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TOPIC : *The removal of fluoride from ground water of rural areas of North West Province by using adsorption (natural adsorbents) and membrane techniques.*

Thesis submitted in fulfilment of the requirements for the degree of Master of Science in the Department of Chemistry in the faculty of Agriculture, Science and Technology at the University of North West.

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ACKNOWLEDGEMENTS

My sincere acknowledgements are directed to the following:

- My supervisors Mr. M. Hlophe, and Dr. D. Isabirye for the support and guidance they offered throughout the study.

- The Membrane Science and Technology group (PU for CHE) for the help and assistance they offered,

- Dr. L. R. Tiedt from the Laboratory For Electron Microscopy of Potchefstroom University for Christian Higher Education (PU for CHE) for Scanning Electron Microscopy (SEM),

- The Department of Mechanical and Material Science Engineering of PU for CHE for the nitrogen (N_2) adsorption / desorption equipment,

- National Research Foundation (NRF) and (PU for CHE) Potchefstroom University for Christian Higher Education for financial assistance,

- University of North West (UNW) and (PU for CHE) for giving me the opportunity to pursue my studies,

- My family and friend (Motshidisi) for being a source of inspiration and encouragement through thick and thin, and
- To God for everything.

gaopalelwe malefo.

ABSTRACT

Flourine, a fairly common element on the earth's crust, is present in the form of fluorides in a number of minerals and many rocks. The routes of human exposure to fluorides are essentially through drinking water and food. Fluoride ingested in water is almost completely absorbed while in the diet is not as fully absorbed. Absorbed flouride is distributed rapidly throughout the body and is mainly retained in the skeleton with a small portion in the teeth.

While traces of flouride occur in many waters, high concentrations are often associated with ground waters of rural areas.

The World Health Organisation (WHO) standards permits only 1 *mg/l* as a safe limit for human consumption. More than 1 *mg l* of fluoride in drinking water can cause a damage to teeth in a condition called chronic dental fluorosis (mottling of teeth) which is common in S.A standards. High doses of fluoride also interfere with calcium metabolism, kidney action, and with action of other glands and tissues. Since this cause an unease feeling on the dental wellbeing and health of individuals, there is a need to bring these high concentrations to acceptable limits.

The main objective of this project is to bring the high concentrations of fluoride in drinking water below 1 *mg l*. The defluoridation process should be effective, affordable, and easy to operate. The process should also be adapted at both domestic and community level.

LAYOUT OF THE THESIS

CHAPTER 1 explains the background of the project, the defluoridation technique used and the objectives of the study.

CHAPTER 2 is a literature review dealing with the background of ground water and fluoride, and the effect of fluoride in ground water. The traditional techniques used for water defluoridation are also discussed with their disadvantages leading to the suggested methods namely adsorption and membrane techniques. Under membrane technique, two types of membrane processes are used, that is, nanofiltration and reverse osmosis. The membranes that were used are NF 70 and TFC-SR. Under adsorption technique, the natural adsorbents namely, activated charcoal, charwood, and charcoal (coal) were used. Also chitosan and maize cob were used but no further experiment was done on them since they turned out to be poor adsorbents of fluoride.

CHAPTER 3 explains the characterisation techniques by SEM (Scanning Electron Microscopy), EDS (Energy Dispersive Spectrometry), and N_2 Adsorption / Desorption. The adsorption process is also done where the effect of variables like temperature and mass of adsorbents, etc, are observed. The results are also given and explained.

CHAPTER 4 explains the experimental procedure for the membrane techniques, the methods used, and finally the results and discussions.

CHAPTER 5 compares the defluoridation ability between the two membranes used and the three adsorbents used. The use of the better membrane and an adsorbent is suggested and finally only one technique (adsorption) is recommended because it is inexpensive and it is easy to operate Then the conclusions and suggestions for future purposes are made.

Membrane and adsorption techniques were used. For adsorption technique, the batch process was used in which the natural adsorbents (activated charcoal, charcoal, and charwood) were used. The use of natural adsorbents was advantageous since they are readily available. For membrane techniques, nanofiltration and reverse osmosis processes were used. Since these are pressure driven techniques, pressure of up to 20 bar were used. For the membrane techniques, concentration of up to 5 *mg l* were used and for the adsorption techniques, NaF concentration of up to 10 *mg l* were used.

CHAPTER 1

OVERVIEW

1.1 BACKGROUND OF THE PROJECT

We generally take our drinking water for granted. Perhaps we should not. The water that we drink must have one overriding characteristic- it must be safe[1]! Each an every member of the public has the right to clean and safe water.

The threats of ground water contamination are occurring coincidentally with a rapid increase in the rate of ground water usage. In many areas, ground water is the only reliable source of fresh water, and in others it is increasingly being used as a deference to surface water to meet the growing demands of an expanding population[2].

Ground water has inorganic pollutants like fluorides, nitrates, nitrites, chlorides, sulphates, phosphates, etc[1]. In this project, much focus will be on fluoride contamination of ground water. It became known that more than 1 mg l of fluoride in drinking water causes mottling of teeth in children, bone changes, crippling fluorosis, cancer, etc[3]. Since most water sources for the public are not of suitable quality for human consumption without some form of treatment, many methods have been suggested from time to time for water defluoridation[4]. These may be divided into two basic groups namely those based on an exchange process or adsorption and those based on addition of chemicals to the water being treated[3]. In this project, two techniques are used. They are membrane and adsorption techniques.

1.2 DEFLUORIDATION TECHNIQUES USED

The membrane process used is nanofiltration. This membrane process deals with low molecular weight solutes such as inorganic salts like fluoride. This membrane can be considered as being intermideate between open porous types of membrane (microfiltration / ultrafiltration) and dense nonporous membrane (pervaporation / gas separation)[5].

Because of its higher membrane resistance, a much higher pressure is must be applied to force the same amount of solvent through the membrane which is 5-20 bar. Nanofiltration has a separation principle of solution-diffusion[5].

Nanofiltration membranes are widely applied in desalination of brackish and sea water productionof ultra-pure water, waste water treatment, water softening, and removal of micropollutants[5]. (See Figure 1)

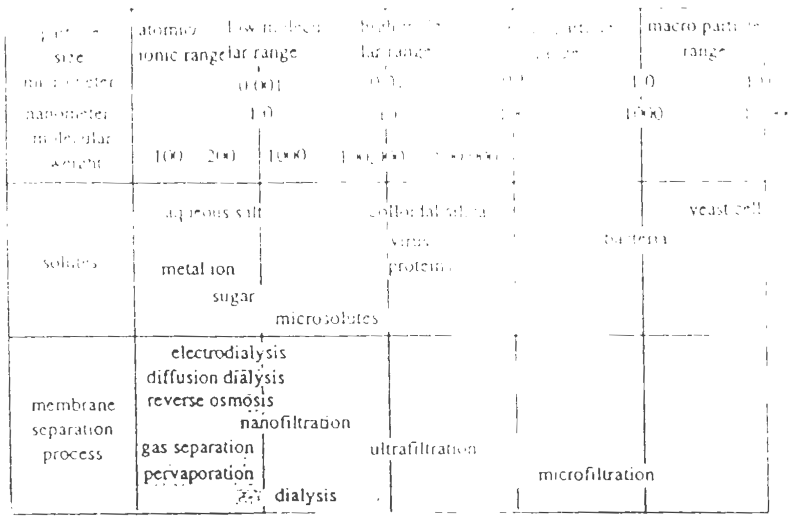


Figure 1 - Application range of various membrane processes[5].

1.2.2 Adsorption processes

Batch method was used for adsorption The natural adsorbents (activated charcoal, charcoal, and charwood) were used The adsorbents were heated up to 300 °C so as to remove impurities[1]. Mass of 2 *g* and ceconcentration of 2 *mg/l* NaF were used

OBJECTIVES

Since water pollution by fluoride is encountered in many parts of the world including South Africa[3], it is of paramount importance to bring those high concentrations of fluoride to accepted limits.

The objectives of this project are:

(a) To analyse fluoride levels in ground water of rural areas of North West Province.

(b) To use affordable, simple and effective methods (Membrane and Adsorption Techniques) to reduce fluorides in water to *1 mg/l*.

REFERENCES

1. Stine, W.R., 1981, **Applied Chemistry,** 2nd Edition, Allyn and Becon, Inc, U.S.S
2. Pye, V.I., Patric, R., and Quarles, J., 1989, **Ground Water Contamination in the United States,** University of Pennysylvania Press, Philadelphia, Chp 9
3. ***Current Science,*** vol.65, no.10, 25 November 1993
4. http://www.hap.edu/books/030905527X/html/48.html
5. Mulder, M., 1996, **Basic Principles of Membrane Technology,** 2nd Edition, Kluwer Academic Publishers, The Netherlands

CHAPTER 2

LITERATURE STUDY

2. GROUND WATER AND FLUORIDE

In recent years, another water pollution problem has become apparent: the contamination of ground water[1]. Ground water contamination is particularly alarming, because once contaminated, an underground aquifers may remain unusable for decades or longer[1].

The majority of people living in the North West Province live in rural areas. More than half of the water used for drinking, washing, and irrigating crops comes from aquifers underground[2]. This ground water is accesed by boreholes, windmills, or wells. It is generally taken for granted that such ground water drawn from wells, is omnipresent and will always be available and clean and safe to drink. But experts are reporting that ground water sources can dry up through overuse, or become contaminated as a result of pollution, poor sanitation or salt intrusions[2].

Ground water has inorganic pollutants like fluorides, nitrates, chlorides, sulphates, etc[3]. Since water is a major source of fluoride intake[2] in rural areas of North West Province (S.A), much focus will be on fluoride content in drinking water in rural areas of North West Province.

2.1 Basic facts about fluoride

Fluoride is a highly reactive element which normally likes to bond with other elements. These combinations are often salts and the fluorine part *is called fluoride*[4]. *Fluoride is known to contaminate ground water reserves globally and it also occurs naturally in ground waters throughout the world. Contamination of water by fluoride may be attributed to its natural presence in the earth's crust and to many agricultural and industrial activities, especially steel, glass, aluminium, phosphate, electroplating, welding, and the ceramic industries*[5,6]

Fluoride can enter ground water by natural processes. The soil at the foot of mountains is particularly likely to be high in fluoride from weathering and leaching of bedrock with a high fluoride content. In ground water, the natural concentration of fluoride depends on the geological, chemical and physical characteristic of aquifers, the porosity and acidity of soil and rocks, the activation of other chemical elements, and the depths of wells. Because of the large number of variables, the fluoride concentration in ground water can range from 1 ppm to more than 35 ppm[2].

High profile of fluoride in shallow zone ground water is due to the geochemical disposition in the vicinity of the ground water extraction structures. The toxicity of fluoride is also influenced by high ambient temperature, alkalinity, calcium and magnesium content in the drinking water[7]

Abnormal level of fluoride in water is common in fractured hard rock zone with pegmatite veins. The veins are composed of minerals like topaz, fluorite(most common fluoride-bearing mineral), fluor-patite, villiamite, cryolite and fluoride-replaceable hydroxyl ions in ferromagnesium silicates[8]. *Fluoride ions from these minerals leach into the ground water and contribute to high fluoride concentration*[9].

Occasionally, mica group of minerals like muscovite and biotite also contribute to water fluoride content[10].

Fluorospar occurs in structurally weak planes like shear fracture zones, joints and at the host rock and vein quartz.Rock minerals weather and form calcium and magnesium carbonates, which serve as good sinks for fluoride ions[11] However it is the leachable state of fluoride ions that determines the water fluoride levels. The leachability is governed by (i) pH of draining solution and (ii) dissolved carbon dioxide in the soil. The present study pertains to the fluoride in phreatic ground water (the top aquifer system) and it is in this regimen that hand pipes, dug and bore wells have been constructed.

2.2 Fluoride concentration in drinking water and its health hazards

Natural contamination of groundwater by fluoride causes irrepairable damage to plants and animals.

Chronic dental fluorosis

Fluoride salts are acute poisons in moderate to high concentrations[1]. World Health Organisation standards permits only 1 ppm as a safe limit for human consumption[12]. 1,5 ppm fluoride in drinking water can cause damage to teeth in a condition known as chronic dental fluorosis which is common in South Africa[13]. The teeth of consumers become mottled with permanent black or grey discoloration, the enamel become so severely pitted that they eventually lose their teeth. This damage is significant only when teeth are first developing. Once the teeth have fully developed (about 12 to 14 years of age) this condition does not develop.

In mild form of fluorosis, a slight swelling and impregnation with globular and crystalline material in the periosteal collagenous fibres is observed. The impregnation and swelling increase and, in severe cases of fluorosis, an irregular orientation of abnormal fine fibre and thick deposits on the bone surfaces occurs[14].

Chronic dental fluorosis has both psychological and economical effect on consumers[15].

Psychological and economical effects of chronic dental fluorosis

The psychological effect in terms of the unsightly brown-stained teeth has induced the adolescent, with fluoresed teeth, to demand that these teeth be extracted and replaced[15]. This is really a problem since the self-esteem of inhabitants especially adolescents is affected.

Certain workplaces could not hire someone with mottled teeth. For example, studies by Mc Caffrey shows that ground water around Pilanesburg area in Rustenburg have fluoride content that exceed the suggested 1 ppm fluoride concentration by South African Bureau of Standards hence the majority of people there cannot work at Sun City or Lost City[15]. This is because with their stained teeth, they cannot attract tourists. This leaves the individual concerned in a very bad economical state.

Development of diseases

Fluoride ion in high doses also interfere with calcium metabolism, kidney action, thyroid function, and with the action of other glands and tissues[1]. Cancer, hip fracture, bone changes and crippling fluorosis may also result from the long term consumption of water containing high fluoride concentrations[16].

Acute fluoride intoxication may lead to sudden deaths. Fluoride ion acts by inhibiting Na^+, K^+, ATPase that stimulates Na^+, Ca^{2+} exchange and conduces to increase kalemia[17,18]. Effectively, in case of acute fluoride intoxication described by Mc Ivor, not only fluoride levels, but also potassium levels increased[19].

Effects in plants

High fluoride levels inhibit germination,cause ultrastructural malformations, photosynthetic capacities, alter membrane permiability, reduce productivity and biomass and inflict other physiological and biochemical disorders in plants[20].

2.3 Available methods for defluoridation of fluoride-rich ground waters

Several physical and chemical methods have been used for the defluoridation of fluoride-rich waters. Amongst others they are: flocculation with silver chloride, softening with lime, filtration through activated alumina, ion exchange, reverse osmosis, and electro dialysis[21,22].

2.3.1 Electrodialysis

It is an electromembrane process which was first developed for desalinating brackish water brine production and demineralisation. It is a simple physical process which enables avoiding many of the defects chemical process have. This approach is found suitable for desalination and defluoridation of water having total dissolved solids of up to 5000 ppm and fluoride up to 10 ppm with an energy requirement of < 1 kWh/kg of salt removed. Electrodialysis suffer the limitation of frequent change of beds and inability to reduce fluoride to non-toxic levels[21,22].

2.3.2 Flocculation

It is the formation of larger particles of a solid phase dispersed in a solution by the gathering together of smaller particles. The process whereby initial aggregates in a solution develop spontaneously into particles of a new stable phase is known as nucleation. When these particles grow to size sufficient to scatter visible light, they are known as colloids. Dispersions of particles of colloidal size are frequently stable, coalescence of the particle into larger aggregates settling under gravitational or centrifugal forces being prevented by their similar residual and mutually repelling charges[2].

By changing the ionic environment in which colloidal particles exist, for example, by adding salts containing multicharged ions, the colloidal particles can be made to undergo further flocculation. Silver chloride is a good example of compounds which can be precipitated as a flocculated colloid[2].

Since flocculation is best carried out under alkaline conditions, lime or bleaching powder are added to water.

2.3.3 Activated Alumina[22]

It is an expensive process. Reactivation of filter material is cumbersome (done by treatment of bed by acid and alkali) and it can be done only with the help of trained persons, who are generally not available in most of our villages. This process also results in moderately high residual aluminium in output water ranging from 0,1 mg/*l* to 0,3 mg/l[22].

2.3.4 Krass Process

In this process, defluoridation is conducted in columns using support material (still patended) in a downflow mode. Effects of recharging solution quantity, initial fluoride concentration and pH effeciency are studied. An attempt was made to develop domestic filter suitable for a rural family[22].

2.4 Methods used for defluoreidation

For this project, membrane and adsorption techniques are used to remove excessive fluoride in ground water.

2.4.1 Membrane techniques

Transport through the membrane takes place when a driving force is applied to the feed. In most membrane processes the driving force is a pressure difference or concentration difference across the membrane. Membrane is a heart of every membrane process[2].

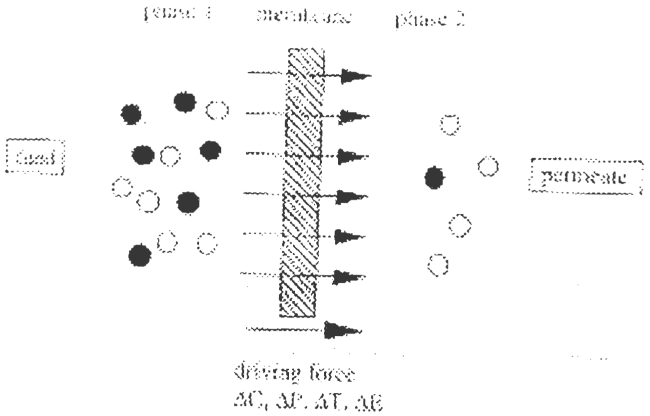


Figure 2.1 Schematic representation of a two-phase system separated by a membrane[23].

Phase 1 of figure 2.1 is the feed which contains both the solute and the solvent separated by a membrane. Phase 2, the permeate, is obtained after a membrane has trapped some solvent and solute particles in the feed. If the membrane is good, it will remove a lot of unwanted material.

Membrane can be thin or thick, its structure can be homogenous or heterogenous, and transport can be active or passive. Asymmetric membranes are used for industrial purposes due to high selectivity with the permeation rate of a very thin membrane. One membrane process will be used in this research namely nanofiltration[23].

2.4.1.1 Nanofiltration

Nanofiltration is a membrane process between reverse osmosis and ultrafiltration. During nanofiltration, substances are rejected by two principles: the rejection of neutral species by size (molecules larger than 200-300 g/mol are rejected), and the rejection of inorganic ions due to the electrostatic interaction between the ions and the membrane[24,25].

Nanofiltration has more open network structure. The pore size is <2 nm and flux range is 1,4-12 ($l.m^{-2}.h^{-1}.bar^{-1}$). Membrane material is polyamide (interfacial polymerisation). The retention is high for micro-pollutants or micro-solutes and for other low molecular like dyes, and sugars. Top layer is 1µm in thickness and sub-layer is 150 µm in thickness. Separation principle is also solution-diffusion[23].

Most nanofiltration membranes are thin composite membranes of hydrophobic polymers with negatively charged groups incorporated. Top-layer and sub-layer are composed of different polymeric materials so that each layer can be optimised separately. Firstly, a porous sub-layer should be prepared. Important criteria for this sub-layer are surface porosity and pore size distribution. Different methods have been employed for placing a thin dense layer on top of this sub-layer viz dip coating, *in situ* polymerisation, and interfacial polymerisation[23].

Nanofiltration can be applied in the removal of micro-pollutants and waste water treatment, and in dairy industry. With nanofiltration, it is possible to separate organic substances from monovalent inorganic substances. It was in fact originally designed to desalt whey. The area of application has, however increased into other fields such as water softening, decolourisation of citrus and sugar molasses, treatment of metal-containing waste waters from metal finishing industries and removal of sulphate from sea water in off-shore oil well application [27,31,32].

The advantage of nanofiltration compared with reverse osmosis and ultrafiltration is that it is possible to separate organic substances from some type of salts. It is also possible to separate different kinds of salts due to negatively charged groups on the membranes. Since the membranes are negatively charged, it is the anion repulsion which mainly determines the solute retention of salt solutions. The degree of retention increases with increasing valence of the anion, due to the increased repulsion by the membrane (for example, the retention of sulphate ions is considerably higher than the retention of chloride ions)[23]. Among other membrane processes, nanofiltration is chosen because it deals with low molecular weight components like inorganic pollutants including fluoride and it is applied in water purification[23].

The filtration process takes place on a selective separation layer formed by an organic semi-permeable membrane. The driving force of the separation is the pressure difference between the feed (retentate) and the filtrate (permeate) side at the separation layer of the membrane (10 - 25 bar)[26].

However, because of its selectivity one or several components of a dissolved mixture are retained by the membrane despite the driving force, while water and substances with a molecular weight 200 Dalton are able to permeate the semi-permeable separation layer. Because nanofiltration membranes also have a selectivity for charge of the dissolved components, monovalent ions pass the membrane and divalent and multivalent ions will be rejected[26].

Various types of commercial nanofiltration membranes are available, and the separation performance of these membranes varies greatly[24,27,28,29,30].

2.4.2 *Adsorption technique*

Adsorption is a type of adhesion that takes place at the surface of a solid or a liquid in contact with another medium, resulting in an accumulation or increased concentration of molecules from that medium in the vicinity of the surface. For example, if freshly heated charcoal is placed in an enclosure with ordinary air, a condensation of certain gases occurs upon it, resulting in a reduction of pressure, or if it is placed in a solution of unrefined sugar, some of the impurities are likewise adsorbed, and thus removed from the solution[33].

The degree of adsorption depends on five factors:

1. Decomposition of the adsorbing material
2. Condition of the surface of the adsorbing material
3. Material to be adsorbed
4. Temperature
5. Pressure (in the case of gas).

The temperature of preparation of adsorbent charcoal is an important factor, high temperatures being deleterious.

On the basis of the adsorbate (or the substance which is adsorbed), adsorption may be polar, when the material to be adsorbed consists of positive or negative ions, so that the adsorbed film has an overall electrical charge. The term polar adsorption is also applied to adsorption chiefly attributed to attraction between polar groups of adsorbents. Example of polar adsorbent is silica gel. It also retains water and may thus reject an organic compound. It can also discriminate more selectively than activated carbon and consequently can be used for the fractionation of organic solvents[33].

Activated carbon is non-polar since it has no affinity for water and it will adsorb organic compounds in preference to water. Specific adsorption is the preferential adsorption of one substance over another, or the quantity of adsorbate held per unit area of adsorbent[33].

On the basis of the process involved, adsorption may be classified as chemical adsorption or chemisorption where forces of chemical or valence nature between adsorbate and adsorbent are involved or van der Waals or physical adsorption where van der Waals forces are involved.
Chemical adsorption may be rapid or slow and may occur above or below critical temperatures of the adsorbent. Physical adsorption occur as a result of relatively non-specific intermolecular forces that are responsible for the condensation of vapour to a liquid. Physical adsorption is usually important only for gases below their critical temperature

The difference is usually indicated by the greater heat of adsorption and more specific nature of chemical process[3]. The heats of adsorption should be in the range of heats of consensation.

Mayor adsorbents are: carbon, clay, sand, activated silica, activated alumna, charcoal, charwood, bonechar, synthetic zeolites, etc. Among these adsorbents, only natural adsorbents will be used. They are activated carbon, charwood, and charcoal.

2.4.2.1 Properties of charcoal

Charcoal is a highly porous form of amorphous carbon derived from wood by destructive distillation. It is a black, brittle solid that is odourless and tasteless. It contains barrels, multi wall paper sacks. It is denser than water, but it often adsorbs enough gas to make it float on water. The ability to adsorb a large quantity of gas is the most remarkable physical properties of charcoal. 1 cubic inch of freshly prepared willow charcoal adsorbs about 90 cubic inches of ammonia gas. Because of its ability to adsorb gases, charcoal is a good deodoriser[34].

Charcoal also removes the odour from certain liquids. It a good fuel but it is more expensive than any other fuel. It has the following uses: filtering medium, component of black powder and other explosives, purifying oils, and solvent recovery from their vapours. A layer of wood charcoal is often used between layers of sand and gravel in water purification. Its efficiency is increased by steam activation[34].

Hazards of charcoal are that it can cause dangerous fire risk in briquette form or when wet. It may also ignite spontaneously in air[34].

Surface area of charcoal

Surface area is the total area of exposed surface of a solid material, usually in the form of powder, including all the irregularities, pores, etc. Since activity is greatest at the surface, that is, the interface between the particle and its environment, the larger the surface area of a given substance, the more reactive it becomes. Thus the reduction to smaller particles is a means of increasing the efficiency of both chemical and physical reactions, for example, twigs and wood fragments ignite more easily than large slabs[34].

2.4.2.2 Properties of activated charcoal

It is an active charcoal that has been treated with oxygen to open up millions of tiny pores between the carbon atom. It is made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperatures of 700-1100 ^{0}C, which result in a porous internal structure (honeycomb). The structure of activated charcoal consists of elementary micro-crystallites of graphite, but these micro-crystallites are stacked together in random orientation and it is the spaces between the crystals, which form the micropores (Table 2)[35]

Table 2 : The pore size ranges in typical activated charcoal[35].

	Micro-pores	**Meso-pores**	**Macro-pores**
Diameter (nm)	<2	2-50	>50
Pore volume (cm^3 /g)	0,15-0,5	0,02-0,1	0,2-0,5
Surface area (m^2 /g)	100-1000	10-100	0,5-2
Particle Density (g/cm^3	0,6	0,7	0,9
Porosity	0,4	0,5	0,6

The actual distribution and the total pore volume associated with each pore size range are however sensitive to the conditions of the initial pyrolysis and activation procedures.

The use of special manufacturing techniques results in highly porous charcoals that have surface areas of 300-2000 m^2 / g. The specific gravity is from 0,08-0,5. The huge surface area of activated charcoal gives it countless bonding sites. The ability of activated carbon to adsorb molecules of gas is due to this factor[36].

Activated carbon is an amorphous form of carbon characterised by high adsorptivity for many gases, vapours, and destructive distillation of wood, nutshell, animal bones, or other carbonaceous material. It is widely used to adsorbs odorous or coloured substances from gases or liquids, decolourising of sugar, water, and air purification, solvent recovery, waste treatment, electroplating, air conditioning, and removal of jet fumes from air pockets[37].

The dangers of activated charcoal are that it is flammable and it can be bad to ones health if it is inhaled[37].

2.4.2.3 Charwood

It is a highly porous form of amorphous carbon. It is derived from destructive distillation of wood. It contains multiwall paper sacks. It is used as a gas adsorbent, decolorizing and filtering medium, and as a component of black powder[33].

2.4.2.4 Theories of adsorption

The Langmuir adsorption isotherm

Using the law of mass action, Langmuir derived adsorption isotherms widely applicable to the adsorption of gases on solid surfaces. Generally speaking, there are two kinds of adsorption: physical or chemical The former involves a weak binding of the adsorbate to the surface by van der Waals forces. The second, usually referred to as chemisorption, involves the formation of chemical bonds. Enthalpies of adsorption for the first case fall in the range of 0-5 kcal/mol whereas for chemisorption the range is 20-100 kcal mol. Adsorption at liquid-vapour and liquid-liquid interface is most often of the physical sort, although it also occurs with some frequency in gas-solid interface[38].

Chemisorption does not occur indiscriminately over all portion of the interface but at specific surface sites that, because of the local compound or topography, are most suitable for binding the adsorbate, these are called the active sites. The derivation starts by considering a gas of species M to be in equilibrium with the appropriate concentration of adsorbed molecules. It is furthermore supposed that the surface contains a specific concentration S_0 of active sites capable of capturing M type molecules. The absorbed molecules are represented by SM and written as chemical reactions, are given by:

$(S_0 - SM) + M \Leftrightarrow SM$ **(Equation 1)**

If the fractional occupation of active sites is defined as $\theta \equiv SM \quad S$, we can write for equilibrium constant equation 1 :

$$K \quad (SM) \quad (SM)(M)$$

$$- \quad \theta S_0 \ / S \ (1-\theta) P_M \qquad \textbf{(Equation 2)}$$

$$- \theta \ / P_M - \theta P_M$$

Where M $\propto P_M$ the partial pressure on M . The algebraic rearrangement of Equation 2 leads to

$$\theta = KP_M / \ (1 + KP_M), \qquad \textbf{(Equation 3)}$$

which is the usual form of the Langmuir adsorption isotherm

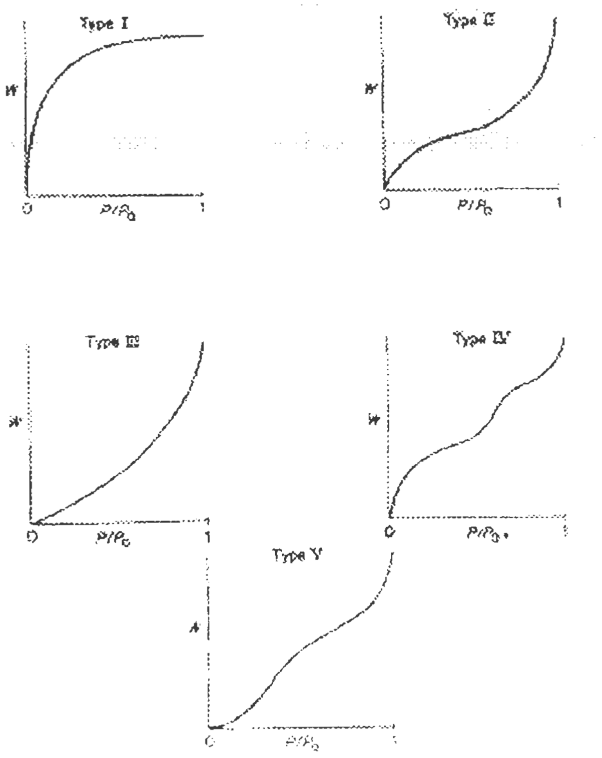


Figure 2.2 The five isotherm classification according to BDDT[29]. *W is the weight adsorbed, P is the adsorbate equilibrium pressure, Po is the adsorbate equilibrium vapour pressure, and P/Po is the relative pressure. Condensation occurs at P/Po≥1.*

Classification of adsorption isotherms

The majority of physisorption isotherms may be grouped into the six types, five of which are shown in Fig 2.2. In most cases at sufficiently low surface coverage the isotherm reduces to a linear form (i.e. $n^a \propto p$*), which is often referred to as Henry's region. On heterogenous surfaces this linear region may fall below the lowest experimentally measurable pressure*[39].

The reversible Type I isotherms are sometimes referred to as Langmuir isotherms, but this nomenclature is not recommended. It is concave to the p/p^0 *axis and* n^a *approaches a limiting value as* $p/p^0 \rightarrow 1$*. Type I isotherms are given by microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides, the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area*[39].

The reversible Type II isotherm is the normal form of isotherm obtained with a non-porous or microporous adsorbent. The Type II isotherm represents unrestricted monolayer-multilayer adsorption. Point B, the beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption is about to begin[39].

The reversible Type III isotherm is convex to the p/p^0 *axis over its entire range and therefore does not exhibit a point B. Isotherms of this type are not common, but there are a number of systems (nitrogen on* *polyethylene) which give isotherms with gradual curvature an indistinct point B. In such cases, the adsorbate - adsorbate interaction plays an important role*[39].

The characteristic features of Type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high $p\ p^0$. *The initial part of Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a nonporous form. Type IV isotherms are given by many mesoporous industrial adsorbents*[39].

Type V isotherm is uncommon, it is related to the Type III isotherm that the adsorbent - adsorbent interaction is weak, but is obtained with certain porous adsorbents[39].

Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height now represents the monolayer capacity for each of adsorbed layer and, in the simplest case, remains nearly constant for two to three adsorbed layers. Amongst the best examples of Type IV isotherms are those obtained with argon or krypton on graphitised carbon black at liquid nitrogen temperatures[39].

Adsorption hysteresis

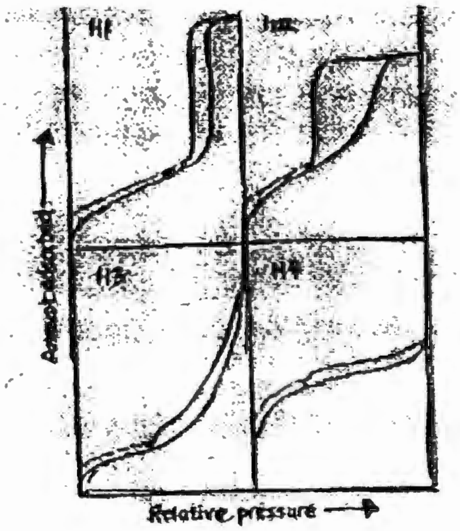


Figure 2.3 Adsorption hysteresis

Hysteresis appearing in the multilayer range of physisorption isotherms is usually associated capillary condensation in mesopore structures. Such hysteresis loops may exhibit a wide variety of shapes. Two extreme types are shown as H1 (formerly known as Type A) and H4 in Figure 2.3 . In the former, the two the two branches are almost vertical and nearly parallel over an appreciable range of gas uptake, whereas in the latter they remain nearly horizontal and parallel over a wide range of p/p^0*. In certain respects Types H2 and H3 (formerly termed Types E and B, respectively) may be regarded as intermediate between these two extremes*[39]*.*

A feature common to many hysteresis loops is that the steep region of the desorption branch leading to the lower closurepoint occurs at a relative pressure which is almost independent of the nature of the porous adsorbent but depents mainly on the nature of the adsorptive (e.g. for *nitrogen at its boiling point at* $p/p^0 \cong 0.42$ *and benzene at* 25^0C *at* $p/p^0 \cong 0.28)$[39].

Although the effect of various factors on adsorption hysteresis is not fully understood, the shapes of hysteresis loops have been identified with specific pore structures. Thus, Type H1 is often associated with porous material known to consist of agglomerates or compacts of approximately uniform spheres in fairly regular array, and hence to have narrow distributions of pore size. Many porous adsorbents tend to give Type H2 loops, but in such systems the distribution of pore size and shape is not well-defined. Indeed, the H2 loop is especially difficult to interpret[39].

The Type H3 loop, which does not exhibit any limiting adsorption at high p/p^0*, is observed with aggregates of plate-like particles giving rise to slit-shaped pores. Similarly, the Type H4 loop is often associated with narrow slit-like pores, but in this case the Type 1 isotherm character is indicative of microporosity*[39].

The BET Isotherm

More often than denoted, additional adsorbate molecules will condense on the initial monolayer before the latter has completely saturated all the available surface sites. These successive layers are bound less tightly, and their relative concentrations (that is, the first, second, third, and so fourth, layers) will follow the customary thermodynamic distribution functions. The (Brauner- Emmett.-Teller) BET isotherms takes account of these successive layers of these adsorbate and thus is an extent of the Langmuir treatment. The adsorption of gases as a function of pressure on nonporous surfaces generally (but not always) follows either of the two isotherms potrayed in figure 2.3 (a, b). Figure 2.3 (a) shows the adsorption of a monolayer in which the gas ultimately saturate all of the adsorption sites without condensation of the second layer and (b) shows the isotherm appropriate for the case where additional supercritical layers develop befpore saturation by the initial monolayer[38]

As in the usual case for a thermodynamic description of chemical reaction, one can proceed via a classical or statistical approach, the fpormer will be used since it is more closely parallel to the previous deviation of the Langmuir isotherm. Defining S_0, S_1, S_2, S_3,...S_i... as the areas covered by 0, 1, 2, 3... I, molecular layers of adsorbate, we have an equation for the first layer only:

$a_1 PS_0 \quad d_1 S_1 e^{-E1/RT}$ **(Equation 4)** *or*

$S_1 = BPS_0^{E1 \quad RT}$

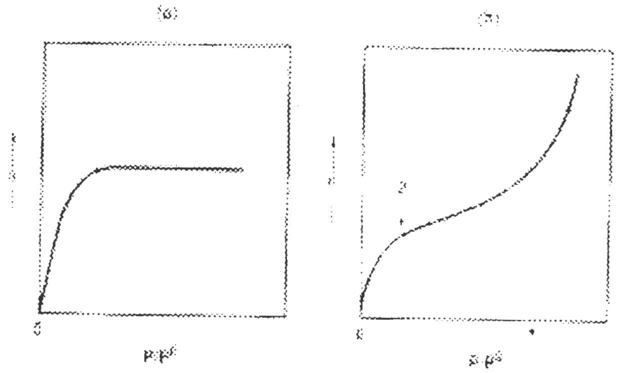


Figure 2.3 (a) and (b) The idealized adsorption isotherms : (a) Langmuir isotherm described by equation 13 and (b) The frequently encountered isotherm with second layer of adsorbate starting as denoted at ~2.

Where a_I and d_I are rate constants for adsorption and desorption, E is the heat of adsorption of the first layer, and $b = a_I / d_I$. Equation 2 is formally equivalent to the Langmuir equation. Similar relations exist in equilibrium, between the first and the second layers, and so on. In the development of BET isotherm, two major approximations are made. First, the proportionality constant b is taken to be the same for all layers. Second, the heat of adsorption for the second and for all the layers beyond the second is taken to be the heat of liquifaction, E_L . Thus, for the second layer:

$$S_2 \quad bPS_1e^{E1 RT} \quad (bP)^2 S_0 e^{E1 RT} e^{E1 RT} \qquad \textbf{\textit{(Equation 5)}}$$

The general form for i layers is then

$$s_i \quad (bP)^i \quad S_0 e^{E1 RT} e^{(i-1) EI RT} \qquad \textbf{\textit{(Equation 6)}}$$

If we substitute i 2 in Equation 6 we go back to Equation 5

It is convenient to let .

$$bPe^{E1\,RT} \qquad x,$$ *(Equation 7)*

to give,

$$S_i \quad bPe^{E1\,RT}S_0x^{i-1}$$ *(Eequation 8)*

Now the total active surface area of the solid is given by

$$A = \sum_{i=0}^{\infty} Si$$

(Equation 9)

and the total volume of gas adsorbed is

$$V^s = V^s0\sum_{i=1}^{\infty} iS_i$$

(equation 10)

where V^s_0 is the volume of gas adsorbed per unit area by a completed monolayer . Hence, for a surface of area we can write

$$\frac{V^s}{AV^s} \qquad \frac{V^s}{V^s_m}$$

$$= \sum_{i=1}^{\infty} S_i \div \sum_{i=0}^{\infty} S_i$$

(*Equation 11*)

Where V is the volume corresponding to a monolayer over the entire surface.

The summation in ***Equation 11*** may be expressed as

$$\sum_{0}^{\infty} S_i = S_0 + S_0 bPe^{E1/RT} (1 + x + x^2 + \dots)$$

$$= S_0 + \frac{S_0 bP e^{E1/RT}}{1 - x},$$

(Equation 12)

$$\sum_{0}^{\infty} iS_i = S_0 bPe^{E1/RT} (1 + 2x + 3x^2 + \dots)$$

$$\frac{S_0 bPe^{E1/RT}}{(1 - x)^2},$$

(*Equation 13*)

and ***Equation 13*** becomes

$$\frac{V^S}{V^S_m} = \frac{bPe^{E1/RT}}{(1 - P/P_0)(1 - P/P_0 \dots)}$$

(Equation 14)

$$\frac{V^S}{V^S_m} = \frac{bPe^{E1/RT}}{(1 - P/P_0)(1 - P/P_0 + bPe^{E1/RT})}, \qquad \textbf{\textit{(Equation 14)}}$$

which is the BET adsorption isotherm.

For matching to experiments, **Equation 14** may be rearranged by calling that $bP_0\exp(E_l/RT) = 1$, as

$$\frac{P}{V^S(P_0 - P)} = \frac{e^{\Delta E/RT}}{V^S_m} + \frac{P(1 - e^{\Delta E/RT})}{P_0 V^S_m}, \qquad \textbf{\textit{(Equation 15)}}$$

where $\Delta E = E_l - E_1$.

The BET method is most commonly used to determine the total surface area of solids. The most commonly used adsorbate is N_2. Figure 2.4 shows particularly good agreement between ***Equation 15*** and the experimental data.

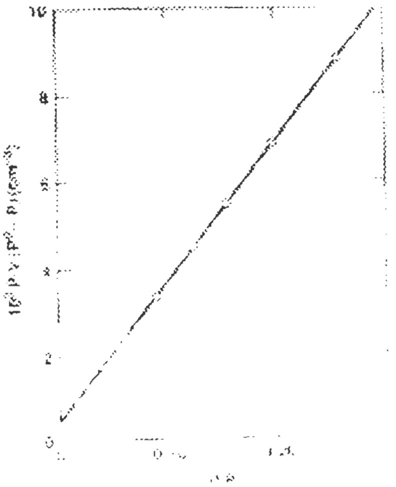


Figure 2.4 Adsorption of N_2 on a fused Cu catalyst at 90.1 K according to equation 15[40].

In conclusion, it should be marked that, although the BET approach is extremely useful for the determination of the surface areas, it is not a rigorous theory, and, in fact, has been shown to violate the principle of microscopic reversibility.

REFERENCES

1. Hill, J.W., 1988, ***Chemistry for changing times,*** Millan Publishing Company, a division of Mac Millan, Inc, U.S.A

2. ***McGraw-Hill, Encyclopedia of Science and technology***, (Elem-Fus) pp 458, (1982), U.S.A, by McGraw-Hill, Inc

3. Stine, W.R., 2nd Edition, 1981, ***Applied Chemistry,*** Allyn and Bacon, Inc, U.S.A

4. http://www.earthlife.org.za

5. Bulusu, K.R., Sunderesan, B.B., Pathak, B.N., Nawlakhe, W.G, Kulkarni, D.N, and thergaonkar, W.P. J. Ins. ***Eng. (India),*** Part EN 60 (1979) 1.

6. Min, B.R., Gill, A.L., Gill, W.N., ***Desalination,*** 49 (1984) 89.

7. Singh, B., and Dass, ***Blu-Jal News,*** 1993, 8, 28-31.

8. Rameshan, V., and Rajagoplan, K.J., J. ***Geol. Soc***. India, 1985, 26, 125-132

9. Karunakaran, B.K., ***Analytical Information on percentage fluorine content,*** 1974.

10. Hanola, B.K., ***Bhu-Jal News,*** 1988, 3, 31-37

11. Jacks, G., Sharma, V.P., and Sharma, G.K., ***Hydrochemical Studies, SIDA- assisted groundwater Resorces of Karnataka State - A Report,*** 1992, vol.2, pp: 35-37.

12. http://www.iwaponline.com

13. http://www.interview.net

14. http://www.uct.ac.za

15. http://www.uct.ac.za

16. Schoeman, J.J., Botha, G, R., ***Water S.A.,*** 11 South Africa (1985) 25.

17. McIvor, M.E., Cummings, C.C., ***Sodium Fluoride produces a K^+ efflux by increasing intracellular Ca^{2+} through Na^+, Ca^{2+} exchange.*** Toxicol Lett 1987; 38: 169-76.

18. McIvor, M.E., Cummings, C.C., Mower, M.M, Wenk, R., Lustgarten, J., Baltazar, R.F., Salomon, J., ***Sudden cardiac death from acute fluoride intoxication : the role of potassium .*** Am J Cardiol 1993; 51: 901-2.

19. McIvor, M.E., Baltazar, R.F., Beltran, J., Salomon, J., *Hyperkalemia and cardiac arrest from fluoride exposure during haemolysis.* Am J Cardiol 1993; 51: 901-2.

20.Miller, G.W., ***Fluoride,*** 1993, 26, 3-22.

21.Adhikary, S.K., Tipnis, U.K., Harkare, W.P., and Govindan, K.P., ***Desalination,*** 71(1989) 301.

22.Jinada, K.B.P.N., Weerasooriya, S.W.R., and Dissaranayake, C.B., ***Intern. J. Environ. Studies,*** 31(1988)305

23. Mulder, M., ***Basic Principles of Membrane Technology,*** 2nd Edition. 1996, Kluwer Academic Publishers, Netherlands,

24.Rautabach, R., and Mellis, R., ***Desalination,*** 95 (1994) 171.

25.Eriksson, P., ***Environ. Prog.***, 7 (1) (1988) 58

26.http://www.ameridia.com

27.Cadotte, J., Forester, R., Kim, M., Peterson, R., and Stocker, T., ***Desalination,*** 70 (1988) 77.

28.Raman, L.P., Cheryan, M., and Rajagopolan, ***Chem.Eng.Prog.,*** 90 (3) (1994) 68.

29.Perry, M., and Linder, C., ***Advanced Nanofiltration Mebranes Possessing High Chemical and Solvent Stability,*** Aachener Mem.Colloquim, Aachen, Germany, 1991

30.Ikeda, K., Nakano, T., Ito, H., Kubota, and Yamamota, S., ***Desalination,*** 68, India (1988) 109.

31.Macoun, R., and Fane A., ***Water (Artarmon, Aust.),*** 19 (2) (1992) 26.

32.De Wette, J.P., ***Recent Prog.*** Genie Procedes, 6 (1992) 61.

33.Douglas, M., ***Scientific Encyclopaedia,*** Considine (A-I) pp 46 (1995), Van Nostrand Reinhold company, Inc.

34.Clifford, A., Hampel and Gessner G. Hawley., ***Glossary of Chemical Terms,*** 1982, Van Nostrand Reinhold company, Inc, U.S.A

35.Ruthven, D.M., ***Principles of Adsorption and Adsorption Process,*** 1984, John Wiley and sons, Canada.

36.http://www.howstuffworks.com

37.***The Condensed Chemical Dictionary,*** 10th Edition, pp 194.U.S.A

38.Borg, R.J., and Dienes, G.J., ***The Physical Chemistry of Solids,*** 1992, Academic Press, Inc.

39.***Pure and Applied Chemistry.,*** Vol. 57, number 4, pp 603-619, 1985 IUPAC, Printed in Great Britain.

40.Brunauer. ***An Introduction to Principles of Surface Chemistry.,*** Cambridge University Press, p. 165, 1994

CHAPTER 3

3. TECHNIQUES FOR THE CHARACTERISATION OF ADSORBENTS

3.1 GAS ADSORPTION - DESORPTION

The term adsorption may be used to denote the process in which adsorptive molecules are transferred to, and accumulative on, the interfacial layer. Its counterpart, desorption, denotes the converse process, in which the amount adsorbed decreased. Adsorption and desorption are often used adjectivally to indicate the direction from which experimentally determined adsorption curve (or point) and the desorption curve (point)[1].

Gas adsorption - desorption is a well-known technique for pore size and pore size distribution in porous material. The adsorption and desorption isotherms of an inert gas is determined as a function of a relative pressure ($p_{rel} = p/p_0$, i.e. the ratio between the applied pressure and the saturation pressure). Nitrogen is often used as adsorption gas the experiments are carried out at boiling point of liquid nitrogen at 77K (at 1 bar)[2].

The adsorption isotherm starts at a relative pressure. At a certain minimum pressure the smallest pores will be filled with liquid nitrogen (with a minimum radius size of about 2nm). As the pressure is increased still further, larger pores will be filled and near the saturation pressure all the pores are filled. The total pore volume is determined by the quantity of gas adsorbed near the saturation pressure[2]

Desorption occurs when the pressure is decreased, starting at the saturation pressure. The desorption curve is generally not identical to the adsorption curve, e.g. a hysteresis effect can be observed. A hysteresis arises when the adsorption and desorption curves do not coincide[2].

The lowering of the vapour pressure for a capillary of a radius is given by the Kelvin relationship:

$$\ln(p/p_0) \quad \underline{2\,\gamma} v \ \cos\theta / r_k \ RTr_m \qquad \textbf{\textit{Equation (i)}}$$

the contact angle θ is assumed to be 0 when the adsorptive is nitrogen (cos 0 = 1),

p^0 = actual pressure (p_a) , γ = liquid surface tensions, v = molar volume of condensed adsorptive ($m^3.mol^{-1}$), r_m = mean radius of curvature of the liquid meniscus (also called the Kelvin radius), R = gas constant ($J.K^{-1}.mol^{-1}$), and T = temperature.

This relation can be simplified for nitrogen adsorption - desorption to r_k in nm:

$$r_k \quad \frac{-4.1}{\log p\,p} \qquad \textbf{\textit{Equation (ii)}}$$

and pore radius may be calculated: $r \quad r_k \quad t$ ***Equation (iii)*** where t is the thickness of the adsorbed layer of vapour in the pores, r_k is the Kelvin radius, and r_p is the pore radius $(r_k \quad r_p)$. The thickness of the t-layer can be estimated from calibration curves[2].

The instrument that was used for gas adsorption-desorption experiment is Micromeritics ASAP 2010 Gas Sorption Analyser. The internal surface areas of adsorbents was measured by a standard technique in which nitrogen gas was contacted with the adsorbent at the atmospheric boiling point of liquid nitrogen (77K). An initial pressure of less than 1 atmosphere was applied. The pressure was then raised slowly. Then nitrogen gradually condensed as a monolayer onto the internal surfaces.

3.1.1 RESULTS AND DISCUSSION

3.1.1.1 Nitrogen Adsorption - Desorption

Natural adsorbents which were used in this project, that is, charcoal, activated charcoal, and char-wood, gave the following results:

3.1.1.1(a) Activated charcoal

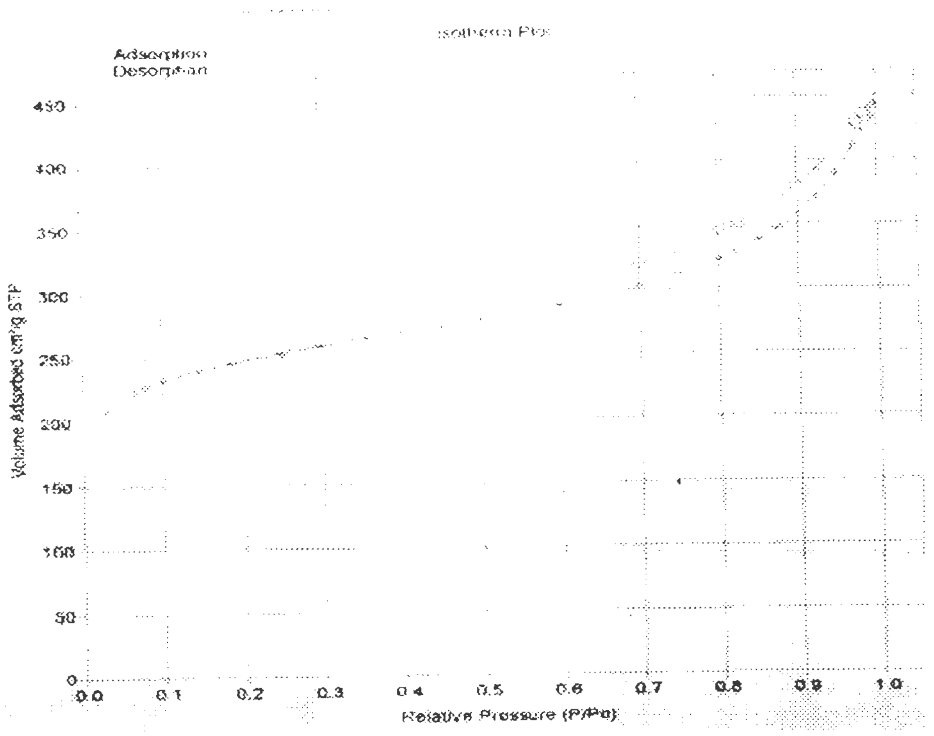


***Figure 3.1** The isotherm plot of Volume Adsorbed (cm^3/g) against Relative Pressure (P/Po) of activated charcoal.*

Figure (3.1) above which is the isotherm plot of volume adsorbed (cm^3/g) against relative pressure (p/p_0) was used to determine which type of isotherm is activated carbon. The shape of the curve shows that activated carbon is a Langmuir Type I isotherm, which is an indicative of microporosity. Type I isotherms are given by microporous solids having relatively small external surfaces. The isotherm plot also shows that hysteresis of type H4 appears. Hysteresis is usually associated with capillary condensation in mesopore structures[1].

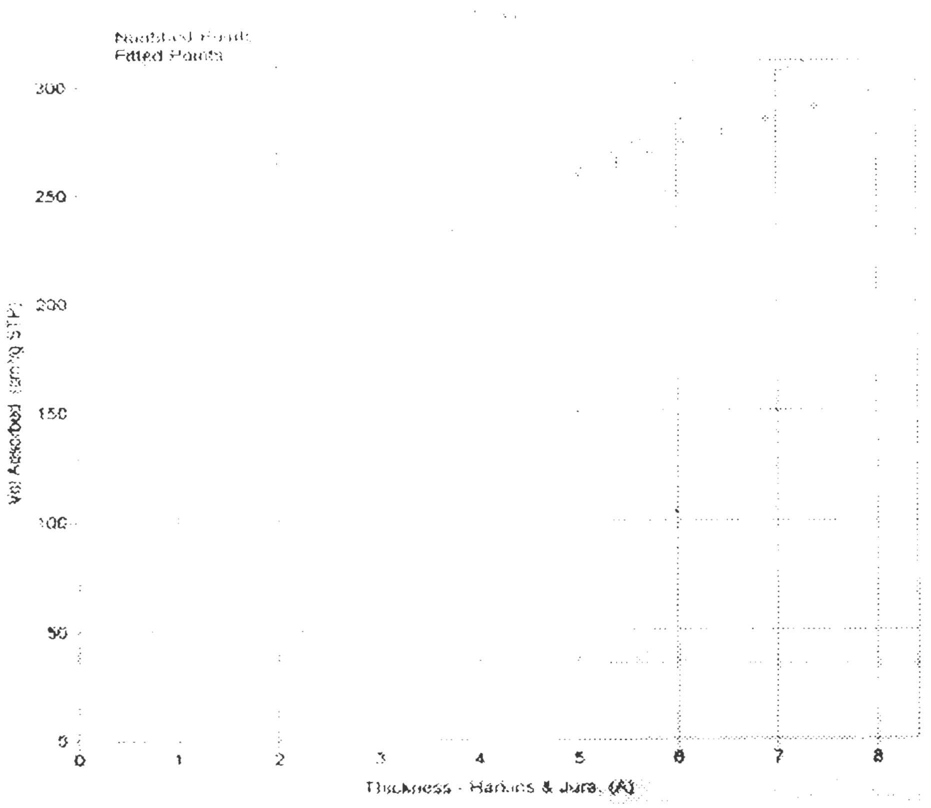


Figure (3.2) is the t - plot of volume adsorbed (cm^3/g STP) against thickness.

The shape of the graph (Figure 3.2) is indicative of microporous material. This is confirmed by the t-plot above which does not start at zero. There are no mesopores in activated charcoal. There are only micropores. carbons. The pore widths do not exceed 2 nm. Carbons have very small diameter.

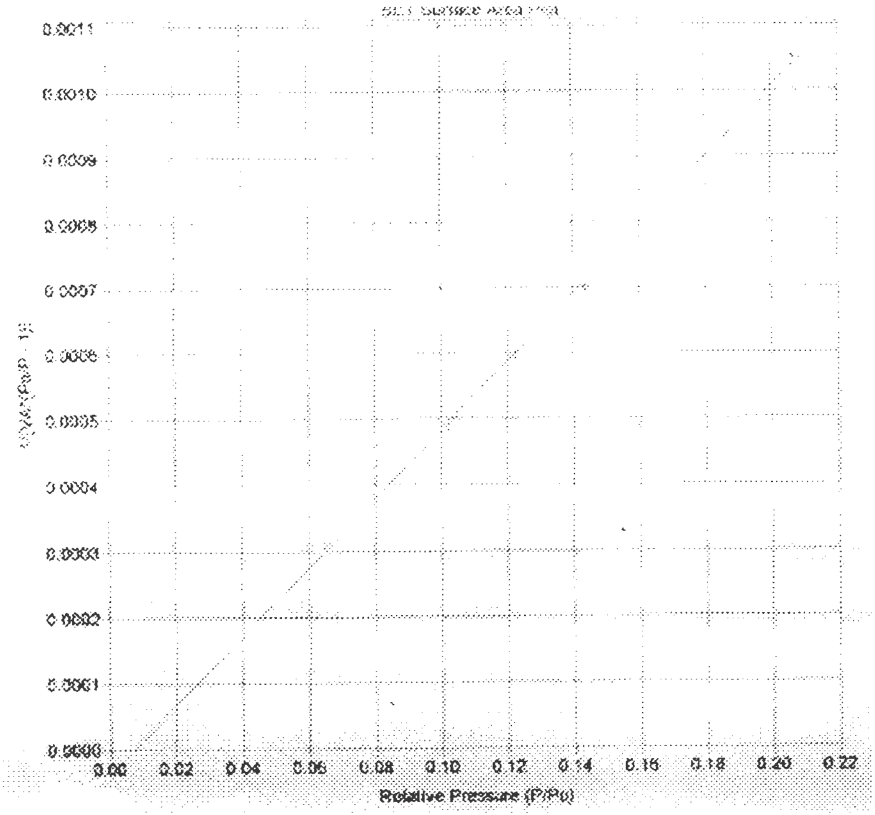


*Figure (3.3) shows the BET surface area plot of 1/[VA * (Po/P - 1)] against relative pressure (P/Po) of activated carbon.*

The graph of Figure 3.3 does not give any linear relationship. The range of linearity is outside the P/Po range of 0.05 - 0.30. Therefore the BET surface area (842 m^2/g) is not applicable.

Pore volume was found to be 0,63 cm^3/g and two types of diameter were found to be mesopores of ~ 30Å and 60 Å.

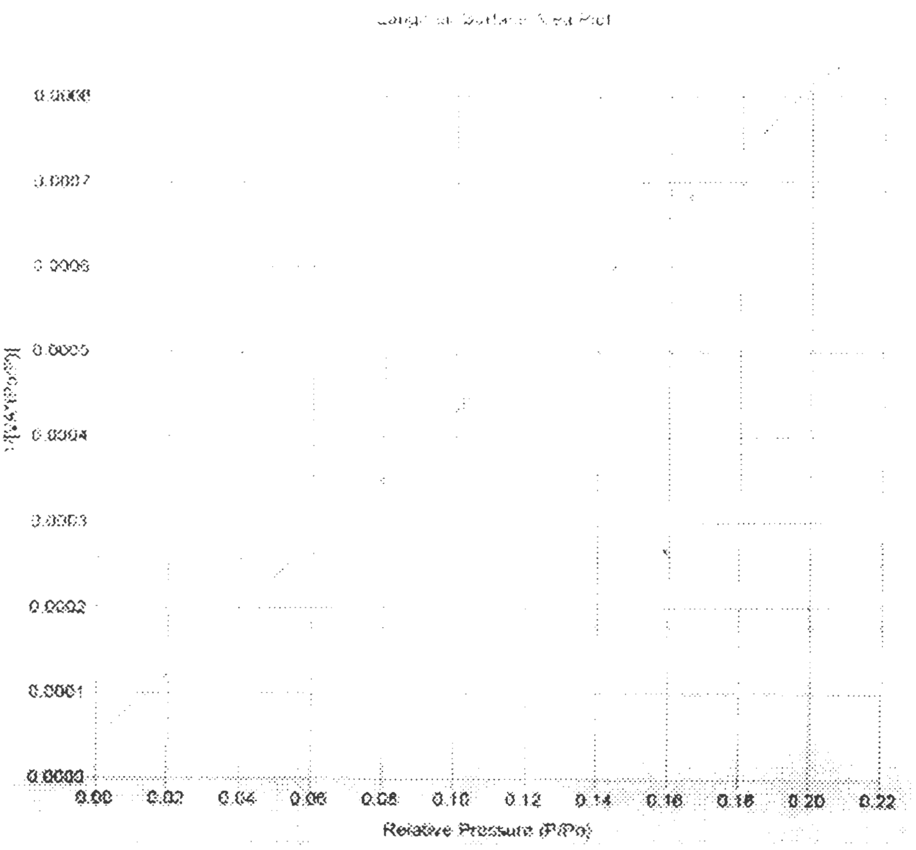


Figure 3.4 The Langmuir Surface Area plot of 1/[VA(P/Po) against Relative Pressuer (P Po) of activated charcoal.*

From the graph (Figure 3.4), a straight line is observed where most of the points are in a straight line. This shows that activated charcoal is a type I Langmuir isotherm. Langmuir surface area was 1136 m^2/g which is very large.

3.1.1.1(b)Char-wood

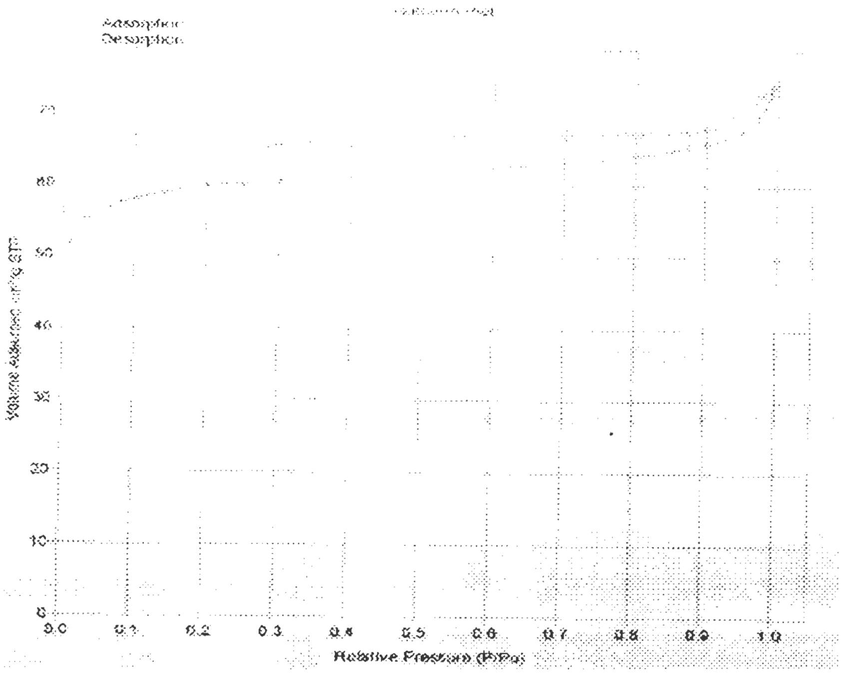


Figure 3.5 The isotherm plot of the volume adsorbed (cm^3/STP) against Relative pressure (P Po) of char-wood.

Like in activated charcoal, Figure (3.5) of the isotherm plot shows that char-wood is a Langmuir Type I isotherm with the appearance of hysteresis of type H4. Hysteresis is observed because at first there is adsorption and then the filling of the pore called capillary condition occur[1].

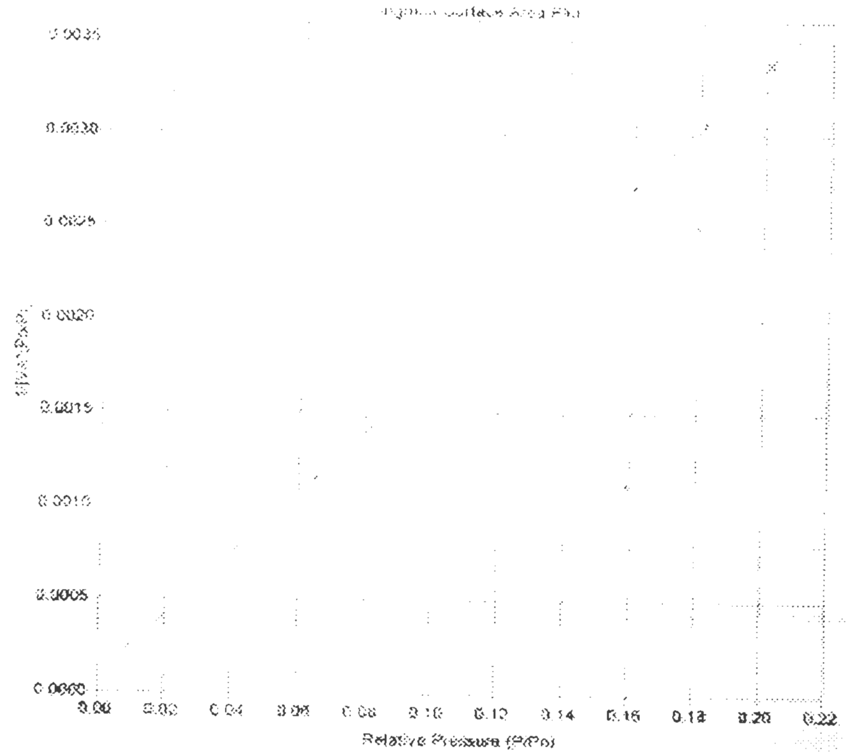


Figure 3.6 The Langmuir Surface Area plot of 1/[{VA(Po/P)] against Relative Pressure of char-wood.*

The straight line in the Langmuir surface area plot shows the validity of Langmuir surface area. Pore volume was 0,1 cm^3/g and two types of pore diameter were mesopores of 21Å and 61Å.

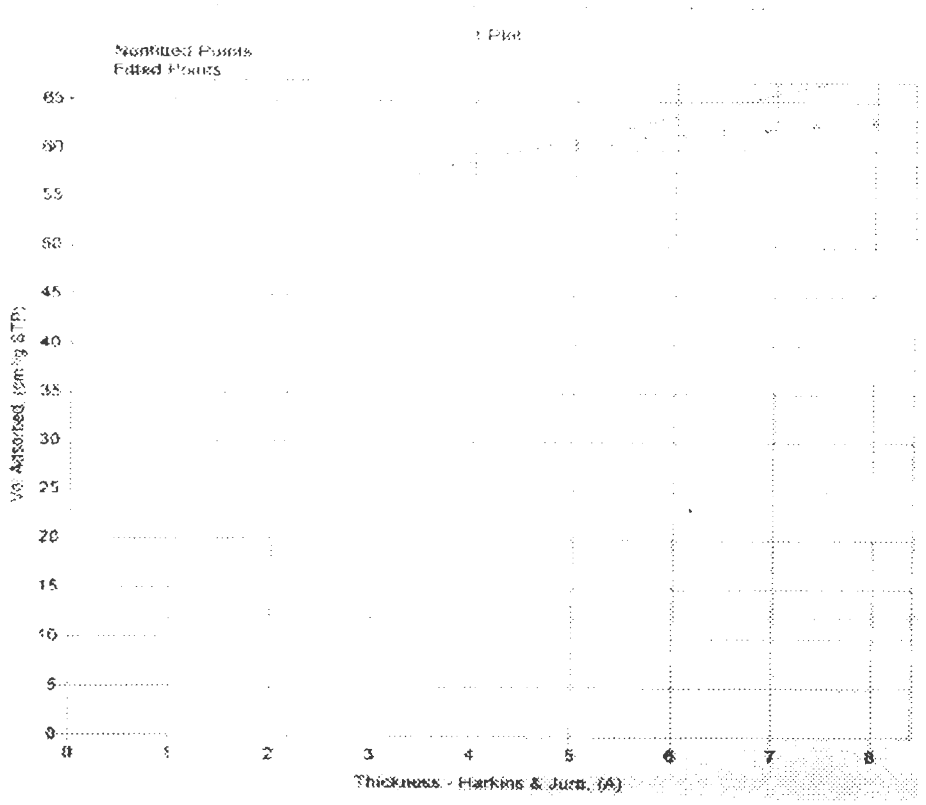


Figure 3.7 The t-plot of the volume adsorbed (cm^3/STP) against thickness of char-wood.

The t - plot figure (3.7) does not start from 0 which is an indicative of microporosity.

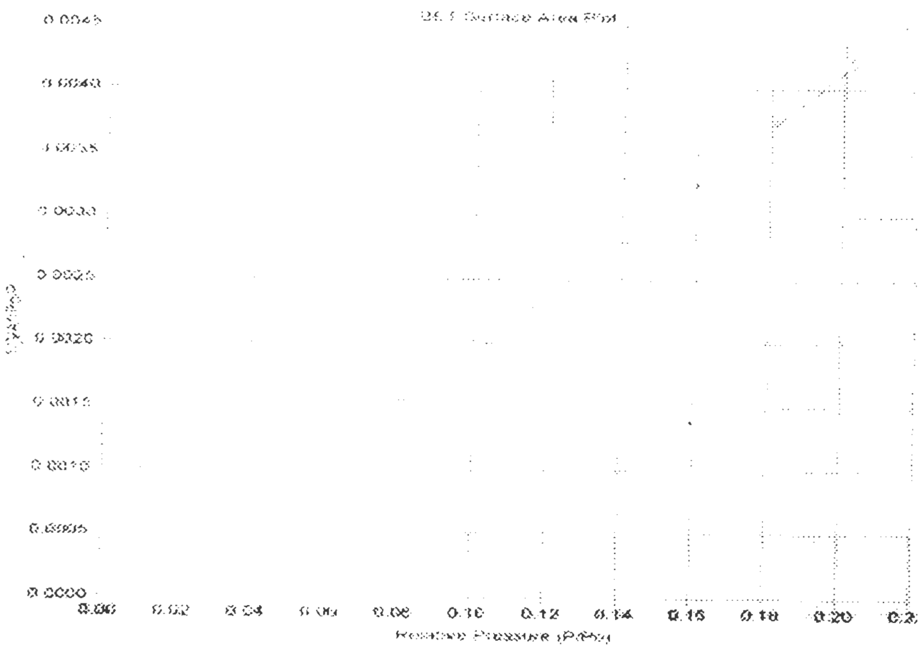


Figure 3.8 The BET Surface Area plot of 1/[VA*(Po/P-1) against Relative Pressure (P/Po) of char-wood.

BET surface area (figure 3.8) is not applicable because char- wood is microporous. BET surface area was 200 m^2/g.

3.1.1.1(c) Charcoal

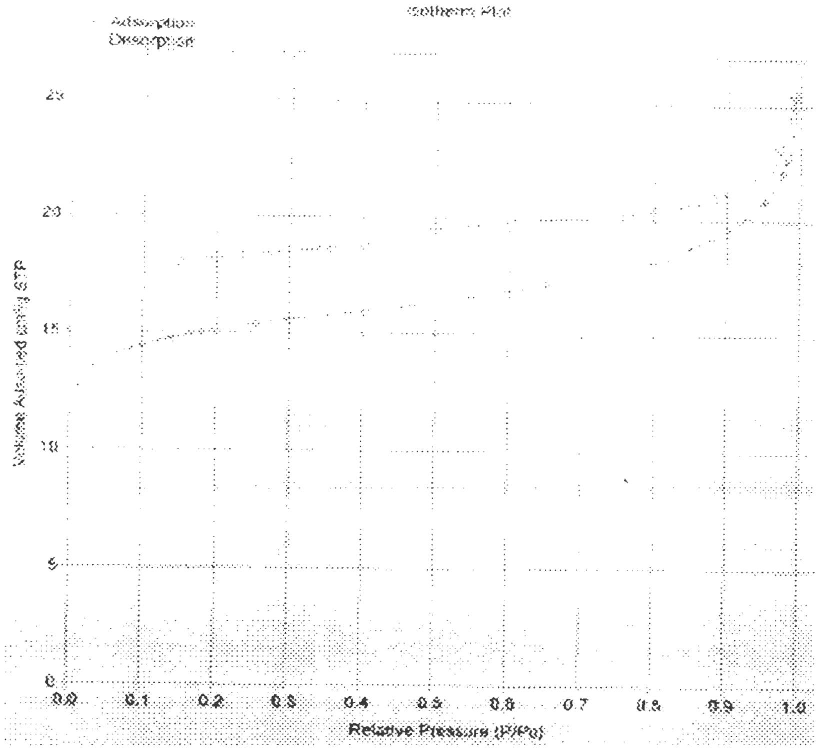


Figure 3.9 The isotherm plot of charcoal (coal).

Figure (3.9) shows that charcoal is more of Langmuir Type I isotherm with hysteresis H4. Therefore like all the other carbons, Langmuir surface area is valid and it was 68 m^2/g.

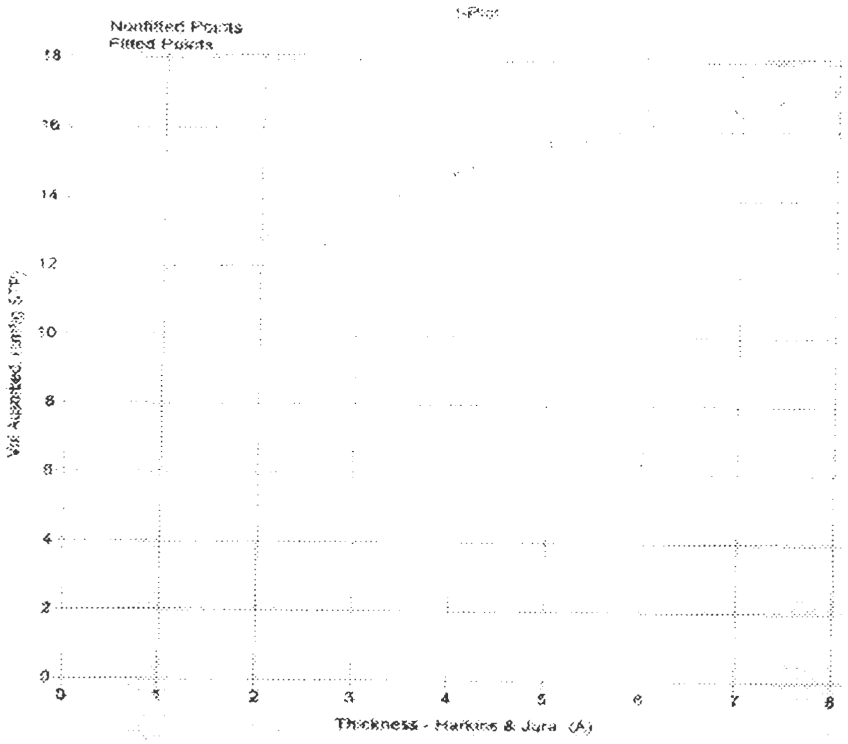


Figure 3.10 The t-plot of charcoal (coal).

The t - plot of figure (3.10) confirms that charcoal is microporous. It has very less pore volume: 0,03 cm^3/g. Its porosity is also very low. Pore diameter was very difficult to estimate. This is because charcoal has very small pores. The BET surface area is not valid, and it was 51 m^2/g.

Basically, it was very difficult to interpret results on charcoal.

3.1.1.2 TABLE OF THE RESULTS

Adsorbents	Pore volume *(cm^3/g)*	Pore size or diameter *($Å$)*	BET surface area *(m^2/g)*	Langmuir surfac area *(m^2/g)*
Activated carbon	0.63	30 and 60	842	1136
Charcoal	0.03	26 and 76	51	68
Charwood	0.1	21 and 61	200	266

3.1.1.3 CONCLUSION.

All the carbons are microporous. This is clearly explained by the t- plot which does not go to zero. The Langmuir surface area is valid for all the carbons since they are all Type I isotherms. Type H4 Hysteresis appeared for all of them. The BET surface area was not obeyed because the carbons are microporous. In general, carbons have smaller pores compared to oxides.

Among the three natural adsorbents, activated carbon has better porosity, larger Langmuir surface area, larger pore volume and pore diameter. Therefore, activated carbon is the better adsorbent, followed by charwood and then charcoal. Basically, it was very difficult to interpret results on charcoal (coal).

3.2 SEM (Scanning Electron Microscope)

The scanning electron microspore (SEM) is commonly used to examine the microstructure of bulk specimen. It is an electron-optical instrument which uses a source of electrons to illuminate specimen. These electrons are accelerated down the column and pass through a combination of electromagnetic lenses and apertures to form a fine probe at the surface of the specimen in the chamber area. Both the column and the chamber are held under vacuum to avoid high voltage discharge and scattering of the electrons along their path by residual gas atom[3].

The SEM is a valuable imaging tool which allows very fine detail to be resolved and, unlike an optical microscope, offers a large depth of field. In addition, it may be combined with appropriate detectors, to serve as a powerful analytical tool[3]. Sample preparation for SEM include polishing, mounting, coating, sputtering, and dehydrating the sample[3].

3.3 EDS (Energy Dispersive Spectrometry)

EDS (Energy Dispersive Spectrometry) is an X-ray spectrometer which collects the characteristic X-rays. The spectrometer counts and sorts the X-rays, usually on the basis of energy. The resulting spectrum plots number of X-rays, on the vertical axis versus energy, on the horizontal axis. Qualitative analysis can be thought of as the "ingredients" of the specimen and it identifies the elements present in the analysed volume of specimen. Peaks on the spectrum correspond to the elements present in the sample. The elements are identified by reference to tables and databases[3].

3.4 RESULTS AND DISCUSSIONS

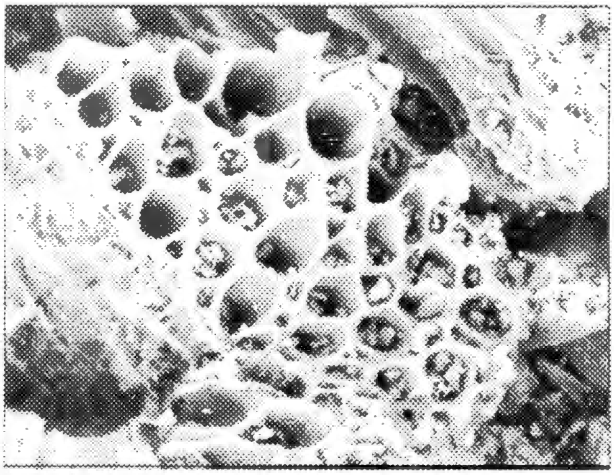
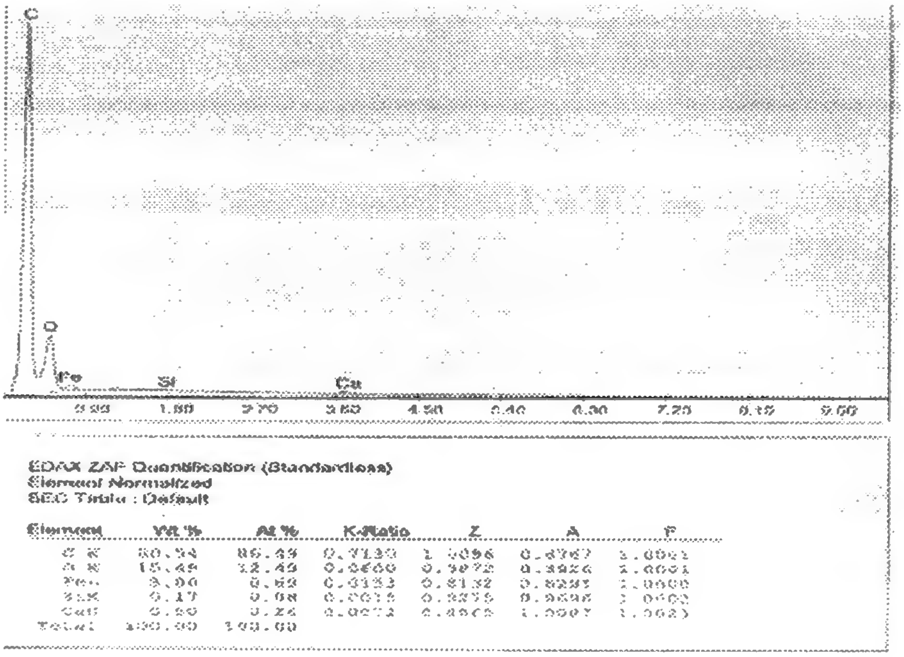


Figure 3.13 The SEM photo of activated carbon.

The above figure shows that activated charcoal is a layered porous material.



EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	80.54	86.49	0.7130	1.0096	0.8767	1.0001
O K	15.49	12.49	0.0600	0.9872	0.3926	1.0001
FeL	3.00	0.69	0.0333	0.8132	0.8285	1.0000
SiK	0.17	0.08	0.0015	0.8355	0.9696	1.0002
CuK	0.80	0.24	0.0072	0.8905	1.0007	1.0623
Total	100.00	100.00				

Figure 3 .14 The EDS analysis for activated carbon

The EDS graph shows that activated charcoal is the purer form of carb since it has less impurities. This is because activated charcoal has been heated to higher temperatures so as to remove impurities. The element composition are 87,56% of carbon, 15,87% of oxygen, 0,14 % of fluorine and 0,86 % of silicon.

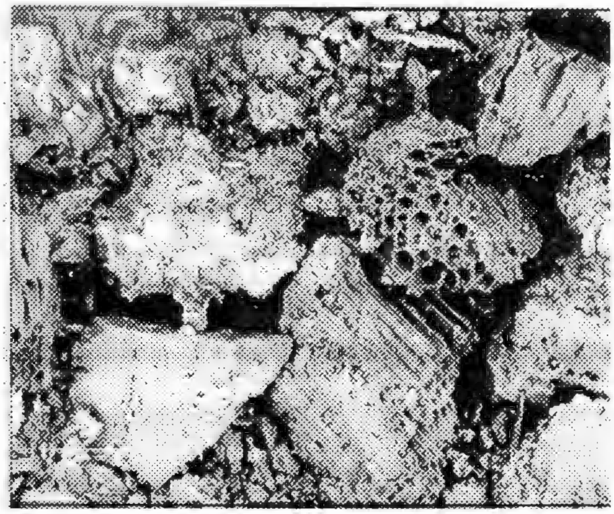
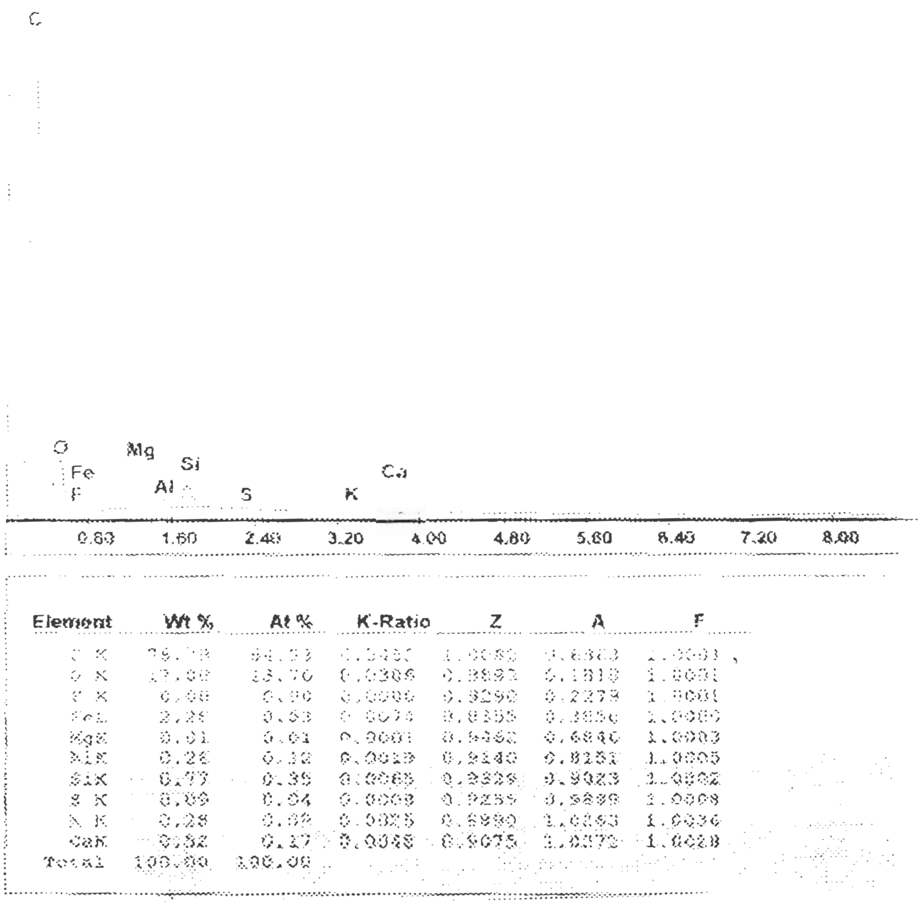


Figure 3.15 The SEM picture for char-wood.

The above figure suggest that char-wood is also a layered material.



Element	Wt %	At %	K-Ratio	Z	A	F
C K	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
O K	17.00	13.70	0.0306	0.3892	0.1310	1.0001
F K	0.00	0.00	0.0000	0.9290	0.2279	1.0001
FeL	2.25	0.53	0.0074	0.8355	0.3856	1.0000
MgK	0.01	0.01	0.0001	0.9462	0.6840	1.0003
AlK	0.26	0.12	0.0019	0.9140	0.8131	1.0005
SiK	0.77	0.35	0.0065	0.9329	0.9023	1.0002
S K	0.09	0.04	0.0008	0.9255	0.9899	1.0008
K K	0.28	0.09	0.0025	0.8990	1.0263	1.0036
CaK	0.32	0.17	0.0048	0.9075	1.0372	1.0028
Total	100.00	100.00				

Figure 3.16 The EDS analysis for char-wood

The above graph (Figure 3.16) shows that charcoal is n as p as activated carbon since it has many elements in it. Carbon a oxy are the main elements of both carbons.

3.5 THE ADSORPTION METHOD

3.5.1 EXPERIMENTS

APPARATUS: a) 250 *ml* beaker
- b) 250 *ml* volumetric flasks
- c) magnetic stirrers
- d) stirrer pieces
- e) Ultrafiltration membrane (PA-100)

CHEMICALS: a) AA water (milli Q water)
- b) HCl
- c) NaOH
- d) SPADNS reagent for fluoride analysis

ANALYTICAL TOOLS: a) HACH DR/890 Colorimeter (Programme 24)
- b) Pressure driven nanofiltration setup
- c) Labotec sieve with aperture opening of 90 *μm*

ADSORBENTS: a) Activated carbon
- b) Charcoal
- c) Charwood
- e) Chitosin (High molecular weight shells)
- f) Red and white maize cob (mixture of the third and second layers)

GROUND WATER SAMPLE COLLECTION- *A case study*

Ground water samples were collected from six different villages around Rustenburg namely Lefaragatlhe, Lerome (Doornkop store), Ledig (Kagiso Section), Ledig (Btshabelo Section), Saulspoort, And Lerome (Moruleng Section). Rustenburg was chosen as the area of study because literature studies, for example, Schoemann and associates, have shown that ground water around that area have fluoride which exceed 1 *mg/l*. Samples were all collected from boreholes during very hot weather when the temperature was about 32 ^{0}C. Samples were then kept in a cold place inside plastic bottles. The experiment was followed for water with excessive fluoride (Moruleng and Saulspoort).

EXPERIMENTAL PROCEDURE

a) Level of fluoride in ground water

Areas around Rustenburg were sampled for underground water. The samples were then analysed for fluoride.

b) Detecting whether the adsorbents have fluoride as one of their elements (purity of the adsorbents)

This was done by mixing 2 g of each of the adsorbents with milli Q water. The solutions were stirred for 1 hour, filtered with PA-100 ultrafiltration membrane, and the analysed for fluoride.

c) The adsorptive capacity of adsorbents

2 *g* of each adsorbent was mixed with 100 *ml* of 2 mg/l NaF solution. The mixture was stirred for 1 hour and the filtered. The permeate was analysed for fluoride.

d) The effect of mass of adsorbents on adsorption

100 *ml* of 2 *mg l* F^- was added to different masses of 0.5, 1 and 2 *g* and stirred for 1 hour. The solution was then filtered and analysed for fluorides.

e) The effect of temperature of adsorbents on adsorption

2 *g* of each adsorbent heated to temperatures of 100, 200, and 300 ^{0}C was added to 2 *mg l* F^- solution. The solution was stirred, filtered and analysed for fluorides.

f) The effect of concentration of fluoride on adsorption

2, 4, 6, and 10 *mg l* F^- solutions were prepared and added to 2 *g* of adsorbent separately.

g) The effect of contact time of fluoride and adsorbent on adsorption

2 g of each adsorbent was mixed with 2 *mg l* F solution. The solution was stirred for three different times : 20, 40, and minutes. The solution was filtered and analysed for fluorides.

h) The effect of pH on adsorption

2 g of each adsorbent was mixed with 100 *ml* of 2 *mg l* NaF at different pH (1, 4, 10 and 12). Analysis was made.

i) The removal of excessive fluoride from collected ground water

2 g of activated carbon was heated to 300 ^{0}C and then added to 100 *ml* of ground water. Experiment was followed only for two water samples since other samples did not show excessive fluoride.

3.5.2 RESULTS AND DISCUSSIONS

a) Fluoride concentrations in collected ground water samples

The following table shows the results which were obtained :

Area (Village)	**Fluoride concentration (*mg/l*)**
Lerome (Doornkop Store)	**0,9**
Lerome (Moruleng Section)	**5,4**
Ledig (Kagiso Section)	**0,0**
Ledig (Botshabelo Section)	**0,4**
Lefaragatlhe	**0,0**
Saulspoort	**4,9**

b) The purity of adsorbents

Maize cob (red and white) showed the presence of fluoride in it. The red maize cob was found to contain 0,29 *mg/l* fluoride and the white one contained 0,55 *mg/l* fluoride. Since maize cob proved to be the poor adsorbent for fluoride, no further experiments were done on it. All the other adsorbents were found to contain no fluoride.

c) The adsorption capacity of adsorbents

All the other adsorbents were found to be good for fluoride removal. For activated carbon, the initial mass of 2 *g* was reduced to 0,44 *g* (up to 78 % was adsorbed), for charwood it was reduced to 0,74 g (up to 63 % was adsorbed) and for charcoal it was 1,07*g* (up to 47 %). These results show that activated carbon is the best adsorbent for fluoride removal, followed by charwood and finally charcoal.

d) The effect of mass of adsorbent on adsorption

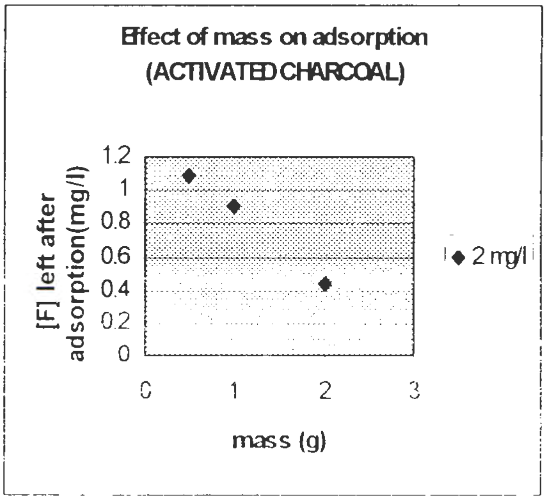


Figure 3.17 The plot of concentration of fluoride left after adsorption against the mass of activated charcoal using 2 mg/l of NaF solution.

From the figure above, it is observed that the larger the mass (2 g) of the adsorbent, the larger the adsorption. This is because when larger mass is used, there is enough available site for bonding. The larger the mass, the larger the surface area hence the better the adsorption.

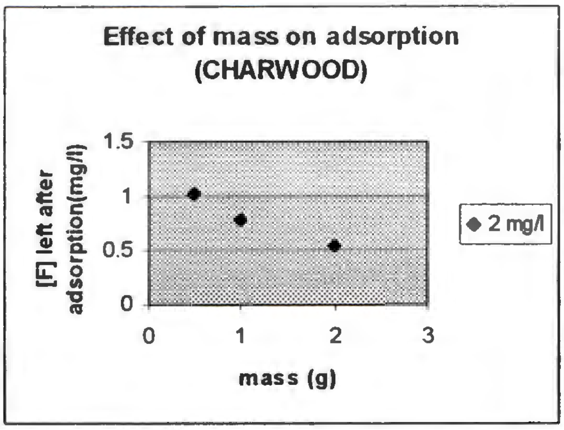


Figure 3.18 The plot of fluoride concentration left after adsorption against mass of char-wood using 2 mg/l of NaF solution.

As the mass of adsorbent increases, adsorption also increases. The use of smaller mass (0,5 g) reduce adsorption since the surface area is small.

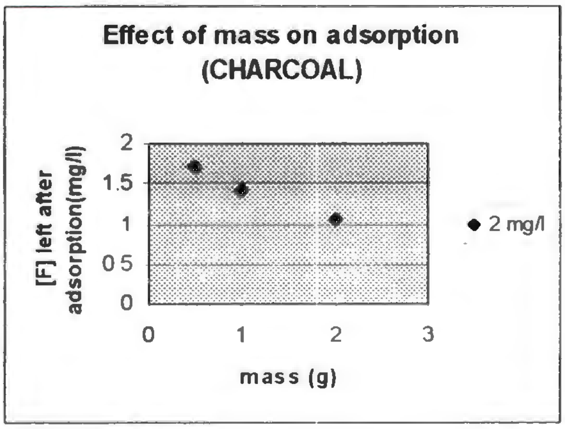


Figure 3.19 The plot of concentration of fluoride left after adsorption against mass of adsorbent using 2 mg l of NaF solution.

From the figure, it is observed that the larger the mass of adsorbent, the larger the adsorption. Charcoal is generally not a better adsorbent for fluoride removal but when larger mass is used, its adsorptive capacity increases.

SUMMARY ON THE EFFECT OF MASS OF ADSORBENT ON ADSORPTION

From the findings above, it is clear that the larger the mass, the better the adsorption because larger mass have large surface area and large bonding site. Activated charcoal gave best results, followed by char-wood and finally charcoal (coal). Activated charcoal has been heated to larger temperatures so as to be active hence it is very porous.

e) Effect of temperature of adsorbent on adsorption.

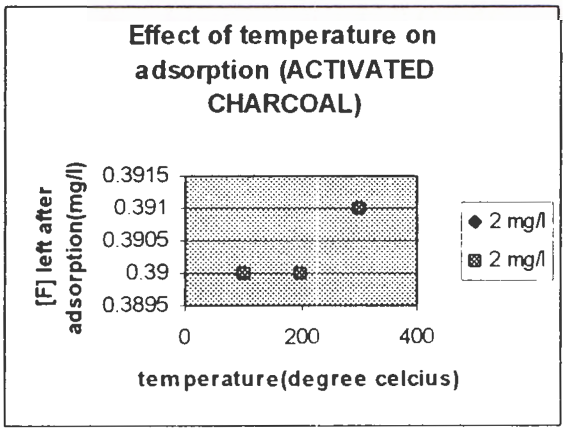


Figure 3.20 The plot of concentration left after adsorption against the temperature of 2 g of activated charcoal using 2 mg l of NaF solution.

From the graph, it is observed that the difference in temperature did not bring any changes to activated charcoal. This is because activated charcoal has already been heated to larger temperatures (600-800 ^{0}C) in its form.. By doing that, it was activated to remove impurities. The temperatures that were used in this research were not good enough to activate it further.

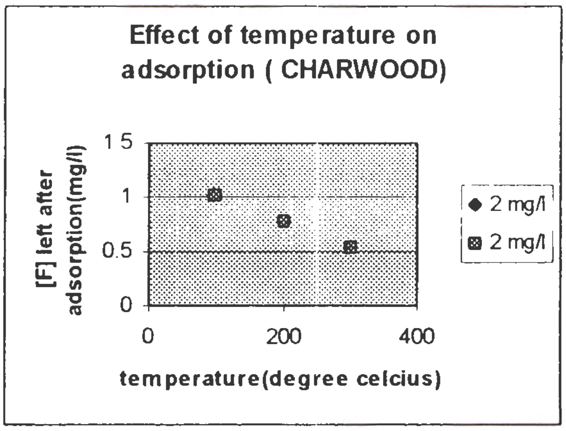


Figure 3.21 The plot of fluoride concentration left after adsorption against temperature of 2 g of char-wood using 2 mg/l of NaF solution.

The higher the temperature, the larger the adsorption. This is because by heating char-wood to higher temperatures, one is activating it and its adsorption capacity increases.

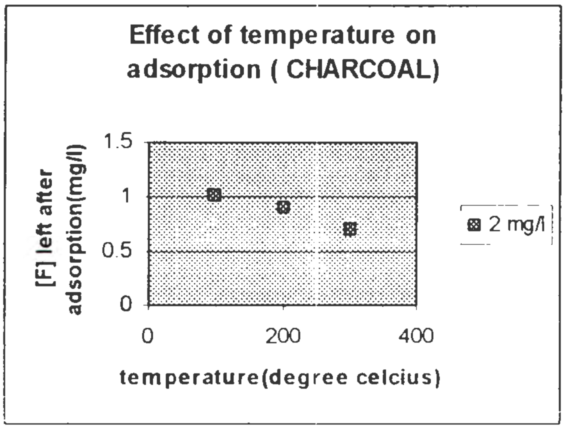


Figure 3.22 The plot of fluoride concentration left after adsorption against the temperature of 2 g of charcoal using 2 mg/l of NaF solution.

From the graph, it is observed that charcoal is the poor adsorbent for fluoride but at high temperatures, its adsorptive capacity increased.

SUMMARY ON THE EFFECT OF TEMPERATURE ON ADSORPTION

From the results obtained for the three adsorbents, it is observed that char-wood performed well under higher temperatures of 300^0C whereas activated charcoal did not show any effect on temperature. Charcoal is the poor adsorbent for fluoride removal but at higher temperatures it can perform better.

f) Effect of contact time of fluoride and adsorbent on adsorption.

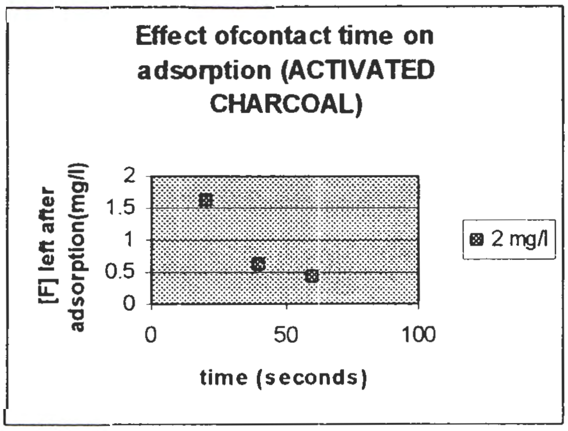


Figure 3.23 The plot of fluoride concentration left after adsorption against the contact time of 2 mg l of NaF solution and 1 g of activated charcoal.

The longer the contact time of activated charcoal and fluoride, the better the adsorption. This is because if the adsorbent is allowed to be in contact with fluoride solution, it will have enough time to adsorb fluoride.

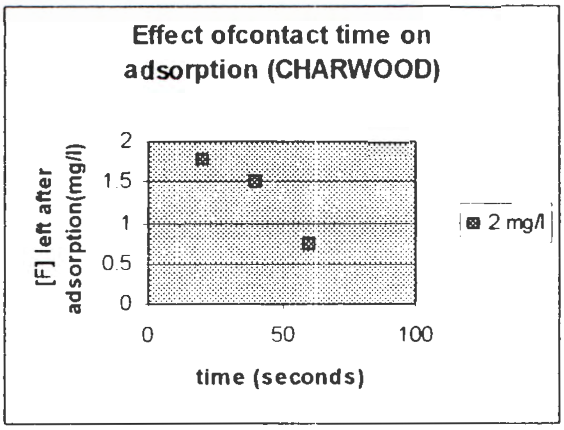


Figure 3.24 The plot of fluoride concentration left after adsorption against the contact time of 2 mg l of NaF and 2 g of char-wood.

The more the contact time of fluoride and the adsorbent, the better the adsorption.

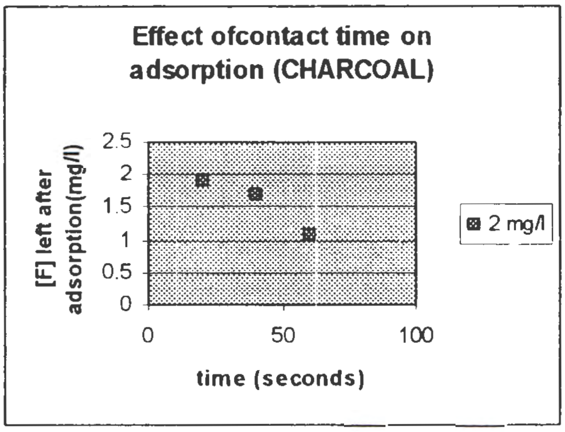


Figure 3.25 The plot of fluoride concentration left after adsorption against the contact time of 2 mg/l of NaF and 2 g of charcoal (coal).

The more the time of stirring of the solution of fluoride and charcoal, the better the adsorption since there will be enough contact time of adsorbent and fluoride.

SUMMARY ON THE EFFECT OF CONTACT TIME OF FLUORIDE AND ADSORBENT ON ADSORPTION

In general, the longer the time of stirring of the solution, the better the adsorption due to enough contact of fluoride and adsorbent. Among the three adsorbents, activated charcoal gave better results followed by char-wood and then charcoal.

g) Effect of concentration of fluoride on adsorption.

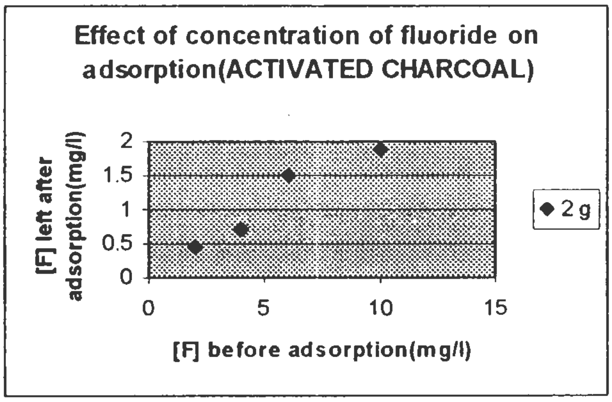


Figure 3.25 *The plot of fluoride concentration left after adsorption against the concentration of fluoride using 2 g of activated charcoal.*

There is a linear relationship between the concentration left after adsorption and the initial concentration of fluoride. The higher the concentration of fluoride, the lesser the adsorption since there will be a competition between the ions.

h) Effect of pH on adsorption

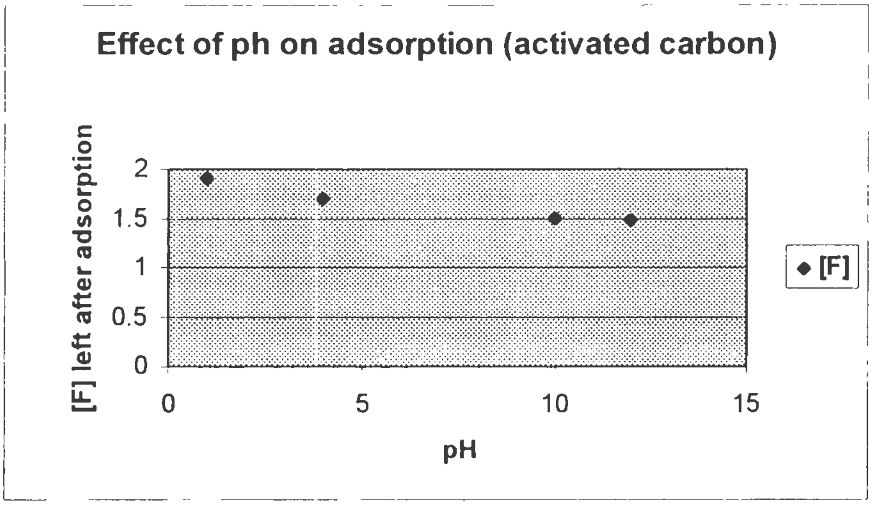


Figure 3.26 *The plot of fluoride concentration left after adsorption versus pH using 2 g of activated carbon.*

From the above graph it is observed that fluoride was adsorbed efficiently on basic medium (pH 10 and 12). Up to 60 % fluoride was adsorbed. In acidic medium (pH 1 and 4) not much fluoride was adsorbed. Less than 40 % fluoride was adsorbed.

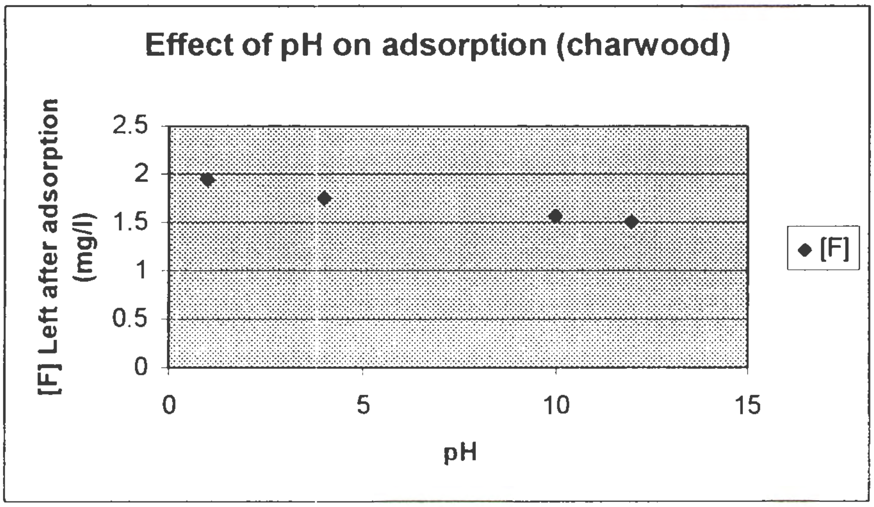


Figure 3,26 *The graph of fluoride concentration left after adsorption versus pH using 2 g of charwood and 2 mg l NaF.*

Charwood also performed better in the basic medium compared to acidic medium. Its adsorptive capacity was lesser than that of activated carbon.

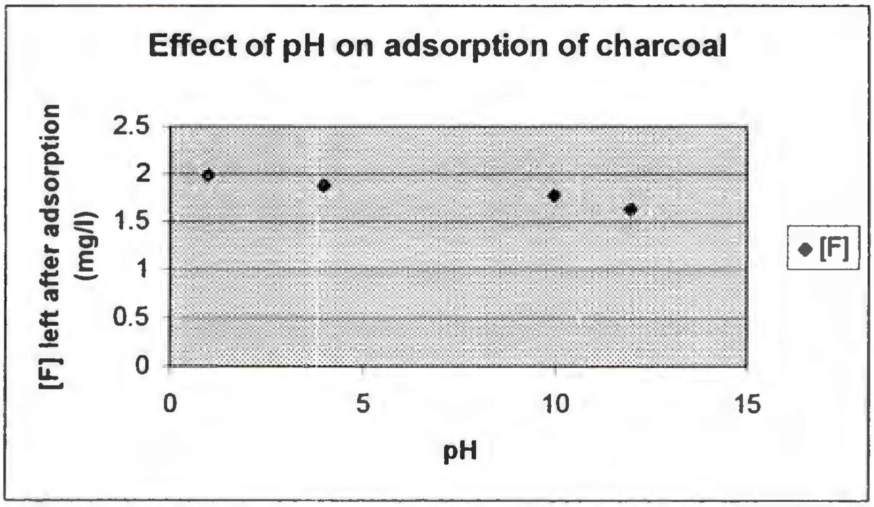


Figure 3.27 *The graph of concentration of fluoride left after adsorption versus pH using 2 g of charcoal and 2 mg/l NaF*

From the graph, it is observed that charcoal was not able to reduce fluoride efficiently. The adsorptive capacity was less than 20 % in both acidic and basic medium.

i) Fluoride concentration in water samples after adsorption

Fluoride concentrations from Moruleng and Saulspoort samples were reduced to considerable limit after the use of activated carbon.. Up to 65% fluoride was adsorbed from Moruleng sample whereas up to 67 % fluoride was adsorbed from Saulspoort sample. The following concentrations of fluoride were found:

Area(Village)	**[F$^-$] before adsorption** *(mg/l)*	**[F$^-$] after adsorption** *(mg/l)*
Lerome (Moruleng Section)	**5,4**	**1,9**
Saulspoort	**4,9**	**1,6**

Conclusion and discussions

Among the three adsorbents, activated carbon proved to be the best under the following conditions: when *larger* mass was used, when *higher* temperatures were applied, when *small* concentration of fluoride was used, when the time of stirring the solution was 1 hour, and when *basic* pH was used. Charwood also proved to be a better adsorbent with adsorption capacity of more than 60 %. Charcoal was the poorest adsorbent for fluoride.

Activated carbon also was efficient even in ground water samples since it was able to adsorb more than 70 % fluoride.

REFERENCES

1. ***Pure and Appl. Chem,*** Vol. 57, No .4, pp. 603-619, 1995
2. Mulder, M., 1996, **Basic Principles of Membrane Technology,** 2nd Edition, Kluwer Academic Publisher.
3. Tiedt, L.R., and Pretorius, W.E., ***An Introduction to Electron Microscopy And X-Ray Microanalysis,*** Laboratory for Electron Microscopy, PU for CHE

CHAPTER 4

4. THE MEMBRANE TECHNIQUE.

4.1 Characterisation of membranes

Membranes need to be characterised to ascertain which one may be used for separation or class of separations. A small change in one of the membrane formation parameters can change (top layer) structure and consequently have a drastic effect on membrane performance. Reproducibility is also often a problem. Membrane characterisation is necessary to relate structural membrane properties such as pore size, pore size distribution, free volume and crystallinity to membrane separation processes. For example, concentration polarisation and fouling of the membrane can cause large discrepancy on the membrane[1].

Membrane characterisation leads to the determination of structural and morphological properties of a given membrane. Irrespective of the structure developed, the first requirement after membrane preparation is to characterise the latter using simple techniques. Since membranes range from porous to non-porous, completely different characterisation techniques will be required in each case[1].

Membranes are characterised by the fact that the feed stream is divided into the retentate or concentrate stream and the permeate stream which implies that either the concentrate or permeate stream is the product

(Figure 4.1). If the aim is concentration, the retentate will usually be the product stream[1].

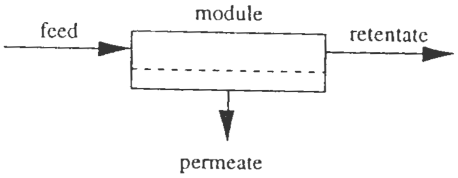


Figure 4.1 Schematic representation of a membrane process where the feed stream has been separated into a retentate and a permeate[1].

For my project, nanofiltration membranes are used. Nanofiltration membranes are intermediate between porous and non-porous membranes but their structure is more of non-porous than porous. In porous membranes, the pore size and pore size distribution mainly determines which particles or molecules are retained and which ones will pass through the membrane. Hence, the material of little importance in determining the separation performance. Examples of porous membranes are ultrafiltration and microfiltration membranes[23].

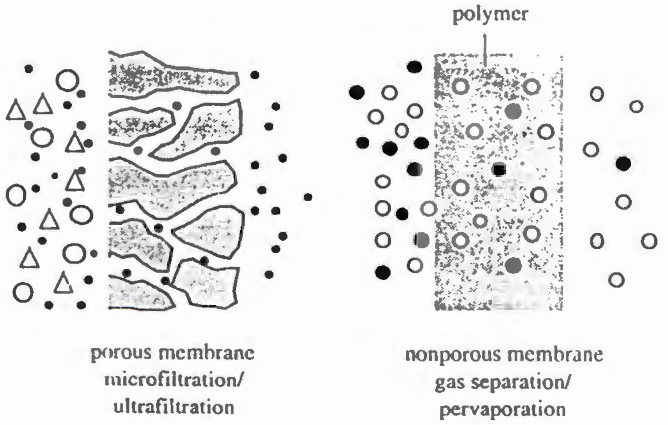


Figure 4.2 Schematic drawing of a porous and a nonporous membrane[1] .

Non-porous membranes are used to perform separation on a molecular level. However, rather than molecular weight or molecular size, the chemical nature and morphology of the polymeric membrane and the extent of interaction between the polymer and permeates are the important factor to consider. Transport through non-porous membranes occur by a solution-diffusion mechanism and separation is achieved either by differences in solubility and / or diffusivity. With non-porous membranes, the determination of the physical properties related to the chemical structure is important. Methods like permeability, plasma etching, surface analysis, and other physical properties are important For example , factors such as temperature and the interaction of the solvent and solute with the polymeric material, have a large influence on the segmental motion. Consequently, the material property will change if the temperature, feed composition and so forth, are changed.

4.2 EXPERIMENTS

APPARUTUS: a) 500 and 250 ml beakers,
b) 4 x 1*l* volumetric flask,
c) magnetic stirrer and stirrer pieces,
d) NF 70 membrane,
e) TFC-SR membrane,
f) nitrogen gas,

CHEMICALS: a) NaF,
b) AA water,
c) HC*l*,
d) NaOH,
e) SPADNS reagent for fluoride analysis
f) NaCl

EXPERIMENTAL PROCEDURE

Different concentrations of NaF solution were prepared (0.5, 1,2,4 and 5 mg/l). 2 mg/l of fluoride was chosen as the concentration that was obtained after the point of equilibrium was reached. Two types of membranes, NF 70 and TFC-SR were used to reject fluorides at pressures of 10, 15, and 20 bar using nitrogen gas. Membranes were first soaked in AA water for 1 hour before they were used so as to enhance wetting. The stirred nanofiltration set-up with the capacity of 1 *l* was used to perform the experiment. The first solution that was collected from the reactor in five minutes interval was thrown away so as to wash the membrane from impurities. The solute can be partly or completely retained while the solvent molecules pass freely through the membrane. The permeate is usually potable water.

The amount of fluoride left in the permeate and retentate was monitored using HACH DR/890 colorimeter and SPDNS reagent. Percentage rejection is given by:

$$R = c_f - c_p/c_f = (1 - c_p/c_f) \times 100\%$$

Where c_f is the solute concentration in the feed, c_p is the solute concentration in the permeate, R is the rejection which is the dimensionless parameter.

The water flux with different amount of NaF (solute flux) and pure water flux (solvent flux) of the membranes was determined. Flux is given by:

$$J = A(\Delta P - \Delta\pi),$$

where J is the flux ($m^3/m^2.s$), A is the permeability coefficient ($m^3/m^2.s.P$), ΔP is the driving force (Pa) and $\Delta\pi$ is the osmotic pressure difference (Pa).

The following parameters were also studied using the two membranes: pH, pressure, salt, and concentration.

Finally, the percentage retention and the water flux of ground water sample were determined using a better performing membrane (NF 70).

METHODS

The following procedure was followed for both NF 70 and TFC-SR

1. *Effect of pressure on pure water flux (solvent flux)*

The membrane was cut then soaked in water for 1 hour. The setup with water inside was pressurised by nitrogen gas at 10, 15, and 20 bar. After five minutes, first permeate was discarded so as to wash off the membrane. In the next five minutes' interval the permeate was collected. The volume flux of pure water ($ml.s^{-1}.m^{-2}.bar^{-1}$) was determined.

2. *Effect of NaF concentrations on pure water flux*

0.1, 1, 2, 4, and 5 mg/l of NaF solutions were prepared. 1*l* of each solution was added into the membrane reactor. These were pressured (10, 15, and 20 bar) and the permeate was collected after 5 minutes. The flux of the permeate was determined.

3. *Effect of NaF concentration on fluoride rejection*

Various concentrations of NaF were used under various pressures. The solution was filtered and the permeate and retentate were collected. Percentage rejection was determined.

4. *Effect of pH*

NaF concentrations of 2 mg/l was used under pressure at various pH of 1and 4 (acidic), 10 and 12 (basic). Unbuffered solution was also used. The flux and rejection of the permeate were determined.

5. Effect of other ions on NaF rejection

NaF concentration was separately mixed with the following solutions to form mixtures: a) 50 mg/l of NaCl

b) 35 mg/l of NaCl and 15 mg/l of HCl

c) 25 mg/l of HCl and 25 mg/l of NaCl

g) 50 mg/l of HCl

6. Efficiency of NF 70 on fluoride retention at pH 10 and 12 and water flux of ground water

Ground water samples with the initial concentrations of 4.9 and 5.4 mg/l fluoride were used under pressure of 20 bar. The final concentration of fluoride was determined.

4.3 RESULTS AND DISCUSSION

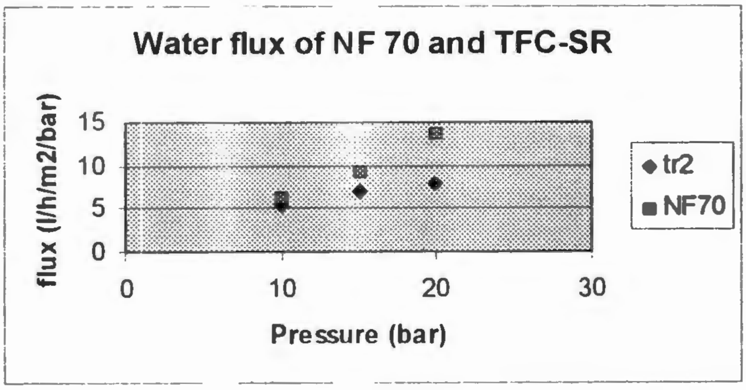


Figure 4.1 The graph of flux versus pressure of NF 70 and TFC-SR

The above graph shows the relationship between the water flux of the two membranes. As pressure increases flux also increases. It is observed from the graph that NF 70 has the high water flux (up to 7,2 $l.h^{-1}.m^{-2}/bar^{-1}$) TFC-SR produced the lower water flux (2,88 $l.h^{-1}.m^{-2}.bar^{-1}$) which was almost two times that of NF 70. This is so because NF 70 is more porous than TFC-SR 2 which has a more compact structure. Membranes with high flux are usually regarded as good .

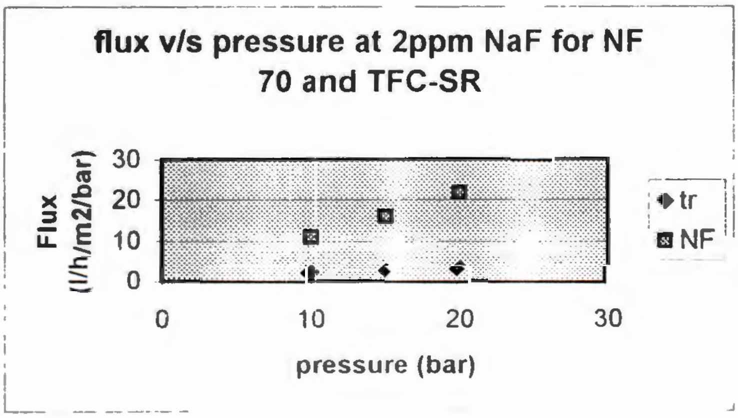


Figure 4.2 The graph of flux versus pressure of the two membranes at 2 mg l NaF.

The above graph shows the effect of concentration on flux of the two membranes. The linear relationship is observed between flux and pressure irrespective of the concentration of fluoride added. TFC-SR 2 gave the high solute flux of up to 13.32 $l.h^{-1}.m^{-2}.bar^{-1}$ whereas NF 70 gave the lowest solute flux of 1.32 $l.h^{-1}.m^{-2}.bar^{-1}$.

The solute flux of NF 70 is lower than its pure water flux since NaF accumulated on the membrane and thus made the passage of water very difficult. On the other hand, TFC-SR gave larger solute flux and lower solvent flux since the membrane film dissolved in the solution of NaF which made it very porous.

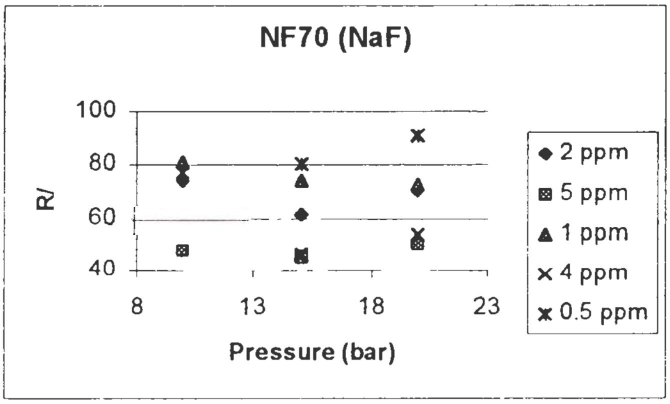


Figure 4.3 the graph of R% versus pressure of NF 70 at various concentrations of fluoride.

The lower the concentration of fluoride, the higher the percentage retention. This was clearly explained by the above graph where the 90 % of retention was obtained at lower concentrations whereas only 50 % retention was obtained at the highest concentration.. There is no linear relationship between percentage retention and pressure because the points on the graph gave a v-shape, that is, retention increased, then decreased and finally increased.

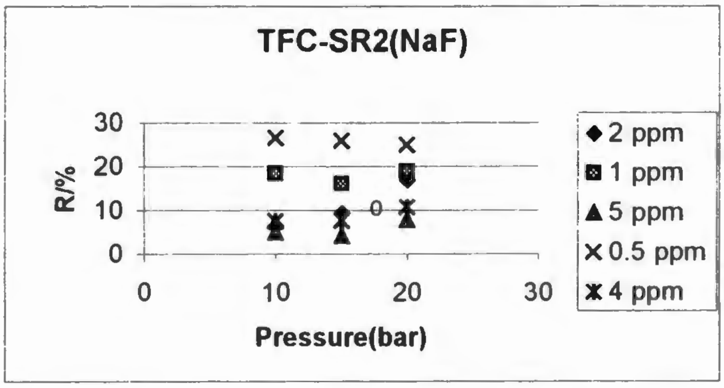


Figure 4.4 The graph of R% versus pressure of TFC-SR at various concentrations of NaF.

Generally, TFC-SR 2 membrane is poor for fluoride removal. This was confirmed by poor retentions that were obtained. The highest retention was only 25 %. Since this membrane gave highest solvent flux, most of the fluoride was allowed to pass through the membrane with water. There is an inverse proportionality between solvent flux and retention, that is, membranes with larger solvent flux produces lower retentions, vice versa.

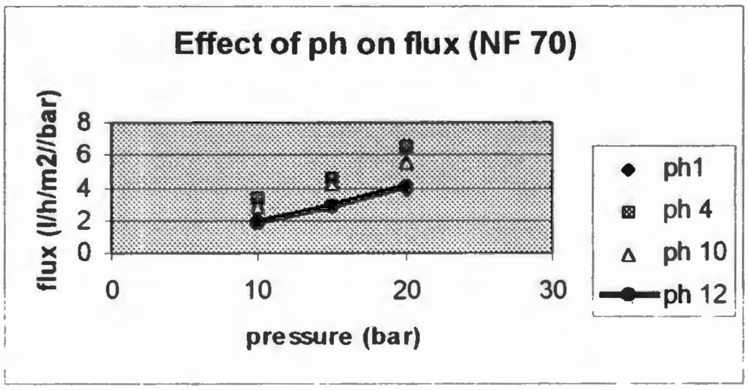


Figure 4.5 The graph of flux versus pressure at various pH and 2 mg l NaF (NF 70).

The linear relationship between flux and pressure is observed but the changes in pH lowered the flux. The highest flux of 3,6 *l.h^{-1}.m^{-2}.bar^{-1}* was obtained at the acidic pH (4). The basic pH lowered the flux to even smaller flux (1.6 *l.h^{-1}.m^{-2}.bar^{-1}*).

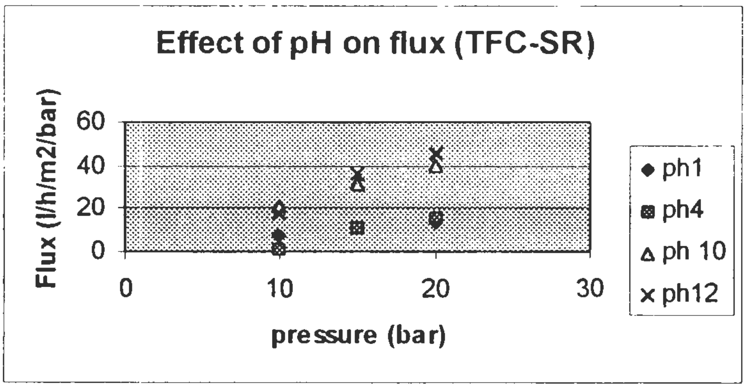


Figure 4.6 The graph of flux versus pressure at various pH and 2 mg/l NaF (TFC-SR).

From the above graph, it is observed that TFC-SR produced the highest flux (27 *l.h^{-1}.m^{-2}.bar^{-1}*) at the higher pH (12 and 10) whereas low pH (1 and 4) reduced the flux (10,88 *l.h^{-1}.m^{-2}.bar^{-1}*). In general, this membrane gave better flux at various pH compared to NF 70. The reason is that the changes in pH led to the improved porosity of TFC-SR since acids and bases reacted with the membrane film. The decreased flux of NF 70 is due to the salts and other chemicals accumulated on the membrane which made it to be compact.

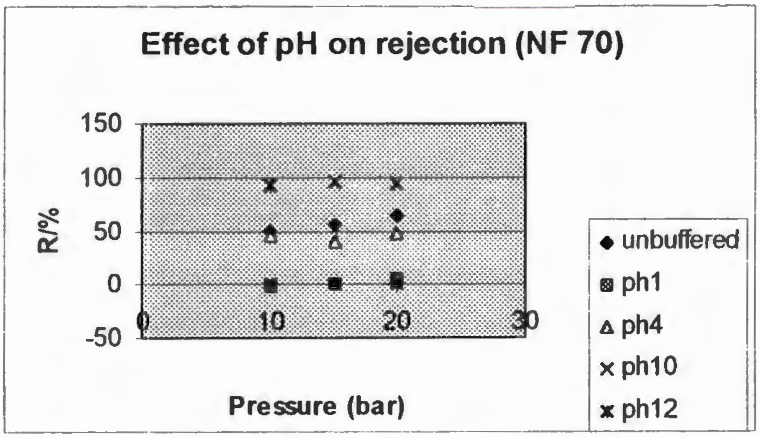


Figure 4.7 The plot of R% versus pressure at 2 mg/l NaF (NF 70)

The higher the pH, the larger the retention. The basic pH of 10 and 12 gave better retentions of up to 96%. Acidic pH (1 and 4) lowered the retention to even negative numbers.

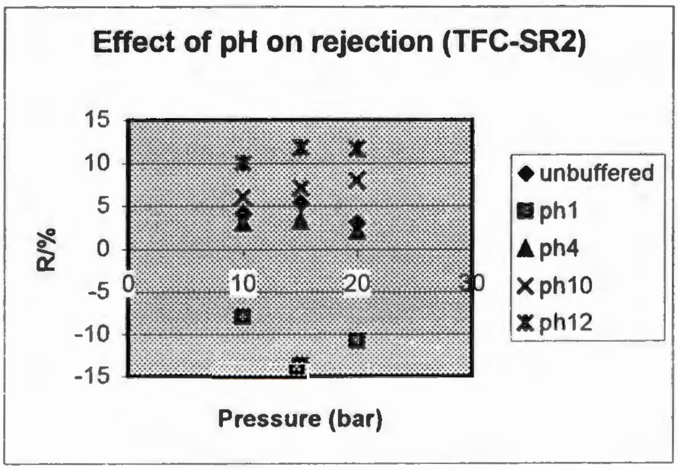


Figure 4.8 The plot of R% versus pressure at 2 mg/l NaF (TFC-SR)

The above graph shows that the acidic solutions yield lower retentions whereas basic ones yield better retentions. Comparing the two membranes, it is clear that both membranes produce better retentions in basic pH but NF 70 membrane produced best retentions.

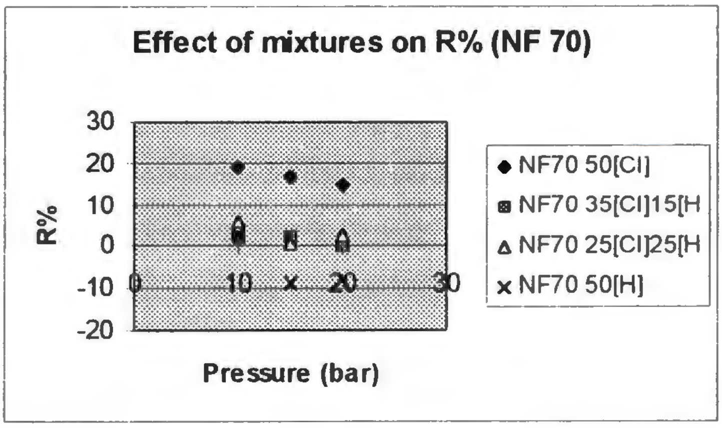


Figure 4.9 The plot of R% versus pressure at multiple concentrations of NaCl, HCl, and 2 mg/l NaF.(NF 70).

The figure above shows that with mixtures, NF70 is generally giving poor retentions. The membrane retained up to 20 % of fluoride. The membrane fluoride retained fluorides better when the concentration of chloride ions was high (50 mg/l) in the absence of acid (HCl). The addition of HCl to NaCl reduced the retention to 5 % and to even negative values when 50 mg/l of acid was added. The poor retention in the presence of chloride and fluoride ions is due to the competition that existed between the ions (ions are competing for the binding side on the membrane).

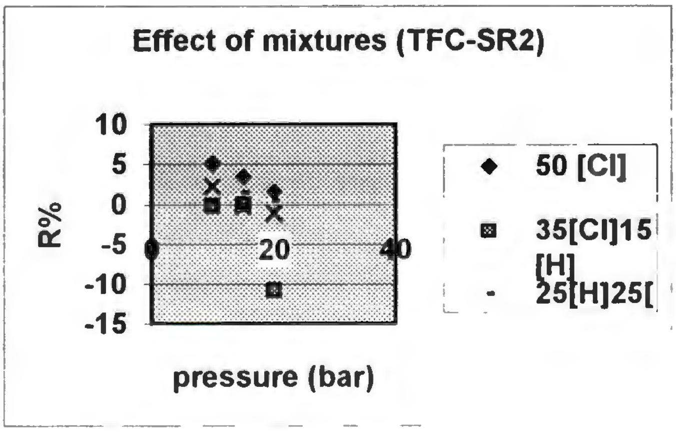


Figure 4.10 The plot of R % versus pressure at multiple concentrations of NaCl, HCl, and 2 mg l NaF (TFC-SR 2).

This membrane generally produced poor retentions but with the addition of mixtures worst results were obtained. The above graph shows that only 12 % retention was produced. Addition of acid (50 *mg/l*) improved the retention rather than NaCl.

The efficiency of NF 70 on the fluoride retention at basic medium and water flux of ground water.

After treatment with NF 70 membrane, the initial concentrations of 4.9 *mg/l* and 5,4 *mg/l* fluoride in ground water were able to reduce to 1,9 and 2.2 mg/l respectively. This shows that the membrane is efficient since it was able to trap more than 50 % fluoride. The water flux of the two samples was 8,44 $l.h.^{-1}.m^{-2}.bar^{-1}$ and 8,29 $l.h^{-1}.m^{-2}.\mathrm{bar}^{-1}$ (See the table below).

Village	**Initial [F^-] (*mg/l*)**	**Final [F^-] (*mg/l*)**	**Water flux ($l.h^{-1}.m^{-2}bar^{-1}$)**
Moruleng (LEROME)	**5.4**	**2,2**	**8,44**
Saulspoort (BAKGATLHA)	**4.9**	**1,9**	**8,29**

Table 2 .*Table of the results on ground water samples.*

DISCUSSIONS AND CONCLUSIONS

From the results, it is clear that NF 70 is the better membrane for fluoride removal compared to TFC-SR. A linear relationship was obtained for both the solute and solvent flux with pressure. NF 70 gave larger water (solvent flux), lower solute flux and better retention (up to 90 %) whereas TFC-SR gave larger solvent flux (fluoride also passed through), lower water flux and poor retentions of even negative values. This made NF 70 to be a better membrane. Membranes with high water flux and low solvent flux are good ones since they lead to larger retentions.

Addition of NaCl, HCl, and NaF and changes in pH (1,and 4) decreased the flux and the retention ability of the two membranes due to the competition for the binding side that occurs between the ions. The basic solutions improved retention and it is an advantage because ground water has some basic salts thus it will not be difficult for one to remove fluoride in the presence of those ions.

The ground water treatment by NF 70 also showed that it is the best membrane for fluoride removal.

In conclusion, NF 70 is more preferred membrane due to the following reasons:

- A better water flux is observed (up to 7,22 $l.h^{-1}.m^{-2}.bar^{-1}$) for laboratory water and 8,44 l/h/m^2/bar and 8,29 l/h/m^2/bar for ground water samples which falls within the flux range for nanofiltration membranes (1,4 - 12 $l.h^{-1}.m^{-2}.bar^{-1}$). This membrane performed better in the absence of acidic media and also in the absence of mixtures but extremely good in the presence of a base.

- A better retention was obtained (Between 90% and 96 %)).

REFERENCES

1. Hill, J.W., 1988, **Chemistry for changing times,** Millan Publishing Company, a division of Mac Millan, Inc, U.S.A

2. Mulder, M., **Basic Principles Of Membrane Technology,** 2nd Edition. 1996, Kluwer Acadamic Publishers, Netherlands

CHAPTER 5

EVALUATION

5.1 Summary on the defluoridation capacity of the two techniques used (Membrane and Adsorption).

5.1.1 The membrane technique.

Between the two membranes (TFC-SR and NF 70), NF 70 yielded better retentions at lower concentrations of fluoride (2 mg/*l)* and at higher pressures of 20 bar. Up to 90 % of fluoride was removed from water using this membrane. NF 70 also produced better water flux and poor solute flux. This was an advantage because if lesser amount of solute pass through the membrane, it means defluoridation is efficient since chances of obtaining water with less amount of fluorides are high.

On the other hand, TFC-SR was found to be the poorest membrane for fluoride removal since it yielded only up to 25 % fluoride retentions. The solute (NaF) reacted with the film of the membrane and hence made the membrane very porous. Retention decreased because the membrane also allowed a lot of fluoride ions to pass through.

Based on the finding outlined above, it is clear that NF 70 is a better membrane for fluoride removal.

5.1.2 Adsorption technique

Among the three adsorbents used, activated charcoal proved to be the better one for fluoride removal, followed by char-wood, and then charcoal (coal). All the adsorbents performed well under the following conditions: when a larger mass of 2 g was used, when contact time of 1 hour was used, when a smaller concentration of 2 g was used, and when a higher temperature of 300^0C was used (in case of char-wood and charcoal). Higher temperatures of 300^0 did not bring any changes to activated charcoal since extremely high temperatures (600^0) are needed to activate it. Activated carbon was able to reduce 2 mg/*l* of fluoride to 0,4 mg/*l*, which is good. Char-wood was able to give 0,7 mg/*l* whereas charcoal gave only 1,09 mg/*l*.

Although activated charcoal was able to remove a larger amount of fluoride in water, it is better to use char-wood due to its availability. Since charcoal (coal) is not a good adsorbent, it will be of no use to use it for defluoridation.

5.2 Conclusions and suggestions

From the two techniques, the membrane technique with the use of NF 70 proved to be the most effective method for defluoridation. This was shown by the larger retentions obtained for both laboratory waters and ground water samples. For practical use, this method is not suitable since it is expensive and it is not easy to use as one might think (especially if it has to be used mainly by people in rural areas).

The membranes are not readily available. They are prepared from the laboratory using a unique support and then coated with expensive chemicals. If this technique is to be used, the government should be willing to spend for the sake of the health of the consumers.

Due to the above pitfalls of membrane technique, I would suggest the use of the batch process by char-wood since the process is cheap (very economical), and it is easy to use with readily available adsorbent. This method can be adapted at both domestic and community level.

Defluoridation by char-wood can be practically done as follows:

People from rural areas have to be trained as to how to defluoridate water. At domestic level, wood will be burnt to produce char-wood, then heated to 300^0C (using stoves). Solution mixture of polluted water and char-wood will then be stirred using any suitable domestic stirrer for a longer time, and then filtering will follow. Sand can be used as a filter. The product obtained is potable water. The amount of water to be defluoridated can be determined by the consumer depending on the size of the family or consumers.

At community level, a big tank (big enough to feed the whole village) has to be filled with water and char-wood, then stirred and filtered. Modern electronic equipment has to be devised and used for stirring and filtering. Of course, this can only be possible if enough funds are available.

APPENDIX 1 (ADSORPTION PROCESS)

TABLE 1.1 THE PRESENCE OF FLUORIDE IONS ON THE ADSORBENTS USING 2g OF EACH ADSORBENT.

Adsorbents	Contact Time (seconds)	Temperature (^{0}C)	[F] mg/*l*
chitosan	60	300	0
Maize cob(red and white)	60	300	0,29 and 0,55
Activated charcoal	60	300	0
Charwood	60	300	0
Charcoal(coal)	60	300	0

EFFECT OF MASS OF THE ADSORBENTS ON THE ADSORPTION OF FLUORIDE IONS.

Table 1.2 Effect of mass of activated charcoal on the adsorption of fluoride ions using 2 mg/l of NaF solution.

Mass (g)	Contact time (sec)	Temperature (^{0}C)	[F] left after adsorption (mg/*l*)
0,5	60	300	1,09
1	60	300	0,9
2	60	300	0,44

Table 1.3 The effect of mass of charwood on the adsorption of fluoride ions using 2 mg/l of NaF solution.

Mass(g)	Contact time (seconds)	Temperature (^{0}C)	[F] solution after adsorption (mg/*l*)
0,5	60	300	1,4
1	60	300	1,1
2	60	300	0,74

Table 1.4 Effect of mass of charcoal on the adsorption of fluoride ions using 2 mg/*l* of NaF solution.

Mass (g)	Contact time (seconds)	Temperature(^{0} C)	[F] left after adsorption (mg/*l*)
0,5	60	300	1,7
1	60	300	1,4
2	60	300	1,07

EFFECT OF TEMPERATURE OF ADSORBENTS ON ADSORPTION OF FLUORIDE ION.

Table 1.5 The effect of temperature of activated charcoal on the adsorption of fluoride ions using 2 mg/l of NaF solution.

Mass (g)	Temperature (^{0}C)	Contact time (seconds)	[F] left after adsorption (mg/l)
2	100	60	0,39
2	200	60	0,39
2	300	60	0,4

Table 1.6 Effect of temperature of charwood on the adsorption of fluoride ion using 2 mg/*l* of NaF solution.

Mass (g)	Contact time (seconds)	Temperature (^{0}C)	[F] left after adsorption (mg/*l*)
2	60	100	1.01
2	60	200	0,78
2	60	300	0,54

Table 1.7 The effect of temperature of charcoal on the adsorption of fluoride ions with 2 mg/l NaF solution.

Mass (g)	Contact time (seconds)	Temperature (^{0}C)	[F] left after adsorption (mg/*l*)
2	60	100	1,01
2	60	200	0,9
2	60	300	0,7

EFFECT OF CONTACT TIME OF ADSORBENT AND FLUORIDE ON ADSORPTION.

Table 1.8 Effect of contact time of activated charcoal and fluoride on adsorption of fluoride ions using 2 mg/l of NaF solution.

Mass (g)	Contact time (seconds)	Temperature (^{0}C)	[F] left after adsorption (mg/*l*)
2	20	300	1,67
2	40	300	0,63
2	60	300	0,44

Table 1.9 Effect of contact time of charwood and 2 mg/l of NaF on the adsorption of fluoride ions.

Mass (g)	Contact time (seconds)	Temperature (^{0}C)	[F] left after adsorption(mg/*l*)
2	20	300	1,78
2	40	300	1,5
2	60	300	0,74

Table 1.10 Effect of contact time of charcoal and 2 mg/l of NaF on adsorption of fluoride ions.

Mass (g)	Contact time (seconds)	Temperature (^{0}C)	[F] left after adsorption(mg/l)
2	20	300	1,91
2	40	300	1,7
2	60	300	1,07

EFFECT OF CONCENTRATION OF NaF SOLUTION ON ADSORPTION OF FLUORIDE IONS.

Table 1.11 Effect of concentration on adsorption using 2 g of activated charcoal.

Temperature (^{0}C)	Contact time(seconds)	[F] before adsorption(mg/l)	[F] after adsorption(mg/l)
300	60	2	0,44
300	60	4	0,7
300	60	6	1,5
300	60	10	1,89

Table 1.12 Effect of concentration of fluoride on adsorption using 2 g of charwood.

Temperature (^{0}C)	Contact time (seconds)	[F] before adsorption (mg/l)	[F] after adsorption (mg/)
300	60	2	0,74
300	60	4	1,09
300	60	6	1,6
300	60	10	1,92

Table 1.13 Effect of concentration of fluoride on adsorption using 2 g charcoal (coal).

Temperature (^{0}C)	**Contact Time (Minutes)**	**[F] before adsorption (mg/*l*)**	**[F] after adsorption(mg/*l*)**
300	**60**	2	**1,07**
300	**60**	4	**1,5**
300	**60**	6	**1,8**
300	**60**	10	**1,96**

EFFECT OF pH ON ADSORPTION

Table 1.14 Effect of pH on adsorption of 2 g of activated carbon and 2 mg/l NaF

Temperature(^{0}C)	**Contact time (minutes)**	**pH**	**[F] after adsorption (mg/l)**
300	**60**	1	**1.9**
300	**60**	4	**1.7**
300	**60**	10	**1.5**
300	**60**	12	**1.46**

Table 1.15 Effect of PH on adsorption of 2 g of charwood and 2 mg/l NaF

Temperature (^{0}C)	***Contact time (minutes)***	*ph*	***[F] left after adsorption (mg/l)***
300	**60**	1	**1,93**
300	**60**	4	**1,75**
300	**60**	10	**1,56**
300	**60**	12	**1,49**

Table 1,16 The effect of ph on adsorption of 2 g of charcoal and 2 mg/l NaF

Temperature (^{0}C)	Contact time (minutes)	ph	[F] left after adsorption (mg/l)
300	60	1	1,98
300	60	4	1,87
300	60	10	1,77
300	60	12	1,63

APPENDIX 2

MEMBRANE PROCESSES.

Table 2.1 Pure water flux of NF 70 and TFC-SR 2 membranes.

Membrane Type	Pressure (bar)	Solvent Flux (l/m^2/h/bar)
NF 70	10	6,228
	15	9,22
	20	13,68
TFC-SR 2	10	7,59
	15	8,17
	20	8,57

Table 2.2 Effect of NaF concentration on flux of NF 70 and TFC-SR 2 using 2 mg/l of NaF.

Membrane Type	**Pressure (bar)**	**Solute flux (l/m^2./h/bar)**
NF 70	10	1,334
	15	1,991
	20	2,675
TFC-SR 2	10	10,83
	15	16,85
	20	23,29

Table 2.3 The effect of NaF concentration on Retention of fluoride using NF 70 membrane.

Initial [F] /mg/*l*	Pressure(bar)	Retention (%)
0,5	10	77,32
	15	80
	20	90,91
1	10	80,65
	15	74
	20	73
2	10	74
	15	61,4
	20	70,09
4	10	30
	15	46,12
	20	53,42
5	10	47,92
	15	45,1
	20	50

Table 2.4 The effect of concentration of NaF on Retention of fluoride using TFC-SR 2 membrane.

Concentration(mg/*l*)	**Pressure(bar)**	**Retention(%)**
0,5	10	26,7
	15	25,9
	20	25
1	10	18,4
	15	16,1
	20	18,9
2	10	6,4
	15	9,2
	20	16,81
4	10	7,5
	15	7,55
	20	10,66
5	10	5
	15	4,1
	20	7,8

Table 25 The effect of pH on flux of NF 70 membrane.

Pressure(bar)	**pH**	**Flux (m^2/lh/bar)**
10	**1**	**3,564**
15		**5,004**
20		**6,48**
10	**4**	**3,53**
15		**5,05**
20		**6,91**
10	**10**	**3,71**
15		**15,54**
20		**7,52**
10	**12**	**3,13**
15		**4,82**
20		**6,12**

Table 2.6 Effect of pH on flux of TFC-SR 2

Pressure(bar)	pH	Flux (*l*/m^2/*h/bar)*
10	1	15,8
15		22,97
20		31,32
10	4	11,99
15		17,75
20		23,25
10	10	20.84
15		29,30
20		43,81
10	12	22,28
15		36,94
20		48,71

Table 2.7 Effect of pH on Retention using NF 70 membrane and 2 mg/l of NaF solution.

Pressure(bar)	**pH**	**Retention(%)**
10	**1**	**-1,2**
15		**1,4**
20		**4,7**
10	**4**	**38,97**
15		**46,1**
20		**47,8**
10	**10**	**0**
15		**95,5**
20		**94,6**
10	**12**	**91,9**
15		**0**
20		**0**

Table 2.8 The effect of pH on Retention of fluoride using TFC-SR 2 membrane with 2 mg/l of NaF solution.

Pressure(bar)	pH	Retention(%)
10	1	0,2
15		-13,7
20		-10,9
10	4	3,2
15		3,7
20		5
10	10	5,6
15		7,4
20		7,8
10	12	8
15		11,8
20		15

Table 2.9 Effect of 2 mg/l of NaF and mixtures (NaCl and HCl) on Retention using NF 70 membrane.

Pressure(bar)	**Mixtures (mg/l)**	**Retention (%)**
10	**50 mg/*l* NaCl**	**19,1**
15		**16,6**
20		**14,6**
10	**35 mg/*l* NaCl + 15 mg/*l* HCl**	**2,25**
15		**2,3**
20		**0**
10	**25 mg/*l* *H*Cl + 25 mg/*l* NaCl**	**5,81**
15		**0,63**
20		**2,6**
10	**50 mg/*l* HCl**	**2,5**
15		**-9,1**
20		**-7,8**

Table 2.10 The effect of 2 mg/l of NaF and mixtures (NaCl and HCl) on Retention using TFC-SR 2 membrane.

Pressure(bar)	Mixtures (mg/*l*)	Retention (%)
10	50 mg/*l* NaCl	-11,3
15		-12,5
20		-3,2
10	35 mg/*l* NaCl + 15 mg/*l* HCl	0
15		-3,6
20		-2,4
10	25 mg/*l* HCl + 25 mg/*l* NaCl	4,9
15		4,8
20		6,5
10	50 mg/*l* HCl	6,5
15		12,02
20		-1,3