maintenance cost of a household water treatment system is one of the factors that determines sustainability of the system in rural areas. A system that has high purchasing and maintenance costs has less chances of being successful. A system might be considered if it had a once off high initial cost but minimal additional maintenance costs. Such a system has better chances of sustained use in rural areas. The initial cost can be taken care off with assistance from government and non-governmental organisations. If there are no maintenance costs to the user, the usage of the technique can be continual.

Other technologies may need continual replacement of broken parts which might be a huge burden to the households and might result in a complete abandonment of the system. Any system that requires a continual replacement of parts is less sustainable in rural areas.

2.4.1.5 Use of local material for construction and maintenance

The system must be constructed from locally available material for it to be sustainable in rural areas. This is to eliminate the cost and time of importing maintenance material.

2.4.1.6 Chemical use and power requirement

The handling of chemicals as well as the dosage of required amounts during water treatment requires skilled individuals. This might not be available in rural areas. Some areas are still without power. Any technology that has power requirement will not be applicable in such areas.

2.4.1.7 Robustness

The conditions in rural areas might be harsh and changing. Systems which are delicate and affected by conditions such as temperature, raw water quality and other parameters are not suitable for application in rural areas.

2.4.2 Woven Fabric Microfiltration Gravity Filter

The WFMFGF shown in Figure 2.2 consists of 15 flat sheet membrane elements. An element consist of a PVC rectangular frame with a permeate outlet on one of the four sides. Two sheets of membrane fabric are glued on either sides of the frame. A spacer is put in between the sheets to enhance the flow of permeate to the outlet (Pikwa *et al.*, 2010).

The membrane elements are then stack together to form a membrane pack. The total membrane surface area of ±1m^2. The membrane pack is placed inside a 40 L container. Each flat sheet membrane element has a treated water outlet pipe connected to a manifold. The manifold connects to a tap located outside the membrane container (Pikwa *et al.*, 2010; Mecha and Pillay, 2014).

The system is simple to operate, water is just fed into the container and the tap is opened to draw out clean water. The system has been designed to produce 20 L of treated water per hour. The modular design of the membrane elements enables the system capacity to be increased easily. This does not cause a significant increase in the volume and weight of the system. The system is light and easy to carry (Pikwa *et al.*, 2010).

Figure 2.2: Photographs of WFMFGF, (left) complete unit, (centre) front view of membrane pack, (right) bottom view of membrane pack

The ability of the system in removing impurities has been established. In a study by Pikwa *et al.* (2010), the system was tested to assess its performance on raw water obtained from Umkomaas river. The system was found to produce treated water with turbidity that is within the SANS 241 standard of 1 NTU from raw water with turbidity above 300 NTU. Total coliforms were reduced to an average of 103 counts per 100 ml from 4838 count per 100 ml. E.coli were reduced to an average of 1 count per 100 ml from 38 counts per 100 ml.

2.4.3 Bio-sand house hold water treatment filter.

Bio-sand household water treatment filters are an intermittent operated slow sand filter (Lea, 2008; Kubare and Haarhoff, 2010; Young-Rojanschi and Madramootoo, 2014). It is a biological process where particulate and microbiological contaminants are removed by a biofilm layer that forms on the top surface of the filter media (Sobsey, 2002). This system is shown in Figure 2.3. It consists of a column or simple bucket packed with filter media. The filter media is normally sand with a diameter of 3.15 mm or less. It is packed to a height of 40 to 50 cm. It is supported by coarse sand of diameter 3.12 to 6.25 mm, packed to a height of 5cm. Below the coarse sand is gravel having a diameter of 6.25 to 12.5 cm, also packed to a height of 5 cm (Lea, 2008).

According to Lea (2008) the system is operated with a constant water level of 5 cm above the top surface of the filtering media. Water level above 5 cm causes poor oxygenation of the biofilm and the level below 5 cm may cause a disturbance of the biofilm during feeding. It may also cause easy evaporation of the water destroying the biofilm layer.

The outlet pipe is made to make a U-turn above the top surface of the filter media. This automatically maintains the 5cm water level above the filter media. The system is easy to use. Water is poured on top of the filter media and clean water collected at the bottom. The system is designed for a velocity of about 0.1-0.3 m/hr (Campos *et al.*, 2002). The prescribed flow rate through the system is 0.6-1 l/minute (Elliott *et al.*, 2008).

After some time of continuous use the top layer of the sand gets clogged by particulate matter and microbial contaminants. At that point it requires maintenance. The filter is maintained by scrapping the top 5 to 10 cm layer of sand and replacing it with fresh one. The removed sand is cleaned and stored for later use (Sobsey, 2002). After cleaning, the filter will take some time to redevelop the bio-film layer (Elliott *et al.*, 2006). It may take about 14 days for the bio-film layer to develop (Campos *et al.*, 2002). This necessitates the use of an alternate bio-sand filter.

The bio-sand household water treatment filter is not recommended for feed water with high turbidity because it easily get blocked and requires frequent cleaning (Lea, 2008; Kubare and Haarhoff, 2010).The maximum recommended feed turbidity is 30 NTU (Kubare and Haarhoff, 2010). If the water has high turbidity, pre-treatment is required.

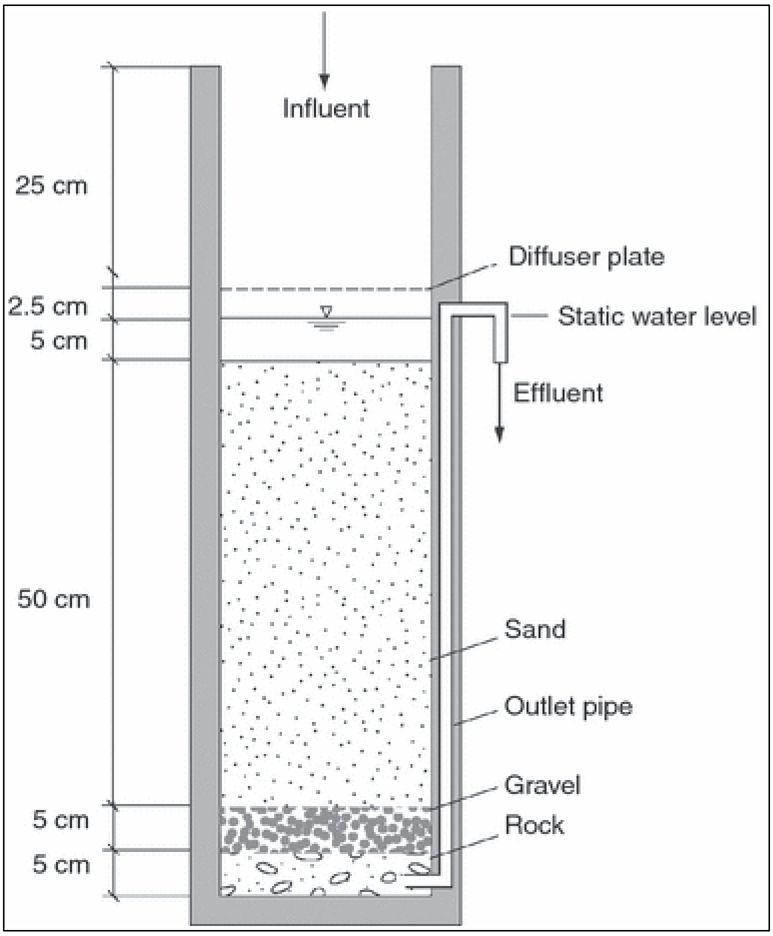


Figure 2.3 Schematic diagram of Bio-sand household water treatment filter (Tiwari *et al.*, 2009)

According to Baig *et al.* (2011), the bio-sand household water treatment filter normally does not achieve high microbial contaminants removal. This may be caused by improper construction, operation and maintenance. This might also be caused by the intermittent operation of the system which sometime disturbs the biofilm (Stauber *et al.*, 2006; Young-Rojanschi and Madramootoo, 2014).

If properly constructed, operated and maintained the system can remove up to 99 percent of enteric waterborne pathogens (Sobsey, 2002). A field study by Fabiszewski de Aceituno *et al.* (2012) conducted in Copan (Honduras) showed that diarrheal disease was reduced by 45 percent in households that used bio-sand household water treatment filters. A field study by Stauber *et al.* (2012) conducted in Tamale (Ghana) reported a 60 percent reduction in diarrheal disease.

Bio-sand filters are generally not recommended for house water treatment. This is because of the skill required for proper construction, operation and maintenance of the system which cannot be found in most households (Sobsey, 2002). A study by Fiore *et al.* (2010) found that after installation the users were happy using the bio-sand household filters. They were encouraged by the reduction in diseases while using the filters, although according to Baig *et al.* (2011) this system cannot provide treated water that meet national and international water quality guidelines.

2.4.4 Ceramic filters

Ceramic filters are made of various types of clay, diatomaceous earth glass and other fine particles (Sobsey, 2002). These materials are blended, manually or mechanically shaped and dried (Sobsey, 2002). They are fired at different temperatures to give different pore sizes. They may also be used unfired to have open pore filters (Sobsey, 2002). Water usually flows from the exterior to the interior which is then connected to a tap. There are however those that are design to filter from interior to exterior. Figure 2.4 shows ceramic filter systems and the different types of filter elements used in rural areas.

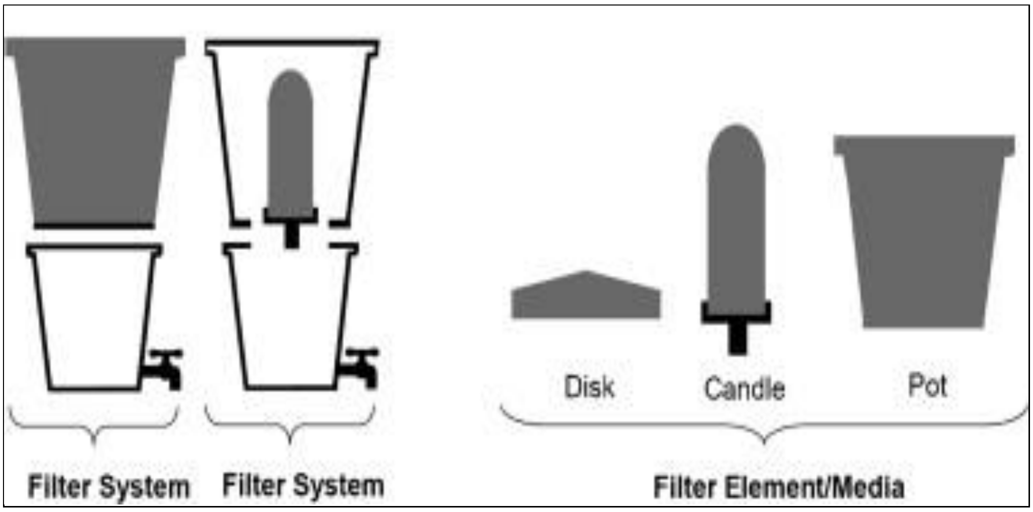


Figure 2.4: Ceramic filter elements and systems used in rural areas (Simonis and Basson, 2011)

After continuous usage, the ceramic filter fouls and requires cleaning. They are cleaned by scrubbing and rinsing with water. Most ceramic filter made in developed countries are in the micron pore size range or even less (Sobsey, 2002). This enables the removal of particulate contaminants as well as bacteria and parasites. Some ceramic filters are made of material that can adsorb viruses (Michen *et al.*, 2013). The problem with this type of ceramic filter is that the adsorption sites can be occupied by competing contaminants which result in poor virus removal (Sobsey, 2002). Most ceramic filters are impregnated with silver for disinfection (Lantagne, 2001; Van Halem *et al.*, 2009).

Developed countries such as the United Kingdom and United States of America have developed ceramic filters that are tested for pore size and microbial contaminants removal capability (Sobsey, 2002). The amount of work required in developing these filters and the transportation of the filters to the users will escalate the cost of these products such that it cannot be afforded by most rural households. There are other filters made in developing countries which are less costly but their contaminant removal capability is uncertain (Sobsey, 2002). A study by Brown and Sobsey (2010) show that ceramic filters are capable of removing 99 percent of bacteria from water, however these results were obtained from a laboratory scale study.

A study by Clasen and Boisson (2006) found that 70.6 percent of samples taken in households using more expensive commercially manufactured ceramic filters met the WHO guidelines for zero themotolerant coliform /100 ml. However after 16 months of the study, 51.3 percent of the filters still with the user were no longer working. This was due to breakages, blockages and expiry of the useful life of the ceramic filters.

The study concluded that compared to other point of use water treatment systems, ceramic filters offer advantages including low cost, high microbial efficacy, good performance in a wide variety of water conditions (pH, Temperature, turbidity), good acceptability by the user. The disadvantages of these filters include low flow rate 1-3 l/hr (Van Halem *et al.*, 2007) and breakages (Clasen and Boisson, 2006). The use of ceramic filter has now spread worldwide with the involvement of governments and international Non- Governmental Organisations (NGO) (Simonis and Basson, 2011).

A study by Ren *et al.* (2013) found that ceramic filters impregnated with silver was an effective way of providing clean water to developing world communities. A study conducted by Du Preez *et al.* (2008) in rural areas in Limpopo South Africa and Zimbabwe found that ceramic filters are well accepted in rural areas. 80 percent reduction in incidents of bloody and non-bloody diarrhoea after the use of ceramic filters was reported. Franz (2005), found that ceramic filters are capable of removing turbidity from 12 NTU down to below 1 NTU, meeting WHO standard for drinking water.

Table 2.1 summarises the performance of WFMFGF, ceramic filter and household bio-sand water treatment filter against the set criteria. The assessment confirms that the WFMFGF system meets all the criteria while the ceramic filters as well as household bio-sand filters do not meet some of the criteria. It is on this basis that the WFMFGF was selected as the preferred pre-treatment system for the adsorption process.

Table 2.1: Summary of performance of WFMFGF, ceramic filter and household bio-sand Water treatment filters (BSF) against the set criteria

Criteria	**WFMFGF**	**Ceramic filter (CF)**	**Household Bio-sand water treatment filter (BSF)**	**Acceptable technology**
Production of enough quantity of water for a household	The WFMFGF produces 20 L/hr of treated water. This is high above the recommended 5 L/hr.	Household ceramic filters produce about 1-3 L of treated water per hour. This is further declined with accumulation of dirt on the surface.	Household bio-sand produces 0.6 to 1 l/min (36 to 60 L/hr).	WFMFGF and BSF
Improvement in the quality of treated water	The system provides good quality treated water irrespective of feed water quality fluctuations.	The operating principle of a ceramic filter is filtration which is similar to that of membranes. It also provides good quality treated water irrespective of feed water fluctuations.	There seems to be uncertainty in terms of the household bio-sand filter constantly providing good quality of treated water	WFMFGF and CF
Ease of maintenance and operation	The system is easy to maintain. The construction material is locally available. Operation is also easy.	The filter element used in this system is not available in some areas. The operation is similar to that of WFMFGF.	Bio-sand filters are generally not recommended for household application. This is because of the skill required to operate and maintain.	WFMFGF
Affordability	WFMFGF is made from locally available and affordable materials. Most parts are less susceptible to breakage. The membrane is made of woven fibre material which cannot be damaged easily.	Ceramic filters are fragile and easy to break. They therefore need to be replaced once they have broken. To obtain and to replace broken ceramics is costly and not sustainable in rural areas.	Household Bio-sand filters are obtained once and require no frequent replacement of parts. Once obtained they have sustained use in rural areas.	WFMFGF and BSF.
Use of local material for construction and maintenance	The whole system is made of material locally available	Good quality ceramics need to be imported	Whole system is made of locally available materials	WFMFGF, and BSF
Chemical use and power requirement	System requires no chemical addition and power to provide clean water.	No chemicals and power required	No chemicals and power required	All
Robustness	System is robust	Ceramics are fragile	System is robust	WFMFGF and BSF

2.5 Membrane treatment

2.5.1 Different membrane processes

A membrane can be described as a barrier that separate particulates, colloidal and dissolved substances from solvent or water (Shirazi *et al.*, 2010). Membrane treatment processes can be divided into micro-filtration, ultrafiltration nano-filtration and reverse osmosis. The processes are differentiated from each other by the membrane pore size. Figure 2.5 shows the different types of membranes, their pore size ranges as well as the impurities they can remove.

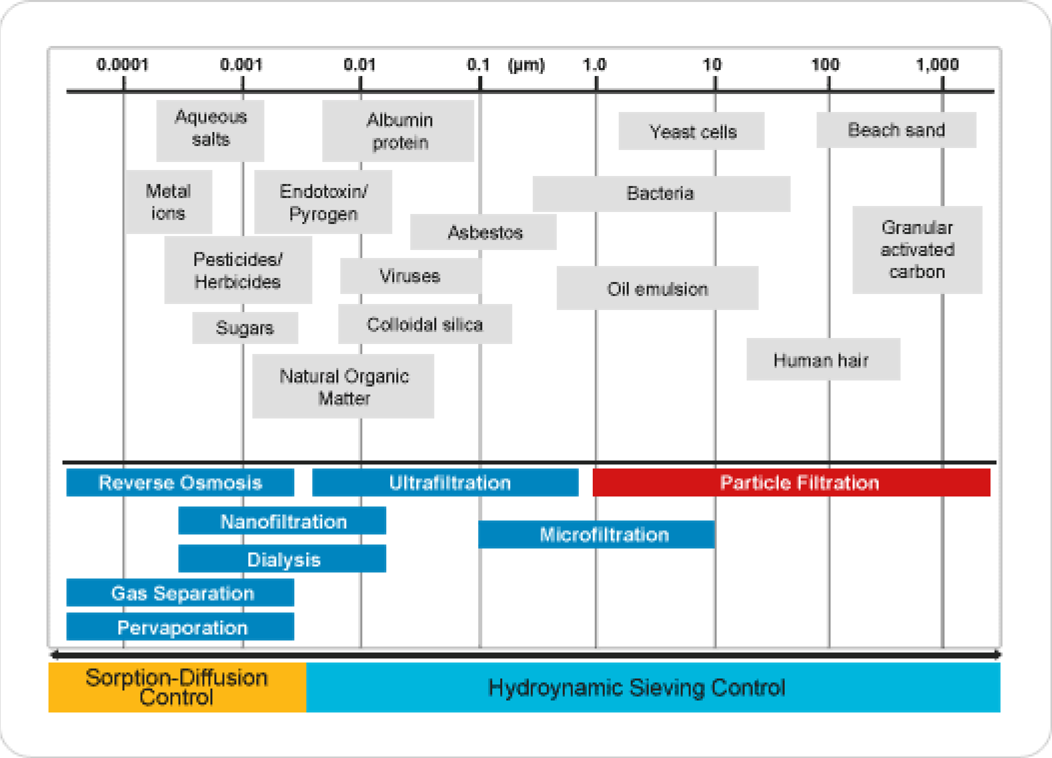


Figure 2.5: Membrane filtration spectrum adapted from (Pearce, 2007a)

Reverse osmosis membranes are one of the oldest type of membranes, commecialised in the 60s (Pearce, 2007a). It is the most used process for desalination. It has an aproximate pore size of 0.0005 micron (Abid *et al.*, 2011). It is capable of removing the smallest substance such as monovalent ions, producing almost pure water as permeate (Fritzmann *et al.*, 2007; Greenlee *et al.*, 2009). This is a pressure driven process. A very high pressure needs to be applied in order to ovecome the osmotic pressure on the feed side. For desalination plants, pressures in the range of 55 to 68 bar are common. Apart from desalination reverse osmosis membranes are used for waste water treatment as well as for the removal of organic and inorganic impurities from water for industrial applications (Fritzmann *et al.*, 2007).

Nano-filtration membranes have pore sizes slighly larger than those of reverse osmosis. They have an aproximate pore size range of 0.0005 to 0.005 micron, operating at pressures between 5 and 40 bar (Abid *et al.*, 2011). Nanofiltration is a newer membane process which can be used for water softening, removing magnesium and calcium. It can also be used to remove by-product trihalomethanes formed in conventional disinfection treatment by chlorine (Bottino *et al.*, 2009).

Ultrafiltration have pore sizes larger that nanofiltration. They have a pore size range of 0.005 to 0.1 micron, operating at a pressure range of 1 to 10 bar (Abid *et al.*, 2011). This membrane removes contaminants from water by size exclusion. It is able to remove micromolecules, colloidal and suspended matter as well as all microbial contaminants such as Giadia, cryptosporidia and bacteria (Hagen, 1998). It can also be used as a pretreatment for reverse osmosis process (Greenlee *et al.*, 2009). Due to its low pressure requirement some attempts have been made to use ultrafiltration to supply clean water to rural households where there is no power supply (Jacobs *et al.*, 1999).

Microfiltration has a pore size ranging from 0.1 to 3 microns operating at pressures below 2 bars (Abid *et al.*, 2011). Microfiltration also remove contaminants from water by size exclusion. The process removes micro-sized particles such as bacteria, colloids yeast cells etc (Zhao *et al.*, 2013). If the feed water to the microfiltration membrane has fine particles, it will start with a high initial flux, after which the flux will reduce to that of an ultrafilter. This is caused by the particles blocking the pores of the membrane (Pearce, 2007a).

The fact that the microfiltration membrane can be operated under gravity means that it is suitable for applications in rural areas where there is no electricity. It is for this reason that the WFMFGF is made of a microfiltration membrane and is gravity driven. The pore size of the membrane is however not definite. The performance of the membrane largely depends on a cake layer that forms on the surface. This enhaces the retention of contaminants present in the feed (Rajagopaul and Pillay, 2004).

2.5.2 Membranes: Past, present and the future

The use of membrane in water treatment has been in existence for decades. According to Sutherland (2009) the earlier membranes were reverse osmosis mainly used for desalination and nano-filtration membranes, mainly used for removal of organic and larger inorganic ions. Later on ultrafiltration and micro-filtration entered the market. Microfiltration is now taking a large portion of the membrane market (Sutherland, 2009).

The use of membranes has previously not been supported. There were a few reasons for this, which include; high capital and operational costs of membranes, conventional water treatment method was able to efficiently treat the water, difficulty with disposal of chemical waste from cleaning and limited knowledge on membrane use (Owen *et al.*, 1995).

Over the last decade a dramatic growth on membrane application for water and wastewater treatment have been observed (Moon *et al.*, 2009).Other recent areas of membrane application include pharmaceutical, textile, pulp and paper, tanning and leather, electroplating, mining, dairy, food and beverage processing as well as biotechnology (Shirazi *et al.*, 2010). The increase in the use of membranes for water and waste water is attributed mainly to increased pollution of water as a result of population growth, climate change and industrialisation (Parish *et al.*, 2012). The reduction in the cost of membranes also had a big impact in the increased usage of membranes (Sutherland, 2009).

Population growth has caused a high demand for water which reduces the water levels in the water sources. On the other hand the increased population has increased the pollution that ends up in the already shrunken water sources. Climate change has resulted in inconsistent weather patterns. Some drought and floods are being experienced. This worsens the pollution level in the water sources.

Increase in industrial activities has led to an increase in the quantity of impurities that ends up in the water sources. Some of the conventional water treatment systems can no longer cope. Apart from battling with handling the increasing contaminants from water sources, conventional water treatment involves addition of chemicals such as chlorine for disinfection. The chlorination of water increases the likelihood of formation of the carcinogenic trihalomethanes (Perez Pavon *et al.*, 2008). Another disadvantage of conventional water treatment is the fact that it is environmentally unfriendly. There is a large volume of chemical rich sludge produced as a result of flocculation and clarification (Perez Pavon *et al.*, 2008).

The above limitations of the conventional water treatment make membranes an option for consideration. The main advantage with membranes is that it can remove all contaminants without being selective. All the impurities are removed in one step. This is a huge advantage since it reduces the required footprint (Pearce, 2007a). Additional advantages of membrane use include low chemical usage which results in low chemical cost and low waste generation. Membranes can also be easily automated and can operate unattended (Pearce, 2007a).

Advances in membranes especially in the area of reduction in energy consumption have also rendered membranes more competitive to previously preferred treatment methods. With the conventional water treatment processes battling with the increasing stringency of the water quality regulations, decrease in the quality of water sources, technical advancement and widening of application of membrane process, it looks like the future demand for membrane processes will increase even more.

2.5.3 Membrane material

According to Sutherland (2009) the continual production of new types of membranes has resulted in an improvement in membrane filtration in terms of performance and cost. There are now a number of membrane materials on the market that has been made to improve membrane filtration. Ways in which membranes are characterised include chemical tolerance, strength as well as whether they are hydrophilic or hydrophobic (Sutherland, 2009).

A hydrophilic membrane is water loving, this means it is easy to wet. Cellulose acetate membrane is an example of a hydrophilic membrane. The advantages with these membranes are that since they are water loving, they are good for water treatment and they are also less fouling and flexible. The disadvantages are that they tolerate a very narrow pH range, are biodegradable and have poor strength (Pearce, 2007c).

Hydrophobic membranes on the other hand are water hating. This means that they don’t easily get wetted. The water forms droplets on the surface of the membrane. Examples of hydrophobic membranes include polypropylene and polyethylene. The advantages of these membranes are good strength and better chemical tolerance (good for cleaning). Disadvantages include poor wetting and easy fouling (Pearce, 2007c).

There are membranes that have been modified to have both hydrophilic and hydrophobic properties. The purpose is to have membranes that have the advantages of hydrophilic membranes yet with strength and better chemical tolerance. Such membranes include polysulfones, polyethrsulfone polyacrylontrile and polyvinylidene fluoride (Pearce, 2007c).

The WFMFGF is made from a robust polyester woven fabric. The membrane is not easily damaged from drying, mechanical and chemical cleaning. It shows hydrophilic properties with an advantage of less fouling. It is cheaper and locally available (Mecha and Pillay, 2014). All of this makes it an ideal material for a rural water treatment system where there are harsh conditions, unskilled people having less income.

2.5.4 Membrane module configuration

Membrane module configuration refers to a setup of a single membrane module. A membrane module can be configured into flat sheet, spiral wound, capillary and hollow fibre membrane modules. Membranes used for water treatment should be characterised by ease of cleaning, low power consumption and high packing density (Bodzek and Konieczny, 1998).

Spiral wound element is made of two long membrane sheets glued on three edges. This is shown in Figure 2.6. The open side is connected to a permeate collection pipe. The sheets are then wrapped around the permeate collection pipe. Spacers are placed inside the two glued sheets (permeate side) as well as outside the sheets (feed side). The feed flows parallel to the central collection pipe. It is partially forced through the membrane. Permeate flows towards the central collection pipe (Fritzmann *et al.*, 2007).

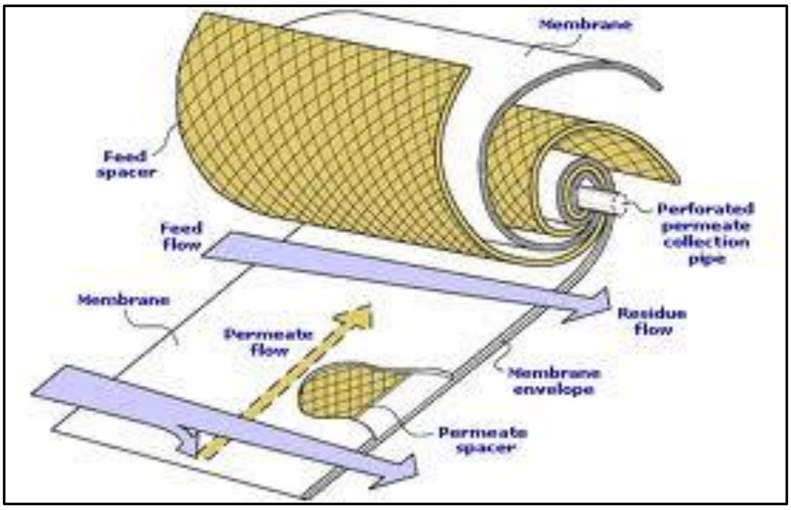


Figure 2.6 Spiral Wound membrane (Baker, 2004)

The advantages of spiral wound modules include ease and affordability of production, high packing density (less than 1000 m^2/m^3), and high flux. Disadvantages include high feed pressure loss, easy to foul and difficult to clean, often requires pre-treatment (Fritzmann *et al.*, 2007). The spiral wound module is mainly used in RO and NF membranes (Pearce, 2007d).

Hollow fibre membrane modules consist of small tubes with inside diameter <0.5 mm mounted inside a vessel (Pearce, 2007d). This module is shown in Figure 2.7. The flow through the membrane is from outside to the inside. This type of membrane module was used for reverse osmosis systems in the early days (Fritzmann *et al.*, 2007). It now dominates the ultrafiltration and micro-filtration membranes (Pearce, 2007d).

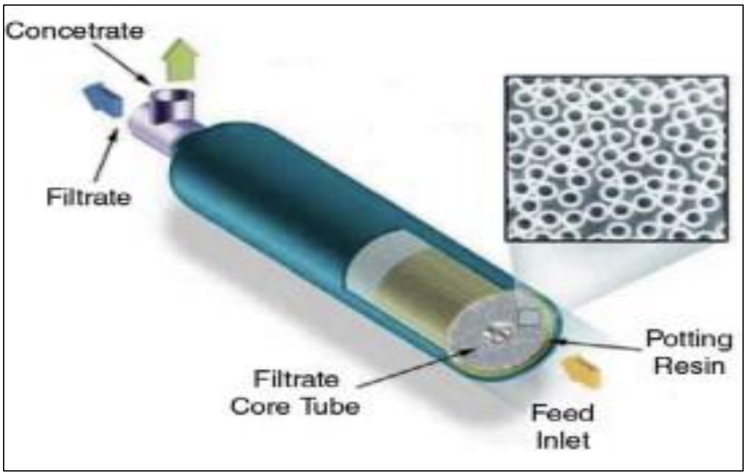


Figure 2.7: Hollow fibre membrane module (Pearce, 2007d)

The advantages of hollow fibre membranes include: high strength, ability of the tubes to resist high transmembrane pressure, hydrodynamic efficient, back washable and it requires a low level of pre-treatment compared to spiral wound membrane modules (Pearce, 2007d; Sutherland, 2009).The disadvantage of this module format is the need for fluid to flow in small passages which makes it prone to blockage. Pre-filtration is often required (Sutherland, 2009).

A capillary module consists of a number of capillaries supported on ends by glue, epoxy resin or silicone (Mulder, 2003). These are similar to hollow fibre membranes but are made of tubes with inside diameter >1mm (Pearce, 2007d). The flow through the capillaries can either be inside out or outside in. This module format is commonly used on ultrafiltration and microfiltration membranes (Pearce, 2007d).

Advantages of capillary membrane modules are similar to those of hollow fibre membrane modules (Pearce, 2007d). They however have larger tube diameters meaning that they are less susceptible to blockage compared to hollow fibre membrane modules. The disadvantage is that they still need pre-treatment (Pearce, 2007d).

Flat sheet elements are made of a frame with flat membrane sheets stuck on either sides of the frame. A spacer is placed between the flat sheet membranes to enhance permeate flow. Water flows from the outside to the inside of the module. Permeate take-off is connected to the module frame. Flat sheet membrane pack is shown in Figure 2.8. The disadvantage of this membrane module is the low packing density while advantages include ability to be operated under gravity and the ease of cleaning (Pillay and Jacobs, 2008).

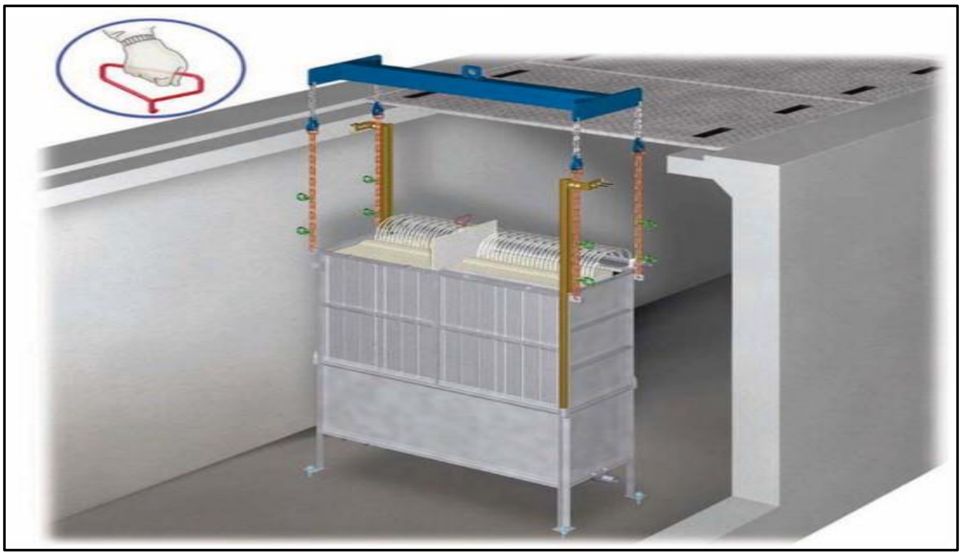


Figure 2.8 Flat sheet membranes (Pearce, 2008)

The woven fabric micro-filtration gravity filter is made from a flat sheet module. The fact that it can be operated under gravity and it is easy to clean makes it more suitable for rural application over the other membrane modules.

2.5.5 Membrane fouling

Membrane fouling can be defined as an undesirable deposit of material on membrane surface (Zhang and Ma, 2009). This occurs when material rejected by the membrane is not returned to the bulk feed. The rejected material causing fouling may include particulate, organic, inorganic as well as microbiological contaminant (Pearce, 2007b).

Membrane fouling results in increased pressure drop across the membrane, low rejection (Fritzmann *et al.*, 2007) and permeate flux reduction (Williams and Wakeman, 2000). In a system where the water is pumped, fouling increases energy costs. It also increases cleaning chemical costs as well as labour costs for maintenance.

Noticeable improvement has been made in the area of high flux operation, high rejection as well as the membrane’s ability to operate at low operation pressure. Despite these improvements the membrane flux ultimately reduces due to membrane fouling (Al-Amoudi and Lovitt, 2007). This shows that membrane fouling is still a persistent problem. According to Al-Amoudi and Lovitt (2007) membrane fouling and cleaning depends on the following:

- Membrane properties such as roughness, pore size distribution, surface charge etc. A membrane with a rough surface as well as small pore size will be easy to foul. Again if the charge of the membrane is opposite the charge of the impurities, the impurities will easily be attracted to the surface resulting in membrane fouling.
- Chemistry of the feed such as solute concentration, type of solute, charge, feed pH, fouling potential etc. High feed solute concentration will easily foul the membrane.
- Process design of the system, configuration, capacity, flow rate, etc. There is high fouling with dead end systems compared to other system configurations. Operating a membrane system above its capacity will increase its rate of fouling.
- Condition of the environment such as temperature and pressure. High organic and high temperature in the feed water will promote biological growth which will foul the membranes. High operating pressure will force the solute onto the membrane surface resulting in increased fouling rates.

The fouling of membranes can be divided into surface fouling which is a build-up of cake (gel-like) layer on the membrane surface and pore blocking fouling where the fouling occupies the membrane pores. Pore blocking can be divided into complete blocking where a particle completely blocks the pore, incomplete blocking where a particle partially blocks the pore, or standard pore blocking where small particles will gradually block the pores (Pearce, 2007b; Kweon *et al.*, 2012).

The raw water has different impurities in it which may result in the above mentioned types of fouling. In order to deal with these different types of fouling, different cleaning methods are required.

2.5.5.1 Inorganic fouling

Inorganic fouling is caused by the existence of one or more inorganic species precipitating on the surface of a membrane. The precipitation of inorganic contaminants is in two stages viz nucleation and crystal growth (Gilron and Hasson, 1987; Pervov, 1991). Gilron and Hasson (1987), report that inorganic fouling occurs when inorganic species deposit and grow on a membrane surface. This is called heterogeneous crystallization.

Pervov (1991) on the other hand reported that nucleation and crystallization may occur in the bulk fluid before being deposited onto the membrane. This is called homogeneous crystallization. Salts that commonly cause membrane scaling include $CaCO_3$, $CaSO_4$. H_2O, silica and $CaPO_4$ (Al-Amoudi and Lovitt, 2007). Physical and chemical parameters that promotes crystallization and membrane fouling include temperature, pH, permeate flow rate, salt concentration, concentration polarization, membrane type and material as well as metal ions.

These salts are commonly found in ground water. The micro-filtration membranes employed in the system being developed cannot remove these salts because of their small size unless nucleation and crystallization occurs in the bulk fluid before being deposited onto the membrane. In such a case the fouling can easily be removed by physical methods.

2.5.5.2 Organic fouling

Membranes can be fouled by natural organic material (NOM). Humic substances are a major fraction of natural organic material (Al-Amoudi and Lovitt, 2007). Humic acids are micro-substances resulting from degradation of organic materials such as plants produce. These substances are found in natural water at concentrations ranging from 0.5 to 20 mg/L in brackish water and up to 100 mg/L in seawater (Redondo and Lomax, 1997). The substances are of polymeric phenolic nature. They form complexes with metal ions such as iron. The complexation of multivalent ions forms a gelly-like substance layer on the membrane surface (Fritzmann *et al.*, 2007).

Other continuants of NOM include hydrophilic acids, proteins, lipids, amino acids and carbohydrates (Kalajdzic *et al.*, 2013). NOM can be classified as hydrophilic or hydrophobic. It is the hydrophobic NOM that mainly contributes to membrane fouling (Nilson and Digiano, 1996).

According to Al-Amoudi and Lovitt (2007), in ground water hydrophobic NOM accounts for about 75 percent while hydrophilic NOM accounts for about 20 percent.

On surface water however hydrophobic NOM accounts for 27 percent while hydrophilic NOM accounts for 65 percent. This shows that in cases where the system will be applied for treating ground water, it will be more susceptible to hydrophobic NOM fouling.

The hydrophobicity of NOM increase with increasing molecular weight (Nilson and Digiano, 1996). The hydrophobicity is the most important parameter determining the retention of molecules within the molecular weight cut off (MWCO) of the membrane. The molecules are presumed to be binding on the membrane surface (Braeken *et al.*, 2005). NOM fouling increases at high pH in the presence of calcium. If the calcium concentration is high it will precipitate at high pH. The NOM adsorbs on the precipitate (Suess, 1973).

Organic fouling can result in reversible and irreversible flux decline. Cleaning can be used to restore reversible flux decline. If organic fouling has resulted in irreversible flux decline, the flux cannot be recovered even with rigorous chemical cleaning (Al-Amoudi and Farooque, 2005).

2.5.5.3 Bio-fouling

Bio-fouling involves fouling of membranes by biological contaminants. Bio-fouling begins with the formation of a conditioning film on a membrane surface. This involves adsorption of micro-molecule substances that naturally exist in water. These micro-molecules include proteins, polysaccharides and extracellular polymeric substances secreted by micro-organisms.

A gel-like film forms where micro-organisms get deposited and grow. The micro-organisms include bacteria, fungi, and other eukaryote. They feed on the micro-molecules as well as organic material and nutrients present in feed water (Shi *et al.*, 2014). When the bio-film grows to a certain level it reduces flux and increases pressure drop. This is the point of membrane fouling.

The membrane surface provides a good site for microbial growth as it returns a lot of nutrient required for microbial growth (Al-Amoudi and Lovitt, 2007). Bio-fouling can be minimised by reducing nutrients in the feed that will promote microbial growth and using appropriate cleaning mechanisms (Al-Amoudi and Lovitt, 2007).

The focus of this study is the application of the system in ground water. The fouling that is expected on the membrane surface of the WFMFGF in such an application is mainly particulate matter that may naturally be present in water and salts that have precipitated in the bulk fluid. The larger pore size of the micro-filter membrane is not expected to return dissolved inorganic substance. To a lesser effect organic substances may be adsorbed on the membrane surface. Most organic contaminants are however used by the micro-organisms resulting in bio-film growth.

2.5.6 Membrane cleaning

The fouling of the membrane results in high trans-membrane pressure and low flux. When this happens, membrane cleaning is required. Appropriate cleaning methods must be used to recover the performance. Available membrane cleaning methods can be classified into physical and chemical cleaning. Physical cleaning involves changing hydrodynamics, creation of turbulence or variation of temperature to force contaminants to leave the membrane surface.

Chemical cleaning on the other hand varies the chemistry of the foulants enabling repulsion of foulants from the membrane surface. Chemicals may also react with the foulants decomposing it into the water (Kweon *et al.*, 2014). The selected cleaning method must be effective against the foulants but not harmful to the membrane material.

2.5.6.1 Physical cleaning

Physical cleaning involves applying mechanical, hydraulic and electrical means to remove fouling from a membrane surface (Shi *et al.*, 2014). Hydraulic cleaning methods involve reversing the trans-membrane pressure across the membrane (backwashing). Backwashing the WFMFGF would be difficult because the system operates under gravity and this pressure would not be enough to remove the fouling on the membrane surface.

Mechanical cleaning methods involve using mechanical means to remove fouling from the membrane surface such as scrubbing and scouring with air or sponge balls (Kweon *et al.*, 2014). The disadvantages of air scouring are as follows (Shi *et al.*, 2014);

- It is difficult to maintain a uniform distribution of air across the whole membrane module.
- The velocity and bubble size has an effect on the effectiveness of the method.
- Compressed air may cause damage to the system.
- There might be high operational cost as a result of compressing the air.

It is clear that air scouring is not suitable for rural area applications because of its sophistication and power requirements. The only available and applicable mechanical cleaning method is scrubbing. This method is simple and has no power requirement.

Electrical cleaning involves putting electrodes on either sides of a membrane creating an electrical field across the membrane (Jagannadh and Muralidhara, 1996). Foulants are then attracted to the electrodes, away from the membrane surface (Huotari *et al.*, 1999). The drawback with this technology is the power requirement as well as poor availability of corrosion resistant and affordable electrodes (Huotari *et al.*, 1999).

2.5.6.2 Chemical cleaning

Chemical cleaning involves the use of cleaning agents to remove contaminants from the membrane surface. The first thing with chemical cleaning is to find a suitable cleaning agent. A suitable chemical agent must be characterised by the following: effective in removing contaminants, low cost, safe to use and easily washable with water. A cleaning chemical should mainly be able to loosen foulants from the membrane surface, keep foulants dispersed in solution and not attack the membrane (Madaeni and Samieirad, 2010).

Chemical cleaning is used to remove organic, inorganic and biological contaminants. Chemical reagents commonly used for membrane cleaning include acid detergents, alkaline detergents, oxidants, enzyme detergents, surfactants etc. These chemicals are used to remove different foulants (Pearce, 2007c).

The alkaline chemical commonly used for membrane cleaning is sodium hydroxide. It can be applied at a pH of 11-12 to dissolve weakly acid organic contaminants including phenolic and carboxylic functional groups (Porcelli and Judd, 2010). According to Fritzmann *et al.* (2007) at a pH >9, both the organic ions and the membrane surface become negatively charged resulting in repulsion. Lower pH must be used with sensitive membrane materials (Porcelli and Judd, 2010).

Acid cleaning chemicals such as hydrochloric and sulphuric acids are used to remove inorganic foulants such as divalent salts and metal hydroxides (Kweon *et al.*, 2012). These metal acids solubilise the inorganic contaminants, removing it from the membrane surface. The pH must not be lower than 1 for pH sensitive membrane material such as Polyvinylidene Difluoride (PVDF) (Porcelli and Judd, 2010). Acids can also remove organic contamination to a lower extent. It oxidises NOM to form soluble aromatic compounds, but generally acids are used for scale removal from membranes surfaces.

2.5.6.3 Oxidants

Oxidants are used to remove biological contaminants. Available oxidants include hydrogen peroxide (H_2O_2) and sodium hypochlorite (NaOCl). Sodium hypochlorite is the most common oxidant. In water it easily hydrolyses to form hypochlorous acid (HOCl). This is a weak acid that dissociates at low pH. This oxidises pathogenic micro-organisms on the membrane surface (Shi *et al.*, 2014). The use of sodium hypochlorite however depends on whether the membrane material is chlorine tolerant or not.

Another problem with the use of sodium hypochlorite is that if the water has high organics in it, chlorine will chlorinate the organics into compounds that may be harmful to humans as well as the environment (Perez Pavon *et al.*, 2008). According to Kweon *et al.* (2012), sodium hypochlorite degrades NOM functional groups to ketone, aldehyde and carboxyl groups. These can react by hydrolysis at high pH. The combination of sodium hypochlorite and sodium hydroxide has been used as an effective membrane cleaning method.

2.6 Adsorption theory

2.6.1 Fluoride

Fluoride is a salt of the most reactive element called fluorine. It is estimated to be the seventeenth most abundant element occupying about 0.065 percent of the earth’s crust (Patil and Ingole, 2012). Since it is reactive, it exists as compounds rather than a free element (Patil and Ingole, 2012). Fluoride bearing rocks include fluorspar, cryolite, fluoroapatite and hydroxyl apatite (Salim, 2011). From rocks, fluoride gets desorbed into ground water through natural weathering of the rocks (Loganathan *et al.*, 2013).

Other factors that contribute to high levels of fluoride in ground water include the velocity of underground flowing water, pH, temperature, as well as the concentration of calcium and bicarbonate ions (Salim, 2011). High pH, high bicarbonates and low calcium concentration results in high fluoride levels. High levels may also be associated to activities such as agriculture.

The addition of fertilizers into the soil and irrigation increases the ground water alkalinity. This promotes adsorption of hydroxide ions into soil, displacing fluoride ions which then get dissolved into the water (Ayoob and Gupta, 2006). This increases the fluoride concentration in the ground water. On surface water, elevated fluoride levels result from industrial activities. Industries such as aluminium, steel, glass, semi-conductors, electronic, tooth paste and fertilizer have waste water that may have high levels of fluoride (Goswami and Purkait, 2012)

In water, fluoride exists as soluble compounds associated with monovalent ions such as Sodium Fluoride (NaF) and Potassium Fluoride (KF) (Patil and Ingole, 2012). It is also prevalent in acidic conditions in a form stable mono- fluoroaluminate, hexa-fluoroaluminate mono-fluoroferrates and hexa-fluoroferrates (Patil and Ingole, 2012). Generally free fluoride is found in alkaline solution (Patil and Ingole, 2012). In general the different ways in which fluoride enters the human body is through drinking water, food, industrial exposure, drugs, cosmetics etc (Meenakshi and Maheshwari, 2006). However the main contributor is drinking water which contributes 75-90 percent of the daily intake (Meenakshi and Maheshwari, 2006).

The problem of high fluoride levels in water is a local as well as an international problem. Ground water with high levels has been reported in countries such as United State of America, Asia, Sri Lanka and Africa (Meenakshi and Maheshwari, 2006). In South Africa, high fluoride levels have been reported in the North West Province, Limpopo, Northern Cape, and KwaZulu Natal (Schoeman, 2009; Odiyo and Makungo, 2012).

Severe cases of high fluoride have been reported in China (Wuyi Wang, 2002), India (Ayoob and Gupta, 2006) and countries along the rift valley in Africa (Sneha Lunge, 2011). In Africa, detailed studies on high fluoride in ground water have been done in Tanzania and Kenya (Mjengera and Mkongo, 2003; Meenakshi and Maheshwari, 2006).

The consumption of fluoride has beneficial and detrimental effects on human health. Since fluorine is a highly electronegative element, it readily reacts with calcium which is abundant in teeth and bone to form calcium fluoride (Shrivastava and Vani, 2009). The formed calcium fluoride protects teeth against decay especially in children. The decay of children teeth is called dental caries (Loganathan *et al.*, 2013). The fluoride must however be consumed at low concentrations, between 0.4 to 1 mg per litre of water.

A problem exists if the fluoride is consumed at concentrations in excess of 1.5 ppm (Fan *et al.*, 2003). Naturally the teeth enamel is made of crystalline hydroxyl apatite. Due to high calcium content of the teeth and bone, the consumption of high concentration of fluoride leads to the formation of calcium-fluoro apatite crystals on the teeth. The hydroxide ion on the teeth gets replaced by fluoride to form a more stable fluoroapatite. This only occurs in growing teeth of children, while the teeth are still developing (Shrivastava and Vani, 2009). The teeth irreversibly lose its shine and might have a yellowish or brownish striation of the front teeth (Salim, 2011).

Over exposure with time may not be noticeable in adults that have fully developed teeth, but they may suffer from other irreversible illnesses caused by a high consumption of fluoride (Shrivastava and Vani, 2009). Overexposure to fluoride results in skeletal fluorosis in adults. This affects children as well. The fluoride gets deposited into joints of the neck, pelvis, shoulder and knees. The backbone can be joined together making it difficult for a person to walk(Shrivastava and Vani, 2009). Ultimately the person may suffer from bone cancer as well as damage to the spine, major joints, muscles, and nervous system (Shrivastava and Vani, 2009).

Too much consumption of fluoride may also cause muscle fibre degeneration, low haemoglobin levels, excessive thirst, headache, skin rashes, nervousness, neurological manifestation, depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pains, reduced immunity etc (Vani, 2009).

The maximum fluoride concentration in drinking water permitted by the World Health Organisation is 1.5 mg/L (Mjengera and Mkongo, 2003). Different areas may have different standards depending on the air temperature. In areas with generally high air temperature, the maximum allowable fluoride concentration is lower. This is because there is high water consumption in those areas (Meenakshi, 2004). For this research the maximum drinking water fluoride concentration of 1.5 mg/L as specified by the World Health Organisation was adopted. This is because the system being used should be able to be used worldwide.

According to Meenakshi and Maheshwari (2006) the problem of fluoride poisoning can be addressed with the following options

- Use of alternate water sources
- Improved nutrition
- Treatment of fluoride contaminated water using available defluoridation technologies.

The alternate water sources include water harvesting, river water and fluoride free ground water sources. The problem with water harvesting would be minimum rainfall in some areas as well as poor storage capacity. River water may have other impurities which might be expensive to treat. The use of fluoride free ground water sources might also prove not to be a better solution since the fluoride concentration changes from source to source (Meenakshi and Maheshwari, 2006). This requires monitoring of all the sources which might be costly. It also means that the user might have to travel a longer distance to a cleaner source which will be an inconvenience.

It has been said that calcium and vitamin C supplements lowers the risk of dental fluorosis. Such supplements would only be effective if used with a technical solution. Practically the supply of such supplements to affected areas seems not feasible because of costs involved. The more practical solution seems to be the use of defluoridation technologies. This can be a once off acquisition, capable of providing fluoride free drinking water regardless of the water source (Meenakshi and Maheshwari, 2006).

2.6.2 Fluoride removal

Fluoride removal is easily done in areas where there is a conventional water treatment system. Adding a unit that removes fluoride in the existing treatment system easily solves the problem. The population that is at high risk is that in rural areas where there is inadequate infrastructure for the supply of bulk water. Point of use (POU) water treatment systems can be used in the interim.

2.6.2.1 Process selection

This section presents the assessment and selection of the best process for fluoride removal, suitable for application in rural areas. The processes were assessed using the criteria presented in section 2.4.1. The available processes for fluoride removal include lime softening, precipitation and coagulation, adsorption, ion exchange resins, contact precipitation and membranes.

2.6.2.2 Lime softening, precipitation and coagulation

This process involves adding lime to fluoride contaminated water to form an insoluble calcium fluoride precipitate. If magnesium is present in the water, fluoride is co-precipitated in the magnesium hydroxide precipitate formed (Fawell *et al.*, 2006). The removal of fluoride by lime is not very effective. It leaves a fluoride residual of about 8 mg/L. Lime has to be used in conjunction with alum for better removal (Meenakshi and Maheshwari, 2006).

A household technology based on these processes is shown in Figure 2.9. This technology is called the Nalgonda defluoridation technology. It was named after the poorest and draught prone district in the state of Andhra Pradesh, southern India. This district is called Nalgonda. The district is affected by severe fluorosis and is where this technology was first constructed (Ayoob *et al.*, 2008). Apart from India, this technology has been used in household and communities in many developing countries such as Kenya, Tanzania and Senegal (Dahi *et al.*, 1996; Ayoob *et al.*, 2008).

The technology consists of two buckets. One for mixing raw water with the lime and alum, the other for treated water. A tap is fitted at the bottom of the raw water bucket to collect treated water. A screen and filter cloth is fitted underneath the tap to prevent precipitates from passing through to the treated water in the bucket.

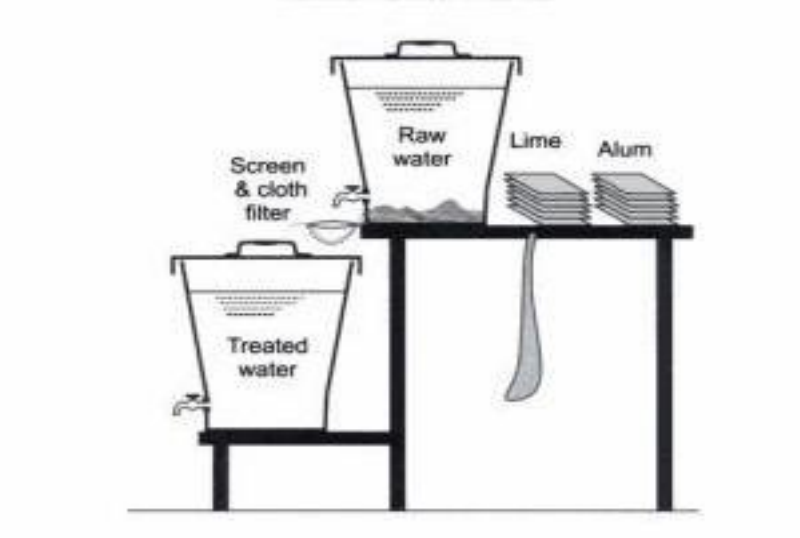


Figure 2.9: The Nalgonda Defluoridation Unit adopted for domestic use in Tanzania (Fawell *et al.*, 2006)

The treatment is done in two steps (Meenakshi and Maheshwari, 2006). The first step involves adding slaked lime [$Ca(OH)_{2\,(aq)}$] into fluoride contaminated water. The slaked lime reacts with the fluoride [F^-] in the water to form calcium fluoride precipitate [$CaF_{2(s)}$]. The reaction is as follows:

$$Ca(OH)_{2\,(aq)} + 2F^-_{(aq)} \rightarrow CaF_{2(s)} + 2OH^-_{\,(aq)} \qquad (2.1)$$

The second step involves adding alum [$Al(SO_4)_{3(aq)}$] into the water. The alum first dissolve into aluminium ions [$Al^{3-}{}_{(aq)}$] and sulphate ions (SO_4^{2-}). The aluminium ions then react with water to form aluminium hydroxide flocs [$Al(OH)_{3(s)}$]. The formation of the aluminium hydroxide flocs attract different kinds of micro-particles and negatively charged ions like fluoride. This occurs as follows:

Alum dissolution

$$Al_2\,(SO_4)_{3(aq)} + 18H_2O_{(aq)} \rightleftarrows 2Al^{3+}_{(aq)} + 3SO_4^{2-}{}_{(aq)} + 18H_2O_{(aq)} \qquad (2.2)$$

Alum Precipitate (Acidic)

$$2Al^{3-}_{(aq)} + 6H_2O_{(aq)} \rightarrow 2Al\,(OH)_{3(s)} + 6H^+_{(aq)} \qquad (2.3)$$

Co-precipitation

$$F^-_{(aq)} + Al(OH)_{3(s)} \rightleftarrows Al(OH)_3 . F \text{ complex} + \text{undefined products} \qquad (2.4)$$

The advantage of this method is its flexibility. It can easily be used at different scales by just varying the dose. The addition of lime increases the calcium content in the water. The calcium reduces fluoride absorption by the human body (Mjengera and Mkongo, 2003).

The following drawbacks were identified with the method: It requires a large dose of alum. The alum dose may be 20 times more than the conventional water treatment where turbidity removal is the focus (Mjengera and Mkongo, 2003). It cannot provide treated water that has fluoride concentration meeting drinking water standards. It converts a large portion of the fluoride to soluble aluminium fluoride complexes (Meenakshi and Maheshwari, 2006).

This method is based on widely available material but the dose of chemicals is costly to people in rural areas. The required dose of chemicals has to be predetermined by skilled individuals which cannot be found in most households. When the quality of raw water changes, the process has to be optimised. This can only be achieved by a skilled individual. Finding the appropriate means of handling the large quantity of sludge produced becomes a problem as well during treatment (Shrivastava and Vani, 2009).

2.6.2.3 Adsorption

Adsorption processes involve the removal of a substance from a liquid phase, by attachment to a surface of a solid phase. The adsorbing material is called adsorbent while the substance being removed is adsorbate. Adsorbents such as activated alumina, and activated carbon have a wide industrial application as well as in water and waste water treatment.

The mechanism of adsorption can be divided into van der waals forces (outer sphere surface complexation), ion exchange (outer sphere surface complexation), hydrogen bonding (inner sphere surface complexation), ligend exchange (inner sphere surface complexation) and chemical modification of the adsorption media surface (Slejko, 1985; Loganathan *et al.*, 2013). The first two mechanisms are weak physical attraction and are not specific to fluoride. The third and fourth mechanisms are strong chemical attractions and are specific to fluoride. The last mechanism can either be specific or nonspecific (Loganathan *et al.*, 2013).

In the presence of other ions fluoride cannot be selectively removed by the first and second mechanism. If there are other ions in the water, there will be high competition for adsorption sites. Fluoride will selectively be adsorbed with the third and fourth mechanism even in the presence of other competing ions (Loganathan *et al.*, 2013).

The van der waals forces is the forces between two atoms. These forces become larger with a large size of the adsorbate. It is for this reason that adsorbate with high molecular weight such as organic matter is adsorbed better than ions such as fluoride on activated carbon(Loganathan *et al.*, 2013). Hydrogen bonding is an attractive force between electropositive hydrogen and electronegative atoms such as oxygen, nitrogen or fluoride (Laurence and Berthelot, 2000). Adsorption by hydrogen bonding is stronger than that of van der waals forces but weaker than ligand exchange.

Ligand exchange mechanism involves adsorption of anions like fluoride onto a metallic cation located on the media surface. The fluoride attraction is by covalent bonds. The process involves the releasing of anion that was attached to the cation. Adsorption by this mechanism is highly selective towards specific anions. It also results in a high adsorption capacity. Adsorption with ligand exchange mechanism can selectively remove an anion even if it is present at low concentration among competing ions of low selectivity present at high concentration (Loganathan *et al.*, 2013).

Available household adsorption units can either be drum, double bucket or column filters. These are shown in Figure 2.10. In these systems the adsorbent is put into the drum, column or the first of the two buckets. Fluoride contaminated water is fed on top of the media. Fluoride gets adsorbed as the water flows through the media. Fluoride free water is then collected from the tap.

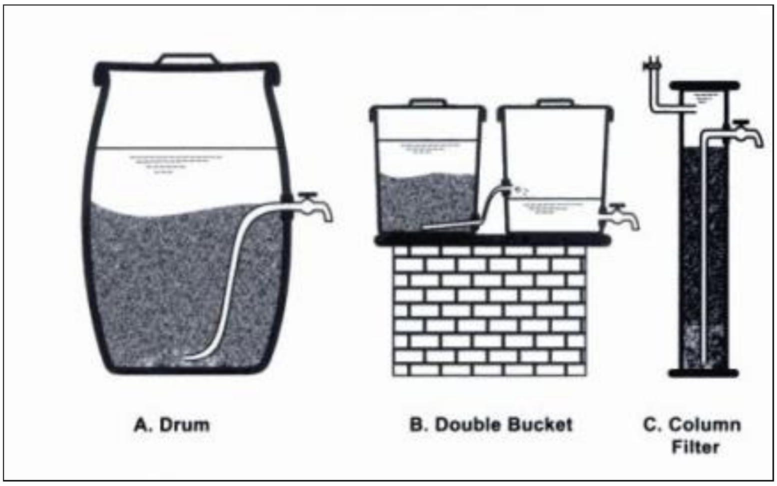


Figure 2.10: Three common domestic systems for fluoride removal by adsorption (Fawell *et al.*, 2006)

According to Loganathan *et al.* (2013), adsorption is an attractive method of fluoride removal compared to other available technologies. This is because of its simple design, effectiveness, less environmental problems, ease of operation, availability of low cost adsorbents that can remove fluoride around neutral water pH and there is also less replacement equipment required.

There are several low cost adsorbents that have previously been investigated for the ability to remove fluoride. These include activated alumina, impregnated alumina, rare earth oxides, activated clay, impregnated silica, zeolite, bone char coal etc. Bone char coal and activated alumina are both effective in fluoride removal and are preferred adsorbents because of their high selectivity for fluoride. These two adsorbents are presented further in the next sections.

a) Activated alumina

Activated alumina is a granular material used to adsorb contaminants such as fluoride, arsenic, selenium, silica and humic materials from water. It consists mainly of aluminium oxide (Al_2O_3) (Pontius, 1990). It is highly porous and has a normal surface area ranging from 200 to 300 m^2/g (Ayoob *et al.*, 2008). It is the most preferred adsorbent for fluoride removal. It is highly selective towards fluoride compared to other ions and very effective in removing fluoride (Ghorai and Pant, 2004). This is a well-established process of fluoride removal used worldwide (Pontius, 1990).

The mechanism of fluoride removal by activated alumina is adsorption by ligand exchange as well as chemisorption (Pontius, 1990). These are strong chemical attraction forces specific to fluoride (Loganathan *et al.*, 2013). It involves the exchange of hydroxide ion for fluoride ion which gets adsorbed by a covalent bond in the inner–sphere surface of the adsorbent. The process begins with hydration of the activated alumina surface and the following groups are formed (Ayoob *et al.*, 2008; Leyva-Ramos *et al.*, 2008): $\equiv AL\text{-}OH_2^+$, $\equiv AL\text{-}OH$, $\equiv AL\text{-}O^-$, where ≡ represents the surface of the activated alumina. The first and the last group exists when the middle group is protonated and deprotonated. This happens as follows:

$$\equiv AL\text{-}OH_{(s)} + H^+_{(aq)} \rightarrow \equiv AL\text{-}OH_2{}^+{}_{(s)} \qquad (2.5)$$

$$\equiv AL\text{-}OH_{(s)} \rightarrow \equiv AL\text{-}O^-_{(s)} + H^+_{(aq)} \qquad (2.6)$$

If the feed water has a pH greater than 7 and high fluoride concentration, the release of hydroxide ions from the adsorbent surface results in an increase in treated water pH. Under this condition, the exchange of hydroxide ion for fluoride ions on the surface of activated alumina can be presented as follows (Ayoob *et al.*, 2008):

$$\equiv Al\text{-}OH_{(s)} + F^-{}_{(aq)} \rightleftarrows \equiv Al\text{-}F_{(s)} + OH^-{}_{(aq)} \qquad (2.7)$$

The increase in treated water pH is less observed if the feed water pH is less than 6. The chemical reaction under these conditions is as follows: (Ayoob *et al.*, 2008).

$$\equiv Al\text{-}OH_2{}^+{}_{(S)} + F^-{}_{(aq)} \rightleftarrows \equiv Al\text{-}F_{(s)} + H_2O_{(aq)} \qquad (2.8)$$

When the activated alumina becomes exhausted, it can no longer remove fluoride. For the activated alumina to be used again it has to be regenerated. This is done by using an excess of strong base such as sodium hydroxide that is contacted with the activated alumina media. The hydroxide ions replaces the fluoride ions on the activated alumina surface as shown by the following reaction (Pontius, 1990):

$$\equiv Al\text{-}F_{(s)} + OH^-_{(aq)} \rightarrow \equiv Al\text{-}OH_{(s)} + F^-{}_{(aq)} \qquad (2.9)$$

The process of fluoride adsorption by activated alumina is highly sensitive to pH. The optimum pH range is 5 to 6. Outside this pH range there is more competition for adsorption sites from other ions. Only the presence of arsenic will affect fluoride removal by activated alumina at this optimum pH. Activated alumina has a higher affinity for arsenic over fluoride at pH 5 to 6. Arsenic is also difficult to regenerate. Again at the optimum pH range, trace heavy metals gets removed, but this is completely removed during regeneration (Pontius, 1990; Ayoob *et al.*, 2008; Leyva-Ramos *et al.*, 2008).

At pH 7, the presence of bicarbonates alkalinity slightly reduces fluoride removal efficiency. At pH 7 to 10, silica and hardness competes with fluoride for active sites. Hardness removal occurs at the beginning of the treatment but since activated alumina has great affinity for fluoride, hardness removal ceases as the treatment progresses. Below the pH of 4, fluoride removal reduces. This is caused by the formation of ionized hydrofluoric acid as well as positively charged alumina complexes (AlF^{2+}, AlF_2^+) which repel from the positively charged alumina (Pontius, 1990; Ayoob *et al.*, 2008; Leyva-Ramos *et al.*, 2008).

The use of activated alumina based household water treatment system has gained popularity in India. It is mainly implemented by two organisations, UNICEF and RGDWM (Rajiv Gandhi Drinking Water Mission) (Ayoob *et al.*, 2008). Apart from India, The Domestic Defluoridation Units has successfully been used in countries including China and Thailand (Ayoob *et al.*, 2008).

The advantages of activated alumina based on the fluoride removal system are as follows (Meenakshi and Maheshwari, 2006; Ayoob *et al.*, 2008):

- It is cost effective
- Easy to assemble
- Easy to use.
- Effective in fluoride removal (can remove up to 90 percent of fluoride).
- It is now a well understood process with a wide application.
- Activated alumina is very selective towards fluoride.

The limitations of this process are as follows (Meenakshi and Maheshwari, 2006; Shrivastava and Vani, 2009):

- The process is dependent on the water pH. It operates well in a pH range of 5 to 6.

- The performance is reduced at total suspended solids above 1500 mg/L because of fouling of the activated alumina bed.
- The process requires regeneration very often. The effectiveness of the adsorbent depreciates after each regeneration.
- Even though less waste is produced compared to other technologies, the waste regenerant is still an environmental issue.
- Adsorption by activated alumina has slow kinetics.

b) Bone char coal

Bone char coal is a porous granular material with an ability to remove fluoride from water. It is made from ground animal bone, carbonised at a temperature of 1100-1600°C. This is a charring process in which organic material such as oil, fat, meat remnants are removed from the bone. What remains is essentially tricalcium phosphate and carbon. The heating also improves the defluoridation capacity of the bone char. (Mjengera and Mkongo, 2003; Ayoob *et al.*, 2008).

According to Fawell *et al.* (2006) the main constituents of bone char are calcium phosphates (57-80 percent), calcium carbonate (6-10 percent) and activated carbon (7-10 percent). The fluoride removal is believed to be as a result of ion exchange of carbonate for fluoride ions on apatite [$Ca_9\,(PO_4)_6.CaCO_3$](Ayoob *et al.*, 2008). The chemical reaction involved can be presented as follows:

$$Ca_9\,(PO_4)_6.CaCO_{3\,(s)} + 2F^-_{\,(aq)} \rightleftarrows Ca_9\,(PO_4)_6.CaF_{2\,(s)} + CO_3^{2-}{}_{(aq)} \qquad (2.10)$$

Another reaction involves an exchange of the hydroxyl group on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ for fluoride as follows (Ayoob *et al.*, 2008):

$$Ca_{10}\,(PO_4)_6(OH)_{2(s)} + 2F^-_{(aq)} \rightarrow Ca_{10}\,(PO_4)_6.F_{2(s)} + 2OH^-_{(aq)} \qquad (2.11)$$

The removal of fluoride by bone char is pH dependent. It increases with a decrease in pH. At low pH the phosphate ions are easily dissociated and replaced by fluoride on the bone char surface. Exhausted bone char is regenerated using 1 percent caustic soda solution. This converts fluorapatite to hydroxyapatite. The regeneration is followed by a caustic rinse and then acid treatment for pH correction. The acid treatment must be done with caution because bone char can dissolve in an acid. The performance of the bone char is however reduced after regeneration (Ayoob *et al.*, 2008).

Mjengera and Mkongo (2003), report successful application of bone char coal for fluoride removal in Tanzania. The process has also been reported to be used in Thailand (Ayoob *et al.*, 2008). The use of the process in India is said to be restricted by religious beliefs (Ayoob *et al.*, 2008). The advantages of this process according to Mjengera and Mkongo (2003), includes production of treated water with very low fluoride levels (0.1 mg/L from a feed concentration of 12 mg/L).The process is also simple, have easy available material and there is a possibility of processing the bone char material locally.

The disadvantage of using bone char is that some religious groups may find the use of animal bone for water treatment unacceptable. Another problem is that if the bone char is not well prepared, the treatment of water with such bone char may cause bad odour and taste in the treated water which can result in a complete rejection of the process. The cost of the media can also be high depending on the methods used for manufacturing (Fawell *et al.*, 2006; Ayoob *et al.*, 2008).

2.6.2.4 Ion exchange resins

Ion exchange is a stoichiometric reaction process where an ion on a media surface is replaced by an equivalent number of moles of another ion to have an electro-neutral ion exchanger. The ion to be adsorbed must have a higher affinity for the adsorbent than the ion on the surface for the exchange to take place. This is a physical adsorption process controlled by electrostatic attraction (Loganathan *et al.*, 2013).

Fluoride can be removed by anion exchange resins. This involves the exchange of an anion on the resin surface for fluoride. Fluoride removal by anion exchange resins is however inefficient because of low selectivity towards fluoride. The selectivity order of anion exchange resins is as follows: citrate > SO_4^{2-} > Oxalate > I^-> NO^{3-} > CrO_4^{2-} > Br^- > SCN^-> Formate > acetate > F^-. This shows that sites on the resins surface can get occupied by other anions before fluoride is taken up (Luo and Inoue, 2004).

According to Luo and Inoue (2004) instead of using anion exchange resin which have poor selectivity for fluoride, cations exchange resins loaded with high valence metals such as iron (III), cerium (IV), Lanthanum (III) and Zirconium (IV) can be used. These multivalent metal ions have a high affinity for the small size and high electronegative fluoride.

An investigation by Kanesato *et al.* (1988) found that Lanthanide (La III) loaded resins are only effective at low pH (3 to 4) for fluoride removal. A research study by Suzuki *et al.* (1989) found that dried amberlite XAD-7 beads impregnated with zirconium can remove fluoride from drinking water. However zirconium leaches out when the resin is reused.

A study by Meenakshi and Viswanathan (2007) proved that chelating type resins are superior for fluoride removal compared to anion exchange resins. In the study chelating type resin (INDION FR-10 resin) was compared to an anion exchange resin (Ceralite IRA 400). The comparison was made on effect of pH as well as the presence of competing ions. The investigation found that chelating type resin (INDION FR-10 resin) was a better resin.

FR10 resin has been developed to selectively remove fluoride. FR-10 ion exchange resin is made of cross linked polystyrene with the sulfonic acid functional group on the surface. According to Meenakshi and Viswanathan (2007), the mechanism of fluoride removal by FR-10 resin is adsorption involving hydrogen bonds. It is because of the hydrogen bond that the highly electronegative fluoride is adsorbed first, followed by the other ions. Fluoride attraction to the resin can be represented as follows:

$$\mathrm{O{-}{-}SO_3H_{(s)} + F^-_{(aq)} \rightleftarrows O{-}{-}SO_3HF_{(s)}} \qquad (2.12)$$

O represents the resin material —SO_3H is the functional group responsible for the adsorption. Unlike activated alumina, fluoride removal by FR-10 resin is not influenced by pH and the presence of competing ions (Meenakshi and Viswanathan, 2007).

The advantages of fluoride removal by ion exchange resin are as follows (Meenakshi and Maheshwari, 2006; Loganathan *et al.*, 2013):

- The process is effective for fluoride removal especially at low concentration. It can achieve high removal (90-95 percent).
- The process does not change the colour and taste of the water.
- It is a widely used process.

- It is simple to assemble and to operate.
- The hydrated surface of this process results in fast kinetics which allows for smaller systems to be used.
- There is less waste produced.
- The granular form of the media allows for easy flow of water through the system.

The disadvantages of the system as highlighted by Meenakshi and Maheshwari (2006) are as follows:

- The efficiency of some ion exchange resins is reduced by the presence of competing ions such as sulfates, phosphates, carbonates and alkalinity.
- Ion exchange resins have to be regenerated. This produces waste which has to be dealt with appropriately to protect the environment.
- The high cost of resin makes the technology to be expensive.
- Some resins are not robust, they become ineffective when allowed to dry.

2.6.2.5 Contact precipitation

This process involves removal of fluoride from water by addition of calcium chloride and sodium dihydrogen phosphate (MSP) and precipitation of the fluoride in a form of calcium fluoride (CaF) and fluoroapatite $Ca_{10}(PO_4)_6F_{2(S)}$ (Ayoob *et al.*, 2008). The chemical reactions involved in the process are as follows:

1. Dissolution of calcium chloride

$$CaCl_{2(s)} + 2H_2O_{(aq)} \rightleftarrows Ca^{2+} + 2Cl^{-} + 2H_2O_{(aq)} \qquad (2.13)$$

2. Dissolution of MSP

$$NaH_2PO_{4(S)} + H_2O_{(aq)} \rightleftarrows PO_4^{3+} + Na^{+} + 2H^{+} + H_2O_{(aq)} \qquad (2.14)$$

3. Precipitation of calcium fluoride

$$Ca^{2+} + 2F^{-} \rightleftarrows CaF_{2(S)} \qquad (2.15)$$

4. Precipitation of fluoroapatite

$$10\,Ca^{2+} + 6PO_4^{-} + 2F^{-} \rightarrow Ca_{10}(PO_4)_6F_{2(S)} \qquad (2.16)$$

The process is limited by slow kinetics. Saturated bone charcoal is used as a catalyst to speed up the precipitation after chemical dosage. It is also used as a filtration media

(Dahi, 1996). The system is shown in Figure 2.11. It consists of raw water and chemical mixing bucket, contacting column and a treated water bucket. Fluoride contaminated water and chemicals are mixed in the mixing bucket. The water then gravitates to the contact column where the fluoride is precipitated and filtered.

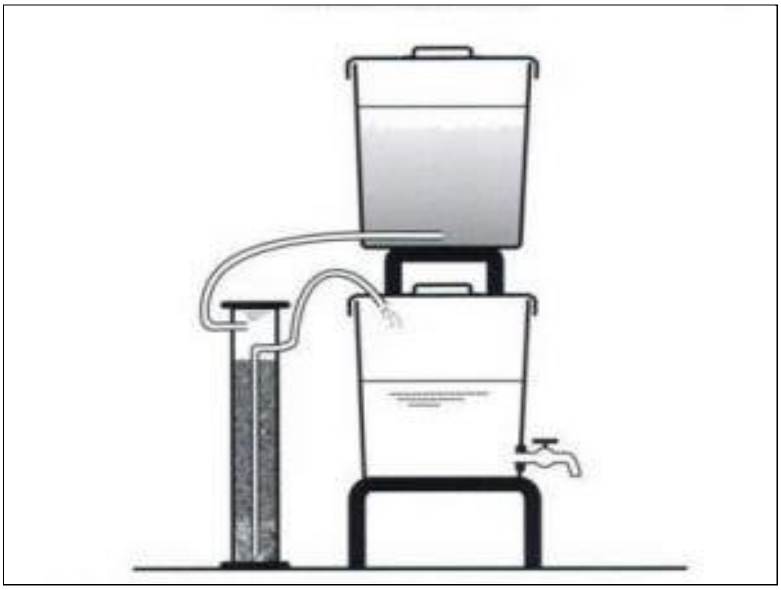


Figure 2.11: Contact precipitation system for household application (Fawell *et al.*, 2006)

The critical design parameter in this process is contact time within the bone char coal. A too short contact time results in poor precipitation. Long contact time on the other hand result in precipitation at the column entrance, resulting in filter column blockage (Fawell *et al.*, 2006). The optimum contact time is between 20 and 30 minutes (Ayoob *et al.*, 2008). This technology has been used in Tanzania as well as in Kenya (Ayoob *et al.*, 2008).

According to Dahi (1996) the system is capable of consistently producing water that have fluoride concentrations below 1 mg/L. The precipitation is thought to be occurring mainly in the pores of the contacting media. This minimizes the chances of filter blockage. After a year of operating the system in Ngurdoto, Northen Tanzania, the head loss through the column was almost unchanged (Dahi *et al.*, 1996). A cost comparison shows that the cost of operating this system is low compared to the Nalgonda process as well as the bone char coal process (Dahi, 1996). The main limitation of the process is the large dose of chemicals required.

2.6.2.6 Membranes

Fluorides can be removed from water using membranes such as nano-filtration, reverse osmosis, dialysis and electrodialysis (Mohapatraa *et al.*, 2009). Reverse osmosis membranes have the smallest pore size among the different types of membranes. It has the ability to remove even the smallest ions from water. The removal is based on the size of the contaminant as well as charge (Meenakshi and Maheshwari, 2006). It has proven to be capable of removing fluoride from water.

Even though reverse osmosis is successfully applied in many developing countries for fluoride removal, there is limited data on the use of the process (Ayoob *et al.*, 2008). A laboratory study by Arora *et al.* (2004) found that reverse osmosis is capable of achieving 95 percent fluoride removal. The study found that the performance is affected by pH, feed water concentration, pressure and flow rate.

The advantages of using reverse osmosis membranes include excellent fluoride removal; it also removes other impurities such as suspended solids, organic and inorganic pollutants as well as pathogens in one step. Pre-treatment may only be required if there are large particulate impurities in the water. There are no chemicals required, minimal waste generation, minimal maintenance, can work on a wide pH range and there is no interference from other ions (Meenakshi and Maheshwari, 2006; Loganathan *et al.*, 2013).

The major disadvantage of using reverse osmosis membranes for fluoride removal is the high capital and operational costs involved. Other disadvantages include no ion selectivity (even the beneficial nutrients are removed together with fluoride), disposal problem of fluoride concentrate residue, some membranes are sensitive to pH, large portion of the water is wasted, and the membrane is prone to scaling, fouling and clogging (Meenakshi and Maheshwari, 2006; Loganathan *et al.*, 2013).

Nano-filtration membranes have pore sizes slightly larger than those of reverse osmosis. The larger pore sizes results in less resistance to passage of the solute and solvent through the membrane. Lower pressure is also required to drive water through this membrane thus nano-filtration membranes are referred to as low pressure reverse osmosis membranes (Ayoob *et al.*, 2008; Mohapatraa *et al.*, 2009).

The contaminants removal on nano-filtration membranes is by size exclusion as well as repulsion. During filtration some anions gets adsorbed on the surface of the membrane. There is then a repulsion effect between the anions on the membrane surface and those on the bulk solution. This increases the ion retention similar to RO membranes but at higher fluxes (Ayoob *et al.*, 2008).

Nano-filtration is fairly new among the available membrane types. It is however gaining popularity as being suitable especially for divalent ion removal (Tahaikta *et al.*, 2008; Nasr *et al.*, 2013). Research work conducted has proven the ability of nano-filtration membranes for fluoride removal. A pilot plant study by Lhassani *et al.* (2001) showed the capability of nano-filtration membranes for fluoride removal. The study revealed that the mechanism of ion removal is by conduction as well as diffusion. Diffusion dominates at low operating pressure while conduction dominates at high operation pressure.

Nasr *et al.* (2013) states that nano-filtration membranes can achieve fluoride removal as high as 88 percent. The main advantage of nano-filtration membranes is that it operates at a lower pressure than the reverse osmosis membrane. It therefore has lower operational costs. Unlike reverse osmosis, nano-filtration membranes offer selective demineralisation and there is no need for remineralisation (Lhassani *et al.*, 2001).

The disadvantages of nano-filtration membranes are that it is more sensitive to pH compared to RO membrane because of the membrane material used (Ayoob *et al.*, 2008). The rest of the disadvantages specified for RO membranes still apply to nano-filtration membranes. The only difference is that less operational costs are incurred because of lower operational pressure with the nano-filtration membrane.

Electrodialysis consists of an anode and cathode placed on opposite sides. A number of cation and anion exchange membranes are placed alternately and parallel to each other in between the cathode and anode. When water with ions is passed across the membranes an electric potential difference is created, an anion gets attracted to the anode, passing through the anion exchange membrane but gets rejected by the following cation exchange membrane.

Cations on the other hand pass through the cation exchange membrane but get rejected by the following anion exchange membrane. This results in one water passage between the membranes having a high collection of ions and the next passage having less ions (Ayoob *et al.*, 2008). A schematic presentation of an electrodialysis membrane system is shown in Figure 2.12.

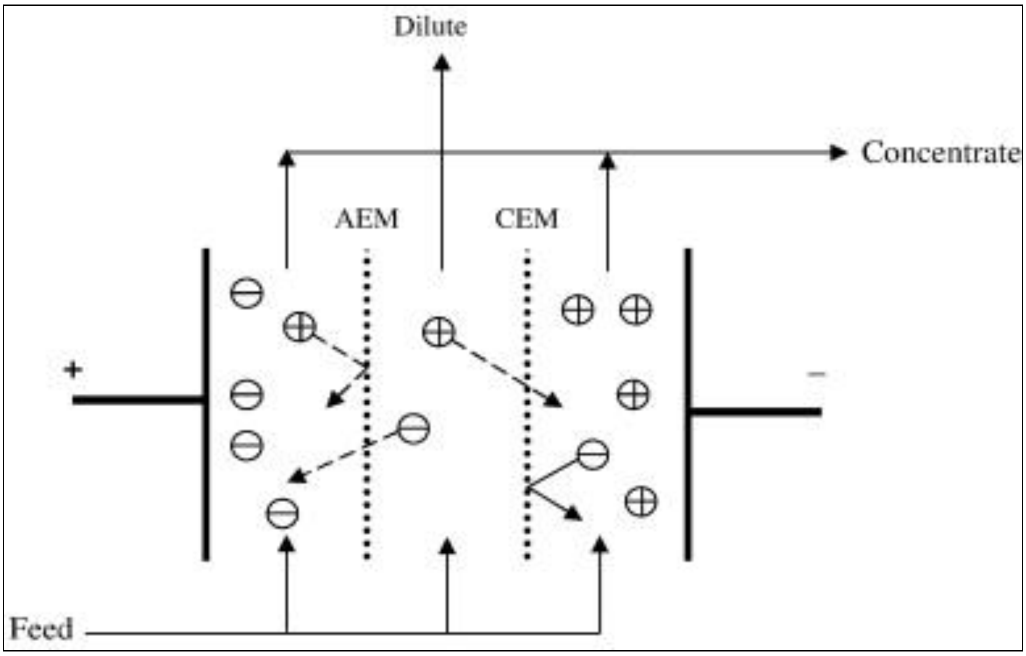


Figure 2.12: Schematic presentation of electrodialysis membrane system (Sadrzadeh and Mohammadi, 2009)

Adhikary *et al.* (1989), in a research on a lab scale system stipulates that the electrodialysis membrane system is capable of removing fluoride from brackish water from levels as high as 15 mg/L to levels less than 1.5 mg/L. A similar study by Amor *et al.* (1998) found that potable water can be produced by treating fluoride contaminated brackish water with electrodialysis membranes. Desalination and defluoridation rates were found to be increasing with temperature, voltage and flow rate.

The advantages offered by electrodialysis membranes include excellent fluoride removal, no chemicals required for treatment and minimal waste generation. The disadvantages include high capital and operational costs, no ion selectivity (even the beneficial nutrients get removed), skilled labour is required to operate the system and there is a problem with polarization on the membrane surface (Loganathan *et al.*, 2013).

Table 2.2 compares the available fluoride removal technologies. It can be seen that adsorption meets all the criteria set for a system that has a potential of being successful in rural areas. Ion exchange resins also have a potential in rural areas. Like adsorption it can easily be made into small water treatment systems and it is easy to use.

Table 2.2: Summary of comparison of available treatment methods for fluoride removal

Criteria	Lime softening, precipitation and coagulation (LSPC)	Adsorption	Contact precipitation (CP)	Ion exchange resins (IER)	Membranes	Acceptable technology
Production of enough quantity of water for a household	With this process any volume can be produced. Only the dose is increased for a high volume of treated water.	Enough quantity of water is produced.	Enough quantity of water is produced.	Enough quantity of water is produced.	Production of high volume of treated water with RO membranes require pumping of the water. This cannot be done in most rural households.	All
Improvement in the quality of treated water	Process cannot produce final water that meets standards	Adsorbents such as activated alumina can produce final water that meets standards	Treated water meets drinking water standards	Treated water meets drinking water standards	Treated water meets drinking water standards	Adsorption, CP,IER and Membranes
Ease of maintenance and operation	Easy to maintain	Easy to maintain	Easy to maintain	Systems are easy to maintain	Requires skilled people to maintain.	LSPC, Adsorption, CP and IER
Affordability	The chemicals may be costly to people in rural areas	Adsorbents for fluoride removal are generally affordable	The chemicals used might not be affordable to people in rural areas	Resins can be expensive and not affordable to people in rural areas	Membranes for fluoride removal have high capital and operational cost	adsorption
Use of local material for construction and maintenance	All the material can be obtained locally	All the material of construction is locally available	Local material is used	The media may need to be imported	The membrane material has to be imported	LSPC, Adsorption and CP
Chemical use and power requirement	Process uses chemicals but requires no power	No Chemicals used for treatment except for regeneration	Chemicals are used requiring skilled labour	No chemicals used for treatment except for regeneration	Chemicals are not required for treatment but only required for cleaning	Adsorption IER
Robustness	It is robust	Very robust	robust	Some resins must not be allowed to dry	Commercial membranes are not robust enough for the harsh conditions in rural areas.	LSPC, Adsorption and CP

Based on the above table, adsorption and ion exchange resins were selected for further assessment. The discussion in the next section is applicable for both adsorption and ion exchange.

2.6.3 Adsorption equilibria

Presented here is available literature on adsorption equilibria. It shows how adsorbent selection is done based on adsorption capacity.

2.6.3.1 Adsorption capacity

Adsorption processes undergo different stages. This includes transport of fluoride from the bulk fluid to the adsorbent surface, transfer of the fluoride from the surface to the pores and the adsorption of fluoride in the pore surface of the adsorbent. Proper design of an adsorber requires that all experimental data is available and the rate controlling step is known. Common practice is to size adsorbers using adsorption capacity obtained from equilibrium studies (Goswami and Purkait, 2012).

Adsorption capacity or solid phase solute concentration is the amount of solute adsorbed per unit weight of adsorbent. It can be used to give a rough estimation of the amount of adsorbent required for a given application through the following expression (Ayoob and Gupta, 2008):

$$M = \frac{(C_o - C_e)V}{q_e} \tag{2.17}$$

Where M is the mass of adsorbent that is required for the adsorption in grams, C_o is feed solute concentration in mg/l, C_e is the desired treated water solute concentration in mg/l, V is treated water volume in L and q_e is the equilibrium adsorption capacity in mg/g. According to Kratochvil and Volesky (1998) it is not possible to select the best adsorbent for a given application unless the desired equilibrium concentration is specified.

The best adsorbent is selected by comparing equilibrium capacities. The equilibrium adsorption capacity generally increases with an increase in equilibrium concentration (Ayoob and Gupta, 2008). Therefore the equilibrium capacity of adsorbents has to be compared on the same equilibrium concentration.

Adsorption capacity is determined through obtaining equilibrium data and developing adsorption isotherms. There are available adsorption isotherm models that are then fitted onto the experimentally determined adsorption isotherm to get the best fit model. The adsorption isotherm model that best fits the experimental data is then used to predict the amount of adsorbent required to achieve a given equilibrium concentration (Slejko, 1985).

2.6.3.2 Adsorption isotherms

Adsorption isotherm is an equilibrium relationship between the solid phase concentration or equilibrium capacity (q_e) and liquid phase concentration (C_e) (Kratochvil and Volesky, 1998). It is called the adsorption isotherm if the adsorption is conducted at constant temperature (Slejko, 1985). Apart from being used to determine adsorption capacity, adsorption isotherms can also be used for the following:

- To establish if adsorption is favourable or unfavourable (Alagumuthu *et al.*, 2010).
- To determine the nature of effluent concentration breakthrough to be expected in a column viz if the breakthrough will be sharp or gradual. A sharp breakthrough is desired as it results in efficient adsorbent usage.
- To determine if continuous or batch mode of operation is suitable for the adsorption (Slejko, 1985).
- To establish if the desired concentration of contaminant in the treated water can be achieved (Slejko, 1985).

Figure 2.13 is a schematic presentation of favourable and unfavourable adsorption isotherms. A favourable isotherm means that the solute being removed prefers being attached on the surface of adsorbent rather than being in the liquid while unfavourable isotherm means the solute prefers the liquid than the adsorbent. Favourable adsorption results in desirable sharper breakthrough in an adsorption column provided the rate of adsorption is high (Slejko, 1985) .

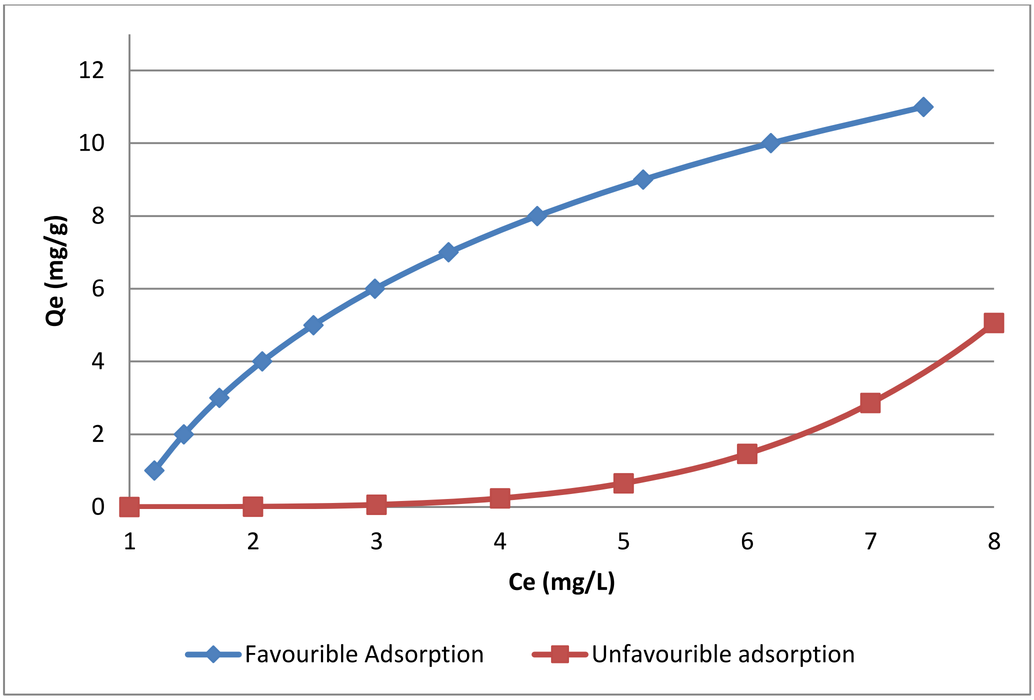


Figure 2.13: Schematic presentation of favourable and unfavourable isotherms adapted from (Slejko, 1985)

A breakthrough is a period in an adsorption column operation where the exit concentration is increasing from low to maximum concentration where the column can no longer remove the contaminant (exhaustion point). A sharp breakthrough means that it will take a very short period of time for the column exit concentration to jump from very low to very high. This ensures efficient usage of the adsorbent. With unfavourable adsorption, the breakthrough is gradual. This results in a column reaching the point of exhaustion while there is still a lot of unused adsorbent inside. This becomes an inefficient usage of adsorption media. A detailed discussion on this is in section 2.6.4.1.

There are also cases where adsorption is less sensitive to equilibrium concentration. This mean that the equilibrium capacity remains high as the concentration is varied from low to high. In such a system an even sharper column breakthrough is achieved. A less efficient batch mode of operation can be used for contaminant removal in such a case (Slejko, 1985).

Column adsorption is generally more efficient compared to batch operation. This is because in a batch mode of operation, once the equilibrium is reached there is no more reduction in the liquid phase solute concentration. If the equilibrium concentration does not meet the required drinking water standards, it means it will never reach it under the same conditions. This is because at equilibrium the rate of adsorption is equal to the rate of desorption.

In column adsorption on the other hand, as the fluid flows down the column it is contacted with fresh media such that the solute concentration is progressively decreased. There is a good chance of the desired effluent concentration being achieved (Slejko, 1985).

In a case where adsorption isotherms show that adsorption is more sensitive to equilibrium concentration, meaning that the equilibrium capacity increases gradually with an increase in equilibrium concentration, the column breakthrough will also be gradual and the adsorbent usage will be less efficient. Batch mode of operation is not suitable for such an isotherm since at low concentration the rate of adsorption is also low. Longer contact time is then required for adsorption to occur (Slejko, 1985). Column mode of operation is more suitable for such an isotherm.

There are a number of existing models that can be used to represent the experimentally determined adsorption isotherms. Most of these models have empirical origin because they are not derived from thermodynamic or molecular principles (Ayoob and Gupta, 2008; Goswami and Purkait, 2012). This means that they can be applied in one set of conditions but fail in another. The commonly used models in water treatment are Langmuir and Freundlich isotherms (Ghorai and Pant, 2005). These will be discussed in the next section. A schematic presentation of Langmuir and Freundlich models is shown in Figure 2.14.

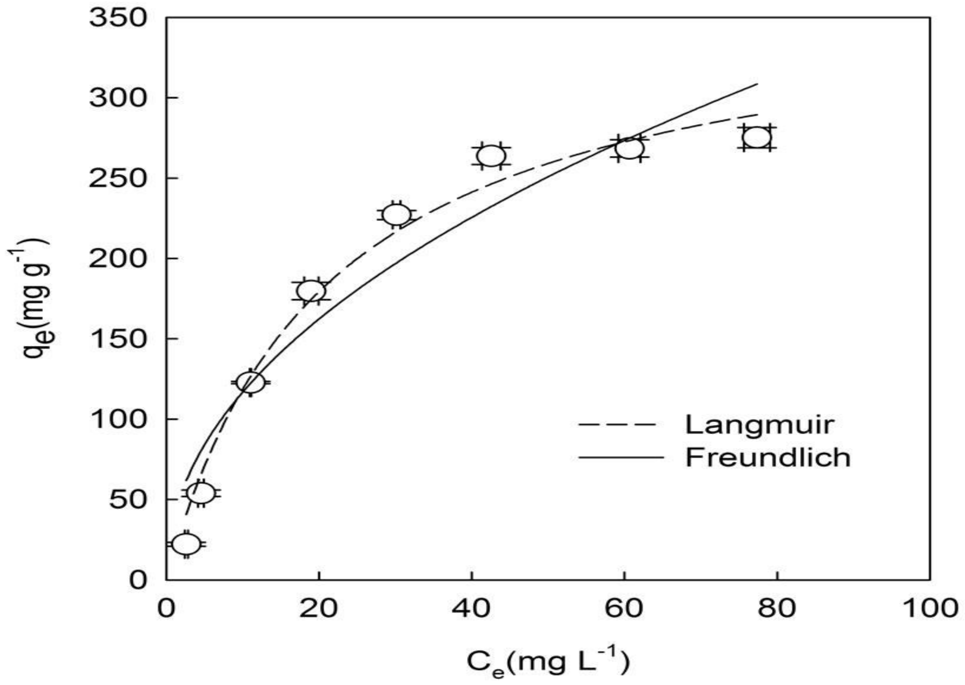


Figure 2.14: Schematic presentation of Langmuir and Freundlich isotherm models (Ren *et al.*, 2011)

a) Langmuir isotherm

The Langmuir isotherm is applicable in cases where uniform surfaces having equivalent adsorption sites are assumed. Each site is assumed to be having equal sorption activated energy. There is monolayer coverage on the surface of the adsorbent and there is no transmigration of adsorbates on the adsorption sites. It is originally derived for solid-gas interface. It can be equally applied in a solid-liquid interface (Slejko, 1985; Ayoob and Gupta, 2008). The model is presented as follows:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{2.18}$$

Where $q_{\max}$ is the maximum adsorption capacity for the adsorbent obtained at high liquid phase concentration in mg/g. b is the equilibrium constant expressed as a ratio of adsorption to desorption rate constant in L/mg. It is directly related to binding energy. At low concentration, the Langmuir model reduces to the following linear equation (Ayoob and Gupta, 2008):

$$q_e = q_{\max} b C_e \tag{2.19}$$

The term bCe becomes too small that it can be neglected. At high concentration the adsorption show no dependency on concentration. The term bC_e becomes too large that the equation reduces to (Ayoob and Gupta, 2008):

$$q_e = q_{\max} \tag{2.20}$$

To evaluate the applicability of the Langmuir isotherm to experimental data the Langmuir constants b and $q_{\max}$ have to be determined. This is done through the use of the linear form of the Langmuir isotherm expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \tag{2.21}$$

The term C_e/q_e is plotted against (C_e). If the resulting graph is a straight line, then it means the adsorption experimental data can be represented by the Langmuir model. From the linear Langmuir equation, the term ($1/q_{\max}$) is the slop. It is used to determine constant $q_{\max}$. The term ($1/bq_{\max}$) is the y intercept. It is used to determine b (Malay and Salim, 2011). The terms in the Langmuir isotherm can also be used to determine if the adsorption is favourable or unfavourable. This is determined using the following equation (Alagumuthu *et al.*, 2010; Malay and Salim, 2011):

$$R_L = \frac{1}{1 + bC_o} \tag{2.22}$$

Where R_L is a dimensionless separation factor, b is Langmuir constant (L/mg) and C_o is the initial fluoride concentration (mg/L). If R_L > 1, adsorption is unfavourable. If R_L = 1, the relationship between equilibrium capacity and equilibrium concentration is linear. If 0<R_L<1 then the isotherm is favourable. If R_L = 0 the adsorption is irreversible (Malay and Salim, 2011).

b) Freundlich isotherm

The Freundlich isotherm is an empirical model indicating surface heterogeneity of an adsorbent. Here the binding energy term represented by a constant b in the Langmuir isotherm varies as adsorption progresses. This is caused by varying heat of adsorption. Unlike the Langmuir isotherm, the Freundlich isotherm does not reduce to a linear form at low concentration. It also does not level off at high equilibrium concentrations (Ayoob and Gupta, 2008). The Freundlich isotherm can be expressed as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{2.23}$$

Where K_f is the adsorption capacity in mg/g, and n is dimensionless adsorption intensity. The linear form of the Freundlich isotherm is shown as follows:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{2.24}$$

If the term $\ln q_e$ is plotted against $\ln C_e$, and the resulting graph is a straight line, this would indicate that the experimental result can be represented by the Freundlich isotherm. $\ln K_f$ in the equation is the Y intercept. It is used to determine the adsorption capacity. $1/n$ is the slope of the equation. It is used to determine the adsorption intensity (Malay and Salim, 2011).

2.6.3.3 Selection of the best fit model

a) Linear and non-linear regression

Normally the model that best fits the isotherm experimental data is easily determined through the linear regression coefficient (R^2). An adsorption isotherm with linear regression coefficient close to one is selected as the best fit isotherm. However according to Ayoob and Gupta (2008), errors associated with development of the linear models affect the results of the linear regression process. The chi-squared analysis can be used as an alternative to the linear regression coefficient for determination of the best fit model. The chi-squared equation is given as follows:

$$X^2 = \sum \frac{\left(q_{e,\exp} - q_{e,cal}\right)^2}{q_{e,cal}} \tag{2.25}$$

Where $q_{e,\exp}$ is the experimental equilibrium capacity and $q_{e,cal}$ is the calculated equilibrium capacity. If the difference between the calculated and experimental equilibrium capacity is large, the X^2 value will be high (Chabani *et al.*, 2009). The best model is therefore the one that has the lowest X^2 value.

2.6.4 Column adsorption

An adsorption column generally consists of a cylindrical vessel packed with the adsorption media. The water can either be fed from the top flowing downwards or from the bottom flowing upwards. The downward flow mode can be used if the feed has high solids. In this case the column will be used for both filtration as well as adsorption. The problem of using the column for filtration is that it results in early blockage. Pre-treatment of the feed prior to feeding the column is a better option. A bottom up mode of operation is more suitable if the feed has low solid content. This mode of operation minimises pressure drop, channelling and adsorbent fouling. (Slejko, 1985).

2.6.4.1 Establishment of mass transfer zone and breakthrough curve

When water contaminated with impurity enters an adsorption column, adsorption begins at the entrance. The concentration of the exiting water will be low provided there is enough adsorbent in the column. As the process continues, the adsorbent at the entrance will get exhausted. An adsorption front normally referred to as the mass transfer zone will form.

The mass transfer zone is located between the section of the media that is saturated with impurity being removed and the section that has fresh media (Kratochvil and Volesky, 1998). Adsorption takes place in this zone. The liquid concentration varies in this zone. It is equal to feed contaminant concentration at the interface with exhausted media and reduces to minimum at the interface with fresh media.

A breakthrough curve is a history of column exit contaminant concentration. A breakthrough point is the limit at which the effluent contaminant concentration must not be exceeded (1.5 ppm for fluoride according to WHO guidelines). The relationship between the mass transfer zone and breakthrough curve can be explained through Figure 2.15. The first column (C_1) shows mass transfer zone that has just developed.

No contaminant concentration is detected on the column exit as shown by the graph of concentration against time of operation.

In column (C2), the mass transfer zone is moving down the column leaving saturated adsorbent behind. There is still no contaminant detected on the column exit. In column (C3) the mass transfer zone has just started moving out of the column. The exit concentration has reached the breakthrough point. In column (C4) the mass transfer zone is exiting the column. In column (C5) the media is saturated and can no longer remove contaminant from water (Kratochvil and Volesky, 1998).

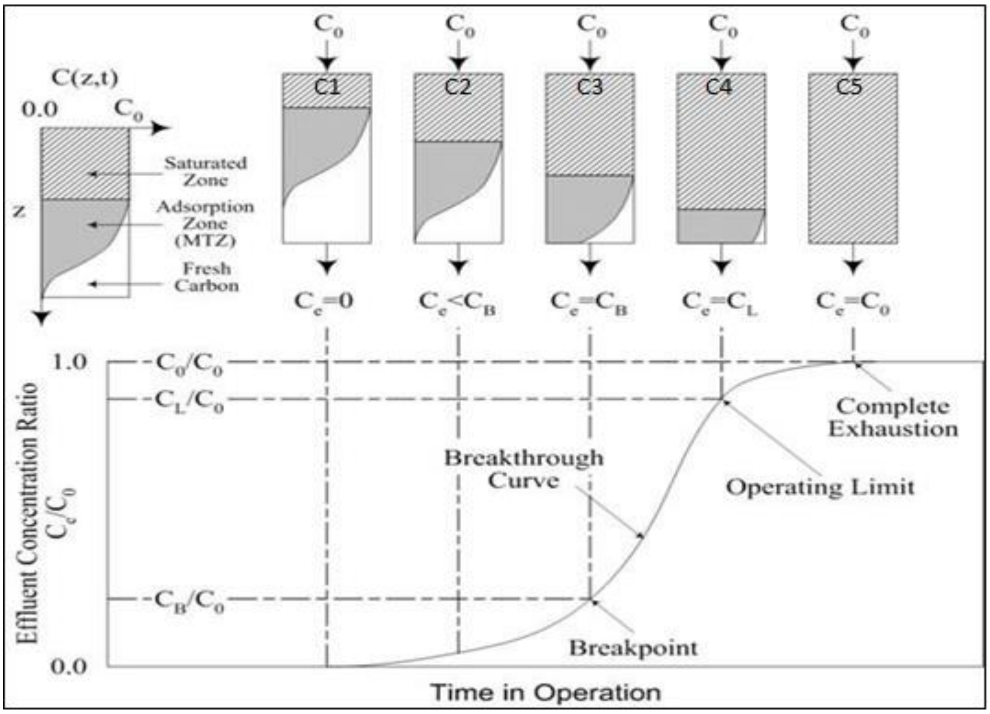


Figure 2.15: Movement of mass transfer zone through an adsorption column adapted from (Slejko, 1985)

The shape of a breakthrough curve gives an indication of the length of a mass transfer zone. The breakthrough can be gradual or sharp. A sharp breakthrough means that the column effluent concentration increases from very low to a maximum in a short period of time or within a small volume of effluent water. A short and sharp breakthrough is desired since it results in efficient usage of the adsorbent (Kratochvil and Volesky, 1998). The shape of the breakthrough curve and the length of mass transfer zone depends on the rate of adsorption, contact time as well as adsorption isotherms (Slejko, 1985).

Apart from observing the shape of the breakthrough curve, the performance of a column can be assessed using the bed volume of treated water at breakthrough as well as adsorbent usage rate (Reed *et al.*, 1996). The bed volume is the volume of water treated at breakthrough per volume of adsorbent used (Ghomshe *et al.*, 2011). Adsorbent usage rate is expressed as the mass of adsorbent used per the total volume of water treated at breakthrough (Reed *et al.*, 1996). The adsorbent usage rate should be low indicating that a small amount of adsorbent is required to provide a large volume of water

2.6.4.2 Effect of contact time on breakthrough curve

If there is infinite contact time in an adsorption column, at first there will be low contaminant concentration in the effluent. When the column reaches the point of exhaustion, the effluent water concentration will jump from minimum to maximum at once. In this case the size of the mass transfer zone is insignificant. Under normal circumstances the contact time is lower and there is a longer mass transfer zone. The breakthrough in such a situation is gradual.

If the contact time is too low which may result from high volumetric flow rate, the mass transfer zone will be longer and the breakthrough becomes more elongated such that the column leaks contaminant very early and the breakthrough is reached while there is a lot of unused material in the column (Slejko, 1985).The contact time in an adsorption column is generally called empty bed contact time (EBCT) (Slejko, 1985) . It is calculated as follows:

$$EBCT = \frac{V}{Q} \qquad (2.26)$$

Where V is the volume of media in the adsorption column in (l) and Q is the fluid volumetric flow rate through the column in (l/hr). True contact time is obviously lower because some of the volume in the column is occupied by the media. The fluid only flows in the void spaces between the media. From the above equation it can be observed that the contact time can be increased by either increasing the volume of the bed or reducing the feed volumetric flow rate.

There is limited information regarding the effect of contact time on fluoride adsorption in a column. Conducted studies have not been specific to fluoride but other impurities removal from water. Findings from these studies have been considered here to observe outcomes that might be expected in the current study. In a study by Reed *et al.* (1996), the effect of contact time on lead removal by granular activated carbon was investigated. The study found that increasing contact time from 1.85 to 5.55 minutes, boosted the column performance such that the volume of treated water at breakthrough increased by 63 percent.

A further increase in contact time from 5.55 to 12.75 minutes resulted in 11 percent increase in the volume of treated water at breakthrough. Increasing contact time gives more time for adsorption to occur hence there is better performance. The less improvement with a further increase in contact time is caused by reduced adsorption rate as the adsorption approaches equilibrium.

2.6.4.3 Effect of velocity on breakthrough curve

An exception in the detrimental effect of column performance as a result of high flow rate is when the high flow rate causes shear on the liquid film around the adsorption particles. This increases the rate of adsorption and compensates for the performance loss resulting from reduced contact time.

The rate of adsorption is governed by film diffusion, pore diffusion and surface adsorption. Resistance in any of the above processes results in low adsorption rates. Film transport depends on the size of fluid film on the surface of an adsorbent. If there is high resistance due to thick film, the creation of fluid turbulence can reduce the resistance (Reed *et al.*, 1996).

Turbulence can be created by mixing in batch adsorption and by increasing fluid velocity in column adsorption. The effect of velocity on fluid film in an adsorption column can be observed though the magnitude of mass transfer coefficient. If mass transfer coefficient is high, it means the rate of adsorption will also be high. The mass transfer coefficient can be expressed as follows:

$$K_F = \frac{Dl}{\delta} \tag{2.27}$$

Where K_F is the mass transfer coefficient, Dl is the liquid diffusivity and δ is the liquid film thickness. From the above expression, it can be seen that reducing the fluid film thickness increases the mass transfer coefficient. The fluid film mass transfer coefficient is related to fluid velocity by the following equations (Slejko, 1985):

$$\frac{K_F}{u} Sc^{0.58} = 2.4\,\mathrm{Re}^{-0.66} \text{ (for } 0.88 < \mathrm{Re} < 125\text{)} \qquad (2.28)$$

$$\frac{K_F}{u} Sc^{0.58} = 0.442\,\mathrm{Re}^{-0.31} \text{ (for } 125 < \mathrm{Re} < 5000\text{)} \qquad (2.29)$$

$$Sc = \frac{\mu}{\rho Di} \qquad (2.30)$$

$$\mathrm{Re} = \frac{\rho a_p u}{\varepsilon \mu} \qquad (2.31)$$

Where μ is the fluid viscosity in Pa.s, ρ is the fluid density in kg/m^3, u is the fluid velocity in m/s, a_p is the adsorbent particle radius in m, ε is the void fraction, Sc and Re are dimensionless Schmidt and Reynolds numbers respectively. From the above expressions it can be observed that by increasing the fluid velocity, the fluid film mass transfer coefficient also increases. The column velocity can be increased by increasing the volumetric flow rate as shown in the following equation:

$$u = \frac{Q}{A_c} \qquad (2.32)$$

Where u is the fluid velocity in m/s, Q is the fluid volumetric flow rate in m^3/s and A_c is the column cross sectional area in m^2. Some studies have been done regarding the effect of velocity on contaminant removal by adsorption. Some studies though have not been specific to fluoride removal. They have however been evaluated here to observe the expected trends in the current study.

In a study by Reed *et al.* (1996), the effect of fluid velocity (hydraulic loading rate) on lead removal by activated carbon was investigated. The study found that the increase of hydraulic loading rate from 4.8 m/hr to 8.9 m/hr enhanced lead removal. This was attributed to the decrease in mass transfer resistance on adsorbent surface at high hydraulic loading rate which increase the rate of adsorption. This trend was observed when the lead concentration was high.

However a similar trend was not observed at low feed concentration. At low lead concentration, increasing the hydraulic loading rate did not increase the rate of lead removal. No reason was given for this observation. According to Slejko (1985) there is low adsorption rate at low concentration. This might be the reason why the effect of velocity at low feed concentration was not observed.

Findings that seems to contradict those of Reed *et al.* (1996) were found by Lorenzen *et al.* (2009). In his study, he found that an increase in fluid velocity from 60 m/hr to 270 m/hr results in poor fluoride removal by activated alumina. This study however used very high velocities. The poor performance with an increase in velocity was attributed to an increase in dispersion resistance. Dispersion resistance increases with an increase in fluid velocity due to increased turbulence (Lorenzen *et al.*, 2009). It therefore seems that at lower velocities an increase in velocity enhances column adsorption performance due to a reduction in fluid film resistance. It also seems like there is a maximum velocity limit beyond which an increase in velocity results in poor column performance due to increased resistance.

2.6.4.4 Column pressure drop

The size of adsorption particles has a significant effect on the performance of an adsorption column. It affects the adsorption rate as well as pressure drop. High adsorption rate is achieved with smaller particle sizes at the expense of high pressure drop. A compromise has to be reached between high adsorption rates and workable pressure drop. Particle geometry determines the initial pressure drop in a column as water is passed through. As the column operation continues, the trapped particles increase the pressure drop. Particle geometry includes size distribution, mean particle diameter, coefficient of uniformity as well as effective size (Slejko, 1985).

Size distribution refers to the size of particle that will pass through or be returned by a screen of a certain size. Mean particle size is the average size determined through sieve analysis. Effective particle size is the largest diameter of the particles in millimetres where below it, is 10 percent of the sample by weight (Slejko, 1985).

Apart from particle geometry, pressure drop is also affected by the velocity of fluid through the column as well as the height of the adsorbent bed in the column. High velocities as well as tall adsorption beds result in high pressure drop. For a clean fluid, pressure drop is represented by the Ergun equation shown as follows (Ergun, 1952):

$$\frac{\Delta P}{L} = A\frac{\mu(1-\varepsilon)^2}{d_p{}^2\varepsilon^3}u^2 + B\frac{\rho(1-\varepsilon)}{d_p\varepsilon^3}u^2 \qquad (2.33)$$

Where ΔP is pressure drop across the packed bed in pascals, L is the bed height in m, ε is the void fraction, μ is fluid viscosity in Pa.s, u is the fluid velocity through the bed in m/hr and d_p is the particle diameter in m. Ergun developed his equation after some work by Black-Kozeny who investigated pressure drop in the laminar flow and Burke-Plummer who investigated pressure drop in the turbulent flow.

Ergun combined the Black-Kozeny and the Burke-Plummer equations into one equation that is applicable to both laminar and turbulent flow (Mayerhofer *et al.*, 2011).The constants A and B are shape factors called Blake-Kozeny-Carman constant and Burke-Plummer constant. They are sometimes called viscous and inertial constants respectively. These constants were originally found through experimentation to be A=150 and B=1.75.

The Ergun equation was developed on a basis of 640 experiments with crushed-coke, spheres of various sizes and sand particles (Ergun, 1952). The investigation was conducted with a gas passed through a fixed column. The constants 150 and 1.75 were obtained through those experiments. Often, the media used in fixed beds is not spherical.

Previous researchers have found that the Ergun equation cannot accurately predict pressure drop in such cases. Nemec *et al.* (2005), found that with non-spherical media, a higher pressure drop is obtained than predicted using the Ergun equation. This was said to be resulting from high tortuosity with non-spherical media. According to Nemec *et al.* (2005) inaccuracies in measurement of specific surface and porosity can have a significant effect on the values of the Ergun constants.

The issue of Ergun constants has been a subject since 1952 (Nemec *et al.*, 2005). Most of the work on the subject was done by Macdonald *et al.* (1979) who proposed that the viscous and inertial constants should be 180 and 1.8 for particles of arbitrary shapes. The study then suggested that for non-spherical particles the values should be 15 percent or more higher than 180 and 1.8 respectively (Nemec *et al.*, 2005). Apart from particle shape, pressure drop is also affected by particle roughness (Macdonald *et al.*, 1979; Crawford and Plumb, 1986). It was proposed by Macdonald *et al.* (1979) that for rough particles, the inertial constant must be increased from 1.8 to 4.

This study focuses on determining if the original Ergun equation can be applied in predicting pressure drop in adsorption columns using activated alumina as well as FR-10 resin.

Chapter 3. Experimental methodology

This chapter presents the methods used in conducting experiments. Section 3.1 describes the raw water used for the investigation. Section 3.2 presents the material used. Section 3.3 describes the adsorbents used. In section 3.4 is the equipment. Finally, section 3.5 is the experimental methodology.

3.1 Raw water used for the investigations

Raw water used for all investigations was obtained from Process Evaluation Facility, Wiggins Water Treatment Works (Umgeni Water). The original source of the water was from Inanda dam. The quality of the raw water is shown in Table 3.1.

Table 3.1: Quality of water used in the investigation

Determinand	**Values**
pH	7 to 8
Turbidity (NTU)	<5
Silica (mg/l)	<1
Bicarbonate alkalinity (mg/l)	<70
Sulphate (mg/l)	<20
Manganese (mg/l)	<0.01
Fluoride (mg/l)	<1

The characteristics of the raw water were not adjusted for the investigations conducted in membrane treatment. It was however spiked with sodium fluoride for the investigation conducted for adsorption. This was done because of unavailability of a fluoride contaminated water source close to Durban where the research was conducted. This was also done to ensure that the desired feed concentration was used.

The fluoridated feed was prepared by first preparing a stock solution. A 2000 ppm fluoride stock solution was first prepared by adding 41.9 g of sodium fluoride into 5 L of water. The water was stirred to dissolve the sodium fluoride. Investigations for the determination of the effect of contact time on fluoride removal as well as the effect of velocity on fluoride removal was conducted using 4 ppm feed solution.

Low feed concentration was used for experimental set up because higher concentration results in treated water not meeting drinking water standards at all when the flow rate was high especially if the amount of adsorbent used is small. The feed was prepared by diluting 160 ml of 2000 ppm stock solution into 80 litres of water. This was prepared in a 100 litre tank. A sample calculation used in preparation of the feed is shown in appendix B.

3.2 Sorbents

The media selected for experimentation is activated alumina and FR-10 resin. Activated alumina is a well-established media and highly selective towards fluoride. FR-10 resin is also highly selective towards fluoride and has high affinity as a result of high electro-negativity for fluoride. Like the well-established activated alumina, FR-10 resin has a potential of successful implementation in rural areas.

The main draw back with FR-10 resin at the moment is the high purchasing cost. However, if the costs can be subsidised by governments or non-governmental organisations it would have huge potential for being successful in rural areas. Unlike activated alumina, FR-10 resin has faster kinetics and may result in the use of even smaller columns (Loganathan *et al.*, 2013).

Activated alumina used in the study is KA-402 Grade, supplied by Zan-Tech. This grade is used specifically for defluoridation. The FR-10 resin used was supplied by Ion Exchange (India) Ltd. It is also highly selective towards fluoride. Properties of activated alumina and FR-10 resin as provided by the suppliers are shown in appendix A. The chemical composition, surface area and attrition loss percent for FR-10 resin was however not given. FR-10 resin has a smaller particle size compared to activated alumina. It is therefore expected to have an advantage of high adsorption rate. It will however have a disadvantage of high pressure drop.

3.3 Equipment

3.3.1 Membrane treatment

The equipment used for the membrane treatment experiments consisted of the woven fabric micro-filtration gravity filter described in section 2.4.2, a stop watch, cleaning brush and sodium hypochlorite for membrane cleaning.

3.3.2 Adsorption

The system for adsorption experiments is shown in Figure 3.1. It consists of a 100L elevated feed tank, which is used to ensure that the water level in the column feed tank is constant. A mesh screen is fitted on the elevated feed tank outlet to remove large suspended material from the water prior to feeding the column feed tank.

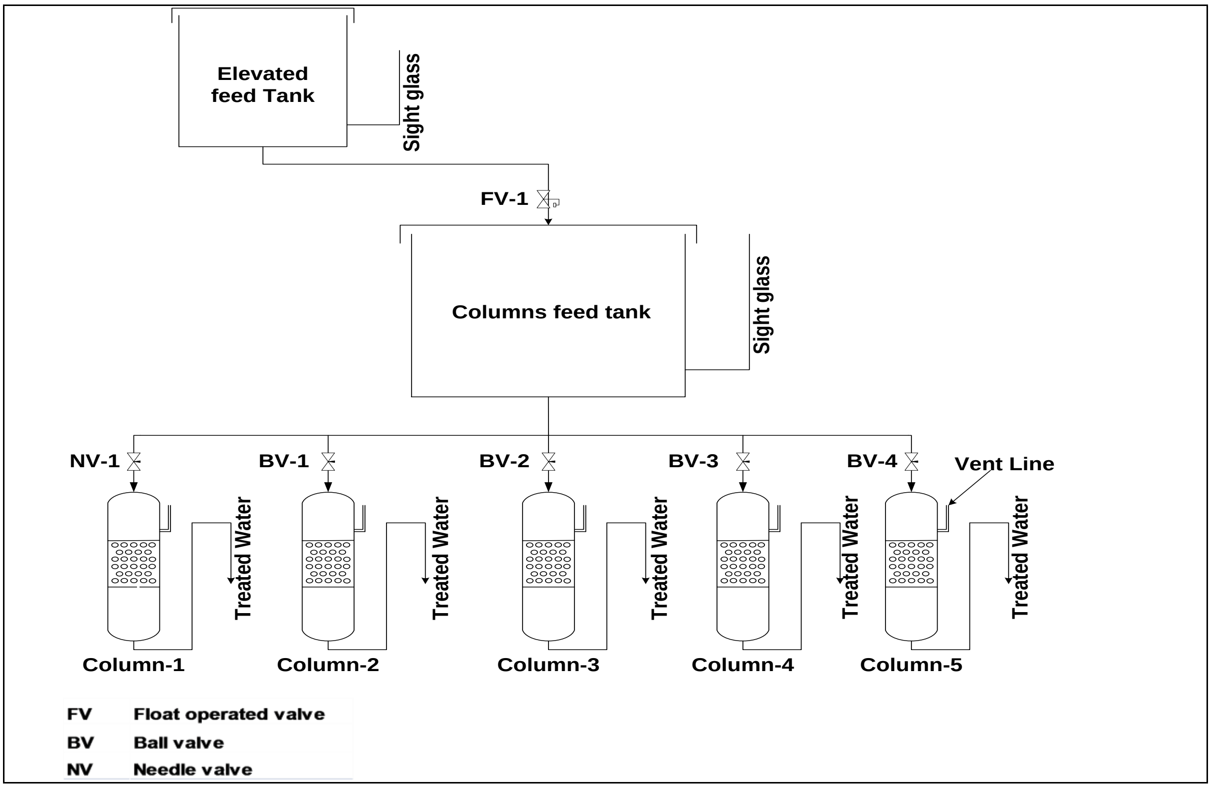


Figure 3.1: P&ID for system used for column adsorption investigations

The elevated feed tank and the column feed tanks were fitted with sight glass to observe water level. The water level in both tanks was maintained at a constant level. Maintaining the water level is important as it ensures constant flow rate through the columns. The level was maintained by manually pouring feed water when the level was going down. The large size of the elevated tank was chosen to ensure that the water level does not decrease at a faster rate. The pipeline connecting the elevated feed tank and the column feed tank has a float operated valve which opens depending on the water level in the column feed tank. This maintained a constant water level in the column feed tank.

At first the elevated feed tank was feeding raw water to a membrane unit which then fed permeate to the adsorption columns. It was then observed that the fouling of the membranes was again reducing the flow rate through the adsorption columns. For investigation purpose it was important that the flow rate is maintained constant. It was then decided that the raw water will be filtered prior to running the column experiments. The water feed to the elevated tank had already been filtered.

From the column feed tank, the water gravitates through the adsorption columns which ran in parallel. The system had five columns of the different sizes. The sizes used were 16 mm, 25 mm, 32 mm, 40 mm and 75 mm outside diameter. All the columns were made of PVC material. The 75 mm column was fed by a 20 mm PVC pipe, fitted with a needle valve for proper flow control.

The feed pipes to the rest of the columns had 5 mm outside diameter, fitted with ball valves for flow control. The smaller pipe diameter was used in these columns because the required flow rates were low. Better flow rate control was easily achieved with the smaller pipe sizes. The media was supported by a mesh screen inside the column. A vent line in the adsorption column was used to prevent air build up that would retard flow.

Each column outlet pipe makes a U-shape leg above the adsorption media. This ensures plug flow through the columns. It also ensured that the media was kept immersed in water after each run. This is particularly important for FR-10 resin whose performance is drastically affected if it is allowed to dry.

Both media was first wetted with deionised water prior to being fed to the columns. This was necessary to ensure that air is expelled from the media surface. Having air on the media surface reduces the total surface area available for adsorption. The flow rate through the columns was occasionally monitored using a stop watch and a measuring cylinder. Fresh media was used for every experiment.

3.4 Experimental methods

3.4.1 Determination of best cleaning method for the woven fabric micro-filtration gravity filter

The reusability of the woven fabric micro-filtration gravity filter depends on finding a suitable cleaning method for the system. This section presents the cleaning methods investigated to find a suitable one for the system. The treatment methods investigated were selected based on available resources in rural areas. Since the fouling that was expected on the membrane surface of the WFMFGF was particulate, biological and adsorbed organic contaminates, it seem that the suitable cleaning method would be physical as well as chemical cleaning with alkaline chemicals or oxidants. These are the methods that were investigated in the study.

The selected physical cleaning method was scrubbing the membranes with a brush. A scrubbing brush that fits in between the membrane elements must be used. This must scrub the membranes without having to dismantle the whole membrane pack. This method is simple and requires no complicated procedures. The brushes are easily available and can be obtained in local shops.

The selected chemical cleaning method was sodium hypochlorite (Jik). This was used to remove micro-biological foulants on the membrane surface. This is easily available in rural areas and can be obtained at an affordable price at shops. Its usage has a minimal safety and health risks. It will therefore be easy to use by people in rural areas. The cleaning methods investigated were designed as follows:

1. The system was filled with raw water and the membranes brushed.
2. The system was filled with permeate and the membranes were brushed.
3. The system was filled with permeate, 300 ml of sodium hypochlorite was added and the membranes were then soaked for 6 hrs, before being brushed.
4. The system was filled with permeate and 300 ml of sodium hypochlorite was added. The membranes were then allowed to soak for 12 hrs prior to being brushed.
5. The system was drained and then filled twice with permeate to rinse off the sodium hypochlorite.

The investigations were started by first running the system with tap water. This was to observe the performance of a clean membrane. After each run with raw water and cleaning, the system was run with tap water again. Comparison of the tap water runs after every membrane cleaning to the initial water run indicated the extent to which the membrane is clean. If the results of the two tap water runs match, it means that the membranes were completely cleaned. A run was conducted by filling the system with water and opening the permeate tap to collect permeate. Each run was performed for an hour and the volume of permeate collected was recorded.

The purpose of running the system with raw water was to foul the membranes. This was achieved by repeatedly filling the system with raw water and collecting permeate until the membrane fouled. It was decided that the membranes were badly fouled when the volume of permeate collected after an hour was half the volume of the first run. At this point the membranes required cleaning. One cleaning method was investigated at a time. The experiments were repeated two more times to ensure that results are repeatable.

3.4.2 Determination of run time for the woven fabric micro-filtration gravity filter

This investigation was conducted to see how long it takes for the system to run before it requires cleaning. A system that requires frequent cleaning might lead to the user being tired and abandoning the system altogether.

This investigation was conducted on the membrane unit using raw water sourced from Umgeni water. Again the system was first run with tap water. This was done to observe the performance of a clean membrane before it was fouled. After the system was used with raw water and cleaned, it was evaluated with clean water again. This was to indicate if the membrane was clean. The system was run by filling it with water and opening the tap to draw permeate. The volume of permeate collected after an hour was recorded.

The filling of raw water and collection of permeate for an hour was repeated until the volume of permeate collected in an hour was half the volume obtained from the first run. At that point it was decided that the membranes were badly fouled and required cleaning.

Since the system is to be used once per day, the number of runs represents the number of days the system can be used before cleaning is required. The system was cleaned by soaking the membrane in 0.0225 percent sodium hypochlorite solution overnight and brushing the membranes in the morning. The experiment was repeated two more times to ensure repeatability of the results.

3.4.3 Determination of maximum and minimum flow rate through the woven fabric micro-filtration gravity filter

The design of an adsorption column requires the knowledge of the flow rate through the system. This is needed for the determination of the required column diameter given the velocity of the fluid through the column. It also indicates if the operation is within the contact time limits. The column contact time is determined using the fluid volumetric flow rate as well as the volume of the bed in the column.

This investigation was conducted by running raw water through the membrane system. Time taken for every litre of permeate collected was recorded. The system was run until the flow rate became insignificant. This data was used to calculate flow rate per volume of water collected. A flow rate profile was then developed with the obtained data. From the profile, the maximum flow rate was obtained at the beginning of the run and the minimum flow rate at the end of the run. The experiment was repeated to ensure that the results were repeatable.

3.4.4 Comparison performance of adsorbents based on adsorption capacity

The adsorption capacity was determined through conducting laboratory scale batch adsorption experiments. From the results of the batch experiments adsorption isotherms were developed. This is a plot of equilibrium concentration against equilibrium capacity of the media. From these results the equilibrium capacity of the adsorbents were compared at the same equilibrium concentration. Adsorption isotherm models were then applied to the experimental data to find the one that best describe the experimental data. The best fit model was then used to predict adsorption capacity at any equilibrium concentration. The best media could also be identified by comparing the model constants.

The isotherm experiments for comparison of adsorbents must be done under the same environmental conditions such as temperature, ionic strength, pH, etc (Kratochvil and Volesky, 1998). This investigation can be conducted by either varying the feed concentration at a fixed amount of adsorbent or varying the amount of adsorbent at a fixed feed concentration. For this investigation, the feed concentration was varied at a fixed amount of adsorbent.

This investigation was conducted with river water spiked with sodium fluoride. The concentration was varied between 5 and 80 mg/L. Since adsorption capacity depends on the feed concentration, a feed concentration as high as 80 mg/L was used to ensure that the adsorbent reaches a point of exhaustion which will then enable experimental determination of maximum adsorption capacity. Plastic beakers of 250 ml were used for these experiments. A sample volume of 100 ml was added into each beaker. An adsorbent mass of 4 g was added into each beaker. The beakers were then placed on a shaker which agitated the samples at a speed of 150 rpm for 24 hours. Samples were then taken from each beaker to be analysed for equilibrium concentration.

3.4.5 Effect of velocity on the adsorption column

This experiment investigated the effect of velocity on fluoride removal. The effect of velocity was investigated while other parameters were kept constant. Parameters kept constant included contact time as well as the amount of adsorbent. This was done with activated alumina and FR-10 resin. The aim was to compare the two adsorbents. An adsorbent that operates at a wider velocity range is the better adsorbent.

This investigation was conducted in five columns run in parallel. The fluid velocity was varied at fixed volume of media in the columns as well as fixed contact time. The fluid velocity was calculated using the following expression:

$$u = \frac{V_B}{A_c Tc} \tag{3.1}$$

Where u is the fluid velocity in m/hr, V_B is the volume of bed in the column in m^3, Tc is the contact time in minutes and A_c is the column cross sectional area m^2. The volume of bed in the column and contact time were kept constant while the cross sectional area was varied in order to vary the fluid velocity. The experimental design for this experiment is shown in Table 3.2. The table shows the inside diameters of the five columns that were used ranging from 14 mm to 86 mm. Fixed contact time, flow rate and volume of adsorbent used were 5 minutes, 20 ml / minute and 100 ml respectively.

The 100ml volume of adsorbent was selected because it can easily be accommodated by all the columns. An increase in the volume would have made the column with 14 mm inside diameter to be even taller. The fluid velocity in the column ranged from 7.8 m/h down to 0.21 m/h.

Table 3.2: Experimental design parameters for effect of velocity on fluoride removal

	Column 1	**Column 2**	**Column 3**	**Column 4**	**Column 5**
Column inside diameter (mm)	14	21	28	36	86
Contact time (min)	5	5	5	5	5
Flow rate (ml/min)	20	20	20	20	20
Volume of media (ml)	100	100	100	100	100
fluid velocity (m/hr)	7,80	3,46	1,95	1,18	0,21

Column feed sample was taken once and column outlet samples were taken at six hour intervals and analysed for fluoride concentration. The fluoride results were used to develop breakthrough curves used for assessment of performance of the columns.

3.4.6 Effect of contact time on adsorption column

In this investigation, contact time was investigated independent from other variables. The contact time was varied at constant velocity as well as constant amount of adsorbent. These variables were kept constant because any variation affects the column performance. An increase in velocity and amount of adsorbent may result in delayed breakthrough as well.

The contact time was varied by varying column cross sectional area as shown by the following equation:

$$Tc = \frac{V_B}{uA_c} \qquad (3.2)$$

V_B is the volume of media in the column in m^3, u is the fluid velocity in m/hr and A_c is the cross sectional area of the column in m^2. From the equation it can be seen that the contact time can be increased at constant fluid velocity and volume of adsorbent by varying the cross sectional area of the column. Table 3.3 shows experimental design for this investigation.

Table 3.3: Experimental design parameters for effect of contact time experiment

	Column 1	Column 2	Column 3	Column 4	Column 5
Column inside diameter (mm)	14	21	28	36	86
Fluid velocity (m/hr)	5	5	5	5	5
Flow rate (ml/min)	13	29	51	85	484
Volume of media (ml)	100	100	100	100	100
Contact time (min)	7,80	3,46	1,95	1,18	0,21

This investigation was conducted using the system shown in Figure 3.1. The feed fluoride concentration was 4 mg/l. The effluent concentration from each column was measured at 6 hour intervals and breakthrough curves were developed.

3.4.7 Effect of pressure drop on the column operation

This section presents the experimental method for the investigation of the effect of pressure drop on column operation. This investigation was conducted on the experimental set up shown in Figure 3.2. The system consists of an elevated feed tank, a column feed tank as well as the adsorption column. A needle valve is fitted on the column inlet line to control the flow rate. The elevated feed tank and float operated valve fitted on the exit pipeline from the elevated tank was used to fix the water level in the column feed tank.

The system was fitted with a head loss measuring device which consists of two glass tubes and a calibrated scale. One of the tubes was connected to the column outlet pipe, just as it exited the column while the other tube was connected to the column structure above the adsorption media. The calibrate scale was placed in between the glass tubes and used to measure the difference in water levels. The water level in one tube relative to the other indicates the head loss through the media. According to Charles (1969), this method is suitable for head loss measurement in a column that is gravity driven.

Raw water used for this investigation was sourced from Inanda dam, obtained through Umgeni water (Wiggins Water Works). It was first pre-filtered using the WFMFGF before feeding into the feed tank. The flow rate used ranged from zero to 100 l/hr. The column velocities used were 0.0014 m/s, 0.0068 m/s, 0.0123 m/s, 0.0177 m/s, 0.0232 m/s and 0.0273 m/s.

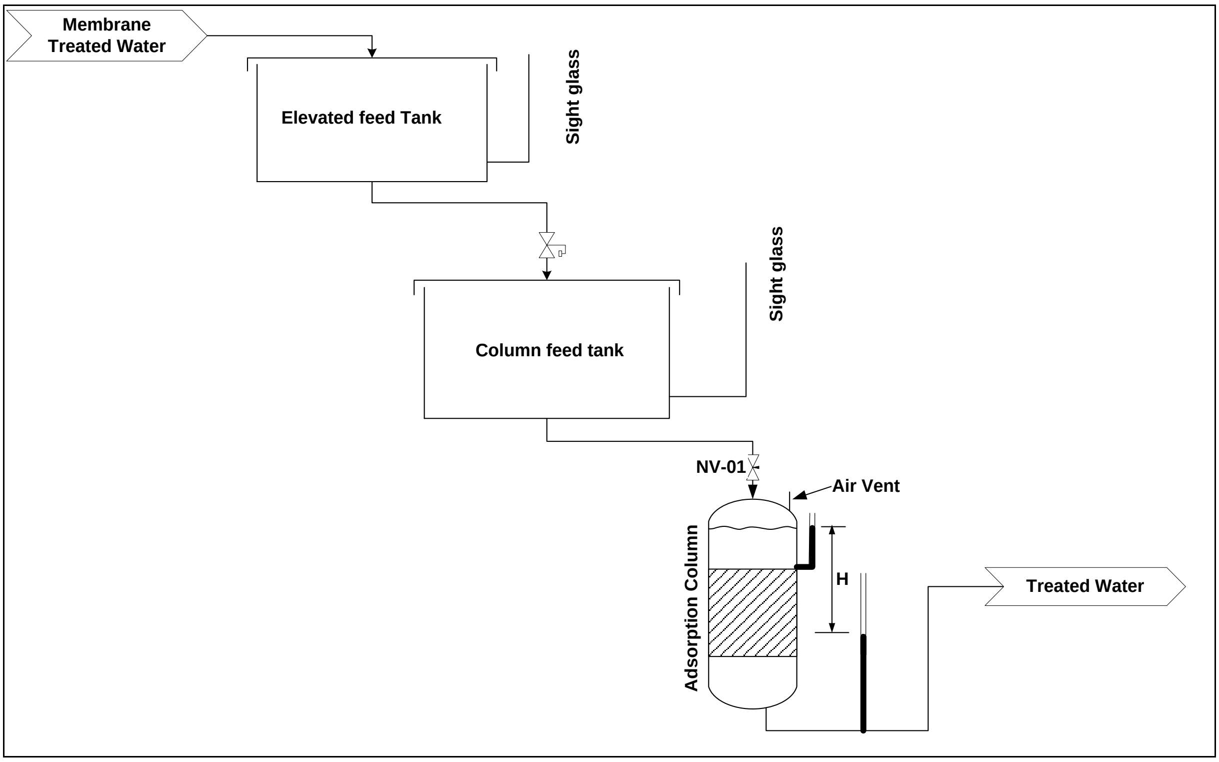


Figure 3.2: Experimental set for column pressure drop investigation

A run with each velocity was conducted by filling the elevated feed tank and the column feed tank with water. The needle valve was opened to allow water to pass through the column. A measuring cylinder and a stop watch were used to measure the flow rate through the system. Once the desired flow rate was set, the system was allowed to run for 5 minutes to stabilise before measurement was taken. The height in between the water levels in the glass tubes was measured. This indicates the head loss in meters of water.

3.5 Analytical methods

3.5.1 Fluoride measurement

The method used for fluoride analysis was the spends photometric method. This method involves the reaction of fluoride in the sample with red ziconium dye (spends) solution. The fluoride in the sample reacts with the ziconium dye to form colourless complexes. The colour change is proportional to the fluoride concentration in the sample. The material used in the analysis included a HACH DR 3900 spectrophotometer for the fluoride measurement, 0.45 µm filter papers used to filter samples before analysis and Spends reagent. To ensure accuracy of the test method, the instrument was calibrated using 1 mg/L standard solutions. The step by step calibration and testing procedure is shown in appendix C.

Chapter 4. Results and discussions

This section presents results obtained from the investigations. Results of investigations conducted on the pre-treatment unit are presented and discussed from sub-section 4.1 to 4.3. Results of adsorption investigations are presented and discussed from subsection 4.4 to 4.7. The selection of the best adsorbent is shown in subsection 4.8.

4.1 Determination of run time for the woven fabric micro-filtration system

The results of the determination of run time for the woven fabric micro-filtration gravity filter are shown in Figure 4.1. The system has been designed to provide 20 litres of treated water per hour and the system is to be run once per day. From the results, it can be seen that the system consistently provides the 20 L for 28 consecutive runs. This means that the system can be used for almost a month providing 20 L of treated water per day. Beyond this period the effect of fouling becomes significant, affecting the performance of the system. However the system can still be used for 16 more runs which is equivalent to about 10 more days. Beyond that the volume of treated water produced by the system is significantly lower and it requires cleaning to regain its performance.

It can be observed from the graph that the first four runs produced high volumes of permeate. After that the volume obtained was constantly around 20 L per hour. The high volume produce in the first four runs is caused by the large pore size of the micro-filtration membrane. The permeate flow rate remains high while the particles in the feed are still occupying the membrane pores. According to (Pikwa *et al.*, 2010) the turbidity of the water at this initial period range from 5 NTU to 10 NTU. This does not meet the SANS 241 Standard of 1NTU. The initial quantity of water can either be discarded or allowed to be diluted with good quality water that will subsequently be produced.

After the pore size of a micro-filtration membrane has been reduced, the cake that forms on the surface of the membrane then performs the filtration. At this point the permeate flow rate becomes constant and the membrane begins to operate like an ultrafiltration membrane (Pearce, 2007a).

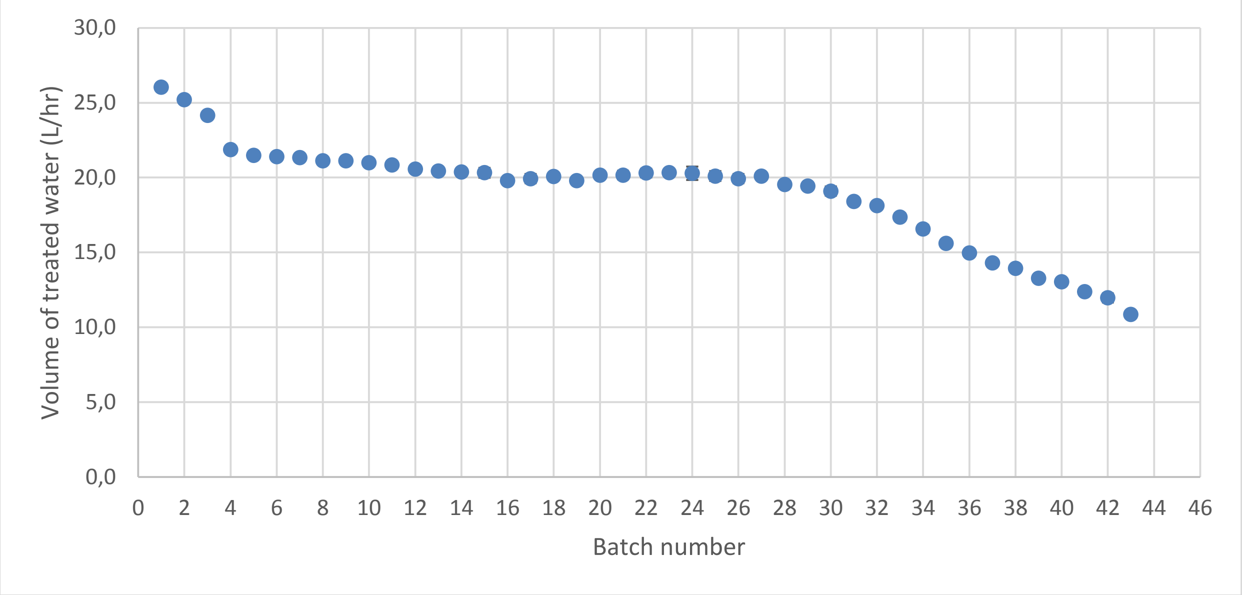


Figure 4.1: Run time for the woven fabric microfiltration gravity filter

From an operational point of view, the longer run time achieved with the system puts it at an advantage for successful applications in remote rural areas compared to other available systems. For example, the conventional water treatment system which consists of flocculation, clarification and filtration, the clarifiers require frequent desludging while the filters require frequent backwashing. Other systems like the conventional membrane systems also require frequent cleaning. These systems required a daily operator to operate them. Alternatively, an automatic cleaning mechanism has to be installed which will escalate the cost.

It is also not easy to automate a system that is to be used in remote rural areas. This is mainly because of the unavailability of electricity in some areas. On the other hand the user would also not be comfortable spending a lot of time each day cleaning the system. The more than 30 days run time before the system requires cleaning makes it more suitable for applications in remote rural areas.

4.2 Determination of maximum and minimum flow rate for the WFMFGF

Presented here are the results of determination of minimum and maximum flow rate through the system. This was done to characterise the system. The results of this investigation are important when designing the adsorption process which follows the membrane treatment process. The design requires that the flow rate coming through is known. As mentioned in section 3.3.1.1, the woven fabric micro-filtration gravity filter has been designed to provide 20 litres of treated water per hour. The flow rate through the system was however varying throughout the experimental period. This was a result of variation in static head.

The flow rate profile of the system gave the minimum and maximum flow rates that can be achieved by the system. The flow rate profile is shown in Figure 4.2. This is presented as instantaneous flow rate measured against volume of permeate collected. It can be seen from the graph that the maximum flow rate through the system obtained at the beginning of a run was about 100 l/hr. The minimum flow rate through the system obtained at the end of a run was about 5 l/hr.

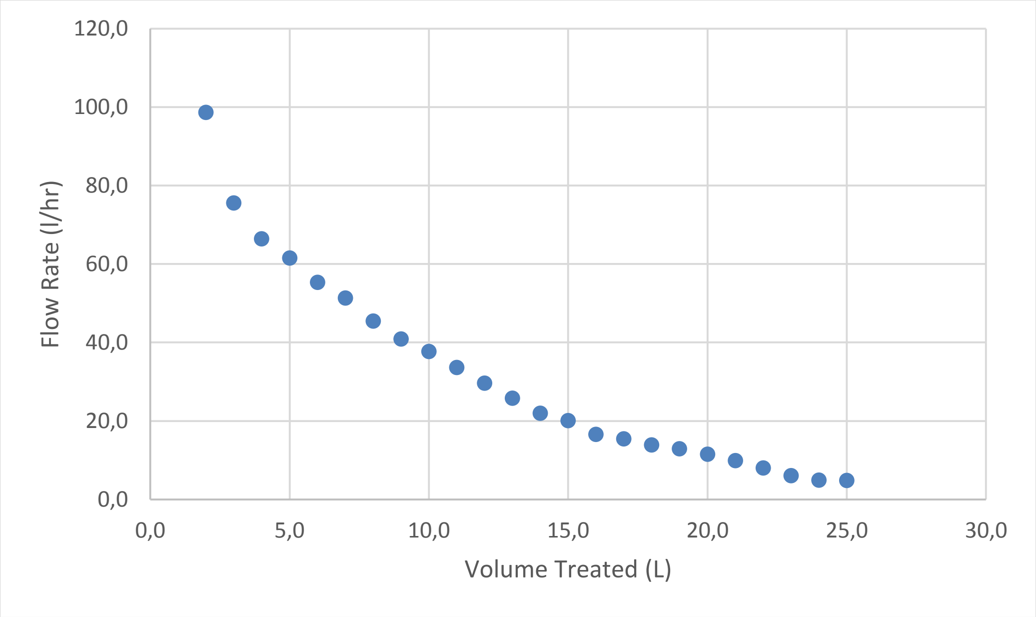


Figure 4.2: Flow rate profile for the Remote Rural Water Treatment system

4.3 Determination of the best cleaning method for the woven fabric micro-filtration system

The results of the determination of the best cleaning method for the woven fabric micro-filtration system are shown in Figure 4.3. The graph shows volume of pure water run for a clean membrane as well as after the membrane had been cleaned with each cleaning method. Shown is the volume of pure water permeate collected after 30 minutes. The best cleaning method is the one in which the pure water run after cleaning matches the pure water run of a clean membrane.

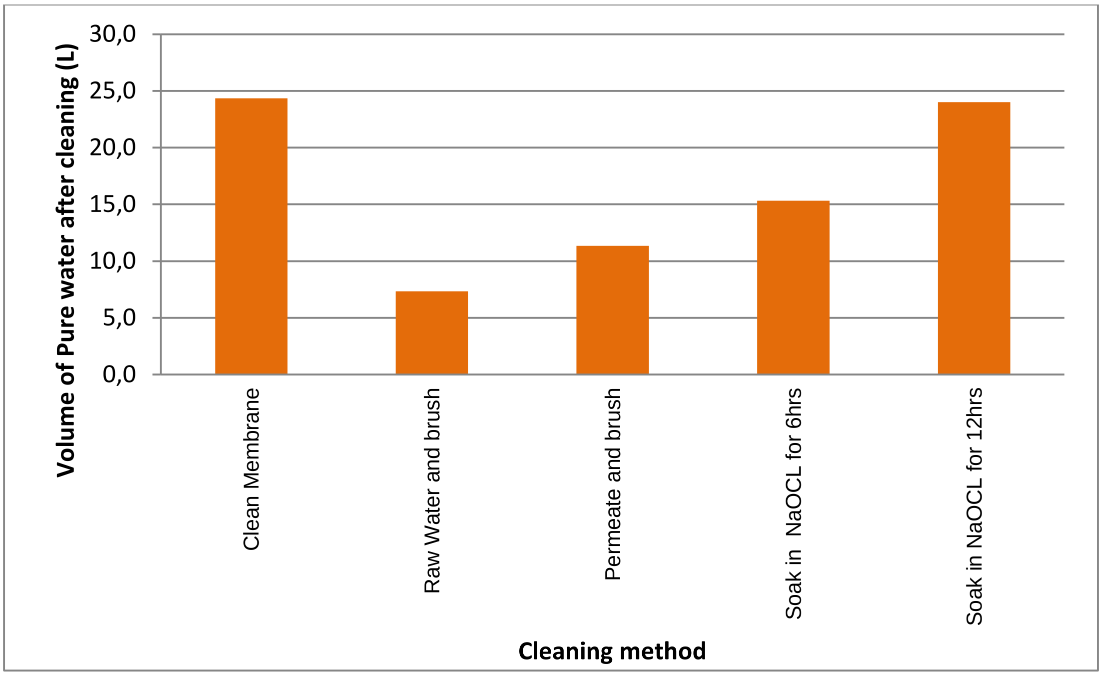


Figure 4.3: Performance of the different cleaning methods

From the results it can be seen that cleaning the system with a brush and permeate is better than cleaning it with brush and raw water. This is because raw water is already highly concentrated with dirt and is therefore not effective in cleaning of the membrane.

What can also be observed is that physical cleaning alone is not enough in recovering the performance of a clean membrane. The pure water run after cleaning with raw water and brushing provided a permeate volume that was 29 percent of the volume received with a clean membrane. Cleaning with permeate and brushing produced permeate volume that was 45 percent of the volume obtained with a clean membrane.

Soaking the membranes in 0.0225 percent by weight of sodium hypochlorite solution for 6 hours and brushing the membranes recovered 60 percent of the permeate volume obtained from a clean membrane. A permeate volume recovery of 100 percent was achieved by soaking the membranes in 0.0225 percent sodium hypochlorite solution for 12 hours and brushing the membranes.

The results also show that the combination of physical and chemical cleaning produces better results. The aspect of membrane soaking time in a chemical solution has not yet been well researched. Few research papers available indicates that a better performance is obtained with longer contact time (Ang *et al.*, 2006). These results confirm those findings.

The results indicate that the membrane is mainly fouled by particulates as well as microbiological contaminants. Particulate fouling is removed by physical methods (Shi *et al.*, 2014). In this case this was achieved by brushing. Sodium hypochlorite on the other hand removes micro-biological contaminants (Shi *et al.*, 2014). It should be noted that these results were obtained using raw water from one source. If the quality of the raw water differs significantly from that used in this research, further investigation might have to be done to find a suitable cleaning combination.

According to Perez Pavon *et al.* (2008), if the raw water has high organics, the use of sodium hypochlorite can result in formation of substances that are harmful to humans. For any application of this system and the use of the sodium hypochlorite for cleaning, the NOM should first be measured in the raw water. If there is evidence of high level of NOM a possible solution to prevent the consumption of harmful substance would be proper rinsing of the system after cleaning. This however requires a detailed investigation.

4.4 Equilibrium studies

4.4.1 Equilibrium studies for fluoride adsorption by activated alumina and FR-10 resin

Figure 4.4 shows equilibrium capacity results for both activated alumina and FR-10 resin. Shown are graphs of equilibrium concentration on the liquid phase against concentration on the solid phase (adsorption isotherm). The shape of the isotherms shows that adsorption of fluoride by both activated alumina and FR-10 resin is favourable. This means that fluoride ions prefer to be in both media surface rather than being in the water. A sharper effluent breakthrough on column adsorption is expected on both media provided the rate of adsorption of fluoride is high.

It was observed that at the same equilibrium concentration, the equilibrium capacity for FR-10 resin was higher than that of activated alumina. This might indicate that FR-10 resin is more selective towards fluoride compared to activated alumina. This observation can be justified by the fact that fluoride is less dependent on pH yet activated alumina is highly dependent on pH, operating efficiently between the pH range of 5 to 6 (Pontius, 1990; Ayoob *et al.*, 2008; Leyva-Ramos *et al.*, 2008).

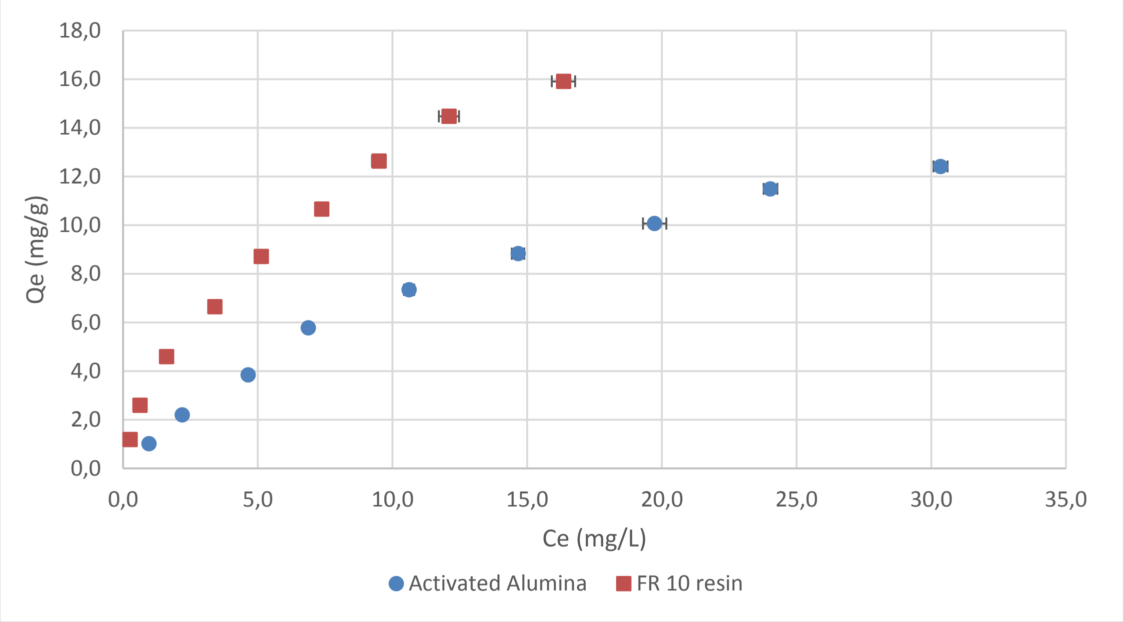
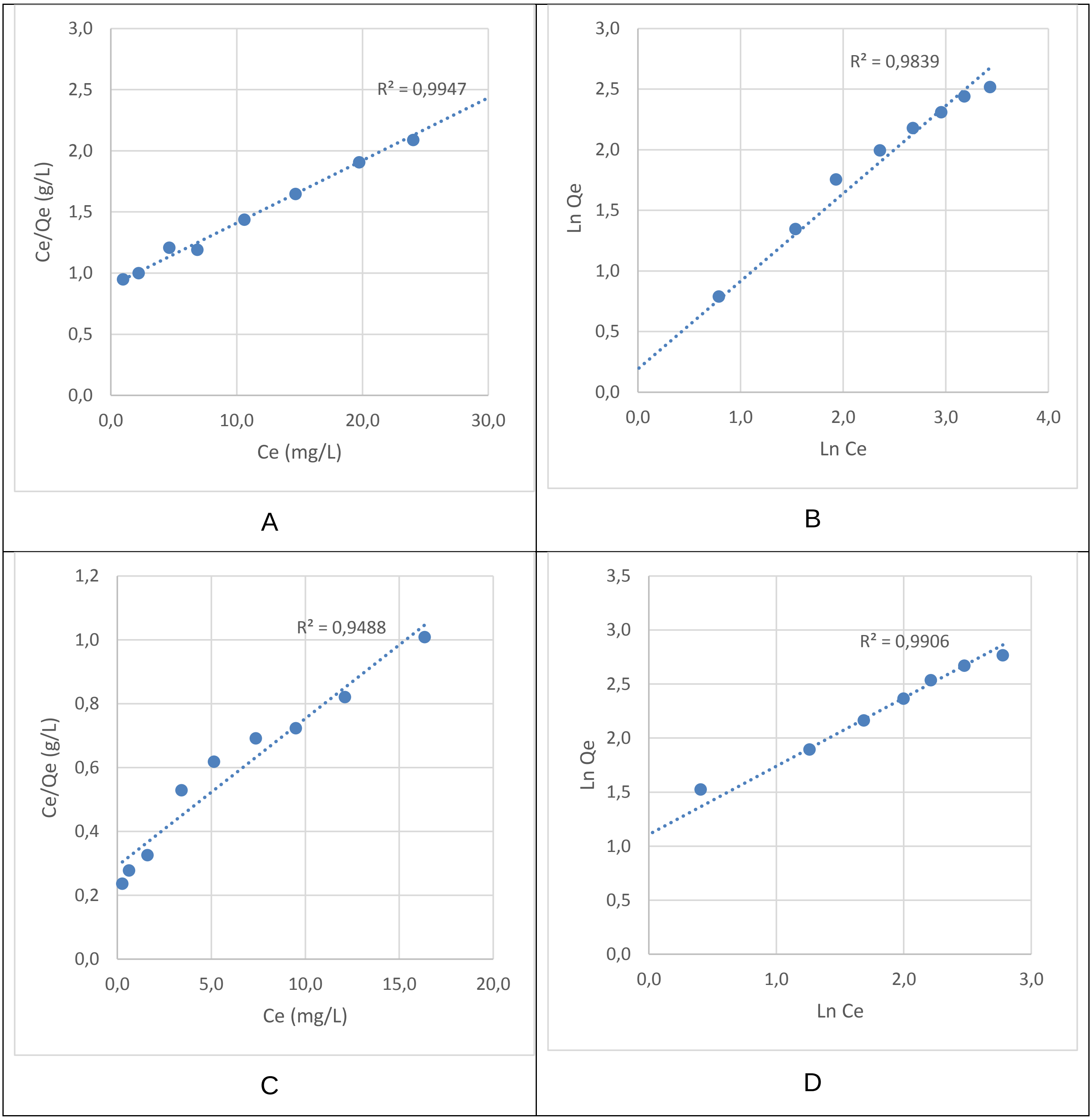


Figure 4.4: Equilibrium capacity results for Activated alumina and FR-10 Resin

An investigation was then done to find out which model can be used to predict equilibrium capacity for activated alumina and FR-10 resin at varying equilibrium concentrations. The model constants can also be compared to find out which adsorbent has a higher capacity for fluoride removal.

In Figure 4.5 are results of application of linear form of the Langmuir and Freundlich models on experimental data for fluoride adsorption by activated alumina and FR-10 resin. These graphs were used to find the model that best fit the experimental data and to determine constants for the models.



A

B

C

D

Figure 4.5: Linear plots of isotherm models for fluoride removal, (A) Langmuir model for activated alumina, (B) Freundlich model for activated alumina. (C) Langmuir isotherm on FR-10 resin, (D) Freundlich model for FR-10 Resin.

To find the model that best fits the experimental data, the coefficient of regression was used. The coefficient of regression indicates how close to a straight line the linear model is. A model with a coefficient of regression closer to unity is the best fit model. The best fit model was also confirmed by using the non-linear chi-squared analysis.

This was done because of the errors associated with the development of the linear models which may affect the results of the linear regression process (Ayoob and Gupta, 2008). The slope and y-intercept of the linear form of Langmuir and Freundlich isotherms were used to determine the isotherm constants.

Table 4.1 shows isotherm constant, coefficient of linear regression and chi- squared values for Langmuir and Freundlich isotherms applied on both activated alumina and FR-10 resin. The value of the coefficient of regression being close to unity and the chi-squared value being lowest for the Langmuir isotherm when fluoride is removed by activated alumina means fluoride removal by activated alumina can be modelled by the Langmuir isotherm. Similarly, the value of the coefficient of regression being close to unity and the lowest value of the chi-squared for the Freundlich isotherm when fluoride is removed by FR10 resin means that fluoride removal by FR-10 resin can be modelled by the Freundlich isotherm.

Table 4.1: Langmuir and Freundlich model parameters

Media	**Freundlich constants**				**Langmuir constants**			
	n	**K_f (mg/g)**	**R^2**	**X^2**	**b**	**Q_{max}**	**R^2**	X^2
Activated Alumina	1,38	1,21	0,98	0,62	0,06	19,53	0,99	0,03
FR-10 Resin	1,58	3,03	0,99	0,30	0,16	21,69	0,95	0,61

Previous researchers also found that experimental equilibrium data for fluoride removal by activated alumina can be modelled by the Langmuir isotherm (Bishop and Sansoucy, 1978; Ghorai and Pant, 2005). However, the adsorption isotherm constants obtained by the different researchers are different. This study also found different results. This might be caused by the types and size of activated alumina used in the different investigations as well as the different conditions in which the experiments were conducted. Differences may also be in the feed concentration used as well as presence of competing ions in the feed.

A study by Bishop and Sansoucy (1978) confirmed that the adsorption capacity is dependent on the size of the adsorption media. In that study the effect of particle size on fluoride removal capacity was investigated. This was conducted in a batch scale experiment using fluoride-spiked tap water. Activated alumina having different particle sizes was used. The results show that by reducing the adsorption media size, the adsorption capacity was increased. It was concluded that the increase was caused by an increase in surface area with a decrease in particle size.

A study for fluoride removal by activated alumina conducted by Ghorai and Pant (2004) found that the value of K_F was 1.78 mg/g and the value of n was 3.13 for the Freundlich isotherm. The value of $q_{\max}$ was found to be 0.74 mg/g and the value of b was 0.31 L/mg for the Langmuir isotherm. The activated alumina used in that investigation was a different grade. It had a lower surface area of 250 m^2/g and the particle size was 2-5 mm, which means that lesser sites on the adsorbent surface were available for adsorption hence the low maximum adsorption capacity as shown by the Langmuir isotherm.

The investigation was also conducted with low fluoride feed concentration (2.5-14 mg/l). Even though equilibrium might be reached during the experiments, the maximum capacity might still not be reached because of the low feed concentration used relative to the mass of adsorbent used.

A study by Meenakshi and Viswanathan (2007) also found that equilibrium results for fluoride removal by FR-10 resin can be modelled by the Freundlich isotherm. At a temperature of 30°C, which is similar to the temperature used in this study, the values of K_f and n for the Freundlich isotherm were 1.032 mg/g and 1.23 respectively. The values of Q_{max} and b for the Langmuir isotherm were 1.038 mg/g and 9.406 L/mg respectively.

These values were different from what was found in the current study. This might have been caused by differences in the experimental conditions. In the study by Meenakshi and Viswanathan (2007), a very low feed concentration was used. This may have resulted in inaccuracies in the determination of the constants.

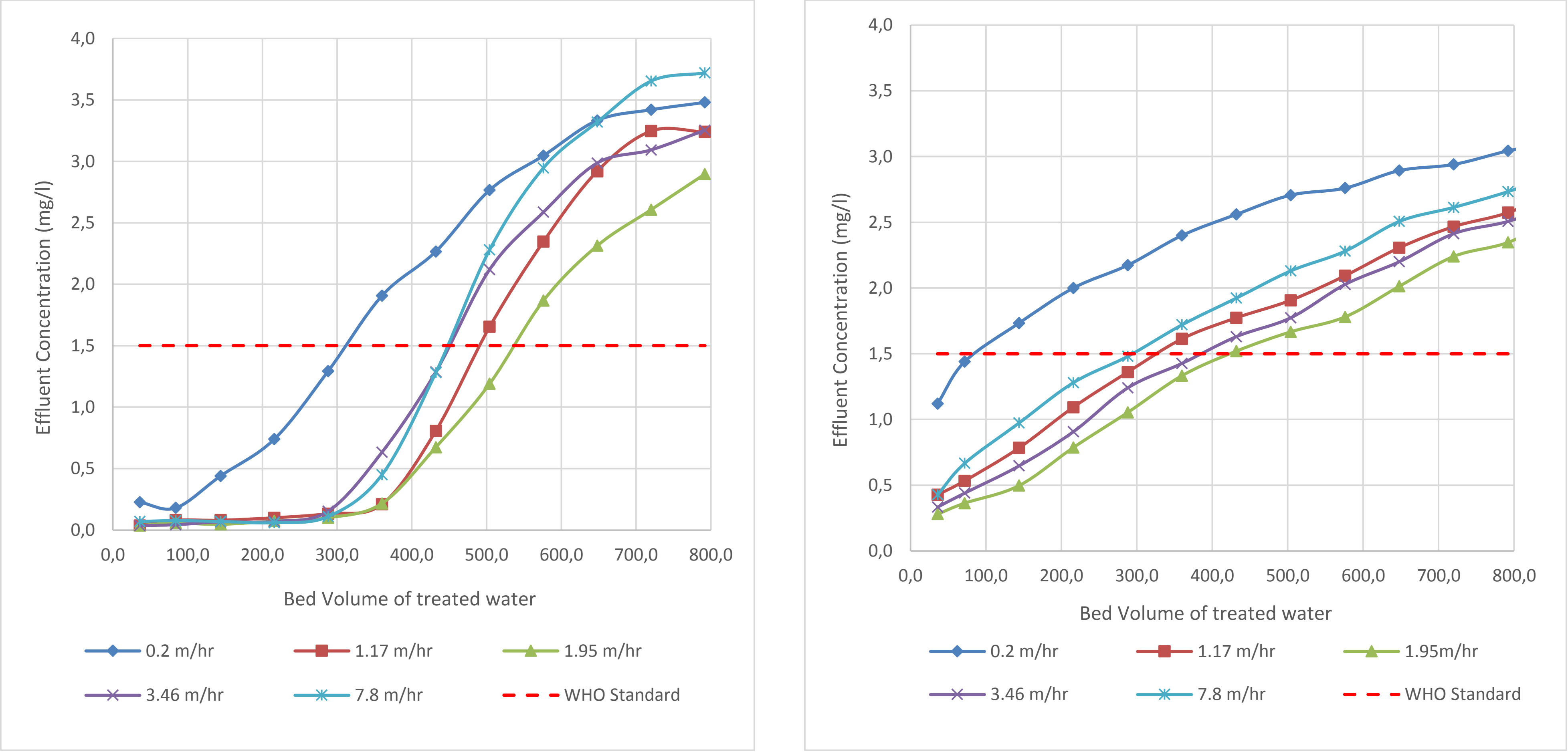
Summary of results

The fact that equilibrium experiments for fluoride adsorption by activated alumina is modelled by the Langmuir model while fluoride adsorption by FR-10 resin is modelled by Freundlich mean that the model constants cannot conclusively indicate which adsorption media has the highest adsorption capacity. However the experimental data for the two adsorbents conducted under the same conditions indicates that at the same equilibrium concentration FR-10 resins have a higher equilibrium adsorption capacity for fluoride compared to activated alumina. With these findings it can then be concluded that based on adsorption capacity, FR-10 resin performs better than activated alumina.

4.5 Effect of velocity on fluoride adsorption by FR-10 resin and activated alumina

This investigation was conducted to see how the two adsorption media are affected by varying fluid velocity in a column. This variation is caused by varying static head that drives the water through the system during treatment. The condition for this investigation is shown in Table 3.2. The adsorption media that performs better under this condition was the preferred media.

Figure 4.6 shows results of this investigation. Shown on the graph is column effluent concentration plotted against bed volumes of treated water for the different fluid velocities. A bed volume is the volume of treated water at breakthrough per volume of adsorption media used. The breakthrough point or the concentration above which the water is not suitable for consumption is shown by the dotted line.



A

B

Figure 4.6: Effect of velocity on fluoride removal by (A) FR-10 resin, (B) activated alumina.

What was observed from both graphs was that with an increase in fluid velocity, the column adsorption performance improved. This was shown by the increase in the bed volume of treated water at breakthrough when the velocity increased. A velocity increase from 0.2 m/hr to 1.95 m/hr, resulted in an increase in the bed volumes of treated water from 300 to 536 with FR-10 resin, while it increased from 50 to 430 with activated alumina.

What is also observed is that in each velocity, FR-10 resin performs better compared to activated alumina. This is shown by the high bed volumes of treated water at breakthrough when using FR-10 resin. This is caused by the fact that FR-10 resin is smaller in size compared to activated alumina. The size range of FR-10 resin is 1-2 mm while the size range of activated alumina is 0.3-1.2 mm. According to Slejko (1985) high adsorption rates are achieved with adsorbents having smaller sizes. This is because with smaller sizes there is large surface area available for adsorption (Slejko, 1985). This then explains the better performance of FR-10 resin.

The results of both media however show that beyond the velocity of 1.95 m/hr, the performance begins to deteriorate. From 1.95 m/hr to 7.8 m/hr, the bed volume of treated water reduced to 450 with FR-10 resin while it reduced to 300 with activated alumina. This means that for both media 1.95m/hr was the maximum velocity in which good performance was achieved.

These results are in agreement with previous findings by Reed *et al.* (1996) as well as Lorenzen *et al.* (2009). A study by Reed *et al.* (1996) who studied the effect of velocity on lead removal by activated carbon found that at a feed concentration of 10 mg/L and contact time of 1.85 minutes, an increase in fluid velocity from 4.9 m/hr to 9.8 m/hr enhances the performance of an adsorption column. The bed volumes of treated water was increased from 190 to 217. This was attributed to the reduction in mass transfer resistance on the fluid film on the adsorbent surface at high velocities. A reduction in the mass transfer resistance resulted in an increase in the rate of adsorption, hence the higher volume of treated water at breakthrough.

Lorenzen *et al.* (2009), investigated the effect of velocity on fluoride removal by activated alumina. High velocities were used compared to the velocities used in the current study. What was found was that an increase in velocity from 60 m/hr to 270 m/hr resulted in deterioration in the performance of the column. This study might have used velocities that are above the optimum velocity. This confirmed that above the optimum velocity, a further increase in the velocity results in deterioration of column performance. Lorenzen *et al.* (2009), attributed this to an increase in dispersion resistance at very high velocity.

The results of the current study also agrees with findings by Rajagopal and Kapoor (2001). In the study, the effect of velocity on adsorption of nitro-organic was investigated. The results showed better performance with an increase in velocity. The result also indicated that there is a limit to which a further increase in velocity will result in the deterioration of the system performance. However, the contact time was not fixed while varying the fluid velocity.

These results were explained on the bases of adsorption mass transfer fundamentals. The increase in fluid velocity decreases the overall mass transfer resistance and reduces the height of mass transfer zone. This delays the column reaching breakthrough and more treated water is obtained. Beyond a certain fluid velocity the effect of the speed of the mass transfer zone through the column turns to be predominant and results in early breakthrough.

What is also observed from the results of the current study is that with FR-10 resin even at a velocity as low as 0.2 m/hr there is higher bed volumes of treated water at breakthrough, with a value of 303. However the breakthrough curve was observed to be increasing gradually, unlike the steeper increasing curves obtained with the higher velocities. An operation with gradual breakthrough is not ideal as it results in larger volume of unused media (Slejko, 1985). The ability of FR-10 resin to operate at varying velocities is good since it means the varying operation flow rate in the system is easily accommodated.

Activated alumina on the other hand produced very small bed volumes of treated water at a velocity of 0.2 m/hr. About 60 bed volumes of treated water was obtained. It is however not beneficial to operate at this velocity. The operation velocity range was therefore limited to 1.17 to 7.8 m/hr. This is narrow compared to FR-10 resin which could operate at a wider range.

The breakthrough curves for activated alumina were also gradually increasing. This was due to the low adsorption rate. This means that at breakthrough, there is still a large volume of unused adsorbent in the column. The intermittent operation of the point of use system however can minimise the problem. More fluoride gets adsorbed when the system is not run. Having the water remaining in contact with the media in the column enables more adsorption to occur (Pontius, 1990).

Apart from bed volumes of treated water at breakthrough, the performance of activated alumina and FR-10 resin was compared based on adsorbent usage rate at breakthrough. Adsorbent usage rate indicates the amount of adsorbent used per volume of treated water at breakthrough. This parameter should be low indicating that a small amount of adsorbent is required to provide a large volume of water. The bed volumes of treated water and adsorbent usage rate achieved when velocity is varied are shown in Table 4.2. The observed trends on adsorbent usage rates are also shown in Figure 4.7.

Table 4.2: Column parameters for effect of velocity on fluoride removal by activated alumina and FR-10 resin

Fluid velocity (m/hr)	**Bed Volume of treated water at breakthrough**		**Adsorbent usage rate (g/L)**	
	Activated alumina	**FR-10 resin**	**Activated alumina**	**FR-10 resin**
0,20	86,73	302,90	13,80	2,67
1,17	327,79	492,00	2,30	1,63
1,95	424,29	538,00	1,60	1,49
3,50	385,97	449,00	2,30	1,78
7,80	294,00	448,00	2,30	1,78

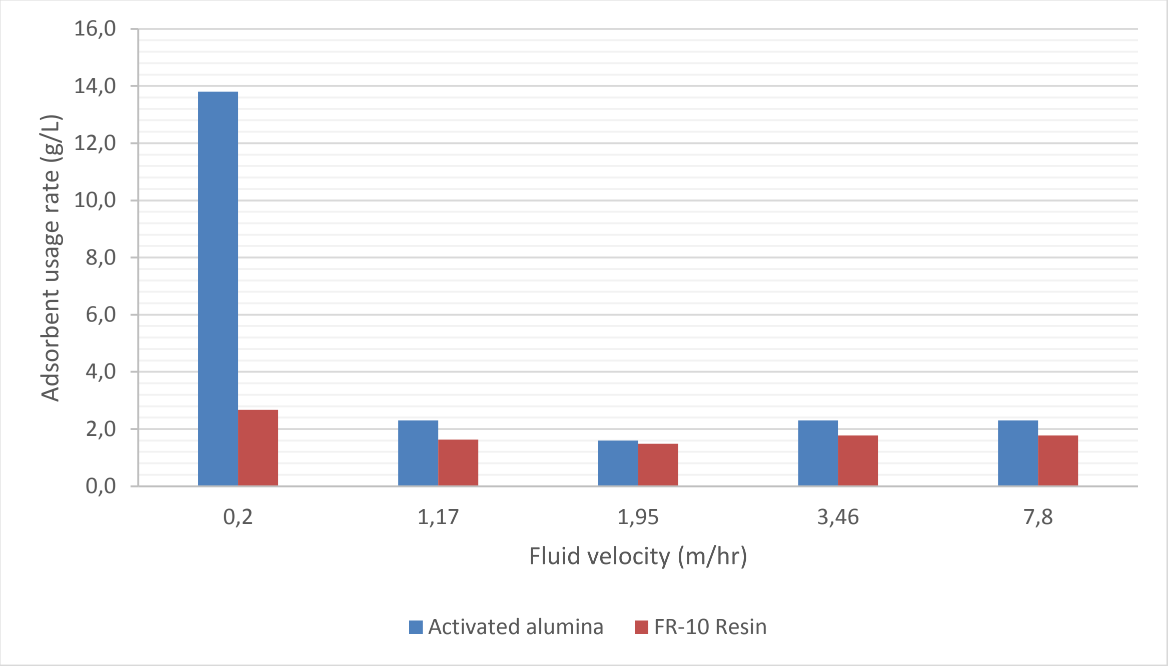


Figure 4.7: Comparison of activated alumina and FR-10 resin on adsorbent usage rate when velocity is varied

The observed trend is that a lower adsorbent usage rate is achieved with an increase in velocity. However beyond the velocity of 1.95m/hr, the adsorbent usage rate begins to increase. Also observed is lower adsorbent usage rate with FR-10 resin compared to activated alumina. The results confirm that better performance is achieved with an increase in velocity. The velocity of 1.95 is the optimum velocity since beyond this velocity, the performance begins to deteriorate. The results also confirms that FR-10 resin performs better compared to activated alumina

Summary of results

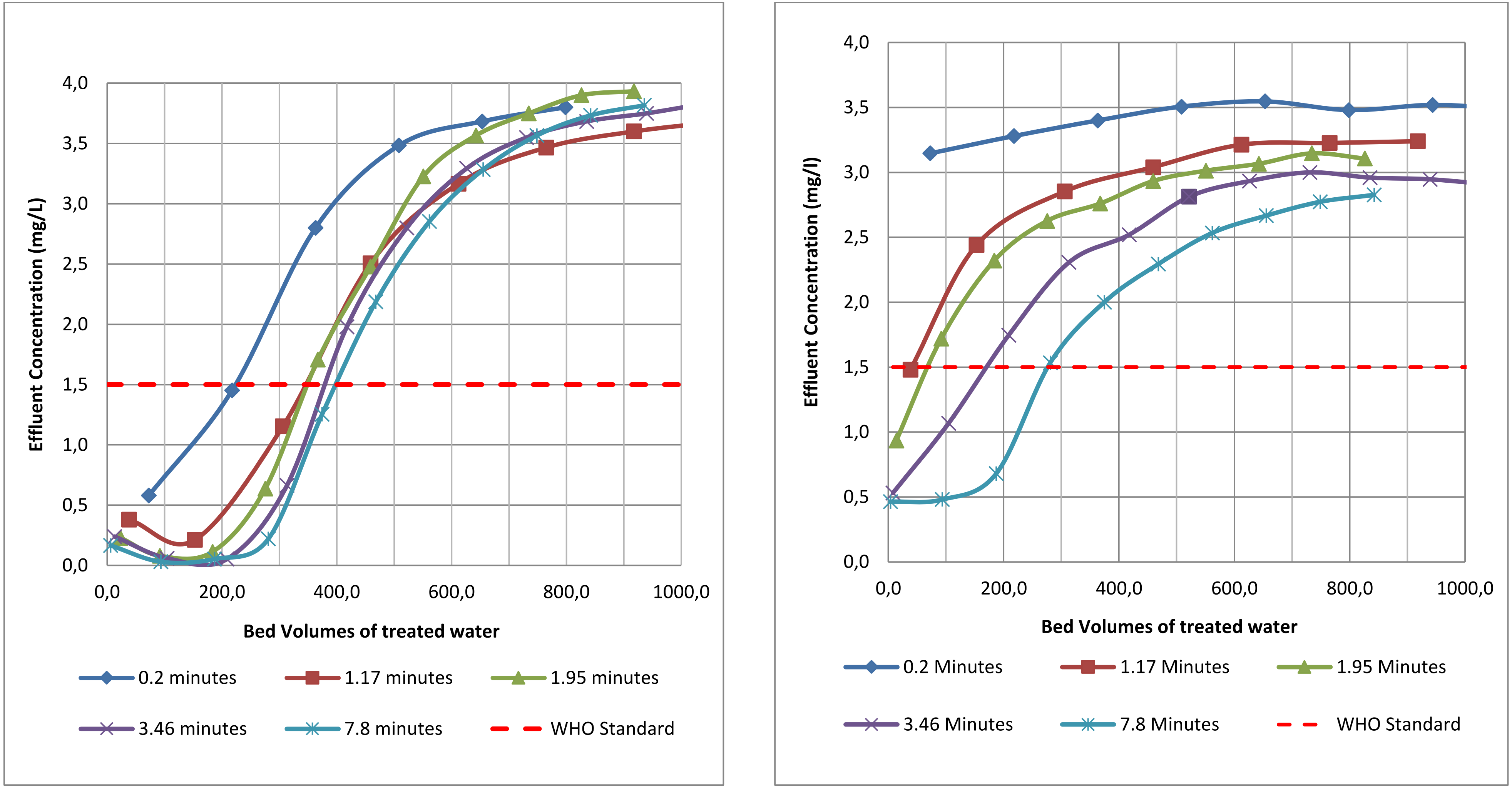
From this investigation, it was observed that with an increase in velocity, fluoride removal improved in both adsorption media. There is however a maximum velocity beyond which the performance began to deteriorate. This maximum velocity was found to be 1.95 m/hr for both adsorption media. The performance parameter used indicated that FR-10 resin performed better than activated alumina in terms of bed volumes of treated water at breakthrough as well as adsorbent usage rate. High bed volume of treated water and less amount of FR-10 was used at breakthrough.

It was also found that all the velocities provided better performance with FR-10 resin, yet with activated alumina very low bed volumes of treated water was obtained at the lowest velocity used. This means that FR-10 resin can accommodate a wider range of velocity. It was then concluded that based on fluid velocity, FR-10 resin was a better adsorbent for fluoride removal.

4.6 Effect of contact time on fluoride adsorption by FR-10 resin and activated alumina

This section presents results obtained from an investigation conducted to compare the performance of FR-10 resin and activated alumina under the condition of varying contact time. The condition for this investigation is shown in Table 3.3. The contact time variation in the adsorption column is caused by variation in system static head.

The results of this investigation are shown in Figure 4.8. Shown are breakthrough curves obtained when contact time was varied while running with activated alumina as well as FR-10 resin. The breakthrough curves show the column effluent concentration against bed volumes of treated water for the different contact times investigated.



A B

Figure 4.8: Effect of contact time on fluoride removal by FR-10 Resin (A) and activated alumina (B)

Results of both adsorbents indicate that the column performance improves with an increase in contact time. This is shown by shaper breakthrough curves when contact time is increased. The observed breakthrough trends can be explained with the size of the mass transfer zone in the column. Short contact time does not allow the fluoride ion to migrate to the adsorption sites. This results in an undesirable long mass transfer zone, an early breakthrough and inefficient usage of the adsorbent.

With long contact times on the other hand, the time is enough for the fluoride ions to migrate to adsorption sites and be adsorbed. The mass transfer zone becomes short, resulting in delayed breakthrough, more efficient usage of the adsorbent resulting in cost savings (Slejko, 1985) and larger volume of treated water with the same amount of adsorbent.

By observation of the graphs it can be seen that the breakthrough curves for FR-10 resin is steeper compared to that of activated alumina. This means that the mass transfer zone is shorter with FR-10 resin (Slejko, 1985). The advantage of this would be even less amount of unused media achieved through using FR-10 resin compared to using activated alumina (Kratochvil and Volesky, 1998). The better performance with FR-10 resin might be caused by higher adsorption rates (Meenakshi and Maheshwari, 2006). Activated alumina on the other hand is known to have low adsorption rates (Pontius, 1990).

The results were also confirmed using the adsorbent usage rate. Table 4.3 show the bed volumes of treated water achieved with both adsorbents while the trends on adsorbent usage rate are shown in Figure 4.9. The results show a decrease in adsorbent usage rate with an increase in contact time. Also observed is lower adsorbent usage rate with FR-10 resin compared to activated alumina. This means that less adsorbent is required at higher contact time and less amount of FR-10 resin is required compared to activated alumina for the same application.

Table 4.3: Column parameters for the effect of contact time on fluoride removal by activated alumina and FR-10 resin

Empty Bed Contact Time (minutes)	Bed volume of Treated Water at breakthrough point		Adsorbent Usage Rate (g/L)	
	Activated alumina	FR-10 resin	Activated alumina	FR-10 resin
0,20	0,00	217,80		3,67
1,17	38,00	345,19	18,16	2,32
1,95	69,98	349,47	9,86	2,29
3,46	170,93	379,54	4,04	2,11
7,80	281,00	399,14	2,46	2,00

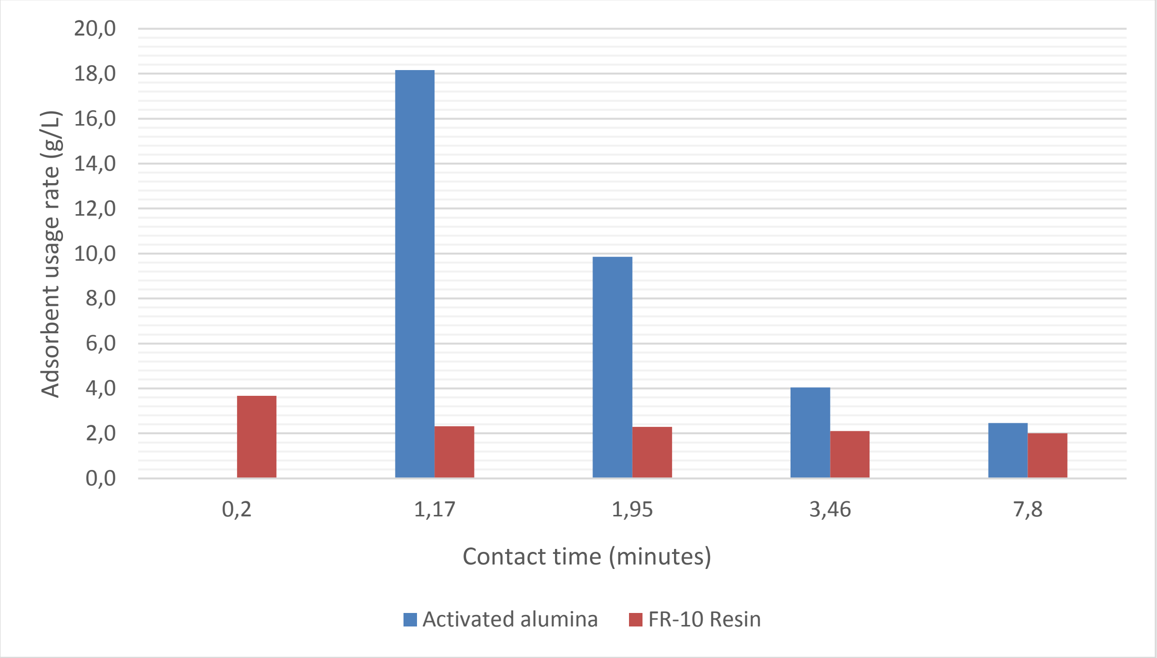


Figure 4.9: Comparison of activated alumina and FR-10 resin on adsorbent usage rate when contact time is varied

A study similar to the current study was conducted by Ghorai and Pant (2004). In their study, the effect of flow rate on fluoride removal by activated alumina was investigated. It was found that with an increase in flow rate from 20 to 30 ml/min, the breakthrough time was reduced and fluoride removal was also reduced from 92 percent to 86 percent. This was attributed to a reduced contact time at higher flow rates.

The study however did not consider the fact that with an increase in flow rate the velocity in the column also increases. The increase in column velocity creates turbulence, which reduces mass transfer resistance and result in improved performance.

Summary of results

From this investigation, it was observed that there is better performance with an increase in contact time. There was no maximum contact time observed within the range investigated. FR-10 resin provided good performance with the range of contact time investigated. Activated alumina on the other hand provided treated water not meeting drinking water standards at low contact time. The breakthrough curves obtained with FR-10 resin was found to be steeper compared to that of activated alumina. This indicated faster adsorption rate which may results in smaller treatment systems and savings on capital cost.

The better performance with FR-10 resin was confirmed using two parameters which were the bed volumes of treated water at breakthrough as well as the adsorbent usage rate. From the results of this investigation it can be concluded that based on contact time, FR-10 resin is a better adsorbent for fluoride removal.

4.7 Effect of pressure drop on column operation

Presented here are the results of an investigation of the effect of pressure drop on column operation. Shown in Figure 4.10 is a relationship between pressure drop and fluid velocity for both activated alumina as well as FR-10 resin. The observed trend is that column head loss increases with an increase in fluid velocity. There is higher pressure drop with FR-10 resin compared to activated alumina. It can also be observed that the Ergun equation predicts pressure drop better with activated alumina. It however fails with FR-10 resin.

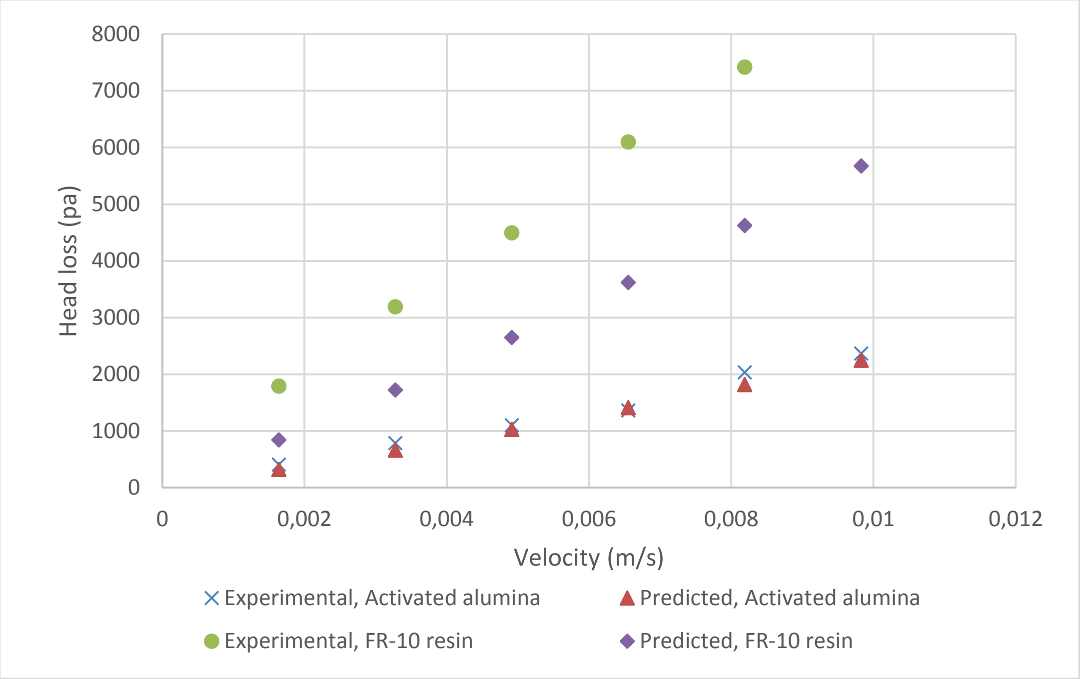


Figure 4.10: Effect of velocity variation on column pressure drop

The increase in pressure drop with an increase in velocity was expected as there is more resistance to flow with increasing velocity. The purpose was however to see if one of the media will have excessive head loss which might affect the operation of the system, since the system is gravity driven. The steeply increasing pressure drop with an increase in velocity when using FR-10 resin means that the operation or the design of the system might be limited by the pressure drop. To accommodate the excessive pressure drop it would mean designing taller columns or running the system only at low velocities. This condition might cause the system not to be operated easily.

The difference in the pressure drop might be caused by the fact that the particle sizes were not the same. Activated alumina was slightly bigger than FR-10 resin. It was 1-2 mm for activated alumina while it was 0.3-1.2 mm for FR-10 resin. This causes the void fraction of FR-10 resin to be slightly smaller, resulting in a higher pressure drop.

The high predicted pressure drop compared to measured pressure drop when using FR-10 resin may also be caused by the particle relative roughness. This particle parameter is not factored in the Ergun equation. Even though Macdonald *et al.* (1979) suggested that the Ergun inertial constant must be changed to 1.8 for smooth pipes and 4 for rough pipes, these constants are however not related to any parameter showing relative roughness. Their use is therefore inaccurate (Nemec *et al.*, 2005).

Summary of results

The results showed that there is an excessive increase in pressure drop when FR-10 resin is used compared to activated alumina when fluid velocity is increased. It was also found that the Ergun equation predicts pressure drop better with activated alumina compared to FR-10 resin. The investigation concluded that based on pressure drop activated alumina is a better adsorbent.

Table 4.4 provides a summary of the performance comparison of the two adsorbents against the set criteria.

Table 4.4: Comparison of the two adsorbents against set criteria

Criteria	**Comparison**	**Best adsorbent**
Cost	FR-10 resin is not available locally. It has to be imported from countries such as India. The total cost of the media includes purchasing the adsorbent as well as transporting it. On the other hand the purchasing cost of activated alumina is lower. The fact that it is locally available means that it is more affordable compared to FR-10 Resin	Activated alumina
Ease of use	FR-10 resin has no safety and health hazards associated with its handling. However the media cannot be used once it has dried. It must also be always kept in the shade, at a temperature between 20 to 40°C. Even though the design of the system can be such that the resin is immersed in water all the time, leaks in the column during off periods can cause the media to be dry. Activated alumina on the other hand has no safety or health issue. It is completely safe and easy to use. Drying up of the media does not affect its performance.	Activated alumina
Adsorption capacity	When comparing activated alumina and FR-10 resin based on adsorption capacity, the equilibrium experimental data obtained under the same conditions indicates that at the same equilibrium concentration, FR-10 resin has higher adsorption capacity.	FR-10 Resin
Effect of contact time on fluoride removal	Good performance was observed with FR-10 resin in all the contact times investigated. The drinking water standard were met, more treated water was obtained and there was more efficient usage of the media. Activated alumina on the other hand did not produce water meeting drinking water standard at low contact times. Lesser amount of water was obtained with less efficient usage of adsorbent.	FR-10 Resin
Effect of velocity on fluoride removal	The results indicated that there are higher bed volumes of treated water with FR-10 resin compared to activated alumina. The performance of FR-10 resin is not affected much by the variation in fluid velocity. This means it can easily accommodate the systems varying velocity which emanates from the varying system static head.	FR-10 Resin
Effect of pressure drop	Pressure drop was found to be high when running the adsorption column with FR-10 resin. The high pressure drop means that tall columns are required for the system. Activated alumina on the other hand showed low pressure drop even at high fluid velocity. This allows the use of shorter columns which is user friendly for the end user.	Activated alumina

4.8 Selected adsorbent

From the above comparison FR-10 resin was found to perform better in adsorption capacity, effect of contact time and effect of velocity on fluoride removal. Activated alumina on the other hand performed better on costs, ease of use as well as pressure drop. Based on the specified criteria the adsorbent performed equally.

FR-10 resin outperformed activated alumina on fluoride removal. However the performance of activated alumina on fluoride removal can be improved in point of use systems through intermittent operation (Pontius, 1990) while it will not be easy to improve FR-10 resin on cost, ease of use as well as pressured drop.

Slow kinetics is the main factor that causes poor performance of activated alumina on fluoride removal. With intermittent operation, the adsorbent gets more time to adsorb fluoride at the time when it is not run resulting in more treated water produced. Activated alumina was therefore the selected adsorbent for the system.

4.9 Summary of the adsorption system and operation regime

The adsorption capacity of adsorbent selected for the system was 1.53 mg/g. The system should operate at a minimum contact time of 3.46 minutes, velocity range between 1.17 and 7.8 m/hour. The pressure drop will have minimal effect on the operation of the system.

4.10 Adsorption column design

The amount of adsorbent required was determined based on the adsorption capacity of activated alumina as well as the volume of treated water before regeneration is required. The system was designed for a run time of 1 week before regeneration and a feed concentration of 10 mg/l. The total volume of water to be treated per week was based on the estimate that 20 L of water will be treated per day. For one week, the total volume is 140 L. The amount of fluoride to be removed on the 140 L of water was found to be 1400 g. The amount of activated alumina required to remove this amount of fluoride was 915 g.

The required column size was determined through an iteration procedure where the column diameter was assumed. The minimum and maximum velocities were then calculated to see if they were within the required range of 1.17 to 7.8 m/hr. The optimum standard size was found to be 75 mm outside diameter with an inside diameter of 71 mm. This column size gave a minimum velocity of 1.278 m/hr and maximum velocity of 6.389 m/hr.

The required media volume was found using the mass of the media as well as the bulk density. The media volume was found to be 0.001m^3. Using the media volume and the column size, the height of the media was determined to be 0.4m. Sample calculations for the design of the system are presented in appendix K.

Chapter 5. Conclusions and recommendations

5.1 Conclusion

The comparison of WFMFGF against existing small water treatment systems for rural areas found that the WFMFGF is superior based on the set criteria. It is therefore suitable for use as a pre-treatment device for the fluoride removal unit. It is easy to use, provides acceptable quantity of water, can remove a wide range of impurities and is cost effective. The investigation conducted on the WFMFGF found that it has flow rates ranging from 5 to 100 litres per hour. This was required information for the design of the fluoride removal unit.

It was also found that the WFMFGF can be used for more than a month providing 20 litres of water per hour operated once per day. This is sufficient for cooking and drinking for a household of five members. The use of the system beyond that does not provide sufficient quantity of water. It therefore requires cleaning. The investigation of the best cleaning method found that filling the system with water, adding 300 ml of 3 percent sodium hypochlorite (Jik), soaking overnight and then brushing the membranes is sufficient in cleaning the system and recovering the initial system flux.

The assessment of available technologies for fluoride removal found that adsorption is the best method for rural water application. It is easy to use, affordable and has a proven record of being applicable and acceptable in rural areas. Among the available sorbents, activated alumina and FR-10 were selected for suitability in the fluoride removal system being developed. The selection was mainly influenced by their high selectivity for fluoride and the fact that the use of activated alumina for fluoride removal is very well established.

FR-10 resin out performed activated alumina on adsorption capacity, the effect of velocity variation and effect of contact time variation. The resin was found to perform well amidst these variations in the system. Activated alumina performed better when it comes to accommodating pressure drop variation. It is more affordable and is better to use when it comes to handling requirements as well as robustness. Since performance of activated alumina in terms of fluoride removal can be improved it was decided that activated alumina is the best adsorbent for the system.

The adsorption system was designed to run for a week before regeneration. The required amount of media was 915 g. The optimum column diameter was found to be 75 mm outside diameter with 71 mm inside diameter. The volume of the media in the column was 0.001 m^3 and the bed height was 0.4 m.

5.2 Recommendations

After the membranes have been washed using sodium hypochlorite there may be residual chlorine at the beginning of treatment mode that might affect the operation of the adsorption column. The chlorine would occupy the adsorption sites and reduce the adsorption capacity of the adsorbent. Further investigation is required to find the suitability of membrane effluent from being fed to the adsorption column immediately after the membrane has been washed with sodium hypochlorite.

The treatment system has shown good performance in the laboratory set up using simulated feed water. Further work needs to be done in the field to assess its performance on real water contaminated by fluoride at the source. The system also needs to be accessed on usability and acceptance by the user.

The adsorption media can be reused after exhaustion if it can be regenerated. Activated alumina is commonly regenerated using sodium hydroxide solution followed by acidification with sulphuric or hydrochloric acid. Such chemicals may be hazardous to unskilled and under resourced people in rural areas. Other methods of regeneration need to be investigated for this application.

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Appendices

Appendix A: Physical properties of activated alumina and FR-10 resin

Table A-1: Physical Properties for KA-402 grade activated alumina and FR-10 resin as provided by suppliers

Media	**Appearance**	**Chemical composition**			**Bulk Density g/ml**	**Surface Area m^2/g**	**Pore Volume ml/g**	**Attrition loss percent**	**Particle size (mm)**
		AlO_3 percent	Na_2O percent	SiO_2 percent					
Activated Alumina	White, Spear, No Ordor, Insoluble in water	≥93	≤0,3	≤0,1	0,69	320	0,45	<1	1-2
FR-10 Resin.	Translucent golden yellow to brown beads	-	-	-	0.81	-	0.4	-	0.3-1.2

Appendix B: Sample calculation for preparation of feed water for fluoride adsorption experiments

The preparation of the feed solution involved calculation of the volume of 2000 ppm stock solution that was to be diluted into 80 L of water to have 4ppm solution. The calculation of the stock volume was done as follows:

$$V_1 = \frac{C_2 V_2}{C_1} \qquad \text{(B-1)}$$

$$V_1 = \frac{4\,mg \times 80\,L}{2000\,mg} \times \frac{1000\,mL}{1\,L}$$

$$V_1 = 160 ml$$

The same approach was used in determination of the volume of stock solution required feed solutions for the equilibrium studies. Here different feed concentrations were prepared. The prepared concentrations were 15 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm, 60 ppm, 70 ppm and 80 ppm. The 2000 ppm solution was first diluted to 100 ppm in a 1L using equation (B-1) as follows:

$$V_1 = \frac{100\,mg/L \times 1\,L}{2000\,mg/L} \times \frac{1000\,mL}{1\,L}$$

$$V_1 = 50 ml$$

The range of concentrations used in the equilibrium studies was prepared using a stock solution having fluoride concentration of 100 ppm. The volume of the stock solution used to prepare 15 ppm in a 0.5 L beaker was calculated using equation (B-1) as follow:

$$V_1 = \frac{15\,mg/L \times 0.5\,L}{100\,mg/L} \times \frac{1000\,mL}{1\,L}$$

$$V_1 = 75 ml$$

Using the above equation the volume of 50 ppm stock solution required to prepare the different feed concentrations were 100 ml for 20 ppm, 150 ml for 30 ppm, 200 ml for 40 ppm, 250 ml for 50 ppm, 300 ml for 60 ppm, 350 ml for 70 ppm and 400 ml for 80 ppm.

Appendix C: Fluoride testing procedure

The samples were collected using plastic sample bottles. The analysed were conducted immediately after collection. The spends photometric method used in this analysis has a testing range between 0 to 2 mg/L. Before the samples were analysed for fluoride, the instruments was calibrated using a 1 mg/L standard solution.

Calibration procedure

The calibration procedure is as follows:

a) Connect the DR3900 spectrophotometer to the power source and switch on.
b) Press the power button on the DR 3900 spectrophotometer to switch it on.
c) Select program 190 for fluoride measurement.
d) Use a pipet to add 10 ml of deionised water into a dry sample cell.
e) Use a pipet to add 2ml of SPANDS reagents into the sample cell.
f) Swirl the sample cells to mix.
g) Start the instrument timer and allow 1 minute reaction time.
h) When reaction time elapses, use a clean cloth to wipe the blank sample cell.
i) Insert the blank cell into the cell holder and press Zero. The display on the screen will show 0.00 mg/L.
j) Used a clean cloth to wipe the standard solution cell and insert it into the cell holder.
k) Press read and the fluoride concentration will appear in mg/L. this should read ±1mg/L.

Testing procedure

Presented here is a step by step procedure followed for fluoride measurement after calibration was done. This was done as follows:

a) Use a pipet to add 10 ml of sample to a dry sample cell.
b) Use a pipet to add 10 ml of deionised water to another dry sample cell.
c) Use a pipet to add 2 ml of SPANDS reagents into each sample cell.
d) Swirl the sample cells to mix.
e) Start the instrument timer and allow 1 minute reaction time.
f) When reaction time elapses, use a clean cloth to wipe the blank sample cell.

g) Insert the blank cell into the cell holder and press Zero. The display on the screen will show 0.00 mg/L.
h) Used a clean cloth to wipe the sample cell and insert it into the cell holder.
i) Press read and the fluoride concentration will appear in mg/L.

If a sample was found to be overage, it was diluted with known volume of deionised water and tested again. The results was then multiplied by the dilution factor.

Appendix D: Determination of the base cleaning method

Table D-1: Results of determination of the best cleaning method

Cleaning Method	Volume of pure Water collected after an hour (L)				STD Deviation	STD Error
	Run 1	**Run 2**	**Run 3**	**Average**		
Clean Membrane	24,00	24,00	25,00	24,33	0,47	0,27
Raw Water and brush	8,00	7,00	7,00	7,33	0,47	0,27
Permeate and brush	11,00	11,00	12,00	11,33	0,47	0,27
Soak in NaOCL for 6 hrs	14,00	17,00	15,00	15,33	1,25	0,72
Soak in NaOCL for 12 hrs	25,00	24,00	23,00	24,00	0,82	0,47

Appendix E: Determination of run time for the WFMFGF

Table E-1: Results of determination of the run time for the WFMFGF

Batch no	Permeate Volume(L)					
	Run 1	Run 2	Run 3	Average	STD Deviation	STD Error
1	26,40	26,03	25,70	26,04	0,29	0,17
2	25,00	25,20	25,40	25,20	0,16	0,09
3	24,20	24,30	24,00	24,17	0,12	0,07
4	21,80	22,10	21,70	21,87	0,17	0,10
5	21,50	21,40	21,58	21,49	0,07	0,04
6	21,50	21,10	21,60	21,40	0,22	0,12
7	21,00	21,60	21,40	21,33	0,25	0,14
8	21,15	21,13	21,10	21,13	0,02	0,01
9	21,13	21,10	21,12	21,12	0,01	0,01
10	20.99	20,97	21,01	20,99	0,02	0,01
11	20,80	20,64	21,10	20,85	0,19	0,11
12	20,20	21,00	20,50	20,57	0,33	0,19
13	20,65	20,65	20,00	20,43	0,31	0,18
14	20,40	20,30	20,40	20,37	0,05	0,03
15	19,50	20,73	20,73	20,32	0,58	0,33
16	20,10	19,46	19,80	19,79	0,26	0,15
17	20,10	20,50	19,20	19,93	0,54	0,31
18	19,60	20,00	20,60	20,07	0,41	0,24
19	19,50	19,80	20,10	19,80	0,24	0,14
20	20,12	20,20	18.5	20,16	0,04	0,02
21	19,60	20,80	20,10	20,17	0,49	0,28
22	20,60	20,70	19,60	20,30	0,50	0,29
23	20,20	20,00	20,80	20,33	0,34	0,20
24	19,20	20,75	20,90	20,28	0,77	0,44
25	20,50	19,30	20,50	20,10	0,57	0,33
26	20,40	20,20	19,20	19,93	0,52	0,30
27	19,90	20,20	20,20	20,10	0,14	0,08
28	19,70	19,30	19,60	19,53	0,17	0,10
29	19,80	19,30	19,20	19,43	0,26	0,15
30	18,50	19,00	19,80	19,10	0,54	0,31
31	18,50	18,00	18,70	18,40	0,29	0,17
32	18,00	18,60	17,80	18,13	0,34	0,20
33	17,50	16,80	17,80	17,37	0,42	0,24

34	15,90	16,80	17,00	16,57	0,48	0,28
35	15,40	15,60`399	15,80	15,60	0,16	0,09
36	14,60	15,00	15,30	14,97	0,29	0,17
37	14,00	14,40	14,50	14,30	0,22	0,12
38	14,00	13,70	14,10	13,93	0,17	0,10
39	13,30	13,10	13,40	13,27	0,12	0,07
40	13,50	13,00	12,60	13,03	0,37	0,21
41	12,00	12,40	12,70	12,37	0,29	0,17
42	12,60	12,00	11,30	11,97	0,53	0,31
43	10,50	11,20	10,90	10,87	0,29	0,17

Appendix F: Determination of maximum and minimum flow rate through the WFMFGF

Table F-1: Results of determination of maximum and minimum flow rate through the WFMFGF

Volume Treated (L)	**Flow Rate (l/hr)**					
	Run 1	**Run 2**	**Run 3**	**Average**	**STD deviation**	**STD Error**
2	99,2	98,1	98,7	98,7	0,4	0,3
3	75,0	75,9	75,6	75,5	0,4	0,2
4	65,8	66,5	66,9	66,4	0,5	0,3
5	61,4	61,0	62,0	61,5	0,4	0,2
6	55,0	55,8	55,2	55,3	0,3	0,2
7	50,9	51,2	51,7	51,3	0,3	0,2
8	45,9	45,4	44,9	45,4	0,4	0,2
9	40,9	40,6	41,1	40,9	0,2	0,1
10	37,4	37,8	37,7	37,6	0,2	0,1
11	33,6	33,4	33,7	33,6	0,1	0,1
12	29,7	29,6	29,4	29,6	0,1	0,1
13	25,6	25,9	25,8	25,8	0,1	0,1
14	21,9	22,0	21,8	21,9	0,1	0,0
15	20,3	19,8	20,0	20,0	0,2	0,1
16	16,2	16,8	16,6	16,5	0,2	0,1
17	15,4	15,6	15,1	15,4	0,2	0,1
18	13,8	13,7	13,9	13,8	0,1	0,0
19	13,1	12,7	12,9	12,9	0,2	0,1
20	11,4	11,6	11,3	11,4	0,1	0,1
21	9,9	9,7	9,8	9,8	0,1	0,0
22	8,1	7,9	8,0	8,0	0,1	0,0
23	6,0	6,0	6,0	6,0	0,0	0,0
24	5,0	4,8	4,9	4,9	0,1	0,0
25	4,8	4,7	4,8	4,8	0,0	0,0

Appendix G: Adsorption equilibrium results

Table G-1: Equilibrium result for fluoride removal by Activated alumina

Feed Concentration (ppm)	**Mass of AA (g)**	**Equilibrium Concentration Ce (mg/l)**					
		Run 1	**Run 2**	**Run 3**	**Average**	**STD Deviation**	**STD error**
5,00	4,00	0,96	1,01	0,90	0,96	0,04	0,03
11,00	4,00	2,20	2,40	2,00	2,20	0,16	0,09
20,00	4,00	4,48	4,64	4,80	4,64	0,13	0,08
30,00	4,00	6,88	7,04	6,72	6,88	0,13	0,08
40,00	4,00	10,56	10,24	11,04	10,61	0,33	0,19
50,00	4,00	14,56	15,20	14,24	14,67	0,40	0,23
60,00	4,00	19,20	20,80	19,20	19,73	0,75	0,44
70,00	4,00	24,60	24,00	23,50	24,03	0,45	0,26
80,00	4,00	30,40	30,88	29,76	30,35	0,46	0,26

Table G-2: Equilibrium results for fluoride removal by FR-10 resin

Feed Concentration (ppm)	**Mass of FR-10 resin (g)**	**Equilibrium Concentration Ce (mg/l)**					
		Run 1	**Run 2**	**Run 3**	**Average**	**STD Deviation**	**STD error**
5,00	4,00	0,28	0,20	0,30	0,26	0,04	0,02
11,00	4,00	0,72	0,60	0,55	0,62	0,07	0,04
20,00	4,00	1,50	1,69	1,63	1,61	0,08	0,05
30,00	4,00	3,52	3,63	3,08	3,41	0,24	0,14
40,00	4,00	5,39	5,06	4,95	5,13	0,19	0,11
50,00	4,00	7,37	7,26	7,48	7,37	0,09	0,05
60,00	4,00	9,13	10,12	9,24	9,50	0,44	0,26
70,00	4,00	11,88	12,98	11,44	12,10	0,65	0,37
80,00	4,00	16,06	15,62	17,37	16,35	0,74	0,43

Appendix H: Effect of velocity on fluoride removal

Table H-1: results of the effect of velocity on fluoride removal by FR-10 resin (0.2m/hr)

Run time (hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3	0,200	0,240	0,240	0,227	0,019	0,011	4	36
7	0,180	0,160	0,200	0,180	0,016	0,009	8	84
12	0,400	0,440	0,480	0,440	0,033	0,019	14	144
18	0,680	0,820	0,720	0,740	0,059	0,034	22	216
24	1,160	1,360	1,360	1,293	0,094	0,054	29	288
30	1,880	2,000	1,840	1,907	0,068	0,039	36	360
36	2,200	2,280	2,320	2,267	0,050	0,029	43	432
42	2,740	2,800	2,760	2,767	0,025	0,014	50	504
48	2,980	3,040	3,120	3,047	0,057	0,033	58	576
54	3,280	3,320	3,400	3,333	0,050	0,029	65	648
60	3,380	3,480	3,400	3,420	0,043	0,025	72	720
66	3,440	3,520	3,480	3,480	0,033	0,019	79	792

Table H-2: results of the effect of velocity on fluoride removal by FR-10 resin (1.2m/hr)

Run time (hrs)	**Effluent fluoride concentration (mg/L)**						**Volume treated (L)**	**BV treated**
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3	0,030	0,040	0,040	0,037	0,005	0,003	4	36
7	0,070	0,080	0,090	0,080	0,008	0,005	8	84
12	0,090	0,080	0,070	0,080	0,008	0,005	14	144
18	0,110	0,100	0,090	0,100	0,008	0,005	22	216
24	0,150	0,130	0,120	0,133	0,012	0,007	29	288
30	0,190	0,200	0,240	0,210	0,022	0,012	36	360
36	0,740	0,830	0,850	0,807	0,048	0,028	43	432
42	1,590	1,660	1,710	1,653	0,049	0,028	50	504
48	2,240	2,440	2,360	2,347	0,082	0,047	58	576
54	2,720	2,920	3,120	2,920	0,163	0,094	65	648
60	3,140	3,280	3,320	3,247	0,077	0,045	72	720
66	3,320	3,240	3,160	3,240	0,065	0,038	79	792

Table H-3: Results of the effect of velocity on fluoride removal by FR-10 resin (1.95m/hr)

Run time (hrs)	**Effluent fluoride concentration (mg/L)**						**Volume treated (L)**	**BV treated**
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3,00	0,030	0,040	0,04	0,037	0,005	0,003	3,60	36,0
7,00	0,060	0,050	0,06	0,057	0,005	0,003	8,40	84,0
12,00	0,050	0,040	0,05	0,047	0,005	0,003	14,40	144,0
18,00	0,080	0,070	0,07	0,073	0,005	0,003	21,60	216,0
24,00	0,110	0,090	0,10	0,100	0,008	0,005	28,80	288,0
30,00	0,230	0,200	0,22	0,217	0,012	0,007	36,00	360,0
36,00	0,670	0,650	0,70	0,673	0,021	0,012	43,20	432,0
42,00	1,130	1,230	1,21	1,190	0,043	0,025	50,40	504,0
48,00	1,820	1,880	1,90	1,867	0,034	0,020	57,60	576,0
54,00	2,360	2,280	2,30	2,313	0,034	0,020	64,80	648,0
60,00	2,580	2,640	2,60	2,607	0,025	0,014	72,00	720,0
66,00	2,840	2,960	2,89	2,897	0,049	0,028	79,20	792,0

Table H-4: results of the effect of velocity on fluoride removal by FR-10 resin (3.46m/hr)

Run time (hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
3,00	0,030	0,040	0,040	0,037	0,005	0,003	4	36
7,00	0,040	0,050	0,040	0,043	0,005	0,003	8	84
12,00	0,070	0,060	0,070	0,067	0,005	0,003	14	144
18,00	0,080	0,060	0,070	0,070	0,008	0,005	22	216
24,00	0,140	0,170	0,150	0,153	0,012	0,007	29	288
30,00	0,600	0,660	0,640	0,633	0,025	0,014	36	360
36,00	1,200	1,360	1,300	1,287	0,066	0,038	43	432
42,00	2,080	2,120	2,160	2,120	0,033	0,019	50	504
48,00	2,600	2,520	2,640	2,587	0,050	0,029	58	576
54,00	2,920	3,040	3,000	2,987	0,050	0,029	65	648
60,00	3,040	3,160	3,080	3,093	0,050	0,029	72	720
66,00	3,280	3,320	3,160	3,253	0,068	0,039	79	792

Table H-5: results of the effect of velocity on fluoride removal by FR-10 resin (7.8 m/hr)

Run time (hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
3,00	0,080	0,070	0,060	0,070	0,008	0,005	4	36
7,00	0,090	0,060	0,080	0,077	0,012	0,007	8	84
12,00	0,060	0,070	0,080	0,070	0,008	0,005	14	144
18,00	0,070	0,050	0,060	0,060	0,008	0,005	22	216
24,00	0,100	0,120	0,110	0,110	0,008	0,005	29	288
30,00	0,430	0,450	0,470	0,450	0,016	0,009	36	360
36,00	1,250	1,300	1,290	1,280	0,022	0,012	43	432
42,00	2,320	2,280	2,240	2,280	0,033	0,019	50	504
48,00	2,960	2,920	2,960	2,947	0,019	0,011	58	576
54,00	3,360	3,280	3,320	3,320	0,033	0,019	65	648
60,00	3,600	3,640	3,720	3,653	0,050	0,029	72	720
66,00	3,760	3,720	3,680	3,720	0,033	0,019	79	792

Table H-6: Results of the effect of velocity on fluoride removal by Activated alumina (0.2m/hr)

Run time (hrs)	**Effluent fluoride concentration (mg/L)**						**Volume treated (L)**	**BV treated**
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3	1,12	1,04	1,2	1,120	0,065	0,038	4	36
6	1,48	1,44	1,4	1,440	0,033	0,019	7	72
12	1,72	1,72	1,76	1,733	0,019	0,011	14	144
18	2,04	2	1,96	2,000	0,033	0,019	22	216
24	2,12	2,24	2,16	2,173	0,050	0,029	29	288
30	2,4	2,44	2,36	2,400	0,033	0,019	36	360
36	2,52	2,6	2,56	2,560	0,033	0,019	43	432
42	2,68	2,68	2,76	2,707	0,038	0,022	50	504
48	2,76	2,72	2,8	2,760	0,033	0,019	58	576
54	2,8	2,92	2,96	2,893	0,068	0,039	65	648
60	2,9	2,92	3	2,940	0,043	0,025	72	720
66	3,01	3,04	3,08	3,043	0,029	0,017	79	792
72	3,09	3,12	3,16	3,123	0,029	0,017	86	864
78	3,23	3,28	3,24	3,250	0,022	0,012	94	936
84	3,28	3,16	3,2	3,213	0,050	0,029	101	1008

Table H-7: Results of the effect of velocity on fluoride removal by Activated alumina (1.2m/hr)

Run time (hrs)	**Effluent fluoride concentration (mg/L)**						**Volume treated (L)**	**BV treated**
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3,000	0,41	0,44	0,43	0,43	0,01	0,01	3,60	36,00
6,000	0,60	0,48	0,52	0,53	0,05	0,03	7,20	72,00
12,000	0,75	0,80	0,80	0,78	0,02	0,01	14,40	144,00
18,000	1,12	1,08	1,08	1,09	0,02	0,01	21,60	216,00
24,000	1,32	1,40	1,36	1,36	0,03	0,02	28,80	288,00
30,000	1,64	1,60	1,60	1,61	0,02	0,01	36,00	360,00
36,000	1,84	1,76	1,72	1,77	0,05	0,03	43,20	432,00
42,000	1,88	1,92	1,92	1,91	0,02	0,01	50,40	504,00
48,000	2,04	2,12	2,12	2,09	0,04	0,02	57,60	576,00
54,000	2,24	2,36	2,32	2,31	0,05	0,03	64,80	648,00
60,000	2,44	2,48	2,48	2,47	0,02	0,01	72,00	720,00
66,000	2,56	2,60	2,56	2,57	0,02	0,01	79,20	792,00
72,000	2,73	2,76	2,76	2,75	0,01	0,01	86,40	864,00
78,000	2,79	2,92	2,92	2,88	0,06	0,04	93,60	936,00
84,000	2,87	2,92	2,88	2,89	0,02	0,01	100,80	1008,00

Table H-8: Results of the effect of velocity on fluoride removal by Activated alumina (1.95m/hr)

Run time (hrs)	**Effluent fluoride concentration (mg/L)**						**Volume treated (L)**	**BV treated**
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3,00	0,32	0,28	0,24	0,28	0,03	0,02	3,60	36,00
6,00	0,33	0,36	0,40	0,36	0,03	0,02	7,20	72,00
12,00	0,49	0,48	0,52	0,50	0,02	0,01	14,40	144,00
18,00	0,88	0,76	0,72	0,79	0,07	0,04	21,60	216,00
24,00	1,12	1,04	1,00	1,05	0,05	0,03	28,80	288,00
30,00	1,32	1,36	1,32	1,33	0,02	0,01	36,00	360,00
36,00	1,36	1,64	1,56	1,52	0,12	0,07	43,20	432,00
42,00	1,76	1,60	1,64	1,67	0,07	0,04	50,40	504,00
48,00	1,78	1,76	1,80	1,78	0,02	0,01	57,60	576,00
54,00	1,96	2,00	2,08	2,01	0,05	0,03	64,80	648,00
60,00	2,20	2,28	2,24	2,24	0,03	0,02	72,00	720,00
66,00	2,32	2,40	2,32	2,35	0,04	0,02	79,20	792,00
72,00	2,48	2,56	2,60	2,55	0,05	0,03	86,40	864,00
78,00	2,74	2,76	2,64	2,71	0,05	0,03	93,60	936,00
84,00	2,82	2,76	2,76	2,78	0,03	0,02	100,80	1008,00

Table H-9: Results of the effect of velocity on fluoride removal by Activated alumina (3.46m/hr)

Time (hrs)	**Effluent fluoride concentration (mg/L)**						**Volume treated (L)**	**BV treated**
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3,00	0,32	0,36	0,32	0,33	0,02	0,01	3,60	36,00
6,00	0,52	0,36	0,44	0,44	0,07	0,04	7,20	72,00
12,00	0,66	0,64	0,64	0,65	0,01	0,01	14,40	144,00
18,00	0,96	0,92	0,84	0,91	0,05	0,03	21,60	216,00
24,00	1,20	1,24	1,28	1,24	0,03	0,02	28,80	288,00
30,00	1,44	1,40	1,44	1,43	0,02	0,01	36,00	360,00
36,00	1,65	1,60	1,64	1,63	0,02	0,01	43,20	432,00
42,00	1,88	1,72	1,72	1,77	0,08	0,04	50,40	504,00
48,00	2,00	2,04	2,04	2,03	0,02	0,01	57,60	576,00
54,00	2,12	2,24	2,24	2,20	0,06	0,03	64,80	648,00
60,00	2,36	2,48	2,40	2,41	0,05	0,03	72,00	720,00
66,00	2,40	2,56	2,56	2,51	0,08	0,04	79,20	792,00
72,00	2,68	2,64	2,64	2,65	0,02	0,01	86,40	864,00
78,00	2,72	2,84	2,76	2,77	0,05	0,03	93,60	936,00
84,00	2,76	2,76	2,84	2,79	0,04	0,02	100,80	1008,00

Table H-10: Results of the effect of velocity on fluoride removal by Activated alumina (7.8m/hr)

Run time (hrs)	**Effluent fluoride concentration (mg/L)**						**Volume treated (L)**	**BV treated**
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
3,00	0,44	0,36	0,48	0,43	0,05	0,03	3,60	36,00
6,00	0,76	0,52	0,72	0,67	0,10	0,06	7,20	72,00
12,00	1,08	1,00	0,84	0,97	0,10	0,06	14,40	144,00
18,00	1,68	1,08	1,08	1,28	0,28	0,16	21,60	216,00
24,00	1,48	1,44	1,52	1,48	0,03	0,02	28,80	288,00
30,00	1,72	1,68	1,76	1,72	0,03	0,02	36,00	360,00
36,00	1,89	1,96	1,92	1,92	0,03	0,02	43,20	432,00
42,00	2,11	2,16	2,12	2,13	0,02	0,01	50,40	504,00
48,00	2,28	2,24	2,32	2,28	0,03	0,02	57,60	576,00
54,00	2,48	2,56	2,48	2,51	0,04	0,02	64,80	648,00
60,00	2,56	2,64	2,64	2,61	0,04	0,02	72,00	720,00
66,00	2,76	2,72	2,72	2,73	0,02	0,01	79,20	792,00
72,00	2,88	2,84	2,92	2,88	0,03	0,02	86,40	864,00
78,00	3,08	2,96	2,96	3,00	0,06	0,03	93,60	936,00
84,00	3,10	2,96	2,96	3,01	0,07	0,04	100,80	1008,00

Appendix I: Effect of contact time on fluoride removal

Table I-1: Results of the effect of contact time on fluoride removal by FR-10 Resin (0.2 minutes)

Run time (hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	Average	STD Deviation	STD Error		
0,25	0,50	0,66	0,58	0,58	0,07	0,04	7,26	72,60
0,75	1,32	1,60	1,44	1,45	0,11	0,07	21,78	217,80
1,25	2,85	3,00	2,55	2,80	0,19	0,11	36,30	363,00
1,75	3,45	3,40	3,60	3,48	0,08	0,05	50,82	508,20
2,25	3,60	3,70	3,75	3,68	0,06	0,04	65,34	653,40
2,75	3,65	3,85	3,90	3,80	0,11	0,06	79,86	798,60

Table I-2: Results of the effect of contact time on fluoride removal by FR-10 Resin (1.2 minutes)

Run time (Hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	Average	STD Deviation	STD Error		
0,75	0,14	0,66	0,34	0,38	0,21	0,12	3,83	38,25
3,00	0,26	0,19	0,19	0,21	0,03	0,02	15,30	153,00
6,00	1,24	1,11	1,11	1,15	0,06	0,04	30,60	306,00
9,00	2,44	2,60	2,48	2,51	0,07	0,04	45,90	459,00
12,00	3,15	3,25	3,10	3,17	0,06	0,04	61,20	612,00
15,00	3,65	3,45	3,30	3,47	0,14	0,08	76,50	765,00
18,00	3,60	3,50	3,70	3,60	0,08	0,05	91,80	918,00
21,00	3,55	3,85	3,65	3,68	0,12	0,07	107,10	1071,00

Table I-3: Results of the effect of contact time on fluoride removal by FR-10 Resin (1.95 minutes)

Run time (Hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
0,00	0,00						0,00	0,00
0,75	0,25	0,24	0,20	0,23	0,02	0,01	2,30	22,95
3,00	0,09	0,07	0,08	0,08	0,01	0,00	9,18	91,80
6,00	0,10	0,13	0,11	0,11	0,01	0,01	18,36	183,60
9,00	0,62	0,65	0,64	0,64	0,01	0,01	27,54	275,40
12,00	1,76	1,64	1,72	1,71	0,05	0,03	36,72	367,20
15,00	2,56	2,40	2,48	2,48	0,07	0,04	45,90	459,00
18,00	3,24	3,16	3,28	3,23	0,05	0,03	55,08	550,80
21,00	3,60	3,45	3,65	3,57	0,08	0,05	64,26	642,60
24,00	3,70	3,90	3,65	3,75	0,11	0,06	73,44	734,40
27,00	3,95	3,90	3,85	3,90	0,04	0,02	82,62	826,20
30,00	3,95	3,95	3,90	3,93	0,02	0,01	91,80	918,00

Table I-4: Results of the effect of contact time on fluoride removal by FR-10 Resin (3.46 minutes)

Run time (Hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
0,00	0,00						0,00	0,00
0,75	0,16	0,28	0,28	0,24	0,06	0,03	1,31	13,05
6,00	0,02	0,08	0,08	0,06	0,03	0,02	10,44	104,40
12,00	0,04	0,06	0,06	0,05	0,01	0,01	20,88	208,80
18,00	0,65	0,67	0,67	0,66	0,01	0,01	31,32	313,20
24,00	1,94	2,00	2,00	1,98	0,03	0,02	41,76	417,60
30,00	2,64	2,88	2,88	2,80	0,11	0,07	52,20	522,00
36,00	3,40	3,28	3,20	3,29	0,08	0,05	62,64	626,40
42,00	3,55	3,60	3,50	3,55	0,04	0,02	73,08	730,80
48,00	3,75	3,65	3,65	3,68	0,05	0,03	83,52	835,20
54,00	3,90	3,75	3,60	3,75	0,12	0,07	93,96	939,60
60,00	3,95	3,85	3,70	3,83	0,10	0,06	104,40	1044,00

Table I-5: Results of the effect of contact time on fluoride removal by FR-10 Resin (7.8 minutes)

Time (min)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
0,75	0,21	0,13	0,16	0,17	0,03	0,02	0,59	5,85
12,00	0,02	0,03	0,04	0,03	0,01	0,00	9,36	93,60
24,00	0,02	0,12	0,02	0,05	0,05	0,03	18,72	187,20
36,00	0,12	0,44	0,10	0,22	0,16	0,09	28,08	280,80
48,00	1,28	1,28	1,20	1,25	0,04	0,02	37,44	374,40
60,00	2,12	2,24	2,20	2,19	0,05	0,03	46,80	468,00
72,00	2,84	2,80	2,92	2,85	0,05	0,03	56,16	561,60
84,00	3,20	3,40	3,25	3,28	0,08	0,05	65,52	655,20
96,00	3,65	3,50	3,55	3,57	0,06	0,04	74,88	748,80
108,00	3,65	3,80	3,75	3,73	0,06	0,04	84,24	842,40
120,00	3,85	3,95	3,65	3,82	0,12	0,07	93,60	936,00

Table I-6: Results of the effect of contact time on fluoride removal by activated alumina (0.2 minutes)

Run time (hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
0,25	3,12	3,20	3,12	3,15	0,04	0,02	7	73
0,75	3,20	3,36	3,28	3,28	0,07	0,04	22	218
1,25	3,36	3,44	3,40	3,40	0,03	0,02	36	363
1,75	3,48	3,60	3,44	3,51	0,07	0,04	51	508
2,25	3,44	3,72	3,48	3,55	0,12	0,07	65	653
2,75	3,48	3,52	3,44	3,48	0,03	0,02	80	799
3,25	3,44	3,60	3,52	3,52	0,07	0,04	94	944
3,75	3,52	3,52	3,44	3,49	0,04	0,02	109	1089
4,25	3,48	3,60	3,52	3,53	0,05	0,03	123	1234

Table I-7: Results of the effect of contact time on fluoride removal by activated alumina (1.17 minutes)

Run time (hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
0,75	1,36	1,36	1,72	1,48	0,17	0,10	3,83	38,25
3,00	2,44	2,52	2,36	2,44	0,07	0,04	15,30	153,00
6,00	2,80	3,00	2,76	2,85	0,10	0,06	30,60	306,00
9,00	2,96	3,16	3,00	3,04	0,09	0,05	45,90	459,00
12,00	3,12	3,36	3,16	3,21	0,10	0,06	61,20	612,00
15,00	3,20	3,28	3,20	3,23	0,04	0,02	76,50	765,00
18,00	3,12	3,28	3,32	3,24	0,09	0,05	91,80	918,00

Table I-8: Results of the effect of contact time on fluoride removal by activated alumina (1.95 minutes)

Time (hrs)	Effluent Fluoride Concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	Run 2	Run 3	AVG	STD Deviation	STD Error		
0,45	0,88	0,84	1,08	0,93	0,10	0,06	1,38	13,77
3,00	1,76	1,72	1,68	1,72	0,03	0,02	9,18	91,80
6,00	2,12	2,36	2,48	2,32	0,15	0,09	18,36	183,60
9,00	2,52	2,64	2,72	2,63	0,08	0,05	27,54	275,40
12,00	2,60	2,84	2,84	2,76	0,11	0,07	36,72	367,20
15,00	2,76	3,00	3,04	2,93	0,12	0,07	45,90	459,00
18,00	2,96	3,08	3,00	3,01	0,05	0,03	55,08	550,80
21,00	2,92	3,12	3,16	3,07	0,10	0,06	64,26	642,60
24,00	2,96	3,20	3,28	3,15	0,14	0,08	73,44	734,40
27,00	2,92	3,16	3,24	3,11	0,14	0,08	82,62	826,20

Table I-9: Results of the effect of contact time on fluoride removal by activated alumina (3.46 minutes)

Time (hrs)	Effluent fluoride concentration (mg/L)						Volume treated (L)	BV treated
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**	**STD Error**		
0,45	0,44	0,60	0,55	0,53	0,07	0,04	0,78	7,83
6,00	1,00	1,20	1,00	1,07	0,09	0,05	10,44	104,40
12,00	1,60	1,76	1,88	1,75	0,11	0,07	20,88	208,80
18,00	2,28	2,20	2,44	2,31	0,10	0,06	31,32	313,20
24,00	2,36	2,60	2,60	2,52	0,11	0,07	41,76	417,60
30,00	2,72	2,88	2,84	2,81	0,07	0,04	52,20	522,00
36,00	2,88	3,00	2,92	2,93	0,05	0,03	62,64	626,40
42,00	3,04	3,08	2,88	3,00	0,09	0,05	73,08	730,80
48,00	2,92	3,04	2,92	2,96	0,06	0,03	83,52	835,20
54,00	2,52	3,16	3,16	2,95	0,30	0,17	93,96	939,60
60,00	2,56	3,04	3,12	2,91	0,25	0,14	104,40	1044,00

Table I-10: Results of the effect of contact time on fluoride removal by activated alumina (7.8 minutes)

Time (hrs)	Effluent fluoride concentration(mg/L)						Volume treated (L)	BV treated
	Run 1	**Run 2**	**Run 3**	**AVG**	**STD Deviation**			
0,45	0,32	0,64	0,43	0,46	0,13	0,08	0,35	3,51
12,00	0,44	0,48	0,52	0,48	0,03	0,02	9,36	93,60
24,00	0,64	0,56	0,84	0,68	0,12	0,07	18,72	187,20
36,00	1,56	1,52	1,52	1,53	0,02	0,01	28,08	280,80
48,00	1,64	2,08	2,28	2,00	0,27	0,15	37,44	374,40
60,00	2,20	2,32	2,36	2,29	0,07	0,04	46,80	468,00
72,00	2,60	2,40	2,60	2,53	0,09	0,05	56,16	561,60
84,00	2,76	2,56	2,68	2,67	0,08	0,05	65,52	655,20
96,00	2,76	2,72	2,84	2,77	0,05	0,03	74,88	748,80
108,00	2,88	2,80	2,80	2,83	0,04	0,02	84,24	842,40

Appendix J: Effect of velocity on pressure drop

Table J-1: Effect of velocity on pressure drop on activated alumina

Flow rate (l/hr)	Column Velocity, (m/s)	Measured Head loss (Pa)						Calculated head loss by Ergun equation (Pa)
		Run 1	**Run 2**	**Run 3**	**Average**	**STD Deviation**	**STD Error**	
6	1,6E-03	441,45	392,4	392,4	408,75	23,12	13,35	320,75
12	3,3E-03	784,8	833,85	735,75	784,8	40,05	23,12	663,05
18	4,9E-03	1128,15	1098,72	1079,1	1101,99	20,16	11,64	1026,89
24	6,6E-03	1373,4	1324,35	1393,02	1363,59	28,88	16,67	1412,28
30	8,2E-03	2030,67	2011,05	2060,1	2033,94	20,16	11,64	1819,21
36	9,8E-03	2334,78	2364,21	2403,45	2367,48	28,13	16,24	2247,68

Table J-2: Effect of velocity on pressure drop on FR-10 resin

Q (l/hr)	Column Velocity, (m/s)	Measured Head loss (Pa)						Calculated head loss by Ergun equation (Pa)
		Run 1	**Run 2**	**Run 3**	**Average**	**STD Deviation**	**STD Error**	
6	1,6E-03	1814,85	1765,8	1795,23	1791,96	20,16	11,64	841,628
12	3,3E-03	3188,25	3207,87	3168,63	3188,25	16,02	9,25	1725,085
18	4,9E-03	4512,6	4463,55	4502,79	4492,98	21,19	12,24	2650,372
24	6,6E-03	6092,01	6082,2	6121,44	6098,55	16,67	9,63	3617,488
30	8,2E-03	7435,98	7416,36	7396,74	7416,36	16,02	9,25	4626,434
36	9,8E-03	3,111						5677,208

Appendix K: Adsorption column design

Determination of amount of adsorbent required

The amount of fluoride to be removed on the on the 140 L of water was found from the following equation:

$$Amount\ of\ \ fluorideto\ be\ removed = C_oV \tag{K-1}$$

$$= 10mg / L \times 140L$$

$$= 1400mg\ of\ \ fluoride$$

The amount of activated alumina required was then determined as follows:

$$Mass\ of\ activated\ alu\min a\ = \frac{Amount\ of\ \ fluoride\ removed}{adsorption\ capacity} \tag{K-2}$$

$$= \frac{1400\,mg}{1.53\,mg/g}$$

$$= 915g$$

The volume of the media was determined as follows:

$$Volume\ \ of\ the\ media = \frac{Mass\ of\ \ the\ media}{bulk\ \ density\ \ of\ \ the\ \ media} \tag{K-3}$$

$$= \frac{915\,g}{1000 \times 690\,g/l}$$

$$= 0.001m^3$$

Column size

By iteration procedure the optimum standard size was found to be 75 mm outside diameter with an inside diameter of 71 mm. The following minimum and maximum velocity were calculated and found to be within the range of 1.17 to 7.8 m/hr.

The minimum velocity was found as follows:

$$u_{\min} = \frac{4Q}{\pi d_c{}^2} \qquad \text{(K-4)}$$

$$u_{\min} = \frac{4 \times 5l / hr}{3.14 \times 1000 \times 0.071m^2}$$

$$= 1.278m / hr$$

The maximum velocity was found using equation (K-4) as follows:

$$u_{\min} = \frac{4 \times 25l / hr}{3.14 \times 1000 \times 0.071m^2}$$

$$= 6.389m / hr$$

The bed height was determined as follows:

$$H = \frac{4V}{\pi D^2} \qquad \text{(K-5)}$$

$$= \frac{4 \times 0.001}{\pi \times 0.071^2}$$

$$= 0.4m$$

Table K-1 Show the design of the fluoride adsorption column using activated alumina as the adsorption media. Highlighted are the optimum parameters.

Table K-1: Design of the fluoride adsorption column

Parameters	**Values**				
Feed Concentration (mg/l)	10				
Minimum Design Flow Rate (l/hr)	5	5	5	5	5
Maximum Design Flow Rate (l/hr)	100	80	60	40	25
Run time before cleaning (days)	7	7	7	7	7
Operating hour per day	1	1	1	1	1
Volume treated per hour (l)	20	20	20	20	20
Total volume treated per week (l)	140	140	140	140	140

Amount of fluoride to be removed (mg)	1400	1400	1400	1400	1400
Required amount of adsorbent (g)	1076,92	1076,92	1076,92	1076,92	1076,92
Contact Time					
Volume of Bed (L)	1,561	1,561	1,561	1,561	1,561
minimum contact time (min)	0,936	1,171	1,561	2,341	3,746
maximum contact time (min)	18,729	18,729	18,729	18,729	18,729
Column size					
Column Diameter (mm)	35,400	45,600	70,600		
Minimum Velocity (m/hr)	5,083	3,063	1,278		
Maximum Velocity (m/hr)	25,413	15,316	6,389		
Bed Height (m)	1,587	0,956	0,399		