A BI-FACETED ADSORPTIVE PERFOMANCE OF TiO_2-COATED CARBON FOR THE REMOVAL OF FLUORIDES IN WATER

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by

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DEDICATION

I dedicate this work to my late parents and late grandmother, to my family and to all the people who believed in me. I also dedicate this study to Mr Zweli Maphanga and Nosipho Maphanga for their undying love and immeasurable support.

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The results obtained from this work have been presented in regional and international conferences and some of them have been submitted for publication in peer-reviewed journals.

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ABSTRACT

In this study, non-impregnated and TiO_2-encapsultaed *Musa paradisiaca* (MP) stem carbon have been synthesized, characterized and applied for removal of fluorides in water samples. It was found that water sources contain fluorides and at some sampling sites, levels were above the maximum contaminant level (MCL) as set by the World Health Organization (WHO) and the South African Department of Water Affairs. The WHO permissible levels of fluorides in drinking water are fixed at 1.5 mg L^{-1}.

Suitable physical and instrumental characterization studies were carried out after the synthesis of the MP carbon materials. Fourier transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) were used for investigating the structural integrity of the adsorbents. The FT-IR spectrum confirmed the functional groups present in the adsorbent materials. The SEM confirmed the surface morphology of the MP carbon materials. The non-impregnated and the TiO_2-coated MP carbon differ in morphology. In the BET results, the temperature difference of 50˚C rise improved the surface area by about 2 folds, which on further rise by another 50˚C, increased the surface area rise in about 5 folds. The surface area of every virgin MPC, up on coating by TiO_2 gets increased to multiple times. The average pore diameters for virgin MPC were 15.37nm and 15.23nm for BJH adsorption and BJH desorption respectively, whereas for TiO_2-coated MPC were 5.16nm and 4.73nm for BJH adsorption and BJH desorption respectively. In the study, the IEP of the TiO_2-coated MPC corresponds to 2.2 and corroborates that the surface charge is positive.

The adsorbent materials synthesized confirmed that the uptake or remediation of fluorides is dependent on a number of factors, including pH, contact time, adsorbent dose, concentration, and temperature. As the optimization of these parameters was carried out, a notable increase in the percentage removal of fluorides was recorded. Optimizing all these parameters gave percentage removals of around 95% for fluorides. Validation using kinetic and isotherm model studies was also carried out.

Overall, TiO_2-coated MP carbon outperformed the virgin/non-impregnated MP carbon in terms of adsorption capacity, and this observation was corroborated by the difference in surface morphology between these adsorbents as well as the presence and absence of some functional groups as confirmed by FT-IR spectroscopy. It was concluded that both the functional group and the surface orientation could be connected to the performance of the adsorbents in the removal of fluorides. The adsorption capacity of TiO_2-coated MP carbon was improved for fluorides. Comparing these adsorbents with other developed adsorbents in literature, these adsorbents are cheap, easy to prepare, environmentally friendly and have high adsorption capacities, capable of removing fluorides and bringing them to acceptable drinking levels set by WHO.

All experiments in this study were performed in triplicate and the standard deviation was calculated, from which all experimental results with standard deviation within 5% were reported in this dissertation.

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LIST OF ABBREVIATIONS

BET	Brannuer Emmett teller
Br^-	Bromides
BSE	Back scattered electrons
CA	Cellulose acetate
CHNS	Carbon Hydrogen Nitrogen Sulphur
Cl^-	Chlorides
ClO_4^-	Perchlorates
CTA	Cellulose triacetate
EDS	Electron dispersion spectroscopy
F^-	Fluorides
FTIR	Fourier transform infrared
GAC	Granular activated carbon
H^+	Hydrogen ions
I^-	Iodides
IC	Ion chromatography
ISE	Ion selective electrode
MCL	Maximum contaminant level
MF	Microfiltration
MgO	Magnesium oxide
MP	Musa paradisiacal
MPC	*Musa paradisiaca* carbon
Na^+	Sodium ions
NaOH	Sodium hydroxide
NF	nanofiltration

NIS	Neurological integration system
POE	Point of entry
POU	Point of use
RO	Reverse osmosis
SE	Secondary electrons
SEM	Scanning electron microscopy
SPE	Solid phase extraction
TiO_2	Titanium dioxide
TEM	Transmission electron microscopy
TFC	Thin film composite
TGA	Thermogravimetric analysis
TTIP	Titanium tetraisopropoxide
UF	ultrafiltration
WHO	World health organisation
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

This chapter gives an overview of the presence of fluoride (F^-) ions in water particularly ground water systems. The problems arising from the presence of excessive amounts of these anionic species in water is also highlighted. In addition to this, the guidelines and regulations for F^- as per the different international and national authorities' guidelines are presented.

1.1 Background

Water pollution is a serious problem in many parts of the world including South Africa and has caused health problems to human beings as well as aquatic and wild organisms[1]. Normally, water used for domestic, agricultural, industrial activities etc, is recycled and if not adequately treated, it ends up contaminating both surface and ground water sources[2]. The implication of these contaminants has resulted into adverse effects on the quality of water thus indirectly has affected both human and ecological systems[3]. Of the many polluting species, pollution due to the presence of anionic species in the environment has widely been reported and among these anions are the fluorides (F^-)[4]. These ionic species are of major concern and therefore of particular interest in this study. Fluorine is one of the elements that make up the earth's crust and due to its reactive chemistry it exists mostly in combination with other elements in forms of fluorspar, cryolite, and fluorapatite [5,6]. It is a trace element (0.08% of the earth's crust) and exists in almost all types of soils[7] and in many rock structures[8,9]. In its elemental form, it is flammable, irritating, toxic (in its gaseous state) and it exhibits strong oxidizing tendencies[10]. It occurs in nature mainly in its reduced (fluoride, F^-) form combined other minerals[7,11]. These ions are released into the aquatic environments through migration phenomena and mechanisms between environmental compartments[12].

Natural waters all over the world including South Africa contain fluorides in varying amounts depending on the underlying geological set up. Fluorine is one of the compositional elements found in skeletal structures (e.g., bones and teeth) in mammals and other organisms. This implies that fluoride is nutritionally important and water is a major source of fluoride intake[13]. Therefore fluoride ion is both a nutritional essential element, a potent environmental pollutant and a toxicant when it occurs at concentrations above the guidelines[14]. According to the World Health Organization (WHO), a F^- concentration level that exceed 1.5 mg/L in drinking water can cause dental and skeletal fluorosis[15]. However, a F^- intake of more than 2 mg/L for a lengthy period of time in humans causes many bone dieses including mottling of teeth and lesions of endocrine glands, thyroid, liver, and other organs thus the need to remove the amount of fluorides in water[16-24].

Pollution of fluoride in groundwater and drinking water is a serious health problem all over the world, including South Africa and in some areas concentrations are higher than the recommended limits set by the WHO for drinking water[25]. Hence there is a need to defluoridate groundwater.

Consequently, the treatment of wastewater and remediation of polluted surface and subsurface waters are of critical concern.

1.2 Problem statement

The major source of fluorides that are released into the environment is processes that are related to the weathering and dissolution of minerals. They are released in emissions from volcanic activities and from marine aerosols as well. Other sources of fluorides in the environment include coal combustion and process waters as well as waste from steel manufacturing processes, primary aluminium, copper and nickel production, phosphate ore processing, fertilizer production and use, glass, brick and ceramic manufacturing, and glue and adhesive production. Consumption of water that contains fluorides in a concentration of approximately 1 mg/L has been found to be effective in reducing tooth decay. For this reason fluoride compounds have been added to water supplies which contain less than the desired concentration. In communities where the fluoride content in the water supply is at an optimum level, tooth decay has been shown to be almost 65% less than in communities with little or no fluoride in the water. However, exposure to drinking levels above 2 mg/L for a prolonged period of time may result in cases of dental, crippling, skeletal and non-skeletal fluorosis[17-19].

These anionic contaminants are present in the water at a wide concentration range, occasionally reaching hundreds of mg/L. At times they have shown clear adverse effects on both human and ecological systems, hence it is important to supply water with safer fluoride levels.

1.3 Justification

The selected study compound is among the most commonly detected and of concern in ground water systems. They are products and by-products spanning across many industries including the chemical, manufacturing, fertilizer production, and the energy sector. The compounds often appear on various lists of compounds of concern such as priority pollutants, endocrine disruptor compounds, emerging contaminants, and others. Hence, the need for the study to focus on the analysis and remediation of this group of compounds and find a way in which they can be removed in contaminated aquatic environments.

Various methods and adsorbents are available to remove fluorides from water and some of these methods have high costs, labour-intensive, and often results in shuffling toxicants from one place to another, as well as the potential to cause secondary pollution and these adsorbents often have low adsorption capacities. Hence low-cost, environmentally compatible technology, highly selective removal methods continue to be sought and the one presented in this dissertation falls on such categories of techniques.

Moreover the use of natural products like plant fibers presents several advantages such as mechanical strength, high disposability, degradability and renewability hence are considered environmentally friendly. Natural products are also abundantly available and their abundant availability renders them inexpensive.

The combination of carbon materials, natural products, and nano particles hold promising techniques for the removal of many waterbone contaminants, hence TiO_2 coated *Musa paradisiaca* stem carbon have been investigated in this study for use in the removal of fluorides in water.

1.4 Aims and objectives

1.4.1 Main aim

The main aim of this study is to investigate the adsorption of fluorides by TiO_2 dispersed on *Musa paradisiaca* (MP) stem carbon.

Specifically this study aims to:

- Development of TiO_2 dispersed on *Musa paradisiaca* stem carbon.
- Application of *Musa paradisiaca* (MP) carbon for the removal of fluorides in surface and ground water sources.

1.4.2 Specific objectives

The objective of this work is to study the removal of fluorides by TiO_2 dispersed on MP stem carbon.

Primary objectives

- Remove the fluorides ions from aqueous solution and natural ground water.

Secondary objectives

- Synthesize carbonized materials from natural sources of remarkable abundance.
- Disperse the TiO_2 on the carbon matrix of carbonized materials.
- Characterize the adsorbent material (TiO_2 dispersed MP stem carbon) using conventional instrumental techniques and applied for the removal of fluorides in water.

- Study the removal efficiency of the adsorbent material on fluorides with respect to other factors such as pH, contact time, temperature, adsorbent dose, adsorbate and effect of other anions.
- Explore the reusability of the exhausted material.

1.5 Thesis outline

Chapter 1 of this dissertation highlights the purpose, reasons and the need for the analysis and removal fluorides in water.

Chapter 2 gives the details of what has been done by other researchers similar to this study. It also gives a summary of detection and pre-treatment methods available in literature for the quantification, removal or monitoring of fluorides in water samples.

Chapter 3 details the experimental work and procedure that was carried out in this study. Procedures for the synthesis and characterization of TiO_2 dispersed *Musa paradisiaca* stem carbon is reported however, details and some specific aspects of methods are reported in each chapter.

Chapter 4 discusses the synthesis, characterization of non-impregnated and TiO_2-coated *Musa paradisiacal* (MP) carbon for the removal of fluorides.

Chapter 5 reports on the adsorption of fluorides from water using both non-impregnated and TiO_2-coated MP carbon

Chapter 6 discusses the general conclusions and recommendations for possible future work regarding the analysis and removal of fluorides in water.

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CHAPTER 2

LITERATURE REVIEW

This chapter provides a literature survey on the methods reported for the analysis and remediation of fluorides in water. An outline of sample preparation methods and techniques, detection and quantification as well as the removal methods is provided in this chapter. The strengths and limitations of these various techniques are as well discussed.

2.1 Anions in aquatic systems

Anions are a group of atoms or radicals that have gained electrons and thus have a negative charge and examples of such species include chloride (Cl^-), bromide (Br^-), iodide (I^-), fluoride (F^-), perchlorate (ClO_4^-) among others. The above examples of anions belong to a group of the monovalent anions which have a combining capacity with only one hydrogen ion. Similarly there also exist some bivalent and multivalent anions which have a combining capacity with more than one hydrogen ion. Anions are termed so because they get attracted towards the anode (the positive electrode). All anions tend to accept a proton (H^+) and they thus categorized as bases. Anions find their way into aquatic environments from a variety of sources, processes and reactions. Contamination of water systems by anions has been a major crisis in many parts of the world causing numerous health problems to individuals who consume contaminated water[1]. This has prompted many national and international regulatory authorities to impose guidelines, regulations and legislations to control the discharge of effluents containing these anions. The World Health Organization (WHO) as well as many regulatory bodies have set maximum acceptable levels for all anions that is allowed to be in drinking water systems in order to protect the health of consumers[2,3].

Anions such as fluorides, chlorides, perchlorates, iodides and bromides have been reported to be present in various water systems including groundwater and surface water[4]. Ingestion of water containing excess levels of these anions has been widely reported to cause many illnesses [5]. For example excessive fluoride intake leads to loss of calcium from the tooth matrix, causing cavity formation, dental fluorosis, as well as skeletal fluorosis after prolonged exposure[6]. Due to these negative health implications caused by F^- anions in water, the WHO has recommended 1.5mg/L for fluorides as the maximum contaminant levels (MCL) in drinking water[7].

Fluoride pollution is a serious health problem in many parts of the world including South Africa[7]. Previous studies showed that fluorides were recorded in many parts of South Africa; however the problems of high fluoride concentrations were found to be present in the Limpopo, Northern Cape, North-West and KwaZulu-Natal Provinces[8]. These provinces have a high population still living in rural areas and most of them still rely on groundwater and surface water for drinking purposes. Currently, the fluoride distribution situation in South Africa is such that some areas have groundwater sources in which the fluoride concentrations are higher than the recommended limits set by the WHO for drinking water[8]. Hence there is a need to remove the amount of fluorides present in water to bring them to optimum levels safe for drinking water purposes.

To date, ecological systems continue to be threatened by the discharge of effluents containing these anions. However, due to high dilution effect some of these anions are mixed with other compounds requiring highly sensitive and selective analytical methods to detect them at such lower concentrations.

2.2 Analytical methods for the analysis of fluorides

Analytical procedures for the analysis of fluorides in water include sampling, sample preparation, separation and detection, data processing and interpretation[9]. Each of these steps is dependent on the preceding one. Sample preparation is key, as it determines the accuracy, precision, limits of detection and quantification of the analysis[9].

2.3 Sampling

The considerations that need to be observed during sampling and analysis of fluorides include the fact that, samples has to be collected from locations that are a representative of the water source of interest (for example, points in the treatment plant such as after disinfection, storage facilities, distribution network, points, points of use) etc.[10,11]. Normally in selecting sampling points, each locality is considered individually. Sampling points should therefore be uniformly distributed throughout a system, taking population distribution into account. In addition, the number of sampling points should be proportional to the number of links or branches[12]. The samples are supposed to be stored in clean and sterilized sample bottles. It is advisable to analyze important physico-chemical parameters on site as some will change during storage and transport[13]. Samples are then transported in ice to ensure rapid cooling. Samples should then be kept in a refrigerator before analysis. In general, the time between sampling and analysis should be kept to a minimum. This ensures that the intergrity of the sample is not changed or compromised[13].

2.4 Sample preparation for anions

All samples should be kept refrigerated until they are analyzed. Therefore, the refrigeration should be done as quickly as possible[14]. Samples must also be free of high molecular weight organics and particulates to avoid reactions with such molecules because of the high electronegativity of halogens[15]. All natural samples need to be filtered for particulates, preferably through a 0.4 μm filter. This is because high molecular weight organics may irreversibly damage the analytical column during the chromatographic separation of the anions[16].

In most cases water samples that are meant for ion chromatography (IC) analysis do not requires stringent sample pre-treatment procedures apart from filtration through an appropriate filter to remove particulates[17]. Other mild sample preparation methods for analyses meant for IC include dilution which is normally carried out for water samples with high ionic strength e.g. wastewater. Dilution corrects the concentrations of anions in the water samples to be analyzed into the working range of the target analyte[18]. In some cases when dealing with more complex aqueous samples, such as sand solid leachates, a chemical modification (or cleanup) procedure may be desirable to enable the elimination of the sample matrix interferents which may mask the signal of interest. Otherwise other preparation techniques such as liquid-liquid extraction, solid phase extraction, solvent extraction, digestion etc, may be incorporated in order to eliminate matrix interferences[19].

2.4.1 liquid-liquid extraction

Liquid–liquid extraction (LLE) or solvent extraction (SE) is a separation method based on the relative solubility of the analyte in one of the two different immiscible liquids, usually water and an organic solvent[20]. During the LLE an analyte present in one of the two immiscible liquids (mainly aqueous) is extracted into another liquid phase (mainly organic). LLE can be performed using separatory funnels, counter current distribution equipment, etc[21].

LLE consists of the transferring process of one (or more) solute(s) contained in a feed solution to another immiscible liquid (solvent). Solvent extraction is one of the most extensively studied and most widely used techniques for the separation and pre-concentration of analytes[22]. The technique has become more useful in recent years due to the development of selective chelating agents for trace metal determination[23]. The solvent that is enriched in solute(s) is called an extractant while the feed solution that is depleted in the solute(s) is called raffinate.

A further advantage of solvent extraction method lies in the convenience of subsequent analysis of the extracted species. However, one major disadvantage of this technique is that it requires a large volume of solvent thus uneconomical and environmentally unfriendly and is time consuming[24].

2.4.2 Solid phase extraction

In solid-phase extraction (SPE), compounds dissolved or suspended in a liquid mixture are extracted based on their retention on the solid stationary sorbent materials packed in a column. The retention mechanisms are based on different principles such as ion exchange, polarity etc[25,26].

SPE cartridges provide an attractive option of eliminating matrix interferences before sample injection into the chromatographic system. The process is simple, rapid and use only small volumes of both the sample and organic solvents[27]. The SPE method involves about four (4) steps which include (i) conditioning of the sorbent with appropriate solvents, (ii) percolating the sample through the sorbent to retain the analytes preferentially over the possible interfering components[27], (iii) washing off interfering molecules from the sorbent and (iv) bleeding out the analytes using an appropriate solvent which can be done using a small volume of solvent to concentrate the analyte to improve the detection limits[28].

2.5 Separation, detection and quantification methods

2.5.1 Ion selective electrode

The ion selective electrode (ISE) method is the technique mostly employed for the measurement of free anionic species in environmental sample solutions due to its convenience, acceptable sensitivity, and reliability. ISE methods are simple and suitable for both field and laboratory applications. For example, fluoride -specific electrodes are commercially available and are widely used to detect only free fluoride species (anions) that are present in solution. The limitation of this technique arises from the fact that a number of other anionic species which include thiocyanate, iodide, nitrate, chloride, phosphate, and acetate always present interference problems with the fluoride electrode[29].

2.5.2 Ion chromatography

Ion chromatography is a separation technique normally used for ions and polar molecules which are discriminated based on their affinity differences when subjected to an ion exchanger such as anionic exchange resins. The technique can be employed to separate any charged organic or inorganic molecules. The basic process of chromatography follows similar steps as in SPE except that the solvent in chromatography is constantly pumped through the column[30].

In most cases, conductivity detectors are the ones used in IC systems although these detectors have shortcomings in that, they cannot specify the ion producing the signal. The separated ions are identified based solely on retention times[31].

2.6 Treatment technologies

There are a number of environmental remediation methods and techniques which may include degradation, sequestration, etc. Some of the techniques that have been employed for the removal of contaminants include membrane based techniques (e.g reverse osmosis, etc), adsorption, ion exchange, flotation, flocculation, chemical precipitation, nanotechnological based techniques among others.

2.6.1 Membrane technology

Membrane technology has received much attention and has actually been regarded as the technologies of choice when it comes to water and wastewater treatment. This is due to the high efficiency and ability to filter-out undesired molecules present in water to produce water fit-for-use. Different types of membranes based on various principles and separation mechanisms have been fabricated[32].

The widely used membrane processes include microfiltration (MF)[33], ultrafiltration (UF)[34], nanofiltration (NF)[35], reverse osmosis (RO)[36], electrodialysis[37], membrane distillation[38], etc. All processes except (electro) dialysis are pressure driven[39]. Membranes can be fabricated in a variety of designs and configurations such as hollow fiber, spiral, and tubular which give varying degrees of separation[40].

The membrane performance efficiency is normally governed by two factors which include (i) the flux defined by the amount of water passing through the membrane per unit time and surface area. (ii) the selectivity or retention which defines the concentration ratio of a component between the filtered 'permeate' and the input feed water[41].

The main limitation of membrane technology includes its requirement for large amount of energy, the frequent fouling and polarization problems. Concentration polarisation results from the concentration increase at the membrane surface which also triggers membrane fouling. The main causes for membrane fouling include particulate and colloidal matters, scaling (precipitation of inorganic salts), bio-fouling and adsorption[42].

2.6.1.1 Reverse osmosis based membranes

Osmosis is a process whereby two liquids with different solute concentrations are separated using a semi permeable membrane whereby the movement is from an area of low solute concentration (high water potential) to high solute concentration (low water potential) until a chemical potential equilibrium is attained[43].

The reverse osmosis (RO) process involves forcing a solvent containing high solute concentration through a semipermeable membrane to a region of low solute concentration by applying a magnitude of pressure higher than the osmotic pressure[44]. This technique has been highly applied in water purification processes to remove pollutants including microorganims from drinking water [40,45]. In the RO process the solute is retained on the pressurized side of the membrane while the pure solvent (water) is allowed to permeate through the membrane to the other side[46].

For example, point of use (POU) reverse osmosis has been used in the reduction of fluoride whereby a cellulose acetate/cellulose triacetate (CA/CTA) membrane was used and it gave rejection rates of 80-90% at pH in the 4-8.5 ranges[47]. Also a thin film composite membrane (TFC) operated on a RO mechanism yielded a higher rejection rate (up to 95 percent) in the 3-11 pH range[47]. Both the CA/CTA and TFC membranes were operated at a minimum membrane pressure differential of at least 30 psi[47]. In principle, RO mechanisms depend on ionic diffusion of the species to effect the separation[48].

2.6.1.2 Filtration based membrane methods

Filtration is a physical method of separation of mainly solid particles present fluids and the solids are separated by interposing a separating medium which allows only fluid to pass through[49].

In filtration process, the separation is made possible due to the interaction between the undesired molecule to be removed and the filter depending on whether the undesired molecule is dissolved or suspended in the fluid[50].

Filtration is only useful for the separation of materials which have different chemical composition such that an appropriate solvent is selected to dissolve one component, at the same time, without dissolving the other such that the dissolved component will pass through the filter and the other will be retained[51].

2.6.2 Flotation

Flotation is one of the techniques widely used in the wastewater treatment and mineral processing industries[52]. In a natural flotation process, particles that are less dense than water will associate themselves with gas bubbles and then rise and float at the stationary liquid surface. Similarly particles heavier than water will attach to air bubbles and move to the liquid surface by flotation[52].

The flotation process has been used for centuries in the mining and metallurgical area, and there have been rapid developments of devices and techniques that use flotation being applied in drinking water and wastewater treatments plants. Flotation in wastewater and domestic sewage treatment has been known, for a number of years and is widely used by civil, chemical and environmental engineers, (especially dissolved air flotation, which offers process advantages)[53]. Advantages of flotation include better treated water quality, rapid start up, high rate operation, and a thicker sludge. This process leads to the production of sludge and cause secondary pollution, a major disadvantage[54].

2.6.3 Chemical precipitation

In chemical precipitation, chemicals such as sulphides, hydroxides, and carbonates) are made to react with organic and inorganic pollutants present in water to form insoluble precipitates[55]. These precipitates will then settle out of solution as solids which can then be filtered, centrifuged, or otherwise separated from the liquid portion using an appropriate technique[56]. This separation treatment technology can be carried out in four phases which are (i) the addition of the chemical to the wastewater, (ii) mixing to homogenize the water, (iii) flocculation (formation of the insoluble solid precipitate) and (iv) filtration, settling, or decanting to remove the flocculated solid particles[56]. The limitation of this technique is that it tends to be effective on a narrower range of contaminants and is also time consuming[57].

2.6.4 Flocculation

In this technique clarifying agents are added to the sample to cause the formation of colloids which will then come out of the suspension in the form of floc or flake[58]. This technique is widely employed in the treatment of drinking water as well as sewage treatment, storm-water treatment and treatment of other industrial wastewater streams. However, this technique is known to limitations in that it causes secondary pollution[59].

2.6.5 Adsorption methods

Adsorption is an interface process that facilitates the stripping of an analyte from sample solution and enriches it to a solid sorbent[60]. The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid material[61].

There are three main classes of adsorbents and these include (i) The hydrophilic and polar oxygen-containing adsorbents such as silica-gel and zeolites[62], (ii) the hydrophobic and non-polar carbon-based adsorbents such as activated carbon[63] and (iii) polymer-based adsorbents possessing either polar or non-polar functional groups in a porous polymer matrix[64].

Adsorption finds applications in tertiary wastewater treatment as a polishing step before final discharge[65]. Adsorption is commonly used in the treatment of industrial wastewaters containing organic compounds which are either toxic or not easily biodegraded during secondary (biological) treatment[65,66].

The adsorption of ionic species has been investigated using various materials and adsorption has proven to be a particularly interesting technique in many applications. It allows for the removal of ions from very dilute solutions and possesses the ability to process large volumes of solutions when other separating methods seem unfavourable.

2.6.5.1 Adsorbents

Various materials have been used as adsorbents in the removal of anions, some of which include activated alumina[67], granular activated carbon[63], bone char[68], ion exchange resins[69], nanoparticles[70], natural fibers[71] among others.

i) Activated alumina

Granulated aluminum oxide (activated alumina) has been used in many applications including in the removal of fluorides[66], arsenic[72], lead[73], cadmium[73] in water. Activated alumina also finds applications in the adsorption of catalysts[75], polyethylene production[76], hydrogen peroxide production[77] in addition to its use as a selective adsorbent for many chemicals including fluoride[74], arsenic[72] and many others[73]. This adsorbent is attractive in that it is porous and as a result it has a very large surface area-to-weight ratio[74]. Studies have shown that, when activated alumina is immersed in a liquid, it retains its integrity[72]. Activated alumina can adsorb gases and liquids without changing its form[72]. The original adsorption efficiency of activated alumina can be restored by heating it at temperatures between 177° to 316°C[74]. When the desiccant is heated as described above, the water stored in its cavities is released thus making it possible for filters incorporating activated alumina to reused[74].

The adsorption process by activated alumina proceeds in two regeneration steps mainly (i) caustic (NaOH) regeneration and (ii) acid (H_2SO_4) neutralization (regeneration process). The main requirement for activated alumina adsorption to proceed optimally is that the pH range has to be maintained at ranges between 5.5 and 6.5[78,79].

Activated alumina is well understood, well established, and reliable. Activated alumina is therefore capable of meeting the desired product water requirements for arsenic and fluoride removal and the adsorption process requires minimal operator involvement. Even though activated alumina has proven to be a good adsorbent, it requires routine monitoring to determine when regeneration is necessary[79].

ii) Bone charcoal

Bone charcoal (bone char) implies to carbonized animal bone which contain porous crystalline matrix formed by hydroxide of calcium phosphate which can thus be exchanged with other ions such as fluorides [68, 81]. The application of bone char has been reported in the adsorption of metal species, such as copper[80], iron[80], nickel[80], and manganese[80]. Regeneration of bone char can easily be achieved by rinsing the adsorbent with 2% NaOH rinse. The main drawback of using bone char as an adsorbent is that the pH of water should be maintained below a value of 6.5 to suppress any ion competition[82].

iii) Ion exchange resins

Generally ion exchange involves the exchange of either positively charged ions (cation exchange), exchange negatively charged ions (anion exchange) or exchange of both cations and anions simultaneously (amphoteric exchange)[69,84,85,88].

However, ion exchangers suffers from the fact that they are not selective to particular ionic species but rather show binding preferences for certain ions or classes of ions, based on their chemistry, size of the ions, their charge, or their structure[86].

Conventional ion exchange resins consist of a cross-linked polymer matrix with a relatively uniform distribution of ion-active sites throughout the structure. Ion exchange materials are commercialized as spheres or sometimes granules with a specific size and uniformity to meet the needs of a particular application[87]. The majority of ion exchange resins are prepared in spherical (bead) form, either as conventional resins with a polydispersed particle size distribution from about 0.3 mm to 1.2 mm (50-16 mesh) or as uniform particle sized resins with all beads in a narrow particle size range[88-92].

iv) Granular activated carbon

Activated carbon is an adsorbent that is widely used in wastewater treatment[67]. The mode of adsorption involve the removal of pollutants by accumulation at the interface between the activated carbon (absorbent) and the wastewater (liquid phase) the adsorbing capacity of activated carbon is always associated with very high surface area per unit volume[93,94]. A number of factors are known to influence carbon adsorption and they include temperature, pH, contact time, nature of adsorbate, presence of competing species as well as the chemistry of the carbon[70,95].

v) Metal based nanoparticles

Nanoparticles have received a wide attention in the adsorption processes bacuse of (i) They possess larger surface areas as compared to bulk particles and (ii) They can be functionalized with various chemical groups to significantly enhance their affinity towards target compounds[96,97,105].

Nanoparticles have been reported in the removal microbial agents in water (or as biocides[98-100], in the removal of anionic species in water[101,102], and also in the removal of organics in water[103].

2.6.6 Nanotechnology

Specific control and design of materials at the molecular level may impart increased affinity, capacity, and selectivity for pollutants. In this regard, nanotechnology could play a key role in pollution prevention technologies[104]. The benefits, which arise from the application of nanomaterials for remediation, would be more rapid or cost-effective clean-up of wastes[105-110].

There are four classes of nanoscale materials that have so far been subject to evaluation as suitable functional materials for water purification. These are dendrimers[111], metal-containing nanoparticles[112], zeolites[113] and carbonaceous nanomaterials[114]. The reason for the attention to these nanoscale materials lies in their broad range of physicochemical properties which include high surface area to mass ratios which enhances their adsorption capacities and also the fact that they possess a wide distribution of reactive and disordered surface regions which also enhance adsorption of the target analytes[116-118].

2.6.7 Titanium dioxide (TiO_2)

Titanium (IV) oxide or titania, is the most widespread form of titanium dioxide-bearing ore around the world[119]. Rutile is the next most abundant and contains around 98% titanium dioxide in the ore[120]. The metastable anatase and brookite phases convert irreversibly to the equilibrium rutile phase upon heating above temperatures in the range 600°C - 800°C[119]. Hence, titanium dioxide crystals are present in three different polymorphs in nature: Rutile, Anatase and Brookite in the order of their abundance. Titanium dioxide nanoparticles have been widely used in water treatment. These nanoparticles have the advantages of being readily available, inexpensive, and low with toxicity[121].

In addition, TiO_2 is one of the popular materials used in various applications because of its semiconducting, photocatalytic, energy converting, electronic and gas sensing properties[122]. Nanoparticulate TiO_2 anatase, is also known to exhibit antibacterial as well as photocatalytic properties. Apart from its photocatalytic property, TiO_2 is also an excellent adsorbent. It has been widely used as an adsorbent for removal of pollutants in water[123].

2.6.8 *Musa paradisiaca* (banana plant) pseudostem fibers

Natural fibers are attractive for use in water treatment due to the fact that they are recyclable and biodegradable. The renewability and degradability of the fibrous materials from plant makes them to be more environmentally friendly compared to their synthetic counterparts[124].

Banana plants (*Musa paradisiaca)* grow in a wide variety of soils, as long as the soil is at least 60 cm deep, has good drainage and is not compacted[125]. The fibre from banana plant is considered as an agricultural waste and an abundantly available renewable resource[126]. Therefore banana plant can be cheaply available for use in various applications especially in water and waste water treatment[127 -129]. Fibres obtained from banana pseudo-stem are characterized by their good mechanical, thermal and spectral characteristics [71].

2.7 Characterisation

2.7.1 Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) is useful in generating images of a sample which have been bombarded with a beam of electrons [130]. The signals can only be generated by SEM if the sample is electrically conductive (SEM active) [131]. If the sample is not electrically conductive it has to be coated with conducting materials such as gold, carbon, chromium, osmium, tungsten or graphite [132].

2.7.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which uses the electromagnetic radiation to cause vibration of asymmetrical heteronucleus and paramagnetic molecules[133]. FTIR identifies chemical bonds in a molecule and also distinctive molecular fingerprints that can be used to screen and scan samples for many different components[134].

2.7.3 X-ray diffraction (XRD)

X-ray crystallography is useful technique in the identification of atomic and molecular structure of a crystal and it does so by giving a measure of angles and intensities of the diffracted beams, which are used to produce a three-dimensional picture of the density of electrons within the crystal. The information obtained from crystallographic measurements of the sample enables the determination of the electron density, the mean positions of the atoms in the crystal type of chemical bonds and their disorder[135].

2.7.4 Brunauer Emmett Teller (BET)

Brunauer–Emmett–Teller (BET) measurements provides the magnitude of the physical adsorption of gas molecules on a solid surface and relate this magnitude to the specific surface area of the material. The technique also provide a measure of other parameters such as external area and pore area evaluations to determine the total specific surface area in m^2/g which provide clues on the effects of surface porosity and particle size[136].

Because gas absorption forms the basis of surface area/pore volume measurements, degassing of the sample before absorption is an important step to be considered[137].

2.7.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a a thermal based technique in which physical and chemical properties of the sample are monitored at the conditions of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss)[138]. TGA is useful in providing (i) sample physical information related to second-order phase transitions such as vaporization, sublimation, adsorption, absorption and desorption (ii) chemical information such as chemisorptions, desolvation, decomposition, and solid-gas reactions[139].

Therefore TGA measurements may reveal the trends for heat treatment of a sample as to whether there is mass loss or gain which may be related to either decomposition, oxidation, or loss of volatiles (such as moisture) depending on the nature of the sample[140].

Generally, TGA can be very useful in the evaluation of the thermal stability of a material such that in cases where the sample is thermally stable, no mass change will be observed and vice versa[141].

2.7.6 Transmission electron microscopy (TEM)

In transmission electron microscopy (TEM) processes a beam of electrons is directed and passes through to an ultra-thin sample specimen and the interaction of electrons and sample specimen results in the image being formed which can then be magnified and detected by an appropriate sensor[142,143].

This technique is therefore very useful in the study of the electron scattering properties of the internal structure of the samples[143].

2.7.7 Raman spectroscopy

Raman spectroscopy is useful in the investigation of the chemical bonds for symmetrical and homonuclei molecules. Like FTIR it uses same region of electromagnetic radiation to cause the vibrations of the molecular bonds[44,146].

2.7.8 Elemental (CHNS) analyzer

A CHNS Analyzer is normally used to measure the elemental composition of a sample mainly a measure of carbon (C), hydrogen (H) and nitrogen (N), sulphur (S) and oxygen (O). A number of principles are normally employed including the combustion process to break down components into simple compounds which are then quantified, usually by infrared spectroscopy[147].

2.7.9 Zeta Potential

Zeta potential is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles, and is a function of the surface charge of the sample in solution. Zeta potential data is used widely in the measurements of the surface charge of the sample which is then useful in ascertaining of the causes of dispersion, aggregation or flocculation[148-150]. There are properties that are crucial when measuring the zeta potential and they include size and sample pH which can be used to locate the isoelectric point for the material being measured[152].

2.7.10 Surface charge

Surface charge is a measure of the magnitude of the electrical potential difference between the inner and the outer surface of the different aggregate state of the material (for example: liquid and gas, liquid and solid or gas and liquid). It can be used to study phenomena like particle repulsions or particle attractions[154].

2.8 Statistical evaluation

Statistical evaluations are carried out to validate data that have been generated from sampling up to detection methods. These include extraction percentages, adsorption capacities, adsorption efficiencies and percentage removal of contaminants, etc. However, other statistical tests that are known and have been carried out include quality control charts, standard deviations, patterns and correlations, linear regression of calibration curves, detection limits of instruments, linear response range, precision of standards and samples, recovery and blank values, student's t-test, the Q-test and the F-test for the complete validation of the data[155,156]. All these are essential to complete the amount of analytical work that have been carried out and validate the results found thereafter.

2.9 Conclusion

Human beings are frequently exposed to fluoride through water and in some areas concentrations are higher than the recommended limits set by the WHO for drinking water. Exposure to such high concentrations of fluoride can cause serious health problems such as dental, crippling and skeletal fluorosis and other neurological disorders. Various methods and adsorbents are available and widely reported in literature to remove fluorides from water, however some of these methods are expensive, labour-intensive, as well as the potential to cause secondary pollution and whereas some of these adsorbents often have low adsorption capacities.

Hence low-cost, environmentally compatible technology, highly selective removal methods continue to be sought. More attention should be directed to the research on cheap adsorbents in solving environmental problems such as fluorides in water to protect public health.

The combination of carbon materials, natural products, and nano particles hold promising techniques for the removal of many waterbone contaminants, hence TiO_2 coated *Musa paradisiaca* stem carbon have been investigated in this study to remove the amount of fluorides present in water to bring them to optimum levels safe for drinking water purposes.

2.10 References

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CHAPTER 3

EXPERIMENTAL METHODOLOGY

This chapter outlines the general procedures and experimental work that was carried out in this project. It includes the procedures that were done for sample preparation, analysis of fluoride ions, sampling of *Musa paradisiaca (MP)*, processing of MP, preparation of carbon material from MP, characterization and application of TiO_2-coated *Musa paradisiaca* stem carbon for the adsorption and removal of fluorides in ground and surface water.

3.1 MP sample collection

MP stems were collected from Mbabane, Hhohho region of Swaziland between July 2014 and May 2015. The MP stems were reduced to smaller equal sized pieces using a sharp house knife and then separated into inner, outer and unseparated parts. The three sets of the materials were autoclaved and bleached using two different bleaching agents mainly 8% sodium hydroxide (after optimization) and 1.7% Sodium chlorite[1] to remove pigments, lignin, and tannin before being dried under shadow light.

3.2 Sampling

Water samples were collected from various treatment plants and ground water sources in Gauteng, Mpumalanga and North West provinces in South Africa. Three samples were taken from each of the sampling points and physico-chemical parameters such as pH, temperature and conductivity were measured on-site. Samples were collected using polypropylene sampling bottles, which were pre-washed with soap and water, rinsed with deionised water, soaked in nitric acid and finally the sampling bottles were rinsed with the sample three times prior to filling up with the water sample. Water samples were stored in a cooler box (with ice bags) and immediately transported to the laboratory for analysis. The amount of total dissolved solids was determined and then samples were stored in the refrigerator at 4^0C to minimize sample decomposition until further analysis.

3.3 Sample preparation

Normally, water samples collected for the analysis of anionic species (chloride, nitrates, sulphates fluorides etc) by ion chromatography (IC) require very minimal sample pre-treatment. In most cases the sample preparation may only involve filtration using appropriate filter such as to eliminate suspended solids. For more complex aqueous samples such as industrial effluents dilution may be employed to correct for the high concentrations of analytes present in such complex matrices.

3.4 Preparation of MP stems carbon

MP stem was collected, cut into slices of equal size (as thin discs) and divided into three portions and autoclaved for an hour. Autoclaved MP stem discs were soaked into a reagent of bleaching action to expel out tannin from soft fibers that is, in 4%, 5%, 6%, 7% and 8% NaOH, for 2 h and 1.7% $NaClO_2$ for 4 h[1] . Tannin expelled

MP was then dried under shadow light. The mass was then carbonized in muffle furnace at 100, 150 and 200˚C for 2 h.

3.5 Preparation of TiO_2-coated MP stem carbon

50 mL of Titanium tetraisopropoxide (TTIP) was mixed with about 5 g of the three portions of MP dried mass and stirred for about 10 min. Double distilled water was then added to the above system drop wise and slowly to facilitate uniformity in the dispersion of TTIP until there is a formation of a precipitate in white color along with the fibers. The wet mass was then filtered before its weight was recorded. The TiO_2 impregnated MP fibers were divided into three sets and carbonized in muffle furnace at 100, 150 and 200˚C respectively for 2 h in an inert atmosphere. Then the carbonized MP dispersed with TiO_2 was desiccated and stored under moisture free conditions. The prepared carbon materials (**Table 3.1**) were expected to have their property identity based on influence of the carbonization temperatures as well as the amount and type of bleaching agents).

Table 3.1 Carbonized materials prepared under this study

Carbon	**Preparation**
MPCExt-Ti200	Exterior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 200 ^{0}C
MPCBoth-Ti200	Both exterior and interior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 200^{0}C
MPCInt-Ti200	Interior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 200 ^{0}C
MPCExt-V200	Exterior part, 8%NaOH, 1.7% $NaClO_{2,}$ virgin/non-impregnated at 20^{0}C

MPCBoth-V200	Both exterior and interior part, 8%NaOH, 1.7% $NaClO_{2,}$ virgin/non-impregnated at 200^0C
MPCInt-V200	Interior part, 8%NaOH, 1.7% $NaClO_{2,}$ virgin/non-impregnated at 200^0C
MPCExt-Ti150	Exterior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 150 ^{0}C
MPCBoth-Ti150	Both exterior and interior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 150^0C
MPCInt-Ti150	Interior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 150 ^{0}C
MPCExt-V150	Exterior part, 8%NaOH, 1.7% $NaClO_{2,}$ virgin/non-impregnated at 150^0C
MPCBoth-V150	Both exterior and interior part, 8%NaOH, 1.7% $NaClO_{2,}$ Virgin/non-impregnated at 150^0C
MPCInt-V150	Interior part, 8%NaOH, 1.7% $NaClO_{2,}$ virgin/non-impregnated at 150^0C
MPCExt-Ti100	Exterior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 100^0C
MPCBoth-Ti100	Both exterior and interior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 100^0C
MPCInt-Ti100	Interior part, 8%NaOH, 1.7% $NaClO_{2,}$ TiO_2-coated at 100^0C
MPCExt-V100	Exterior part, 8%NaOH, 1.7% $NaClO_{2,}$ virgin/non-impregnated at 100^0C
MPCBoth-V100	Both exterior and interior part, 8%NaOH, 1.7% $NaClO_{2,}$ Virgin/non-impregnated at 100^0C
MPCInt-V100	Interior part, 8%NaOH, 1.7% $NaClO_{2,}$ virgin/non-impregnated at 100^0C

3.6 Characterization experiments

3.6.1 Fourier transform infrared (FTIR) spectroscopy

Perkin Elmer Spectrum 100 FTIR spectrometer, (Massachusetts, USA) was used to investigate the presence of organic and inorganic functional groups present in the MP carbon material[3]. All TiO_2-coated MP carbon adsorbents were crushed into fine powder (<45 µm) and analysed over the spectral range of 4 500 cm^{-1} and 500 cm^{-1}. The difference between the virgin (non-impregnated) MP carbon and TiO_2-impregnated MP carbon in terms of the presence and/or absence of functional groups were monitored by FT-IR. Moreover the influence of the carbonization temperatures and bleaching properties on the functional groups on the carbonized materials were followed from the FTIR spectra.

3.6.2 Scanning electron microscopy (SEM)

The surface structures/morphology of the MP stem carbon was analysed by Tescan VEGA 3 XMU scanning electron microscopy (Brno, Czech Republic). SEM was used to acquire the information about the morphology of the carbonized material and its changes with respect to thermal and chemical effects[4]. The adsorbents were crushed into fine powder and sieved to uniform size (<45 µm). All micrographs were taken at the same magnification, working distance and beam capacity. XMAX Oxford instruments EDS was also carried out to understand the presence of elements dispersed on the carbon matrix.

3.6.3 X-ray diffraction (XRD)

The Rigaku Ultima IV X-ray diffractometer XRD (Tokyo, Japan) was used in this study to find out the crystal and phases of TiO_2 on the adsorbent material. XRD was carried out to ascertain the crystalline/armophous nature of the material and crystalline if any bound to the carbon's surface[5].

3.6.4 Brunauer, Emmett, Teller (BET)

The nitrogen sorption porosimetry was carried out using a Micrometrics ASAP 2020 surface area and porosity analyzer (Atlanta, Georgia, USA). Brunauer, Emmett and Teller (BET) analysis is the main technique that was used to determine specific surface area, specific pore volume, pore size distribution and average pore diameter values of the MP stem carbon. This is done to understand the surface properties of the MP carbon and its variation with respect to external modification by thermal and chemical effects[6]. The surface properties include pore size, pore volume, surface area etc along with the prediction of particle size range based on adsorption-desorption hysteresis curve type. Samples were degassed at 150 ^{0}C for 180 min and analyzed under nitrogen atmosphere.

3.6.5 Thermogravimetric analysis (TGA)

Thermal stabilities of the adsorbents were investigated using a Perkin Elmer TGA 4000 (Massachusetts, USA). This was used to investigate the behavior of the MP carbon under thermal effect and to understand its thermal stability. Adsorbent sample weight was monitored as the temperature increased from 30°C to 800°C at 10°C/min under a nitrogen atmosphere with the flow rate set at 20 mL/min. A thermal analysis curve was generated by plotting the temperature change against the weight loss in percentages whereby a weight loss at any given temperature signify a thermal activity which means a thermal decay of a particular constituent of the adsorbent material[7].

3.6.6 Elemental (CHN) analysis

A LECO CHN Analyzer (St Joseph, Michigan, USA) was used in this study for elemental analysis of the adsorbent material to substantiate the influence of the percentage of C, H and N in the adsorption pattern for fluoride. Moreover, the calculations of these elements along with analysis of ash content can be used to predict the suitability of the carbonized material for solid fuel applications[8].

These techniques were at our disposal, some were available from our collaborators and neighboring institutions.

3.6.7 Zeta potential

Zeta potential of the adsorbent material (carbon) was carried out using a Malvern ZEN 3600 zeta sizer (Malvern, U.K). The zeta potential measurements are useful in obtaining a detailed insight into the causes of dispersion, aggregation or flocculation also as a function of surface charge of the carbonized material[9].

To consolidate the result obtained from pH versus Zeta potential plot, the iso-electric point (IEP) of the adsorbent material was determined using electrophoretic mobility in electrolytic medium of an ionic strength of 0.01 M and 0.001 M NaCl.

3.6.8 pH of carbon materials

25 mg of carbon was weighed and added in 50 mL of distilled water and then stirred for 30 min and the pH of the carbon materials was then recorded.

3.6.9 Moisture content

3.6.9.1 Moisture content in biomass

For the moisture content of biomass, the amount of MP taken initially (W1), amount of MP remaining after bleaching (after drying) (W2), and amount of carbon after carbonization process (W3), were recorded. It was expected that the trend would be W1 > W2 > W3. The difference obtained for the three weights, was used in the interpretation of the estimation of the amount of water and lignin contents. The moisture content was also estimated by taking a defined amount of MP in an oven at a temperature of 105 ± 5^{0}C for 2 h and the moisture content was then estimated by subtracting the final mass from the initial mass.

3.6.9.2 Moisture content in MP carbon

For the moisture content of MP carbon, a well cleaned crucible was weighed and 1 g of MP carbon was taken in the crucible. The crucible with the 1 g of MP carbon was kept in an oven at 110^{o}C for about 90 min. The hot crucible was then removed from the oven and kept in a desiccator to bring down its temperature to ambient temperature and finally the crucible was weighed.

3.6.10 Ash content

3.6.10.1 Ash content in biomass

The mass of a covered high silica or porcelain dish was weighed and then the oven-dried specimen (biomass) from a moisture determination step was placed in the weighed porcelain dish and the mass of the dish and specimen were determined.

The cover was then removed and the porcelain dish was placed in a muffle furnace. The temperature in the furnace was gradually brought to 750°C and temperature was held until the specimen was completely ashed (no change of mass occurs after a further period of heating).

The dish was then covered with the retained aluminium foil cover, cooled in a desiccator, and the mass was again determined and the ash percentage in the sample was worked out according to **Equation 3.1**[10].

$Ash\ content, \% = (C\ X\ 100)/\ B$ ………………………………………………….. 3.1

where:

C= ash weight (g), and

B = oven-dried test specimen, g.

3.6.10.2 Ash content in MP carbon

For the ash content of MP carbon, a well cleaned crucible was weighed and 1 g of MP carbon was put in the crucible. The crucible with the 1 g of MP carbon was kept in a furnace at 750^{o}C for about 1 h. The hot crucible was then removed from the furnace and kept in a desiccator to bring down its temperature to ambient temperature. Finally the crucible was weighed.

The procedure was repeated till the weight of MP carbon remained constant.

3.6.11 pH of zero point charge (pH_{ZPC})

This measurement was carried out to study the nature of the carbonized material, whether it contains positive or negative charges on the carbon surface. This property suggests the suitability of MP carbons to have affinity with anions in the solution.

A solution of 0.005 M $CaCl_2$ was boiled to remove dissolved CO_2 and then cooled to room temperature. The pH of the solution was adjusted to a value between 2 and 10 using 0.1 M HCl or 0.1 M NaOH. The MP carbon 0.06 g was added into 20 mL of the pH-adjusted solution in a capped vial and equilibrated for 24 h. The final pH was measured and plotted against the initial pH. The pH at which the curve crosses the $pH_{initial}$) pH final line is taken as pH_{ZPC}. The above procedure was followed for all the 18 carbon samples for the determination of their pH_{ZPC} values.

3.6.12 Calculation of percentage carbon

The amount of the dried initial mass of MP and the amount of carbonized mass were recorded and the percentage carbon was the calculated using the **Equation 3.2**:

$\% Carbon = MPc/MPi * 100$……………………………………………..3.2

Where:

MP_i =initial dried mass of MP

MP_c = Carbonized MP mass

3.6.13 Amount of TiO_2 impregnated

On hydrolysis, TTIP gives $Ti(OH)_4$ and 3 molecules of isopropyl alcohol. The purity of TTIP calculated based on g/mL was worked out which was then multiplied by the volume (mL) of TTIP added. This gave the amount of TTIP (g) in that particular solution/volume from which the amount of $Ti(OH)_4$ is formed. Then the amount of TiO_2 that can be impregnated was calculated.

3.7 Analyte determination

Fluorides analysis was carried out using Dionex ICS 2000 RFIC ion chromatography (California, USA).

3.8 Statistical validation

Statistical evaluations were carried out to validate data that have been generated from sampling up to detection methods. These include adsorption capacities, adsorption efficiencies and percentage removal of contaminants. Other statistical tests that were carried out include standard deviations, patterns and correlations, linear regression of calibration curves, detection limits of instruments, linear response range, precision of standards and samples, recovery and blank values.

3.9 Batch adsorption experiments

The batch mode experiments were conducted to explore the uptake potential of fluoride by the adsorbent material.

The parameters that were studied and optimized include pH, contact time and dose to study the maximum efficiency of sorption onto the adsorbent materials. In addition, the effect of temperature, initial fluoride concentration on the sorption efficiency was explored. Batch adsorption experiments were performed in a wide base container at 25°C with shaking. A weighed amount of adsorbent material (0.2g) was placed in 50 mL of sample in a capped vial and shaken at 125 rpm for 1 h except for effect of contact time experiments.

The experiments were conducted as follows.

3.9.1 Optimization of pH

Initial concentrations of fluorides were prepared at different pH values (between 2 to 10). This study was conducted at fixed contact time, fluoride concentration and the dose.

3.9.2 Contact time

This is based on the nature of adsorbent material as the equilibrium takes place between adsorbent and adsorbate (F^-) Defined adsorbent quantity (0.2 g) was taken with the fluoride concentration (2 mg/L) at optimised pH.

3.9.3 Adsorbent dose

This is the dose at which maximum removal is optimized for all the subsequent studies (adsorbent dose was varied from 0.2 g to 1 g). In this study, contact time, pH was kept constant but dose was the variable.

3.9.4 Effect of adsorbate (F^-) on the removal efficiency

Different F- concentrations were prepared (2 – 20 mg/L) and at each of them, the adsorbate removal efficiency was worked out using a fixed adsorbent dose, at a fixed pH and contact time.

3.9.5 Effect of temperature on the removal efficiency

In this study, the removal efficiency of adsorbate from the solution at constant pH, adsorbent dose and adsorbate concentration was carried out at different temperatures (10, 20, 30, 40 and 50 ^{0}C).

3.9.6 Effect of competitive species (other anions) on the removal efficiency

This study was conducted with a known concentration of F- at an optimized pH and contact time but together with other anions (binary system). The other anions were chloride, nitrate, and sulphate. The F- removal in an environment with these competitive anions in a particular ratio was also carried out.

3.10 Field trials (real sample adsorption)

The removal efficiency of F- in groundwater using the prepared MP carbon that showed maximum F- adsorption (MPCExt-Ti200, 8%NaOH, 1.7%$NaCl_2$) was studied. The practical feasibility of adsorbent in the removal was thus studied.

3.11 Validation

The sorption system was validated with respect to kinetic and isotherm models. **Equations 3.3 and 3.4** were used to calculate the adsorption capacity and percentage removal respectively.

$$\boldsymbol{AC} = \left[\frac{\boldsymbol{Ci - Cf}}{\boldsymbol{M}}\right] \boldsymbol{X\, V} \ldots\ldots\ldots\ldots 3.3$$

$$\%\boldsymbol{R} = \frac{\boldsymbol{Ci - Cf}}{\boldsymbol{Ci}} \boldsymbol{X\, 100}\% \ldots\ldots\ldots\ldots 3.4$$

where:

AC is adsorption capacity (mg/g)

%R is percentage removal (%)

Ci is initial concentration before adsorption (mg/L)

Cf is final concentration after adsorption (mg/L)

m is mass of adsorbent material (g)

V is sample volume (L)

3.11 References

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CHAPTER 4

ATMOSPHERE CONTROLLED-LOW TEMPERATURE SYNTHESIS OF VIRGIN AND TiO_2-ENCAPSULATED *Musa paradisiacal CARBONS (MPCs):* INTERPRETATION THROUGH SUITABLE PHYSICAL AND INSTRUMENTAL CHARACTERIZATION STUDIES

This chapter outlines the procedures that were carried out for the synthesis and characterization of the carbon materials that were prepared from *Musa paradisiaca* (MP). Various spectroscopic and elemental measurements were conducted to ascertain the properties of materials before and after some specific treatments.

4.1 Introduction

Carbon is an amazing element, not just because it is the element required for all life processes, but also due to the fact that it can exist in numerous allotropic forms[1]. Carbon technology development efforts have been critical to the advancement of analytical techniques such as chromatographic separations, sample preparation, and many applications such as adsorbents. Carbon adsorbents are used to remove organic pollutants and toxins from different media[1,2]. Some of these adsorbent carbons include: non-porous graphitised carbon blacks (GCB), carbon molecular sieves, highly porous activated carbons, charcoals and many more others.

Various methods, such as electrochemical separation[3], ion exchange[4], precipitation[5], membrane processes[6] and reverse osmosis[7] have been widely used for removing fluoride from aqueous solution[8,9]. However, these techniques are time consuming, inefficient (as some are unsuccessful in bringing concentrations to acceptable levels), energy use and high operating cost[10]. Among these methods, adsorption is generally considered to be relatively more effective and suitable due to the simplicity of its design, selectivity, relatively low cost and environmentally friendlyness[11-13]. For these reasons, a wide variety of natural and modified adsorbents have been fabricated and used to remove fluoride ions in aquatic environments[14].

A number of researchers have come up with various technologies to remove fluoride from aquatic systems using different types of adsorbents including natural, synthetic, low-cost and biomass materials such as activated alumina/ aluminium based materials[15,16], alum sludge[17,18], chitosan beads[19,20], flyash[21], amberlite resin[22], synthetic hydroxyapatite[23,24], calcite[25], quicklime[26], hydrated cement[27] layered double hydroxides[28,29], clays and soils[30-32], modified zeolites[33], ion exchange resins[34], carbon based materials, etc. [35-37].

Adsorbents can be prepared from a variety of sources, for examples clays such as bentonite, etc[31,38]. However, in this work, the adsorbent was prepared from wastes originating from plant sources mainly banana pseudo-stems which remain as waste after the harvest of the banana fruit.

Banana plantation generates huge volumes of these pseudo-stem wastes, which are then discarded into the rivers, lakes and on highways, causing a serious environmental problem[39]. Banana pseudo-stems are known to contain fibers which are rich in lignin and cellulose, and other components with functional groups, including carboxylic acids, phenols, carbonyls and ethers. Which make pseudo stems attractive for use as adsorbents for the removal of pollutants from wastewater[40,41].

Human beings are frequently exposed to fluoride through water, food and other daily products[42]. Exposure to high concentration of fluoride can cause serious health problems such as fluorosis, osteoporosis, arthritis, brain damage, cancer and other neurological disorders[43-45]. Therefore, more attention should be directed to the research on cheap adsorbents in solving environmental problems such as fluorides in water to protect public health[46]. This chapter thus reports on the synthesis of non-impregnated and TiO_2-impregnated MP carbon and characterization of the prepared MP carbon materials.

4.2 Materials and methods

4.2.1 Chemicals

Nitric acid (65%), hydrochloric acid (32%), sodium hydroxide, sodium chlorite, titanium tetraisopropoxide (TTIP) supplied by Sigma Aldrich (St Louis, Missouri, USA), and they were all of analytical grade and were used without any further purification. Deionised water (18.4 MΩ conductivity) was obtained from an in-house reverse osmosis system and was used for most dilutions and the preparation of standards.

4.2.2 Synthesis of MP carbon

MP stem was collected at Mbabane, Hhohho region of Swaziland and cut into slices of equal size (as thin discs) and were divided into three portions and autoclaved for an hour. Autoclaved MP stem discs were soaked into a reagent of bleaching action to expel out tannin from soft fibres that is, in 4%,5%, 6%, 7% and 8% NaOH, for 2 h and 1.7% $NaClO_2$ for 4 h[47]. Tannin expelled MP was dried under shadow light. The mass was then carbonized in muffle furnace at 100, 150 and 200^oC for 2 h.

4.2.3 Synthesis of TiO_2-coated MP carbon

50 mL of Titanium tetraisopropoxide (TTIP) was mixed with about 5 g of the three portions of MP dried mass and stirred for about 10 min. Double distilled water was then added to the above system drop wise and slowly to facilitate uniformity in the dispersion of TTIP until there is a formation of a precipitate in white color along with the fibers. The wet mass was then filtered before its weight was recorded. The TiO_2 impregnated MP fibers were divided into three sets and carbonized in muffle furnace at 100, 150 and 200˚C respectively for 2 h in an inert atmosphere. Then the carbonized MP dispersed with TiO_2 was desiccated and stored under moisture free conditions.

4.2.4 Characterization

4.2.4.1 Fourier transform infrared spectroscopy (FTIR)

Perkin Elmer Spectrum 100 FTIR spectrometer, (Massachusetts, USA) was used to investigate the presence of organic and inorganic functional groups present in the MP carbon material. All TiO_2-coated MP carbon adsorbents were crushed into fine powder (<45 µm) and analyzed over the spectral range of 4 500 cm^{-1} and 500 cm^{-1}. The difference between the virgin (non-impregnated) MP carbon and TiO_2-impregnated MP carbon in terms of the presence and/or absence of functional groups were monitored by FT-IR. Moreover the influence of the carbonization temperatures and bleaching properties on the functional groups on the carbonized materials were followed from the FTIR spectra.

4.2.4.2 Scanning electron microscopy (SEM)

The surface structures/morphology of the MP stem carbon was analysed by Tescan VEGA 3 XMU scanning electron microscopy (Brno, Czech Republic). SEM was used to acquire the information about the morphology of the carbonized material and its changes with respect to thermal and chemical effects. The adsorbents were crushed into fine powder and sieved to uniform size (<45 µm). All micrographs were taken at the same magnification, working distance and beam capacity. XMAX Oxford instruments EDS was also carried out to understand the presence of elements dispersed on the carbon matrix.

4.2.4.3 X-ray diffraction (XRD)

The Rigaku Ultima IV X-ray diffractometer XRD (Tokyo, Japan) was used in this study to find out the crystal and phases of TiO_2 on the adsorbent material. XRD was carried out to ascertain the crystalline/armophous nature of the material and the presence of any bound materials to the carbon's surface.

4.2.4.4 Brunauer, Emmett, Teller (BET)

The nitrogen sorption porosimetry was carried out using a Micrometrics ASAP 2020 surface area and porosity analyzer (Atlanta, Georgia, USA). Brunauer, Emmett and Teller (BET) analysis is the main technique that was used to determine specific surface area, specific pore volume, pore size distribution and average pore diameter values of the MP stem carbon. This was done to investigate the surface properties of the carbonaceous material and its variation with respect to external modification by thermal and chemical effects. The surface properties investigated include pore size, pore volume, surface area etc along with the prediction of particle size range based on adsorption-desorption hysteresis curve type. Samples were degassed at 150^{o}C for 180 min and analyzed under nitrogen atmosphere. Specific surface areas were calculated according to the BET method[48], and the pore size distribution was obtained according to the Barret–Joyner–Halenda (BJH) method[48] from the adsorption data.

4.2.4.5 Thermogravimetric analysis (TGA)

Thermal stabilities of the adsorbents were investigated using a Perkin Elmer TGA 4000 (Massachusetts, USA) to obtain information about the behaviour of the MP carbon under thermal treatment as well as its thermal stability. Adsorbent sample weight was monitored as the temperature was increased from 30°C to 800°C at the rate of 10°C/min under a nitrogen atmosphere with the flow rate set at 20 mL/min. A thermal analysis curve was generated by plotting the temperature change against the weight loss in percentages whereby a weight loss at any given temperature signify a thermal activity which means a thermal decay of a particular constituent of the adsorbent material.

4.2.4.6 Elemental (CHN) analysis

A LECO CHNS analyzer (St Joseph, Michigan, USA) was used for elemental analysis of the adsorbent material to substantiate the influence of the percentage of C, H, N and S in the adsorption pattern for fluoride. Moreover, the calculations of these elements along with the analysis of ash content were used to predict the suitability of the carbonized material for solid fuel applications.

4.2.4.7 Zeta potential

Zeta potential of the adsorbent material (MP carbon) was carried out using a Malvern ZEN 3600 zeta sizer (Malvern, U.K). The zeta potential measurements are useful in obtaining a detailed insight into the causes of dispersion, aggregation or flocculation also as a function of surface charge of the carbonized material.

To consolidate the result obtained from pH versus Zeta potential plot, the iso-electric point (IEP) of the adsorbent material was determined using electrophoretic mobility in electrolytic medium of an ionic strength of 0.01 M and 0.001 M NaCl.

4.2.4.8 pH of zero point charge (pH_{ZPC})

This measurement was carried out to study the nature of the carbonized material, whether it contains positive or negative charges on the carbon surface. This property suggests the suitability of MP carbons to have affinity with anions in the solution.

A solution of 0.005M $CaCl_2$ was boiled to remove dissolved CO_2 and then cooled to room temperature. The pH of the solution was adjusted to a value between 2 and 10 using 0.1M HCl or 0.1M NaOH. The carbon material 0.06g was added into 20 mL of the pH-adjusted solution in a capped vial and equilibrated for 24 h. The final pH was measured and plotted against the initial pH. The pH at which the curve crosses the $pH_{initial}$) pH final line is taken as pH_{ZPC}.

4.2.4.9 Moisture content

Moisture content in biomass

For the moisture content of biomass, the amount of MP taken initially (W1), amount of MP remaining after bleaching (after drying) (W2), and amount of carbon after carbonization process (W3), were recorded. It was expected that the trend would be W1>W2>W3. The difference obtained for the three weights, was used in the interpretation of the estimation of the amount of water and lignin contents. The moisture content was also estimated by taking a known amount of MP in an oven at a temperature of 105 ± 5^0C for 2 h and the moisture content was then estimated by subtracting the final mass from the initial mass.

Moisture content in MP carbon

For the moisture content of MP carbon, a well cleaned crucible was weighed and 1 g of MP carbon was taken in the crucible. The crucible with the 1 g of MP carbon was kept in an oven at 110 ^{0}C for about 1h 30 min. The hot crucible was then removed from the oven and kept in a desiccator to bring down its temperature to ambient temperature and finally the crucible was weighed.

4.2.4.10 Ash content

Ash content in biomass

The mass of a covered high silica or porcelain dish was weighed and then the oven-dried specimen from a moisture determination step was placed in the weighed porcelain dish and the mass of the dish and specimen were determined.

The cover was then removed and the porcelain dish was placed in a muffle furnace. The temperature in the furnace was gradually brought to 750°C and temperature was held until the specimen was completely ashed (no change of mass occurs after a further period of heating).

The dish was then covered with the retained aluminium foil cover, cooled in a desiccator, and the mass was again determined and the ash percentage in the sample was worked out according to **Equation 4.1**[49].

$Ash\ content, \% = (C\ X\ 100)/\ B$ ………………………………………………….. 4.1

where:

C= ash weight (g), and

B = oven-dried test specimen, g.

Ash content in MP carbon

For the ash content of MP carbon, a well cleaned crucible was weighed and 1g of MP carbon was put in the crucible. The crucible with the 1g of MP carbon was kept in a furnace at 750 ^{0}C for about 1h. The hot crucible was then removed from the furnace and kept in a desiccator to bring down its temperature to ambient temperature. Finally the crucible was weighed. The procedure was repeated till the weight of MP carbon remained constant.

4.3 Results and discussion

4.3.1 Optimization of concentration of bleaching solution

The effect of increasing concentration of the bleaching solution was also investigated. It was observed that bleaching was effective in the samples that were bleached in a higher concentration of the bleaching solution. A more fibrous appearance was observed in SEM images for samples that were soaked in more concentrated bleaching solutions than in less concentrated bleaching solutions (**Figure 4.1 (a) – (c)**). The increase in efficiency in bleaching with increase in concentration of the bleaching solution was also attributed to the delignification process.

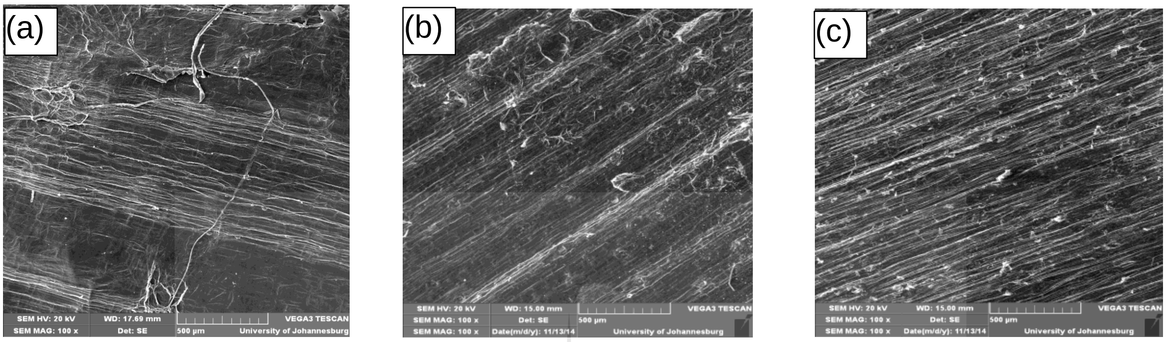


Fig 4.1: SEM images (a) 4% NaOH-bleached (b) 6% NaOH-bleached (c) 8% NaOH-bleached

4.3.2 Optimization of bleaching temperature

The effect of bleaching with respect to heating the bleaching solution was investigated. Autoclaved MP fibers were soaked in a 4% NaOH without heating the bleaching solution and on the other hand, the autoclaved MP fibers soaked in heated 4% NaOH bleaching solution. It was observed that bleaching was effective in the samples bleached in heated solution as these samples had a more fibrous (thread-like) appearance than the one that was not heated (**Figure 4.2 (a)- (b)**). This is as a result of the delignification process. It is known that effective bleaching result in more threadlike structures in the fibre, bright colour in appearance and soft and slimy in texture.

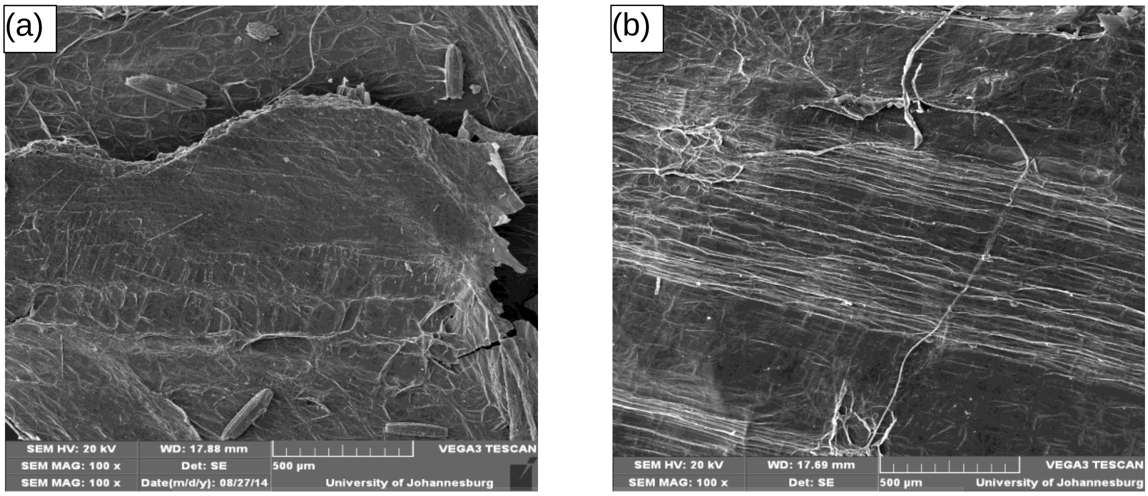


Fig 4.2: SEM images (a) 4% NaOH bleached-not heated (b) 4% NaOH bleached-heated 80 ^{0}C

4.3.3 Scanning electron microscopy (SEM) results

The surface morphology was characterized by scanning electron microscopy and it showed the difference between the adsorbents. The surface texture and morphology of non-impregnated and TiO_2-imprenated MP carbon were found to differ from each other, as shown in **Figure 4.3 (a) and (b)**, with TiO_2-impregnated MPC showing loaded TiO_2 nanoparticles embedded on the fibers, compared to non-impregnated MP carbon. There was a morphological change on the SEM image of the carbonized material impregnated with TiO_2 (**Figure 4.3(b)**). This indicates that TiO_2 was successfully impregnated. This characteristic could either promote the surface area available for adsorption or may have an effect on the adsorption sites for fluorides.

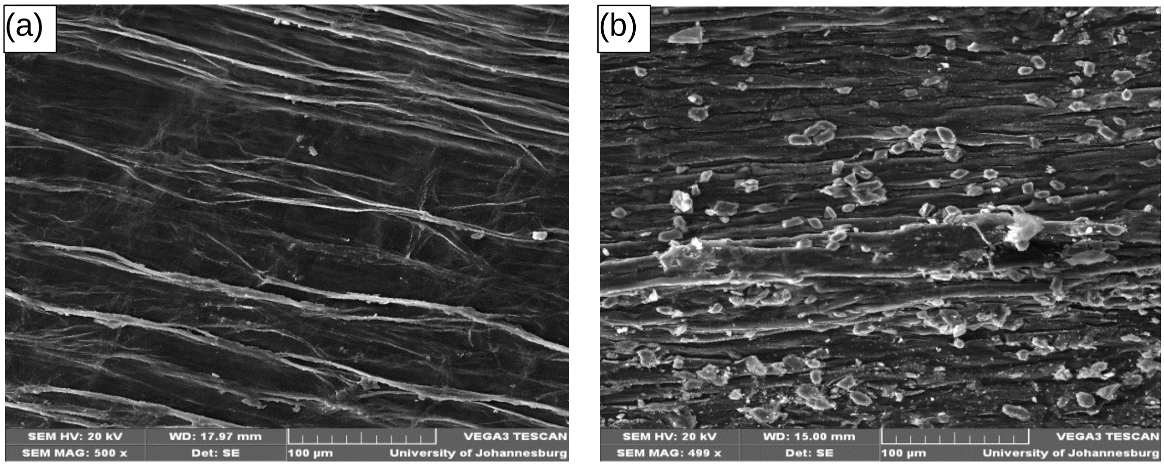


Fig 4.3: SEM images (a) Non-impregnated carbon (b) TiO_2-coated carbon

Elemental composition of the bleached and carbonized samples and all the MP carbon materials were confirmed by Energy dispersive spectroscopy (EDS) as shown in **Figure 4.4 (a).** The presence of Ti was also confirmed by EDS and the results are depicted in (**Figure 4.4 (b)**).

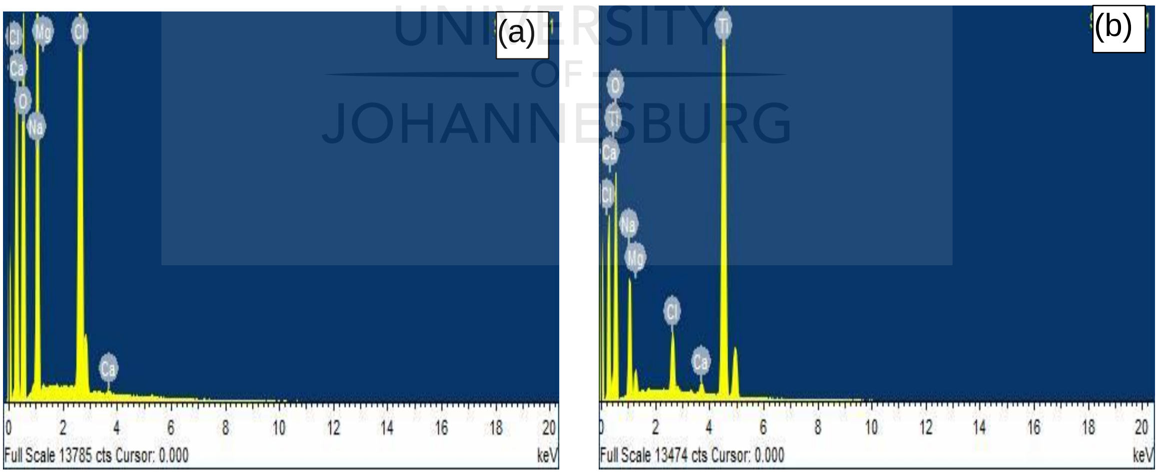


Fig 4.4: EDS spectra (a) Non-impregnated Carbon (b) TiO_2-coated Carbon

4.3.4 Fourier transform infrared (FTIR) spectroscopy results

The presence or absence of specific functional groups in adsorbents does play a major role in the adsorption of different adsorbates. In this study, FT-IR spectroscopy was used to determine the type of functional groups present in each adsorbent used. It was found that the constitutions of the functional groups in the various adsorbents differed.

4.3.4.1 Raw MP fibers

The presence of functional groups on the raw MP fibers was confirmed by FTIR as shown in **Figure 4.5** and **Table 4.1**. The absorption bands at 3600-3000 cm-1 can be assigned to stretching vibrations and other polymeric associations of hydroxyl groups (O-H). Peaks at 3700-3500 cm-1 due to amides (N-H). Symmetric stretching at 3100-2913cm-1 is assigned to the C-H groups present in polysaccharides. Angular deformations of C-H linkages of aromatic groups were observed at 860-680 cm-1. Other peaks were observed between 1700-1500 cm-1 due to aromatic C=C and 1210-1080 cm-1 due to C-O, and CH and C-OC vibrations due to polysaccharides.

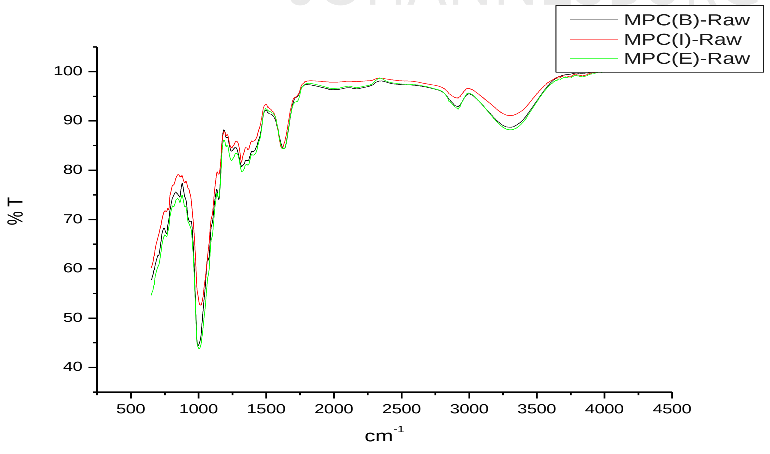


Fig 4.5: FTIR spectra for raw MP fibers

Table 4.1 FTIR results of Raw MP fibers

MPC	**Wave numbers**	**Vibration**	**Functional group**
Raw MP			
MPCExt	3838.97, 3308.98, 2918.11, 2162.51, 2015.97, 1622.96, 1508.37, 1406.56, 1363.37, 1319.16, 1243.56, 1203.80, 1147.36, 1003.97, 861.53, 815.52, 763.99	N-H, O-H, C-H, C≡H, C=C,C-N, C-O,C-O-C, Aromatic C-H	Amines, alcohols, alkane, alkynyl, alkenyl, aromatic amine, polysaccharides
MPCInt	3838.90, 3751.89, 3672.97, 3646.11, 3308.15, 2916.99, 1999.16, 1618.15, 1508.40, 1363.61, 1317.06, 1242.18, 1202.89, 1149.30, 1017.35, 896.36, 863.81, 777.89, 758.57	N-H, O-H, C-H, Aromatic C=C, aromatic C-H, C-N	Amide, alcohol, alkanes, Aromatic amine
MPCBoth	3310.61, 2917.31, 2162.47, 1967.58, 1635.22, 1318.32, 1241.71, 1204.69, 1148.55, 1074.53, 995.43, 934.30, 860.24, 762.54	O-H, C-H, aromatic C=C, Aromatic C-H, C-N, C-O	Alcohol, alkanes, aromatic amine

4.3.4.2 Bleached MP fibers

The differences in the FTIR spectra between the raw and bleached MP fibres are seen clearly in **Figure 4.6 and Table 4.2.** The change in the spectra occurs between wavelengths 2913cm^{-1} and 1654 cm^{-1}. The removal of hemicelluose on other impurities after scouring and bleaching is indicated in between the stated wavelengths. C-O bonds of alcohols at 3500-3200 cm^{-1} and C-H bonds at 3100-3000 cm^{-1} are still observed. Other peaks that were observed were at 2200-2400 cm^{-1} due to C≡N nitrile. Aromatic C=C bonds were also observed at 1700-1500 cm^{-1}.

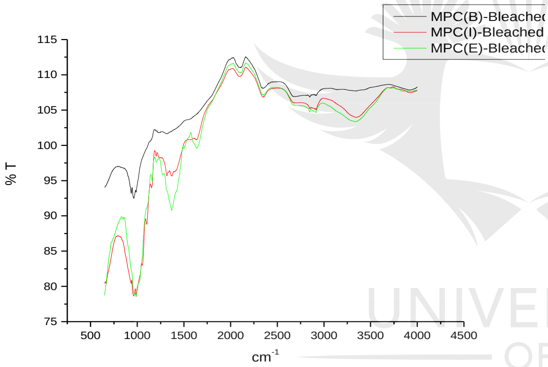


Fig 4.6: FTIR spectra for bleached MP fibers

Table 4.2: FTIR results for bleached MP fibers

Bleached	**Wave numbers**	**Vibration**	**Functional group**
MPCExt	3932.02, 3337.13, 2914.61, 2848.37, 2352.64, 2098.92, 1637.48, 1499.15, 1368.59, 1276.60, 1203.53, 1159.34, 987.50, 971.57, 851.98	O-H, C-H, C≡N, C≡C, C=C, C-O, C-H	Alcohols, alkane, alkenyl

MPCInt	3926. 27, 3345.51, 2917.24, 2850.76, 2352.44, 2090.19, 1629.05, 1370.65, 1317.79, 1202.84, 1153.97, 1102.72, 1053.15, 987.20, 961.63, 935.60, 668, 02	O-H, C-H, C≡N, C≡C,C=C, C-N	Alcohol, alkane, aromatic amine
MPCBoth	3918.18, 3347.93, 2915.50, 2850.40, 2693.74, 2337.20, 2109.27, 1317.38, 1222.67, 987.21, 962.88, 936.13	O-H, C-H, C≡N, C≡C, C-N	Alcohols, alkane, aromatic amine

4.3.4.3 Virgin/non-impregnated MP carbon

Again the differences in the FTIR spectra of virgin MP carbon are seen clearly in **Figure 4.7**.

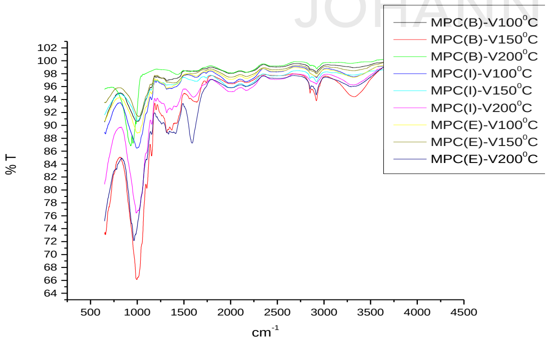


Fig 4.7: FTIR spectra for virgin/non-impregnated MP carbon

Table 4.3: FTIR results for virgin/non-impregnated MP carbon

Virgin MPC	Wave numbers	Vibration	Functional group
MPCExt-V200	3295.66, 2916.94, 2851.45, 2513.22, 2162.28, 2008.15, 1587.41, 1412.51, 1379.93, 1334.86, 1260.52, 1153.80, 964.45	O-H, C-H, N-O, C-O, C≡C	Alcohols, alkane, alkenyl
MPCInt-V200	3309.19, 2917.97, 2484.61, 2161.16, 2012.91, 1600.93, 1420.45, 1368.89, 1315.14, 1200.10, 1156.49, 988.74	O-H, C-H, C-O, C≡C	Alcohols, alkane, alkenyl
MPCBoth-V200	3278.06, 2925.74, 2436.01, 2162.06, 2011.83, 1560.73, 1431.30, 987.05, 953.35, 928.75	O-H, C-H, C≡C, C=C	Alcohols, alkane, akenyl, aromatic
MPCExt-V150	3319.09, 2917.58, 2463.64, 2163.69, 1999.89, 1394.79, 1199.56, 1150.88, 1017.19	O-H, C-H, C≡C, C-O	Alcohol, alkane, alkenyl
MPCInt-V150	3305.04, 2921.52, 2850.68, 2443.90, 2165.98, 2008.09, 1744.97, 1637.20, 1316.24, 1200.67, 1010.02	O-H, C-H, C≡C, C=O, C=C	Alcohols, alkane, alkenyl
MPCBoth-V150	3324.55, 2918.88, 2851.24, 2529.62, 2166.31, 2016.16, 1737.27, 1637.74, 1370.14, 1316.22, 1201.30, 1153.75, 1101.99, 659.34	O-H, C-H, C≡C, C=C, C-O	Alcohols, alkane, alkenyl
MPCExt-V100	3322.19, 2921.00, 2461.40, 2177.60, 2009.14, 1632.98, 1316.98, 1200.12, 1153.22, 1001.02	O-H, C-H, C=C, C-O	Alcohol, alkane
MPCInt-V100	3671.93, 3318.28, 2922.40, 2488.30, 2155.61, 1984.34, 1737.92, 1633.03, 1316.07, 1199.35, 1153.90, 996.18, 659.20	O-H, C-H, C=C, C-O	Alcohols, alkane
MPCBoth-V100	3323.37, 2916.69, 2487.23, 2158.19, 1984.45, 1623.54, 1315.89, 1199.81, 991.20	O-H, C-H, C-O, C=C	Alcohols, alkane

4.3.4.4 TiO_2-impregnated MP carbon

Presence and/or absence of functional groups on the TiO_2-impregnated MP carbon were also confirmed (**Table 4.4 and Figure 4.8**). Bands at 2940 can be assigned to O-H and 1060 cm-1 to C-O-C ethereal group. The ionic character of Ti-O bonds in TiO_2 is manifested in the strong IR absorption below about 950cm^{-1} FTIR spectra peaks for TiO_2 impregnated were observed at 987.05, 1153.68, 1321.29, 1630.02, 2895.12, 3283.35, 3949.15 confirming C-H, O-H, C=C, C=O stretch.

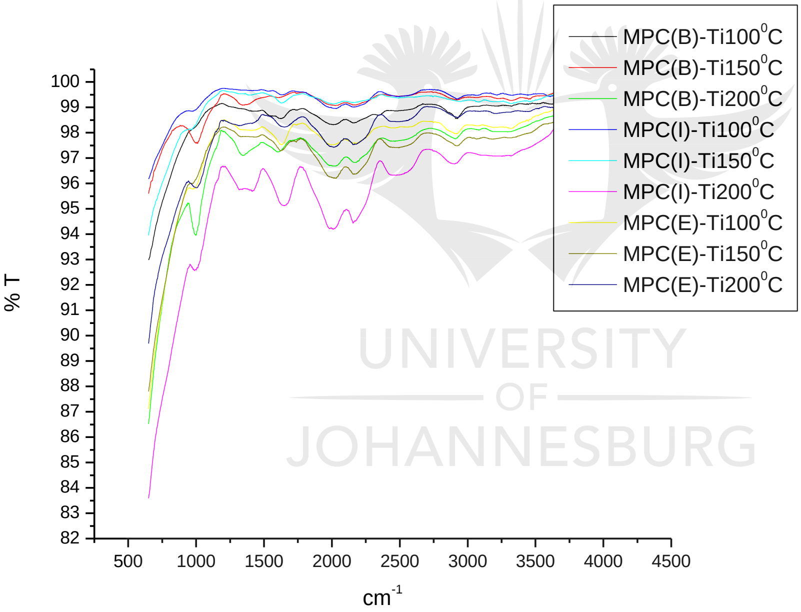


Fig 4.8: FTIR spectra for TiO_2-coated MP carbon

Table 4.4: FTIR results for TiO_2-coated MP carbon

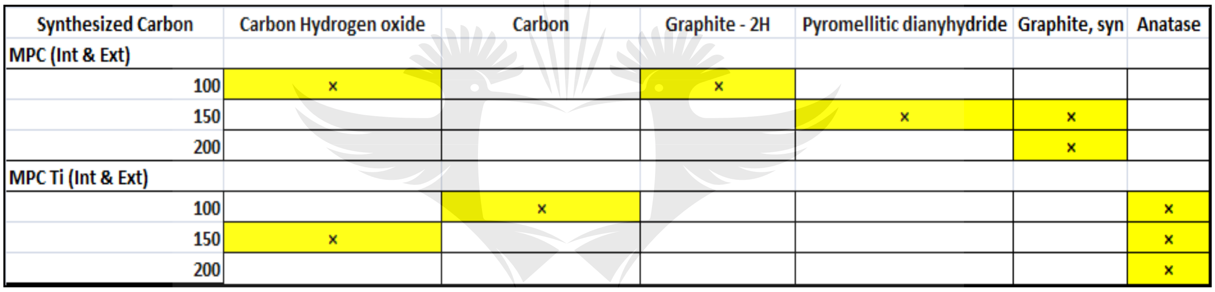
TiO_2-coated MPC	Wave numbers	Vibration	Functional group
MPCExt-Ti200	2924.04, 2493.37, 2155.91, 2014.64,	C-H, C≡C, C=C	Alkane, alkenyl

	1650.80, 1316.24, 1000.61		
MPCInt-Ti200	3931.21, 3253.00, 2901.28, 2449.40, 2156.00, 2008.17, 1648.99, 1412.95, 986.61	O-H, C-H, C=C	Alcohol, alkane, alkenyl
MPCBoth-Ti200	3685.35, 3295.40, 2910.52, 2463.92, 2166.78, 2027.00, 1606.11, 1346.50, 997.50	N-H, O-H, C-H	Amide, alcohol, alkane
MPCExt-Ti150	3901.15, 2920.72, 2493.00, 2156.69, 2030.96, 1623.03	C-H, C≡C, C=C	Alkane, alkenyl,
MPCInt-Ti150	3313.32, 2008.22, 1624.28	O-H, C=C	Alcohol, alkenyl
MPCBoth-Ti150	3323.97, 2921.51, 2024.90, 1340.06, 1010.23	O-H, C-H	Alcohol, alkane
MPCExt-Ti100	3902.73, 3319.00, 2922.15, 2178.61, 1999.13, 1623.55, 1411.98	O-H, C-H, C=C	Alcohol, alkane, alkenyl

MPCInt-Ti100	3607.36, 2918.25, 2490.01, 2155.28, 2030.99, 1633.01	N-H, C-H, C=C	Amide, alkane, alkenyl
MPCBoth-Ti100	2911.81, 2155.25, 2009.84, 1623.14	C-H, C=C	Alkane, alkenyl

4.3.5 X-ray diffraction (XRD) results

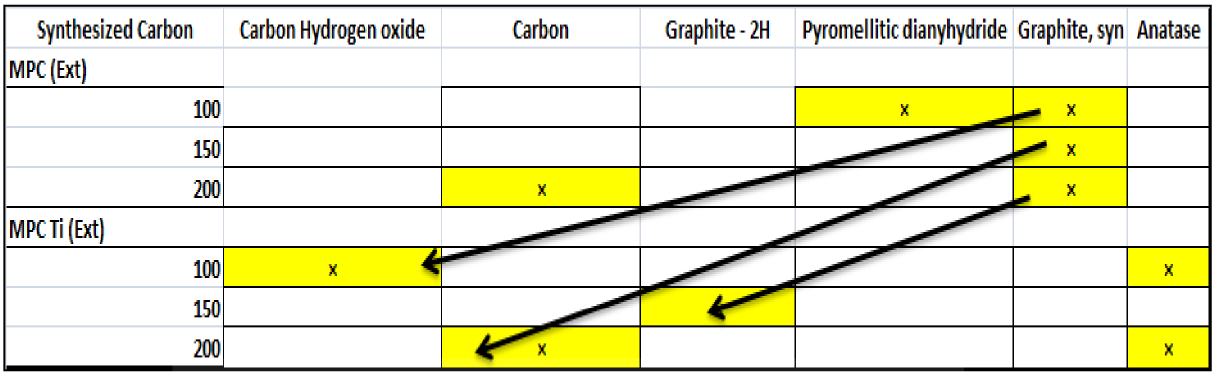
Table 4.5 The presence of different phases in virgin and TiO_2 coated MPC



Synthesized Carbon	Carbon Hydrogen oxide	Carbon	Graphite - 2H	Pyromellitic dianyhydride	Graphite, syn	Anatase
MPC (Int & Ext)						
100	×		×			
150				×	×	
200					×	
MPC Ti (Int & Ext)						
100		×				×
150	×					×
200						×

The percentage of anatase dominates on increasing the temperature from 100˚C to 200˚C. The existence of dominating phase of graphite (syn) is quite apparent from (**Table 4.5**) at 200˚C unlike the existence of different phases at the lower temperatures of 100˚C and 150˚C.

Table 4.6 The presence of different phases in virgin and TiO_2 coated MPC (Ext)



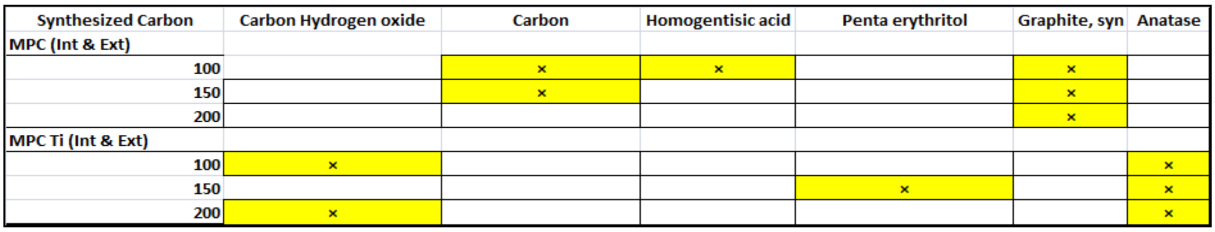
Synthesized Carbon	Carbon Hydrogen oxide	Carbon	Graphite - 2H	Pyromellitic dianyhydride	Graphite, syn	Anatase
MPC (Ext)						
100				x	x	
150					x	
200		x			x	
MPC Ti (Ext)						
100	x					x
150						
200		x				x

MPC (Ext) – Carbon synthesized from Internal part of *Musa Paradaisica*

MPC Ti (Ext) – TiO_2 encapsulated Carbon, synthesized from Internal part of *Musa Paradaisica*

It is interesting to observe that the crystallite size of graphite (syn) decreases from 423 Å to 32 Å on increasing the temperature from 100˚C to 200˚C. Conversely the strain increases from 0.06% to 1.15% with respect to the decrease in the crystallite size. Also, the graphite (syn) tends to change its phase during the encapsulation of TiO_2 at different temperatures (**Table 4.6**). Encapsulation of TiO_2 on carbon particles tends to change the phase from graphite (syn) into carbon hydrogen oxide (at 100˚C), graphite – 2H (at 150˚C) and carbon, C60 (at 200˚C) . The higher the temperature (from 100C to 200C) leads to the minimization of the crystallite size and maximization of the strain.

Table 4.7 Different phases in virgin and TiO_2 coated MPC (Int & Ext)

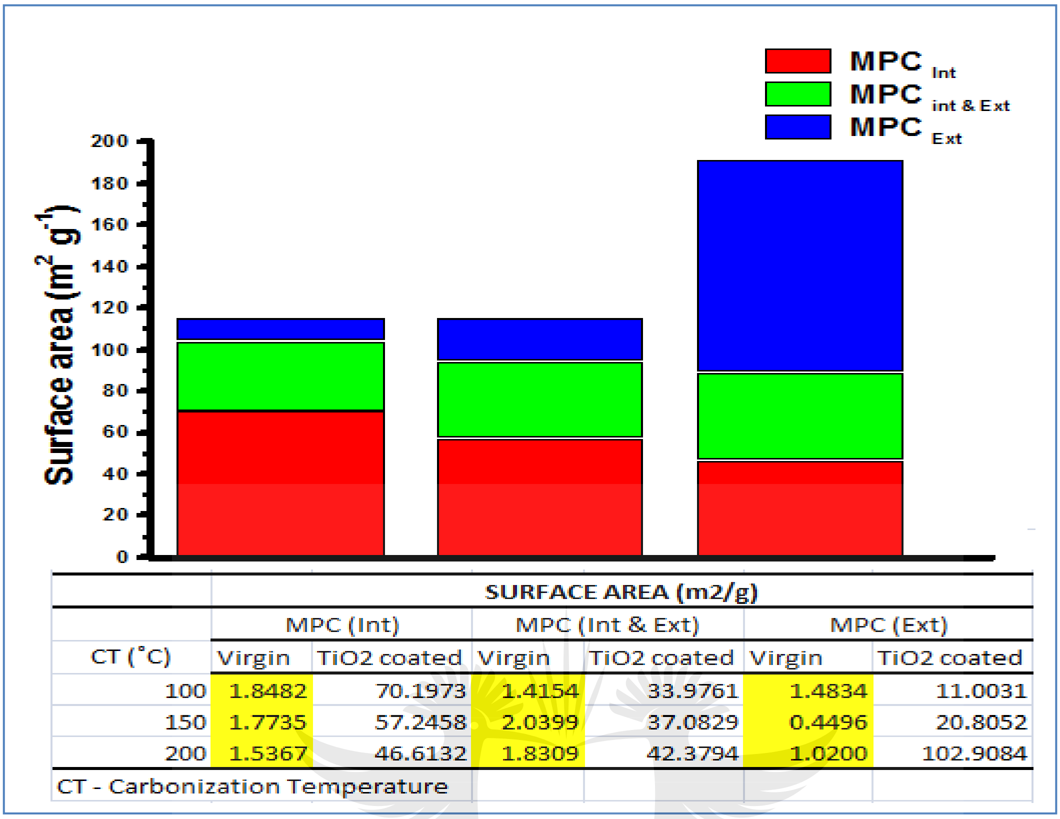


Synthesized Carbon	Carbon Hydrogen oxide	Carbon	Homogentisic acid	Penta erythritol	Graphite, syn	Anatase
MPC (Int & Ext)						
100		x	x		x	
150		x			x	
200					x	
MPC Ti (Int & Ext)						
100	x					x
150				x		x
200	x					x

Similar to the above MPC (Int), the crystallite size decreased from 362 Å to 139 Å on increasing the temperature from 100˚C to 200˚C. Conversely the strain for the graphite (syn) increased from 0.05% to 0.198%. The graphite (syn) tends to change its phase during the encapsulation of TiO_2 at different temperatures (**Table 4.7**). Encapsulation of TiO_2 on carbon particles tends to change the phase from graphite (syn) into carbon hydrogen oxide (at 100˚C), penta erythritol (at 150˚C) and carbon hydrogen oxide, $(CH_2)_3O_3$ (at 200˚C).

4.3.6 Brannauer Emmet Teller (BET) results

There was no appreciable change in the surface area with respect to temperature gradient for the virgin MPCs except MPC (Int) which shows little gradation of about 0.3 $m^2\ g^{-1}$ of surface area. The decrease in the surface area for the TiO_2 coated MPC (Int) was about 23.5 $m^2\ g^{-1}$ with respect to 100˚C rise. In contrast to this, the increase of about 8.40 $m^2\ g^{-1}$ for Ti-MPC (Int & Ext) and 89.91 m^2g^{-1} forTi- MPC (Ext) was corroborated. The increased gradation in the case of Ti-MPC (Ext) was about 10 times more than that of MPC (Int & Ext). The temperature difference of 50˚C rise improved the surface area by about 2 folds, which on further rise by another 50˚C, increased the surface area rise in about 5 folds. The surface area of every virgin MPC, up on coating by TiO_2 gets increased to multiple times as shown in **Figure 4.9, 4.10 and Table 4.8**.



	SURFACE AREA (m2/g)					
	MPC (Int)		MPC (Int & Ext)		MPC (Ext)	
CT (˚C)	Virgin	TiO2 coated	Virgin	TiO2 coated	Virgin	TiO2 coated
100	1.8482	70.1973	1.4154	33.9761	1.4834	11.0031
150	1.7735	57.2458	2.0399	37.0829	0.4496	20.8052
200	1.5367	46.6132	1.8309	42.3794	1.0200	102.9084

CT - Carbonization Temperature

Fig 4.9: BET results for MP carbon materials

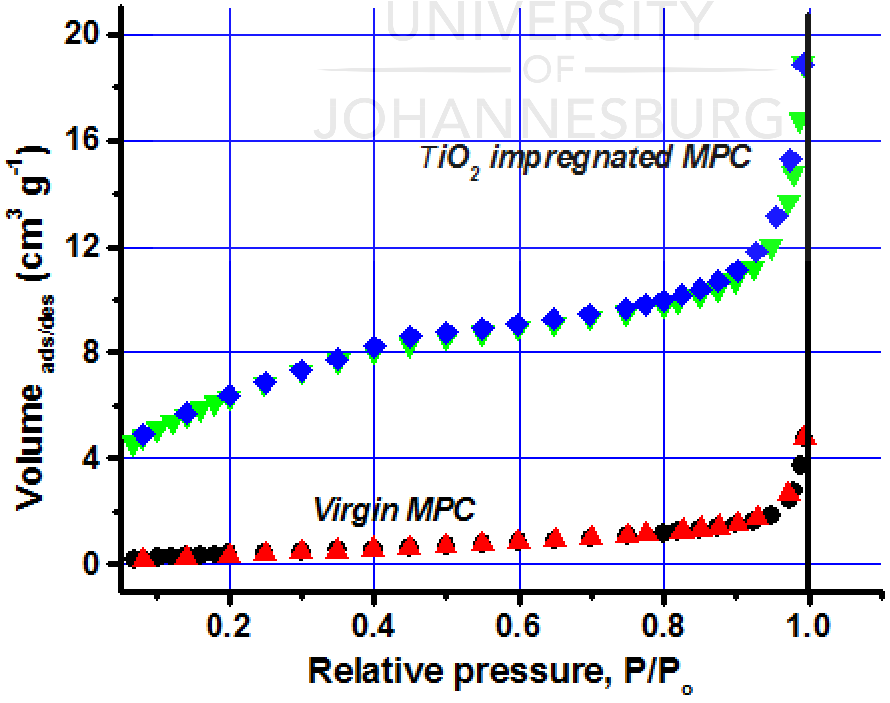


Fig 4.10: Relative pressure vs Volume plot for MP carbon materials

Table 4.8 BET results

Textural data	MPC (Virgin)	MPC (Ti coated)
Single point surface area (m^2g^{-1})	1.5019	22.1672
BET surface area (m^2g^{-1})	1.8091	23.2716
Total pore volume (cm^3g^{-1})	0.0074	0.0292
Average pore width (nm)	16.39	5.02
Average pore diameter (nm) during		
BJH adsorption	15.37	5.16
BJH desorption	15.23	4.73

4.3.7 Thermogravimetric analysis (TGA) results

Thermal stability studies were performed on all the adsorbents under study and the results are shown by the thermal analysis curves in **Figure 4.11** below. The TGA programme was such that the flow rate of the nitrogen gas was set at 20 $mL\cdot min^{-1}$ with the temperature programmed from 30°C to 900°C and a ramp rate of $10°C\cdot min^{-1}$.

It was observed that there was a small change in sample mass around 100 ^{0}C which was attributed to vaporization of moisture. The decomposition of all MP carbon materials began slowly at about 300 ^{0}C with the rate increasing at about 320 ^{0}C for the non-impregnated MP carbon and at 350 ^{0}C for the TiO_2-coated MP carbons signifying the loss of most functional groups and finally another loss at around 700 ^{0}C due to ashing of carbonates. The TGA curve for the TiO_2 -coated MP carbons shifted to higher temperatures, by about 20 ^{0}C, compared to the TGA curves for the virgin/non-impregnated carbons. This result indicates that a higher activation energy is needed to decompose the TiO_2-coated MP carbon which can be explained by the higher carbon content.

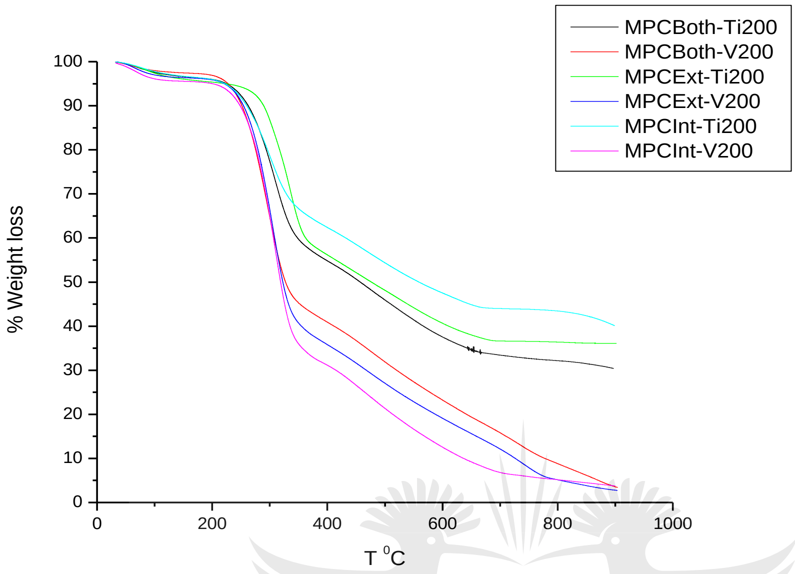


Fig 4.11: TGA curves for virgin and TiO_2-coated MP carbon

4.3.8 Elemental (CHN) analysis

Table 4.9 Elemental analysis and corresponding ratios of MPCs

	C	H	O	N	H/C	O/C	O+N/C	C	H	O	N	H/C	O/C	O+N/C
	HT = 100˚C													
MPC (E+I)	33.70	5.46	60.72	0.12	0.16	1.80	1.81	21.40	4.25	74.29	0.06	0.20	3.47	3.47
MPC Int	34.80	5.43	59.46	0.33	0.16	1.71	1.72	24.80	4.50	70.60	0.10	0.18	2.85	2.85
MPC Ext	35.30	5.56	59.02	0.12	0.16	1.67	1.68	29.00	4.70	66.18	0.10	0.16	2.28	2.29
	HT = 150˚C													
MPC (E+I)	33.90	5.43	60.57	0.11	0.16	1.79	1.79	23.70	3.90	72.30	0.10	0.16	3.05	3.05
MPC Int	35.00	5.38	59.47	0.35	0.15	1.70	1.70	26.00	3.90	69.90	0.11	0.15	2.69	2.70
MPC Ext	36.70	5.36	57.81	0.13	0.15	1.58	1.58	30.10	4.40	65.37	0.11	0.15	2.17	2.18
	HT = 200˚C													
MPC (E+I)	34.10	5.23	60.52	0.11	0.15	1.77	1.78	29.60	3.40	66.84	0.10	0.11	2.26	2.26
MPC Int	35.60	5.30	58.77	0.33	0.15	1.65	1.66	29.40	3.30	67.04	0.11	0.11	2.28	2.29
MPC Ext	37.70	5.30	56.86	0.14	0.14	1.51	1.51	34.70	4.20	61.02	0.08	0.12	1.76	1.76

Note: C, H, O and N are expressed in percentage

The degree of carbonization may be described by the molar H/C ratio, because 'H' is primarily associated with plant organic matter[50]. The observed H/C ratios (**Table 4.9**) in the range 0.14 – 0.16 and 0.11 – 0.20 for virgin MPCs and TiO_2 encapsulated MPCs respectively indicate that these carbons are carbonized as compared to the activated carbons reported by Chun et al. 2004 and Chen et al. 2008 with the respective H/C ratios of 0.12 and 0.256. These low H/C ratios suggest that both biochars likely contain no appreciable amount of original plant organic residues such as cellulose[51,52]. The molar oxygen to carbon (O/C) ratio of biochar has been used as a surrogate for surface hydrophilicity since it is indicative of polar-group content, derived most likely from carbohydrates which could facilitate the formation of water clusters on MPCs surface[51]. Conventional pyrolysis results in graphite-like structures with low O/C and H/C ratios and, therefore, few functional organic groups. Based on this, the polar structure of MPCs are especially interesting as a soil conditioner, since they can play an active role in soil CEC and reactivity.

The carbonization process tends to increase the content of mainly due to the loss of oxygen and hydrogen in the dehydration of sugars. As the temperature of hydrothermal carbonization increased, the carbon content increased up to 37.7% and 34.7% for virgin MPCs and TiO_2 encapsulated MPCs respectively. However, at the same time the content of nitrogen remains constant which suggests that nitrogen was incorporated within the carbon matrix upon hydrothermal carbonization and that, upon further heat treatment, it can actually be incorporated in the aromatization/ pseudo-graphitization process of the carbon structure[53-55].

4.4 Conclusion

MP Pseudo-stem carbon materials have been studied with respect to their chemical and textural properties. The surface morphology was characterised by scanning electron microscopy and also shows the difference between the adsorbents. The surface texture and morphology of non-impregnated and TiO_2-imprenated MP carbon was found to differ from each other. The surface texture and morphology of the MP carbon may play a major role in the adsorption of adsorbate. The MP carbon has been successfully modified using TiO_2 and the modification of the functional groups present in the materials has been confirmed by FT-IR. There is a loss as well as gain of functional groups after the impregnation of TiO_2 on the MP carbon which is clearly shown in the FTIR spectra. The presence of these functional groups in the MP carbon also may play a major role in the adsorption of the adsorbate in this study.

There is also an increase in the surface area of the MP carbon materials after impregnation of TiO_2 which means that the TiO_2 does improve the surface area of the MP carbon materials, this is shown clearly in the BET results. The higher the surface area means the higher the percentage removal in the adsorption process. The phases of TiO_2 on the MP carbon were confirmed by XRD and were found to be mostly anatase. TGA studies showed that the adsorbent materials degraded only after 300°C which is still acceptable because adsorption is not normally carried out at such high temperatures. The elemental composition and percentage carbon on the MP carbon materials were also carried out using elemental analyser. In conclusion, this study was successfully carried out.

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CHAPTER 5

FLUORIDE ADSORPTIVE PROFILE OF VIRGIN AND TiO_2-ENCAPSULATED *Musa paradisiacal CARBONS (MPCs):* VALIDATION USING KINETIC AND ISOTHERM MODELS

This chapter outlines the details of the performance of TiO_2 coated carbon prepared from *Musa paradisiacal* (MP) for the removal of fluorides in water. The effect of pH, contact time, adsorbent dose, concentration and temperature were investigated. The effect of other competitive anions on the adsorption capacity was also explored. Adsorption studies on real water samples were also carried out.

5.1 Introduction

Contamination of water sources has aggravated the scarcity of potable water for human consumption. Fluoride ions are among the common pollutants mostly found in many aquatic systems[1]. These anions have both beneficial and harmful effects on humans depending on the concentrations at which they occur in water[2]. High concentrations of fluorides can be harmful to humans and it is thus very important to remove them from water[3]. According to the World Health Organization (WHO) reports, a fluoride (F^-) value that exceed 1.5 mg/L in drinking water can cause dental and skeletal fluorosis[4]. However, the U.S. Environmental Protection Agency has set a maximum contaminant level for fluoride of 2.0 mg/L for drinking water for public water systems. The U.S. Public Health Service has set the optimal fluoride content in drinking water in the range of 0.7–1.2 mg/L. In 2011, the U.S.

Department of Health and Human Services proposed a recommendation of 0.7 mg/L to replace the current range of 0.7–1.2 mg/L[5]. Indian standards for drinking water recommend an acceptable fluoride concentration of 1.0 mg/L and an allowable fluoride concentration of 1.5 mg/L in potable waters[6-8].

Fluoride exists in the form of fluorides in various minerals such as fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$) and it also be found in rocks, and soils[9,10]. Groundwater constitutes 97% of global freshwater consumed for drinking purpose by more than 50% of the world population[11]. In many remote and communities in the developing world where basic water distribution systems are unavailable, groundwater serves as the most economically viable option[12]. However, groundwater often contains inorganic contaminants such as fluoride, arsenic among many others[13-15]. Long term exposure to such contaminants causes health effects in humans. For example, excessive fluoride ingestion leads to dental and skeletal fluorosis[16].

A number of approaches to remediate water containing high levels of fluorides have been reported. For example conventional water treatment methods which involve a combination of adsorption[17-19], ion exchange[20-22], precipitation-coagulation[23-24], Donnan dialysis[25-26], electrodialysis[27,28], nanofiltration[29,30], membrane separation processes[31,32] and reverse osmosis[33,34]. However, some of these technologies have major drawbacks. Ion-exchange for example, can remove fluoride up to 90–95% but it is mostly dependent on the use of resins and the regeneration of resin is still a challenging issue. The technique is costly due to high cost of resin and post-treatment is required due to low pH[35].

Reverse osmosis, nanofiltration, electro dialysis and Donon dialysis fit into the category of membrane process which has disadvantages in terms of economic viability and maintenance cost[36]. Membranes do not require additives but these are relatively expensive to install and operate and are prone to fouling, scaling, or membrane degradation[12]. The electro dialysis, in general suffers due to the high cost factor, during installation, operation and maintenance[12]. The precipitation methods suffers from ineffectiveness and often lead to secondary pollution (generation of toxic sludge etc, high residual aluminium concentration, 2-7mg/L in the treated water whereas the set standard by WHO is 0.2 mg/L) [12,37]. Coagulation methods are found to be effective in defluoridation, but they are unsuccessful in bringing the fluoride to desired concentration levels[12,37].

Adsorption process seems to be most versatile and most effective method that has been recommended for the removal of fluorides present in water[38,39]. Adsorption seems to be a more attractive method for the removal of fluorides in terms of cost, simplicity of design and operation[38,39,40,41]. It has been reported to be one of the most economic and environment friendly among various defluoridation techniques[42,43]. This work therefore investigates the adsorption of fluorides using a non-impregnated and TiO_2-coated MP carbon.

5.2 Materials and methods

5.2.1 Chemicals

The fluorides standards were supplied by Sigma Aldrich (St Louis, Missouri, USA). Other chemicals used in this study include nitric acid (65%), hydrochloric acid (32%), sodium hydroxide, sodium chlorite, titanium tetraisopropoxide (TTIP) which were also supplied by Sigma aldrich. All chemicals used were of analytical grade. Deionised water (18.4 MΩ) was obtained from an in-house reverse osmosis system and was used for most dilutions and the preparation of standards.

5.2.2 Instrumentation

The determination of fluorides concentrations was performed using Dionex ICS 2000 RFIC ion chromatography (California, USA). A Tescan VEGA 3 XMU scanning electron microscopy (Brno, Czech Republic) was used for the surface morphology whilst for functional group characterization a Perkin Elmer Spectrum 100 FTIR spectrometer (Massachusetts, USA) was used. The thermogravimetric analysis was done using a Perkin Elmer TGA 4000 (Massachusetts, USA). For specific surface area, pore volume and pore diameter, a Micrometrics ASAP 2020 surface area and porosity analyzer (Atlanta, Georgia, USA) was used and for the phases of TiO_2 on the MP carbon, a Rigaku Ultima IV X-ray diffractometer XRD (Matsubara-cho, Akishima-shi, Tokyo, Japan) was used. For elemental analysis, a LECO CHN analyser (St Joseph, Michigan, USA) was used. For the zeta potential a Malvern ZEN 3600 zeta sizer (Malvern, U.K) was used.

5.2.3 Synthesis of MP stem carbon

MP stem was collected and cut into slices of equal size (as thin discs) and were subdivided into three portions and autoclaved for an hour. Autoclaved MP stem discs were soaked into a reagent of bleaching action to expel out tannins from soft fibres that is, in 4%,5%, 6%, 7% and 8% NaOH, for 2 h and 1.7% $NaClO_2$ for 4 h.[44] Tannin expelled MP was dried under shadow light. The mass was then carbonized in muffle furnace at 100, 150 and 200^oC for 2 h.

5.2.4 Synthesis of TiO_2-coated MP carbon

50 mL of Titanium tetraisopropoxide (TTIP) was mixed with about 5 g of the three portions of MP dried mass and stirred for about 10 min. Double distilled water was then added to the above system drop wise and slowly to facilitate uniformity in the dispersion of TTIP until there is a formation of a precipitate in white color along with the fibers. The wet mass was then filtered before its weight was recorded. The TiO_2 impregnated MP fibers were divided into three sets and carbonized in muffle furnace at 100, 150 and 200˚C respectively for 2 h in an inert atmosphere. Then the carbonized MP dispersed with TiO_2 was desiccated and stored under moisture free conditions.

5.2.5 Characterization

Different techniques were employed to ascertain the presence or absence of structures, functional groups, etc that were expected after different types of treatments of the MP carbon. The techniques that were used for characterization include microscopy, spectroscopy etc.

Scanning electron microscopy (SEM)

The morphology and mean diameter of the fibers were examined via Tescan VEGA 3 XMU scanning electron microscopy (Brno, Czech Republic), operating at an accelerating voltage of 15 kV.

Fourier transform infrared (FTIR) spectroscopy

The structure of the MP carbon was studied by Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra were recorded with a Perkin Elmer Spectrum 100 FTIR spectrometer (Massachusetts, USA) in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed to obtain information about the thermal stability of the prepared MP carbon. The analysis was performed with a Pekin Elmer TGA 4000 (Massachusetts, USA) using 8.0 mg of sample with a heating rate of 10 °C/min under nitrogen flow of 20 mL/min.

Brannauer Emmet Teller (BET)

The textural characterization of the MP carbon was obtained by N_2 adsorption/desorption isotherms using a Micrometrics ASAP 2020 surface area and porosity analyzer (Atlanta, Georgia, USA). Prior to measurement, the samples were degassed under nitrogen atmosphere at 150°C for 3 h. Specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was obtained according to the Barret–Joyner–Halenda (BJH) method from the adsorption data.

X-ray diffraction (XRD)

The Rigaku Ultima IV X-ray diffractometer XRD (Tokyo, Japan) was used in this study to find out the crystallinity and phases of TiO_2 on the adsorbent material. XRD experiments were carried out to ascertain the crystalline/armophous nature of the material and the presence of any bound materials to the carbon's surface.

Elemental analysis

Elemental analysis for C, H, N and S was performed in an elementary analyzer by LECO CHN analyzer (St Joseph, Michigan, USA).

Zeta potential

Zeta potential of our adsorbent material was carried out by a Malvern ZEN 3600 zeta sizer (Malvern, U.K). The zeta potential measurement were performed in order to obtain detailed insight into the causes of dispersion, aggregation or flocculation also as a function of surface charge of our material

The pH of point of zero charge (pH_{ZPC})

The pH of the point of zero charge (pH_{ZPC}) was determined. $CaCl_2$ (0.05 M) solutions of pH 2 - pH 10 were prepared using 0.1 M NaOH or 0.1 M HCl. 0.06 g of banana fibers were added to 20 mL of solution of different initial pH values, and the equilibrium pH was measured after 24 h of agitation (125 rpm) at 25 ± 2 ^{o}C.

5.2.6 Analyte determination

The analysis of anions in water was carried out using Dionex ICS 2000 RFIC ion chromatography (California, USA).

5.2.7 Batch adsorption experiments

Batch-adsorption experiments were carried out by shaking 0.2 g of adsorbent in 50 mL of Fluorides solution of the initial concentration (2 mg/L) at a temperature of 25°C for 1 h (except for effect of contact time experiments) at 125 rpm agitation speed. The effect of pH on adsorption was investigated in the range between pH 2 to pH 10. The effect of contact time on the adsorption time was studied by varying the exposure time from 2 min to 180 min at optimum pH while the effect of the adsorbent dose was carried out by varying the mass of the adsorbent from 0.2 g to 1 g. The effect of initial concentration of fluorides on adsorption was investigated using the optimum adsorbent dose (0.6 g) of adsorbent in 50 mL solution of varying concentrations of F^- (2 mg/L to 20 mg/L). The effect of temperature on the removal efficiency was also studied at temperature varying between 10^{o}C and 50^{o}C. After every adsorption experiment, the solutions were filtered using 0.45 µm pore membrane filters and the filtrate was analyzed for Fluorides using IC and adsorption capacity (AC) and percentage removal calculated using **Equations 5.1 and 5.2** respectively:

$$\boldsymbol{AC = \left[\frac{Ci - Cf}{M}\right] X\, V} \quad \textbf{5.1}$$

$$\%\, \boldsymbol{R = (Ci - Cf)/Ci * 100} \quad \textbf{5.2}$$

where:

AC adsorption capacity (mg.g^{-1})

Ci is the initial concentration (mg/L)

Cf is the final concentration after adsorption (mg/L)

V is the sample volume (L)

% R percentage removal (%)

m is the mass of adsorbent (g)

All the adsorption experiments were done in triplicate and the average values are reported.

5.3 Results and discussion

5.3.1 Effect of pH

Initial concentrations of fluorides were prepared at different pH values (between 2 to 10). This study was conducted at fixed contact time, fluoride concentration and the dose. The adsorption of fluorides into non-impregnated and TiO_2-impregnated MP carbon was investigated and the results are shown in **Figure 5.1**. Using the non-impregnated and TiO_2-impregnated carbon for adsorption of fluorides, the

TiO_2-impregnated MP carbon showed a better adsorption of fluorides than the non-impregnated. This could be as a result of the availability of many adsorption sites engineered to favour the attachment of fluorides in the TiO_2-impregnated MP carbon. This could also be as a result of the difference in the surface orientation and the presence or absence of particular functional groups in the respective adsorbents. This suggests that functional groups play an important role in the adsorption of F^- as does the surface orientation.

At pH 2, fluorides adsorption was highest with percentage removal of 73% and 79% for both non-impregnated and TiO_2-coated MP carbon respectively. Then from pH 3 to 7, there was a decline in the adsorption with a further peaking at pH 8. This could be as a result of different functional groups responsible for the adsorption at the different pH solutions. It should be noted however that throughout the investigated pH range, some fluorides was adsorbed nonetheless.
It was then concluded that optimal fluorides adsorption by non-impregnated and TiO_2-impregnated MP carbon occurs when the sample solution is adjusted to pH 2, hence for further experiments, adsorption of F was fixed at pH 2.

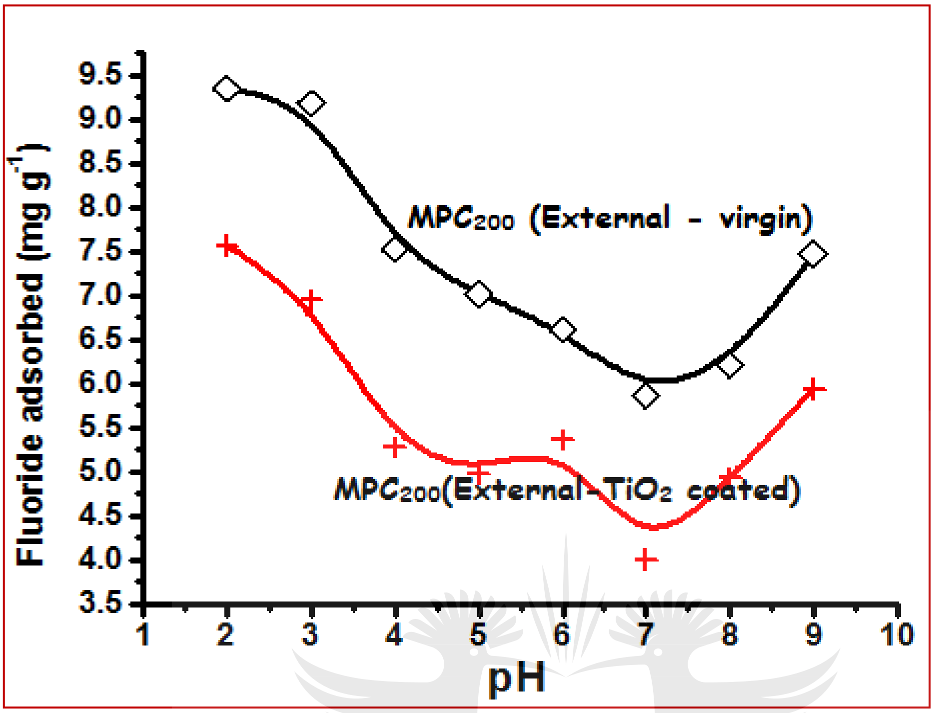

Fig 5.1: Effect of pH on adsorption of fluorides

The Zeta potential of the adsorbent material was also carried out because its measurement brings insight about the surface charge of the carbonized material and results are shown in **Figure 5.2**.

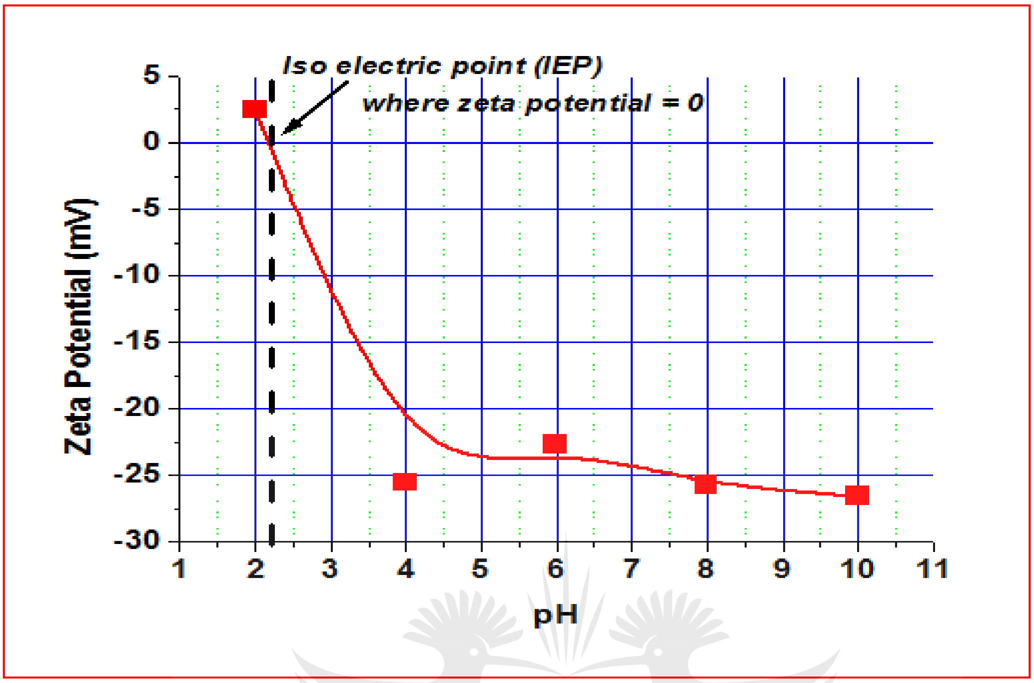

Fig 5.2: Results of pH versus Zeta potential

To consolidate the result obtained from pH versus Zeta potential plot, the iso-electric point (IEP) of the adsorbent material was determined. The surface charge assessed by IEP is defined as the point at which the zeta potential was found to be zero. When pH < pH_{IEP}, the surface charge is positive, and when pH > pH_{IEP}, the surface charge is negative, and when the pH = pH_{IEP}, it indicates neutral surface. In the above study, the IEP of the MPC corresponds to 2.2 and corroborates that the surface charge is positive.

To consolidate the result obtained from pH versus Zeta potential plot, the iso-electric point (IEP) of the adsorbent material was determined using electrophoretic mobility in electrolytic medium of ionic strengths of 0.001 M and 0.01M NaCl solutions as shown in **Figure 5.3.**

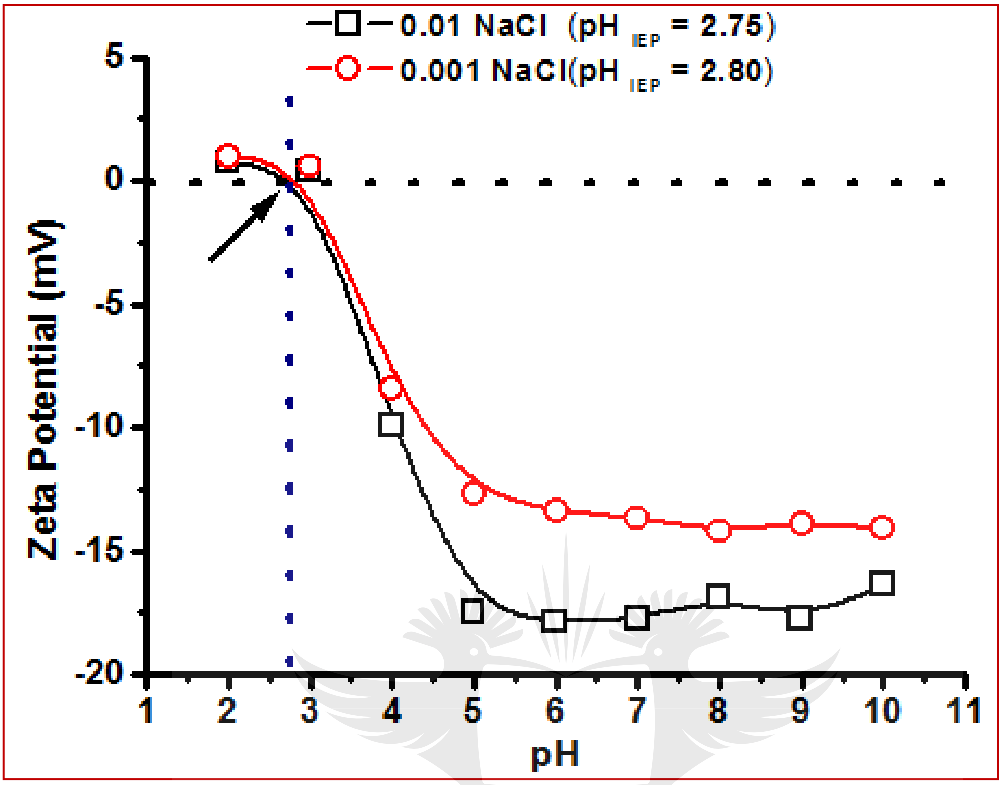

Fig 5.3: Results of pH of 0.01M & 0.001M NaCl versus Zeta potential

The surface charge of the carbon can be assessed by compete with the fluoride ion for the active sites, thus titration or electrophoresis[45] both methods have advantages and drawbacks[46]. Usually the titration method provides the point of zero charge (PZC) and the electrophoresis the IEP[47]. The IEP and the PZC are the same when the background electrolyte does not adsorb on the surface. Nevertheless, both terms provide a qualitative assessment of the carbon surface charge.

To consolidate the result obtained from pH versus Zeta potential plot, the iso-electric point (IEP) of the adsorbent material was determined using electrophoretic mobility in electrolytic medium of ionic strengths of 0.001 M and 0.01 M NaCl solutions. The surface charge assessed by IEP is defined as the point at which the zeta potential was found to be zero[47]. When $pH < pH_{IEP}$, the surface charge is positive, and when $pH > pH_{IEP}$ [46,47] the surface charge is negative, and when the $pH = pH_{IEP}$, it indicates neutral surface[48]. Thus at, $pH < pH_{IEP}$, the anions from the solution will be drawn to the surface of MPC and at $pH > pH_{IEP}$, the cations will be drawn. In the present study (Figure 5.3), the pH_{IEP} of the MPC corresponds to 2.75 is less than the pH value of 2 at which the maximum fluoride removal was achieved. This corroborates that the surface of MPC is positive.

The pH_{IEP} for 0.001 M NaCl and 0.01 NaCl was found to decrease with 2.80 and 2.75 respectively. The pH_{IEP} was probably due to the adsorption of background electrolyte (NaCl) used in the electrophoresis measurements. The anions (Cl^-) adsorbed on the surface of MPC and get neutralized by some of the surface positive charges, causing a decrease in pH_{IEP}.

5.3.2 Effect of contact time

The contact time between the adsorbent and the adsorbate plays a major role in ensuring that maximal adsorption of pollutants is achieved[49–51]. The adsorption of fluorides by the non-impregnated and TiO_2-impregnated MP carbon was investigated over a contact time of 2 min to 180 min and the results are presented in **Figure 5.4 and Figure 5.5**. Defined adsorbent quantity (0.2 g) was taken with the fluoride concentration (2 mg/L) at optimized pH.

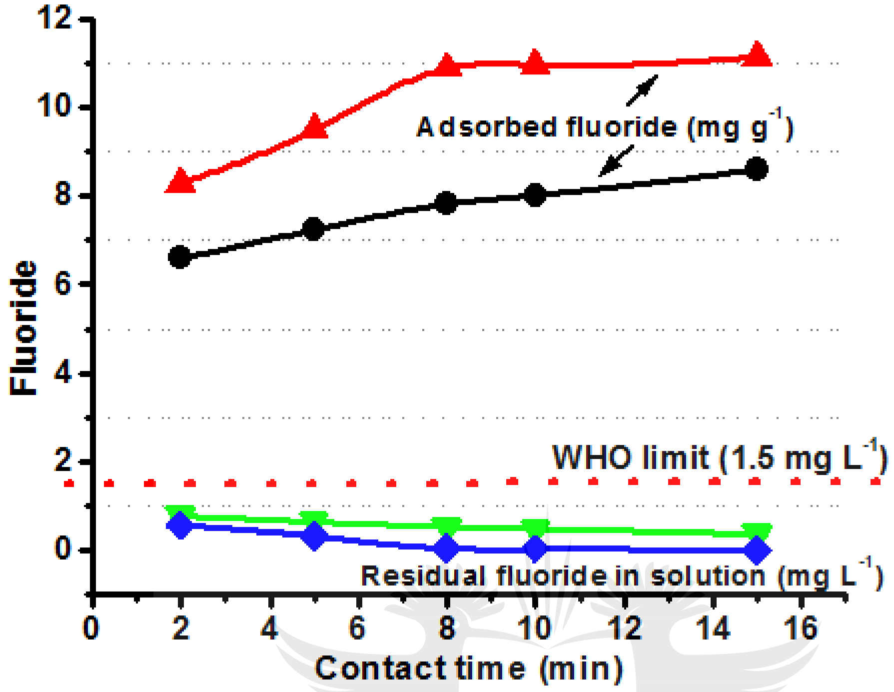

Fig 5.4: Effect of contact time on adsorption of fluorides

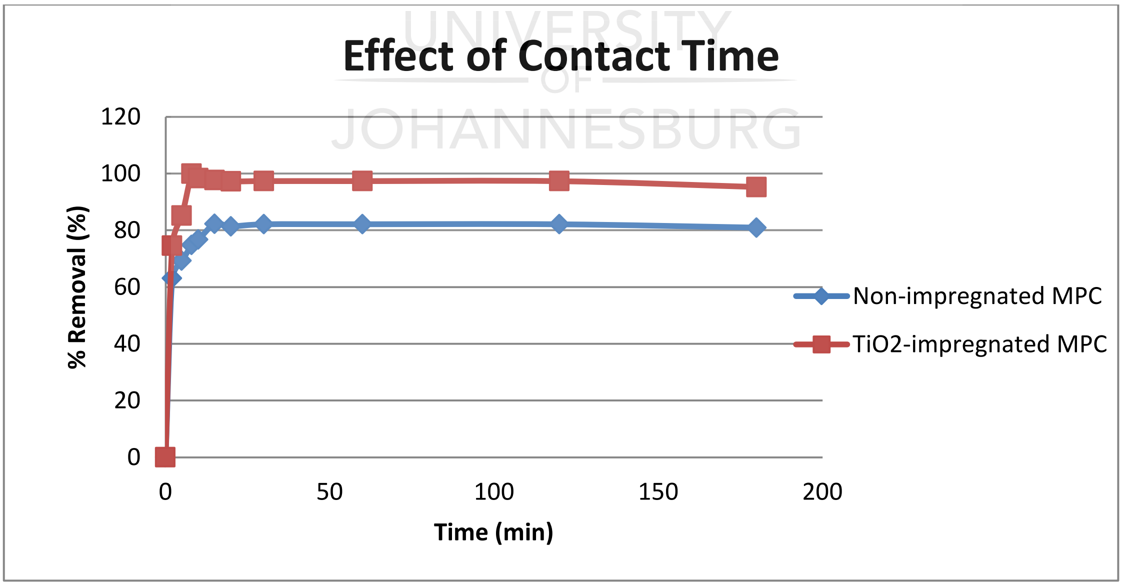

Fig 5.5: Contact time vs percentage removal

Using both non-impregnated and TiO_2-impregnated MP carbon for the adsorption of fluorides, both adsorbents showed a strong dependence on the contact time.
An increase in the adsorption with an increase in contact time finally reached a maximum for TiO_2-coated MP carbon after 8 min (99% removal) and stagnated after 8 min whilst for non-impregnated MP carbon, the maximum adsorption took a little longer to achieve, namely 15 min (82% removal) with not much difference being observed even after 180 min as shown in **Figure 5.5**.

To be noted again is the improvement in the adsorption of both adsorbents in comparison to the results achieved when adsorption was determined with pH as the only variable, i.e. 78% against 99% for TiO_2-impregnated MP carbon. This shows that appropriate optimization of both the pH and contact time is fundamental in the adsorption of fluorides[52–54].

As the maximum adsorption was found to be in 8 min for the TiO_2-impregnated MP carbon and 15 min for the non-impregnated MP carbon therefore, the rest of the adsorption process was carried out in 8 min and 15 min for TiO_2-impregnated and non-impregnated MP carbon respectively.

5.3.3 Effect of adsorbent dose

This is the adsorbent dose at which maximum removal was optimized for all the subsequent studies (adsorbent dose was varied from 0.2 g to 1 g). In this study, contact time, pH was kept constant but dose was the variable and results are shown in **Table 5.1**.

Table 5.1 Results of Effect of Adsorbent dose on adsorption

Adsorbent Dose	**F_{ads} (mg/L)**	**F_{ads}/g (mg/g)**	**$F_{initial}$ (mg/L)**	**K_D**	**log K_D**	**1+log K_D**	**% F removal (%)**
0.2	1.4805	7.4025	2.1632	3.4220	0.534282	**1.534**	74.03
0.4	1.9479	4.8698	2.1632	2.2512	0.35241	**1.352**	97.40
0.6	2.1452	3.5754	2.1632	1.6528	0.218228	**1.218**	99.17
0.8	2.0788	2.5985	2.1632	1.2012	0.079626	**1.080**	96.10
1.0	1.8798	1.8798	2.1632	0.8690	-0.06099	**0.939**	93.99

The fluoride removal by MPC was calculated in the range 74 – 99% on increasing the dose from 0.2 g to 1.0 g. A steep typed increase was observed from 0.2 g to 0.4 g with a difference of about 23 % but after this, no appreciable difference was observed. After achieving the maximum removal of 99.17% at 0.6 g, a decreasing trend was observed as the amount of MPC was increased from 0.6 g to 1.0 g. This may due to the overlapping of active sites at higher dosage as well as the decrease in the effective surface area resulting in the conglomeration of exchanger particles[55].

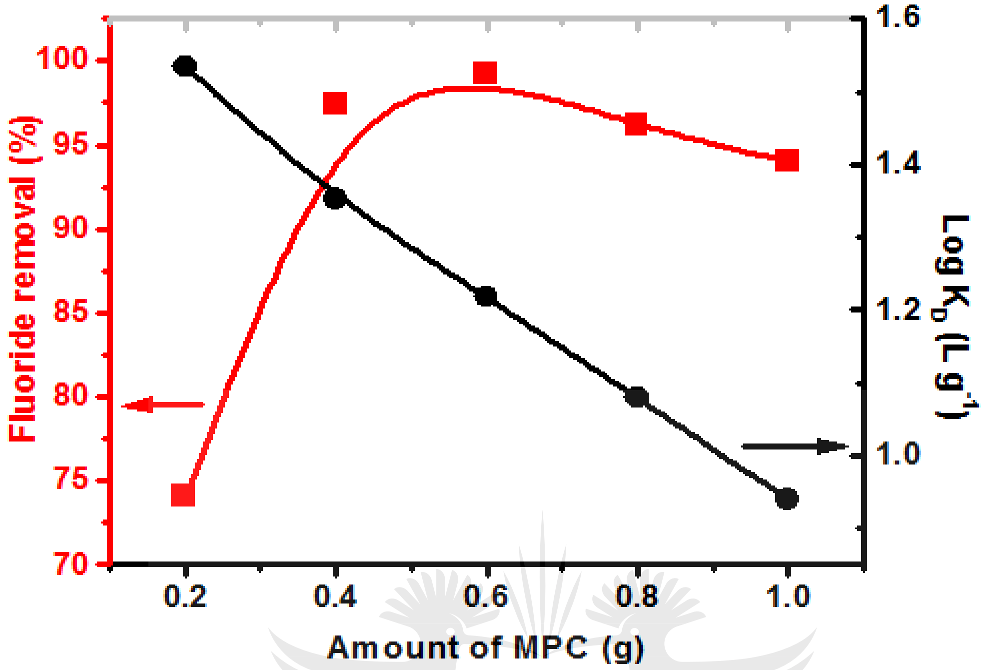

Fig 5.6: Effect of adsorbent dose on adsorption of fluorides

The fluoride uptake increase with respect to the increase in dose of MPC was attributed to the higher availability of surface pore volume of the carbon materials. Although the percentage of fluoride removal was found to increase with respect to the increase in adsorbent dose, the fluoride sorption capacity (mg g^{-1}) for a particular adsorbent approaches the descending trend due to the following facts:

- Better utilization of active sites at lower doses but the sites become superfluous at higher doses for the limited quantity of fluoride.
- The operation of driving forces responsible for fluoride sorption becomes negligible despite the usage of high doses.

A distribution coefficient K_D is one which reflects the binding ability of the surface of an adsorbent and depends on the pH of the solution and the surface of the adsorbent[56]. K_D can be calculated with **Equation 5.3**.

$$\boldsymbol{KD = Cs/Cw\,(L\,kg\ -1)} \text{..........} \mathbf{5.3}$$

where C_s is the concentration of fluoride on the solid particles (mg kg^{-1}) and C_w is the equilibrium concentration in solution (mg L^{-1}). **Figure 5.6** shows that the log K_D value decreases as the dose of MPC increases at the constant pH and it implies the increasing surface heterogeneity of the adsorbent as reported by earlier researchers[57].

5.3.4 Effect of concentration on removal efficiency

Different F^- concentrations were prepared (2 – 20 mg/L) and at each of them, the adsorbate removal efficiency was worked out using a fixed adsorbent dose, at a fixed pH and contact time. The effect on the removal efficiency of fluorides by both TiO_2-coated and non-impregnated MPC was studied and results are shown in **Table 5.2**.

Table 5.2 Results of Effect of initial concentration on adsorption

TiO_2-coated MPC				
Conc (mg/L)	**$F_{Initial}$ (mg/L)**	**F_{Final} (mg/L)**	**$F_{Adsorbed}$ (mg/L)**	**% Removal (%)**
2	2.0506	0.0316	2.0190	98.06
5	4.8735	1.2393	3.6342	74.57
8	7.1746	3.9003	3.2743	45.64
10	8.7458	5.8376	2.9082	33.25
15	12.4017	6.1386	6.2631	50.50
20	15.7875	6.2902	9.4973	60.16
Non-impregnated MPC				
2	2.0506	0.2874	1.7632	85.98
5	4.8735	1.4451	3.4284	70.35
8	7.1746	4.0111	3.1635	44.09
10	8.7458	5.8376	2.8534	32.63
15	12.4017	6.1594	6.2423	50.33
20	15.7875	6.4150	9.3725	59.37

From **Table 5.2** an increase in the adsorption capacity was observed with the increasing initial concentration suggesting that adsorption is taking place rather than precipitation or masking of the adsorbate. These results were then validated with respect to Freundlich and Langmuir plots and results are shown in **Figure 5.7**.

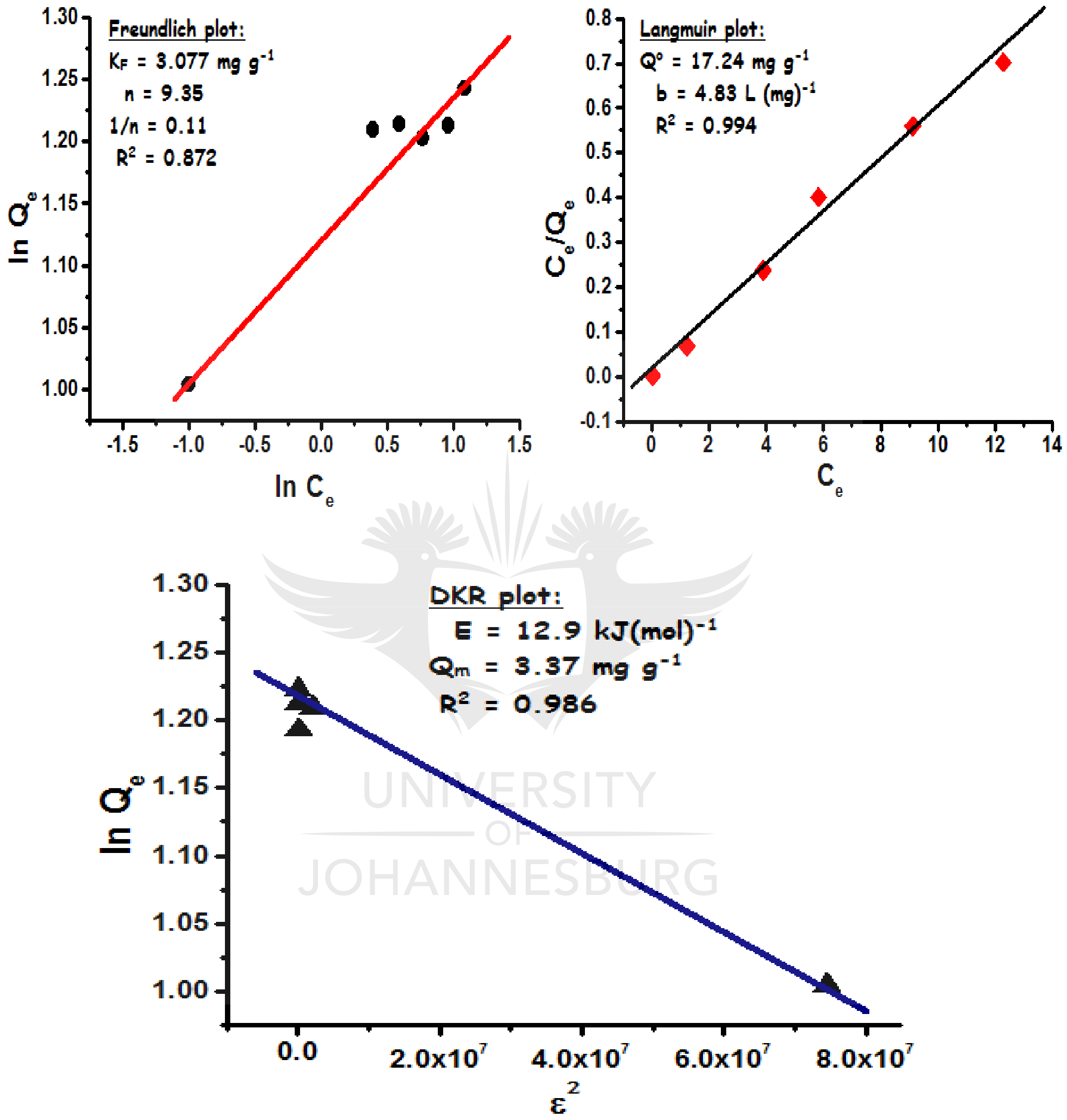

Fig 5.7: Kinetic and isotherm plots for sorption of fluorides

Equilibrium data can be analyzed using well known adsorption isotherms, which provide the basis for the design of adsorption systems. The most widely adopted isotherm equations for modeling of the experimental data are Langmuir and Freundlich equations[58-59]. The former is being purely empirical and the later assumes that maximum sorption occurs when the surface is covered by the adsorbate. The details of equations are gathered in **Table 5.3.**

Table 5.3: Kinetic, isotherm model equations and associated parameters.

Model	**Equation**	**Plotting parameters as**		**Description and units**	**Ref.**	**Equation number**
		X	**Y**			
Kinetic type:						
1.Pseudo – first – order	$\ln (q_e – q) = \ln q_e – k_1(t)$	time (t)	$\ln (q_e-q)$	k_1 → Pseudo – first – order rate constant in min^{-1}	[60]	(5.4)
2.Pseudo – second – order	$dq/dt = k_2 (q_e – q)^2$ $t/q_t = 1/k_2q_e^2 + (1/q_e)t$	time (t)	t/q_t	k_2 → Pseudo – second – order rate constant in g mg^{-1} min^{-1}; h (= kq_e^2) → initial sorption rate in mg g^{-1} min^{-1}	[61]	(5.5) (5.6)
3.Intra – particle diffusion	$q_{t\,=} k_i t^{1/2} + C$	time $^{1/2}$ $(t)^{1/2}$	q_t	k_i →intraparticle rate constant in mg g^{-1} $min^{-0.5}$; C → thickness of the boundary layer in mg g^{-1}	[62]	(5.7)

4.Elovich	$q_t = (1/B) \ln AB + (1/B) \ln t$	time (t)	ln(t)	A → initial adsorption rate in mg $g^{-1}min^{-1}$; B→ constant of desorption in g mg^{-1}	[63]	(5.8)
In the above kinetic models, q_t and q_e are the amount of fluoride adsorbed at time, t and equilibrium respectively in mg g^{-1}						
Isotherm type:						
1.Langmuir	$q_e = Q^o bC_e/1+bC_e$	C_e	q_e	Q^o→Sorption capacity in mg g^{-1}; L→Langmuir isotherm constant in L mg^{-1}	[58]	(5.9)
2.Freundlich	$q_e = K_F Ce^{1/n}$	log C_e	log q_e	C_e→equilibrium concentration of fluoride in solution in mg L^{-1}; K_F→ adsorption capacity in mg g^{-1}; 1/n →adsorption intensity or surface heterogeneity ($0.1 \leq 1/n \geq 1.0$ and $1 \leq n \geq 10$ →favorable for sorption	[59]	(5.10)

3. DKR	$\ln q_{ed} = \ln q_{md} - k\,\varepsilon^2$ $E = -1/\sqrt{-2\beta}$ $\varepsilon = RT \ln (1/C_e)$	ε^2	$\ln q_e$	q_{ed} – amount of fluoride adsorbed per unit weight of adsorbent (mmol g^{-1}) q_{md} – monolayer adsorption capacity (mmol g^{-1}) β – constant related to adsorption energy (mol^2 $(kJ)^{-1}$	[64]	(5.11) (5.12) (5.13)
Thermodynamic parameters:						
1.Free energy of sorption	$\Delta G = -RT \ln K$ $\ln K = -\Delta H/RT + \Delta S/R$	$\ln q_e$	C_e	ΔG→ Free energy change in kJ mol^{-1} ; ΔH→ Enthalpy change in kJ mol^{-1}; ΔS → Entropy change in kJ mol^{-1} K^{-1}; K → Sorption equilibrium constant	[65]	(5.14) (5.15)

The Freundlich model (**Equation 5.10**) is based on the sorption which takes place on a heterogeneous phase. The degree of non – linearity between fluoride in solution and MPC is indicated by the values of ‘n’. When n = 1, then sorption of fluoride is linear. The values of 1/n predicts the nature of sorption to be whether normal (1/n<1) or cooperative (1/n>1) and also reported to represent a joint measure of both the relative magnitude and diversity of energies associated with a particular sorption process[59]. In the present system, a cooperative or S – type or solvent affinity – type isotherm is associated where the marginal sorption energy increases with increasing surface concentration[66]. It can also be interpreted with strong adsorption of solvent, strong inter-molecular attraction within the adsorbed layers, penetration of the solute (fluoride) in the adsorbent (MPC) and mono – functional nature of the fluoride adsorbate.

The fluoride sorption capacity (K_F) of 3.08 mg g^{-1} was determined for the variation of initial fluoride concentration (2 – 20 mg L^{-1}). The value of 1/n was calculated to be 0.11. The present observation is in agreement with early researchers[67,68]. Even though, the agreeable fit (R^2 = 0.986) of experimental data, Freundlich model does not provide a conclusive evidence for the fluoride sorption mechanism, it provides an indirect evidence for site heterogeneity and /or surface heterogeneity. On the basis of energy possessed by each affinity site, the sorption of fluoride takes place in preference primarily to the stronger binding sites followed by other sites in the order of decreasing energy till the sorption of fluoride is complete.

According to Langmuir model (**Equation 5.9**), the amount of fluoride adsorbed onto MPC was 17.24 mg g^{-1} with the corresponding Langmuir isotherm constant of 4.83 L mg^{-1}. The feasibility of Langmuir isotherm can be expressed in terms of a dimensionless constant or equilibrium parameter, R_L which is equal to $[1/(1+bC_0)]$. The data of dimensionless constant was found between 0 and 1 and thus the favorable sorption of fluoride could be inferred.

Dubinin–Radushkevich (D–R) isotherm is more general than Langmuir isotherm owing to its disagreement for a homogenous surface or a constant adsorption potential. Using D-R equations (**Equation 5.11–5.13**) with reference to the present system, the constant β gives the free energy, E (kJ mol^{-1}) for the transfer of 1 mol of fluoride from infinity to the surface of MPC and can be computed using the relationship. The magnitude of E is helpful in understanding the nature of fluoride sorption. The recorded value of E was 12.9 kJ mol^{-1} with the Qm of 3.37 mg g^{-1}(**Figure 5.7**). It is very apparent that E > 8 kJ mol^{-1} ascertained the present fluoride sorption onto MPC demonstrated the bonding between fluoride and MPC under the governance of chemical forces[69].

5.3.5 Effect of temperature

Temperature plays an important role in the mobility of molecules and ions in solution[70]. This can, however, be extended to the adsorption of ions since ions need to be mobile to ‘collide/interact’ with the adsorbent to facilitate adsorption, especially for batch adsorption experiments[71,72].

To study the effect of temperature, adsorption studies were conducted at temperatures varying between 10°C and 50°C at constant pH, contact time, adsorbent dose and adsorbate concentration and the adsorption of fluorides by both TiO_2-coated and non-impregnated MPC was monitored; the results are presented in **Table 5.4**.

Table 5.4 Results of effect of temperature on adsorption

TiO_2-coated MPC				
Temp (^{0}C)	**$F_{Initial}$ (mg/L)**	**F_{Final} (mg/L)**	**$F_{Adsorbed}$ (mg/L)**	**% Removal (%)**
10 ^{0}C	2.0466	0.9445	1.1021	53.85
20 ^{0}C	2.0466	0.6215	1.4251	69.63
30 ^{0}C	2.0466	0.3678	1.6788	82.03
40 ^{0}C	2.0466	0.0374	2.0092	98.17
50 ^{0}C	2.0466	0.5832	1.4634	71.50
Non-impregnated MPC				
10 ^{0}C	2.0466	0.9788	1.0678	52.17
20 ^{0}C	2.0466	0.8231	1.2235	59.78
30 ^{0}C	2.0466	0.4612	1.5854	77.46
40 ^{0}C	2.0466	0.2094	1.8372	89.76
50 ^{0}C	2.0466	0.6934	1.3532	66.12

Maximum percentage removal is observed at 40°C, a percentage removal of 98% for fluorides was achieved. Beyond 40°C a decrease was observed, probably due to the expansion of active sites thus hindering the specialized adsorption and also the formation of unstable interactions between the adsorbent and the adsorbate. Results were also validated with respect to kinetic and isotherm plots.

5.3.6 Effect of other anions (competitive species)

The effect of competitive species on the removal efficiency of fluorides was also explored at the rest of the parameters at optimum and results are shown in **Table 5.5**.

On adsorption with TiO_2-coated MP carbon, percentage removal of 79%, 53%, 74%, and 100% were achieved for fluorides, chlorides, sulphates, and nitrates, respectively. It is noted that there is a slight decrease in the percentage removal of fluorides when they are accompanied by other anions and thus it is concluded that these anions compete with the fluorides. This might have been caused by the fact that, when less ions are adsorbed, there is more space for interfering ions to adsorb onto the surface of the adsorbent not necessarily adsorbing on the engineered cavities but also on the surface of the carbon matrix.

Table 5.5 Results of effect of other anions on adsorption

TiO_2-coated MPC				
Anion	**$F_{Initial\ (mg/L)}$**	**$F_{Final\ (mg/L)}$**	**$F_{Adsorbed\ (mg/L)}$**	**% Removal (%)**
fluorides	2.0672	0.4250	1.6422	79.44%
Chlorides	2.0270	0.9545	1.0725	52.91%
Sulphates	1.9929	0.5187	1.4742	73.97%
Nitrates	1.9955	No peak	1.9955	100%
Non-impregnated MPC				
fluorides	2.0672	0.4848	1.5824	76.54
Chlorides	2.0270	0.9949	1.0321	50.92
Sulphates	1.9929	0.6307	1.3622	68.26
Nitrates	1.9955	0.2697	1.7258	86.38

5.3.7 Analysis of real water samples

After successful optimization of the pH, contact time, adsorbent dose and concentration on the adsorption, the non-impregnated and TiO_2-impregnated carbon were then selected to evaluate the adsorption in real water samples and results are shown in **Table 5.6**.

Table 5.6 Results of the analysis of real water samples

Well 2				
Anion	**$F_{Initial\ (mg/L)}$**	**$F_{Final\ (mg/L)}$**	**$F_{Adsorbed\ (mg/L)}$**	**% Removal (%)**
Fluorides	2.7374	0.1299	2.6075	95.25%
Chlorides	7.5778	0.8144	6.7634	89.25%
Sulphates	0.0384	0.0041	0.0343	89.32%
Nitrates	8.2637	3.7394	4.5243	54.75%
Raw water-Treatment Plant MP				
Anion	**$F_{Initial\ (mg/L)}$**	**$F_{Final\ (mg/L)}$**	**$F_{Adsorbed\ (mg/L)}$**	**% Removal (%)**
fluorides	1.0386	0.1284	0.9102	87.64%
Chlorides	28.0602	11.8879	16.1723	57.63%
Sulphates	17.0501	3.4494	13.6007	79.77%
Nitrates	0.9725	0.3271	0.6454	66.37%
Treated Water-Treatment Plant MP				
Anion	**$F_{Initial\ (mg/L)}$**	**$F_{Final\ (mg/L)}$**	**$F_{Adsorbed\ (mg/L)}$**	**% Removal (%)**
fluorides	0.9905	0.0162	0.9743	98.36%
Chlorides	8.3042	0.9428	7.3614	88.65%
Sulphates	7.7772	3.4556	4.3216	55.57%
Nitrates	7.3970	1.4835	5.9135	79.94%

These samples were found to have fluorides, chlorides, nitrates, and sulphates with concentrations of fluorides being above 2 mg/L in some samples, which is above the permissible maximum contaminant in drinking water. The adsorption by TiO_2-coated MP carbon brought the levels of fluorides to the admissible levels of less than 1.5 mg/L. On adsorption with TiO_2-coated MP carbon, percentage removals of 98%, 89%, 89% and 79% were achieved for fluorides, chlorides, sulphates, and nitrates, respectively, with the highest percent removals of more than 95% for fluorides.

5.4 Data validation

Statistical evaluations were carried out to validate data that have been generated from sampling up to detection methods. These include adsorption capacities, adsorption efficiencies and percentage removal of contaminants (95%). Other statistical tests that were carried out include standard deviations (< 5%), patterns and correlations (0.9995), linear regression of calibration curves, detection limits of instruments, linear response range, precision of standards and samples, recovery and blank values.

5.5 Conclusion

Natural organic materials of low cost have been used as alternative adsorbents for the removal of anions from aqueous solutions. MP carbon materials were successfully synthesised for remediation of fluorides from water samples. They were characterised using SEM for the surface morphology and FTIR for presence and/or absence of functional groups. Thermogravimetric analysis showed the difference in the thermal stabilities between the MP carbon and all thermal functions taking place with temperatures varying between 30°C and 900°C. On batch adsorption, TiO_2-impregnated MP carbon adsorbed fluorides maximally at pH 2 and both MP carbon materials showed a performance dependent on the contact time and sample temperature.

Both the functional group and the surface orientation could be connected to the performance of the adsorbents in the removal of fluorides. Better performance of non-impregnated and TiO_2-impregnated MP carbon was achieved at a contact time of 8 min and a sample pH of 2 with TiO_2-impregnated having the maximum percentage removal and being able to reduce the amount of fluorides to the acceptable levels. Optimizing all these parameters gave percentage removals of around 95% for fluorides. The non-impregnated MP carbon also reduce more efficiently of the F- species and although these MP fibers present low surface area and porosity in relation to the TiO_2-impregnated MP carbon, these MP fibers show promise as a material for the removal of anionic F^- species from aqueous solution.

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CHAPTER 6

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 General conclusions

This study was successfully carried out based on the aims and objectives of the study. Conclusions were thus drawn. Fluorides were found to be present in underground sources and in some treatment plants that were sampled. Although the levels of fluorides were within acceptable levels in most sampling sites, some amounts were above the permissible maximum contaminant levels (MCL) in some sampling sites. *Musa paradisiaca* (MP) carbon were successfully synthesized and were successfully characterized using different physical and instrumental characterization techniques.

Virgin/non-impregnated MP carbons and TiO_2-coated MP carbon have different functional groups and surface morphologies which are linked to their different adsorption capabilities and patterns for fluorides removal. Impregnation of TiO_2 on the MP carbon improved the surface area and hence improved the adsorption capacities of these materials, the TiO_2-coated MP carbon showed better adsorption performance than the non-impregnated MP carbon. These MP carbon materials were able to remove fluorides in real water samples, such that the amounts measured in the samples after the adsorption were in compliance with the WHO standards.

6.2 Recommendations for future work

Although this work may be considered as successful, it still leaves some scope of work for further investigation. Some of the recommendations for future research include possible removal of other contaminants using MP carbon materials, all carbonaceous materials can be used to explore their potential on heavy metal removal from drinking water and industrial effluents.

Others studies that could be done include toxicity studies of the TiO_2 used as well as the monitoring of the possible leaching of the TiO_2 into water and the stability of the material. Other nanoparticles can also be incorporated in the MP carbon materials other than TiO_2, nanoparticles such as manganese dioxide (MnO_2).

Reusability of the exhausted carbonaceous adsorbents can be envisaged for the application of fabricating electrode materials and as solid fuel as well.