ACTIVATED CARBON FROM MAIZE TASSEL AND POLYMER COMPOSITES FOR WATER DECONTAMINATION

by

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DEDICATION

The work presented in this thesis is dedicated to Him the father of light, ‘who deliver my soul from going down into the pit and make my life to see the light, who made His candle to shine upon my head by His light I walked through darkness, be enlightened with light of the living, the fountain of life in thy light shall I see light’.

Thank you for the Light you have given me.

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PUBLICATIONS AND CONFERENCES

PUBLICATIONS

A number of papers have emanated from the work presented in this thesis; some have been presented at conferences and some have been published in peer-reviewed journals or submitted for publication. These papers are listed below and will be referred to in the text. Conference presentation titles are also included in this section.

PAPER I (Chapter 4)

Olorundare, O.F., Krause, R.W.M., Okonkwo J.O. and Mamba, B.B. Potential application of activated carbon from maize tassel for the removal of heavy metals in water. *Journal of Physics and Chemistry of the Earth* 50-52 (**2012)**: 104-110.

PAPER II (Chapter 5)

Olorundare, O.F., Msagati, T.A.M., Krause, R.W.M., Okonkwo, J.O. and Mamba, B.B. Steam activation, characterization and adsorption studies of activated carbon from maize tassels. *Chemistry and Ecology Journal* (**2014**). **In press**.

PAPER III (Chapter 6)

Olorundare, O.F., Msagati, T.A.M., Krause, R.W.M. Okonkwo, J.O. and Mamba, B.B. Activated carbon from lignocellulosic waste residues: Effect of activating agent on porosity characteristics and use as adsorbents for organic species. *Water, Air and Soil Pollution Journal* (**2014**). **In press**

PAPER IV (Chapter 7)

<u>Olorundare</u>, O.F., Msagati, T.A.M. Krause, R.W.M. Okonkwo, J.O. and Mamba, B.B. Preparation and use of maize tassels' activated carbon for the adsorption of phenolic compounds in environmental wastewater sample. **This paper has been submitted for possible publication to** *Applied Surface science Journal* (**2014)**

PAPER V (Chapter 8)

<u>Olorundare</u>, O.F., Msagati, T.A.M., Krause, R.W.M., Okonkwo, J.O. and Mamba, B.B. Polyurethane composite adsorbent using solid phase extraction method for preconcentration of metal ion from aqueous solution. **This paper has been accepted for publication in** *International Journal of Environmental Science and Technology* (**2014**).

PAPER VI (Chapter 9)

<u>Olorundare</u>, O.F., Msagati, T.A.M., Krause, R.W.M., Okonkwo, J.O. and Mamba, B.B. Preparation of polyurethane composite adsorbent and its enrichment of polychlorinated biphenyl from environmental sample.

This paper has been submitted for possible publication to *Journal of Physics and Chemistry of the Earth* (**2014**).

Research paper presentations at international and/or local conferences

1. **<u>Olorundare,</u> O.F**., Krause, R.W.M., Okonkwo J.O. and Mamba, B.B. Potential application of activated carbon from maize tassel for the removal of heavy metals in water. **Poster presentation** at the 12th WaterNet/WARFSA/GWP-SA International Symposium. 26-28 October **2011**, Maputo, Mozambique.

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3. **Olorundare, O.F**., Msagati, T.A.M., Krause, R.W.M., Okonkwo, J.O. and Mamba, B.B. Preparation of Polyurethane Composite Adsorbent and its Enrichment of Polychlorinated Biphenyl from Environmental Sample. Oral presentation at the 14th WaterNet/WARFSA/GWP-SA International Symposium. 30 October – 1November **2013**, Dar es Salaam, Tanzania.

ABSTRACT

This study presents work on the preparation, characterisation and application of agricultural waste residue, maize tassel in the production of activated carbon (AC) using both physical and chemical methods of activation in their production. The activated carbon produced from maize tassel (MTAC) or steam-produced activated carbon (STAC) were later added as a filler – together with beta-cyclodextrin (β-CD), and raw tassel (RT) – in the production of polyurethane composite adsorbent (PUCAD) material for the removal of selected inorganic (such as Cd^{2+}, Cr^{3+}, Pb^{2+}) and organic pollutants (phenolic compound - bisphenol A (BPA), ortho-nitrophenol (O-NTP), para-chlorophenol (PCP), polychlorinated biphenyl (PCB), and methylene blue (MB) as adsorbate/analytes from aqueous medium. Both batch and solid-phase extraction adsorption methods (SPE), were used for separation and preconcentration. The investigations included reactivity using Fourier transform infrared (FT-IR) spectroscopy, surface morphology analysis using scanning electron microscopy (SEM), thermal stability using thermogravimetric analysis (TGA), heat flow using differential scanning calorimetry (DSC), and crystallinity using X-ray diffraction (XRD) coupled with energy dispersive X-ray spectrometry (EDX).

The FT-IR analysis revealed that there was interaction between the polymeric material and all the fillers. The hydrogen bonding and N-H group interaction between all the materials and the polyurethane polymer composite (PCAD) showed compatibility between the polymeric materials and the fillers.

The polyurethane polymer composite was produced by cross-linking a glycol- prepolymer and polyol with diisocyanate linker, together with other additives such as AC, β-CD, ACCDRT and RT as fillers. Two types of diisocyanate were used as linkers, namely hexamethylene diisocyanate (HMDI) and methylene diphenyl diisocyanate (MDI).

The adsorption properties of the polymer synthesised using different ratios of HMDI and MDI were compared. The diisocyanate together with AC, β-CD, ACCDRT and RT were used to separate and preconcentrate a mixtures of three PCB compounds (PCB 105, PCB 126 and PCB 153) from environmental samples. The polymeric composite materials (HMDIACCD and MDIACCD) have the highest recovery rate of over 90% and 80% for HMDI and MDI produced polymeric composites. The limit of detection (LOD) and limit of quantitation (LOQ) ranged from 0.0048-0.013 μg/L and 0.015-0.04 μg/L, respectively.

The adsorbent AC and polymeric composite material PUCAD were evaluated for their surface areas using Brunauer–Emmett–Teller (BET) surface area, pore structure characteristics and adsorption performance by both batch adsorption processes for inorganic Pb^{2+} and dye solution MB and extraction/preconcentration methods using the SPE method for phenolic compounds and PCB.

The surface functional groups produced by AC modified by physical and chemical activation processes were investigated by FT-IR and revealed carboxylic acid, lactone, phenolic groups, quinine and nitro groups, while the PCAD showed N-H groups and H bonding. A chemical method, the Boehm method, was further used for identifying the surface-bound acidic and basic functional groups of the AC.

The morphology results using SEM showed images that reveal good porosity and inner pore structure for AC produced from agricultural waste and polymeric material.

The polymeric material PCAD applied in separation/extraction and pre-concentration of metal ions prior to its determination by ICP-OES showed that pH 7 is the optimal pH for maximum recovery of all the metal ions, ranging from 70% to 85%. The LOD and LOQ results for the metal ions ranged from 0.249-0.256 μg/L and 0.831-0.855 μg/L, respectively.

The application of AC as adsorbent from maize tassel for the separation and pre-concentration of phenolic compounds using GC×GC TOFMS chromatography showed 90%, 92%, and 95%, respectively, for the recovery of BPA, O-NTP and PCP.

Preparing activated carbon with different/varying impregnation ratios (IRs) showed that IR plays an important role in surface area determination; a high surface area of about 1 263 m^2/g and a pore volume of 1.592 cm^3/g were achieved with chemically produced activated carbon (CCA). Activated carbon produced from steam (STAC) revealed good adsorption capacity of about 200 mg/g and $r^2 = 0.97$ for MB adsorption.

The findings in this study generally revealed that good adsorbents in the form of activated carbon can be produced from agricultural waste and also that their application as a filler in composite material production is good. The results suggest that a combination of PCAD with various fillers can produce a viable mixed-matrix adsorbent composite for water treatment without compromising its integrity in the area of leaching.

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LIST OF ACRONYMS AND ABBREVIATIONS

1/n	Adsorption intensity
α-CD	Alpha cyclodextrin
β-CD	Beta cyclodextrin
S_{BET}	Brunauer–Emmett–Teller surface area
^{o}C	Degree Celsius
ΔH_{ads}	Heat of adsorption
γ-CD	Gamma cyclodextrin
µm	Micrometre
mg/L	milligram per litre
%	Percentage
% R	Percentage removal
% T	Percentage transmittance
AA	Activated alumina
AC	Activated carbon
ACF	Activated carbon fibre
ATR	Attenuated total reflection
AWR	agricultural waste residue
BET	Brunauer–Emmett–Teller
b_T	Temkin equation parameter
CD	cyclodextrin
C_e	equilibrium concentration
CE	capillary electrophoresis
CEPB	Chinese Environmental Protection Board

CI	Chemical Inertness
C_o	initial concentration
DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
ECD	Electron Capture Detector
ECOSOC	Economic and Social Council
EGDE	Ethylene glycol diglycidyl ether
EPA	Environmental Protection Agency
EPI	Epichlorohydrin
eq.	equation
FID	Flame Ionisation Detector
FT-IR	Fourier transform infrared
GC	Gas Chromatography
GLA	glutaraldehyde
h	hour
HMDI	Hexamethylene diisocyanate
HMDIAC	Hexamethylene diisocyanate - activated carbon
HMDIACCD	Hexamethylene diisocyanate - activated carbon - beta(β) cyclodextrin
HMDICD	Hexamethylene diisocyanate - beta(β) cyclodextrin
HMDIRT	Hexamethylene diisocyanate-raw tassel
HPLC	High Performance Liquid Chromatography
ICP OES	Inductively Couple Plasma – Optical Emission Spectroscopy
IN	Iodine Number
IR_r	impregnation ratio

IS	ionic strength
ISA	internal surface area
IUPAC	International Union of Pure and Applied chemistry
IWRM	Integrated Water Resource Management
KBr	Potassium Bromide
K_F	Freundlich constant
K_L	Langmuir constant
K_1	equilibrium rate constant
K_T	Temkin constant
kV	Kilovolt
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantification
M	mass
MB	Methylene Blue
MDI	Methylene diisocyanate
MDIAC	Methylene diisocyanate - activated carbon
MDIACCD	Methylene diisocyanate - activated carbon - beta(β) cyclodextrin
MDICD	Methylene diisocyanate - beta(β) cyclodextrin
MDIRT	Methylene diisocyanate raw tassel
min	minute
MIP AES	Microwave Induced Plasma - atomic emission spectroscopy
MS	Mass Spectroscopy
MT	Maize Tassel

MTAC	Maize Tassel Activated Carbon
NCO	Polyurethane bond
PACF	Polyacrylonitrile activated carbon fibre
PCA	Polyurethane composites
PCAD	Polyurethane adsorbents composite
PK_a	Acid dissociation constant
PS	Pore structure
PT	Purge and Trap
PTFE	polytetrafluoroethylene
PU	Polyurethane
PV	Pore Volume
q_m	adsorption capacity
Q_m	equilibrium adsorption capacity
q_t	equilibrium adsorption at time t
r^2	correlation coefficient
R	percentage removal
R_L	dimensionless separation factor
s	second
SEM	Scanning Electron Microscopy
SPE	Solid-Phase Extraction
SPME	Solid-Phase Microextraction Extraction
SSA	Specific Surface Area
STAC	Steam-produced activated carbon
SuSA	Sub-Saharan Africa
temp	temperature

TPV	Total Pore Volume
TOFMS	Time-of-Flight Mass Spectrometry
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet visible
V	Volume
V_{Meso}	mesopore volume
V_{Micro}	micropore volume
V_{Total}	total pore volume
W	Weight
XRD	X-ray diffraction

CHAPTER ONE

INTRODUCTION

BACKGROUND

Environmental pollution caused by both organic and inorganic pollutants worldwide is a problem of major concern, mostly due to anthropogenic impacts. Industry, mining, uncontrolled landfill practices and transportation are considered the main sources of release of these pollutants into the environment [1]. When released, these contaminants are either retained or they migrate into the environmental strata (air, soil and water). The ability of soil to retain or transport these contaminants influences groundwater and surface-water contamination processes. Although, soil tends to retain a large portion of contaminants once released, some contaminants are equally released into the atmosphere and water bodies. The release of contaminants into water bodies may therefore constitute a major factor in terms of the drastic decline in clean water supply [1, 2]. The global water consumption is increasing by the day at a rate that doubles the global population growth [1, 2]. Climate change, population growth (urbanisation) and pollution are major increasing environmental indicators which are likely to combine and produce a severe decline in water quality and supply in the near future, thus leading to the scarcity of clean and safe water. It can be a very demanding and challenging task to turn raw water from various sources into potable water, i.e. water that is clean, clear, odourless, or tasteless. These challenges have prompted scientists to seek for novel techniques for water treatment, because some of the pollutants occur in very low concentrations and tend to bioaccumulate.

While some existing water-purification processes have some affinity for organic pollutants (e.g. pesticides, natural organic matter (NOM), phenolic compounds, persistent organic pollutant (POPs) and other), they fail to remove these contaminants to acceptable levels, i.e. the removal of these pollutants to microgram per litre (µg/L) and nanogram per litre (ng/L) [3]. This may be attributed to the fact that some organic pollutants, for example NOM, reduce the effectiveness of water treatment by interfering with flocculation processes, fouling membranes and adsorbents, and interfering with oxidation and precipitation of dissolved iron and manganese [3, 4]. Apart from the problems associated with NOM, the continued use of some POPs, especially the use of polychlorinated biphenyls (PCBs) in developing countries, phenolic compounds, and brominated flame retardants (BFRs), particularly the lower brominated diphenyl ethers and polybrominated biphenyls, have been of major concern because of their ecotoxicity. These have been found to be persistent, bioaccumulative, biomagnifying and highly toxic to living organisms, including humans [5, 6].

An understanding of the behaviour of these emerging organic contaminants in various environmental matrices, particularly water and soil is extremely essential, as their matrices could play an important role in the environment. Therefore, it is of crucial importance to study in detail the mutual influence of persistent organic pollutants, phenolic compounds, flame retardants, especially polybrominated diphenyl ether (PBDEs) in soil-retention processes as well as to establish their potential to leach into groundwater and their removal from contaminated water using effective adsorbent materials.

Activated carbon (AC) has undoubtedly remained the most popular and widely used adsorbent in wastewater treatment and water purification, but its high cost, non-selectivity and hydrophobicity has placed limitations on its application. Zeolite which could serve as a better alternative also has limitations in terms of flow properties, varying temperatures and electrolytes [7-9]. Polysaccharides which could also have been considered a better option, have drawbacks such as a low surface area, being pH dependent, as well as hydrothermal limitations and column fouling [10]. Furthermore, biosorbent materials such as agro wastes, which would have been a good alternative have leaching problems as organic matter is leached out from the biosorbent material during biosorption processes and this leads to a change in taste and colour of the final treated drinking water, thus causing secondary pollution of the treated water [11]. Metal ions embedded in the biosorbent can also be leached out into water when a raw precursor (biosorbent material) is used, causing adverse effects on the biosorption process [12]. These drawbacks have limited the effective application of biosorbents for water treatment, particularly drinking water. Therefore, it becomes imperative to incorporate material that will overcome these drawbacks.

In recent years, attention has been focused on various adsorbents, composite materials from both natural and synthesised processes that have both organic and inorganic binding capabilities and are capable of removing unwanted pollutants from contaminated water. .

1.1 PROBLEM STATEMENT

Water contamination due to industrial and human activities has led to the evaluation of the efficiency of existing water-treatment processes, such as ozonation, electro-coagulation, reverse osmosis, membrane filtration, ozonation/biofiltration and adsorption. All these processes have limitations which render them ineffective in water treatment [13]. Previous interventions with adsorption techniques using various composite materials revealed their capability to remove organic pollutants from water to $\mu g / L$ levels [11-13].

There have been a number of unit processes employed in water and wastewater treatment for the treatment of both inorganic and organic compounds, which include bacterial and chemical techniques, extraction, steam distillation, ion-exchange [13], electrochemical oxidation [14], reverse osmosis [15], photocatalytic degradation [16], physicochemical and biological treatment, including membrane filtration [17].

However, numerous drawbacks are associated with some of these aforementioned techniques or processes, which include high cost of operation, unsatisfactory treatment of effluent quality (treated effluent), large usage of chemicals for oxidation processes, thus causing secondary pollution, as well as disposal issues due to difficulty in regeneration of materials employed in the unit operation. Furthermore, processes such as biodegradation that involve the use of microorganisms such as algae, bacteria, fungi and yeast, bioaccumulate and degrade different types of pollutants or contaminants. These processes also have a drawback of restricted application because of technical constraints, for example, the process requires large tracts of land for its optimal application. The process is also constrained by sensitivity toward diurnal variation, which includes flexibility in design and operation and toxicity of some chemicals [17]. Other processes such as chemical methods, i.e. flocculation precipitation, coagulation, electrokinetic coagulation and conventional oxidation by oxidising agents are often expensive and secondary pollution may also arise from their application or usage [17, 18]. Physical methods like membrane filtration are often associated with periodic cost of replacement and membrane fouling [17, 18]. However, the adsorption process through the application of a single adsorbent (AC) has remained the most popular and widely used adsorbent which appears to be superior to other techniques for the removal or concentration of both inorganic and organic compounds at low levels. This is mainly due to their flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants, and initial cost; its use also does not result in the formation of harmful substances. However, AC also presents some drawbacks which include regeneration issues after saturation of the activated carbon (producing spent carbon), high thermal cost which results in over 10% to 15% of AC being lost, just because AC is regenerated using an *ex situ* high-temperature process. There are also high initial costs associated with AC, as well as non-selectivity and hydrophobicity issues which impose limitations on its usage in an adsorption process [17, 18]. Due to these high costs and other highlighted issues AC applications have been limited to the point of discharge in water and wastewater treatments

Other adsorbents such as zeolite and polysaccharide have certain drawbacks between them which include flow property limitations under varying conditions of temperature and electrolytes, low surface area, hydrothermal limitations and column fouling as limitation [7-10]. Therefore, it becomes imperative to incorporate material that will produce a good blend in order to overcome these drawbacks. On the other hand, water-insoluble polysaccharide (cyclodextrin polymers composite), their functionalised derivatives and a host of composite materials/nanocomposites have been reported for their superior ability to remove organic contaminants from water [19-38].

In our laboratories, cyclodextrin (CDs) polyurethanes have been co-polymerised with carbon nanotubes (CNTs) to improve their adsorption efficiency and structural integrity. However, these materials have never been integrated with different forms of adsorbents using pre-monomer material to polymerise polyurethane. Polyurethane composites, carbon nanotubes and synthetic zeolite have been synthesised, characterised and used in water treatment, except for polyurethane composites which have only been used in air pollution clean-up but not extensively used in incorporating different materials as composites. Incorporating narrow carbon nanotubes in nanostructure adsorbents can in principle achieve organic pollutant removal from water far exceeding current existing technologies [39]. The high strength imparted by a small amount of nanotubes added to composites holds promise for these materials. Whilst many studies have been carried out on the usage of nanoparticles of other materials including polymers in the removal of organic pollutants from contaminated water, there have been little or no studies on using nanosized composite materials derived from agricultural waste residue (AWR), natural zeolite, synthesised zeolite, and polysaccharides (cyclodextrin). In addition, the use of pre-monomer polyol and isocyanate group as linker to form the hard segment part in the urethane group has not been reported in water treatment. As far as we know, there has been no attempt to ascertain the possibility of synthesising a multifunctional adsorbent composite from the polymerised AC/CDs/AWRs or CDs/ACs/natural zeolite and synthesised zeolite/AC/CD, CD/AC/HMDI.

Activated carbon (AC) is known for its adsorption properties, mechanical strength, large surface area and thermal stability. A composite of polyurethane and activated carbon/other adsorbents is an excellent catalyst or catalyst support. It can be used in the selective chemisorption and preconcentration of unwanted chemical species or ions from drinking water. The polyurethane through its cell formation enhances the specific surface area and the adsorption ability of the composite. Bioadsorbents such as maize tassel have shown promise in application in water treatment as it has been used in the adsorption of metals and organic compounds from aqueous media [40]. A composite of cyclodextrin, activated carbon, maize tassel and other adsorbents should provide a composite adsorbent for the removal of pollutants from water.

In the light of the above-mentioned advantages of zeolite and activated carbon which have a wide range of applications, they have recently been used extensively for the prevention of environmental pollution [39, 40]. Due to the unique properties of these two adsorbents, such as hydrophilic properties, high adsorption capacity, great selectivity, remarkable surface area, enhanced accumulation of organic substances and non-polar compounds from gaseous and liquid phase, a blend of these adsorbents will provide enhanced separation properties in separation and purification technology.

1.2 RESEARCH AIM OF THE STUDY

Thus, the aim of this research project is to synthesise novel multi-purpose nanostructure composite adsorbents with increased affinity, capacity, selectivity for organic and preconcentration ability (especially for POP, phenolic compounds, NOM, BFR and inorganic compounds) and other contaminants, using low-cost, naturally occurring and available material, be it conventional material (agricultural waste residue (AWR)) or non-conventional material (industrial waste (IW) or natural zeolites (NZ)) and polysaccharides.

1.3 OBJECTIVES

The research objectives/aims are outlined as follows:

- Synthesis of a novel multipurpose nanostructure composite adsorbents using low-cost, naturally occurring and available material, such as conventional material -agricultural waste residue (AWR) or non-conventional material -industrial waste (IW) and polysaccharides .
- Production of activated carbon (AC) through carbonisation of agricultural waste residue (AWR), i.e maize tassel (MT) by chemical vapour deposition (CVD).
- Preparation of cyclodextrin (CD) based polymers (cyclodextrin polyurethane) through the polymerisation of cyclodextrins and diisocyanate linkers/suitable linkers.
- Surface characterisation of the composite adsorbent materials using Fourier transform infrared (FT-IR), scanning electron microscopy - energy dispersive x-ray micro analysis (SEM-EDX), Transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), differential scanning calorimetry (DSC)/differential thermal analysis (DTA), Thermogravimetric analysis(TGA), Nuclear magnetic resonance spectroscopy (NMR), x ray diffraction analysis (XRD)

- Chemical characterization of the adsorbents' material using Boehm titration method, iodine number.

- Application of the composite materials produced in water decontamination treatment using two dimensional time of flight mass spectroscopy gas chromatography GCXGC TOFMS, Ultra violet visible spectroscopy (UV-Vis), high performance liquid chromatography (HPLC), inductively coupled plasma optical emission spectroscopy (ICP-OES).

- Application of composite materials in water decontamination, soil phytoremediation and comparison of synthesized composites materials with commercially available composite adsorbent material.

- Application of the various composite adsorbents produced (HMDI (composite material without filler), MDI (composite material without filler), HMDI/AC, and MDI/AC) in water treatment. Performance of the adsorbent composites for pre-concentration and the removal of pollutants will be tested using two-dimensional gas chromatography/time-of-flight mass spectrometry (GC×GC TOFMS), and high performance liquid chromatography (HPLC).

1.4 THE THESIS STATEMENT

Adsorbent composites should have suitable adsorption properties that can make them applicable as adsorbent material in both pre-concentration and unwanted species/substances removal, in contaminated environmental samples.

1.5 RATIONALE BEHIND CHOICE OF COMPOSITE ADSORBENT

Composite material has been in use for various types of applications especially in water-treatment processes (Literature Review: Chapter Two). The usage and application of polyurethane polymer from pre-monomer polyol and isocyanate group as linker to form the hard segment part in the urethane group has not been explored in water treatment. In addition, the composite is cheap and easy to produce and synthesise.

1.6 BRIEF OVERVIEW OF CHAPTERS IN THE THESIS

This thesis is organised into ten chapters:

- Chapter one presents a general introduction, motivation, thesis statement and research aim and objectives.

- Chapter two deals with the literature review and provided an account of the fundamental principles and applications relating to the research conducted and published by other researchers.

- Chapter three provides details on the methods used. This chapter features the list of materials used, the research design and methods. A theoretical discourse of the analytical techniques used is also presented. The experimental section consists of a general section that explains procedures common to the work in general, and those peculiar to each milestone covered.

- Chapters four to nine: These chapters comprise of various milestones, some of which have been published in peer-reviewed journals or submitted for publication. A chapter is allocated to each of the milestones. It also presents the results obtained with a sub-conclusion at the end of each chapter.

- Chapter Ten provides the general conclusions and recommendations.

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CHAPTER TWO

LITERATURE REVIEW

BACKGROUND

Nanoscience as an emerging field in material science has blossomed in the past two decades, mainly due to research drifting towards nanotechnology as miniaturisation to nanometre scales is taking the centre stage in the world of science today. This is reflected in areas such as the biomedical field, sensors, computing, separation technology especially water treatment and numerous other applications [1, 2]. Progress and/or technological advancements in these areas depend basically on the ability to produce nanoparticles, of difference materials, shapes and sizes, as well as incorporating these into complex architectural matrices of material sciences. However, nanomaterials have major applications mainly due to their structural integrity. This fact has prompted researchers in the materials science field to be looking for materials with improved physicochemical properties that can be applied in nanoscience, especially in separation technology [3, 4]. In this regard, the discovery of polyurethane-based polymer, activated carbon composite, metal oxide such as nanoparticles, cyclodextrins polymer composites, are important inclusion in the area of nanotechnology and materials science [3, 4].

Polymer nanocomposites discovery by the Toyota research group has opened a new dimension in the field of materials science with numerous applications [5]. The application of both organic and inorganic nanomaterials as fillers in the preparation of polymer/inorganic/organic composites has attracted growing interest due to their huge potential application and unique properties in areas such as construction, aerospace, electronics, water purification and allied industries[4, 6-13]. However, most research studies are concentrated on polymer nanomaterials based on layered materials of natural origin such as montmorillonite type of layered silicate compounds or synthetic clay, clinoptilolite, and bentonite [4, 6-15]. Because of the poor electrical and thermal conductivity of clay materials, these are no longer in use[16-18]. In order to address this issue, for instance in the preparation of polymer-based nanocomposites, carbon-based nanofiller materials such as carbon nanotubes, carbon nanofibres, carbon black or activated carbon, and exfoliated graphene were incorporated into clay materials [2, 14, 19-22]. Amid these excellent materials, carbon nanotubes (CNTs) have proven to be very effective as conductive fillers, because they possess high adsorption capacity and other numerous applications in water and wastewater treatment[23-28]. The only limitation of CNTs as nanofillers is their high production cost [27, 29]. Therefore, the industrial mass production of CNT-based functional composite materials is very difficult.

2.1 WATER AND WATER POLLUTION

Water scarcity is one of the greatest challenges that face mankind in the 21st century. The lack of access to fresh clean water is a worldwide problem. In their report, the World Bank stated that 40% of the world population of about 7 billion people lack access to sanitation, clean and safe water [27, 29-31]. The demand for clean water is ever increasing at a geometrical rate due to urbanisation and population explosion [30]. This has placed a heavy strain on already scare water resources. Water resources are limited or scarce in arid populated areas of the world, especially in developing countries such as South Africa, which is known to be water -scarce country [30]. The shortage of freshwater for mankind calls for efficient, cost-effective management and simple operational technologies for water and wastewater treatment/purification.

Population growth due to urbanisation, industrialisation, domestic, agricultural activities, as well as climate change and other contributing anthropogenic activities have contributed heavily to the poor state of our clean water resources due to pollution [31-33].

Furthermore, the water crisis is compounded by pollution which has made clean and safe water more scarce. Statistics released by the United Nations showed that more than 2 tons of anthropogenic wastes are disposed of on a daily basis in our water courses; 70% of these, are industrial wastes which are due to anthropogenic activities and are dumped indiscriminately, often untreated or only partially treated, into rivers, lakes and oceans and this has invariably polluted/contaminated the already scarce freshwater resources. Anthropogenic activities have introduced numerous contaminants into freshwater resources such as surface water, groundwater or aquifers. Included among the contaminants resulting from anthropogenic activities are conventional pollutants such as inorganic compounds, distillates, emerging micro-pollutants, and antibiotic residues as well as other persistent organic compounds/pollutants (POCs/ POPs). A number of these pollutants/contaminants cannot efficiently be removed from water via traditional water and wastewater treatment methods. However, more effective and low-cost technologies are used to decontaminate and disinfect water for point-of-use (POU) applications; this water-treatment technology is needed to provide clean water to communities living in the rural areas.

Water pollution refers to contamination of water with chemicals or foreign substances that are detrimental to animal and human life [31, 34]. These contaminants include inorganic compounds such as arsenic, mercury, lead, chromium, cadmium and other heavy metals or organic compounds such as pesticides, polychlorinated biphenyl (PCB), fertilisers from agricultural runoff, phenolic compounds from chemical or industrial effluents and solid or liquid hazardous wastes [35]. Over 2 billion people do not have access to safe and clean water and this situation has a negative effect on their health [32-36]. In developing countries access to fresh water is becoming even more difficult due to water scarcity caused by deforestation, urbanisation, river damming, wetlands destruction, industrial revolution, mining activity through acid mine drainage, agriculture, energy use, and accidental water pollution due to oil spillages, etc. All these have led to an increase in pollution and destruction of water catchment areas [36]. Figure 2.1 shows water classification in terms of abundance and application. The figure also shows the percentage of earth's water distribution, fresh water percentage due to anthropogenic activities, and fresh surface water distribution, respectively [36].

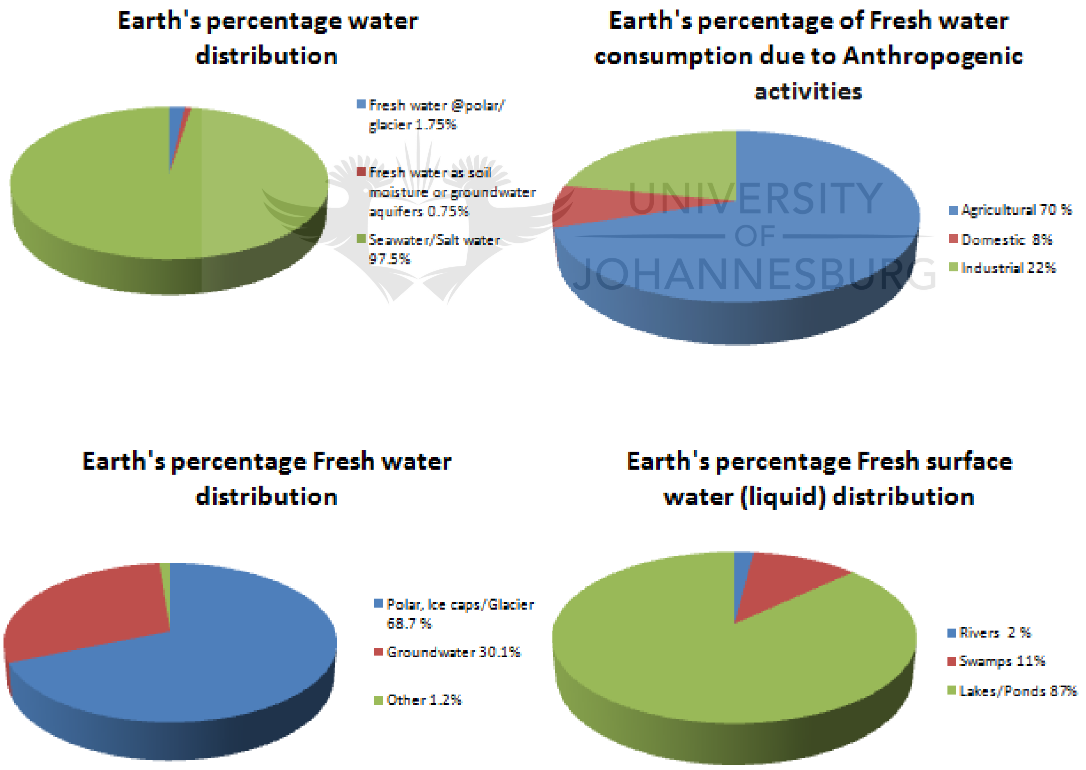

Figure 2.1: Classification of water distribution on earth [36]

2.1.1 Classification of water pollution

Water can be classified into three main groups, namely natural water, polluted water and purified water:

- Natural water includes rain water, surface water, groundwater, seawater, rivers, streams, springs and lakes.
- Polluted water includes industrial effluents, sewage or sullage.
- Purified water includes potable, distilled/treated water.

Among water categories, natural water stands out because it contains largest groups of water bodies that contain surface water and groundwater. These two are interrelated and are often studied as separate resources or entities. Surface water seeps through the soil and becomes groundwater while on the other hand groundwater can also feed the surface water.

2.1.2 Types of water pollution

Water pollution can be classified into three main entities/groups biological, chemical and physical, while chemical entity can be inorganic and organic pollutants.

2.1.2.1 Inorganic pollutants in water

Inorganic pollutants are contaminant-containing compounds without elemental carbon within their structural entity. These pollutants are introduced into the environment by various means which include natural means by way of weathering activity of the parent igneous rocks, agricultural runoff from farmland and industrial wastewater [37]. These inorganic pollutants include, anionic compounds such as chlorides ion (Cl^-), fluoride ion (F^-), nitrate ion (NO_3^-), phosphate ion ($P_3O_4^-$) and cyanide ion (CN^-), heavy metals such as Cd^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} Zn^{2+}, etc., and dissolved gases such as nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), sulphur dioxide (SO_2), etc. Furthermore, these inorganic pollutants are of environmental concern due to the health risks they pose to living organisms mainly because of their tendency to bioaccumulate in the body which can result in chronic negative health effects [38]. Many of these inorganic pollutants are non-biodegradable and can poison the food chains of living organisms if not mitigated [38].

2.1.2.1.1 Metals

Metals are major part of globally distributed pollutants, which are natural elements that have been extracted from the earth's crust and harnessed for the benefit of mankind through industrial application. Inorganic compounds, especially metals, are notable for their widespread application in environmental dispersion; their tendency to bioaccumulate in human tissue and their potential toxicity even at low levels of exposure are well-known. Presently, metals/inorganic ions are abundant in environmental compartments such as air, sediment, soil and water. They are virtually present in every sphere of human endeavour, from construction materials to cosmetic accessories to personal care products, medicines to processed foods. It is very difficult for anyone to avoid exposure to these metals prevalent in our society. Some inorganic metals, such as copper, iron and sodium are essential to life and play a significant role in normal functioning of the critical enzyme systems. However, other metals are xenobiotic, mainly because of their toxicity in living organisms especially humans and also play no useful role in human physiology [39, 40]. Those metals that belong to this group include arsenic, cadmium, mercury, lead, etc. Although metals classified as essential can in turn be harmful at elevated concentrations during exposure; hence reflection of a basic tenet of toxicity which states that 'dosage make the poison'.

2.1.2.1.2 Cadmium

Cadmium, classified as a heavy metal with atomic number 48 in the periodic table of elements, is very toxic and tops the toxicity list of heavy metals [41]. It was discovered as impurity in zinc carbonate by Sromeyer and Hermann around 1817 in Germany [42]. Its concentration in the earth's crust is between 0.1 ppm and 0.5 ppm (part per million). Due to its mobility and chemical form, Cd constitutes a severe environmental problem in many areas thereby putting human health at risk. Cd plays an active role as an inducer of biosynthesis of metallated protein and also its bioaccumulation in living organisms [43].

Cadmium is usually found in the environment, mainly due to anthropogenic activities. It finds applications in numbers of special alloys which include electronic compound (Cu, Pb, or Zn-based alloys, in pigments, stabilisers for PVC, nickel/cadmium batteries and coatings for other non-ferrous metals). Cadmium is also present as an impurity in a number of products which include refined petroleum products and phosphate fertiliser. Its speciation form in many industrial wastewater effluents/streams, especially paint, battery and metal finishing electroplating industries is +2 ions [44, 45]. It has been reported that Cd is an organically bound, exchangeable and water-soluble species in soil and is also fairly mobile [44, 46-48].

It has been reported that an average person living in the United States of America (USA) consumes about 30 μg of cadmium in their diet on a daily basis [49]. Furthermore, in a polluted environment the daily intake of cadmium can be as high as 100 μg. Guo and his co-workers reported that Wonderfonteinspruit, South Africa, is a water catchment area which is heavily contaminated with cadmium due to the mining activity in that area [49].

Nogawa *et al.* [50] reported cadmium poisoning of kidneys, while other researchers have reported cadmium poisoning to include liver and blood [51] lung insufficiency, cancer and changes in the elemental constitution of bone [50].

Renal abnormalities, including proteinuria and glycosuria, and itai-itai disease, have been associated with cadmium bioaccumulation in food crops, especially rice [43, 52]. Thus, any compounds containing cadmium are known to be carcinogenic [52]. Long-term exposure to cadmium is associated with renal dysfunction due to the bioaccumulation and non-biodegradability of Cd once absorbed by living organisms [52]. It is associated with bone defect-such as ostomalacia and osteoporosis in both animal and human being. It has been reported that the average cadmium daily intake in human being lies between 0.15 µg (air) and 1.0 µg (water) [53-55]. The WHO permissible limit for cadmium in drinking water is 0.005 mg/L (Central Pollution Control Board (CPAB) but this may vary from one country to another [53].

2.1.2.1.3 Chromium

'Chroma' the word for colour in Greek is chromium element which was discovered by Vauquelin in 1797 [56]. Special interest for chromium arises from the fact that chromium exists in different oxidative states, i.e., the trivalent oxidation state and the hexavalent oxidation state. While the latter is essential for animal and human nutrition, the former is very toxic and has been reported to be carcinogenic and can damage DNA [56]. Chromium has been reported to be the second most inorganic contaminant of groundwater and the seventh most abundant element on earth [56]. The naturally occurring chromium is found in the trivalent state and is commercially available as chromite ore in which the chromic oxide content, the main constituent, makes up 15% to 65%. The main deposit of chromium is in southern African states of which South Africa forms a part.

Chromium is a steel gray, lustrous, hard and brittle metal that takes a high polish, and can readily be dissolved in non-oxidizing mineral acids, but not in cold aqua regia or nitric acid, due to its passivation. Its trivalent form exhibits a d^3-electronic configuration and it forms many compounds, including complexes with nitrogen and oxygen. Chromium Cr(lll) hydroxo complexes are dominant in nature which includes $CrOH^{2+}$, $Cr(OH)_3^0$, $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$, $Cr(OH)^{2+}$; its poly nuclear complexes have also been reported in the literature but are of no importance/significance in natural systems. The United States Environmental Protection Agency (USEPA) [57-59] and their Chinese counterpart, Chinese Environmental Protection Board (CEPB) [59, 60] have listed hexavalent chromium (Cr(Vl) as one of the priority pollutants. The maximum permissible limit of hexavalent chromium in drinking water, industrial wastewater, and inland surface water are 0.05 mg/L, 0.25 mg/L and 0.1 mg/L, respectively [61]. Chromium has been reported to be mutagenic and carcinogenic [62, 63]. Chromium is a relatively reactive pollutant which finds its way into ecosystems through various anthropogenic activities which include textile dyeing, wood preserving, electroplating, leather tanning chromate preparation, metal finishing and mining [64].

2.1.2.1.4 Lead

Organolead compounds have been with us for many decades. The massive application of lead in household utensils and water pipelines dates back to the Roman Empire. Industrialisation through industrial activities and vehicle emissions, especially in big urban cities where there are large numbers of vehicles on the road, compound the problem of lead pollution on the global scale. Lead has been recognised as one of 'the big three' of heavy metals (together with cadmium and mercury) that have high toxicity and its accumulation leads to health issues in living tissues [65, 66]. Hamidpour *et al.* [66] reported that lead poisoning leads to a condition known as plumbism, colica, Pictonum, saturnism which is a medical condition caused by exposure to increased levels of lead in the body. Lead is regarded as toxic pollutant due to its severe or hazards potential to the environment and organisms [67]. Lead pollutions occur in both air and water. In the air, lead pollution emanates from lead emission through automobile exhaust pipes mainly because of its application as an anti-knocking agent in the form of tetraethyl lead (TEL) in gasoline /petrol. TEL application in gasoline is to prevent premature spontaneous explosion of air/gasoline mixture in the engine. Other anthropogenic activities introduce lead into the environment and this includes metallurgy, manufacture, battery and electroplating. Lead usage in the automobile industries accounts for more than half of the 1.15 million metric tons of the total lead usage, especially in car batteries, etc. [39]. Lead is the traditional base metal for organ pipes in which lead is mixed with varying amounts of tin in order to control the pipe tone [39]. However, lead does not naturally exist in the human body and thus, there is no minimum level in man that does not constitute toxicity/toxic to man’s living cells. Sgarlata *et al.* [68] reported that exposure to lead, no matter how little can lead to health issue which include headache, confusion, irritability, memory and learning deficiencies, severe cases of seizures, high blood pressure, coma, abdominal pain, kidney damage and death. The USEPA has set the acceptable permissible limit of lead (Pb (II) in potable water to be 0.015 mg/L [69, 70]. Presently, the removal or preconcentration of lead in drinking water/wastewater is a major problem facing water regulatory agencies [71]. In water bodies, lead is released via effluents from lead treatment and recovery industries.

In many countries, especially in developing countries, lead is present in water in concentrations higher than the permissible limit of 50 μg/L [71].

Lead tends to form complexes in the human body that can interfere with severe metabolic and synthetic processes. Thus, its removal is very important to ensure the general well-being of the human race.

2.1.2.2 Organic pollutants in water

Organic pollutants are contaminants that constitute environmental issues to human health even at low concentrations. Many of these pollutants are called POP because of their toxicity and tendency to bioaccumulate in the environment and non-biodegradability. These POPs include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), phenolic compounds, pesticides such as atrazine, herbicides and dye solution. These POPs are usually absorbed by plants and animals and hence they find their way into the food chain of other living organisms. Several health issues are linked to these POPs and these include cancer, damage to the nervous system, disruption of the immune system and reproductive disorders have all been linked to POPs [72].

2.1.2.2.1 Dye solution

Colourful materials or substances are a source of attraction to the eyes but comes with a high price. Colours that appear in many industrial effluents are due to dye products [73, 74]

Dyes are classes of any intensely coloured complex organic compounds used for the purpose of colouring textile, leather, paper and other materials. They contain ionising and aromatic organic compounds which show affinity toward the substrate to which it is being applied. Dyes have been known to the ancient before modern civilisation, and come from plant materials (lignin, tannin, melanoidin) such as Indigo and madder, from mollusc sea shells from coal tar and petrochemicals such as synthetic dye [74]. The chemical structures of dyes are relatively easy to modify, thus making it easier to synthesise new dyes with new colour. Dye molecules are deposited from solution onto the materials in such a way that they cannot be removed by ordinary original solvent [75]. Many fabrics are dyed with fibre reactive dye which forms a covalent bond with the fibre. Other forms of dyes require prior treatment before application; these include mordant dyes, an inorganic material that causes the dye to precipitate as an insoluble salt. Another technique of dyeing is Vat dyeing, in which a soluble colourless compound is absorbed by the fibre and then oxidized to the insoluble coloured compound, making it remarkably resistant to either chemical attack, or to the fading effect of washing and sunlight [75]. Azo dyes are any classes of large synthetic organic compounds containing two nitrogen atoms joined by a double bond in the form –N=N—as part of their molecular structure. Presently, half of commercially available dyes belong to the class of azo dyes. They are classed according to fibres for which they have an affinity or the method by which they are applied.

Direct dyes are absorbed from solution by the fibres but others require a second solution or mordant/or second step before the colour is fast

2.1.2.2.2 Classification of dyes

Dyes can be classified into several groups. Each class of dye has a unique way of bonding, chemistry and structure. Some dyes can react chemically with substrates to produce strong bonds in the process, while others can be held by physical forces of attraction. Below is the most important way of grouping dyes into different classes:

- According to the dyeing methods
    - Anionic (for protein fibre)
    - Direct (cellulose)
    - Disperse (polyamide fibres)
- By area and method of application
- By nature of the electronic excitation (i.e., energy transfer colorants, absorption colorants and fluorescent colorants)
- Chemical classification – based on the nature of their respective chromophores
- Organic/inorganic

- Natural/synthetic

Table 2.1: Classification of dyes based on groups and application [74, 75]

Group	Application
Direct	Cotton, cellulosic and blended fibres
Vat dyes	Cotton, cellulosic and blended fibres
Sulphur	Cotton, cellulosic fibre
Organic_pigments	Cotton, cellulosic, blended fabric, paper
Reactive	Cellulosic fibre and fabric
Disperse dyes	Synthetic fibres
Acidic dyes	Wool, silk, paper, synthetic fibres, leather
Azoic dyes	Printing inks and pigments
Basic dyes	Silk, wool, cotton

2.1.2.2.3 Methylene blue

Methylene blue (MB) is a bright greenish blue organic dye belonging to the phenothiazine family of dyes (Figure 2.2). Methylene blue is mainly used in bast fabric or vegetable fabrics such as flax, jute and hemp material. It also finds application though to a lesser extent in leather, mordanted cotton and paper. Methylene blue is also employed as a biological stain used in testing milk for tubercular infection and also as chemical oxidation indicator [75]. Methylene blue is widely used by textile industries to colour their products. One of the key problems concerning textile wastewaters is coloured effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to aquatic life/organisms [76]. MB dyes are known to cause eye burns, which may be responsible for permanent injury to the eyes of humans and animals. On inhalation, it can give rise to short periods of difficult or rapid breathing. Ingestion through the mouth produces a burning sensation and may cause mental confusion, nausea, vomiting, profuse sweating, methaemoglobinaemia and painful micturition [77, 78]. Thus, the treatment of wastewater effluent containing such MB dyes is of interest due to its aesthetic impacts on receiving waters.

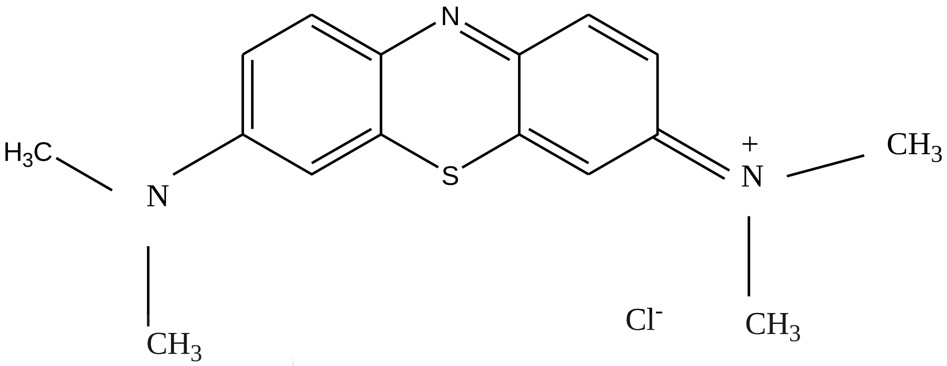

Figure 2.2: Chemical structure of methylene blue

2.1.2.2.4 Phenolic compounds

Phenolic compounds are present in aquatic environments as a result of anthropogenic activities of man especially through industrial activities. These compounds are generated in the production of anti-oxidants, drugs, dyes, paper, pesticides and petrochemicals [79], hence the need to remove them from the environment. There are several types of phenolic compounds which include bisphenol A BPA, chlorophenol nitrophenol, etc.

2.1.2.2.4.1 Bisphenol A

Bisphenol A (BPA) is a colourless crystalline solid belonging to the family of phenolic organic compounds (Figure 2.3). The compound has a general molecular formula of $C_{15}H_{16}O_2$ and is best known for its application in manufacturing of polycarbonate plastics and epoxy resins especially those found in baby feeding bottles, water bottles, beverages and other food containers [80]. In addition, BPA is also employed as a stabiliser or antioxidant in many plastics such as polyvinylchloride (PVC) for use in water pipes, pharmaceuticals, perfumes, cosmetics, medical devices, food packaging, automobile upholstery, as well as computer devices [81]. Bisphenol A has also been grouped as part of plastics additives which are responsible for making plastics less brittle and soft. Other plastic additives include phthalates and polybrominated diphenyl ether PBDE. Bisphenol A is of environmental concern because of its tendency to leach from these products. The compounds are commonly introduced into the environment, especially aquatic habitats, through agricultural runoff, industrial and municipal effluent or wastewater. The compound has been reported in different environmental matrices such as sediments, sewage, sludge, soil and water samples [82]. Bisphenol A and other plastics additives are known to be endocrine disruptors in humans, especially in children and women of reproductive age. Bisphenol A toxicity has been extensively studied over the years and has been shown to have adverse effects on animals through exposure even at low concentration levels [81, 83]. Human exposure to BPA has been reported to be responsible for altered body weight, abnormal early puberty, abnormal karyotype, attention deficit hyperactivity disorder, breast cancer and prostate cancer, developmental and reproductive toxicity, infertility, obesity, and polycystic ovary syndrome [81, 82].

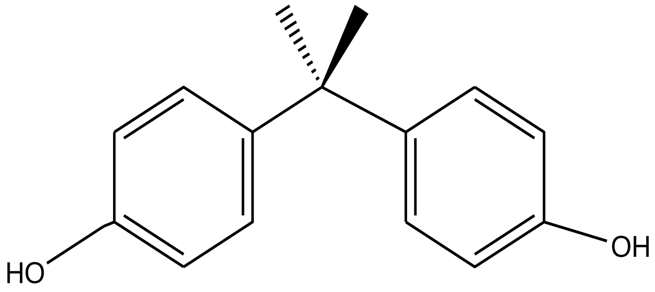

Figure 2.3: Chemical structure of BPA (4, 4′ (propane -2, 2-diyl) diphenol))

2.1.2.2.4.2 Chlorophenol

Chlorophenol (CP) has a total of 19 congeners and belongs to a group of chemicals with chlorine atoms (which can be substituted between positions 1 and 5) attached to the phenolic structure (Figure 2.4). Chlorophenol has been employed as synthesis intermediate for industries or as raw materials in manufacturing of pharmaceuticals, dyes, herbicides, insecticides and wood preservatives [84-87]. There is a fairly large market for CP because its world production is about 100 kt/yr [87]. Nevertheless, taste and odour problems at low concentrations have been associated with CP [87, 88]. They also cause severe adverse health effects on human, mainly due to their toxicity and carcinogenic tendency [88]. They also result in degradation of water quality especially the potable drinking water. Chlorophenol is listed by USEPA and the European Parliament and Council (Decision No. 2455/2001/EC) as a toxic pollutant [89, 90].

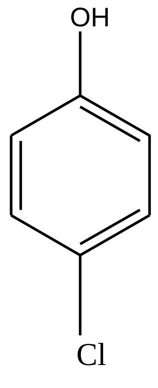

Figure 2.4: Chemical structure of chlorophenol substituted in the para position

2.1.2.2.4.3 Nitrophenol

Ortho-nitrophenol (O-NTP) belongs to the phenolic family of aromatic compounds having phenol as its parent family name substituted in the ortho position of the benzene aromatic ring (Figure 2.5). It is a light yellow colour solid compound with a characteristic aromatic odour. O-NTP is slightly soluble in cold water and can be produced industrially by manufacturing from process plants. This compound is a common organic pollutant present in agricultural wastewaters and they are also common by-products of industrial processes. Ortho-nitrophenol has been reported as being released into the environment without proper regulation [91]. They are found in treated wastewater from manufacturing industries such as electrical/electronic components production, iron and steel manufacturing (where NTP is formed as a by-product during the coke-making process), pharmaceutical production and rubber processing [69]. Nitrophenol is used as an intermediate for the production of dyestuffs and pigments, fungicides and rubber chemicals. Furthermore, few quantities of O-NTP are used as an inhibition for the degradation of glucose by *Pseudomonas fluorescens* and also as an acid-base indicator [92]. Ortho-nitrophenols may be released into the environment through wastewater effluent and as a fugitive emission during its production and application as a chemical intermediate [93]. Ortho-nitrophenols are bioplasmic poisonous compounds which pose high health risks due to their physiological and carcinogenic activity. In addition, they decrease the self-purifying ability of water by restraining microorganism growth. They are present in about 14 out of 1 177 hazardous waste sites listed on the National Priorities List of hazardous waste materials identified by USEPA and as the USEPA evaluates more sites, the number of sites at which NTPs are found also increases [94]. The USEPA have listed 2-NTP, PCP, BPA, and other phenolic compounds on the National Priorities List and also recommends their concentrations in natural waters to be below 10 ng/L [95].

Thus, anthropogenic activities are solely responsible for their presence in the environment.

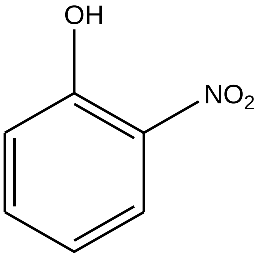

Figure 2.5: Chemical structure of nitrophenol substituted in the ortho position

2.1.2.2.5 Polychlorinated biphenyl

Polychlorinated biphenyl (PCB) refers to a synthetic chlorinated organic compound derived from the biphenyl by substitution of one to ten hydrogen atoms by chlorine atoms. PCB groups have each of its homolog group attached to a particular number of isomers such as mono-chlorobiphenyl 3, di-12, tri-24, tetra-42, penta-46, hex-42, hepta-24, oct-12, nona-3 and decachlorobiphenyl-1. Polychlorinated biphenyl has a total of 209 possible congeners. The coding system is used for the 209 congeners starting from 1 (mono-Cl) to 209 (deca-Cl), i.e. chlorobiphenyl CB. The production of PCB has a global output of ca. 1.3 million tons produced annually and they are commonly produced as a complex mixture in many industrial applications. It has found application in hydraulic oils, as additives in plastics, as transformer oils, cutting oils, carbonless copying paper, and metal casting which releases oil and heat transfer fluids.

The compound PCB comes under different trade names in many developed countries such as the United States (Aroclors), Kanechlor (Japan), Fenclor (Italy), Chlophen (Germany) until it was banned in the late 1970s and early 1980s [96, 97]. Its production was censored mainly because of its adverse effects on human health issue *vis-a-vis* bioaccumulation, persistency and toxicity in the environment [98, 99]. Thus, their widespread application, cum improper disposal, chemical stability and toxicity makes them to be of environmental concern to regulatory bodies in many countries [34, 98, 100-105]. Thus, the empirical formula for PCB is C_{12} H_{10}-nCI$_n$ where n = 1 to 10, i.e. mono-chlorobiphenyl through decachlorobiphenyl [98, 106, 107]. The structural formula of the un-substituted biphenyl molecule with each carbon atom in the ring has its own numbering system (Figure 2.6).

In the past two decades, a lot of attention has been drawn to the fate of PCB in the environment especially their toxicology and particularly congeners that show similarity in toxicity as in those present in polychlorinated dibenzo-p-dioxines (PCDDs) and dibenzofurans (PCDFs). It has been reported that some PCBs that lack chlorine substituents in their ortho position present a high dioxin-like toxicity. This PCB includes PCB, 77, PCB, 126, PCB, 169. The mono-ortho substituted chlorobiphenyl (CB) also presents similar toxicity, as in dioxin types, although to a lesser degree. Thus, dioxin-like toxicity of CB is compared to those of toxic dioxin 2,3,7,8-tetrachlorodibenzo-p-dioxin(2,3,7,8-TCDD) and CB has toxic equivalency factor (TEF) (Table 2.3) [61, 108, 109].

Polychlorinated biphenyls are insoluble in water but easily dissolve in hydrocarbon fats and other organic compounds and they are readily absorbed by fatty tissue [107] (WHO 1993). Polychlorinated biphenyl has a hydrophobic property which makes them resistant to biodegradation and breakdown. Polychlorinated biphenyls have excellent dielectric properties [110, 111] electrically insulating/insulator) and also possess low electrical conductivity and high capacity. This has made them find application as a cooling liquid in electrical equipment.

Polychlorinated biphenyls have unique chemical and physical properties and are therefore desirable components for a number of industrial applications. However, these properties have also made them to be environmentally hazardous and cause human health issues [112]. The pure PCB congeners are colourless, crystalline compounds, while the commercial components of PCB are a mixture of these congeners, and are clear, dark or light yellow colour in appearance [107]. Polychlorinated biphenyls turn into solid resin instead of crystallising at low temperature. The chlorine atom substituent in PCB molecules makes them to have high density. Polychlorinated biphenyls also possess other properties, which include low vapour pressure at room temperature, thermal stability resistance to acids and bases and other chemical agents, compatibility with organic materials and resistance to oxidation and reduction [112].

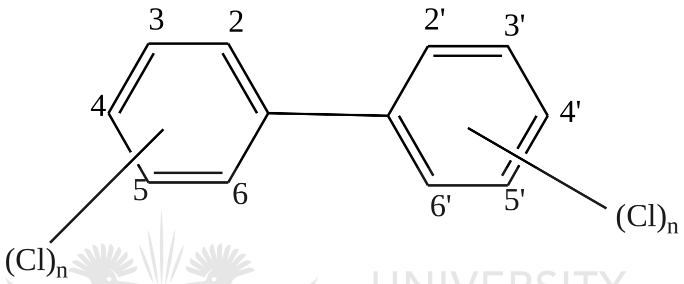

Figure 2.6: General chemical structure of PCB

2.1.2.2.5.1 Polychlorinated biphenyl nomenclature

Table 2.2: Polychlorinated biphenyl nomenclature classification table

Category	Number of individual compounds
Congener	209
Isomer group/homolog	10
Isomers/group	1-46

2.1.2.2.5.2 Composition of PCB isomer

Table 2.3: Composition of PCB isomer congeners

PCB isomer groups	Empirical formula	Percentage chlorine	Number of isomers
Monochlorobiphenyl	$C_{12}H_9Cl$	19	32
Dichlorobiphenyl	$C_{12}H_8Cl_2$	32	12
Trichlorobiphenyl	$C_{12}H_7Cl_3$	41	24
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	49	42
Pentachlorobiphenyl	$C_{12}H_5Cl_5$	54	46
Hexachlorobiphenyl	$C_{12}H_4Cl_6$	59	42

Heptachlorobiphenyl	$C_{12}H_{3}Cl_{7}$	63	24
Octachlorobiphenyl	$C_{12}H_{2}Cl_{8}$	66	12
Nonachlorobiphenyl	$C_{12}H_{1}Cl_{9}$ / $C_{12}HCl_{9}$	69	3
Decachlorobiphenyl	$C_{12}Cl_{10}$	71	1
Total			209

Examples of typical PCBs are shown in Figure 2.7a-c.

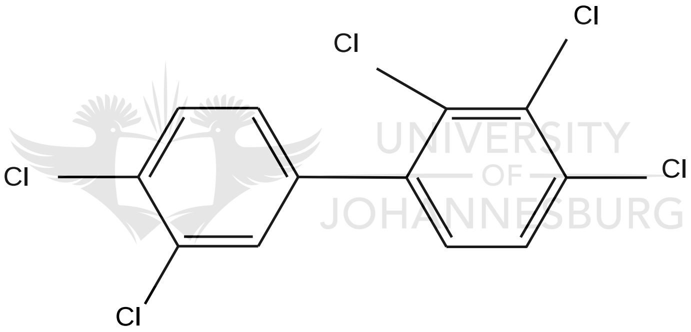

Figure 2.7a: PCB 105 (1,1′-Biphenyl-2,3,3′,4,4′ pentachloro)

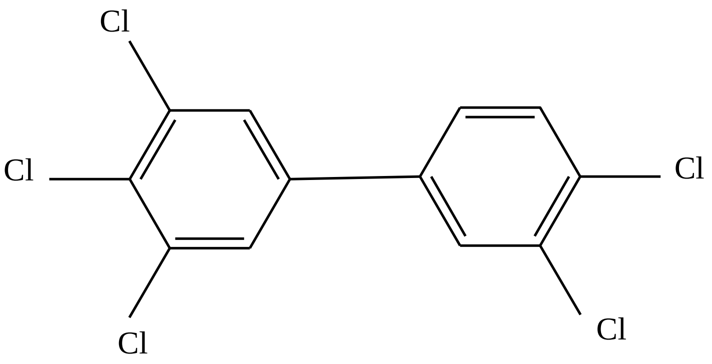

Figure 2.7b: PCB 126 (1,1′-Biphenyl 3,3′,4,4′,5 pentachloro)

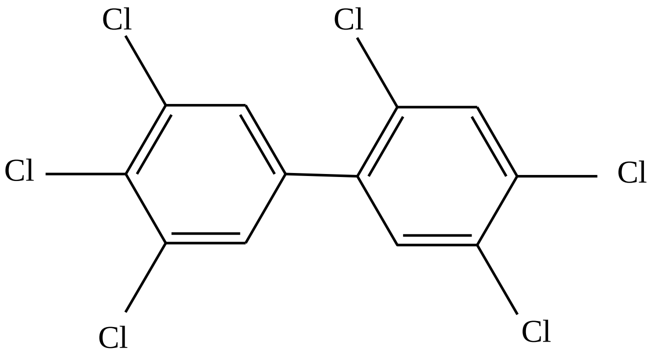

Figure 2. 7c: PCB 153 (1,1′-Biphenyl 2,2′,4,4′,5,5′ hexachloro)

2.1.2.2.6 Sampling and sample pretreatment for PCB analysis

Polychlorinated biphenyl can be analysed in different kinds of environmental matrices, which include sewage sludge, marine mammals, fish, fresh water, wastewater, sea water, benthic organism, food, human blood, adipose tissue and sediments (Table 2.4). In handling sample preparations, all samples require a specific method of handling. Polychlorinated biphenyl is extremely difficult to analyse in water due to its low concentration and low solubility, thus, there is a need for pre-concentrating it in water matrices before analysis and also to reduce background contamination. Polychlorinated biphenyl concentration in an air matrix is determined after extraction from sampling air filters or passive sampling systems. However, sediment and biota samples of PCB can be collected intertidally or by means of a variety of grab samples from a vessel. This is because PCB concentration in sediment has a patchy distribution and several grab samples from different locations are combined to one pooled sediment sample [61, 108, 109].

Table 2.4: Toxic equivalency factors for dioxin-like compounds for humans and wildlife derived at a WHO meeting in Stockholm Sweden, 15-17 June 1997 [108]

$Congener$	$Toxic\ equivalency\ factor\ TEF$	$Factor\ (WHO)$	
$Dioxins$	$Human/Mammals$	$Fish^a$	$Birds^a$
$1,2,3,7,8\ P_eCDD$	1.0	1.0	1.0
$1,2,3,4,7,8\ H_xCDD$	0.1^a	0.5	0.05
$1,2,3,6,7,8\ H_xCDD$	0.1^a	0.01	0.01
$1,2,3,7,8,9\ H_xCDD$	0.1^a	0.01^a	0.1
$Non\ ortho\ PCBs$			
$2,3,4,4',5\ P_eCB\ (114)$	$0.0005^{a\ b\ c}$	$<0.000005^b$	0.0001^a
$2,3',4,4',5\ P_eCB\ (118)$	0.0001	<0.000005	0.00001
$2',3,4,4',5\ P_eCB\ (123)$	$0.0005^{b\ c}$	<0.000005	0.0001
$3,3',4,4',5\ P_eCB\ (126)$	0.1	0.005	0.1
$2,3',4,4',5,5'\ H_xCB\ (153)$	$0.00001^{a\ d}$	$<0.000005^b$	0.00001
$2,2',4,4',5,5'\ H_xCB\ (167)$	$0.00001^{a\ d}$	$<0.000005^b$	0.00001
$Mono\ ortho\ PCBs$	-	-	-
$3,3',4,4'\ TCB\ (77)$	0.0001	0.0001	0.05
$3,4,4',5\ TCB\ (81)$	$0.0001^{a\ b\ c\ e}$	<0.0005	0.1^e
$2,3,3',4,4'\ P_eCB\ (105)$	0.0001	$<\prec 0.000005$	0.0001
$2,3,4',4,4',5\ H_xCB\ (156)$	$0.0005^{\ b\ c}$	$<\prec 0.000005$	0.0001
$3,3',4,4',5,5'\ H_xCB\ (169)$	0.01	<0.0005	0.001
$Furans$	-	-	-
$2,3,7,8\ TCDF$	0.1	0.05	1.0^f

1,2,3,7,8 $P_e CDF$	0.05	0.05	0.1^f
2,3,4,7,8 $P_e CDF$	0.5	0.5	0.1
1,2,3,4,7,8 $H_x CDF$	0.1	0.1	0.1^c

a - limited data; b structural similarity; c QSAR quantitative structure activity relationship; d No new data review from 1993; e *in vitro* induction; f *in vivo* of induction after *in vivo* exposure

CDD Chlorinated dibenzodioxins, *CDF* Chlorinated dibenzofurans, *CB* Chlorinated biphenyl, *T* Tetra, H_x Hexa, P_e Penta

2.2 ADSORBENTS

Adsorbents are substances or materials which are usually porous and have a high surface area that can be used to adsorb or attach substances onto its surface by intermolecular van der Waals forces. These substances can also serve as extraction/preconcentration materials for the purposes of removing trace inorganic/organic analytes/ions from large volumes of aqueous environmental samples especially in solid-phase extraction. However, numerous indices determine the effectiveness of an adsorbent; apart from surface area, these include its chemical nature or structure, pore size, pore volume and particle size. Furthermore, the simplicity and the ease of operation, together with application of low-cost adsorbent, adsorbent composite materials and their relative availability and cost-effectiveness have led to an increase in research on the direct application of these materials in both the liquid-phase adsorption process and the solid-phase adsorption process, especially in extraction/preconcentration processes using the solid-phase extraction method [32, 113]. The application or utilisation of agricultural waste residue as activated carbon and in composite materials for water and wastewater treatment processes would serve as an alternative to the expensive commercially available activated carbon and would be economically viable for water purification processes, especially in developing countries such as South Africa.

2.2.1 Classes of adsorbents

Adsorbents can be classified based on their mode of application into two classes:

- Direct application through batch adsorption process; and
- Through extraction or preconcentration processes

2.2.2 Direct application through batch process

2.2.2.1 Batch adsorption process

Batch adsorption consists of contacting finely divided adsorbent such as AC with the wastewater for a given period of time in a mixing vessel. The adsorbent such as AC used in this process must be in the powdered form, i.e. powdered activated carbon (PAC) in order to maximise specific surface area (SSA) for mass transfer and to minimise agitation for suspension. Typical carbon particle size of an adsorbent such as AC is 10 to 50 mm. After the process is complete (contact time varies depending on when equilibrium is reached, i.e. saturation point of the adsorbent), the spent adsorbent (AC/carbon) is separated from the wastewater (e.g., by filtration) and thereafter regenerated or disposed of.

2.2.2.2 Extraction/preconcentration process

Preconcentration or extraction treatment process is often considered to be an essential step in the process of successful analysis of environmental pollutants, mainly with the view to achieving low detection limit and also to assist in the cleanup of the sample matrix. This is where SPE comes into play. SPE is a separation process for sample preparation in which compounds that are dissolved or suspended are separated from other compounds in the mixture according to their chemical and physical properties [114-118]. Solid-phase extraction is an effective sample preparation/handling method which employs sample enrichment techniques in order to determine low concentrations of analytes in environmental samples. It offers capabilities for a wide range of applications such as biochemical analyses, environmental analyses, food analyses, organic chemistry and pharmaceutical assays. It provides higher enrichment efficiency and requires a lower volume of solvent than the traditional method of liquid- liquid extraction (LLE). In addition, the merit of SPE over LLE includes low solvent consumption, the enormous time saving, it offers potential for automation, yields quantitative extractions that are easy to perform, and is rapid. It also prevents many of the problems associated with LLE, such as incomplete phase separations, less-than-quantitative recoveries, and use of expensive solvents [114, 117, 119].

2.2.3 Adsorbent for extraction/adsorption

2.2.3.1 Types of adsorbent

2.2.3.2 Agricultural waste residue/biomass

Agricultural waste residues (AWR) such as maize tassel (MT) are produced in millions of tons annually due to high consumption of maize as a staple food and livestock feeds in South Africa [120]. Hence, huge wastes are generated by this grain and disposal problems are inevitable. This AWR is relatively abundant in South Africa and consists predominantly of carbohydrates, protein and phenolic compounds, which have metal-binding functional groups, such as carbonyl, hydroxyl, sulphate, phosphate, and amino groups [120, 121]. The International Institute of Tropical Agriculture (IITA) reported that 785 metric million tons of maize are produced globally and 6.5% of this is from sub-Saharan Africa (SuSA) [122]. Several researchers have applied low-cost adsorbents as potential alternative to commercially available AC, which is expensive, for the removal of both inorganic and organic pollutants from aqueous stream and these include the following:

Coconut bunch waste [123], miswak leaves (*Salvadora persica*) [124], banana pith, orange peel [125], guava (*Psidium guajava*) leaf powder [126], salts treated beech sawdust [127], cellulose based wastes, giant duckweed [128, 129] sunflower seed shells [130], palm oil shell [131], furniture waste [132], bamboo [133], bamboo dust [134], groundnut shell [134], rice husk [134], straw [134], pineapple leaf powder [135], sludge ash [136], spent activated clay [137], magnetic Fe_3O_4 nanoparticle [138], spent green tea leaves [139], marine green alga (*Ulva lactuca*) [140], maize tassel as biosorbent and AC [121, 141, 142], banana-based activated carbon [143], periwinkle shell-based activated carbon [144], peat and bentonite [145], rice husk, rice husk ash and rice husk silica [146], zeolites [147], rubber seed coat pine wood-based activated carbon [148], rubber seed coat [149], bagasse and wood charcoal [150], clays and fertiliser wastes, pillared clays and mesoporous alumina [151], carbonised slash pine bark [152] and kenaf (*Hibiscus cannabinus*) [153], all of which have been evaluated for use as adsorbents for the removal/separation of contaminants from aqueous water streams or solutions. However, AWR, i.e. maize tassel applied in this study has only been used as AC [142] already published, but not as fillers in composite materials especially polymeric composite material. Similarly, adsorbents such as beta cyclodextrin β-CD, AC, raw biomass powder form have been previously reported by researchers [154-183] on their application in technologies such as water separation processes, soil amendment extraction/preconcentration of both inorganic and organic analytes and other applications in separation technology. The application of maize tassel-produced activated carbon (MTAC) and its usage as a filler in polymeric material to produce composite materials for the uptake, separation and preconcentration of inorganic and organic contaminants in wastewater is considered a distinctive and new investigation based on the fact that their previous application in adsorption/preconcentration of inorganic/organic compounds is limited and unknown.

2.2.3.3 Activated alumina

Activated alumina (AA) can be produced from a mixture of amorphous and gamma alumina which is prepared from dehydration of $Al(OH)_3$ under low temperature (300 ^oC to 600^oC), with SSA in the range of 250 m^2/g to 350 m^2/g [154]. This adsorbent has been used in wastewater treatment and is reported to have high adsorption capacity for the removal of both inorganic and organic compounds, and has the advantages of chemical inertness (CI), ionic strength (IS), pore structure (PS) and SSA [155]. Konstantinou and his co-workers reported successful removal of phenolic compounds such as 2,4 chlorophenol, 2,4,6 trichlorophenol, pentachlorophenol and pesticides such as atrazine, molinate and propazine from wastewater using microporous alumina pillared with montmorillonite (clay) material [151]. The removal efficiency of the pillared clay material for the herbicide was found to be higher than mesoporous aluminium phosphate due to the substitution of the alkyl lateral chains of the aluminium phosphate during the adsorption of atrazine and the increase in phosphorus/aluminium (P/Al) ratio during the adsorption of propachlor. Furthermore, Faust and Aly recommended AA for the removal most inorganic compounds due to its affinity for inorganic anions, which they reported to have 100% recovery ratio especially for As (V), Se (VI), and the F^- ion [156].

2.2.3.4 Cyclodextrin

Cyclodextrin (CD) was first reported by Villier in 1891 based on his study on enzymatic degradation of starch by the starch-degrading enzyme (amylase) in *Bacillus macerans*; this he called ‘cellulosine’ [157]. Franz Schardinger [158] and his co workers developed a detailed method of isolation, synthesis, separation and elucidation of CDs [158]. This developed method takes advantage of the solubility of CD oligomer to be easily manipulated using organic solvents to induce the selective precipitation. Formation of inclusion complexes such as host-guest types with organic compounds is very common with CD moieties. CDs are non-reducing cyclic oligosaccharides resulting from the cyclomaltodextrin glucanotransferase which is catalysed by the degradation of starch. There are three common types of CDs with 6 (α-CD), 7 (β-CD) or 8 (γ-CD)-glucopyranosyl residue linked by α-1, 4 glycosidic bonds (Figure 2.8). β-CD is the most useful, less expensive and commonly explored among all the CDs [159, 160]. Moreover, higher-molecular-weight CDs have been synthesised and isolated although this has limited their industrial application. All CDs are organised by 6 to 8 glucopyranoside units, and have a toroidal or hollow truncated cone shape (Figure 2.8).

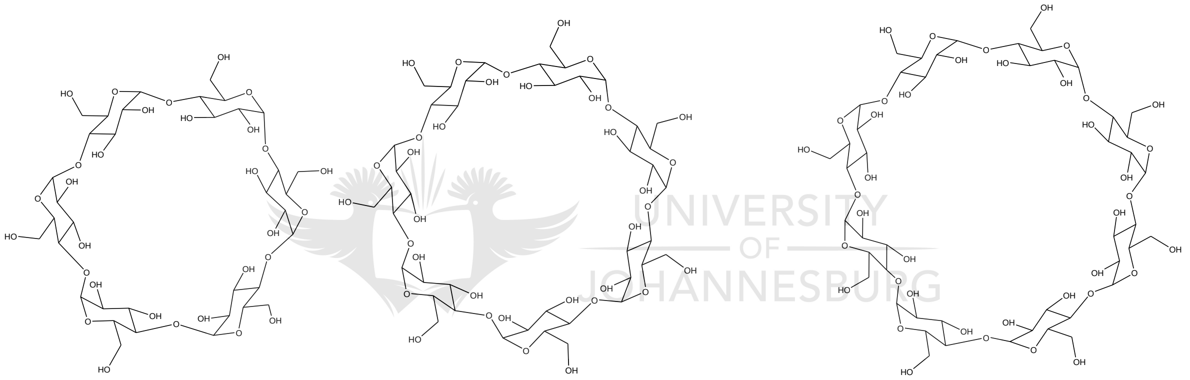

Figure 2.8: (a) α-CD, (b) β-CD, (c) γ-CD

The toroidal openings which CDs employ during reactions are of two types; the larger opening is exposed to the solvents during secondary hydroxyl groups, while the smaller opening is exposed to primary hydroxyl groups. This arrangement enables the toroid to have a hydrophobic interior when compared to the aqueous environment that enables hosting of molecules in the CD cavity. In contrast, the toroid exterior is hydrophilic, thus enabling CDs or their complexes to be water-soluble (Figure 2.9).

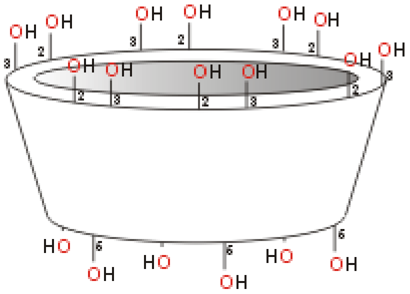

Figure 2.9: Hydrophobic interior and hydrophilic exterior of CD

2.2.3.4.1 Modification in cyclodextrin

Cyclodextrins can be chemically modified in order to vary their solubility properties or behaviour which enables it to entrap pollutants. In modifying CDs, their complexation properties (stability constant and guest selectivity) are manipulated in order to introduce functional groups that can achieve a specific purpose in trapping pollutants [161]. The need to convert CD to a highly crosslinked polymer is necessary in order to achieve this pollutant trapping due to CD water solubility [162].

2.2.3.4.2 Mono-functionalisation

This is a type of functionalisation that involves only one hydroxyl group out of the numerous hydroxyls that are present in CDs. This can be achieved by a reaction of the hydroxyl group with electrophile. This type of reaction is difficult to achieve due to complications experienced in enabling modification at a single desired position.

2.2.3.4.3 Per-functionalisation

This is functionalisation of an entire set of hydroxyl groups. Di- and tri-functionalisations exist but are difficult to produce due to limited studies done on it.

2.2.3.4.4 Polymerisation in cyclodextrins

Cyclodextrin applications have been hindered substantially due to their solubility especially in water treatment. Thus, converting CD into water-insoluble CD entities is very important if CD is to be fully utilised in water-treatment processes. To make this possible CD and its derivatives may be polymerised with suitable bi-functional linkers to produced water-insoluble CD polymer [163-165]. This is done by allowing the hydroxyl groups present in the CD or its derivatives to react with a suitable linker (i.e. monomer) in order to produce insoluble polymers. The result obtained during the polymerisation step depends largely on the type of linker employed during polymerisation reaction. The product solubility in both inorganic and organic solvents depend largely on the crosslinked chain produced during polymerisation [166].

2.2.3.5 Zeolite

The drawbacks of high regeneration and production cost which limit AC applications have made researchers to turn to zeolites as an alternative adsorbent. Zeolites are a group of natural or synthetic hydrated aluminosilicate minerals which contain both alkaline and alkali earth metals or accommodates a wide variety of cations. Zeolites have large surface areas and a well-defined porosity. It has been employed as an adsorbent, catalysts, ion-exchangers and molecular sieve over the past decades, due its large effective surface area and chemical properties which give them their superior adsorptive qualities [167]. There are several types of zeolites such as MCM-22, ZSM-5, ZSM-22, BETA, and Y. Denayer and his co workers studied the adsorption equilibrium of zeolites and established that the synthetic zeolites have a higher adsorption capacity than the natural zeolites for the removal of dyes and ink from polluted wastewater [168]. Treacy and Newsman reported that BETA zeolite was first synthesised in 1967 by Mobil but its configuration was only determined in 1988 [169]. It has a large pore structure and it is widely used as catalyst support and adsorbent for separating mixtures consisting of aromatic compounds [170]. However, they show little affinity for organic compounds in water. Because of this limitation, zeolites are not often employed for the effective removal of organic compounds from aqueous media.

2.2.3.6 Polymeric adsorbent

The polymeric adsorbent composite is another promising adsorbent material in separation technology, especially in wastewater and water treatment. The polymeric adsorbents are produced by crosslinking different polymers with a wide range of functional groups to give rigid microporous structures having high surface areas [171-174]. These materials possess high adsorption capacities for selected organic compounds and can be regenerated more easily and rapidly than other adsorbents especially AC [159]. They are regenerated by thermal regeneration using steam, hot nitrogen or air, microwave heating or indirect contact heating. Polymeric adsorbent composites find application in both reactive and control organic compounds which can undergo a variety of surface chemical reactions on the AC [172, 173, 175]. The main drawback of this material is the cost and it is more expensive than zeolite and AC [173, 176].

2.2.3.7 Polyurethane adsorbent

In polymer science material polyurethanes (PUs) stand tall because of their versatility and applications in material science. Their applications range from electronic appliances to thermoplastics used in footwear and medical devices production, roof and rigid foam applicable as insulators in walls, to flexible foam in furniture upholstered, to applications as sealant, elastomer, coating, adhesives, automobile interiors, tile floors and carpets [177, 178].

Polyurethanes are environmentally friendly and their applications have steadily been on the increase in the past three decades mainly due to their cost benefits, energy saving cost, and increased comfort. [177]. Polyurethane toughness and durability have contributed to the long shelf life of many products, thus making it a sought-after polymer material. These factors listed cum resource conservation and product shelf life extension are the key environmental factors considered in many applications of products development. Polyurethanes belong to a class of thermoset and thermoplastic polymers which can easily be tailored through their chemical, mechanical and thermal properties by reaction of various polyols (monomers) and polyisocyanates which serve as linkers, to produce either the hard or soft segment part of the urethane chain in the polymerisation reaction. PU based polymer has significant amount of urethane (-HN-COO-) group, irrespective of the number of the molecules [179-183]. However, attention has been of recent drawn to applicability of polyurethane in composite material in order to improve thermal stability and adsorption capacity of adsorbent in water and wastewater treatment. This new area of PU application is gaining more recognition in separation technologies thus, making researchers interest on the material to be on the increased.

2.2.3.7.1 Modification in polymeric material as adsorbent

Surface modification of polymeric material with AC or other inorganic substances involve process reactions such as oxidation which is followed by grafting onto AC with polymeric material by methods which include electrochemical [184-188], chemical[187-189], plasma or ozone [190], and microwave treatment [191] in a bid to introduce, for instance, organic functional groups like amine or carboxylic onto it [192, 193]. This oxidation process is achieved basically by using an oxidising agent, which includes hypochlorite, hydrogen peroxide, nitric acid, perchlorate and permanganate [192]. Oxidation which is described as a radical mechanism [194] normally favours an aromatic system during nitration, while the homolytic cleavage process favours an aliphatic hydrocarbon system [194]. Furthermore, in cyclodextrin CDs, especially β-CDs, modification can occur electrochemically by attachment of β-CDs onto the surface of the carbon fibre through covalent attachment of a chitosan polymer [187]. The covalent attachment of β-CDs, chitosan and carbon nanotubes (CNTs) has also been reported [195-197]. In another study a chemical carbamate bond formed between single-walled nanotube (SWNT) surface acid group and β-CDs crosslinked 1-4 phenylene diisocyanate (PDI) has been reported [198]. Polymer surface modification of the hydroxyl groups on β-CDs using glutaraldehyde (GA) as linker produced during the formation of a hemiacetal bond between the hydroxyl groups of polyvinyl alcohol polymer or polyacrylate micro-beads [199] has also been reported. The formation of a polyurethane or urethane bond, ethylene glycol di-epoxypropyl ether (EGDE) and epoxides is a strategic polymerisation of CDs that is open to surface grafting of CDs onto AC by employing a cross-linker such as isocyanate, by forming a hemiacetal bond [200], polyether, or glutaraldehyde [162]. The polymer-based CD materials provide a synergistic binding behaviour due to the presence of CD inclusion sites or intrinsic micropores and non-inclusion micropore domains or interstitial micropores in the composite materials [201-203].

2.2.3.8 Activated carbon

Activated carbon belongs to classes of microporous materials employed in diverse commercial applications as an adsorbent for the removal of both inorganic and organic pollutants in either liquid or gaseous phase, together with other numerous applications. Activated carbon is a carbonaceous adsorbent material with amorphous structure and highly developed internal pore structure, pore size and pore volume. Activated carbon can be produced from a number of carbonaceous (carbon-rich) materials such as agricultural waste residue (AWR), coal, coconut shell, peat/lignite, lignin, wood, etc. The adsorption capacity of AC results from its large microporous specific surface area (SSA). This large SSA is the major contributing factor to its ability of removing large amounts of impurities/contaminants in a relatively small enclosed space. The adsorptive nature of AC is due to its large microporous surface area; AC is composed of ordered carbon atoms in AC aromatic planes. These graphitic planes from the AC aromatic planes form crystallites, which are similar to those found in graphite. However, the differences between AC and graphite are in the angular orientations of the planes which are random to each other in ACs, but are well-ordered in graphite. Activated carbon is associated with numerous amounts of heteroatoms such as hydrogen, nitrogen, oxygen, phosphorus and sulphur that exist in the form of atoms chemically bonded to their structure and/or functional groups. Furthermore, in the carbon matrix, oxygen is the predominant heteroatom present in the form of functional groups, together with others, which include carboxyl, carbonyl, phenols, lactones, quinones and others. The unique adsorption properties of AC can be significantly influenced by these functional groups. The surface chemistry present in AC, i.e. surface oxygen complexes, is created by two major oxidation methods, namely dry and wet. The dry method involves reacting oxidising gases (such as steam, CO_2, air, etc.) with carbonaceous material at high temperatures (> 500°C), while wet oxidation involves reaction between oxidising solutions such as aqueous nitric, hydrogen peroxide, ortho-phosphoric and sulphuric acids at low/reflux temperatures (300° C) with AC surfaces [204-206].

2.2.3.9 Water contaminants and removal technique

The most common toxic pollutants present in water and wastewater streams include inorganic heavy metals such as Cd^{2+}, Cr^{3+}, Cr^{6+}, Pb^{2+}, Hg^{2+}, As^{2+}, ionic compounds such as fluoride and cyanide, organic pollutants such as phenolic compounds (PCB, PBDE, dyes, etc.), and microbial contaminants [204]. There are numerous techniques employed in wastewater purification and these include ion exchange, reverse osmosis (RO), as well as intensive processes like chlorination and ozonation and adsorption. The adsorption process is one of the most economically viable and effective techniques in water purification, and AC has been in the centre of the achievement by its proven record as an effective adsorbent for the removal of a number of contaminants from drinking water and wastewater. Activated carbon has tremendous affinity toward both inorganic and organic contaminants in water. In order to enhance its adsorption capacity and make it more competitive toward specific contaminant /pollutants like inorganic or organic species, it is of paramount importance to modify the AC surface. The surface modifications of AC result in the change in the surface reactivity, chemical, physical and structural properties.

2.2.3.10 Types of surface modification techniques in AC

One of the most interesting things about the properties of AC is that its surface can be suitably modified to change its adsorption capacity and characteristics in order to tailor this adsorbent to suit a particular application [206].

The surface of AC may be modified based on the type and nature of the adsorbates in order to enhance the affinity toward a targeted contaminant. Activated carbon, an inert porous carrier material, has a large specific surface area (SSA) that is capable of attracting a number of chemical ions onto its internal surface which has hydrophobic properties. There are different methods by means of which AC can be modified to improve its surface accessibility; this depends on its application. Generally, surface modification of AC is normally carried out after an activation step. The modification can be classified into three categories, namely: chemical modification, biological modification and physical modification. Chemical modifications can further be divided into two categories: Firstly, by the impregnation with chemicals to modify the surface of AC with alkali metals and their oxides; and secondly, by impregnation with chemicals resulting in an acidic and basic AC surface.

The biological modification of AC is a relatively new approach of surface modification and this is done by using biological methods of environmental control for water-treatment applications. The physical modification involves thermal treatment of AC for surface modification [204, 206].

2.2.3.10.1 Chemical modification

The activated carbon surface can either show acidic, basic or neutral behaviour depending on the surface functional group present on the AC. These functional groups, for instance in the removal of metal ions from wastewater samples, the acidic functional groups present on the carbon surfaces of AC highly favour the metal removal by forming metal complexes with negatively charged ions from the acid [204, 206]. During the chemical modification process all the chemicals employed are oxidising agents which are used mainly to create acidic surfaces on AC which leads to reduction in SSA, due to destruction of the porous structures of AC [204]. However, the chemical modification of the AC surface which produces basic groups is carried out by surface treatment of AC with ammonia or alkali hydroxide [204]. Moreover, in chemical modification techniques the oxidation processes result in reduction of internal surface area (ISA) and pore volume (PV).

2.2.3.10.2 Physical modification

This method of treatment, i.e. heat/thermal method, has been the most commonly mentioned method for surface treatment of AC. Thermally treated AC in an inert atmosphere often results in a basic nature [204, 206]. Physical modification using thermal or heat treatment results in enhancement of physical characteristics (such as S_{BET} surface area and total pore volume (TPV). However, this physical enhancement is limited as a result of decomposition at high temperature which makes the surface oxygen functional groups to be thermally unstable. This can result in the reduction of adsorption capacity of AC. It is because of this drawback that plasma treatment was introduced to enhance thermal treatment without changing the characteristic properties of AC [204, 206].

2.2.3.10.3 Physical modification with gaseous treatment

These groups of modification include: Carbon-halogen surface groups formed by treatment of AC with halogen in solution or gaseous phase; carbon-hydrogen surface group formed by treatment of AC with hydrogen gas at a very high temperature; carbon-nitrogen surface group formed on treatment of AC with ammonia; carbon-oxygen surface group formed on treatment of AC with oxidising solution or gases; carbon-sulphur surface group formed on treatment of AC with elemental sulphur, carbon disulphide (H_2S) and sulphur (IV) oxide (SO_2).

All of these surface groups are attached by being bonded or retained at the edge of the carbon aromatic sheet present in AC. These edges constitute the main adsorbing surface in AC which they expect to modify, i.e. the adsorption behaviour of AC and its adsorption properties and characteristics [206]. Furthermore, AC modification can also be done by degassing and by impregnation of the surface with an oxidising agent.

2.2.3.10.4 Method of surface modification

The concentration and nature of AC surface functional group can be modified by tailoring it through suitable chemical or thermal post treatment method. This can be done, for instance in carbon-oxygen surface groups, by firstly oxidising the AC material/substance in the liquid or gaseous phase in order to increase the concentration of surface oxygen groups while heating the substance in an inert environment. This will thus increase the concentration of the hydroxyl and carbonyl surface groups if oxidation is done in the gaseous phase, while if in the liquid phase oxidation increases the concentration of carboxylic acid on the surface of AC [207, 208]. However, ammonisation of AC could introduce basic groups such as amino, cyclic amides, C-H, C=N groups, nitrile and pyrrole-like structures onto it [209].

2.2.3.10.4.1 Acid treatment

This type of treatment is generally used to oxidise the porous carbon surface in order to enhance its acidic property, improve the hydrophilic of the AC surface and remove the elemental mineral from the carbon surface [210]. Nitric and sulphuric acids are mostly used in these types of method. Coconut-based AC produced by acid method showed excellent adsorption performance for Cr^{6+} (Cr (IV)) removal from aqueous solution [211], where the modification caused the specific surface area to decrease and increased the total number of surface oxygen acidic groups. Shim and his co-workers modified pitch-based activated carbon fibre (ACF) with nitric acid and sodium hydroxide. The results obtained showed a three-fold increase in total acidity when compared to untreated ACF and a decrease in specific surface area [212].

2.2.3.10.4.2 Ammonia treatment

Ammonia treatment method of AC gives AC produced through this method an advantage because of the nitrogen-containing surface groups which tend to increase the ability of AC to adsorb acidic gases [213]. Nitrogen can be introduced into the structure of AC through several ways, including preparation of AC adsorbent from polymers, such as acrylic textile, Nomex® aramid fibre or polyacrylamide, or treatment of AC with ammonia [214-216]. Mangun and his co-worker reported the formation of a new ACF that contains C-N and C=N groups, cyclic amides, nitrile groups produced by heating phenol formaldehyde based ACF in atmosphere of dry ammonia at an elevated temperature of between 500^{o}C and 800^{o}C [217].

2.2.3.10.4.3 Heat treatment

The heat-treatment method favours the concentration and nature of surface functional groups that are modified by thermal or chemical post-treatment. Heating AC substance/material in gaseous or liquid phase tends to increase the surface concentration of oxygen surface groups, while heating in an inert atmosphere/environment tends to selectively remove these functional groups [218]. Activated carbon produced by thermal method which has a basic character and as such had been applied in the treatment of organic hydrocarbon, has been reported [218]. Thermal treatment of AC in an inert environment, such as in hydrogen (H_2), nitrogen (N_2), or argon (Ar) flow, has been known to increase AC hydrophobicity by removing hydrophilic surface functionalities, i.e. various acidic groups [219-222]. Hydrogen treatment of AC has been reported to be more effective than inert treatment because of its ability to effectively stabilise the carbon surface by deactivation of carbon active site by forming stable C-H bonds and gasification of unstable reactive carbon atom found at the edge of the carbon crystallites [220, 223].

2.2.3.10.4.4 Microwave treatment

The merit of microwave heat treatment is in the reduction of treatment time which in many cases represents reduction in the energy cost and consumption. Polyacrylonitrile activated carbon fibre (PACF) has been produced through microwave thermal treatment [224]. The

PACF produced by microwave treatment affected the porosity of the ACF, by causing a reduction in the micropore size and micropore volume. However, the microwave treatment was very effective for surface modification of the surface chemistry of ACF with the production of pyrone groups due to the introduction of basic carbon [225].

2.2.3.10.4.5 Ozone treatment

Ozone is a strong oxidizing agent, and can be applied in organic degradation of the carbon surface, i.e. it can also oxidise the carbon material surface in order to introduce oxygen-containing groups to the surface of the material. The resultant oxygen-containing groups and oxygen concentration on the carbon surface are affected by the amount of dosage of ozone and oxidation time employed [225, 226]. Alvaraz and his co-workers reported the impact of ozonation treatment of two coal-based ACs on their textural and chemical surface characteristics and ability to adsorb phenol, p-nitrophenol and p-chlorophenol from aqueous solution [71].

2.2.3.10.4.6 Plasma treatment

The plasma treatment which is a more recent method is regarded as a promising technique of modifying the surface property of porous carbon material by producing chemically active species that can affect the adsorbability or adsorption capacity of AC. In plasma treatment, the chemical reaction tends to be slower by chemically active species; these reactions take place on the surface of AC without changing its bulk properties. At low pressure during the duration of the treatment [204, 227], plasma could introduce acid and basic functional groups that determine the gaseous resources [227]. Furthermore, plasma treatment can also be an oxidation process wherein AC is exposed to plasma under vacuum or atmospheric pressure in the presence of controlled air or oxygen. The oxidation process takes place with substantial changes in the surface chemistry of AC in contrast to few textural changes in the AC texture, thus leading to an increase in the surface acidity of AC due to the reaction of free radical oxygen with carbon atoms located at the peripheral surface of the graphitic platelets [204, 228].

2.2.3.10.5 Other modification treatments

Other forms of modification include air and steam activation which is commonly used for pore formation and introduction of oxygen-containing functional group onto the AC surface. Air oxidation of rayon ACF has been reported to increase the amount of surface oxygen-containing functional groups such as carboxylic acids and quinines [228, 229]. Furthermore, Budinova and his co-workers reported furfural-based porous AC to have shown basic and acidic character after its activation with steam and air and its ability to be an effective adsorbent for the removal of mercury from aqueous solution [230].

2.2.3.10.6 Modification of porous carbon for electrode material application

Porous active carbon can also be employed as electric double layer capacitance of the material mainly by improving the wettability of the material, producing the pseudo-capacitance effects and increasing the capacitance [231-233]. This effect has been qualitatively investigated in terms of temperature-programmed desorption of oxygen-containing functional groups on electrical characteristics [228, 231-233].

2.2.3.10.7 Modification by impregnation

Activated carbon impregnated with metals and their oxides dispersed as small particles have been widely used in several gas-phase reactions in both industry and for human protection against hazardous gas or vapour. The impregnation of metals onto carbonaceous material can modify the gasification characteristic and alter the pore structure of the final AC. Thus, impregnation has also been used to obtain active carbon with a microporous structure [234].

2.2.3.10.8 Mechanism of contaminant removal from water by AC

The mechanism/pathway of the AC adsorption process occurs in two ways; physisorption and chemisorption. Physisorption is a process of physical attraction of the adsorbate molecular structure onto AC, while chemisorption is the chemical attraction of the adsorbate onto AC by repelling water on the AC structure. The AC adsorption process occurs through three major steps; these are:

- Adsorption of the adsorbates to the exterior of the carbon surface
- Movement of the adsorbate into the adsorption pore of carbon/AC with highest adsorption potential energy
- Adsorption of the adsorbates into the interior graphitic platelets

The starting carbonaceous material with different composition and the activation process results in varying unique pore distribution and pore size of AC. Activated carbon pore size in terms of its diameter is commonly described as micropore (< 2 nm in diameter), mesopore (2 nm to 50 nm in diameter), and macropore (>50 nm in diameter). The most commonly employed AC in water separation/treatment technology includes AWR, anthracite and bituminous coal, coconut-based AC, etc.

2.3 EXISTING TECHNOLOGIES AVAILABLE FOR WATER DECONTAMINATION

There are numerous technologies employed in the water-decontamination process in order to make water safe for human consumption. These processes include the following:

2.3.1. Adsorption process

The adsorption process is a well-known equilibrium separation process and has been found to be superior compared to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. It has also been recognised as an efficient, effective and economical method for application in the water-decontamination process, separation or extraction analytical procedure [235]. In adsorption processes, the choice of adsorbent is a critical step for an effective water-treatment process. The adsorbent choice may be of biological, mineral, organic or biomass origin [235]. Examples of adsorbents include AWR [236, 237], biomass [238, 239], AC [240-242], low-cost adsorbents of industrial by-products [243, 244], clays [245, 246], polymeric materials (organic polymeric resins) [247, 248], macroporous hyper-crosslinked polymers [249], silica beads, [250], and zeolites [251].

2.3.2. Biological treatment

The biological treatment process can be achieved by either the degradation or transformation of organic/inorganic compounds in wastewater by biological means, i.e. by using specific microorganisms such as aerobic and anaerobic bacteria and fungi to biodegrade waste [252]. Kornaros and Lyberatos have reported that biological processes such as the advanced oxidation process, aerobic and anaerobic digestion, and trickling filters are some of the most feasible and cost-effective processes for removing inorganic and organic compounds from wastewaters stream [253].

The biodegradation process is also a form of biological treatment which involves the use of microorganisms such as bacteria, yeasts, algae and fungi which can accumulate and degrade different kinds of pollutants. However, their application in the water-treatment process is often restricted due to the technical constraints encountered in the course of its operation. Biological treatment is a highly sensitive and complex operation that requires flexibility in design and operation due to its usage of large tracts of land in order to be sensitive toward diurnal variation as well as toxicity of some chemicals. With current conventional biodegradation processes, biological treatment is incapable of satisfactorily removing some classes of organic pollutants [254].

In addition, Kornaros and Lyberatos [253] reported that a trickling filter is a biological process developed for treating combined effluent or wastewater. They stated that the filter is operated aerobically, either in sequencing batch reactor operation mode or continuous reactor operation mode [253]. The process takes place in a dynamic reactor consisting of bacterial supporting growth material (silica gravel), feed wastewater and the filter. They also stated that conventional biological treatment methods for treating organic compounds are not the most effective means of removing pollutants generated from organic synthesis operations, such as dyes. This is due to the presence of high POP, improper population of microbial and high concentration of toxic organic compounds [253].

2.3.3. Chemical oxidation treatment

Chemical oxidation treatment is a process performed on wastewater to either selectively modify pollutant's toxicity by way of altering its chemical nature or prepare a specific contaminant for removal from the aqueous medium. The process requires the utilisation of strong chemical oxidisers in order to destroy and remove organic pollutants within polluted wastewaters [255]. A number of oxidising agents are employed in wastewater treatment; these include: ozone, potassium permanganate, chlorine dioxide, chlorine and hydrogen peroxide [252, 255]. Recently, Kurniawan and his co-workers reported the combination of ultraviolet light with ozone and hydrogen peroxide which they applied in various advanced oxidation technologies in treating recalcitrant organic compounds [256].

2.3.3.1 Chemical oxidation with ozone

Application of ozone wastewater treatment is not a new method. Ozone application in wastewater treatment is a tertiary wastewater treatment method for removal of POP which comes after bulk removal of the pollutants has been accomplished by less expensive processes.

Kurniawan and his co-workers in their studies reported that ozone oxidation occurs either by direct electrophilic attack of the ozone molecule on the pollutants or by the generation of the hydroxyl radicals due to ozone decomposition and subsequent attack by the radicals on the pollutant [256]. The use of ozone as an oxidant does not create any secondary pollutants in the environment when compared to the carcinogenic halogenated hydrocarbons or chlorinated by-products obtained during the application of chlorine as oxidant [257]**.** The only limitation of the process is cost.

2.3.3.2 Chemical oxidation with hydrogen peroxide

Hydrogen peroxide in chemical oxidation reaction cannot alone efficiently degrade organic pollutants mainly due to its slow self-decomposition and slow reaction rates with organic pollutants. However, Neyens and Baeyens, have demonstrated the ability of hydrogen peroxide to remove organic compounds which depends on an intermediate association to yield hydroxyl radicals, $OH\cdot$ and HO_2 [258]. Titus and his co-workers also stated that these hydroxyl radicals are responsible for the removal of organic compounds from aqueous solutions [86]. In addition, hydrogen peroxide can be used to initiate reactions in chemical oxidation process of wastewater solution by producing free radicals which rapidly react with the targeted organic compounds [255].

2.3.3.3 Chemical oxidation with potassium permanganate

Potassium permanganate is known to be a strong oxidising agent; its efficiency can be improved when combined with other water-treatment methods. Potassium permanganate has been reported to readily react with impurities such as inorganic ions, phenol and radio-active contaminants. Furthermore, Weber also reported application of potassium permanganate in the complete removal of iron and manganese in a wastewater subjected to aeration treatment [255]. Al-Kdasi and his co-workers in their investigation reported that highly toxic organic compounds in wastewater such as phenol can be quantitatively degraded or mineralised to carbon dioxide and water or transformed to less harmful compounds with a strong hydroxyl radical [259]. The oxidation conditions and strength of an oxidant determined the intermediate oxidation products formed after this reaction [255]. In addition, Lagrega and his co-workers stated that formation of unwanted products as a result of by-products in chemical oxidation of wastewater treatment will lead to further treatment which is not economical due to the increase in oxidation time and the production cost of the oxidising agent employed. Chemical oxidation processes are more economical when the concentrations of the organics to be removed are very low [252].

2.3.4 Conventional treatment

The conventional wastewater treatment method includes coagulation, flocculation, precipitation-flocculation coagulation with $Fe(II)/Ca(OH)_2$, electrokinetic treatment, reverse osmosis, conventional oxidation by oxidising agents, sonochemical treatment, filtration and an electrochemical method. The above-mentioned are some of the most common conventional treatment methods employed in developed countries, especially in the United States [252, 254].

2.3.4.1 Air stripping

Another method applied in conventional treatment process is air stripping. This is a phase change process that is employed in removing volatile organic compounds VOCs from contaminated wastewater by providing contact between the gas (air) and pollutant in wastewater. The air stream acts as a means of transferring the pollutant into the atmosphere [252]. Although, this process leads to secondary air pollution, it is very effective for water purification. Thus, the transferred pollutant also causes air pollution thereby increasing the operation complexity and the cost of cleaning the air stripper unit. Chang and his co-workers reported the utilisation of the combination of air stripping and biodegradation for the removal of BOD from wastewater by using a laboratory-scale submerged membrane bioreactor [260].

2.3.4.2 Sonochemistry

Sonochemistry is another form of conventional treatment employed in wastewater treatment. Sonochemistry is the study of mass transfer and chemical reaction rates within a liquid phase under different ultrasonic conditions. The application of ultrasound to treat organic wastewater involves the destruction of targeted pollutants either indirectly through the production of oxidation species such as hydroxyl radicals or directly through activating their thermal decomposition [261]. Kidak and Ince [262] reported that the removal of pollutants depends on the process operating parameters such as frequency, pH, dissolved gases, reactor geometry, chemical reagents and catalyst used [261].

Petrier and his co-workers reportedly carried out an investigation on the dechlorination of 4-chlorophenol at 500 kHz, [263], while Lin and Ma [162, 264] also investigated the effects of initial solute concentration, pH and $FeSO_4$ on the decomposition of 2-chlorophenol in an aqueous solution containing a chemical oxidant (H_2O_2) under varying ultrasonic conditions.

They found that the decomposition rates were 6.6 times and 9.8 times higher, respectively, at pH 3 than at pH 11 [264].

2.4 COMPOSITE MATERIALS IN WATER DECONTAMINATION

Composite materials represent a well-defined combination of structurally and chemically different constituent materials that are heterogeneous. This is done by ensuring that they retain required properties which include low density, mechanical strength, stiffness or other characteristics depending on their application. In addition, they are materials which comprise two or more physically distinct phases whose combination produces aggregate properties and synergistic effects that are different from those of its original constituents [30, 265]. These qualities enable composite materials to find application in water/wastewater treatment.

2.4.1 Batch adsorption process

A number of polymeric composite adsorbents have been tested for their pollutant-binding capability under different condition. Chiou and Li [266, 267] reported the adsorption of dyes onto crosslinked chitosan beads prepared from glutaraldehyde (GLA), epichlorohydrin (EPI) and ethylene glycol diglycidyl ether (EGDE) as crosslink agents. The beads recorded high uptake of dye solutions which increased with decreasing particle size due to high effective surface area of small-size particles. Furthermore, in their own study Wan Ngah and his co-workers using various crosslinked chitosan composite, i.e. chitosan-GLA, chitosan-EPI, and chitosan-EGDE reported application of the composite in removing metal ions from aqueous solutions. They reported that the process is pH-dependent [268]. Guibal *et al.* [269] have also done numerous studies on chitosan composites. They reported using the chitosan beads composite for the removal and the recovery of toxic or valuable precious metals such as arsenic [269], molybdenum[270, 271], vanadium [271], platinum [272, 273], palladium [274], osmium [275], iridium [275] and gold [276]. However, from a literature survey of plant polymer application in wastewater treatment, it is clear that for water-decontamination applications, the principal polymer employed or of interest is chitosan. However, the tides are changing due to increasing attention being given to the other carbohydrate polymers such as cyclodextrins and starch [235]. Zhang and Chen [277] reported crosslinked-starch graft copolymers containing amine groups and applied it for the removal of Pb(II) and Cu(II) ions from aqueous solutions. The polymer employed was prepared by grafting dimethylaminoethyl methacrylate onto commercial starch. They established that 2 hours of adsorption was enough to reach adsorption equilibrium and adsorption capacity.

In another development Janus and his co-workers [278] proposed the use of 2-hydroxy-3-methacryloyloxy-propyl-beta-cyclodextrin as monomer for the synthesis of cyclodextrin-based materials. The composite materials, i.e. the newly formed hydrophilic β-CD adsorbents were prepared by radical copolymerisation in water using 2-hydroxyethyl methacrylate or vinylpyrrolidone as co-monomers. Several materials with various degrees of CD were synthesised and then applied for wastewater treatment. The experimental adsorption results showed that they exhibit high adsorption capacities especially toward benzene and its derivatives.

Ann and his co-workers reported application of nanocomposite materials prepared (by liquid phase mixing cum casting) from polylactic acid (PLA), graphene oxides (GO) and polyurethane (PU PLA/GO/PU). The produced composite material exhibited good antibacterial activity against gram-positive *Staphylococcus aureus* and the gram-negative *Escherichia coli*, due to the excellent antibacterial property of GO sheets with high specific surface area produced on the surface of the composite [279].

2.4.2 Solid-phase extraction procedure

Numerous materials with varying degrees of CDs have been synthesised and then applied in wastewater treatment. The ability to control the crosslinking reaction is the key factor that governs adsorption capacity or properties of a polymer adsorbent. Yu and his co-workers [280] reported a novel adsorbent for the solid-phase extraction (SPE) procedure which they employed in trace aromatic compounds extraction from aqueous solution. The method they employed is based on the use of cyclodextrin–EPI copolymer as adsorbent. This composite adsorbent produced very high extraction efficiency with recovery percentage ranging between 90% and 100% for aromatic compounds. Kitaoka and Hayashi [281] in their own study reported the possibility of the removal of bisphenol A (BPA) from wastewater by using highly crosslinked cyclodextrin–EPI copolymer. This was done by stirring 5 mg/ml of copolymer in a 0.2 mmol BPA solution for 2 h, more than 98% of the BPA was removed by the process. Fan and his co-workers [282] investigated the use of a cyclodextrin bonded silica as sorbent for on-line solid-phase extraction (SPE) coupled to a chromatographic system. The resulting adsorbent produced showed strong capacity in adsorbing p-nitrophenol. While in their own finding, Phan and his co-workers [283, 284] studied different series of supports containing cyclodextrin for their ability to adsorb aromatic pollutants. The adsorbents are produced by coating or grafting cyclodextrin derivatives (in particular, monochlorotriazinyl and methacryloyl derivatives) [284]. The sorption capacity of the two kinds of supports was very close for a given pollutant. Lue and Peng [285] have prepared polyurethane membranes containing CD by using a two-stage synthesis procedure. The product formed demonstrated outstanding pervaporation properties on benzene/cyclohexane separation. The CD membrane permeability and selectivity properties are very good when compared with those of other polymers. Pervaporation experiments for separation of xylene mixtures were carried out by Chen and his co-workers [286] using polyvinyl alcohol (PVA) membranes filled with CD. The results indicated that the pervaporation rate was effectively enhanced by the performance of the new membranes. Steenkamp and his co-workers [287] reported adsorption of Cu(II) ions onto composite alumina/chitosan membranes. They found the metal-ion capacity of adsorption was about 0.2 g Cu/g chitosan. The hybrid materials, as in this case, are preferred due to their chemical stability as a function of pH. Le Thuaut *et al.* and Martel *et al.* [288, 289] reported a novel method for the preparation of immobilised CD on polypropylene non-woven fabrics. The new composite materials were prepared by graft-polymerisation of glycidyl methacrylate onto filters using the electron beam technique, following the coupling of CD with the epoxide group.

Furthermore, quaternary ammonium such as poly(dimethyldiallyl ammonium chloride (PDDA), a water-soluble cationic polyelectrolyte polymeric material, has been used when dissolved in aqueous solution to coat negatively charged surface of multiwall carbon nanotube MWCNT by electrostatic interaction, which was applied in removal of PCB from aqueous stream through formation of inclusion complex [290]. The removal of PCB was achieved by grafting polymeric material PDDA on the surface of MWCNT which enhanced both extraction efficiency and the solubility of the composite [22].

Presently, many studies have reviewed incorporation of different materials, by way of incorporating special functional groups on the surface of adsorbents in a bid of enhancing their adsorption capacity for both inorganic and organic compounds, and improving dispersion properties in aqueous solutions [45, 291].

Nanomaterial adsorbent composites have played a huge role in separation process technology due to their excellent extraction efficiency and great solubility [292, 293]. These adsorbent nanomaterials cannot easily be separated or completely recovered in the aqueous phase during water purification which is due to their small particle size. In order to amend this limitation, a method such as solid-phase extraction was developed; for instance, mixing ionic surfactants with nanosized modified MWCNT where magnetic nanoparticles are adsorbed onto the ionic surfactant MWCNT +COO^-/ PDDA Fe_3O_4. Zeng *et al.* [294] reported the usage/application of magnetic Fe_3O_4 MWCNT composite in preconcentration of PCB from aqueous stream/solution [294]. When compared with the traditional solid-phase extraction (SPE) method adsorbent, the Fe_3O_4 attached properly to the modified MWCNT adsorbent, while the magnetic property of Fe_3O_4 enhanced the separation ability of the composite, thus reducing the run-time of the time-consuming SPE separation step [294].

2.5 INSTRUMENTAL ANALYSIS IN WATER TREATMENT

2.5.1 Organic compounds/pollutants analysis

2.5.1.1 Gas chromatography

Gas chromatography (GC) analytical technique is one of the most widely used instrumentation techniques for quantitative determination of organic pollutants in wastewater/effluent streams. This is because of its unparalleled sensitivity of detection and resolving power and its relative ease of operation. The concept behind GC is based on the selective interaction of the analyte (gaseous or semi volatile compounds) with the column film or column packing as the vaporised sample/analyte is forced through the column by a chemically inert carrier gas. The hallmark of a good GC analysis is to have good separation in the shortest possible period of time. The criteria responsible for this include the liquid phase of column, length (column length), internal diameter, temperature, and film thickness. The GC consists of basic components that include the following:

- a carrier gas cylinder with regulator
- a flow controller for the gas
- an injection port for sample introduction
- column, primary or secondary (1^o or 2^o) column
- the detector and recorder which can be coupled to a mass spectrometer (MS)

A number of detectors have been developed for GC technique especially for the analysis of organic pollutants, and they include electron capture detector (for halogenated hydrocarbons, halogenated pesticide residues, nitro group or oxygen-containing groups); nitrogen/phosphorus detector (for application to phosphorus and nitrogen-containing pesticides, organophosphates and carbamates); and the flame ionisation detector (suitable mainly for compounds containing the C-H bond/aliphatic organic compounds). Gas chromatography remains the technique of choice for many volatile or semi-volatile organic pollutants (VOC or SVOC) which can be derivatised. Gas chromatography offers excellent selectivity with good increasing detectors.

Moreover, the detector technology in GC has also developed in other areas outside/apart from GC. These include Fourier transform infrared (FT-IR) spectrometry and the atomic emission detector (AED) which can provide structural insight into eluted compounds. The atomic emission detector (AED) allows analysts to move away from the carbon-based detector to focus on other elements such as Br, Cl, F, N, P and S allowing molecules with particular elemental constituents to be identified.

In recent years significant improvements have been made in terms of column technology development in GC analysis/technique with the introduction of chiral column which is based on β-cyclodextrin. This new column development has the ability to separate enantiomers in SVOC in the field of environmental studies, thus allowing significant insights into their different degradation patterns and mode of action of chemical behaviour. The application of an enantiomer fraction gives a good description of compounds such as trans-chlordane, PCB 95 and 136, chiral hexa-chloroborane (CHCB) which has led to new insights into the behaviour in both biotic and abiotic environments. The amounts of input into decreasing analytical time have largely depended on improving the response time in detectors. A number of researchers have reported applications where fast GC has recorded complete separation within a few minutes. The two-dimensional gas chromatography with time-of-flight mass spectrometry (GC-GC TOFMS) has been reported to possess this quality. The coupling of time-of-flight mass spectrometry (TOFMS) into GC detectors is a selected detection system where the quadrupole system has sufficiently fast scan time to be in service or operation.

For instance, an online rapid membrane introduction mass spectrometry (MIMS) system has been reported to have permitted $\rho g / L$ analysis of several trihalomethanes (THMs) in water with a sample throughput of about 20 samples per hour. This fast GC-GC TOFMS combination has been applied in PCB analysis using GC with pulsed electron capture detection (ECD). Polybrominated diphenyl ethers (PBDE) in sewage sludge have been analysed by fast GC coupled with inductively coupled plasma MS (ICP-MS) with low $\eta g / L$ detection limits which was achieved within an analysis time of about 10 min.

The trends of improving selectivity in GC from single GC columns to the application/usage of two-column GC, or two-dimensional GC, have yielded good results. The merits of two-dimensional GC over single-column GC include affording analysts very high resolving power and can also be used to accomplish the separation of specific analytes from complex matrices where, on any single column analytes coelutes with several other compounds which makes their analysis difficult.

2.5.1.2 Separation methods in organic compounds

In chemical separation of organic compounds from water, there are two main methods employed; they are described in the sections that follow.

2.5.1.2.1 Separation of volatile organic compounds

2.5.1.2.1.1 Purge-and-trap method

The purge-and-trap (PT) method involves the separation of the volatile compounds from the aqueous matrix (for instance wastewater) by passing an inert gas through the matrix in order to purge. The separation takes place by desorbing the target VOC from the aqueous phase to the gas phase and separation takes place by trapping the gas through the adsorbent filter (which can be AC, or carbon, porous polymer beads or polymeric material, silica gel, etc.). The PT method uses very effective analytes that are insoluble or slightly soluble in water and have boiling-point temperatures lower than 200^{o}C/573K.

2.5.1.2.1.2 Headspace

The headspace (HS) method, when compared to the PT method, is less sensitive and it works by placing the sample in a sealed container, such as a vial, and leaving it in the container at a constant temperature until the gases in the liquid phase are in equilibrium. The target substance in the sample, which is in the gas phase (HS) is then collected by a gas-tight syringe and later injected into the GC-MS for analysis.

2.5.1.2.2 Separation of semi-volatile organic compounds

The methods are employed in the extraction of SVOC from wastewater/water streams includes LLE, SPE, and SPME.

2.5.1.2.2.1 Liquid-liquid extraction (LLE)

This method is the most common method for isolation and separation of SVOC and non-volatile organic compounds (NVOC) from wastewater/water sample. It is a method based on the partitioning of analytes from the aqueous phase to the liquid organic phase, thus a large amount of solvent is involved in its operation. In LLE, the hydrophobic analytes are extracted into an organic phase. The method is carried out by placing the sample (water sample) and the solvent in a separatory funnel, shaker bottle/flask and later this is shaken continuously or rotated in order to increase the surface area contact between the sample and the solvent.

2.5.1.2.2.2 Solid-phase extraction

This is a method where the water sample/analyte is passed through a cartridge and adsorbed onto a solid support, and this is then extracted by suitable solvent or by thermal desorption. The method is gaining recognition and rapidly emerging as a commercially viable method. It employs a variety of solid supports in a packed column; solid-phase extraction cartridges and disks are commercially available, for example, rigid disks, speed disks, resins, polymeric resin/adsorbents/materials, and silica gel. These cartridges/columns are filled with various phases of bonded material.

2.5.1.2.2.3 Solid-phase microextraction

This method is a modified form of the SPE technique. Analytes are isolated by passive isolation. SPME is a solvent-free method whose approach is to eliminate the usage of solvent when compared to the SPE method based on equilibrium sampling. Fused silica fibre coated with polymer phase bonded to a stainless steel plunger is the extraction medium and a holder that has a form of a microlitre syringe. In addition, SPME technology can also be based on application of hollow fibres which are internally coated with a small quantity/amount of suitable adsorbent/adsorbent of interest. The attractive features of this technology include:

- compatibility with both aqueous and gaseous samples case of integration into GC systems
- its relatively low cost and absence of liquid solvent
- the quantity of analyte removed from the system is normally a negligible proportion of the whole system

2.6 ANALYSIS OF ORGANIC COMPOUNDS PRESENT IN WATER/WASTEWATER

Presently, there has been increasing attention focusing on the identification, detection and quantification\quantitation of organics and emerging new pollutants in wastewater/water sample analysis. The analytical techniques employed for determining organic compounds in industrial wastewater require four general steps, which include

- Isolation (extraction and separation) of the target chemicals from sample matrix including surface water, wastewater, drinking water.
- Separation and purification of the target chemical from co-extracted non-target chemicals - sample clean-up.
- Sample concentration.
- Identification and quantitation by highly selective and sensitive analytical equipment.

The chromatography technique has been widely used for organic pollutant analysis in wastewater/effluent water streams. Gas or liquid chromatography is the most common chromatography instruments that are commonly employed in analytical techniques, especially in the analysis of organic compounds. LC is a technique employed when the sample involved in the analysis cannot be easily converted to gas from the liquid phase. Mass spectrometer (MS) should be employed for accurate quantification and identification of compounds. Although MS has lower sensitivity than other GC detectors, it gives more accurate and confirmatory result involving organic compound identification in a particular sample. PCB congeners and other trades names (such as Ancholor) are determined by either single/dual column analysis system or electron capture detector GC. The compound identification is based on single-column analyses which are confirmed on a second column or supported by confirmation technique of GC/MS (GC coupled with MS) for quantification analysis. The PCB extract use in the analysis may undergo clean-up using sulphuric acid (H_2SO_4) or potassium permanganate ($KMNO_4$) in order to remove the co-eluting organochlorine or organophosphorus pesticide, while the usage of sulphur clean-up is to remove interferences due to elemental sulphur.

2.6.1 Analytical techniques for determining pollutants in adsorption process

In order to determine pollutant in environmental samples, wide range of analytical procedures or methods are employed.

2.6.2 Selection of extraction method for sample preparation

In order to obtain good results from environmental samples, the selection of a technique for the extraction of sample analytes from the environmental matrices is crucial. Thus, the extraction method is selected on the basis of the chemical substance and their water solubility (solubility in water), depending on their physical/physicochemical characteristics which include boiling point, polarity and molecular weight. The method for isolating chemical compounds/organic compounds from water is based on the chemical category shown below in Tables 2.5 and 2.6.

Table 2.5: Classification of organic compounds by physicochemical properties (volatility) [293, 294]

↑	Volatility →			
	Types	Volatile	Semi-volatile	Non-volatile
	Polar	Alcohol, ketones, carboxylic acid, etc.	Alcohol ketones carboxylic acids Phenolic compounds, PCB	High molecular weight electrolytes, carbohydrates, fulvic acid
	Semi-polar	Ethers, esters, aldehydes	Ethers, esters, aldehydes, epoxides, heterocyclic compounds	Proteins, carbohydrates, humic acids
	Non-polar	Aliphatic compounds, aromatic compounds	Aliphatic compounds, aromatic compounds, alicyclic compounds	Non-ionic polymers, lignin
		Small	Medium	Large
Polarity	Molecular weight →			

Table 2.6: Chemical separation methods for water samples [293, 294]

↑	Volatility	→	→	
		Volatile	Semi-volatile	Non-volatile
	Polar	None Liquid-solid phase extraction Distillation	Derivatisation Liquid-liquid, extraction Liquid-solid extraction pH adjustment	Reduced pressure Distillation Freeze dry
	Semi-polar	Distillation Purge and trap	Liquid-liquid extraction Liquid-solid extraction	Reverse Permeation
	Non-polar	Headspace	Liquid-liquid extraction Liquid-solid extraction	Ultrafiltration
		Small	Medium	Large
Polarity	Molecular weight	→	→	

2.7 INSTRUMENTAL ANALYSIS OF INORGANIC POLLUTANTS

2.7.1 Metal analysis

Metal adsorption can be analysed using inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma atomic emission spectrometry (ICP-AES). The merit of ICP emission spectrometry in term of its environmental analysis application is that it can determine several metals simultaneously.

The chemical interference in this method is minimal, unlike in the case of atomic absorption spectrometry (AAS). This method effectively eliminates chemical interference associated with AAS by not allowing the formation of molecular compounds to take place. ICP OES/AES has been reported to have been applied in the analysis of some selected toxic elements in groundwater, surface water, wastewater and potable water, and also in leachate from waste. In the ICP AES/OES technique, samples are nebulised which is then followed by resulting aerosol transfer into plasma and later the ionised ions are excited. This is then followed by emission of light from each element at its characteristic wavelength. This lines obtained can then be used for quantitative analysis after calibration. A new and more advanced expensive technique of ICP coupled with MS, i.e. inductively coupled plasma mass spectrometry has been introduced to the market as a routine tool of analysis. The merit of this new ICP-MS is that it offers the advantage of ICP AES/OES (which is having lower detection limit) and graphite furnace atomic absorption spectrometry (GF-AAS).

CONCLUSION

The application of AC as an adsorbent in adsorption technology processes has proven to be an effective process for wastewater treatment of both inorganic and organic compounds, especially POP and heavy-metal ions. However, the optimum utilisation of AC has not been fully explored as an adsorbent in developing countries, especially in sub-Saharan Africa (SuSA) due to its drawbacks such as the regeneration cost of spent adsorbent, residual issue with disposal and high operational cost associated with AC. Researchers are aware of these limitations and research studies in South Africa are now focusing on investigating the feasibility of employing agricultural waste residue (AWR) in the form of AC as an alternative adsorbent and also as a filler in a polymer matrix in order to decontaminate water or wastewater streams.

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CHAPTER THREE

EXPERIMENTAL METHODS

3.1 MATERIALS

The maize tassels (MT) used as the precursor material were collected locally from Vereeniging (Gauteng, South Africa). The material was thoroughly washed with deionised water, and thereafter oven-dried for 24 h at a temperature of 110^{o}C. The washed and dried tassels were milled with a laboratory hammer-mill to obtain a fine powder. The resultant powder was fractionated into different sizes using analytical sieves. This was later used in AC production.

All reagents were analytical grade (AR) unless otherwise stated and Millipore water (Merck, Darmstadt, Germany) of 18 MΩ was used throughout the experiments. Concentrated nitric acid (HNO_3) (70%) and hydrochloric acid (HCl) (w/v 37%) were purchased from Sigma-Aldrich (St. Louis, MO., USA). Ammonium acetate buffer solution (1M) was prepared by mixing appropriate amounts of 25% ammonia solution (Sigma-Aldrich St. Louis, MO., USA) and glacial acetic acid (97%) ((Sigma-Aldrich St. Louis, MO., USA), which was then followed by dilution with water to a final pH of 9.0 using Mettler Toledo pH meter Model 20, Greifensee, Switzerland. All the polychlorinated biphenyls (PCB 105, 126, 153) were of analytical grade and obtained from Sigma-Aldrich (St Louis, MO, USA). The HPLC grade acetonitrile, hexane and dichloromethane were purchased from Merck (Merck, Darmstadt, Germany). Hydrochloric acid (HCl 0.1 M) and sodium hydroxide (NaOH 0.1 M) solution were used to adjust the pH values of the working solutions. 1,2-dimethoxy-3-(1-methoxypropan-2-yloxy)propane (Sigma-Aldrich St Louis, MO, USA) was used as a triol, dibutyltin dilaurate (DBTL > 97%, Merck, Darmstadt, Germany) was used as a catalyst, and silicone oil and castor oil (Sigma-Aldrich St Louis, MO, USA) were used as a foam stabiliser. The isocyanates used were 4, 4′ methylene diphenyl diisocyanate (MDI> 98% Sigma-Aldrich St Louis, MO, USA) and 1,6 hexamethylene diisocyanate (HMDI > 98% Lupanat, M 50, BASF Lemförde, Germany).

A Strata™ C18-E SPE C_{18} (EC) cartridge (0.5 g, 6 mL, and polypropylene column) purchased from Phenomenex companies, Torrance CA, USA was used for preconcentration. The porous frit was placed at the bottom end and at the top end of the column to allow the adsorbent to settle. The solid-phase extraction was carried out in a VasMaster-20 sample SPE station (Supelco, PA, USA). The SPE station was used for both sample loading and elution desorption flow rate.

3.2 METHODS

3.2.1 Preparation of activated carbon

3.2.1.1 Physical activation

A quartz tube reactor was filled with 5 g of tassel material and was pyrolysed in a tubular electric furnace (Gallenkamp) at various temperatures ranging from 300^{o}C to 700^{o}C under an inert atmosphere, i.e. nitrogen flow at 200 cm^{3}/min. The heating rate was controlled at 10^{o}C/min starting from room temperature. Samples were held at the desired temperature for a carbonisation time of 1 h. The resulting chars from the maize tassel were activated by CO_2 at various temperatures ranging from 300^{o}C to 700^{o}C. The nitrogen gas was switched to CO_2 at the char temperature and continued until the temperature reached 700^{o}C. The produced AC materials were coded PAC (i.e. PAC1, PAC2, PAC3, etc.) depending on the carbonisation temperature used [1].

3.2.1.2 Chemical activation

A sample of 20 g of the milled maize-tassel powder (particle size of about 106 µm) was added to 20 mL of phosphoric acid solution (85% by weight) and manually stirred for few minutes and left to stand for 1 h, and then further heated at 500^{o}C in an inert atmosphere. Activation temperature was set at 500^{o}C, based on the fact that carbon originating from plant species reveals highest specific surface area when carbonised at temperatures of between 450^{o}C and 500^{o}C. The physicochemical properties of the carbon-impregnated material (Xp) were investigated by varying the weight of precursor to acid ratios, i.e. 1:1, 1:2, 1:3 and 1:4, respectively. The produced activated carbons were coded as CCA (i.e. CCA1, CCA2, CCA3 and CCA4) based on their impregnation ratios), where CCA means chemical activation. The impregnated materials were dried at 110^{o}C for 24 h and then activated at 500^{o}C under an inert atmosphere, i.e. nitrogen flow at 200 cm^{3}/min. The residual phosphoric acid was eliminated from the activated carbon by washing with hot deionised water until the pH of the leachate was between pH 5 and pH 6 after which the powder was dried at 110^{o}C for 3 h; the final material was then ground and stored for further analysis [2-5].

3.2.1.3 Steam produced activated carbon

3.2.1.3.1 Activation

The initial carbonisation resulting in the formation of char was produced according to Olorundare *et al* [2]. The fine powder fraction produced of diameter size 106 µm was carbonised at 500^{o}C under an inert atmosphere, i.e. argon flow at 200 cm^{3}/min, and the carbonisation time was 1 h. The resultant char produced was activated by steam at three different temperatures (700^{o}C, 750^{o}C and 800^{o}C) and different activation times (20 min, 40 min, and 60 min) and 10 g of sample were used in each run [2, 6].

3.2.1.4 Chemical vapour deposition CVD

Chemical vapour deposition is a process by which a material especially solid is deposited from a vapour which is form by a chemical reaction occurring in or around the surrounding of a heated substrate surface in an enclosed environment. The final product a solid is obtained as a powder, a coating or single crystal layer covering. This occur by varying the experimental conditions including, the substrate material, substrate temperature, composition of reacting gas mixture, gas flow and total pressure of the gas flow.

3.2.2 Preparation of polyurethane composite using different fillers

The polyurethane composite was prepared according to the method described by Pinto et al. [7] with slight modifications. A bulk total of 50 g of the material, i.e. quantities required for the formation of the polyurethane composite, such as polyol, distilled water, castor oil/silicone oil (1:1) and catalyst were added into a polyethylene flask and mixed vigorously for 1 min with a mechanical stirrer to obtain a formulated polyol prepolymer. The isocyanate was then added to the same flask followed by addition of the various fillers and stirred vigorously for about 20 min. The resulting mixture, a composite material, was left to stand undisturbed for about 60 s to allow the formulation to grow and form a PU polymer composite. The PU polymer composite was then immediately placed into a mould and kept inside the oven at 60^{o}C for 60 min. The resulting product was thereafter ground to a powder and kept in desiccators until further analysis. Several formulations were tested for clarity but only one is reported here (Table 3.1). In order to maintain the urethane NCO index, the isocyanate and water composition were varied (Table 3.1) for the series formulation.

Table 3.1: Composites of formulation of polyurethane composite adsorbent

	Formulation series[a]	
	HMDI (A)	MDI (B)
Polyol (g)	30	30
DBTL (g)	0.23	0.23
Silicone oil: castor oil (1:1) v/v	0.8	0.8
Water content (%)	3-5	1-5
Diisocyanate (g)	14.2	14.2
Fillers (g)	0.2	0.2

[a]NCO index = 105% [7-10]

3.2.3 SPE cartridge preparation

The SPE commercial cartridge was replaced with polyurethane composite adsorbent (PCAD) (polymeric material containing polyurethane, AC and β-CD as filler) packed cartridge which was prepared by modifying a Strata™ C18-E SPE C_{18} (EC) cartridge (0.5 g, 6 mL polypropylene). The C_{18} packing of the cartridge was evacuated, and then 0.5 g of PCAD was packed into the cartridge. The 20 µm polypropylene lower and upper frits remained at each end of the cartridge to serve as support holders for the PCAD packing. The outlet tip of the cartridge was connected to a vacuum pump and the inlet end of the cartridge was connected to the PTFE suction tube whose other end was inserted into sample solution. The entire solid-phase extraction set-up assembly was carefully washed with methanol before use in order to reduce the interferences of the organic and inorganic contaminants.

3.2.4 Procedure

In the preconcentration enrichment step, the PCAD packed cartridge was firstly preconditioned by washing with 10 mL of acetonitrile, 5 mL hexane, and then hexane: dichloromethane (50:50) v/v was added before a new SPE preconcentration procedure was started. The pH of samples was adjusted accordingly with 1 mL of 0.1M HCl or 0.1M NaOH solution. Thereafter a known volume of spiked water samples was aspirated through the modified SPE C18 column at a controlled flow rate of 3 mL/min and the elute obtained was discarded. However, once the entire sample had passed through the SPE column, 10 mL of purified water was used to clean the impurity or the co-adsorbed matrix materials from the cartridge. The SPE column was then dried by negative pressure for 10 min and the targeted analytes were eluted with optimum volume of mixture hexane: dichloromethane (50:50). The resulting eluate was later air-dried with gentle flow of nitrogen gas to 1 mL, before subsequent determination by injecting 2 µL of the final elute into the GC×GC TOFMS instrument.

3.3 ACTIVATED CARBON CHARACTERISATION

3.3.1 Fourier transform infrared (FT-IR)

Spectra were collected on a Nicolet IS10 SMART 1TR Spectrometer and were recorded with characteristic peaks in wave numbers ranging from 550 cm^{-1} to 4 000 cm^{-1}.

3.3.2 Scanning electron microscope (SEM)

The AC was also characterised for surface morphology using both scanning electron microscope (TESCAN VEGA 3SBU (SEM) and high resolution scanning electron microscope (HRSEM) (Nova NanoSEM 200 (FEI) imaging techniques, irradiating the AC sample with a beam of electrons at 10 kV and 15 kV. Prior to applying the technique, the AC was properly processed by carbon coating and placed in the sample holder in order to obtain cross-sectional SEM micrographs.

3.3.3 Brunauer-Emmett-Teller (BET)

The surface area, pore size and pore volume of the AC were studied by using Micromeritics ASAP 2020 surface and porosity analyser by N_2 adsorption at -196°C. About 0.3 g of the sample was weighed and degassed at 180°C for 24 h.

3.4 POLYURETHANE COMPOSITE ADSORBENT CHARACTERISATION

3.4.1 Fourier transform infrared (FT-IR)

The procedure described in Section 3.3.1 was used to determine the functional group present on the PCAD.

3.4.2 Scanning electron microscope (SEM)

The procedure described in Section 3.3.2 was used to characterise the surface morphology present on the PCAD.

3.4.3 Brunauer-Emmett-Teller (BET)

The procedure described in Section 3.3.3 was used to determine the surface area, pore size and pore volume of the PCAD.

3.4.4 Differential scanning calorimetry (DSC)

The thermal analysis heat flow in the polymeric composite material was measured by using SDT Q600 differential scanning calorimetry at 10°C/min over a temperature range of 25°C to 450°C.

3.4.5 Thermal gravimetric analysis (TGA)

The thermal stability of the composite material was determined by Perkin Elmer TGA 4000 thermogravimetric analyser at a heating rate of 10^{o}C/min over a temperature range of 30^{o}C to 900^{o}C in oxygen and nitrogen. About 10 mg of polymeric composite material was weighed and used for carrying out the test.

3.4.6 X-ray diffraction (XRD)

X-ray diffraction was used to determine the crystallinity of the prepared PCAD.

3.5 ADSORPTION STUDIES

The experimental design for the adsorption studies includes the batch adsorption process which is used to determine the adsorbent rate of saturation, i.e. the time taken for the adsorbent to reach equilibrium capacity.

3.5.1 Organic compounds

The isotherm adsorption studies were undertaken to assess the efficiency of the adsorbent for the removal of organic compounds (OC) from aqueous solution. Batch adsorption experiments were carried out in a 250 mL Erlenmeyer flask by shaking a constant mass (0.8 g) of a pre-determined size of adsorbent with a constant volume (50 mL) of organic compound solutions of increasing initial concentration (50 mg/L to 300 mg/L) to maintain a constant mass to volume ratio. The pH of the solutions was adjusted accordingly by adding either 0.1M HCl or 0.1M NaOH. Each flask was sealed using a rubber bung and kept in a state of agitation (150 r/min) using a mechanical laboratory shaker for the material to reach equilibrium. Upon equilibrium, the samples were filtered and analysed using analytical instrument such as UV-Vis for the detection of dyes, and GC× GC TOFMS for the detection of PCB and phenolic compounds. The effects of pH, contact time and initial concentration of the adsorbent on the adsorption process were studied.[11, 12]. The percentage removal of organic compounds determines the efficiency of the adsorbent, and is denoted by Eq. (1):

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (3.1)$$

where:

R is the percentage organic compound removed
C_o is the initial concentration
C_e is the concentration at equilibrium

At equilibrium, $q_t = q_e$ and $C_t = C_e$; therefore the amount of dye adsorbed, i.e. the equilibrium adsorption capacity (q_e) of the AC at predetermined time intervals was determined based on the adsorbate mass balance using Eq. (2):

$$q_e = \left(\frac{C_o - C_e}{M}\right) V \qquad (3.2)$$

where:

C_o and C_e are the initial and equilibrium concentrations of the MB (mg/L), respectively
V is the volume of the aqueous solution (L)
M is the mass of activated carbon used (g)

The concentration of organic compounds adsorbed at time *t* is given by Eq. (3):

$$q_t = \left(\frac{C_o - C_t}{M}\right) V \qquad (3.3)$$

where:

q_t is the equilibrium adsorption at time t
C_o and C_t are initial and equilibrium concentration, respectively, at time t
V is the volume of the aqueous solution (L)
M is the mass of AC used (g)

3.5.2 Inorganic compounds

Batch-mode adsorption studies were carried out on the prepared AC using a 250 mL stoppered Erlenmeyer flask containing 50 mL of test solution at the desired pH value, contact time and adsorbent dosage level. Various initial concentrations of Pb(II) solution were prepared by proper dilution of the stock standard solution, 1 000 mg/L Pb(II). The pH of the experimental solution was adjusted by adding 0.1M HNO_3 and 0.1M NaOH solute ion as required. About 0.8 g of the adsorbent (AC) was then added and the contents in the flask were shaken in an electrically thermostatted reciprocating shaker at a constant speed of 130 r/min for 24 h to reach equilibrium (adsorption equilibrium condition). The contents of the flask were then filtered and the Pb(II) concentrations were determined using flame atomic absorption spectrometry (GBC Varian model). The percentage of Pb (II) removed was calculated from the difference between the concentrations of Pb (II) in aqueous solution before and after contact with the adsorbent AC.

3.6 RECOVERY STUDIES

This is the experimental design to determine the holding capacity of an adsorbent to selectively retain some ions of interest in their matrix and to elute effectively with appropriate solvent.

3.6.1 Inorganic compounds

Percentage recovery of the metal ions retained on the PUCAD polymeric material was stripped from the column using nitric acid. The percentage recovery could be calculated as a function of pH carried out using the PUCAD composite materials.

3.6.2 Organic compounds

Percentage recovery of the organic compounds retained on the PUCAD polymeric material was eluted from the column using a mixture of n-hexane and DCM at a ratio of 1:1 (v/v) for PCB, while in the case of the phenolic compounds HPLC grade menthol was used at optimum pH. The percentage recovery could be calculated as a function of pH carried out using the PUCAD composite materials [13-15].

3.7 ULTRAVIOLET VISIBLE (UV-VIS) SPECTROPHOTOMETRY

A Shimadzu UV 2450 UV-Vis spectrophotometer was used to study the absorbance of dye solution methylene blue (MB) on AC.

3.8 GC×GC TOFMS TWO-DIMENSIONAL GAS CHROMATOGRAPHY

Two-dimensional gas chromatography/time-of-flight mass spectrometry (GC×GC TOFMS) was used to determine all the organic compounds, i.e. phenolic compounds and PCB while MB was analysed by using UV-Visible spectrophotometry.

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CHAPTER FOUR

PREPARATION AND CHARACTERISATION OF ACTIVATED CARBON FROM RAW MAIZE TASSEL AND ITS APPLICATION IN WATER TREATMENT

Potential application of activated carbon from maize tassels for the removal of heavy metals in water

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Abstract

Water-pollution problems worldwide have led to an acute shortage of clean and safe water for both domestic and human consumption. Various technologies and techniques are available for wastewater treatment which includes the use of activated carbon. In this study activated carbons used for the removal of lead (II) ions from water samples were prepared from maize tassels (an agricultural waste residue) which were modified using physical and chemical activation. In the physical activation CO_2 was used as the activating agent, while in chemical activation H_3PO_4 with an impregnation ratio ranging from 1 to 4 was employed. The maize tassel was pyrolysed at different temperatures ranging from 300°C to 700°C in an inert atmosphere for a period of 60 min and activated at 700°C for 30 min. The effects of activation temperature, impregnation ratio and duration were examined. The resultant modified tassels were characterised by measuring their particle-size distribution, porosities, pore volume, and pore-size distribution using scanning electron microscopy (SEM). The activated carbon produced by chemical activation had the highest BET surface area ranging from 623 m^2/g to 1 262 m^2/g. The surface chemistry characteristics of the modified tassels were determined by FT-IR spectroscopy and Boehm's titration method. The experimental data proved that the properties of activated carbon depend on the final temperature of the process, impregnation ratio and duration of the treatment at final temperature. The adsorption studies showed that chemically prepared activated carbon performed better than physically prepared activated carbon.

Keywords: activated carbon, maize tassel, adsorption, activation, lead

4.1 INTRODUCTION

Freshwater resources are crucial for the sustainability of human life on planet earth. However, access to clean and safe water is continuing to be a major problem for both human beings and other organisms. For some time now, this has been a serious problem faced by policy-makers and other key players in human settlement. At the beginning of this millennium, the Economic and Social Council (ECOSOC), established under the United Nation's Charter, set an eight-point agenda in which water for all was clearly spelt out. Water is a resource that is of direct interest to the general population which has a linkage to all developmental sectors and social issues like poverty alleviation and regional income redistribution among communities. Integrated water resource management (IWRM) is one of the ways aimed at achieving this goal. The entire concept of IWRM is aimed at a holistic approach of solving water-related problems in the real world in a timely and cost-effective way [1, 2].

Currently, this treasured resource is becoming scarcer due to the fast-growing world population and increasing human activities which include mining, agriculture, manufacturing industries, etc. For most developing countries there has been no clear policy for water resource management till recently when integrated water resource management (IWRM) was introduced worldwide. The aim of IWRM is to alleviate poverty, create access to clean water, encourage resource management and come to an agreement on how to use this scarce resource. The already limited water resource available for consumption is now being polluted by industries by taking clean water for manufacturing purposes and releasing wastewater into the environment.

The presence of heavy metals, especially lead ions, in the aquatic environment is of great concern as they are reported to be a source of major environmental and health hazards due to the unabated discharge of toxic effluents, their resistance to degradation, and adverse effects on both aquatic life and human consumption [3]. Physicochemical techniques for their removal, which include electrochemical reduction, membrane separation, chemical precipitation, reverse osmosis, electro-coagulation, chemical oxidation, ion exchange and adsorption processes, have been explored to comply with strict laws as per the concentration limits for safe discharge of lead-metal ions to waste streams or wastewater discharge [4, 5]. Although these technologies on their own merit are very suitable for the removal of heavy metals they have some drawbacks, which include financial implications involving their treatment and disposal as well as the inability to remove metals present in effluent streams or wastewater at their trace levels [3].

Adsorption technology by activated carbon has gained wide acceptance and patronage among researchers, more than any other form of wastewater treatment technologies, due to their low cost, simplicity, ease of implementation and effective removal of heavy metals at trace level in effluent streams or wastewater [3, 6-8]. Activated carbon (AC) is an amorphous carbon-based material characterised by a large surface area (~ 1 000 m^2/g) and consisting primarily of graphitic (sp^2 hybridisation) layers. The type of surface functional groups, specific surface area, surface charge and pore-size distribution are some of the properties that affect the adsorption capabilities of activated carbon for metal ions and these give it an edge in wastewater treatment [3, 9].

At the moment, attention is focused on two methods of production of activated carbon with high qualities due to their properties which depend on the precursor materials and activation method. The first factor considered in selecting a suitable method is the type of precursor or raw materials. The second factor is to explore an appropriate activation method which includes activation temperature and chemical activator [3]. Generally, two types of activation methods are employed in the production of activated carbon, namely physical and chemical activation. The physical activation involves carbonisation or pyrolysis of raw material at a higher temperature under an inert atmosphere which is then immediately followed by oxidation which is termed as activation using an activating agent such as carbon (IV) oxide, air or steam. Chemical activation involves impregnation of the precursor or raw material with dehydrating agents such as alkali metal hydroxides or acids, which include phosphoric acid, sulphuric acid, nitric acid, $ZnCl_2$, KOH, NaOH, K_2CO_3, and $NaCO_3$ [10-16].

There is increasing research interest lately in the use of biomass materials as adsorbents, especially agricultural waste residues, such as cassava peel, rice husk and maize tassels, due to their availability, low production cost, minimisation of chemical sludge, renewability, possibility of metal recovery and regeneration ability [17, 18]. The maize tassel is part of the discarded stalk from the maize plant after harvesting. The tassel is the topmost male portion of the maize plant which extends out of the stalk top and sheds pollen to fertilise the corn ears, which is the female part of the maize flower that develops into the corn cob. The gestation period of maize is about three to four weeks after pollination and fertilisation in which the tassel plays a vital role. This means that outside of pollination and fertilisation the tassel serves no other useful purpose to the maize farmer [19]. Local maize growers usually cut off the tassels after pollination and fertilisation to facilitate strands that will produce seeds instead of hybrids which do not produce seeds.

The objective of this study was to produce AC, modified with both physical and chemical methods. In this study wastewater was treated using activated carbon made from maize tassels to remove heavy metals and the results are reported in this paper. These biomass materials were selected based on their availability, and the low cost for production of activated carbon. The effect of modification processes on the produced activated carbons was investigated. Characterisation of the produced activated carbon using different techniques is presented. Lastly, its ability to adsorb lead ions from aqueous solution was studied and reported.

4.2 EXPERIMENTAL SECTION

4.2.1 Sample collection

Maize tassels, agricultural waste residues, were collected locally from a farm settlement, near Vereeniging, 70 km away from the City of Johannesburg, South Africa.

4.2.2 Sample pre-treatment

The dried woody parts of the maize plant were thoroughly washed and rinsed with deionised water and were thereafter oven-dried for 24 h at 110^{o}C. The tassels were then milled in a laboratory hammer mill to obtain a fine powder. The resultant powder was fractionated into different sizes using analytical sieves. Particles of various diameters ranging from 45 µm to 212 µm were obtained and used for the preparation of activated carbon.

4.2.3 Preparation of activated carbon

Activated carbon was prepared using two approaches, namely physical and chemical methods. The activated carbons produced using these two methods were used in adsorption of lead ions from water and the results of their removal performance were compared.

4.2.3.1 Physical activation method

A quartz tube reactor was filled with 5 g of tassel material and was pyrolysed in a tubular electric furnace (Gallenkamp) at various temperatures ranging from 300^{o}C to 700^{o}C under an inert atmosphere, i.e. nitrogen flow at 200 cm^3/min, and the heating rate was controlled at 10^{o}C/min, starting from room temperature. Carbonisation was held for 1 h for all samples. After this procedure the resulting chars from the tassel were activated by CO_2 at various temperatures ranging from 300^{o}C to 700^{o}C. The nitrogen gas was switched to CO_2 at the char temperature and continued until the temperature reached 700^{o}C. The produced materials were coded PAC (i.e. PAC1, PAC2, PAC3, etc.) depending on the carbonisation temperature used.

4.2.3.2 Chemical activation

An aliquot of 20 g of the milled maize-tassel powder was added to 20 mL of phosphoric acid solution (85% by weight) and manually stirred for a few minutes and left to stand for 1 h, and thereafter further heated at 500^{o}C in an inert atmosphere. Activation temperature was set at 500^{o}C, based on the fact that carbon originating from plant species reveals highest specific surface area when carbonised at temperatures of between 450^{o}C and 500^{o}C. The physicochemical properties of the carbon-impregnated material (*X*p) were investigated by varying the weight of precursor to acid ratios, i.e. 1:1, 1:2, 1:3 and 1:4, respectively. The produced activated carbons were coded as CCA (i.e. CCA1, CCA2, CCA3 and CCA4, based on their impregnation ratios), where CCA means chemical activation. The impregnated materials were dried at 110°C for 24 h and then activated at 500°C under an inert atmosphere, i.e. nitrogen flow at 200 cm^3/min. The residual phosphoric acid was eliminated from the activated carbon by washing with hot deionised water until the pH of the leachate was between pH 5 and pH 6 after which the powder was dried at 110°C for 3 h; the final material was then ground and stored for further analysis.

4.3 CHARACTERISATION OF PREPARED AC

Characterisation of the prepared AC was performed using different techniques. The Boehm titration [20] was performed for assessing the basic and oxygenated acidic surface groups. Infrared spectroscopy was used for the determination of the surface functional groups, while the iodine test was used for the assessment of the quality of the AC and giving a rough estimate of the porosity and surface area of the AC [21-23], and N_2 adsorption was used in determining specific surface area, pore-size distribution and porosity of the AC. Heteroatoms present in carbon material before and after combustion were determined using an elemental analyser. X-ray diffraction was used to determine the crystallinity of the prepared AC, and scanning electron microscopy (SEM) was used for determining the morphology of the AC.

4.4 ADSORPTION STUDIES

Batch-mode adsorption studies were carried out on the prepared AC using a 250 mL stoppered Erlenmeyer flask containing 50 mL of test solution at the desired pH value, contact time and adsorbent dosage level. Various initial concentrations of Pb(II) solution were prepared by proper dilution of the stock standard solution, 1 000 mg/L Pb(II). The pH of the experimental solution was adjusted by adding 0.1M HNO_3 and 0.1M NaOH solution as required. About 0.06 g of the adsorbent (AC) was then added and the contents in the flask were shaken in an electrically thermos tatted reciprocating shaker at a constant speed of 130 r/min for 24 h to reach equilibrium (adsorption equilibrium condition). The contents of the flask were then filtered and the Pb(II) concentrations were determined using flame atomic absorption spectrometry (GBC Varian model). The percentage of Pb(II) removed was calculated from the difference between the concentrations of Pb(II) in aqueous solution before and after contact with the adsorbent (activated carbon).

4.5 RESULTS AND DISCUSSION

4.5.1 Determination of physical properties of activated carbon

The adsorption of pollutants such as heavy metals from aqueous systems by activated carbon is governed by different types of parameters which include its adsorption capacity, surface area, pore-size distributions and pore volume with the surface functional group. The surface characteristics of the AC are influenced by the method of preparation of activated carbon. In this study surface characterisation of the prepared activated carbons was performed by using Fourier transform infrared spectroscopy (FT-IR), BET and SEM analysis.

It was observed (Table 4.1) that the surface area of the AC increased with an increase in carbonisation and activation temperature for the physically produced activated carbon. Pore volume follows the same trend while pore size decreased with an increase in temperature for the entire sample treated except PAC3 (5.969 cm^3/g) which showed a slight increase in pore size. These observations indicate that the burn-off level of the AC has a pronounced effect on the increase in surface area. The loss of volatile substances was most likely responsible for the formation of both mesopores and micropores in some samples with high surface area. Similarly, for chemically treated samples the surface area increased with an increase in impregnation ratio, i.e. CCA2 (1:2) was observed to have a higher surface area than CCA1

(1:1). This observation was quite different for CCA3 which had lower surface area than CCA2. CCA4 was observed to have the highest surface area of all (1 263 m^2/g). The pore volume and pore size follow the same pattern of increasing with an increase in impregnation ratio. The specific surface area of AC obtained in this study, can be successfully compared favourably with other reported AC produced from lignocellulosic materials [24-26]. The increase of surface area with activation temperature and impregnation ratio is due to the burn-off effect on the activated carbon and also the retention of volatile materials by activating agent [4, 27]. A similar trend was observed for iodine absorption (Table 4.1) where the increase in activation temperature and increase in impregnation ratio leads to an increase in surface area in both physically and chemically prepared materials. The iodine number (mg/g) which is a means of evaluating adsorptive capacity of activated carbon has been established to measure the porosity of pores with dimensions of less than or equal to 1 nm [28]. The results obtained for the iodine number (Table 4.1) show that the number increases significantly with an increase in activation temperature and impregnation ratio. This increase was observed for both physically and chemically prepared activated carbons. This result is in agreement with what has been reported previously [4, 27, 29, 30]. The greatest accessibility for iodine molecules to adsorption sites occurs mostly in the case of chemically prepared activated carbon which is directly related to the amount of surface area accessible to the gas molecules (Table 4.1).

Table 4.1: Physical characteristics of activated carbon prepared maize tassel (obtained by applying the BET model to adsorption isotherms of nitrogen at −196°C)

Sample code	Single point *P*/*P*$_o$	BET surface area (cm^2/g)	T plot micropore (cm^2/g)	Pore volume (cm^3/g)	Pore size (cm^2/g 4V/A BET)	Iodine number (mg/g)
RT	2.705	2.74	1.2067	0.0153	22.305	
PAC1	6.092	5.82	5.709	0.0077	5.320	607
PAC2	4.596	4.21	9.2066	0.0053	5.034	627
PAC3	6.939	6.46	9.439	0.0096	5.969	661
PAC4	13.839	13.04	16.408	0.0134	4.111	650
PAC5	78.150	75.60	65.678	0.0364	1.924	698
CCA1	697.94	712.16	182.39	0.373	2.095	1 488
CCA2	747.53	776.23	47.42	0.622	3.209	1 679
CCA3	600.32	623.26	56.87	0.617	3.959	1 724
CCA4	1214.24	1262.50	106.32	1.541	4.881	1 855

PAC – physically activated samples; CCA – chemically activated samples

Activated carbons can be influenced not only by the chemistry of the surface but also by the porosity. Surface chemistry and structural surface parameters depend on the method of activation and origin of the precursor. The surface chemistry of activated carbon is associated with the nature of heteroatoms present, such as nitrogen, hydrogen, oxygen, phosphorus, sulphur and chlorine. These heteroatoms are bound to the edges of graphite-like layers and form organic functional groups such as phosphate carboxylic acid, lactones, phenols, carbonyl, aldehyde, ether and nitro-compounds which can either be acidic, basic or neutral in their chemical nature [31]. Boehm titration results for the prepared AC are presented in Table 4.2. The result shows that the surface is more basic and clearly indicates that the surface groups are related to the impregnation ratio in the chemically prepared AC with the values of phenolic, phosphorous acid group contents, and carbonyl and carboxylic group contents decreasing with an increase in impregnation ratio. However, in physically prepared AC the carboxylic group content increases with an increase in activation temperature while lactone and phenolic group content decreases with an increase in temperature. This result is in agreement with other similar studies reported in the literature [4, 27].

Table 4.2: Boehm titration results

Sample code	Carboxylic (mmol/g)	Lactonic (mmol/g)	Phenolic (mmol/g)	Acidic (mmol/g)	Basic (mmol/g)	Total (mmol/g)
PAC1	0.118	0.025	0.056	0.199	0.508	0.707
PAC2	0.124	0.010	0.034	0.168	0.483	0.651
PAC3	0.133	0.005	0.046	0.184	0.480	0.664
PAC4	0.133	0.007	0.048	0.188	0.463	0.651
PAC5	0.126	0.012	0.025	0.163	0.462	0.625
CCA1	0.047	0.031	0.036	0.114	0.472	0.586
CCA2	0.036	0.014	0.054	0.104	0.471	0.575
CCA3	0.001	0.008	0.078	0.087	0.460	0.547
CCA4	0.001	0.003	0.086	0.090	0.453	0.543

PAC – physically activated samples; CCA – chemically activated samples

4.5.2 Electron microscopic examination of activated carbon

The scanning electron microscope (SEM) images of the raw tassel and treated samples are illustrated in Figure 4.1 and Figure 4.2. The surface of the raw tassel (Figure 4.1A) is fairly smooth, fluffy and has fewer cracks and voids, while in the case of the treated sample (Figure 4.1B-F) the heat treatment on the samples has an appreciable impact on the raw tassel material and created large holes and some grains in the various sizes. The gasification on the sample opens the pores on the precursor. It could be shown from the micrograph that heat treatment widens the pores as the temperature increased from 300^{o}C to 700^{o}C. Pore development was more pronounced in PAC5 (Figure. 4.1F) than in the rest of the physically prepared AC. The chemically activated carbon was prepared using phosphoric acid and shows irregular and heterogeneous surface morphology (Figure 4.2A-D). It can be deduced from the micrograph that the interaction of the acid with the precursor generates voids or holes of different sizes, grainy surfaces and brittleness. The impregnation ratio also contributes to pore development because the impregnation ratio CCA2 (1:2) (Figure 4.2B**)** has a more distinct pore distribution than the others, except for CCA4 (1:4) shown in Figure 4.2d. This micrograph result was supported by the result obtained for iodine number determination and BET surface area result which shows that CCA4 has the highest surface area (1 263 m^2/g) of all the activated carbons produced.

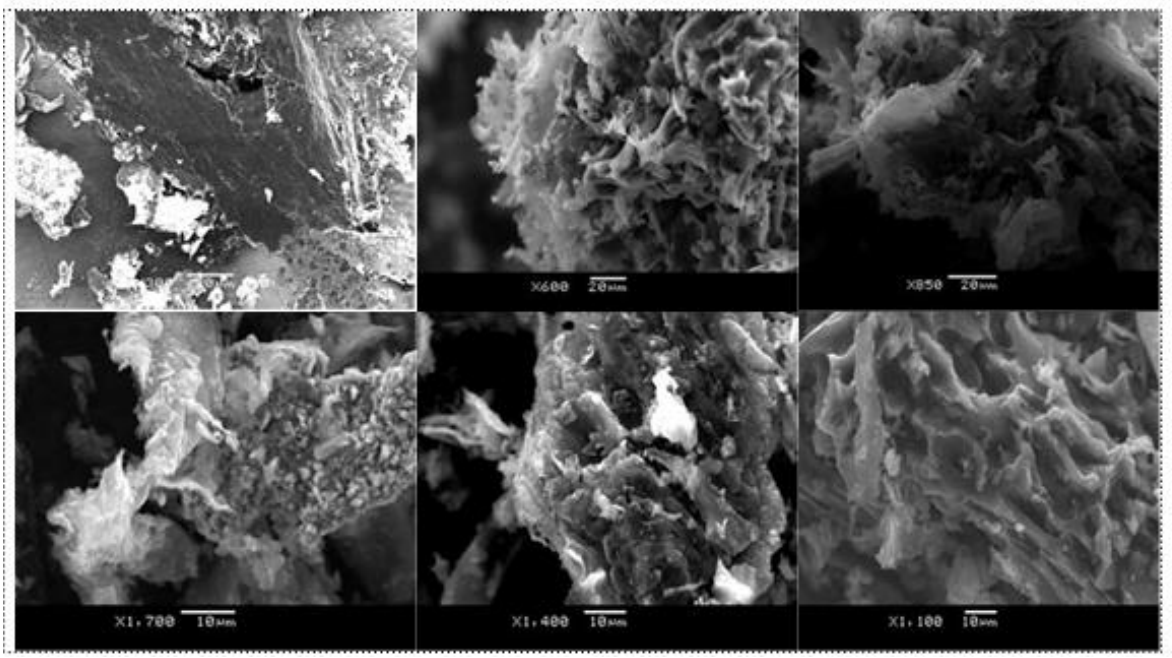

Figure 4.1: SEM Monograph of raw tassel (RT) and physical treatment PAC at different temperature

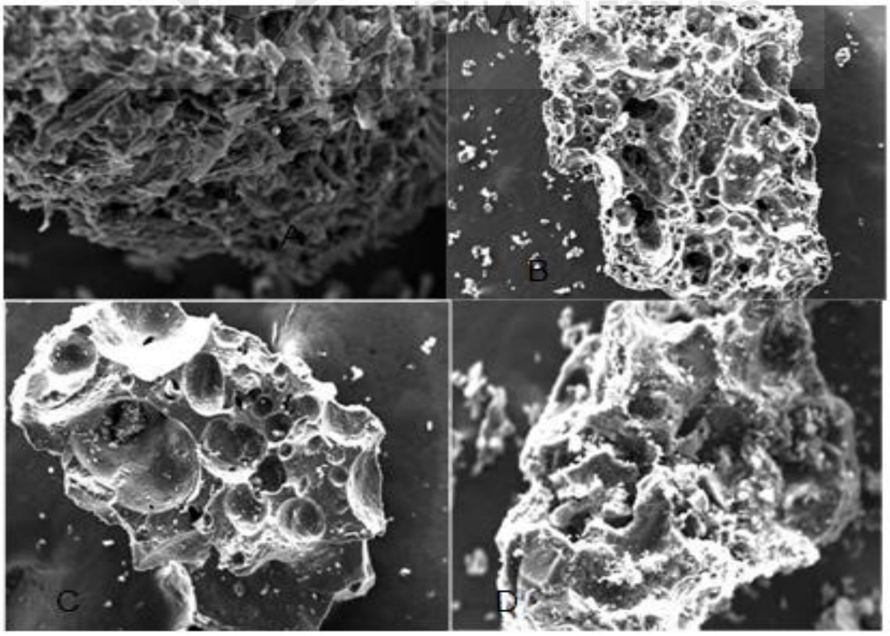

Figure 4.2: SEM Monograph of chemical treatment A-D

4.5.3 Surface chemistry

The Fourier transform infrared (FT-IR) spectroscopy results of raw tassel and activated tassel materials produced by both chemical and physical methods are shown in Figure 4.3, Figure 4.4 and Figure 4.5. The FT-IR spectrum of the raw tassel is depicted by Figure 4.3. The bands associated with various degrees of treatment, which includes temperature, activating agent or chemical treatment, are illustrated in Figure 4.4 and Figure 4.5. In Figure 4.3 the band located around 3 466 cm^{-1} corresponds to *v* (O-H) vibrations in the hydroxyl group, while the strong peaks at 2 921 cm^{-1} and 2 853 cm^{-1} bands correspond to *v* (C-H) vibration in the saturated aliphatic (alkane/alkyl) groups which could be in methyl and methylene groups [32].

In the infrared spectra of the chemically prepared AC, the adsorption band at 3 200 cm^{-1} and 3 500 cm^{-1} with a maximum at 3 300 cm^{-1} is characteristic of the stretching vibration of hydrogen bonded to the hydroxyl group (from alcohol, phenol or carboxyl) and water adsorbed by the activation carbon. The AC which is chemically prepared through impregnation (Figure 4.4**)** breaks many bonds in the aromatic and aliphatic species present in the raw tassels. A broad band is observed in all FT-IR spectra (Figure 4.4**)** in the finger-print spectral region between 950 cm^{-1} and 1 300 cm^{-1} with the maximum at 1 200 cm-1 and 1 150 cm^{-1} and 1 250 cm^{-1}. The absorption peak observed around 1 000 cm^{-1} to 1 200 cm^{-1}, indicates the existence of the C-O single bond in the carboxylic acids, alcohols, phenols and ester or the P=O bond in the phosphate esters, the O-C bond in P-O-C linkage and the POOH bond [33] (Puizy et al., 2002). A small band at about 1 700 cm^{-1} was observed and this is usually assigned to CO stretching vibration of ketones, aldehyde carboxyl groups or lactones. The prepared AC also showed a strong band in the region between 1 500 cm^{-1} and 1 680 cm^{-1} due to C-C vibration in the aromatic ring.

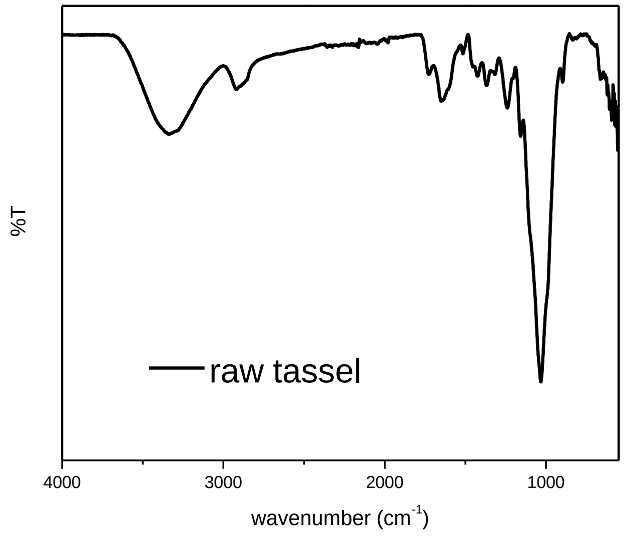

Figure 4.3: FT-IR Spectrum of raw tassel

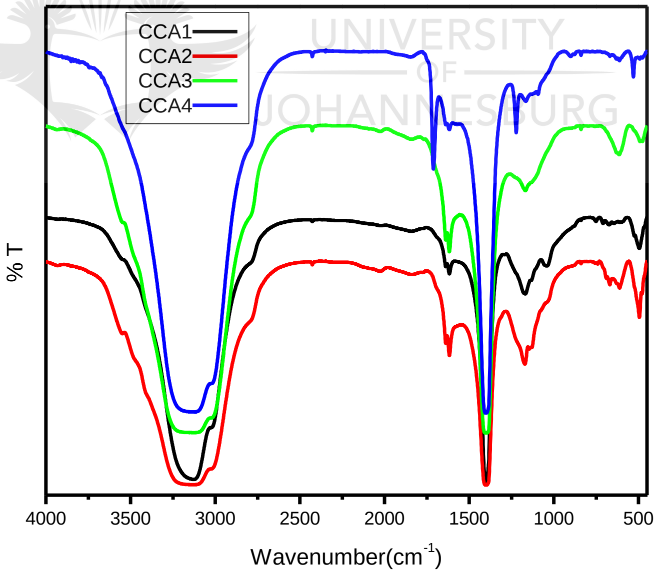

Figure 4.4: FT-IR spectra of chemically treated tassel

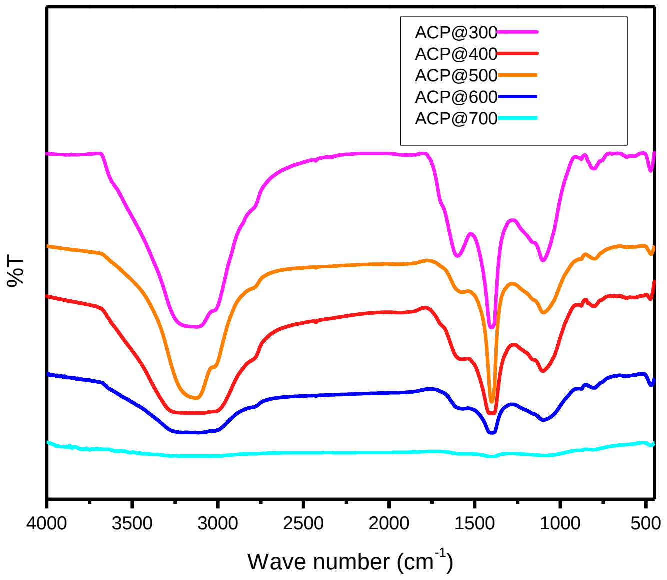

Figure 4.5: FT-IR spectra of physically treated tassel

A comparison between the spectra of activated carbon produced at different temperatures and raw tassels shows that the C-H vibrations in the methylene and methyl groups of alkane, which correspond to 2 921 cm^{-1}, 2 853 cm^{-1} and 1 453cm^{-1}, disappeared in the activated carbon prepared by physical treatment except for PAC1 and PAC4 in which the band at 1 453 cm^{-1} has shifted to 1 400 cm^{-1} and 1 405 cm^{-1}, respectively. This showed that heat treatment reduces the aliphaticity of the precursor [34, 35]. Moreover, a new peak emerged on PAC1 and PAC2 at 801 cm^{-1} which is ascribed to the aromatic C-H out of plane-bending vibrations. This peak was observed despite increased aromatisation in the active carbon prepared through physical treatment. Furthermore, the olefinic *v* (C=C) functional groups indicated by the band at 1 643 cm^{-1} on the raw precursor completely disappeared after the physical treatment while the skeletal C=C vibration corresponding to the band at 1 586 cm^{-1} is intensified. The reduction in oxygen-containing functional groups such as alcohol and ether due to the carbonisation indicates that these functional groups are thermally unstable [36].

4.5.4 Adsorption studies

An adsorption study of lead ions was performed by first investigating the effect of different factors which play a significant role in the process. Some of the important factors which were investigated include effect of the amount of activated carbons (effect of dosage), sample pH and contact time.

4.5.4.1 Effect of dosage

Effect of dosage on the adsorption (Figure 4.6A) clearly revealed that the percentage removal increases with an increase in adsorbent dosage (i.e. from 0.01 g to 0.006 g). This might be due to availability of surface area and pore volume on the adsorbent providing more functional groups on the carbon and active adsorption sites for lead ions. CCA recorded more than 94% removal compared to the PAC removal efficiency of 78%. There is a great improvement in the adsorption capacity in terms of time for metal uptake from aqueous solution when compared to raw maize tassels [18].

4.5.4.2 Effect of contact time

The effect of contact time on adsorption of Pb(II) ions on PAC and CCA (Figure 4.6B) showed a rapid increase in adsorption for the first 100 min. It was observed that Pb(II) ion adsorption increases with initial concentration for both PAC and CCA. The rapid adsorption might be due to fast transfer of metal ions caused by the effect of associated driving forces such as shaking and concentration gradient on the active surface area of the adsorbent. It is also influenced by the availability of uncovered surface area and the active sites [37, 38].

4.5.4.3 Effect of initial pH

The effect of initial pH of a solution is a major factor used to determine the adsorption property of an adsorbent due to its effect on speciation of the adsorbate, degree of ionisation and surface charge of the adsorbent. Figure 4.6C shows the influence of initial sample pH on the removal of Pb(II) ions. A low desorption was observed at lower pH which can be explained by the competition for adsorption between hydrogen ions and lead ions on the available active sites of adsorbents (i.e. PAC and CCA). However, the adsorption property increased with an increase in pH and this was further enhanced by the presence of –COOH in both PAC and CCA. This result obtained is in line with those reported by other researchers [3, 39-42]. Generally, wastewater treatment requires the use of more effective and environmentally friendly techniques. It has been stated, that different methods of preparing adsorbent materials have an effect on the performance of the resulting activated carbon as the properties of the chemically activated carbon differ from those obtained by physical activation. In this paper, it has been shown that there is a difference in the removal of Pb(II) ions from aqueous solution by AC prepared using chemical and physical activation; the difference in the method of activation affects the surface morphology of the produced AC and therefore its adsorption capability. The results obtained in this study showed that chemically prepared AC is more effective in removing metal ions from an aqueous system with more than 94% removal within a very short period of time as compared to physically prepared AC which produced 78% Pb(II) removal.

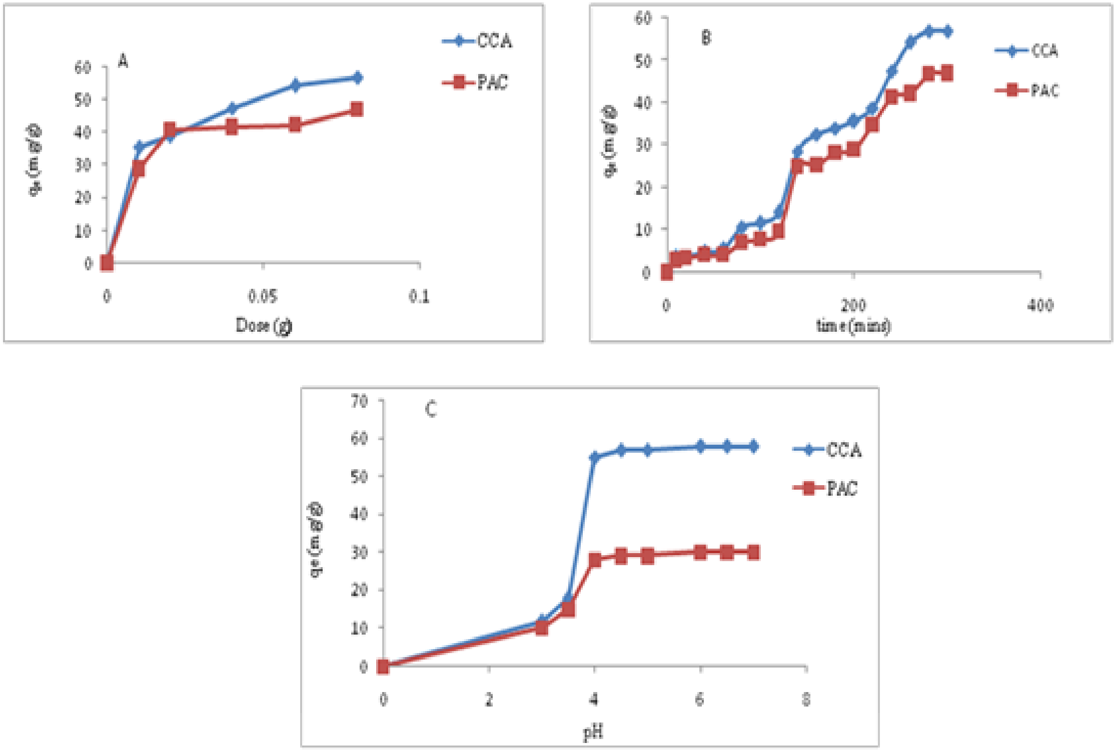

Figure 4.6: Effect of (A) dosage; (B) contact time; and (C) sample initial pH on CCA4 and PAC 5

CONCLUSION

In this work an attempt was made to prepare more effective activated carbon for the removal of heavy metals. Activated carbon prepared from maize tassels using both physical and chemical activation were characterised using various methods before their application. The results obtained from N_2 adsorption, SEM and FT-IR studies showed that activated carbons were indeed produced. The FT-IR results confirmed the presence of the phenolic group, the lactonic group, and the carboxylic group on the surface of the activated carbon, which was corroborated by the Boehm titration. The iodine number further confirmed this and showed that an increase in temperature and impregnation ratio affects pore development in the activated carbon produced. The chemically activated samples have the highest surface area (1

263 m^2/g) and pore size among all treated samples. This study has shown that activated carbon prepared using the chemical activation method was superior in removing Pb(II) ions compared to the physical activation method. From this observation, it can be concluded that chemical treatment produces more effective activated carbons from maize tassels for the removal of heavy metals from water.

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CHAPTER FIVE

STEAM-PRODUCED ACTIVATED CARBON, CHARACTERISATION AND APPLICATION IN REMOVAL OF METHYLENE BLUE FROM AQUEOUS MEDIUM

Steam activation, characterization and adsorption studies of activated carbon from maize tassels

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Abstract

In this paper, steam-produced activated carbon (STAC) from maize tassel (MT) was evaluated for its ability to remove basic dye (methylene blue (MB)) from aqueous solution in a batch adsorption process. The equilibrium experiments were conducted in the range of 50 mg/L to 300 mg/L initial MB concentrations at 30°C, for effect of pH, adsorbent dosage and contact time. The experimental data were analysed by Langmuir, Freundlich and Temkin isotherm models of adsorption. The Freundlich adsorption isotherm was found to have highest value of r^2 (r^2 = 0.97) compared to Langmuir and Temkin models having r^2 = 0.96 and r^2 = 0.95, respectively. STAC has a high adsorptive capacity for MB dye (200 mg/g) and also showed favourable adsorption for the dye with the separation factor (R_L <1) for the dye-activated carbon system. The kinetic data obtained were analyzed using the pseudo-first-order kinetic equation and the pseudo-second-order kinetic equation. The experimental data fitted well into pseudo-second-order kinetic equation as proven by the high value of r^2.

Keywords: activated carbon, steam activation, adsorption isotherm, methylene blue, activated maize tassel

5.1 INTRODUCTION

Synthetic dyestuffs are pollutants that are widely employed in the textile, leather, food, cosmetic, printing and paper industries. This industry and its subsidiaries represent a large group of chemical industries that contributes 40% of industrial wastewater among aqueous pollutants [1]. The sudden increase in production of different synthetic dyes due to industrialisation occurring in many countries has led to a huge surge in their production [2, 3]. These synthetic dyes and their intermediates are of environmental concern due to their toxicity on human health and aquatic systems [3, 4]. It has been reported that the presence of colour substances in an aqueous stream or water body reduces light transmission, thus reducing the photosynthetic activity, which leads to an increase in bacterial growth and invariably reduces the biodegradation of impurities in water stream [5]. The inhalation of these dyestuffs causes short periods of difficult or rapid breathing, while oral ingestion of small amounts may cause nausea or produces a burning sensation in the throat, gastritis, diarrhoea and vomiting [6]. Vanderivere et al. [7] reported that incomplete degradation of dyes by bacteria in the sediment resulted in the production of harmful amine and carcinogenic substances [7].

Methylene blue which is a basic dye has been extensively used in the textile, paper and printing industries and has been found to be a non-biodegradable dye [3]. The wide application of this dye can lead to serious health risk or cause considerable environmental pollution hence the need for their treatment before discharge.

Numerous techniques have been applied to water and wastewater treatments contaminated with dyes; these include ion exchange [8, 9], oxidation [10], ozonation [10], precipitation [11], adsorption [11], irradiation [11], photo-degradation [10], chemical coagulation [3, 8, 9] and flocculation [4, 8, 9]. Critical reviews of emerging and existing processes have been published [11, 12]. However, a number of these existing techniques have some drawbacks, which make them expensive and require various tools [3]. Among these existing processes adsorption on activated carbon (AC) has proven to be an effective method for dye and other pollutant removal [8]. Commercial AC as an adsorbent is very expensive, especially those that are of high quality. On the other hand, the regeneration of spent AC is also expensive for both chemical and thermal regeneration. It is also impracticable to recover all of the spent carbon, which results in loss of the adsorbents. These drawbacks have led several workers to search for the use of abundant, efficient and cheap alternative precursors as adsorbents without compromising the quality of the material. These include: coconut bunch waste [1], miswak leaves [3], banana pith, orange peel [13], guava (*Psidium guajava*) leaf powder [14], salts-treated beech sawdust [15], cellulose-based wastes, giant duckweed [13, 16], sunflower seed shells [17], palm oil shell [18], furniture waste [19], bamboo [20], bamboo dust [21], groundnut shell [21], rice husk [21], straw [21], pineapple leaf powder [22], sludge ash[23], spent activated clay [24], magnetic Fe_3O_4 nanoparticle [25], spent green tea leaves [26], marine green alga (*Ulva lactuca*) [27], banana-based AC [28], and periwinkle shell-based AC [29].

A considerable amount of work on the preparation of AC using methods such as steam/CO_2/N_2 from various sources has been reported [30-34]. Fossil materials and agricultural wastes have been used as raw materials in the production of AC using physical activation [32, 35-43]. Steam activation at higher temperatures has been reported to give better activation and enhanced widening of the narrow micropore network [30, 31, 44, 45]. The steam gasification of coke char can produce carbon with less microporous structure when compared to CO_2 gasification. This suggests that the pore structure and adsorption properties of activated carbon are strongly influenced by the physicochemical nature of precursor materials and the thermal history during the manufacturing process [36, 45, 46].

Maize tassel (MT) powder has been used in the removal of heavy metals. Maize tassel is the male inflorescence of the maize plant that forms at the top of the stem. It is discarded with the rest of the plant in large quantities by local communities in South Africa and elsewhere once the cobs have been harvested [47, 48]. It is proposed that MT contains cellulosic surface hydroxyl groups that can bind positively charged metal ions. This implies that the tassel surface exhibits a high energy surface. This has confirmed the ability of tassel powder to remove heavy metals from aqueous solution from earlier studies [47-49]. To this end, MT has not been applied in the removal of MB dyes or any organic compounds. Also, limited work has been done on the activation of MT.

In the present study, MT has been used as the precursor for the production of activated carbon. To the best of our knowledge, STAC from MT has not been reported in the literature hence, maize tassel is selected for the preparation of AC using steam. The present work reports the effect of activation time, activation temperature, pH and adsorption studies on the properties of STAC in a high-temperature chemical vapour deposition (CVD) environment.

5.2 MATERIALS AND METHODS

5.2.1 Materials

The maize tassels used as the precursor material were collected locally from Vereeniging (Gauteng, South Africa). The material was thoroughly washed with deionised water, and thereafter oven-dried for 24 h at a temperature of 110°C. The washed and dried tassels were milled with a laboratory hammer mill to obtain a fine powder. The resultant powder was fractionated into different sizes using analytical sieves. Particle diameter size has a direct relationship with adsorption properties of AC and can influence adsorption capacity, thus a particle size of 106 µm was used for the production of AC in this study.

5.2.2 Activation conditions

The fractionated fine powder produced, with selected diameter size of 106 µm, was carbonised at 500ºC under an inert atmosphere, i.e. argon flow at 200 cm^3/min, and carbonisation was conducted for a residence time of 1 h. The resultant char produced was activated by steam at three different temperatures (700ºC, 750ºC and 800ºC) and different activation time (20 min, 40 min, and 60 min) and 10 g of samples were used in each run.

5.3 CHARACTERIZATION OF STAC

5.3.1 Fourier transform infrared (FT-IR) analysis

The functional groups on the surface of the carbon were determined by Fourier transform infrared (FT-IR) spectroscopy. A Perkin Elmer Spectrum 100 FT-IR Spectrophotometer (United Kingdom) was used to collect spectra and recorded characteristic peaks in wave numbers ranging from 450 cm^{-1} to 4 000 cm^{-1} at a resolution of 4 cm^{-1}. The FT-IR spectra of STAC were obtained by diluting the sample in the ratio 1:20 in potassium bromide (KBr).

5.3.2 Iodine number of the activated carbon

The prepared activated carbon was characterised for its adsorptive capacity of iodine (mg of iodine adsorbed/g of carbon), which is referred to as the iodine number (IN). The iodine adsorption was determined using a sodium thiosulphate method [1, 50]. The burn-off weight percentage which measures the degree of activation process was calculated using the following equation:

$$burn-off\ (\%)=\left(\frac{W_1-W_2}{W_1}\right)\times 100 \tag{5.1}$$

where:

W_1 is the weight of char material
W_2 is the final mass of carbon after activation of the product

5.3.3 Scanning electron microscopy (SEM)

The STAC was also characterised for surface morphology using a high-resolution scanning electron microscope (HR-SEM) (Nano 2000 High Resolution SEM (HR-SEM), Jeol JSM-6500F, Japan). Prior to applying the technique, the STAC was properly processed in order to obtain cross-sectional SEM micrographs. The STAC sample used was a finely processed powder which was added to the surface of the SEM sample holder already coated with carbon template which served as a base for the sample. The sample was then sprayed with a sample spray coat in order to firmly attach all the particles in the sample and to prevent cross-contamination of the sample in the sample-holder compartment of the instrument. Afterwards and during the segmentation stage, the micrograph section corresponding to the porous region of STAC was identified.

5.4 ADSORPTION STUDIES

The isotherm adsorption studies were undertaken to assess the efficiency of the adsorbent for the removal of MB from aqueous solution. Batch adsorption experiments were carried out in a 250 mL Erlenmeyer flask by shaking constant mass (0.8 g) of a pre-determined size of adsorbent with constant volume (50 mL) of MB solutions of increasing initial MB concentration MB_i (50 mg/L to 300 mg/L) to maintain constant mass to volume ratio. The pH of the solutions was adjusted accordingly by adding either 0.1M HCl or 0.1M NaOH. Each flask was sealed using a rubber bung and kept in a state of agitation (150 r/min) using a mechanical laboratory shaker for the material to reach equilibrium. Upon equilibrium, the samples were filtered and analysed using UV-2450 UV/Vis spectrophotometer (Shimadzu, Japan). The first part of the filtrate was discarded to avoid the effects of MB adsorption on the filter paper. All the measurements were made at a wavelength corresponding to the maximum absorbance of 665 nm, the wavelength which was obtained after a full scan at a range of 200 nm to 800 nm. The amount of MB adsorbed onto the AC was measured by subtracting the remaining concentrations of the MB solution from the initial concentration. The effects of pH, contact time and initial concentration of the adsorbent on the adsorption process were studied. The dye percentage removal (R) is denoted by Eq. (5.2) which determines the efficiency of the adsorbent:

$$R(\%)=\frac{C_o-C_e}{C_o}\times 100 \tag{5.2}$$

where:

C_o is the initial concentration
C_e is the concentration at equilibrium

At equilibrium, $q_t = q_e$ and $C_t = C_e$; therefore the amount of dye adsorbed, i.e. the equilibrium adsorption capacity (q_e) of the AC at predetermined time intervals was determined based on the adsorbate mass balance using Eq. (5.3a):

$$q_e = \left(\frac{C_o-C_e}{M}\right)V \tag{5.3a}$$

where:

C_o and C_e are the initial and equilibrium concentrations of the MB (mg/L), respectively
V is the volume of the aqueous solution (L)
M is the mass of activated carbon used (g)

The equilibrium adsorption (q_t) at time t is the concentration of MB adsorbed at time t and is given by Eq. (3b):

$$q_t = \left(\frac{C_o - C_t}{M}\right)V \tag{5.3b}$$

where:

C_o and C_t are initial and equilibrium concentration, respectively, at time t
V is the volume of the aqueous solution (L)
M is the mass of AC used (g)

5.5 ISOTHERM MODELLING

The equilibrium experimental data between the concentration of the dye adsorbed from solution (C_e) and amount of dye adsorbed (q_e) onto STAC at constant temperature and pH were described by optimum isotherm model. The linear forms of isotherm model of Langmuir, Freundlich and Temkin equations were used to describe the equilibrium experimental data, using the correlation coefficients (r^2) to compare these equations [23, 51-60].

5.5.1 Langmuir isotherm

The Langmuir isotherm is a mechanistic model that is used to predict the adsorption of aqueous compounds onto the solid phase [23, 51-53]. The model assumes that adsorption is done over a uniform adsorbent surface at a constant temperature by a monolayer of adsorbed material (in a liquid, such as dye), and that the equilibrium constant controls the distribution of the compound between the two phases. Thus, at equilibrium both adsorption and desorption rate are equal, as described by the Lineweaver-Burk plot (Langmuir-II) [3, 54, 55]. Thus, the Langmuir-II equation is given as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5.4}$$

where:

q_m (the maximum capacity of adsorption, mg/g) and K_L (constant related to affinity of the binding sites, L/mg) are the Langmuir isotherm constants

5.5.2 Freundlich isotherm

The Freundlich isotherm model describes the adsorption process that takes place on a heterogeneous surface [23, 51, 52]. Thus, the Freundlich exponential equation is given as:

$$q_e = K_F C^{1/n} \tag{5.5}$$

where:

K_F (L/mg) is indicator of the adsorption capacity

$\frac{1}{n}$ is the adsorption intensity which indicates the heterogeneity of the adsorbent sites and the relative distribution of energy

The linear form of this model is derived by taking the logarithm of the term in Eq. (5.5) as shown in Table 5.1.

5.5.3 Temkin isotherm

The Temkin model takes into account the effects of adsorbate-adsorbate interactions on the adsorption process and it assumes that the heat of adsorption (ΔH_{ads}) of all molecules in the layer decreases linearly by increasing the coverage layer. Thus, this model was used to test the applicability or adsorption potential of STAC on the dye. The linear form of the model is given below:

$$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e \qquad (5.6)$$

Table 5.1: Different linear and non-linear isotherm models used in this study

Isotherm	Non-linear form	Linear form	Plot*
Langmuir-II	$q_e = \frac{K_L C_e}{1+K_L C_e}$	$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \left(\frac{1}{q_m}\right)$	$\frac{1}{q_e}$ *vs.* $\frac{1}{C_e}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	$\log q_e$ *vs.* $\log C_e$
Temkin	$q_e = \frac{RT}{b_T}\ln(K_T C_e)$	$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e$	q_e *vs.* $\ln C_e$

Where R is the gas constant (0.008314 KJ/mol K), T is the absolute temperature (K), $\frac{1}{b_T}$ is the Temkin constant related to heat of adsorption (KJ/mol) which is the adsorption potential of the adsorbent, and K_T (L/g) is the adsorption capacity related to the Temkin constant.

*The linear plot of q_e *vs.* $\ln C_e$ enhances the determination of the constants K_T and $\frac{1}{b_T}$ from intercept and slope, respectively [3, 20, 53-55].

5.6 RESULTS AND DISCUSSION

5.6.1 Fourier transform infrared (FT-IR) analysis

The results from the FT-IR characterisation of the STAC from MT indicated the presence of functional groups such as – CO and –C-O-C- which are capable of binding to MB ions on the adsorbent. The sorbent was subjected to various degrees of activation using steam at different activation times. Figure 5.1 shows the resulting FT-IR spectra of STAC with activation at 700°C, 750°C and 800°C for ADG(I,II,III), BEH(I,II,III), CFI (I, II,III) at 20 min, 40 min and 60 min, respectively. The FT-IR spectrum of STAC was used to identify functional groups that could be responsible for the uptake of organic species from aqueous solution. The spectrum of the adsorbent was measured within the range of 4 000 cm^{-1} to 450 cm^{-1} [28, 47, 48]. All spectra show weak bands associated with aliphatic C-H vibration at approximately 2

934 cm^{-1}. Bands associated with C=O stretch, carboxyl and lactone are present at 1 761 cm^{-1} [28, 47-49]; this band is pronounced in both samples B and C at 700°C and 750°C at 40 min (Figure 5.1 (II)) but weak for both samples at 700°C and 750°C at 20 min (Figure 5.1 (I)).

The aromatic hydroxyl groups adsorb infrared radiation at 1 260 cm^{-1} to 1 180 cm^{-1} and aliphatic hydroxyl groups at 1 210 cm^{-1} to 1000 cm^{-1}. The absorption of energy in the spectral region between 1 310 cm^{-1} and 1 000 cm^{-1} may be caused by ether structure as the (C-O-C) vibration for the carbon to carbon band [56, 57].

The C=O stretch, carboxyl and lactone peak are weaker in sample C at 20 min and 40 min compared to samples A and B at 700°C and 750°C. The higher the activation time and temperature, the more intense the peak is at 1 761 cm^{-1} (Fig. 5.1 (III)). However, at 800°C the bands 1 310 cm^{-1} to 1 000 cm^{-1} reduced in intensity compared to other bands, especially for 60 min in (Figure 5.1 (I) and Figure 5.1 (III)). The presence of the bands 1 447 cm^{-1} to 1 199 cm^{-1} indicates phenol, O-H bend in carboxylic and C-O stretching vibration. This change observed in the spectrum of STAC surfaces indicates the likely involvement of these functional groups on the adsorption process of the dye solution. Many researchers have shown that MB adsorption is dependent on both the porosity and the presence of surface groups [3, 6, 16, 20, 23].

5.6.2 Effect of activation temperature and time on iodine number

Iodine number (IN) was measured to evaluate the adsorptive capacity of the AC. It has been established that IN (mg/g) measures the porosity for pores with dimension ≥1.0 nm) [57]. Figure 5.2 illustrates the effect of activation temperature and time on IN. Iodine number increased significantly with an increase in activation temperature from 700°C to 750°C and started to decrease at temperatures higher than 750°C. The increase in activation temperature increases the micropore development, which in turn increases the adsorptive capacity of AC. A similar trend has been reported by other researchers [56-58].

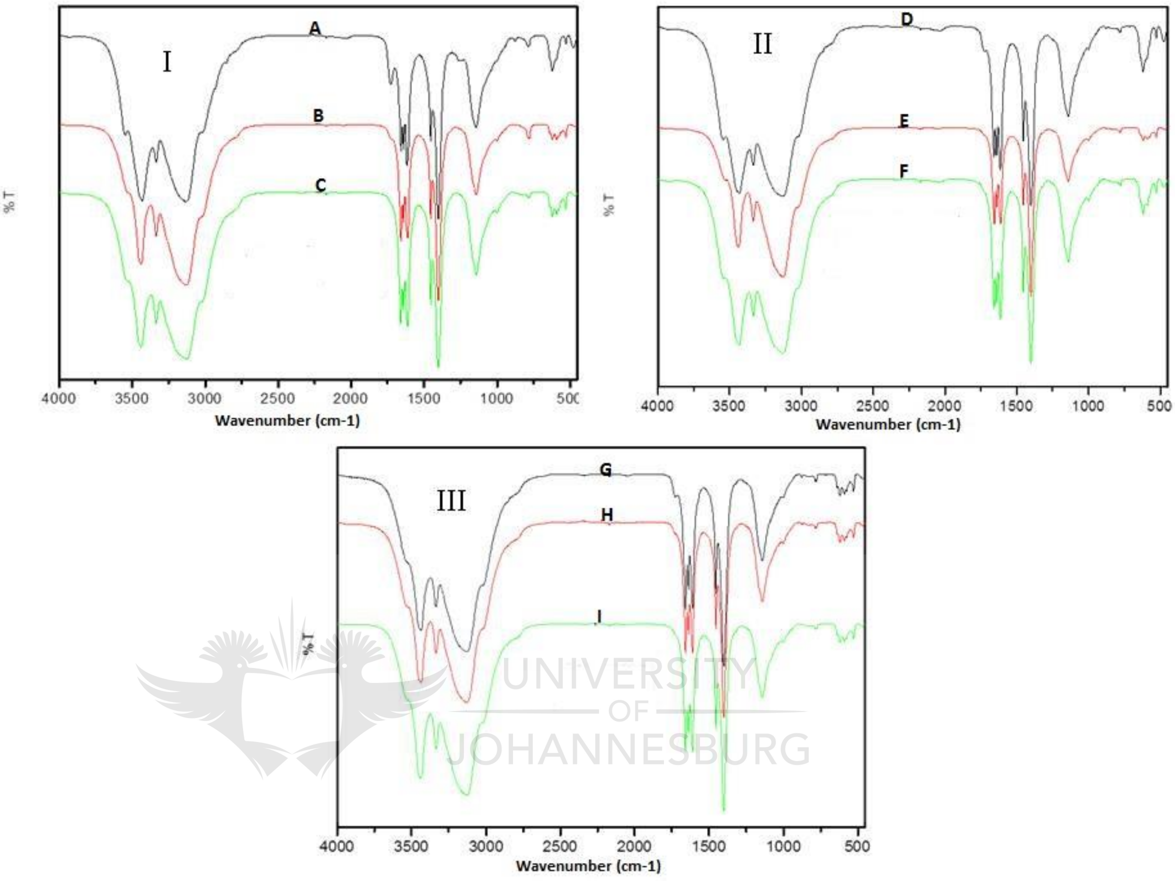

Figure 5.1: FT-IR spectra of STAC with activation at 700°C, 750°C, 800°C for ADG(I,II,III), BEH(I,II,III), CFI (I, II,III) at 20 min, 40 min and 60 min, respectively

The iodine number also increases with an increase in activation time; as activation time increases, the development of porosity in the AC increases, hence an increase in adsorptive capacity of AC. The iodine adsorption capacity of the AC decreases at temperatures higher than 750°C; this result indicates the micropore capacity of the AC [56-59]. The reduction in iodine adsorption is due to the widening of the pores leading to mesopore or macropore development.

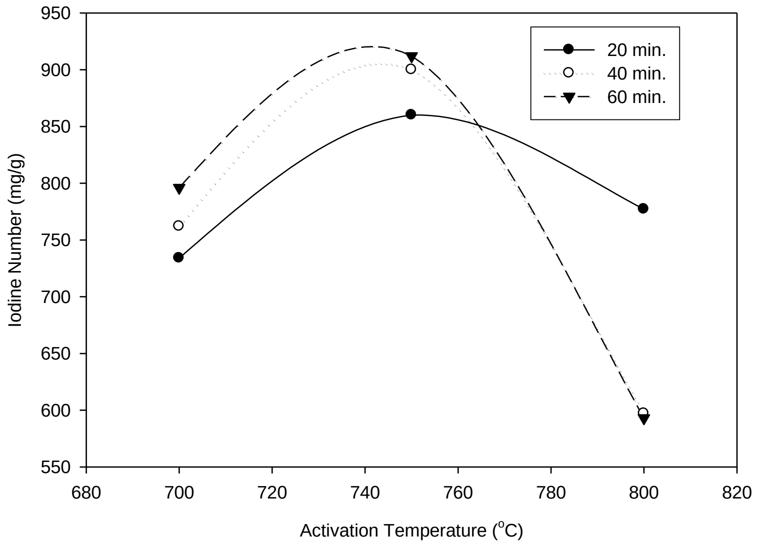

Figure 5.2: Effect of activation time and temperature on iodine number (IN) of AC

5.6.3 Effect of activation time on burn-off

Figure 5.3 shows the effect of activation time on burn-off for the tassel-based activated carbon at different temperatures. Steam activation results in weight loss of the produced char and occurs as a result of the reaction between carbon and water leading to the removal of carbon atoms. This is the process pathway of development of micropore volume, diameter and pore size in produced char [58, 59]. This process of reaction between the carbon surface and pore walls is initiated during the earlier stage of activation, which later reaches a maximum at 50% burn-off. As the burn-off increases, mesopores are formed from micropores [31, 57-59]. This observation was evident at temperatures greater than 750°C which led to the formation of mesopores.

The correlation coefficients (r^2) are greater than 0.96 in all cases between burn-off and activation time. The result indicates that the slope representing the gasification burn-off is almost constant throughout the experiment. Similar observations were made by Chang et al. [59] and Demiral et al. [58].

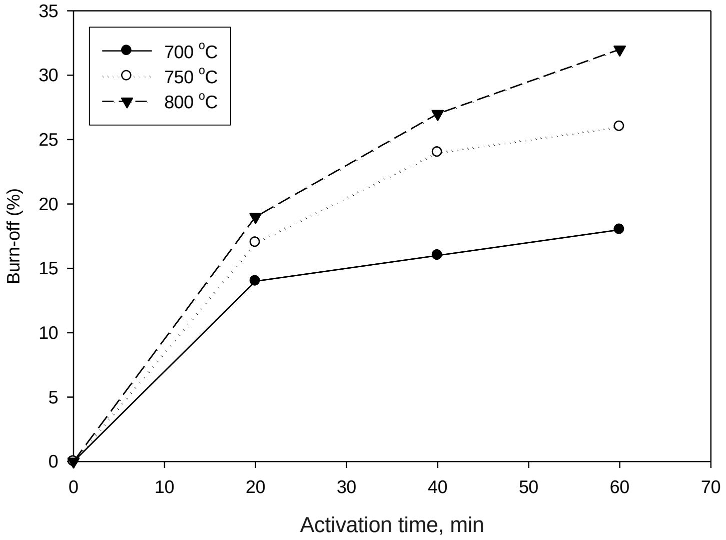

Figure 5.3: Effect of activation time and temperature on burn-off of AC

Whenever, the activating agent comes in contact with the char, it reacts with the exterior and the interior of the char sample, in which most of the disorganised carbon is removed. With regard to the effect of activation temperature, the results indicate burn-off range of 14% to 32%. When the activation temperature was increased to above 750˚C, it was found that the samples were almost burnt completely due to high gasification rates. The highest iodine number of 912 mg/g was obtained for the sample at 60 min and 750˚C, which indicates development of micropores. For the steam-activation process, greater mesoporosity development was reported in the literature [30, 45].

5.6.4 Scanning electron microscopy (SEM) studies

Figure 5.4A and Figure 5.4B present the surface morphologies of the STAC determined using scanning electron microscopy (Nano 2000 High Resolution Scanning Electron Microscope HRSEM, Jeol-Japan). The SEM monograph Figure 5.4 (A and B) shows STAC at 750˚C and 60 min activation time at 10 000× and 20 000× magnifications. It was observed that the STAC micrograph has smooth surface areas with long ridges, resembling a series of parallel lines. The straight tubes each with nearly uniform dimensions are evident in these figures. The outward appearance shows that the pores are not cross-linked. Figure 5.4 (B) revealed some pores on the surface. This type of precursor gives cross-interconnected pores, which are vital in the adsorption process, because it is at this point that the ions of organic compounds react with the adsorbent [45, 59].

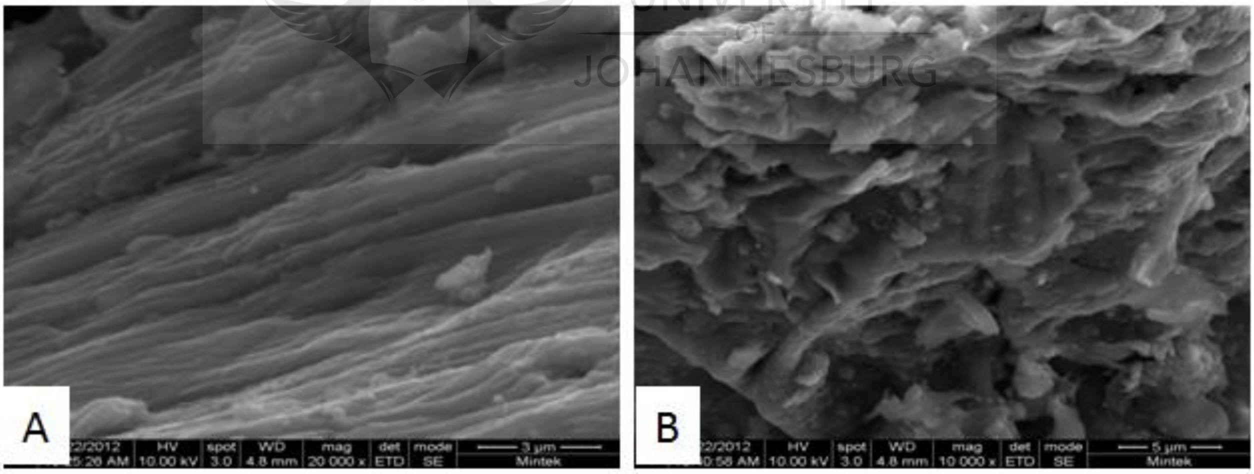

Figure 5.4: SEM micrographs of STAC (A); and (B)

5.6.5 Effect of contact time and initial concentration on MB adsorption

Figure 5.5 shows the effect of contact time on the removal of MB at various initial concentrations of MB_i (50 mg/L to 300 mg/L). The saturation curve rises gradually during the initial stages, indicating that plenty of adsorption sites are readily accessible. The result also shows that MB_i of the dye solution increased six fold (between 50 mg/L and 300 mg/L). This increase occurred in two stages: there was a threefold increase from 50 mg/L to 150 mg/L and a twofold increase from 150 mg/L to 300 mg/L. This result showed that the uptake of the dyes depends on contact time and concentration of MB_i. After a contact time of 120 min, there was a decrease in adsorption which led to a slight plateau indicating that the adsorbent had reached saturation point at this stage. It can also be seen from Figure 5.5 that the contact time needed for the dye solutions with MB_i concentrations of 50 mg/L to 150 mg/L to reach equilibrium was 110 min. However, for the dye solutions with higher initial concentrations, somewhat longer equilibrium times were required which indicated a decrease in adsorption capacity. It could also be seen that an increase in initial dye concentration resulted in increased MB uptake. This may be due to the boundary layer effect which is the time taken for the dye molecules to diffuse from the boundary layer to the surface of the adsorbent and later to diffuse through the porous structure of the adsorbent STAC [52-56]. Similar observations were reported by other researchers [3, 57, 58]. The removal curve in Figure 5.5 is single, and continuous, indicating the formation of monolayer coverage of the dye molecules onto the outer surface of the adsorbent.

A removal efficiency rate of 60% was achieved. The adsorption capacity at equilibrium (q_e) increased from 24.11 mg/g to 164.01 mg/g with an increase in the MB_i from 50 mg/g to 300 mg/L using the optimised pH (pH 10). The mass transport steps are determined by the adsorption of solute from solution by porous adsorbent [60]. This occurs by the adsorbate migrating through the solution by film diffusion, which is then followed by solute movement from the particle surface into the interior site by pore diffusion and then the adsorbate is absorbed onto the active sites in the interior of the adsorbent carbon particle [58, 60]. Furthermore, Figure 5.5 shows that there was only a slight increase in adsorption at initial dye concentrations ranging between 150 mg/L and 300 mg/L. Thus, 200 mg/L of MB was selected as the optimum concentration (MB_o) and subsequently used for other experimental tests.

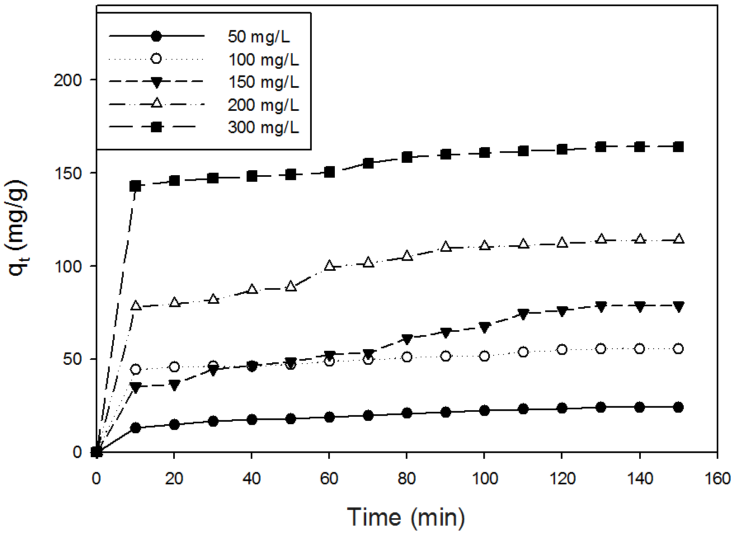

Figure 5.5: Effect of variation in adsorption capacity with time at various initial concentrations of MB at 30°C; pH = 10; Mw = 0.8 g/L; MB_i = 50 mg/L to 300 mg/L; and V = 0.05 L

5.6.6 Effect of pH on adsorption properties of activated carbon

The influence of pH on the adsorptive capacity of the steam-produced AC was determined at a temperature of 30°C and an initial concentration of 200 mg/L using solution pH values from pH 2 to pH 12. Figure 5.6 demonstrates that the MB adsorption rises steadily at the pH range between pH 2 and pH 10, and increases sharply at pH values greater than pH 8, before reaching its maximum at pH 10. A similar trend of the effect was reported by other researchers using commercial and laboratory produced AC [1, 3, 20]. The result shows that the value q_e of the dye reached a maximum in a basic medium and minimum in an acidic medium. Thus, subsequent adsorption processes were performed at this optimum pH value of pH 10. The differences in the pH values would affect the adsorption rate, because of the variation between the surface properties of the adsorbent STAC and the degree of ionisation of the dye molecules. Thus, this result is similar to observations made by other researchers, namely that increasing the electrostatic attraction also increases the adsorption process [1, 3, 20, 22]. At a low pH value the anionic dyes tend to be favourably adsorbed due to the presence of H^+ ions, while the cationic dyes tend to be favoured by high pH values. This observation leads to an increase in electrostatic attraction in each of the dyes, due to an increase in the presence of OH^- ions [1, 3, 20, 22]. The usage of the optimum pH value in the studies increases the negative charge on the adsorbent STAC surface thereby causing an increase in the electrostatic attraction between the STAC surface and the dye molecules which eventually leads to an increase in the adsorption rate of the dye by STAC [1, 3, 20, 22].

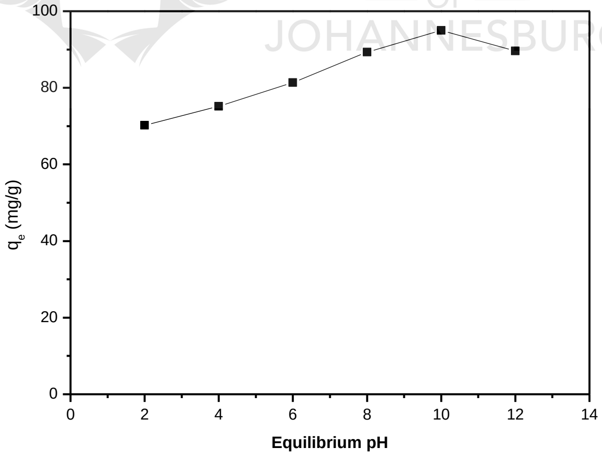

Figure 5.6: Effect of pH on adsorption properties of STAC at 30ºC; Mw = 0.8 g/L; MB_o = 200 mg/L; and V = 0.05 L

5.7 ADSORPTION ISOTHERM PROCESS

Basically, adsorption isotherm is an important tool used to describe the way in which solutes interact with adsorbents and also applicable in optimising the use of adsorbent in adsorption studies. Experimental data obtained for the adsorbed MB against initial concentration MB_o, were analysed using different types of isotherm which include Langmuir, Freundlich and Temkin equations. [3, 20, 55-59].

Langmuir, Freundlich and Temkin isotherm models were used to describe the relationship between the amounts of MB adsorbed and its equilibrium concentration in solution. The isotherm that best describes monolayer adsorption on a finite number of identical sites is Langmuir. The model does not consider transmigration in the plane of the surface, but assumes uniform adsorption on the surface [34, 55-57].

The Langmuir values of r^2, q_m and K_L are presented in Table 5.2. The results obtained revealed a minimal deviation from the integral equation which was indicated by a high value of r^2 (0.96). It has been reported that adsorption data with an r^2 value greater than 0.89 will follow the Langmuir model, hence the adsorption obeys the Langmuir model (not shown) [2, 3, 20]. However, the maximum adsorption capacity (q_m) for MB adsorption onto STAC is 200 mg/g as shown in Table 5.2. This result shows by way of experimental data both the formation of the monolayer coverage of the dye molecules at its outer surface and the homogeneous nature of the STAC surface [1, 3, 20, 27, 28]. Similar observation have been reported for various AC and biomass on the adsorption of dyes from various sources in aqueous solution [20, 28, 29, 60].

Table 5.2: The adsorption process isotherms of Langmuir, Freundlich and Temkin constants for adsorption of MB onto STAC at 30°C

Langmuir constants			Freundlich constants			Temkin constants		
q_m (mg/g)	K_L (L/mg)	r^2	K_F (L/mg)	n	r^2	b_T (KJ/mol)	K_T (L/mg)	r^2
200	0.0054	0.96	1.355	0.85	0.97	0.012	1.004	0.95

A plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ gives a linear graph by using the experimental data obtained, suggesting the applicability of the Langmuir model (r^2= 0.96). The workability of the model suggests that monolayer coverage of the adsorbate at the outer surface of the adsorbent is significant. The Langmuir constants q_m and K_L calculated from the plot are shown in Table 5.2. The significant characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor (R_L) given in Figure 5.7 which is defined by the following equation [3, 20, 56, 57]:

$$R_L = \frac{1}{1 + K_L C_o} \tag{5.7}$$

where:

K_L (L/mg) is the Langmuir constant
C_o (MB_i) is the different concentrations of MB (mg/L)

The value of R_L indicates the type of the isotherm to be unfavourable $(R_L > 1)$, linear $R_L = 1$, favourable $(0 < R_L < 1)$ or irreversible $R_L = 0$. The value for R_L ranges between 0 and 1, which supports favourable adsorption. The plot of R_L versus C_o (MB_i) of the initial MB concentration at 30°C is shown in Figure 5.7. The adsorption of MB onto STAC shows a favourable process by the value of R_L obtained **(**Eq. (5.7)**)** which ranges from 0.38 to 0.79. This confirms that the Langmuir adsorption isotherm plot was favourable adsorption of MB onto STAC at 30°C.

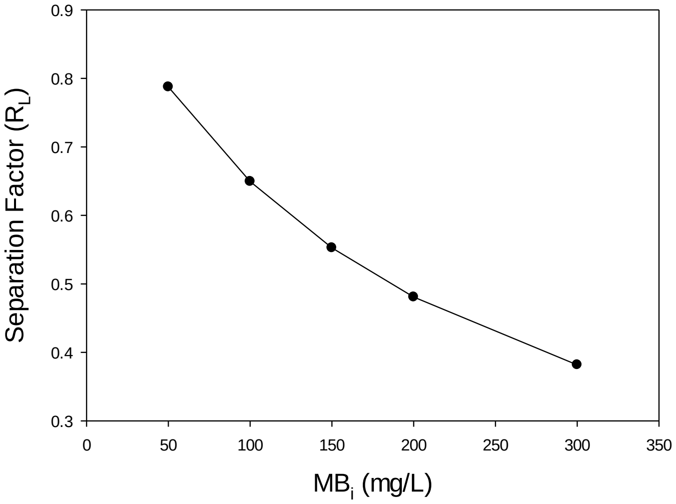

Figure 5.7: Separation factor of MB adsorption process onto STAC at 30°C; pH = 10; Mw = 0.8 g/L; MB_i = 50 mg/L to 300 mg/L; and V = 0.05 L

The equilibrium adsorption data of the initial dye concentration onto STAC were later fitted to the Freundlich isotherm (not shown). The linear plot of the model was engaged in determining the value of slope $\frac{1}{n}$ and intercept value of K_L together with r^2 value (0.97). The r^2 value (0.97) of this model is slightly higher than the Langmuir model r^2 value of (0.96). The value of $\frac{1}{n}$ is 0.85, which is nearer to unity, suggests the favourability of the Freundlich adsorption isotherm for the adsorption process [1, 3, 20, 55-58].

The Temkin adsorption isotherm was also applied to the experimental adsorption data to establish whether it would fit into the equilibrium adsorption data. The plot (not shown) is linear in nature. The Temkin equation parameters b_T and K_T have been calculated from the dye solution adsorbed (Table 5.2). The adsorption capacity of the dye onto STAC is somewhat low for both K_T (1.004 L/g) and the r^2 value (0.95). Hence the Temkin isotherm model poorly describes the equilibrium data of the adsorption process of the dye onto STAC. Table 5.3 shows a comparison between the maximum monolayer adsorption capacity (q_m) for dye uptake onto different adsorbents obtained during the present work (200 mg/g) and q_m obtained by other researchers using alternative adsorbents. The q_m for STAC is 200 mg/g, which shows that STAC is an effective adsorbent for dye molecules, especially for cationic dyes.

Table 5.3: Model parameters of maximum monolayer adsorption capacity (q_m) for comparison of MB adsorption on various adsorbents

Adsorbents	q_m (mg/g)	References
STAC	200	This study
AC from oil palm shell	243.90	[18]
AC from furniture (850°C)	200	[19]
Bamboo-based AC	454.2	[20]
Bamboo dust AC	143.20	[21]
Coconut shell AC	277.90	[21]
Groundnut shell AC	164.90	[21]
Rice husk AC	343.50	[21]
Straw AC	472.10	[21]
Pineapple leaf powder (PLP)	294.26	[22]
Miswak leaves	200	[3]
Banana peel	20.8	[23]
Coconut bunch waste	70.92	[1]
Orange peel	18.6	[23]

Table 5.3 summarises the computed maximum monolayer adsorption capacity for q_m of MB onto STAC. The adsorption capacity is due to IN adsorptive capacity which has a direct relationship to the surface area [57, 58].

5.7.1 Adsorption kinetics

The adsorption kinetics application was carried out with the STAC sample that had the highest iodine adsorption value. The experimental data obtained were integrated into different kinetics which included pseudo-first-order and pseudo-second-order kinetic equations [1, 20, 22, 23, 55-58]. The Lagergren pseudo-first-order and pseudo-second-order rate equation was used in analysing the kinetics of adsorption. The kinetic data were analysed using Lagergren's pseudo-first-order kinetics equation, a simple differential equation, generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5.8}$$

Integrating Eq. (5.10) for the boundary conditions $t = 0$ to t and $q = 0$ to q, gives:

$$\log \frac{q_e}{(q_e - q_t)} = \frac{k_1}{2.303} t \tag{5.9}$$

or linear form of the equation:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{5.10}$$

where:

q_t and q_e are the amounts of MB adsorption at any time t (min) and equilibrium (mg/g)

k_1 is the equilibrium rate constant of first-order adsorption $\left(\frac{1}{\text{min}}\right)$

The values of k_1 and q_e were calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t at different MB concentrations (MB$_i$). The pseudo-first-order Lagergren kinetic equation, as reported by some researchers [53-56], is generally appropriate for the initial stages of adsorption processes and does not fit well with the whole range of contact time. This observation was evidenced in this study, see Figure 5.8. Hence the values of q_e and k_1 were evaluated from the slope and the intercept from the plot of $\log(q_e - q_t)$ versus t at different concentrations (Table 5.4).

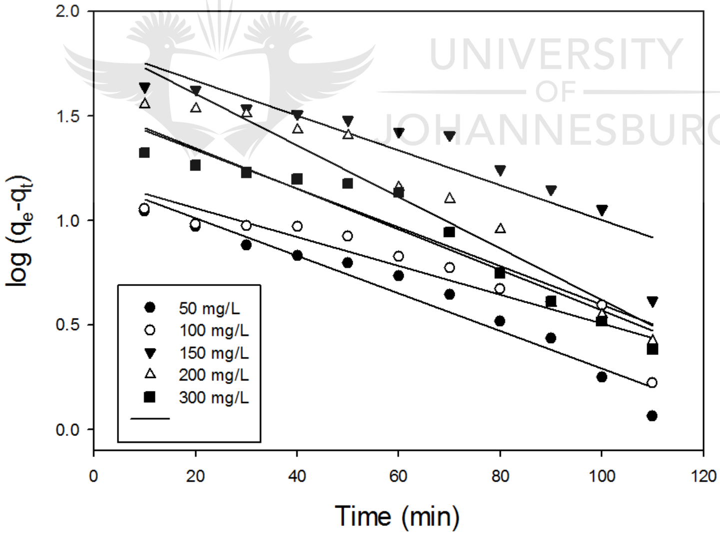

Figure 5.8: Pseudo-first-order kinetics for adsorption of MB onto STAC at 30^{o}C; pH= 10; Mw = 0.8 g/L; MB$_i$ = 50 mg/L to 300 mg/L; and V= 0.05 L

The adsorption rate constant and reaction order have to be determined by experiment in order to establish how rate is dependent on adsorption capacity and not on the concentration of the adsorbate [53-55]. The rate of sorption to the surface should be proportional to a driving force multiplied by an area. The rate constant first- and second-order kinetic model reaction may be dependent on the uptake capacity at equilibrium and amount of solute on the surface of the STAC at any time (*t*). The rate expression for the sorption could be expressed as $(q_e - q_t)$. The kinetic rate constant equation can be written as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{5.11}$$

where:

k is the rate constant of the sorption (g/mg min)
q_e is the amount of MB adsorbed at equilibrium (mg/g)
q_t is the amount of MB adsorbed on the surface of the STAC at any time t (mg/g)

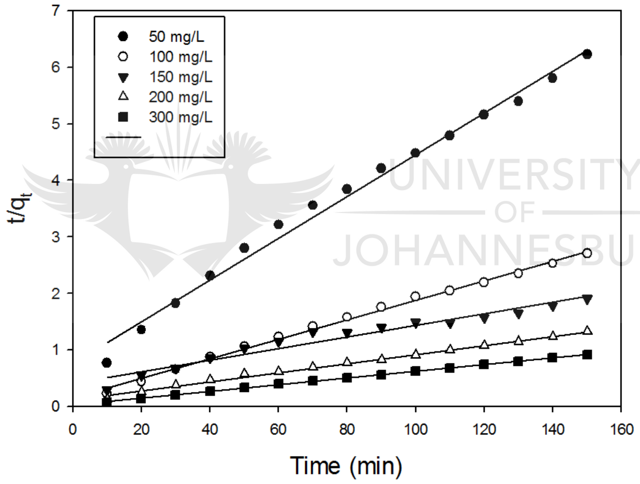

Figure 5.9: Pseudo-second-order kinetics for adsorption of MB onto STAC at 30^{o}C; pH = 10; Mw = 0.8 g/L; MB$_i$ = 50 mg/L to 300 mg/L; and V= 0.05 L

Thus the plot of $\frac{t}{q_t}$ against t should give a linear relationship with a slope of $\frac{1}{q_e}$ and an intercept of $\frac{1}{kq_e^2}$ as shown in Figure 5.9. The information obtain is in agreement with chemisorptions mechanism which is the rate controlling step and can be used to know the behaviour of adsorption processes [46, 53-55]

The values given in Table 5.4 revealed that there is an agreement between q_e experimental and q_e calculated values for the pseudo-second-order model. Thus, the pseudo-second-order model shows a better representation of the MB adsorption kinetics onto STAC (Figure 5.9).

Table 5.4: Pseudo-first-order and pseudo-second-order kinetic model parameters for MB adsorption on STAC at 30°C pH = 10; Mw = 0.8 g/L; MB_i = 50 mg/L to 300 mg/L; and V= 0.05 L

Pseudo-first-order kinetic equation model						Pseudo-second-order kinetic equation model			
(C_o)	q_e,exp	q_e, cal	k_1	R^2	SSE	q_e, cal	k_2	R^2	SSE
50	24.11	15.57	0.021	0.948	2.58	27.10	0.00179	0.990	0.90
100	55.41	15.66	0.016	0.867	11.99	57.80	0.00199	0.996	0.72
150	78.71	68.17	0.019	0.829	3.18	98.04	0.00025	0.949	5.83
200	113.80	70.96	0.028	0.932	12.92	125.00	0.00058	0.995	3.38
300	164.01	34.56	0.022	0.920	39.03	69.49	0.00127	0.999	1.65

Units of terms used above: C_o= mg/L; q_e = mg/g; k_1 = min^{-1}; SSE = %; k_2 = g/mg/min

The results shown in Table 5.4 reflect the list of the kinetic rate constant studies for various initial MB concentrations by the pseudo-first and pseudo-second-order kinetic model. The kinetic rate model especially for the pseudo-second-order model shows that there was a general increase with an increase in the initial concentration of MB. The correlation coefficients R^2 obtained for the second order on the average were greater than 0.986 as against 0.899 for the first-order reaction (Table 5.4). The applicability of both models was verified through the sum of squared errors $(SSE, \%)$ which is defined as:

$$SSE = \frac{\sqrt{\left(q_{e,\exp} - q_{e,cal}\right)^2}}{N} \tag{5.12}$$

where the subscripts ‘exp’ and ‘cal’ denote experimental and calculated values, respectively, while N is the number of data points

The validity of the adsorption kinetics was tested at different initial concentrations for MB and each model tested with the sum of squared errors (SSE) in percentage. It could be deduced that the higher the R^2 value the lower the $(SSE, \%)$ value, the better the fit for the experimental data. The result shows that adsorption of MB onto STAC is better described by the pseudo-second-order kinetic equation.

The values obtained in Table 5.4 indicate that the pseudo-second-order adsorption mechanism was dominant and the overall summation of the MB adsorption process seems to be driven by the chemisorption process rather than by physisorption. Similar observations have been reported by other researchers [19, 20, 52-54, 58].

CONCLUSION

In this study the ability of STAC, an AC adsorbent produced from steam activation of maize tassel, to remove MB from aqueous solution was investigated. Experimental results show that STAC was effective for the removal of MB from aqueous solution. Since the precursor employed in the production of STAC (AC), used in this work is freely available, abundant, and can be sourced locally, the resulting sorbent is expected to be economically viable for the removal of basic dye from aqueous solutions. Results obtained were modelled using three isotherm models, namely Langmuir, Freundlich and Temkin. The equilibrium isotherms were well described by both Freundlich and Langmuir equation, giving maximum adsorption capacity of 200 mg/g at 30°C for the Langmuir equation. In summary, the MB adsorption process seems to be driven by chemosorption rather than by physisorption. The adsorption kinetics can be well described by the pseudo-second-order model equations. The STAC produced AC appeared to be suitable for the removal of MB from aqueous solutions.

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CHAPTER SIX

EFFECT OF ACTIVATING AGENT ON PRODUCTION OF ACTIVATED CARBON AND ITS ADSORPTION CAPACITY FOR ORGANIC POLLUTANTS

Activated carbon from lignocellulosic waste residues: Effect of activating agent on porosity characteristics and use as adsorbents for organic species

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Abstract

This paper reports on the effect of activating agents (AA) such as impregnation ratio of phosphoric acid (1:1-1:5) at constant activation temperature on the performance of porous activated carbon from waste residues (maize tassel). The variation in the impregnation ratio of produced activated carbon (AC) from 1:1-1:5 enabled the preparation of high surface area (1 263 m^2/g) and large pore volume (1.592 cm^3/g) of AC produced from maize tassel as raw material using the conventional chemical activating agent (phosphoric acid). Impregnation ratios of the precursors were varied between 1:1 and 1:5 in which it was found that the ratio of 1:4 was optimal based on the high surface area while a ratio of 1:5 was found to have the optimal pore volume value for the produced activated carbon.

Keywords: *activating agents, impregnation ratio, maize tassel, porous activated carbon*

6.1 INTRODUCTION

The disposal of lignocellulosic wastes, particularly those generated from agricultural wastes, is a major environmental problem, and an issue of concern for environmentalists and ecofriendly activists. Millions of tonnes of wastes generated annually, especially of biomass origin, have turned our cities into glorified dumpsites. The lignocellulosic agricultural wastes have no specific technical usage apart from the generation of fossil fuel. Maize tassel (MT), an agricultural waste, is the male flower of the maize plant. The tassel is the group of stemmy flowers that grow on the apex of the maize stalk. These tassels, during pollination through cross-fertilisation, are responsible for the production of the kernel which in turn produces the maize cob. The whole process involved in the tassel production, is that the tassel producing pollen is blown off by the wind in order to reach the silk of the ear (female flowering part of maize plant) for fertilisation. Maize tassel has no production value after fertilisation except for the farmer to cut them off in ensuring maximum utilisation of the maize grain production.

The possible use of MT as biosorbent for inorganic compounds has been extensively explored by various researchers [1-3], while its application in the commercial production of activated carbon (AC) has not been fully explored. Apart from maize tassels, activated carbon has been produced from other diverse organic materials rich in carbon, such as different agricultural wastes, coal, lignite and wood [4-6]. The possible use of agricultural residues in the production of good quality AC has been highlighted by a number of researchers, mainly due to their availability, low cost, and being a renewable resource [5, 7-14].

Activated carbon (AC) can be defined as final product of an activation process of carbonaceous materials from diverse sources and having over 60% as carbon content [15]. Activated carbon is composed of interconnected domains of benzene rings and graphite plates organised with some localised order on a molecular level [15, 16]. It also displays extended inter-particulate surface area and a high degree of porosity [15]. The properties of the raw materials, both physical and chemical compositions, as well as the process condition and method employed for the activation determine the adsorption properties of AC and its pore-size distribution [17]. Activated carbon can be produced in two ways, namely physical and chemical methods. These two methods employ two-stage processes in their operation, i.e. carbonisation and activation. In the physical activation method, carbonisation of precursors is followed by activation with an oxidant such as steam, air or CO_2, while in the chemical activation method, these two processes occur simultaneously, with the impregnation of the precursor with dehydrating agents (such as acid or alkali) and oxidants. The reason for carbonisation is to create initial porosity, some ordering of the carbon structure and to enrich the carbon material. The purpose of the activation process is to enhance the carbon structure by widening the pores thereby making it more porous [4]. There are various parameters that affect the production of AC, its structure or porosity. These parameters include: (i) activating agents such as phosphoric acid, HNO_3, steam, CO_2, nitrogen, $ZnCl_2$, H_2O_2, KOH and NaOH; (ii) activation temperature; (iii) dynamic process in the films; (iv) high density of precursor; (v) low ash content of precursor; and (vi) high adsorption capacity. However, the activation process can only be assured under a particular condition, which is a non-limiting mass transfer condition which makes the reaction to occur at the particle's internal surface [4, 5]. For example, in chemical activation, the activation of the precursor takes place at a temperature lower than that of physical activation, and also its yield is much higher than by physical activation [18, 19]. Chemical activation also favours a good porous structure [20], while the type of oxidant or dehydrating agents is crucial in porous development during the activation process, especially in lignocellulosic materials that have not been carbonised. Among the dehydrating agents employed as activating agents, phosphoric acid is the most preferred oxidant. This is because of the environmental problems associated with others, such as zinc chloride, that cause corrosion and inefficient chemical recovery [12]. The nature of porosity and the surface area have been reported to have a major influence in the processing or production of AC [5, 12, 19, 21]. Generally, dehydrating agents such as phosphoric acid can be grouped into two categories, namely one- and two-stage activation process (impregnation and carbonisation) carried out in either self-generated or inert made atmosphere. Optimising the process parameters such as impregnation ratio, activating temperature and activating time, goes a long way to determine the nature of the produced AC. It has been reported that the ratio of the activating agents to the precursor is an important variable to porosity development in AC [22]. Other operational variables like method of mixing, activation temperature and activation time have a direct effect on the porosity development [22, 23].

To the best of our knowledge, very little or nothing has been published in the literature about the effect of impregnation ratio on AC produced from maize tassel.

The objective of this study was to produce AC, modified with chemical method as activating agent. In this study, phosphoric acid was used as activating agent for the production of AC from maize tassel and the effect of the impregnation ratio (IR) on the porosity and surface characterisation of the AC produced is investigated, as well as pore characterisation using various techniques.

6.2 EXPERIMENTAL METHOD

6.2.1 Reagents

The phosphoric acid and phenol used in the synthetic procedures of this work were of analytical grade and obtained from Sigma-Aldrich (St Louis MO., USA). Distilled water was applied for all synthesis and treatment processes.

6.2.2 Preparation of activated carbon

The precursor for the AC was acquired by collecting maize tassel (MT) ‘grace green’ cultivar variety from a local farm settlement near Vereeniging, about 70 km away from the city of

Johannesburg, South Africa. The dried woody parts of the maize plant were thoroughly washed and rinsed with deionised water and were thereafter oven-dried for 24 h at 110^{o}C. The tassels were then milled in a laboratory hammer mill (Janke & Kunkel micro-hammer mill) to obtain a fine powder. The resultant powder was fractionated into different sizes using analytical sieves. Particles of various diameters ranging from 45 µm to 212 µm were obtained and particle size 106 µm was used for the preparation of the AC. The dried reduced powdered MT was then stored in a desiccator before use.

A chemical activation method using phosphoric acid was used to activate the precursor. The final sample preparation was done according to Olorundare *et al.* [6] with little modification: A sample of 20 g of MT powder was added to 20 ml of phosphoric acid solution (85% by weight) and manually stirred for 30 min and left to stand overnight. The physicochemical properties of the carbon-impregnated material (*X*p) were investigated by varying the weight of precursor to acid ratios, i.e. 1:1, 1:2, 1:3, 1:4 and 1:5, respectively. The produced AC were coded as ACC, (i.e. ACC1, ACC2, ACC3, ACC4 and ACC5, respectively, based on their impregnation ratios), where ACC denotes chemical activation. The resulting slurry, the mixture of the precursor and phosphoric acid then turned black, yielding a black and sticky dry powder (depending on the ratio of impregnation). This was then semi-carbonised during the first stage before activation during the second stage (the black and sticky dry powder) at 500^{o}C in a horizontal tubular reactor furnace for an hour under inert atmosphere. The carbonisation was performed under a nitrogen flow of 200 cm^{3}/min for a period of 60 min. After activation, the AC produced was collected and cooled in a desiccator. The AC produced was then washed repeatedly with hot deionised water until constant pH of the solution was reached. The AC produced was then dried in a vacuum oven at 110°C for 24 h, before being stored in a desiccator for later experimental use.

6.3 CHARACTERISATION OF ACC

The pore structures of the resulting ACs were analysed using N_2 adsorption BET (Brunauer–Emmett–Teller) method for surface area, X-ray diffraction (XRD) for crystallinity, scanning electron microscopy (SEM) for morphological determination and Fourier transform infrared (FT-IR) for surface functional group.

6.3.1 N_2 adsorption

The pore structure characterisation of the resulting ACs was determined by nitrogen adsorption-desorption isotherm measured at 77 K using ASAP 2020 Micromeritics Instrument. Prior to gas adsorption measurements, the AC was degassed at 250^{o}C under vacuum condition for a period of at least 5 h. Nitrogen adsorption isotherms were measured over a relative pressure (P/Po) range from approximately 0.005 to 0.995. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.05 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.995 and at this relative pressure all pores were completely filled with nitrogen gas.

6.3.2 Scanning electron microscopy (SEM)

The SEM images were recorded for studying the surface morphology using a scanning electron microscope (SEM) (Nano 2000 High Resolution SEM (HRSEM), Jeol-Japan). Prior to applying the technique, the ACC was properly processed in order to obtain cross-sectional SEM micrographs. The ACC sample used was a finely processed powder which was added to the surface of the SEM sample holder already coated with carbon template which served as a base for the sample. The sample was then sprayed with sample spray coat in order to firmly attach all the particles in the sample and to prevent cross-contamination of the sample in the sample-holder compartment of the instrument. The samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 5 kV, eight spot size, four aperture and 20 mm working distance. Afterwards and during the segmentation stage, the micrograph section corresponding to the porous region of ACC was identified.

6.3.3 X-ray diffraction

The composition and structure of the samples were analysed by X-ray powder diffraction XRD (Shimadzu XRD 3000 diffractometer) at 40 kV and 40 mA and a scanning rate of 6^o/min with 2θ ranging from 5^o to 60^o at a step size of 0.01^o.

6.3.4 Fourier transform infrared (FT-IR) spectroscopy

The characterisation of the AC was performed by Fourier transform infrared (FT-IR) spectroscopy to identify its surface functional groups.

A quantitative analysis of produced AC was conducted by obtaining FT-IR transmission spectra of the produced AC samples by KBr technique using a ratio of 1:20. The technique involved placing dried KBr powder, alone and later with the sample, in an agate mortar and then grinding it into a fine powder before placing the mixture into the sample cup and thereafter compressing the powdered samples in a pellet press to form sample pellets. The two pellets (KBr and KBr sample mixture) were mounted one after the other onto the instrument to make a background measurement and sample measurement in the transmittance %T mode. FT-IR spectroscopy was then performed using a Perkin Elmer® Spectrum 100 FT-IR spectrometer and spectra were recorded with characteristic peaks in wave numbers from 450 cm^{-1} to 4 000 cm^{-1} at a resolution of 4 cm^{-1} with 16 runs per scan.

The elemental analysis of the produced AC was carried out using a Perkin Elmer 2400 C, H, N, O analyser.

6.4 ADSORPTION STUDIES

The isotherm adsorption studies were undertaken using simulated wastewater to assess the efficiency of the adsorbent to remove phenol from aqueous solution using the batch method. The batch adsorption experiments were carried out in a 250 mL Erlenmeyer flask by shaking at constant mass (0.04 g) of a pre-determined size of adsorbent with constant volume (50 mL) of phenol solutions of increasing initial phenol concentration (50 mg/L to 250 mg/L) to maintain a constant mass to volume ratio. The pH of the solutions was adjusted accordingly by adding either 0.1M HCl or 0.1M NaOH. Each flask was sealed using a rubber bung and kept in a state of agitation (150 r/min) using a mechanical laboratory shaker for the material to reach equilibrium. Upon equilibrium, the samples were filtered and analysed using a UV-2450 UV/Vis spectrophotometer (Shimadzu, Japan). The first part of the filtrate was discarded to avoid the effects of phenol adsorption on the filter paper. All the measurements of ten scans were made at a wavelength corresponding to the maximum absorbance of 270 nm, the wavelength obtained after a full scan at a range of 200 nm to 600 nm. The amount of phenol adsorbed onto the activated carbon was measured by subtracting the remaining concentrations of the phenol solution from the initial concentration. The effects of pH, contact time and initial concentration of the adsorbent on the adsorption process were studied. The percentage removal (*R*) is denoted by Eq. (6.1) which determines the efficiency of the adsorbent:

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{6.1}$$

where:

C_o is the initial concentration
C_e is the concentration at equilibrium

The equilibrium adsorption capacities (q_e) of the activated carbon at predetermined time intervals were determined based on adsorbate mass balance using Eq. (6.2):

$$q_e = \left(\frac{C_o - C_e}{M} \right) V \tag{6.2}$$

where:

C_o and C_e are the initial and equilibrium concentrations of the phenol (mg/L), respectively
V is the volume of the aqueous solution (L)
M is the mass of activated carbon used (g)

The equilibrium adsorption (q_t) at time t is the concentration of phenol adsorbed at time t and is given by Eq. (6.3):

$$q_t = \left(\frac{C_o - C_t}{M} \right) V \tag{6.3}$$

where:

C_o and C_e are initial and equilibrium concentrations at time t
M is the mass of activated carbon used (g)
V is the volume of the aqueous solution (L)

6.5 RESULTS AND DISCUSSION

Parameters such as impregnation ratio, concentration of oxidant, activation time and activation temperature could impact significantly on the characteristic of porous structure of produced AC. The above parameters have been reported by other researchers to impact significantly on the characteristics of surface chemistry and porosity of AC [8, 12-14]. The impregnation ratio and pre-carbonisation process were investigated in this study. All the experiments were repeated thrice with relative standard deviation less than 10%.

6.5.1 Effects of impregnation ratio on elemental analysis and pore structure of produced AC

The effect of impregnation ratio (IR_r) on the elemental composition and pore volume is discussed. The result obtained in this study are given in Table 6.1 and show that the precursor MT has a high percentage of fixed carbon; an indication of its applicability in AC production. However, the specific surface area (S_{BET}) and total pore volume (V_{Total}) of the AC at different IR_r values were also investigated. From the results of elemental analysis, it was observed that the content of elements were almost the same for different IR_r values, except in the value of nitrogen where all the elemental nitrogen was reduced to nitrogen gas. However, the values of specific surface area (S_{BET}) and total pore volume (V_{Total}) of the produced AC prepared with different IR_r values were obviously different, as shown in Table 6.2. The results showed that S_{BET} and V_{Total} increased with an increase in IR_r, reaching maximum for S_{BET} at 1 263 m^2/g and 1.59 cm^3/g for V_{Total} when the IR_r was 1:4 and 1:5, respectively. The reason was that with an increase in IR_r the acid was able to penetrate the interior of the particle of the produced AC to a certain extent until no further reaction could take place. This result is similar to those obtained by Prahas *et al.* [14] and Wang et al. [24].

Table 6.1: Elemental analysis of maize tassel and produced activated carbon

Sample Code	C	H	H/C	N	S	O^a	% Yield
Maize tassel	53.25	5.63	0.11	1.15	0.081	39.88	-
IR(1:1)ACCT500	41.65	1.37	0.033	0	0	56.37	56.96
IR(1:2)ACCT500	56.17	1.66	0.030	0	0	42.18	46.67
IR(1:3)ACCT500	56.43	1.99	0.035	0	0	41.55	42.36
IR(1:4)ACCT500	51.51	1.47	0.029	0.034	1.090	45.93	39.50
IR(1:5)ACCT500	50.45	1.38	0.029	0	1.040	47.13	38.40

IR_r = impregnation ratio; ACC = chemically activated carbon; H/C = hydrogen carbon ratio; a = obtained by difference

Table 6.2: Pore structure of produced activated carbon

Sample code	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	$S_{singlepoint}$ (m^2/g)	V_{Total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
IR(1:1)ACCT500	712	967	698	0.373	0.0803	0.292
IR(1:2)ACCT500	776	1068	748	0.623	0.0141	0.609
IR(1:3)ACCT500	623	850	600	0.617	0.0197	0.597
IR(1:4)ACCT500	1263	1735	1214	1.541	0.0327	1.508
IR(1:5)ACCT500	1240	1713	1182	1.592	0.0262	1.566

6.5.2 Effect of impregnation ratio on yield of produced activated carbon

Figure 6.1 shows the effect of IR_r on the yield of AC produced, which is usually defined as the final weight of AC after activation, washing and drying divided by the initial weight of the precursor on dry mass basis [8]. The figure shows that the yield of AC produced from MT at different IR_r values decreases with increasing IR_r. In this study the values obtained ranged from 38.40% to 56.96%. This result was similar to what was reported by other researchers using cellulose 42% to 51% [23], fruit stones 31.9% to 48.5% [14], rubber wood sawdust 46.63% [12] and chestnut wood 37.2% to 42.3% [13]. The yield obtained for the phosphoric acid activated MT was higher than those obtained for fixed carbon in the precursor (Table 6.1). This is because carbonisation at high temperature affects the polymeric structures which easily decompose to liberate gaseous substances from the lignocellulosic material in the form of liquid/or tar before forming a rigid carbon skeleton in the form of aromatic sheet [25, 26].

Figure 6.1 also revealed that the carbon yield decreased with an increase in IR_r from 1 to 5. It has been reported [27, 28] that during lignocellulosic reaction with phosphoric acid, the first acid attack occurs immediately after the mixing of the lignin and hemicelluloses. This can be explained by the fact that cellulose is more resistant to acid hydrolysis [27]. This reaction is followed by a series of other reactions, namely dehydration, degradation and condensation. Phosphoric acid was adjusted to give a specific impregnation ratio (IR_r); an excess of phosphoric acid will promote gasification of char, thereby increasing the total weight loss of the carbon [5, 26-36].

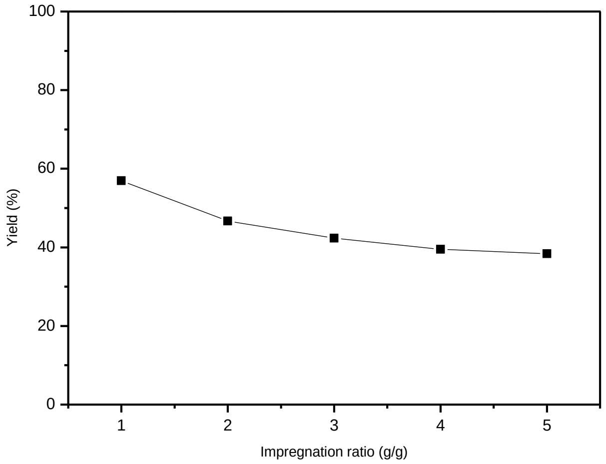

Figure 6.1: Effect of impregnation ratio on produced activated carbon

6.5.3 Effect of impregnation ratio on the surface area and pore volume of produced activated carbon

The effect of impregnation ratio on the BET surface area, micropore volume, and total pore volume are given in Table 6.2. The total pore volume, V_{Total}, was calculated from nitrogen adsorption data as volume of liquid nitrogen at a relative pressure of 0.995. The micropore volume, V_{micro}, was determined by DFT method, and the mesopore volume, V_{meso}, was obtained by subtraction of micropore volume and total pore volume, V_{Total}.

The specific surface area (S_{BET}) and total pore volume (V_{Total}) increase with the increase in IR_r. The increase in porosity with temperature greater than 450^{o}C can be attributed to formation of tars which is caused by the acid treatment on the lignocellulosic material [29]. At temperatures greater than 450^{o}C (i.e. 500^{o}C, the activation temperature for this study), an increase in IR_r also increased the micropore volume, but the increase in micropore volume at IR(1:2) ACCT500 and IR(1:3) ACCT500 was not significant (Figures 6.2 and 6.3). On the other hand, the mesopore volumes increased with an increase in IR_r, while phosphoric acid produced mesopores, as has been reported by some researchers [26, 28, 30]. Moreover, it was observed that the IR (1:3) ACCT500 produced a pore structure with low specific surface, micropore and mesopore volumes. This might have resulted from contraction of carbon structures which in turn resulted in low porosity of the pore structure of AC. Similar results have been reported by other researchers [5].

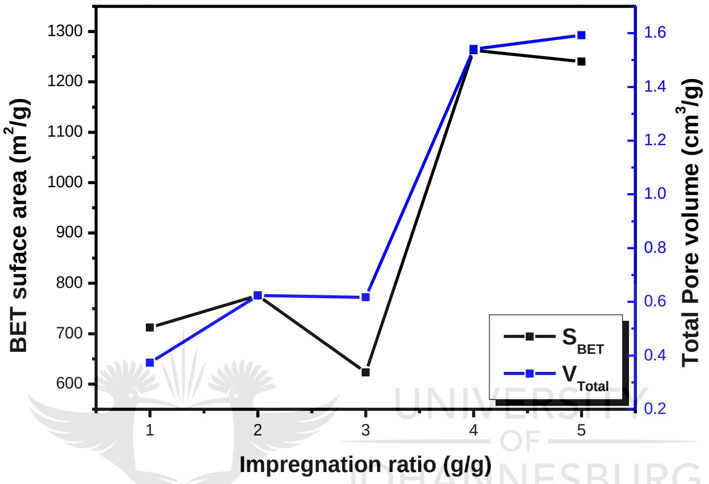

Figure 6.2: Effect of impregnation ratio on specific surface area and total pore volume of produced AC

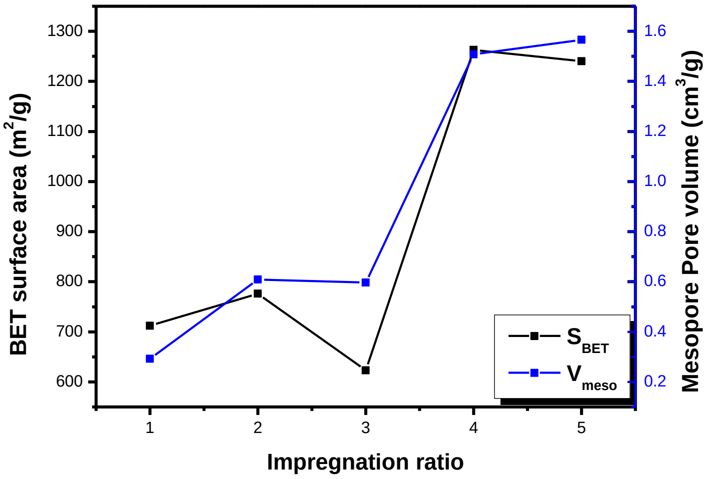

Figure 6.3: Effect of impregnation ratio on specific surface area and mesopore volume of produced AC

6.5.4 Effect of impregnation ratio on N_2 adsorption desorption isotherms of porous carbons

Figure 6.4 shows the N_2 adsorption desorption isotherms of the AC prepared under different IR_r values at 500°C for 60 min. The isotherm classification was done according to BET Bansal and Goyal, [16] and Namane *et al.* [36], in this study IR(1:1) ACCT500 belonged to type I (1:1); IR(1:2) ACCT500 to type II (1:2); IR(1:4) ACCT500 to type III (1:4); and IR (1:3) ACCT500 and IR(1:5) ACCT500 to type IV (1:3 and 1:5). For the samples IR (1:1) ACCT500 and IR (1:2) ACCT500 the adsorption of N_2 increased rapidly at lower relative pressure which indicates that the AC produced had a well-developed mesopore in its matrix, while in the case of samples IR (1:4) ACCT500 and IR (1:5) ACCT500 the volume of N_2 adsorbed was found to increase with an increase in IR_r at higher relative pressure greater than 0.05. The hysteresis loop for the samples occurred at a relative pressure of around 0.45. The volume of the adsorbed N_2 was different in all cases for the samples indicating that changes in the value of IR have a significant impact on the porosity of the AC.

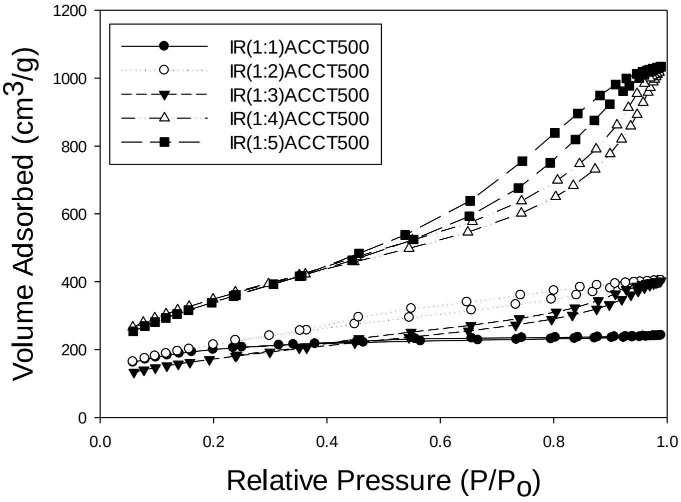

Figure 6.4: Effect of impregnation ratio on N_2 adsorption of the activated carbon

6.5.5 Effect of impregnation ratio on the crystallinity of the produced activated carbon

Figure 6.5 shows the X-ray diffraction patterns of produced AC prepared under different IR_r at an activation temperature of 500°C for 60 min. The figure shows two broad peaks at 26° and 43° and these are assigned to reflection from the plane (0 0 2) and the overlapped reflections from planes 100 and 101, respectively. The appearance of these peaks in produced AC indicates increasing of crystalline structure with increasing IR_r, which results in better layer alignment. The pattern shows a broad diffraction peak in 2θ range of 10° to 30°. The XRD pattern obtained in this study is similar to what has been reported previously by other researchers [5, 24, 31-33].

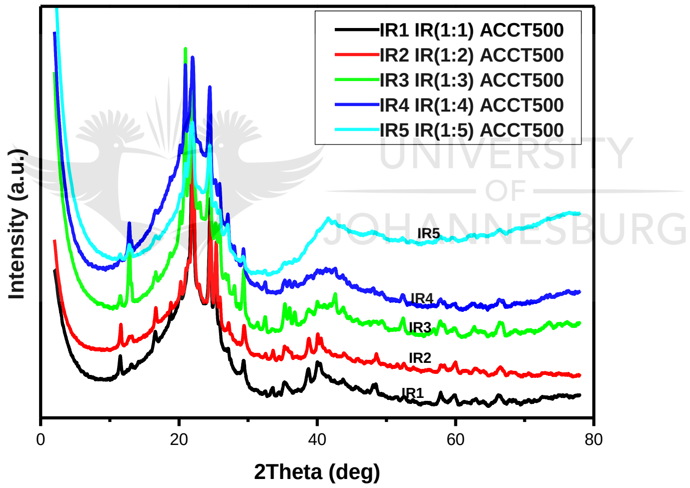

Figure 6.5: XRD of produced activated carbon at different impregnation ratios

6.5.6 Scanning electron microscopy (SEM analysis)

The scanning electron micrograph result of the surface morphology of produced AC is illustrated in Figure 6.6. The result shows that IR_r has a significant impact on the AC porosity. This is obvious in the differences of the exterior surfaces of the AC produced. In samples IR (1:2) ACCT500, IR (1:3) ACCT500, IR (1:4) ACCT500 and IR (1:5) ACCT500 there are pronounced cavities on the exterior surfaces which might have resulted from the evaporation of the phosphoric acid during the carbonisation, thereby leaving spaces previously occupied by the dehydrating agent. Figure 6.6 IR (1:4) ACCT500 revealed that the surface of the produced AC was quite dense with both large and small pores and spongy white patches for occasional cracks in the carbon matrix. This accounts for its large surface area, while in the case of IR (1:3) ACCT500 the surface revealed smooth collapsed surfaces having depressions with some blocked pores which explain its low surface area and pore volume. However, as the ratio of impregnation increases with adequate mixing the surface area increases as shown in IR (1:4) ACCT500 but decreases in IR (1:5) ACCT500. This might be due to evaporation of dehydrating agent previously occupying the cavities or excess activating agents that are still filling the pores of porous carbon.

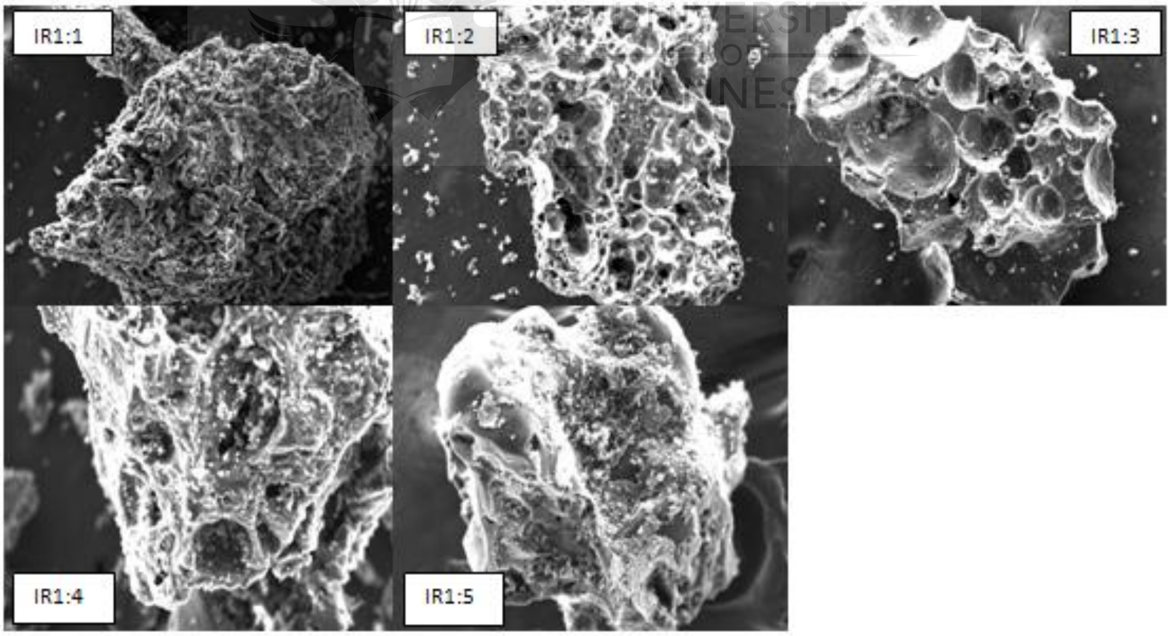

Figure 6.6: SEM micrographs of produced activated carbon at different impregnation ratios

6.5.7 Fourier transform infrared (FT-IR) analysis

Figure 6.7 shows the FT-IR spectra of produced AC with various IR_r values at the activation temperature of about 500°C. All the samples show broad band absorption spectra at around 3 400 cm^{-1} to 2 850 cm^{-1}. A peak at around 1 760 cm^{-1} to 1 640 cm^{-1} shows the presence of C=O stretching vibration of aldehyde, carboxylic acid, ketones and esters. The presence of a broad band at around 3 400 cm^{-1} to 2 850 cm^{-1} and a peak at around 1 670 cm^{-1} indicates the presence of carboxylic acid [23, 34]. A broad peak of relatively low intensity at an absorption band of 3 300 cm^{-1} to 3 100 cm^{-1} of the broad band at around 3 400 cm^{-1} to 2 850 cm^{-1} may be assigned to O-H stretching vibration in phenol and C-H stretching in alkane. The weak peak at around 2 850 cm^{-1} is the C-H stretching vibration in the methyl group [34]. A strong band at 1 646 cm^{-1} can be assigned to C=C aromatic ring stretching vibration which is enhanced by polar functional and alkene groups [14]. Furthermore, there is a sharp peak at 1 410 cm^{-1} which corresponds to C-H stretching alkane and also a broad band between 1 300 cm^{-1} and 1 000 cm^{-1} with the strong band at around 1 220 cm^{-1} and a shoulder at around 1 100 cm^{-1} (which occurred in all the samples with various intensity). Puziy et al. [14] reported similar peaks at 1 220 cm^{-1} to 1 180 cm^{-1} which were assigned to the O-C stretching vibrations in P–O–C, the stretching mode of hydrogen bonded P=O and P=OOH linkage. The shoulder at 1 203 cm^{-1} to 1 118 cm^{-1} can be assigned to symmetrical vibration in a chain of P–O–P and ionised linkage $P^+–O^-$ in acid phosphate esters. The phosphorus-containing group becomes more obvious as the IR increases with the help of activation temperature.

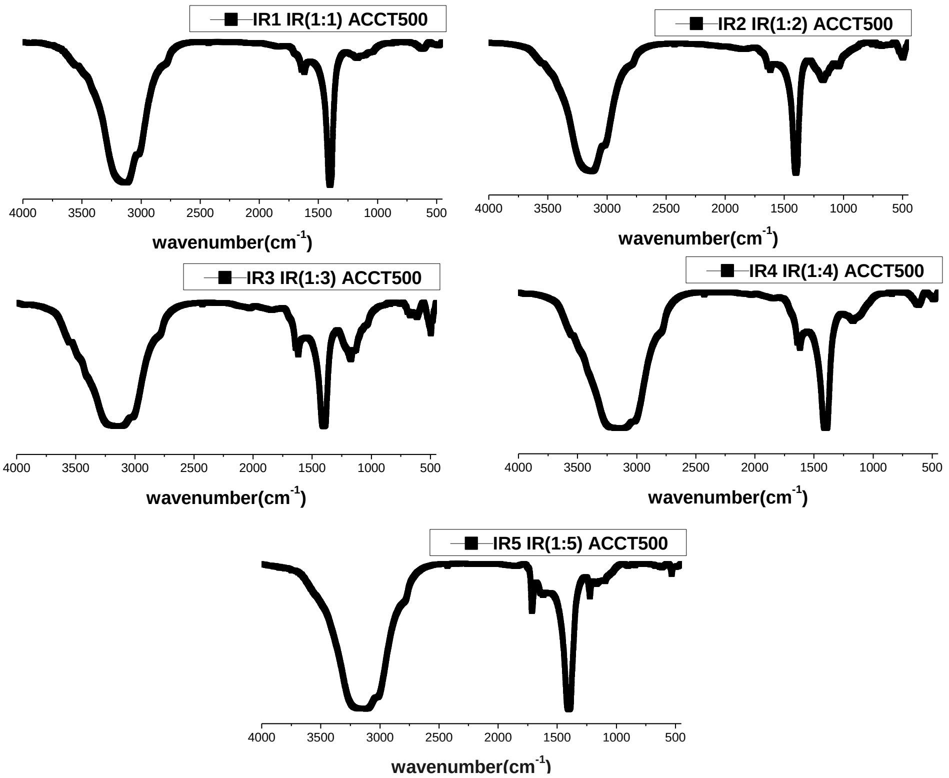

Figure 6.7: FT-IR spectra of produced activated carbon at different impregnation ratios

6.6 Pore-size distribution

Pore-size distribution in produced AC characterises the structural heterogeneity of a porous material which also represents a model of solid internal structure [16, 35]. The pore size distribution has been reported to be closely related to both equilibrium and kinetic properties of a porous material [19]. However, according to the International Union of Pure and Applied Chemistry (IUPAC) structural characterisations in terms of pore size are classified into three groups, namely micropore (diameter <2 nm), mesopore (diameter between 2-50 nm) and macropore (diameter >50 nm) [35, 36]. In all the results obtained the pore-size distribution falls between micropore and mesopore (Table 6.2 and Figure 6.8). Figure 6.8 reveals the pore-size distribution of the produced AC. From Figure 6.8 IR (1:1-1:4)

ACCT500, it could be deduced that a major peak lies in the mesopore region for all the samples, while the other minor peak is in the micropore region which is not visible. The mesopore volume is larger than the micropore volume (Table 6.2). The ratio of V_{meso} to V_{Total} ranges from 0.783 to 0.983. As IR_r increases the mesoporosity of the produced AC increases because the dehydrating agent reacts first with lignin and hemicelluloses to create the mesopore structure. Similar results have been reported by other researchers [5, 24].

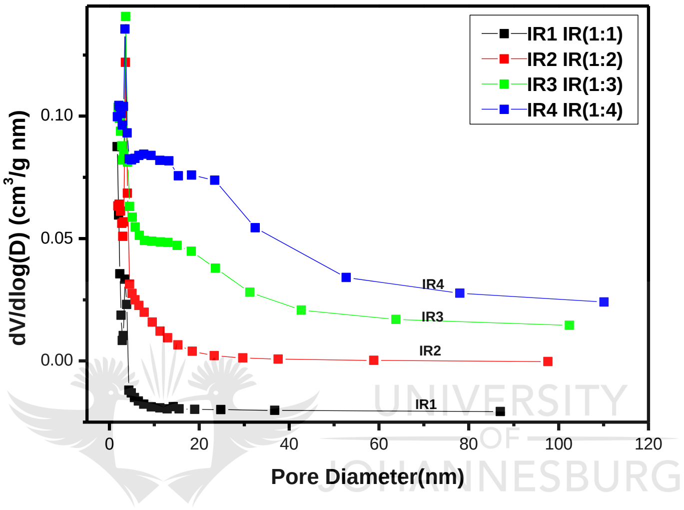

Figure 6.8: Pore-size distribution of produced activated carbon

6.7 Effect of contact time and initial concentration on phenol adsorption

Figure 6.9 shows the effect of contact time on the removal of phenol at various initial concentrations (50 mg/L to 250 mg/L). The saturation curve rises sharply at the initial stages, indicating that plenty of sites were readily accessible. After some time, there were decreases in adsorption which led to a slight plateau which indicates that the adsorbent had reached saturation point at this stage. However, as indicated in Figure 6.10, there was the formation of plateaus indicating the saturation point of the adsorbent. It can also be seen from Figure 6.10 that the contact time needed for phenol solutions with initial concentrations of 50 mg/L to 150 mg/L to reach equilibrium was 120 min. However, for phenol solutions with higher initial concentrations, longer equilibrium times were required which indicate a decrease in adsorption capacity (Figure 6.9). It was also seen that an increase in initial phenol concentration resulted in increased phenol uptake. The removal curve shown in Figure 6.10 is single, and continuous, indicating the formation of monolayer coverage of the phenol molecules onto the outer surface of the adsorbent. A similar observation has been reported about the adsorption behaviour of mono-substituted phenols of different solubilities on activated carbons produced from both demineralised and original bituminous coal [37].

The removal efficiency percentage was over 90 percent (Figure 6.10). The adsorption capacity at equilibrium (q_e) increased from 12.51 mg/g to 75.29 mg/g with an increase in the initial phenol concentrations from 50 mg/L to 250 mg/L. The mass transport steps are determined by the adsorption of solute from solution by porous adsorbent [38]. This occurs by the adsorbate migrating through the solution by film diffusion, which is then followed by solute movement from the particle surface into interior sites by pore diffusion and then the adsorbate is absorbed on the active sites at the interior of the adsorbent particle [38-40]. The relative affinity between the carbon surface and phenolic molecules has been reported to be related to the complexes formed between the organic ring of the phenol and the basic sites on the carbon surface [37].

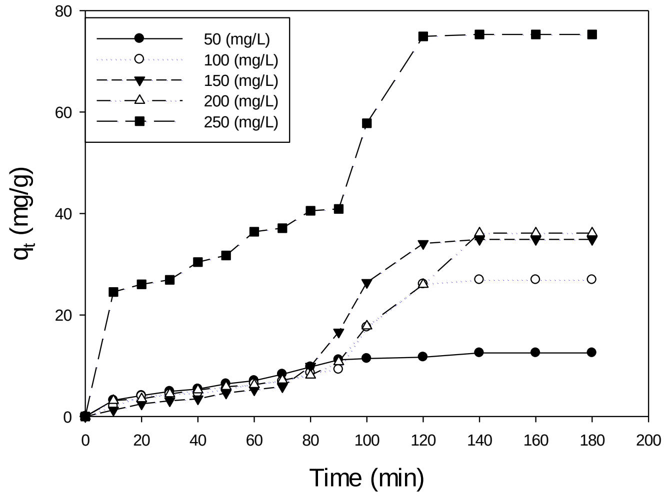

Figure 6.9: Effect of initial concentration and contact time on adsorption of phenol onto ACC

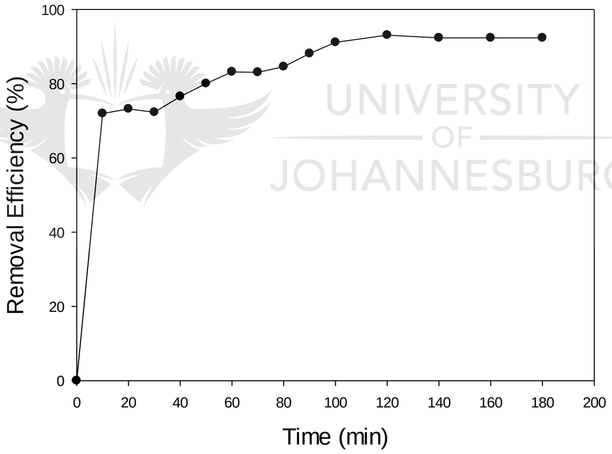

Figure 6.10: Effect of initial concentration and contact time on adsorption capacity of ACC

6.8 Effect of pH on adsorption properties of activated carbon

The influence of pH on the adsorptive capacity of the chemically produced activated carbon were determined at room temperature and the initial concentration of 50 mg/L using solution pH values from pH 2 to pH 12. Figure 6.11 demonstrates that the phenol adsorption was unaffected when the pH was low in the range of pH 2 to pH 4 and later showed increases at pH values of greater than pH 4 and a maximum at pH 6. A similar trend of the effect was reported by other workers using commercial and laboratory produced activated carbon [41-43]. The pH of the solution affects the surface charge of the adsorbent and the degree of ionisation of the adsorbate [40, 44]. Phenol as a weak acid compound (pKa≈9.89) often dissociates at pH>pKa [40, 45]. The adsorption decrease at high pH values is attributed to ionisation of the adsorbate molecules and electrostatic repulsions between the negative surface charge and the phenolate-phenolate anion in the solution [40, 45].

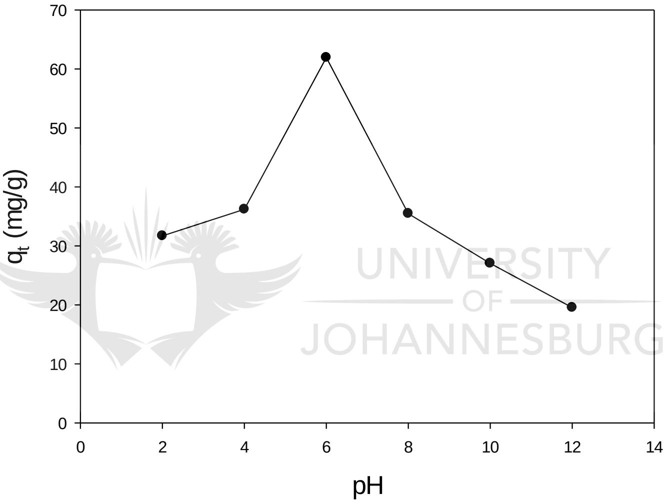

Figure 6.11: Effect of pH on adsorption properties of ACC

6.9 Adsorption isotherms

Basically, the adsorption isotherm is an important tool used to describe the way solutes interact with adsorbents and is also applicable in optimising the use of adsorbent in adsorption studies. Experimental data obtained for the adsorbed phenol against initial concentration were analysed using different types of isotherm which include Langmuir and Freundlich equations [43].

Langmuir and Freundlich isotherm models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solution. The isotherm that best describes monolayer adsorption on a finite number of identical sites is Langmuir. The model does not consider transmigration in the plane of the surface, but assumes uniform adsorption on the surface [42, 46]. The linear form of the isotherm can be denoted by the following equation:

$$\frac{1}{q_e} = \left(\frac{1}{K_L\, q_m}\right)\frac{1}{C_e} + \left(\frac{1}{q_m}\right) \tag{6.4}$$

where:

$C_e\ (mg/g)$ is the equilibrium concentration, i.e. phenol ion concentration remaining in the solution at equilibrium

q_e is the phenol ion concentration taken up by the sorbent per unit mass of the sorbent at equilibrium

q_m is the maximum capacity of adsorption (mg/g)

K_L is the constant related to affinity of the binding sites, L/mg)

The plot of $\frac{1}{q_e} vs. \frac{1}{C_e}$ gives a linear plot indicating that the sorption obeys the Langmuir model. Figure 6.12 shows a linear plot of $\frac{1}{q_e} vs. \frac{1}{C_e}$ using the experimental data obtained, suggesting the applicability of the Langmuir model (R^2=0.95) (Table 6.3).

The Freundlich isotherm model describes the adsorption process that takes place on a heterogeneous surface [42, 47, 48]. Thus, the Freundlich exponential equation is given as:

$$q_e = K_F C^{1/n} \tag{6.5}$$

where:

K_F ((L/mg) is indicator of the adsorption capacity

$\frac{1}{n}$ is the adsorption intensity which indicates the heterogeneity of the adsorbent sites and the relative distribution of energy

The linear form of this model is derived by taking the logarithm of the term in Eq. (6.5), as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6.6}$$

The plot of $\log q_e$ *vs.* $\log C_e$ from Eq. (6.6) gives a linear plot with $\frac{1}{n}$ as slope and K_F as the intercepts (Figure 6.13). The value of $\frac{1}{n}$ is 0.738, which is nearer to unity, suggests the favourability of the Freundlich isotherm for the adsorption process.

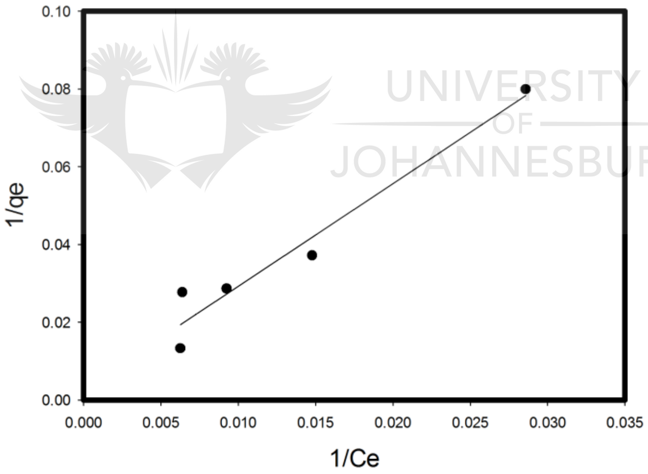

Figure 6.12: Langmuir adsorption isotherm of phenol onto ACC at 30^{o}C

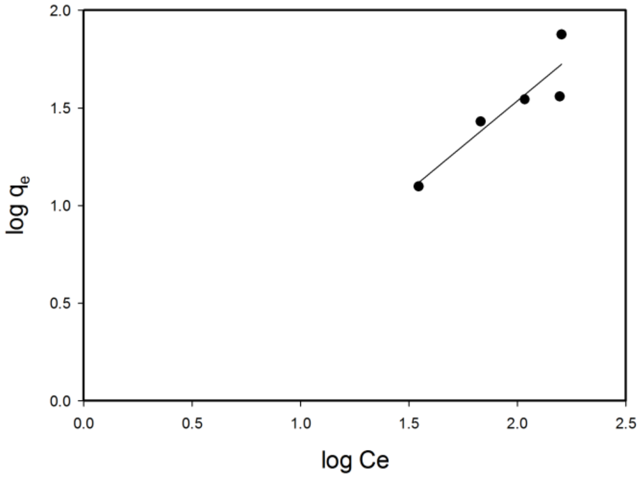

Figure 6.13: Freundlich adsorption isotherm of phenol onto ACC at 30°C

Table 6.3: Langmuir and Freundlich constants for adsorption of phenol onto ACC

Langmuir constants			Freundlich constants		
$q_m (mg/g)$	$K_L (L/mg)$	R^2	$K_F\ (L/mg)$	n	R^2
344.8	0.0000314	0.950	2.51	1.355	0.835

CONCLUSION

The porous activated carbon AC was prepared from maize tassel (MT) using phosphoric acid as an activating agent. The effect of impregnation ratio (IR_r) on the pore structure and surface chemistry was studied. The pore structure of the porous carbon produced was investigated by XRD, N_2 adsorption, FT-IR and SEM. The result obtained showed that there is a direct relationship between impregnation ratio (IR) and pore structure. The activated carbon (AC) produced was porous having a maximum surface area (1 263 m^2/g) and total pore volume (1.592 cm^3/g). In addition, increasing the IR also increases the acid functional groups.

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CHAPTER SEVEN

APPLICATION OF ACTIVATED CARBON FROM MAIZE TASSEL AS AN ADSORBENT IN SOLID-PHASE EXTRACTION FOR THE ENRICHMENT OF PHENOLIC COMPOUNDS

Preparation and use of maize tassels' activated carbon for the adsorption of phenolic compounds in environmental wastewater sample

Paper IV: submitted to *Applied Surface science Journal* **2014**

Abstract

The determination and remediation of three phenolic compounds bisphenol A (BPA), ortho-nitrophenol (o-NTP), and para-chlorophenol (PCP) in wastewater is reported. The analysis of these molecules in wastewater was done using GC×GC TOFMS while activated carbon derived from maize tassel was used as an adsorbent. During the experimental procedures the effect of various parameters such as initial concentration, pH of sample solution, eluent volume and sample volume, on the removal efficiency with respect to the three phenolic compounds was studied. The results showed that maize tassel-produced activated carbon (MTAC) cartridge packed solid-phase extraction (SPE) system was able to remove the phenolic compounds effectively (90%, 92% and 95% for BPA, o-NTP and PCP, respectively) . The MTAC cartridge packed SPE sorbent performance was compared to commercially produced C18 SPE cartridges and found to be comparable. All the parameters investigated were found to have a notable influence on the adsorption efficiency of the phenolic compounds from wastewaters at different magnitudes.

Keywords: bisphenol A, ortho-nitrophenol, para-chlorophenol, maize tassel activated carbon, adsorption

7.1 INTRODUCTION

The quality of water and wastewater streams in the urban settlements has been an issue of concern, thus calling for increased attention in their monitoring, assessment and purification. In the recent past there has been an increase in the release of organic compounds such as phenolic compounds mainly bisphenols A, 2, 2 bis (4-hdroxyphenyl) propane (BPA) (contained in polycarbonate plastic and epoxy resin), ortho-nitrophenol (o-NTP) (formed photochemically in the atmosphere from vehicle exhaust) and para-chlorophenol (PCP) (generated from phenols in the chlorination of drinking water) into the hydrosphere [1-3]. These chemicals are often used as raw materials or synthesis material intermediates in many manufacturing industries such as chemical plants, wood preservative plants, plastics, dye, epoxy, resins, pharmaceutical, oil refineries, textiles, leather industries, paper and pulp [4-7]. These compounds find their way into the aquatic environment through direct discharge of industrial wastewater or effluents [7].

The phenolic compounds that contaminate water systems have been identified to have organoleptic properties, and are carcinogenic and toxic to both aquatic and human life [2, 4]. They are also known to produce unpleasant odours and tastes in drinking water even when present at very low concentrations [2, 8]. These compounds and their derivatives have been placed among the priority list of pollutants by both the European Union and the United States Environmental Protection Agency (USEPA) [9-11]. The release of phenolic compounds into the environment has attracted a great deal of attention, because of their potential estrogenic activity [2, 8, 12, 13]. Therefore, it is necessary to monitor and remove these chemicals from the environment by developing simple and cheap analytical methods.

Several analytical techniques are available for the determination of phenolic compounds, which include high-performance liquid chromatography (HPLC) [14-16], gas chromatography (GC) [16], using a variety of detectors, such as flame-ionisation detection (FID) [2, 14, 15, 17], and electron-capture detection (ECD) [14, 18], capillary electrophoresis (CE) in combination with ultraviolet detection (UV) [16, 18-21], fluorescence detection [17, 20], electrochemical detection or mass spectroscopy (MS) [18, 22], and MS or microwave-induced plasma atomic emission spectroscopy (MIP-AES) [17, 18, 22, 23]. Nevertheless, a preconcentration step is necessary in the analytical scheme for the determination of phenolic compounds, as none of the above-mentioned combinations can achieve the quantification limits required for the direct determination of phenolic compounds in drinking water or wastewater streams [2].

Furthermore, low concentrations of phenolic compounds in actual water samples make direct determination difficult. Therefore, suitable sample pre-treatment methods are often employed. To have an ideal sample pre-treatment procedure, the following criteria are crucial for optimum selection: (i) the set-up should be simple; (ii) able to extract the largest number of target compounds; (iii) efficient; (iv) inexpensive; and (v) compatible with various determination techniques. All these pre-treatment methods are the basis for moving toward simplification [3, 24-27].

Various techniques for sample enrichment or preconcentration for the determination of phenolic compounds have been reported and these include liquid-liquid extraction (LLE), which is still being used in the preconcentration step for determining phenolic compounds in water and wastewater streams [2, 3]. Currently, solid-phase extraction (SPE) and solid-phase microextraction (SPME) are being considered a better alternative to LLE [2]. This is due to the drawback presented by LLE which includes foaming during the process, difficulties in the automation of the LLE procedure, length of time of analysis and consumption of large volumes of organic solvents making the technique uneconomical and environmentally unfriendly. SPE has been in operation in terms of development and usage for concentration of several pollutants for several decades [3, 24, 26-28]. It is very effective as a sample-handling technique resulting in high preconcentration factors, due to its simplicity, ease of automation and operation, low usage of organic solvent and being less time consuming [3, 25, 26, 29-32].

However, the choice of adsorbent is another crucial factor in order to obtain higher enrichment efficiency of analytes in SPE. Different types of solid-phase extraction sorbents such as C_{18}, or C_8 silica, [33-35] polystyrene-divinylbenzene copolymer [16, 24, 33-38], carbonaceous sorbents [17, 33, 35, 39] and carbon nanotubes have been employed for the purpose of enrichment [24]. C_{18} has been the most widely used, but shows low recovery for some polar analytes such as phenolic compounds [24, 33-35]. Activated carbon produced from agricultural waste residues (maize tassel-produced activated carbon (MTAC)) has attracted more attention in environmental field applications in recent times, due to its large surface area and pore diameter [32, 40-42]. This is due to their low cost and ease of availability compared to other adsorbents. The main advantage of this material is its suitability for routine adsorption of pollutants due to its low consumption and cost.

From the above-mentioned facts activated carbon prepared from maize tassel may have great analytical potential as an effective SPE sorbent for the extraction of some suitable compounds such as phenolic compounds. However, to the best of our knowledge, there have been no reports on the usage of maize tassel-produced activated carbon (MTAC) for the removal of phenolic compounds from aqueous solutions.

The objective of this study was to produce AC, modified with physical method by using steam as activating agent and also pre concentrate organic species from aqueous medium. In this study, the applicability of MTAC as packing adsorbents for SPE was investigated using three phenolic compounds, namely BPA, o-NTP and PCP, as model compounds.

7.2 EXPERIMENTAL SECTION

7.3 MATERIALS AND METHODS

7.3.1 Chemical reagents and standards

All the phenolic compounds, BPA (>97 % Purity), o-NTP (>98% Purity), PCP (>99% Purity) were of analytical grade and obtained from Sigma-Aldrich (St Louis MO, USA). The standard stock solutions (100 mg/L) containing these compounds were prepared in methanol and stored at 4°C. The working solutions were freshly prepared on a daily basis by the appropriate dilution of the stock solution with deionised water. Acetic acid (96% purity) and ammonia solution (25%) were used to adjust pH values of the working solutions, and were obtained from Associated Chemical Supplies Ltd, Fluka Analytical (Buchs, Switzerland) and Rochelle Chemicals Ltd (Johannesburg, South Africa). All the glassware used was decontaminated overnight using 6 mol/L nitric acid and thoroughly washed with deionised water before use. Strata™ polypropylene C18-E SPE (EC) cartridges (0.5 g, 6 mL) were purchased from Phenomenex, Torrance CA, USA.

7.3.2 Instrument

The chromatographic separations were performed using a LECO Pegasus® 4D GC×GC TOFMS instrument (LECO Corporation, 3000 Michigan, USA). A Restek fused silica GC column (Rxi®-5ms; Crossbond® 5% diphenyl/95% dimethyl polysiloxane) with length 30 m, 0.25 mm ID, 0.25µm df with maximum temperature of 340°C min bleed at 320°C, and second dimension column (Rtx®200 with length 2 m, 0.18 mm ID, 0.18 µm df with maximum programme temperature 350°C min bleed at 330°C) were used for all separations.

7.3.3 Sample preparation

In this experiment, the sorbent used for cartridge packing of MTAC was produced by chemical method according to Olorundare et al. [41]. An aliquot of 20 g of the milled maize-tassel powder was added to 20 mL of phosphoric acid solution (85% by weight) and manually stirred for 4 minutes and left to stand for 1 h. The impregnated materials were dried at 110°C for 24 h and then activated at 500°C under an inert atmosphere, i.e. nitrogen flow at 200 cm^3/min. The produced activated carbons were coded as MTAC. The residual phosphoric acid was eliminated from the activated carbon by washing with hot deionised water until the pH of the leachate was between pH 5 and pH 6 after which the powder was dried at 110°C for 3 h; the final material was then ground and stored for further analysis. The MTAC used was the one with the highest BET surface area.

The MTAC prepared was characterised by using nitrogen adsorption-desorption isotherm measured at 77 K using ASAP 2020 Micromeritics Instrument for the BET surface area at relative pressure range (P/P_o = 0.05-0.3) and total pore volume at a relative pressure of 0.995. The surface morphology of the sorbent MTAC was determined using scanning electron microscope (SEM) (Nano 2000 High resolution SEM (HRSEM), Jeol - Japan) which gives a rough indication about the porosity of the material. Two water samples were selected from a local dam situated in the City of Johannesburg. Before application, all the environmental water samples were filtered through 0.45µm micropore membrane filter and stored under low temperature (4°C) until use.

7.3.4 Solid-phase extraction cartridge

The SPE commercial cartridge was replaced with an MTAC packed cartridge which was prepared by modifying a Strata™ C18-E SPE C_{18} (EC) (0.5 g, 6 mL) cartridge. The C_{18} packing of the cartridge was evacuated, and then 0.5 g of MTAC was packed into the cartridge. The 20 µm polypropylene lower and upper frits remained at each end of the cartridge to serve as support holder for MTAC packing. The outlet tip of the cartridge was connected to a vacuum pump (Shimadzu, Japan) and the inlet end of the cartridge was connected to the PTFE suction tube whose other end was inserted into the sample solution. The entire solid-phase extraction set-up assembly was carefully washed with methanol before use in order to reduce the interference of the organic and inorganic contaminants.

7.3.5 Procedure for SPE extraction

Before the preconcentration enrichment step, the MTAC packed cartridge was firstly preconditioned by washing with 6 mL of methanol and then 10 mL of purified water were added before a new SPE preconcentration procedure was started. The pH of the samples was adjusted accordingly with 1 mL of acetic acid or ammonia solution. Then a known volume of spiked water samples was aspirated through the modified SPE C18 column at controlled flow rate and the elute obtained was discarded. However, when the whole sample had passed through the SPE column, 10 mL of purified water was used to clean the impurities or the co-adsorbed matrix materials from the cartridge. The SPE column was then dried by negative pressure for 10 min and the targeted analytes were eluted with optimum volume of methanol (Figure 7.1). The resulting eluates were later air-dried with a gentle flow of nitrogen gas to 1 mL before proceeding with the subsequent determination by injecting 2 µL of the final elute into GC×GC TOFMS.

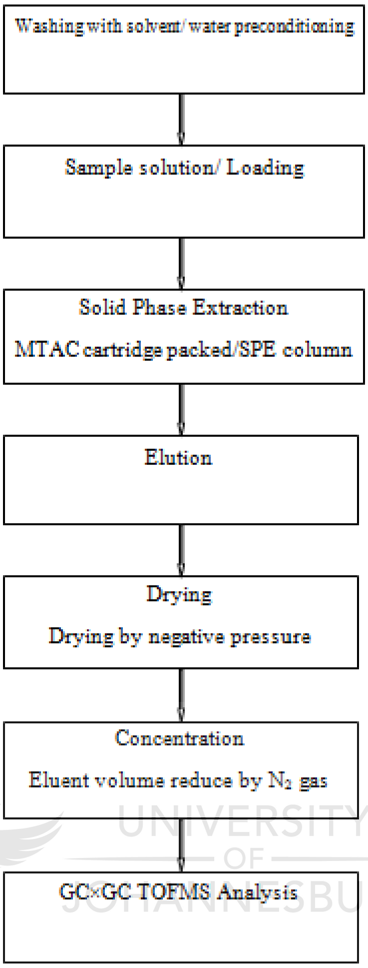

Figure 7.1: Sample flow analysis during SPE extraction process

7.4 RESULTS AND DISCUSSION

7.4.1 Physical characterisation of MTAC

7.4.1.1 Scanning electron microscopy (SEM) studies

In order to study the morphology and porosity development of MTAC prepared, scanning electron microscopy (SEM) was employed. The SEM results reveal that MTAC is characterised with distinct cells and specific surface structure. The SEM images of the

MTAC at high magnification are shown in Figures 2A and 2B (having the same magnification × 200 10 μm) and from the micrographs presented, wide pores can be observed with characteristic spongy surfaces. The micrograph shows the changes in the microstructure of maize tassel after being impregnated with phosphoric acid and subsequent isothermal holding at 500°C. Pore enlargements were observed on the surface of the AC produced (Figure 2B), while its original cell structure is completely preserved (Figure 2A). In addition, on closer inspection of the AC surface (Figure 2B) it was revealed that the large pores on the surface are connected with the smaller pores, thus forming a whole network in the interior of the carbon material.

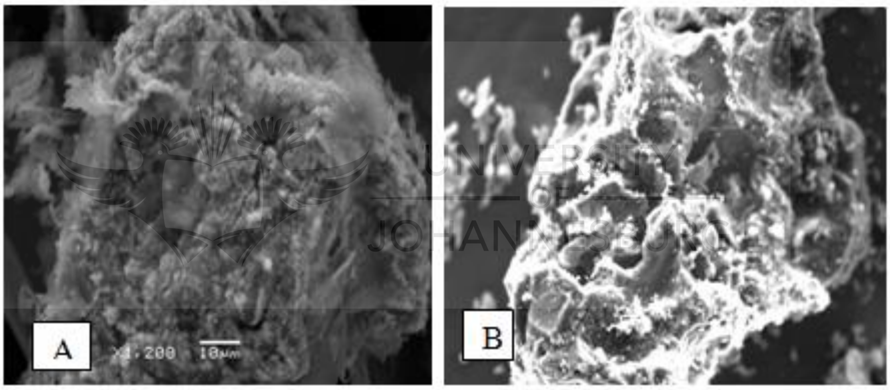

Figure 7.2: SEM images of MTAC powder

7.4.1.2 BET N_2 adsorption

Identifying the pore structure of an adsorbent is a crucial factor in adsorption process and inert gas adsorption is a good method using adsorption instrument for this function [43, 44]. Figure 7.3 shows the isotherms of N_2 adsorption/desorption at 77 K on the MTAC. The isotherm for the MTAC overlaps completely at low relative pressure but the hysteresis exists at high relative pressure (P/Po>5), irrespective of the precursor source. The factors such as the presence of the ‘inkbottle types of pores’ and slit-shaped pores are major influences on the types of hysteresis produced [43, 44]. Furthermore, a common feature of hysteresis loops is that the steep region of the desorption branch leads to the lower closure point at a relative pressure for a given adsorption, which also depends mainly on the nature of the adsorption rather than on the nature of the porous adsorbent [45, 46]. Thus, this explains the reason for the large pores and the high BET surface area of about 1 263 m^2/g and total pore volume of 1.54 cm^3/g on MTAC. The pore diameter also play crucial role in phenolic compound adsorption, because the smaller the pore diameter the larger the available surface area for adsorption. This factor comes into play, for example, when substances such as humic acid which may interfere with the adsorption of phenolic compounds in the later analytical process, will be prevented from entering the pore matrix [2].

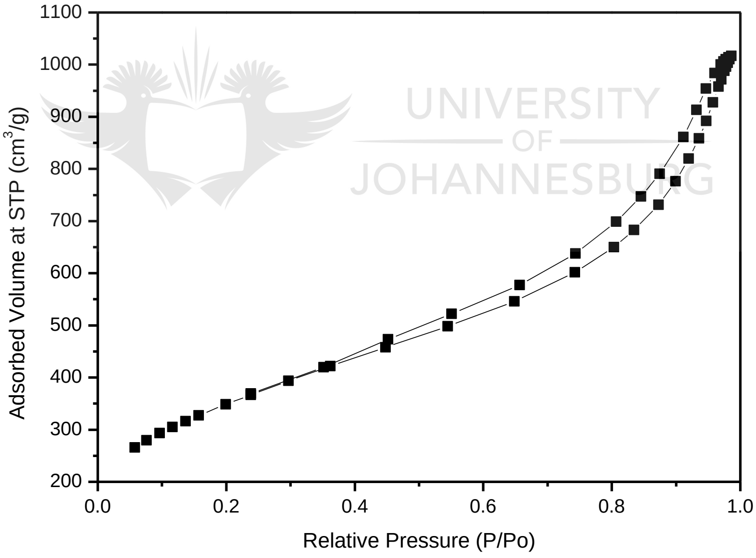

Figure 7.3: Adsorption/desorption isotherm of N_2 at 77 K on MTAC

7.4.1.3 Evaluation of MTAC as solid-phase extraction adsorbent

To determine the analytical potential of MTAC as sorbent in SPE, BPA, o-NTP and PCP were adopted as the model samples. In this experiment, there are a few parameters that may influence the enrichment efficiency; these include initial concentration, pH of the sample solution, sample volume, the eluent and its volume. All these parameters were critically investigated, because they play an important role in the concentration of the target analytes. In addition, they also have an impact on the optimisation of the adsorption efficiency.

7.4.1.4 Influence of eluent types and volume on the MTAC adsorption capacity

In achieving the above goal, four types of eluting solvents including acetone, acetonitrile, dichloromethane and methanol were experimentally tested. The results showed that BPA was the least eluted one among the analytes. It was difficult to elute BPA with dichloromethane (The difficulty in elution has to do with different behaviour in solution of phenolic compounds in terms of acidity and polarity [2]. This could also be due to the difference in pKa and octanol-water partition coefficient (log Kow) between the three analytes which has a different influence on the mobile phase of all three analytes [2]. However, methanol was found to elute all three analytes effectively. This is because methanol is a water-miscible solvent which can enhance the hydrophobic surface of the sorbent and also help in the partitioning process which involves the differences in solubility of the analytes between the aqueous and the solid polar phase [2, 3]. Therefore, methanol was used in this study as eluent. The volume of methanol used was also investigated and the results show that optimal recoveries were achieved when the volume of methanol was 8 mL (Figure 7.4), after varying the volume of methanol between 4 mL and 12 mL. Thus 8 mL of methanol was then used throughout this experiment. Methanol has the optimum elution at 8 mL because there is high mass transfer between water and the sorbent at this methanol volume. Methanol has more than 90% recovery for all of the analytes at this volume. However, from Fig. 7.4 it was observed that an increase in the volume of methanol from 4 mL to 8 mL increases the recovery of the analytes. When the volume of methanol is greater than 8 mL there was a slight reduction in the recovery of all three analytes; this might be due to a reduction in mass transfer efficiency at a volume greater than 8 mL [2].

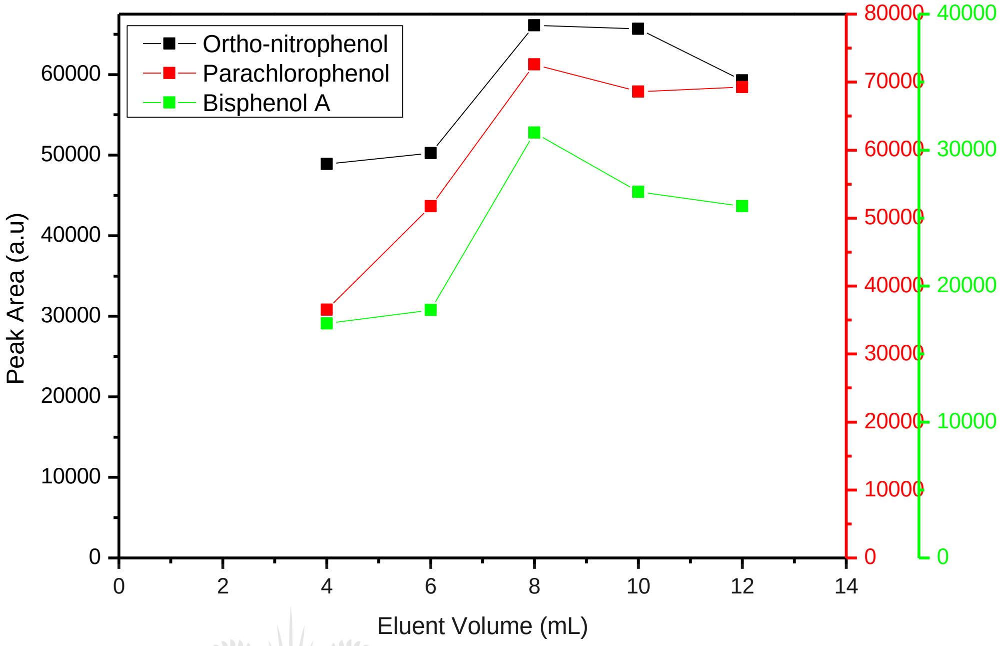

Figure 7.4: Effect of eluent volume on the MTAC adsorption capacity. The graphing was on the first and secondary y axis in order to accommodate the value differences, which needed different scales**.**

7.4.1.5 Influence of initial concentration

The influences of initial concentration play a significant role in the adsorption of phenolic compounds onto MTAC sorbent. Figure 7.5 shows the amount of analytes adsorbed for all the three phenolic compounds. The results show that among all the analytes PCP has the highest extraction shown by the peak area, while the least extractive analytes was BPA. It was observed that an increase in initial concentration of the solute results in increasing uptake of all the solutes. This is more pronounced in PCP than others due to the fact that increasing the initial concentration generally increases the overall mass transfer driving force between the solid and liquid phase of the adsorbate [7, 47], thus leading to an increase in the interaction between the adsorbent and the adsorbate, which consequently enhances the adsorption process [6, 8, 47]. Furthermore, the bonding between adsorbent and water must be broken first before adsorption can take place and also greater solubility provides stronger bonding between the adsorbate and adsorbent [48], which explains why BPA is the least adsorbed among all the analytes.

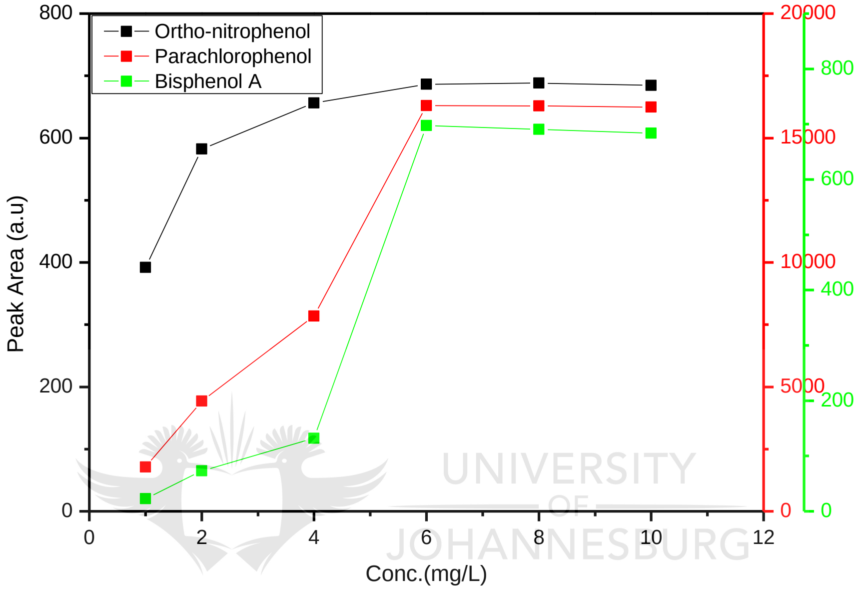

Figure 7.5: Effect of initial concentration on the MTAC adsorption. The graphing was on the first and secondary y axis in order to accommodate the value differences, which needed different scales.

7.4.1.6 Influence of sample solution pH

The sample solution pH also plays important role in the SPE procedure, because the pH values of the solution reveal the analytes' state and also the target analytes' extraction efficiency. In this study, a sample pH range of pH 3 to pH 11 was investigated. The difference in the extracted amounts by means of peak area versus sample pH is shown in Figure 7.6. The maximum enrichment efficiency was achieved with a sample solution pH of 9. At a pH above or below this value a decrease in extraction efficiency was observed; this might be due to the pKa value of the three compounds which also may decompose in either acidic or alkaline condition [2, 8, 48]. The adsorption capacity for all the three analytes increases with increasing pH values. The pH values of water constitute a major influence on the adsorption capacity of compounds that can be ionised [49]. The increase in the pH value is because of the alkali species of the solution produce changes on the carbon surface by reacting with the surface functional groups [3, 24].

By considering the pKa values of the solutes and taken these into account, it is expected that the electrostatic interaction between adsorbent and adsorbate was not dominant in the adsorption process. However, in this case the adsorption of o-NTP is controlled by the dispersive interaction between the π electron of the aromatic ring of the analytes and those of the graphene layers of the carbon surface of AC [2, 50]. This is because the presence of electron-donating groups on the ring of the hydroxyl group of phenolic compounds would lead to higher adsorption of energy while the electron-withdrawing groups would lead to lower analyte affinity for AC. Thus, the order of affinity for adsorption capacity is PCP>o-NTP>BPA. A similar result was reported by Alvarez et al. [50]. This result confirms earlier observations.

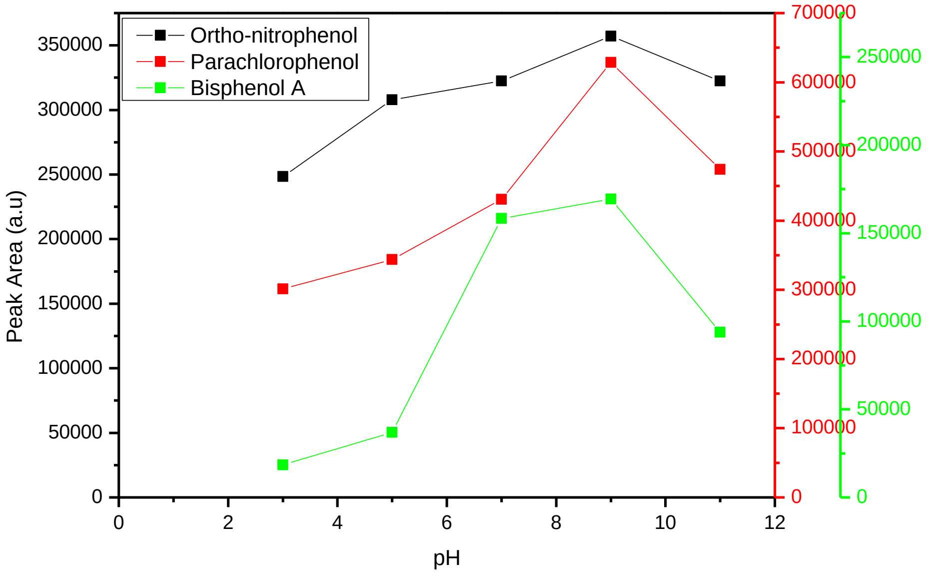

Figure 7.6: Effect of sample pH on the adsorption of phenols by MTAC. The graphing was on the first and secondary y axis in order to accommodate the value differences, which needed different scales.

7.4.1.7 Influence of analyte nature

Generally, AC is mainly hydrophobic and displays a strong affinity for organic molecules with a partial solubility in water. Thus, compounds which are hydrophilic are less adsorbed than those which are hydrophobic, because hydrophobic compounds will tend to be pushed to the adsorbent surface. This explains why PCP and o-NTP which are hydrophobic compounds tend to adsorb better than BPA which is hydrophilic [51-54].

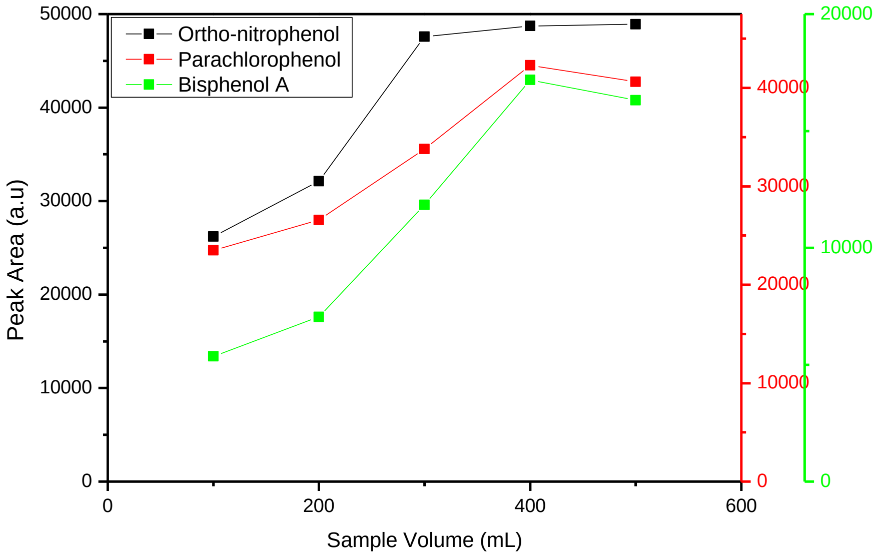

Figure 7.7: Effect of sample volume. The graphing was on the first and secondary y axis in order to accommodate the value differences, which needed different scales.

7.4.1.8 Influence of sample volume

The sample volume is another important parameter that influences the sensitivity of the SPE method. To investigate its influence, sample volumes in the range of 100 mL to 500 mL spiked with purified water were investigated and optimised. Figure 7.7 shows the results of using different sample volumes. It was found that the increasing sample volume has an obvious influence from 100 mL to 400 mL after which there was no significant increase in the recovery of the analytes. A sample volume of 400 mL was adopted as the sample volume for this study as it reduces extraction time based on the excellent adsorption properties of MTAC; the results are shown in Figure 7.7. The extraction of PCP and o-NTP was similar to that of BPA but, smaller in terms of the peak area when compared to the other two analytes.

7.5 APPLICATION

In order to validate the feasibility of the method used in this study to analyse these three compounds BPA, o-NTP and PCP, the performance of the method was evaluated with two environmental water samples from a local dam. It was discovered that there were no peaks at the related location for all three compounds in the sample solution. In order to show the merit of this method the environmental water sample was spiked with these three compounds; even though the MTAC was reused more than 20 times, a good spiked recovery (85% to 95%) were achieved for all the water samples.

7.6 COMPARISON OF THE ENRICHMENT PERFORMANCE

The enrichment performance of MTAC and C18 was compared by using two environmental water samples. The optimal conditions for the recoveries of the spiked water samples were obtained at the highest peak area for all the compounds. The results are shown in Figure 7.8. It was observed that good recoveries were obtained for all the analytes employed on the MTAC packed cartridge. Figure 7.8 reveals that the MTAC cartridge was as effective as the C18 cartridge for all of the analytes used. This result also shows that the MTAC packed cartridge offers a great advantage for the solid-phase extraction of BPA, o-NTP and PCP.

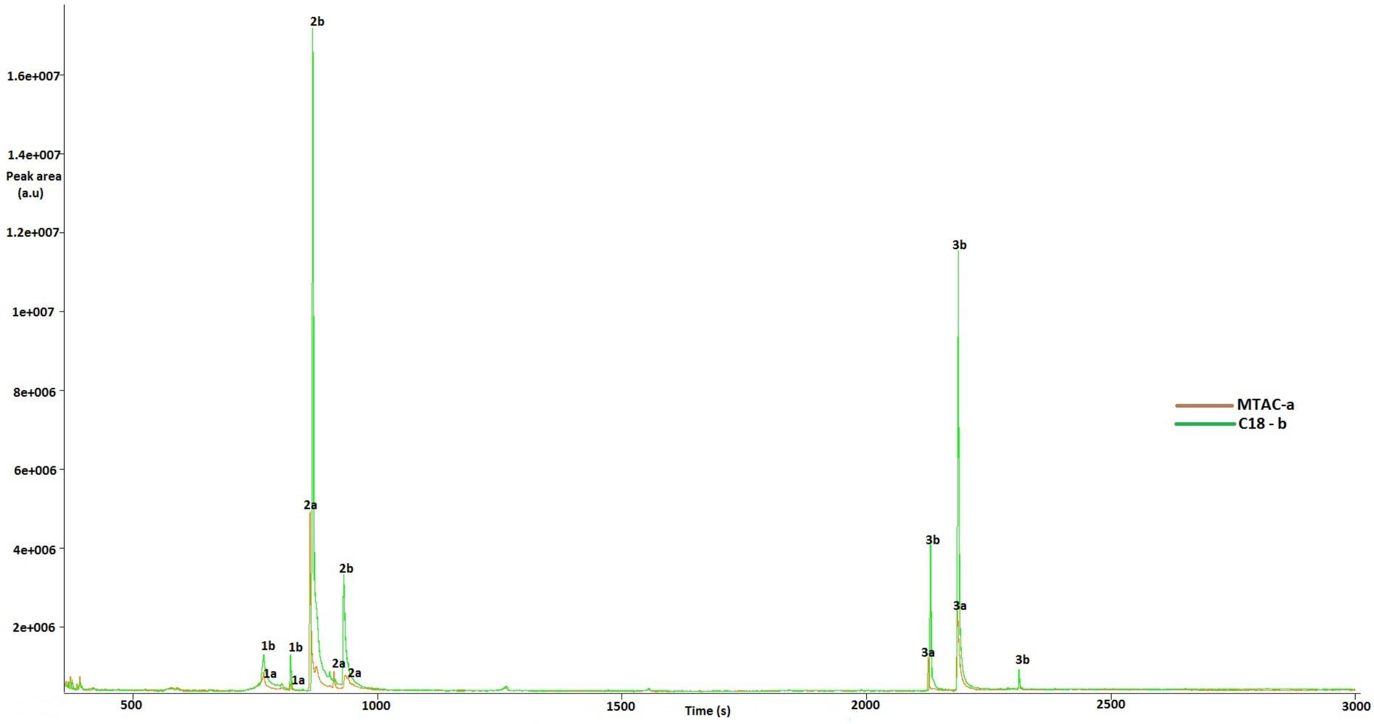

Figure 7.8: GC-TOFMS chromatogram of environmental samples containing the phenolic compounds with both MTAC-a and CI8-b SPE results. Peaks: a-MTAC; 1a-o-NTP; 2a-PCP and 3a-BPA, while Peaks: b- C18 SPE; 1b-o-NTP; 2b-PCP; and 3b-BPA.

CONCLUSION

This study describes a cheap and simple method of analysis of BPA, o-NTP and PCP in an environmental sample. The method was based on SPE and GC×GC TOFMS. It was shown that MTAC, activated carbon produced from agricultural waste residue, is less expensive and also an excellent material that can be employed in SPE columns for the enrichment of BPA, o-NTP and PCP. This method allows concurrent determination of multiple phenolic compounds without complicated protocols. The MTAC packed cartridge can be reused as many times as possible.

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CHAPTER EIGHT

PREPARATION OF POLYURETHANE COMPOSITE AND ITS APPLICATION IN METAL-ION ENRICHMENT

Polyurethane composite adsorbent using solid phase extraction method for preconcentration of metal ion from aqueous solution

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Abstract

Polyurethane composite adsorbent (PCAD) polymeric material was prepared and investigated for selected solid-phase extraction (SPE) for metal ions, prior to its determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The surface characterisation was done using FT-IR. The separation and preconcentration conditions of the analytes investigated includes influence of pH, sample loading flow rate, elution flow rate, type and concentration of eluents. The optimum pH for the highest efficient recoveries for all metal ions, which ranged from 70% to 85%, is pH 7. The metal ions were quantitatively eluted with 5 mL of 2 mol/L HNO_3. Common coexisting ions did not interfere with the separation.

The percentage recovery of the metal ions ranged between 70% and 89%, while the results for the limit of detection (LOD) and limit of quantification (LOQ) ranged from 0.249 to 0.256 and 0.831 to 0.855, respectively. The experimental tests showed good preconcentration results of trace levels of metal ions using synthesised PU polymer adsorbent composite (PCAD).

Keywords: heavy metals, PCAD, preconcentration, SPE, ICP-OES

8.1 INTRODUCTION

Analyses of inorganic compounds in environmental samples, especially waste and natural water samples, have been performed on a continuous basis in order to monitor and assess the level of environmental pollution associated with health issues which have been on the increase in recent times [1-4]. Moreover, direct analysis of these inorganic compounds especially metal ions by atomic spectroscopy method, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma optical emission spectroscopy (ICP-OES), and flame atomic absorption spectroscopy (FAAS), is often difficult due to the matrix interference and low concentration. Thus, a preconcentration method for the enrichment of these metal ions is necessary [1, 3, 5-14].

Numerous preconcentration and separation techniques application have been reported for metal-ion analysis, which include cloud-point extraction (CPE) [15, 16], co-precipitation [17], electrochemical deposition (ECD) [18], flotation [19], liquid-liquid extraction (LLE) [20], solid-phase extraction (SPE) [21-25], solid-phase microextraction (SPME) [24, 26], etc. However, SPE is the preferred method mainly due to its simplicity, direct application in microlitre (µL) volume, speed, minimal sample loss, higher preconcentration factor, rapid phase separation, cost and time saving [2, 24, 27].

The SPE method is based on the principle of analyte transfer from the aqueous medium, i.e. phase, to the active sites on the solid phase of an adsorbent [2]. Numerous technologies involving adsorbents have been applied as preconcentration adsorbents for metal ions, including alumina [28-30], activated carbon AC [31-35], C18 cartridge silica, chelex-100 [36], polyurethane foam [16, 37, 38], microcrystalline naphthalene [20, 22], silica gel [39] cyclodextrins CDs [40], zeolites [41], and clay [42]. However, the development of purification and extraction methods using these adsorbents for the enrichment of metal ions in environmental samples has been a challenge due to drawbacks which have limited their application for effective monitoring and curtailments of pollutants in the environment [7, 37, 43].

Recently, there has been a growing interest in environmentally safe application of these adsorbent materials [37, 44]. This is because most of these adsorbents, available in the market for environmental application, are either obtained in pellets or powder form [37, 45]. The present form of these adsorbents' physical appearance hinders their optimum application in the water-treatment process. Furthermore, these factors have restricted the industrial application of these adsorbent materials, especially those applied in separation technology [37, 44]. Apart from their physical properties, the regeneration of the spent adsorbent materials to their original state of adsorption capacity is a challenge because of its cost implication and heat-controlled environment required for their treatment [46]. This operational drawback has raised questions of development of composite support materials that could be easily regenerated without the thermal energy input [46]. An approach of mitigating a solution to these drawbacks is production of an adsorbent material as a support in the form of a composite material applicable for water treatment [37]. The material for composite production as in the case of a polymer must be a blend of polymeric material that will be able to improve or modify the physicochemical properties of the new polymeric composite material [47].

This method is a way of obtaining materials with the required engineering characteristics such as better chemical properties, biocompatibility, biological activities, thermal stability, open cell content, specific gravity and hydrophobicity properties. An improved way of enhancing the application of polymeric adsorbent material is to support the adsorbent materials in a template of porous matrices. This template can be used to support adsorbent material with desired characteristics for purification purposes, thus allowing for easier formulation cum production of blend filler with both physical and chemical characteristics closer to the desired adsorbent composite [37, 44, 47].

The objective of this study was to produce polymeric composite adsorbents using AC and CD as fillers. In this study, polymeric composite adsorbent material (PCAD) was synthesised and characterised. The prepared composite material showed great affinity, high enrichment and less binding time with metal ions. The SPE extraction method was studied for Cd (II), Cr (III), and Pb(II) metal ions. The parameters that influence the sorption, extraction and elution efficiency of the metal ions were also studied.

8.2 MATERIALS AND METHODS

8.2.1 Reagents and standards

All reagents were analytical grade unless otherwise stated and Millipore water (Merck, Darmstadt, Germany) of 18 MΩ was used throughout the experiments. Concentrated nitric acid (HNO_3) (70%) and hydrochloric acid (37% HCl w/v) were purchased from Sigma-Aldrich (St. Louis, MO., USA). All plastics and glassware were cleansed by soaking in dilute HNO_3 and were rinsed with distilled water prior to use. The metal-ion stock solution (1 000 mg/L) (Merck, Darmstadt, Germany) was prepared daily for obtaining reference and working solutions. The working standard solutions were prepared by mixing appropriate dilution of the stock standard solutions with distilled water. Ammonium acetate buffer solution (1M) was prepared by mixing appropriate amounts of ammonia 25% solution (Sigma-Aldrich St. Louis, MO., USA) and glacial acetic acid 97% solution (Sigma-Aldrich St. Louis, MO., USA), which was then followed by dilution with water to a final pH of 9.0 using Mettler Toledo pH meter model 20, Greifensee, Switzerland.

The working solutions were freshly prepared on a daily basis by the appropriate dilution of the stock with deionised water, while the calibration standards were prepared with serial dilutions of the stock mixture at 10 ng/L, 20 ng/L, 40 ng/L, 60 ng/L, 100 ng/L, 200 ng/L and 500 ng/L. Hydrochloric acid HCl 0.1 M and sodium hydroxide NaOH 0.1 M solution were used to adjust the pH values of the working solutions. 1,2-dimethoxy-3-(1-methoxypropan-2-yloxy)propane (Sigma-Aldrich St Louis, MO, USA) was used as a triol, dibutyltin dilaurate (DBTL > 97%, Merck, Darmstadt, Germany) was used as a catalyst, silicone oil and castor oil (Sigma-Aldrich St Louis, MO, USA) were used as a foam stabiliser. The isocyanates used were 4,4′ methylene diphenyl diisocyanate (MDI> 98% Sigma-Aldrich St Louis, MO, USA) and 1,6 hexamethylene diisocyanate (HMDI > 98% Lupanat, M 50, BASF Lemförde, Germany).

A Strata™ C18-E SPE C_{18} (EC) cartridge (0.5 g, 6 mL, and polypropylene column) purchased from Phenomenex companies, Torrance CA, USA, was used for preconcentration. The porous frit was placed at the bottom and at the top of the column for allowing the adsorbent to settle. The solid-phase extraction was carried out in a VasMaster-20 sample SPE station (Supelco, PA, USA). The SPE station was used for both sample loading and elution desorption flow rate.

8.2.2 Instruments

The analytes (metal ions) were determined using Spectro ARCOS inductively coupled plasma optical emission spectrometry ICP-OES with radial plasma equipped with Cetac ASX-520 auto-sampler (Borscht, Kleve, Germany). The operating conditions used for ICP-OES spectrometry during the measurements were as follows: RF generator forward power; 1 400 W, plasma argon flow rate 13 L/min, auxiliary argon flow rate 2.00 L/min, and nebuliser argon flow rate 0.95 L/min. The most prominent atomic and ionic analytical lines of metal ions selected for this experimental study were Cd 226.5 nm, Cr 205.55 nm, and Pb 220.35 nm. A cross-flow nebuliser and double-pass spray chamber were used throughout the measurement process. The calibration standards for ICP-OES analysis were prepared from high-purity compounds by diluting commercially available 1 000 mg/L solutions (Merck, Darmstadt, Germany) of varying elements in 1% HNO_3.

8.3 POLYURETHANE SYNTHESIS

The method of preparation was done according to Pinto *et al.* [37] with slight modifications. A bulk total 50 g of the material, i.e. quantities required for the formation of a polyurethane composite such as polyol, distilled water, castor oil/silicone oil (1:1) and catalyst were added into a polyethylene flask and mixed vigorously for 1 min with a mechanical stirrer to obtain a formulated polyol prepolymer. The isocyanate was then added to the same flask followed by addition of the various fillers and stirred vigorously for about 20 min. The resulting mixture, a composite material was left undisturbed for about 60 s to allow the formulation to grow and form a PU polymer composite. The PU polymer composite was then immediately added into a mould and kept inside the oven at 60^{o}C for 60 min. The resulting formulation was thereafter ground to a powder and kept in desiccators until further analysis. Several formulations were tested for clarity but only one is reported here (Table 8.1). In order to maintain the urethane NCO index, isocyanate and water composition were varied (Table 8.1) for the series formulation.

Table 8.1: Composites of formulation of polyurethane composite adsorbent

	Formulation Series[a]	
	HMDI (A)	MDI (B)
Polyol (g)	30	30
DBTL (g)	0.23	0.23
Silicone oil:castor oil (1:1) v/v	0.8	0.8
Water content %	3-5	1-5
Diisocyanate (g)	14.2	14.2
Fillers (g)	0.2	0.2

[a] NCO index = 105%

8.4 SOLID-PHASE EXTRACTION (SPE) CARTRIDGE

The SPE commercial cartridge was replaced with polyurethane composites adsorbent (PCAD) (polymeric material containing polyurethane, AC and β-CD as filler) packed cartridge, which was prepared by modifying a Strata™ C18-E SPE C_{18} (EC) cartridge (0.5 g, 6 mL polypropylene). The C_{18} packing of the cartridge was evacuated, and then 0.5 g of PCAD was packed into the cartridge. The 20 µm polypropylene lower and upper frits remained at each end of the cartridge to serve as support holders for PCAD packing. The outlet tip of the cartridge was connected to a vacuum pump (Shimadzu, Japan) and the inlet end of the cartridge was connected to PTFE suction tube whose other end was inserted into sample solution. The entire solid-phase extraction set-up assembly was carefully washed with methanol before use in order to reduce the interferences of the organic and inorganic contaminants.

8.5 PROCEDURE

Before the preconcentration enrichment step, the PCAD packed cartridge was firstly preconditioned by washing using triple distilled water followed by conditioning with 10 mL of ammonium acetate buffer (1.0 M, pH 9.0). The sample solutions were then loaded onto the preconditioned PCAD cartridge at a constant flow rate. After the loading stage, the PCAD packed cartridge was then washed with 5 mL ammonium acetate buffer. The washing stage before metal-ion desorption was engaged in order to eliminate concomitant elements that could be partially adsorbed by the PCAD polymeric material. The retained metal ions were then eluted with nitric acid at a constant flow rate into ICP vials. The metal concentrations in the final solutions were then determined by ICP-OES. The same protocol was employed for the blank solutions. After each run, the PCAD polymeric material in the cartridge was washed with 20 mL of distilled water and then stored for further experiments. The pH of samples was adjusted accordingly with 1 mL of 0.1 M HCl or 0.1 M NaOH solution. Thereafter a known volume of sample solutions were aspirated through the modified SPE C18 column at a controlled flow rate and the eluate obtained was discarded. However, when the whole sample had passed through the SPE column, 10 mL of purified water was used to remove the impurities or the co-adsorbed matrix materials from the cartridge. The influence of sample solution pH, sample volume, sample loading flow rate, elution flow rate, type and concentration of eluents were investigated.

8.6 RESULTS AND DISCUSSION

8.6.1 Characterisation of the polyurethane composite adsorbents

The structure and surface functional groups on the PCAD with different fillers was investigated and compared by using Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM) for their characterisation.

8.6.1.1 FT-IR spectroscopy

The surface functional groups on the PCAD material were investigated using FT-IR spectroscopy (Nicolet IS10 SMART ITR, Madison, WI, USA) equipped with Golden Gate single reflection attenuated total reflection (ATR) accessory. All the polymeric materials, i.e. methylene diisocyanate (MDI), methylene diisocyanate - activated carbon (MDIAC), methylene diisocyanate - beta(β) cyclodextrin (β-CD) (MDICD), methylene diisocyanate - activated carbon - beta(β) cyclodextrin (MDIACCD), and methylene diisocyanate raw tassel (MDIRT) were prepared onto FT-IR grade KBr crystals at a sample-to-crystal ratio of 20:80. Figure 8.1 shows the FT-IR spectra of the polymeric materials.

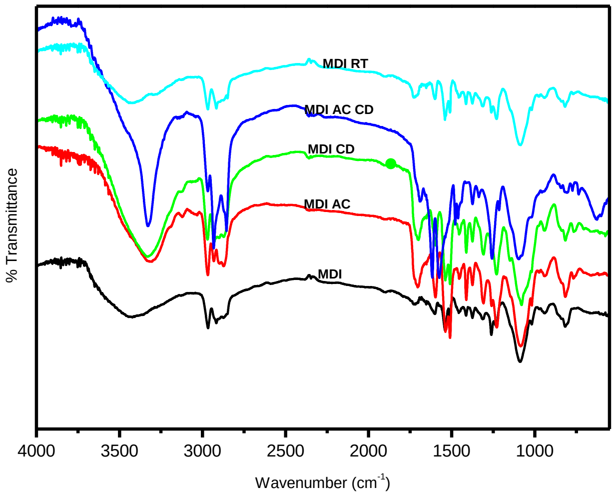

Figure 8. 1: FT-IR transmission spectra of PCAD spectra of (a) MDI; (b) MDIAC; (c) MDICD; (d) MDIACCD; and (e) MDIRT

The typical FT-IR spectra of the polymeric material PCAD for the composite adsorbent are shown in Figure 8.1. All the characteristic absorption peaks of PCAD polymeric materials, around 3 430 cm^{-1} to 3 300 cm^{-1} (free O-H stretching vibration, N-H stretching of hydrogen bonded amino group), 2 970 cm^{-1} to 2 840 cm^{-1} (CH_2 and CH_3 stretching vibration), 1 720 cm^{-1} to 1 600 cm^{-1} (C=O stretching of bonded carbonyl), 1 400 cm^{-1} to 1 305 cm^{-1} (C-N) and 1 100 cm^{-1} to 1 000 cm^{-1} (-C-O-C) revealed the existence of the urethane in the synthesised cross-linked PCAD and fillers in the polymeric materials. The absorption of NCO from the PCAD polymeric materials takes place between 2 300 cm^{-1} to 2 200 cm^{-1} in different spectra for MDI-based PCAD polymeric materials which was not observed in any of the resulting polymeric materials, thus indicating the absence of free NCO groups. All the peaks at 3 430 cm^{-1} to 3 300 cm^{-1} were very broad for the PCAD except for MDIACCD that has a sharp peak at this region. These peaks were shifted to higher absorption band than 3 300 cm^{-1} when compared to the broad absorption of OH stretching vibration in the range of 3 500 cm^{-1} to 3 300 cm^{-1}. This might be due to the OH stretching vibration from β-CD [37, 45, 48].

However, with the introduction of more filler into the PU matrix, in the PCAD polymeric material, the peak at 1 095 cm-^{1} for MDIACCD shifts to 1 018 cm^{-1} for MDI (Figure 8.1). Similar observations were noticed at peak 784 cm^{-1} for MDIAC which shifted to 773 cm^{-1} for MDIACCD and was completely absent in both MDI and MDIRT. This peak shift is attributed to out-of-plane vibration of the CO-NH group. The stretching vibration observed for MDI and MDICD at 940 cm^{-1} is due to the C-O bond stretching vibration. The C-O bond stretching vibrations observed at 818 cm^{-1} to 816 cm^{-1} in MDI, MDICD, and MDIRT were due to anhydroglucose ring stretching vibration [37, 45, 48]. The hydroxyl (-OH) groups and the -O- groups from the filler, especially beta-cyclodextrin (β-CD) and activated carbon (AC), form H bonds with C=O groups and N-H groups from the polymeric PCAD material. This formation, i.e. hydrogen bond formation between the PU macromolecules and the fillers, results in the increase of physical cross-links in the PCAD polymeric composite materials [37, 45, 48].

8.6.1.2 Surface morphology of PCAD using SEM

The surface morphology of PCAD polymeric material was observed by scanning electron microscope (SEM) (TESCAN VEGA 3 SBU, Czech). The representative SEM images (Figure 8.2) reveal the microstructure transformation on the surface of the polymeric material. All the PCAD polymeric material shows different surface morphology. The results show that the filler contributes significantly to the final texture of the polyurethane composite material PCAD. The addition of the filler, indicated in Figure 8.2A (MDI) to Figure 8.2E (MDIRT), shows that the soft segment part of the urethane chain NCO plays a predominant role, compared to the hard segment, especially in Figure 8.2B-8.2D. As can be seen in Figure 8.2D the MDIACCD containing β-CD and AC is shown to be more porous than the remaining PCAD polymeric material. This might be due to the effect of β-CD which has inclusion properties and can incorporate AC as a guest into its moiety. The result for Figure 8.2E (MDIRT) shows that the raw tassel RT is acting as a binder to reinforce the hard segment part of the PU chain, hence the flatter and smoother surface. The MDI surface (Figure 8.2A) is smoother than the other because of the absence of the filler in the polymeric material.

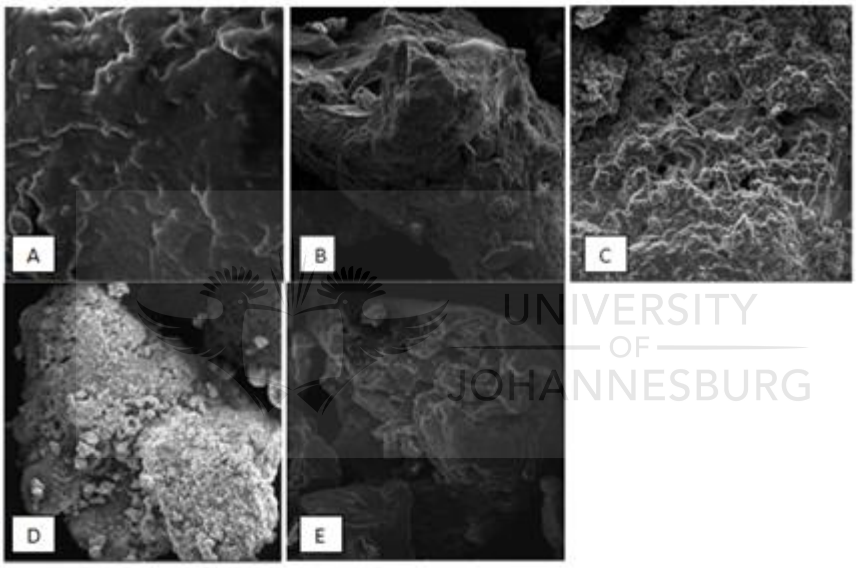

Figure 8.2: Scanning electron microscope (SEM) images of PCAD polymeric material at × 50 nm: (A) MDI; (B) MDIAC; (C) MDICD; (D) MDIACCD; and (E) MDIRT

8.6.1.3 Influence of solution pH

The pH of aqueous solution sample plays major role for quantitative retention of analytes because of the competitive reactions nature, between metal ions and hydrogen ions in aqueous solution [49]. Furthermore, pH influences both the chemistry of metal ions and functional groups on polymeric material due to its metal-retention ability from aqueous solution which is a pH-dependent process [50].

The influence of pH on the retention of analytes (Cd(II), Cr(III) and Pb(II) ions) onto the polymeric material was investigated in the pH range of pH 4.0 to pH 10.0 . The sample solutions of each metal ion were investigated by varying the pH of metal solutions subjected to extraction experiments by using dilute sodium hydroxide or dilute nitric acid solution. The experiment was carried out using 100 mL of 4 ng/L for Cd, 20 ng/L for Cr and 80 ng/L for Pb which were passed through the PCAD packed cartridge.

The retained metal ions on the PCAD polymeric material were stripped from the column using nitric acid. The percentage recovery as a function of pH for all the metal ions is shown in Figure 8.3. The plots (Figure 8.3) reveal that the PCAD polymeric material can be applied easily in extraction experiments in acidic-neutral medium, because it showed more than 70% average recovery for all the metal ions in the pH range of pH 5.0 to pH 8.0 and having the maximum recovery at pH 7. At a pH value of above 5, the main group responsible for metal extraction, carboxylic acids, [43, 51] is protonated due to the high concentration of H^+ species. The result also reveals that as the pH of sample solution increases the concentration of the metal ions also decreases. The recoveries were slightly lower at lower pH values. This could be due to the competition between the metal ion and hydrogen ion/hydronium ions species for active sites which is responsible for metal-ion retention [52]. Thus, the increase in recoveries with increasing pH (Figure 8.3) could be due to a decrease in positive charge density on the PCAD polymeric material. Thus, the reduction of positive charge density will result in the enhancement of metal-ion retention [52].

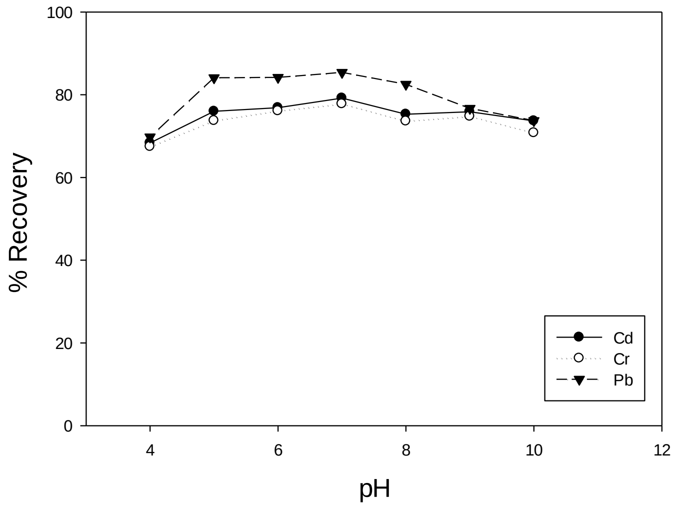

Figure 8.3: Influence of solution pH values on the recoveries of metal ions in aqueous medium

8.6.1.4 The influence of eluent flow rate

The influence of the eluent flow rate is one of the vital parameters affecting preconcentration and recovery percentage of the metal ions. It was observed from the results obtained as shown in Figure 8.4, that the recoveries of the metal ions changed between 64% and 82% for sample flow rates of between 1 mL/min and 2 mL/min and between 65% and 87% for sample flow rates of between 3 mL/min and 5 mL/min. Thus, the recoveries of metal ions for the various elution (desorption) flow rates were found to be between 64% and 86%. The variation of the elution flow rate was minimal with not much significant effect. The flow rate of 3 mL/min was selected as the optimum flow rate for the desorption elution and was subsequently used for other experimental test runs.

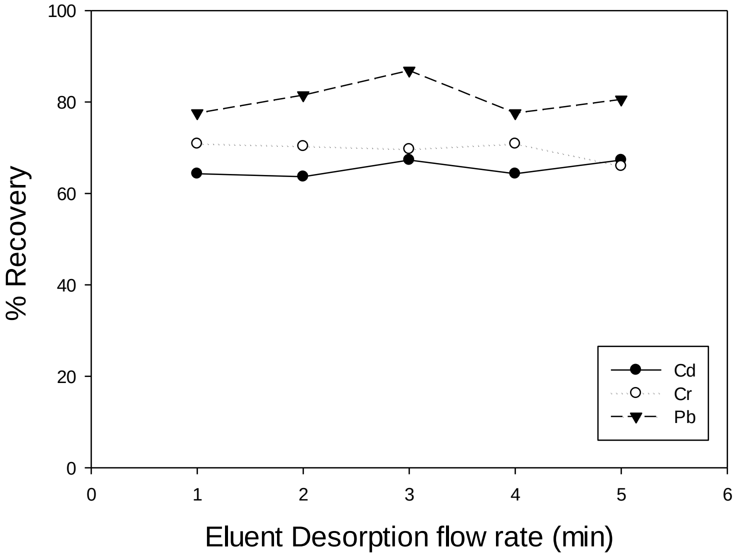

Figure 8.4: Influence of desorption flow rate on the recoveries of metal ions in aqueous medium

8.6.1.5 Influence of sample loading flow rate

The sample loading flow rate is one of the most important parameters in obtaining both the quantitative retention and elution of the analytes, respectively [53, 54]. The influence of sample loading flow rates on retention of metal ions was investigated in the flow rates ranging between 1 mL/min to 5 mL/min. The result (Figure 8.5) shows that at a flow rate of between 1 mL/min and 2 mL/min, there was a sharp increase in the recovery of metal ions. At the flow rates greater than 3 mL/min, there was a decrease in metal-ion recovery. This could be due to the speed at which the sample solution passes through the cartridge column. Thus, the timing is not adequate for the equilibrium to be established between the surface of the adsorbent and the analytes which eventually leads to a reduction in analyte recovery [53, 54]. Thus, a flow rate of 2 mL/min was selected for subsequent experimental test runs.

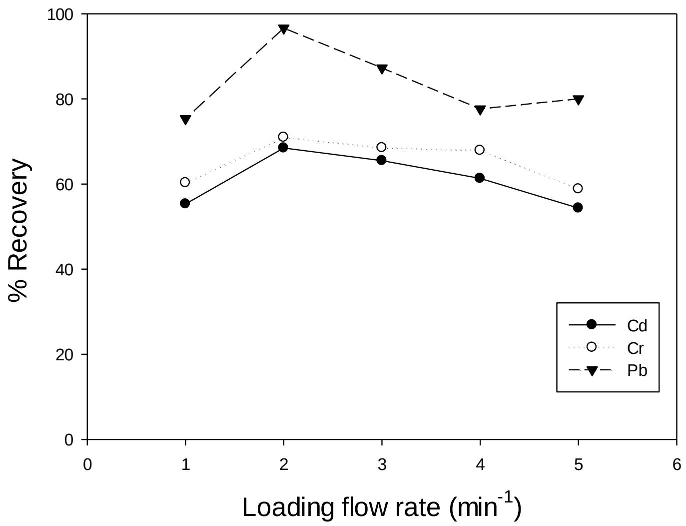

Figure 8.5: Influence of sample loading flow rate on the recoveries of metal-ion mixtures in aqueous medium

8.6.1.6 Influence of the type and concentration of eluents

The quantitative recovery of retained metal ions on PCAD polymeric materials using various concentration and volumes of nitric and hydrochloric acids were investigated. The influence of eluents type on the recovery of metal ions was also studied using nitric acid. The results given in Figure 8.6 show that the quantitative recoveries (80%) for the metal ions were obtained with 50 mL of 2 mol/L of HNO_3. Thus, in this study 20 mL of 2 M HNO_3 was selected as eluents for the metal recovery.

The effect of different concentrations of nitric and hydrochloric acids on the preconcentration yields of the metal ions under the optimum pH condition was studied. The result shows that both acids can effectively elute the metal ions from PCAD polymeric materials in the cartridge (Figure 8.6). However, HNO_3 has higher recoveries than HCl and one would expect both acids to have the same recovery capacities as shown in Figure 8.6. However, this is not the case, despite both acids having the same hydroxonium ion. HNO_3 has an edge due to its oxidation capacity [55]. It was also observed that HCl has a low recovery at 3.0 M as shown in Figure 8.6. This could be due to the formation of stable complexes in the presence of chloride ions which explain the low recovery experienced for HCl when used as eluents [56]. Thus, HNO_3 was selected as eluents for desorption of the metal ions from PCAD polymeric material.

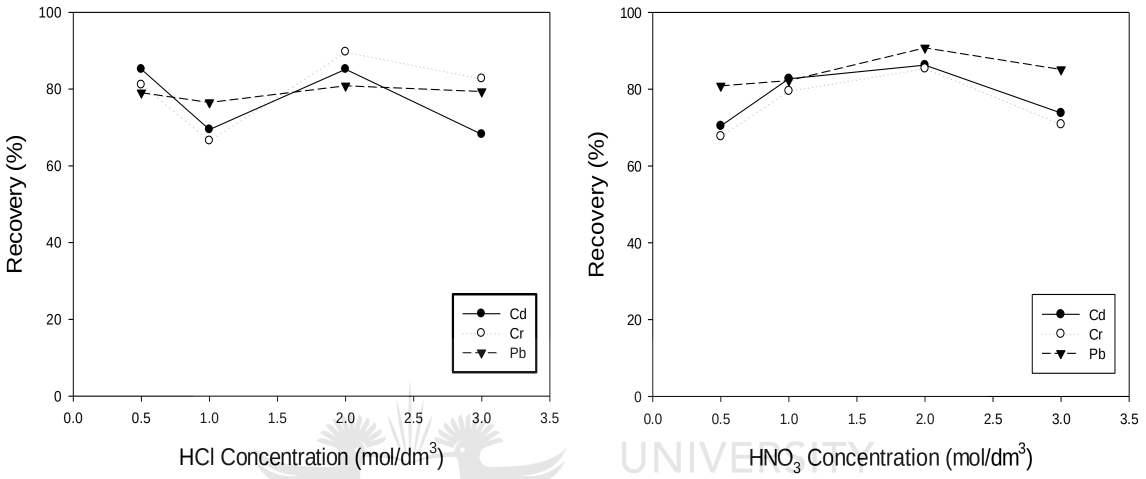

Figure 8.6: Influence of type and concentration of eluents on the recoveries of metal ions in aqueous medium

8.6.1.7 Influence of sample volume

The influence of the sample volume on the recovery and preconcentration factor is one of the vital parameters for obtaining high exchange capacity [57]. In order to determine the maximum applicable sample volume for analyte concentration, there is a need to examine the possibility of enriching low concentrations of analytes from large sample volumes. To achieve this purpose, the concentrations of each metal ion were kept relatively constant with increasing sample volume. The influence of sample volume was studied by passing 100 mL to 500 mL of model sample solution through PCAD polymeric materials packed cartridge under the optimum conditions (Figure 8.7). The recoveries of the metal-ion analytes were greater than 70%. The preconcentration factor was calculated by the ratio of highest volume to the lowest volume of eluents. Hence, 5 mL sample volume solution was adopted for the preconcentration factor.

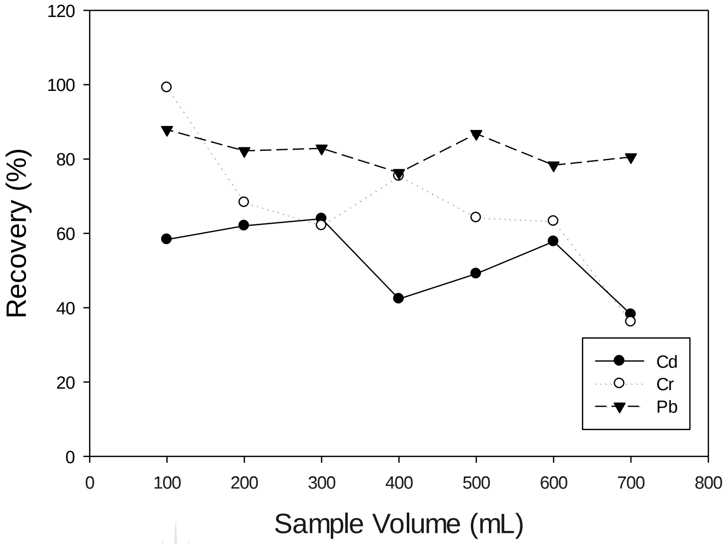

Figure 8.7: Influence of sample volume on the recoveries of metal ions in aqueous medium

8.6.1.8 Comparison of PCAD polymeric material with other methods of metal-ion extraction

The comparison of PCAD polymeric material with other methods of extraction was carried out to show the extraction efficiency and determination of metal ion in water sample. The comparison result (Figure 8.8) showed that PCAD polymeric materials were applied as a stationary phase to preconcentrate and purify metal ions in aqueous solution. The average recoveries of PCB analytes for all PCAD polymeric material including AC and C18 (59% for MDI, 82% for MDIAC, 85% for MDICD, 92% for MDIACCD, 65% for MDIRT, 70% for AC and 76% for C18 cartridge) revealed that the PU composite material with the filler β-CD and AC, i.e. MDIACCD (Figure 8.8) enhances the extraction efficiency of PCBs more than the other extraction techniques.

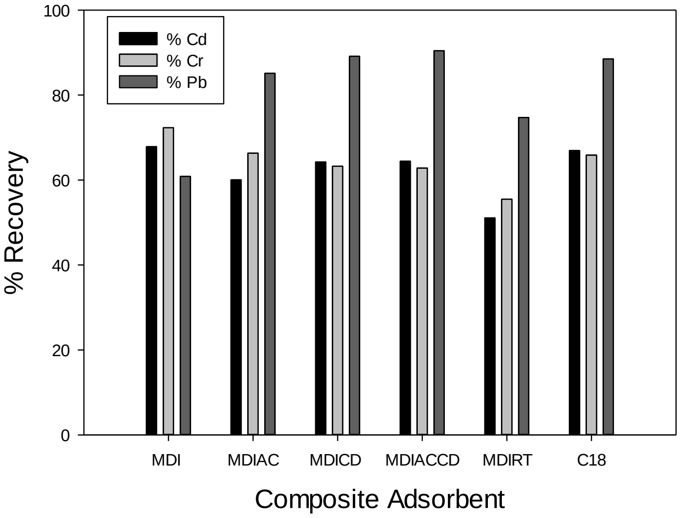

Figure 8.8: Influence of composite adsorbents on the recoveries of metal ions in aqueous medium

8.7 METHOD VALIDATION

A series of standard solutions were prepared to obtain a linear range for each of the metal-ion analytes. Table 8.2 shows the linearity range of the prepared standard solutions. The correlation coefficient (r^2) of the PCB analytes ranges between 0.936 and 0.988. The limit of detection LOD which is a signal-to-noise ratio (3:1) or response of standard deviation to the slope of analytical curve $\left(3.3 \times \frac{s}{b}\right)$ ranges from 0.249 to 0.256. The limit of quantification (LOQs) based upon the signal-to-noise ratio (10:1) or standard deviation of the blank on the residual regression line $\left(10 \times \frac{s}{b}\right)$ ranges between 0.831 and 0.855 of the metal-ion analytes.

A comparison of the method and adsorbent material is shown in Figure 8.8. The obtained LOD and LOQ are comparable with some reported studies [6, 21, 23, 25, 31, 53, 58, 59].

Table 8.2: The limit of detection, limit of quantification and reproducibility method

Analytes	Calibration equations	Linear correlation coefficients (r^2)	LOD (ng/mL)	LOQ (ng/mL)
Cd^{2+}	Y = 0.269x + 1.731	0.936	0.256	0.855
Cr^{3+}	Y = 0.186x + 11.15	0.988	0.249	0.831
Pb^{2+}	Y = 0.276x + 1.555	0.963	0.252	0.841

CONCLUSION

The present study demonstrates the preparation and use of an adsorbent based on polyurethane synthesis with different kinds of fillers. The modification of the polymeric composite material is simple and the composite material produced remained firm and could easily be packed into the SPE cartridges which invariably allowed it to be used several times. It could be concluded from the results that the PCAD produced is an effective adsorbent for preconcentration of metal ions from various sample solutions. The merit of the composite material includes high enrichment factor of (90), reproducibility, and low cost. The reusability of the adsorbent is high; about 10 cycles without any loss in its adsorption capability.

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CHAPTER NINE

PREPARATION OF POLYURETHANE COMPOSITE ADSORBENT USING DIFFERENT CROSS-LINKERS AND ITS ENRICHMENT OF PCB

Preparation of polyurethane composite adsorbent and its enrichment of polychlorinated biphenyl from environmental sample

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Abstract

Polyurethane (PU) polymer composite was synthesised by cross-linking a glycol-prepolymer and polyol with isocyanate linker together with other additives as filler. The comparison of the adsorption properties of the polymer synthesized using different ratios of 1,6-hexa methylene diisocyanate (HMDI) and 4, 4′ methylene diphenyl diisocyanate (MDI) were investigated. The diisocyanate, together with cyclodextrin (β-CD), activated carbon (AC), and raw tassel (RT) were used to preconcentrate three mixtures of polychlorinated biphenyl (PCB 105, PCB 126 and PCB 153) from environmental samples. The polymers were successfully synthesised and applied in the extraction of PCB from a large volume (0.5 L) of wastewater solution. The extraction procedure using solid-phase extraction (SPE) resulted in a short extraction time of about 10 min and preconcentration of PCB from 500 mL of water sample. With the eluent condensate to about 1 mL, recovery percentage of the PCB ranged between 90% and 95%. While the limit of detection (LOD), limit of quantification (LOQ) and relative standard deviation (RSD) results ranged from 0.0048 ng/mL to 0.013 ng/mL, 0.015 ng/mL to 0.04 ng/mL and 1.50% to 4.4%, respectively. The experimental tests showed good preconcentration results of trace levels of PCB using the synthesised PU polymer adsorbent composites.

Keywords: *composites, polyurethane, polymer, PCB, SPE*

9.1 INTRODUCTION

Polychlorinated biphenyls (PCBs) belong to the group of persistent organic pollutant (POP) which is a class of chlorinated aromatic hydrocarbon chemicals that have become an issue of research due to their toxicity and resistance to environmental degradation [1-4]. Despite the restriction or even total ban on their application, manufacturing, and marketing, they are still present in various environmental compartments and are subject to long-range transport and recycling processes, especially in developing countries where their monitoring is very low or completely absent [4-6]. The concern over these chemicals is not abating; in fact there is growing public concern because of their accumulation and toxic effects in the animal food chain on a global scale [5-8]. Soil, sediments and water bodies (surface and groundwater) are the major reservoirs, sources of emission and largest sinks for PCBs [4, 9, 10]. The contamination of groundwater or surface water by PCBs may be associated with point-source discharges such as wastewater effluents from plant or industrial discharges which are often associated with diffuse sources of particle transport, precipitation and runoff [6, 10]. There have been numerous technologies that have been employed in the removal or preconcentration of organic pollutants from environmental samples [4, 6, 11]. Thus, having a good understanding of the sorption behaviour of PCBs on different adsorbent composites is vital for the enrichment of organic pollutants, especially PCBs in aqueous solution, using these technologies.

Cyclodextrins (CDs) and their polymer derivatives have been the subjects of numerous investigations, since their first discovery and application in 1891 and structural elucidation in 1930 [12-14]. Considerable work has been done using CDs as synthetic material in the past two decades [1, 14, 15]. The merit of using CDs is due to their well-known guest-host chemistry which is pivotal to more complex polymeric material chemistry. This polymeric material/polymer often expresses distinct differences in their chemical and physical behaviour from their monomeric precursors. This behaviour has drawn the interest of many researchers to this material [12-14].

Cyclodextrins belong to the class of cyclic oligomers of glucose; they have a toroidal shape which consists of six (α), seven (β) or eight (γ) glucopyranose units: D- glucopyranose units are linked by α (1→4) glycosidic bonds [12-15]. They possess an axial open cavity which has an electron-rich hydrophobic character and are capable of including other apolar molecules; they also have a doughnut-shaped surface structure with a hydrophilic outer surface [12-14]. Their excellent property of strong hydrocarbon backbone atoms, numerous oxygen (O) atoms from the glycosidic bonds and hydroxyl groups located at the periphery of the cycle position them as good host receptors of non-covalent types of interactions which is appropriate for the stabilisation of lipophilic guest molecules by a range of non-covalent interaction [13, 14].

Activated carbon (AC) is a carbon-based nanomaterial with a relatively high porosity and surface area [15-17]. The AC structure is comprised of 3 to 4 parallel hexagonal carbon ring layers separated by graphite interlayer spacing with distances of between 0.34 nm to 0.37 nm; carbon atoms are sp^2 hybridised in the lattice [15, 16]. Activated carbon is composed of microcrystalline (amorphous) graphitic-like sheets, which are randomly cross-linked, unevenly stacked and surrounded by a number of unpaired electrons [16]. These structural features make AC to be highly porous; due to these useful properties AC has found application in both catalysis and adsorption processes.

The adsorption process is one of the most effective and simplest technologies of removing toxic and recalcitrant pollutants from aqueous systems in which activated carbon is one of the most widely used adsorbents. It has been reported that activated carbon (AC) has been successful in removing numerous pollutants, such as heavy metals, dyes, phenolic compounds, pesticides and organic acids from aqueous streams [16-18]. However, there are drawbacks associated with the use of AC, such as the high initial cost of the material, attrition rate and high cost of regeneration of spent carbon [15]. They also tend to adsorb organic chemicals indiscriminately, making it difficult to selectively recover certain organic chemicals for reuse [16, 19]. Furthermore, low-cost adsorbents have recently gained wide interest among researchers in water purification, due to their cost-effectiveness and simple and practicable approach. Their wide application is limited due to their mechanical strength and adsorption capacity [15, 16].

Recently, polymeric adsorbent composites have clearly emerged as alternative to AC or CDs due to their mechanical strength, adjustable surface chemistry, feasible regeneration under mild conditions and surface area [18, 20, 21]. It has been reported that polymeric composite adsorbents can effectively remove numerous organic pollutants [22-24]. The organic chemicals adsorbed can be desorbed upon regeneration and the polymeric material/composites can be reused [22-24]. Thus, in order to improve adsorption capacity in terms of performance of polymeric material for water-soluble compounds such as PCBs, heavy-metal ion functionalisation or surface modification has been effective approach because the functional groups bound to the polymeric matrix are expected to provide attraction towards targeted contaminants/pollutants [22, 23]. Polymeric hybrid adsorbents, a recently improved fabricated material for trace contaminants, can be made by dispersing inorganic nanoparticles within the polymeric support material [22].

Polyurethane foam (PUF) composite has been reported to have a high surface area and porous structure which enables it to act as matrix materials to immobilise various kinds of adsorbents, such as zeolite bentonites, chitosan, activated carbon and hydroxyapatite [20, 21, 25]. The aim of this study was to develop a polymeric composite material as stationary phase of solid-phase extraction (SPE) and potential applications in enrichment of PCB from environmental water samples. The viability of this method was carried out by selecting three major toxic PCBs, such as 2,3,3′,4,4′-pentachlorobiphenyl (PCB 105), 3,3’,4,4′,5-pentachlorobiphenyl (PCB 126), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153) as model compounds. This was then combined with SPE technique and the analytes analysed using the two-dimensional GC×GC TOFMS analytical technique. The performances of the polymeric materials in preconcentrating the PCB were compared with C18 and other composite materials.

9.2 MATERIALS AND METHODS

9.2.1 Reagents and standards

All the polychlorinated biphenyls (PCB 105, PCB 126 and PCB 153) were of analytical grade and obtained from Sigma-Aldrich (St Louis, MO, USA). The HPLC grade acetonitrile, hexane and dichloromethane were purchased from Merck (Merck, Darmstadt, Germany). The standard stock solutions (100 mg/L) containing these PCB compounds were prepared by mixing all three PCBs in hexane and dichloromethane in the ratio of 50:50 v/v and used for the method development. This mixture was thereafter stored at 4^{o}C. The working solutions were freshly prepared on a daily basis by the appropriate dilution of the stock with deionised water, while the calibration standards were prepared with serial dilutions of the stock mixture at 10 ng/L, 20 ng/L, 40 ng/L, 60 ng/L, 100 ng/L, 200 ng/L and 500 ng/L. Acetic acid and ammonia solution were used to adjust the pH values of the working solutions. 1,2-dimethoxy-3-(1-methoxypropan-2-yloxy)propane (Sigma-Aldrich St Louis, MO, USA) was used as a triol, dibutyltin dilaurate (DBTL > 97%, Merck, Darmstadt, Germany) was used as a catalyst, silicone oil and castor oil (Sigma-Aldrich St Louis, MO, USA) were used as a foam stabiliser. The isocyanates used were HMDI (Sigma-Aldrich St Louis, MO, USA) and MDI (Lupanat, M 50, BASF Lemförde, Germany).

Before use, all the glassware was decontaminated overnight in 6 mol/L nitric acid and thoroughly washed with deionised water. A Strata™ C18-E SPE C_{18} (EC) cartridge (0.5 g, 6 mL, and polypropylene) was purchased from Phenomenex Companies, Torrance CA, USA.

9.2.2 Instrument

The chromatographic separations were performed with a LECO Pegasus® 4D GC×GC TOFMS instrument (LECO Corporation, 3000 Michigan, USA). A Restek GC×GC column (Rtx®200 with length 2 m, 0.18 mm ID, 0.18 µm df with max temp. 340°C and min bleed at 320°C), and a second dimension column (Rxi®-5ms (Crossbond® is 5% diphenyl/95% dimethyl polysiloxane) length 30 m, 0.25 mm ID, 0.25µm df with max prog. temp. 350°C min bleed at 330°C) were used as the columns.

9.3 POLYURETHANE SYNTHESIS

The method of preparation was done according to Pinto et al. [18] with slight modifications. A bulk total 50 g of the material, i.e. quantities required for the formation of polyurethane composite such as polyol, distilled water, castor oil/silicone oil (1:1) and catalyst were added into a polyethylene flask and mixed vigorously for 1 min with a mechanical stirrer to obtain a formulated polyol prepolymer. The isocyanate was then added to the same flask followed by addition of the various fillers and stirred vigorously for about 20 min. The resulting mixture, a composite material, was left undisturbed for about 60 s to allow the formulation to grow and form a PU polymer composite. The PU polymer composite was then immediately added into a mould and kept inside the oven at 60°C for 60 min. The resulting product was thereafter ground to a powder and kept in desiccators for further analysis. Several formulations were tested for clarity but only one is reported here (Table 9.1). In order to maintain the urethane NCO index, the isocyanate and water composition were varied (Table 9.1) for the series formulation.

Table 9.1: Composites of formulation of polyurethane composite adsorbent

	Formulation Series[a]	
	HMDI (A)	MDI (B)
Polyol (g)	30	30
DBTL (g)	0.23	0.23
Silicone oil:castor oil (1:1) v/v	0.8	0.8
Water content %	3-5	1-5
Diisocyanate (g)	14.2	14.2
Fillers (g)	0.2	0.2

[a]NCO index = 105% [18, 19]

9.4 SOLID-PHASE EXTRACTION (SPE) CARTRIDGE

The SPE commercial cartridge was replaced with polyurethane composites adsorbent (PCAD) (polymeric material containing polyurethane, AC and β-CD as filler) packed cartridge which was prepared by modifying a Strata™ C18-E SPE C_{18} (EC) cartridge (0.5 g, 6 mL polypropylene). The C_{18} packing of the cartridge was evacuated, and then 0.5 g of PCA was packed into the cartridge. The 20 µm polypropylene lower and upper frits remained at each end of the cartridge to serve as support holders for the PCAD packing. The outlet tip of the cartridge was connected to a vacuum pump (Shimadzu, Japan) and the inlet end of the cartridge was connected to the PTFE suction tube whose other end was inserted into the sample solution. The entire solid-phase extraction set-up assembly was carefully washed with hexane before use in order to reduce the interferences of the organic and inorganic contaminants.

9.5 PROCEDURE

Before the preconcentration process, water samples (5 L) were collected in two 2.5 L pre-cleaned glass bottles from a local dam in Johannesburg at a depth of approximately 0.3 m below the water surface. Water samples were pre-filtered through 0.45 mm fibreglass filters (Whatman) to remove debris and suspended materials. Samples were preserved by adding 5 mL of concentrated H_2SO_4 to prevent biological activity [26]

In the preconcentration enrichment step, the PCA packed cartridge was firstly preconditioned by washing with 10 mL of acetonitrile, 5 mL of hexane, and then hexane: dichloromethane (50:50) v/v was added before a new SPE preconcentration procedure was started. The pH of samples was adjusted accordingly with 1 mL of 0.1M HCl or 0.1M NaOH solution. Then a known volume of spiked water sample was aspirated through the modified SPE C18 column at a controlled flow rate and elute obtained was discarded. However, when the whole sample had passed through the SPE column, 10 mL of purified water was used to clean the impurity or the co-adsorbed matrix materials from the cartridge. The SPE column was then dried by negative pressure for 10 min and the targeted analytes were eluted with optimum volume of mixture hexane: dichloromethane (50:50). The resulting eluate was thereafter air-dried with a gentle flow of nitrogen gas to 1 mL before subsequent determination by injecting 2 µL of the final elute into the GC×GC TOFMS gas chromatography instrument.

Recovery analyses were carried out on samples fortified at 10 ng/L. After extraction and solvent evaporation, the samples were analysed according to the proposed method. The recovery values were calculated from calibration curves constructed from the concentration and peak area of the chromatograms obtained with standards of the polychlorinated biphenyl (PCB). Detection limits of the method were found by determining the lowest concentrations of the residues in each of the matrices that could be reproducibly measured at the operating conditions of the GC×GC TOFMS. Blank analyses were also performed in order to check interference from the sample. All analyses were carried out in triplicate and the mean concentrations were calculated based on the total number of each sample.

9.6 CHARACTERISATION OF PCA POLYMERIC MATERIAL

9.6.1 Fourier transform infrared (FT-IR) analysis

The functional groups on the surface of the carbon were determined by Fourier transform infrared (FT-IR) spectroscopy. A Nicolet IS10 SMART ITR, Madison, WI, USA spectrometer was used to collect FT-IR spectra and characteristic peaks were recorded over the wave-number range of 450 cm^{-1} to 4 000 cm^{-1} at a resolution of 4 cm^{-1}.

9.6.2 Scanning electron microscopy (SEM)

The PCA polymeric material was also characterised for surface morphology using SEM (TESCAN VEGA 3 SBU, Czech). Prior to applying the technique, the PCAD polymeric material was properly processed in order to obtain cross-sectional SEM micrographs.

9.7 RESULTS AND DISCUSSION

9.7.1 Characterisation of the polyurethane composite adsorbents

In order to investigate and compare the structure of the polyurethane composite adsorbents using different fillers, Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM) were used for their characterisation.

9.7.1.1 FT-IR spectroscopy

The surface functional groups on the PCAD material were investigated using FT-IR spectroscopy (Nicolet IS10 SMART ITR , Madison, WI, USA); all the polymeric materials, i.e. hexamethylene diisocyanate (HMDI), hexamethylene diisocyanate - activated carbon (HMDIAC), hexamethylene diisocyanate - beta(β) cyclodextrin CD (HMDICD), hexamethylene diisocyanate - activated carbon - beta(β) cyclodextrin (HMDIACCD), and hexamethylene diisocyanate raw tassel (HMDIRT) were prepared onto FT-IR grade KBr crystals at a sample-to-crystal ratio of 20:80. Figure 9.1 shows the FT-IR spectra of the polymeric materials.

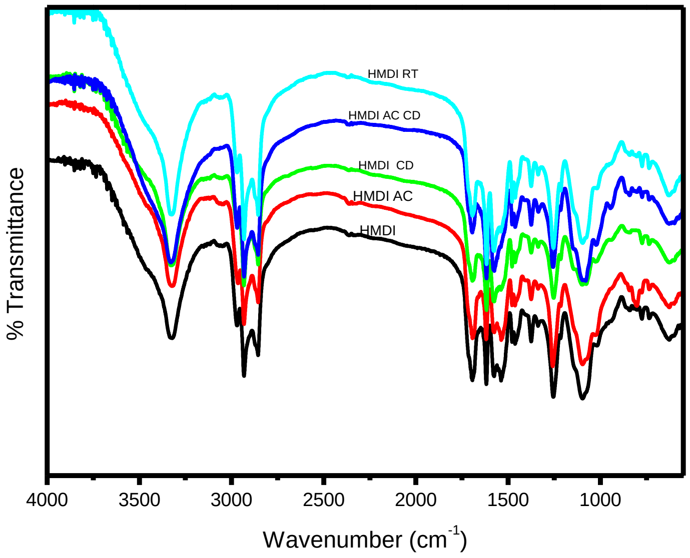

Figure 9.1: FT-IR transmission spectra of polyurethane composite adsorbent PCA spectra of (a) HMDI; (b) HMDIAC; (c) HMDICD; (d) HMDIACCD; and (e) HMDIRT

The typical spectra of the polymeric material PCAD for the composite adsorbent display characteristic bands for the free amide group N-H stretching vibration, at 3 330 cm^{-1} to 3 320 cm^{-1}, for the CH_3, CH_2, C-H groups stretching vibration at 2 970 cm^{-1}, 2 933 cm^{-1}, 2 856 cm^{-1} and for C= O carbonyl group stretching due to the urethane bands at 1 700 cm^{-1} to 1 620 cm^{-1}. The hydrogen bonded NH stretch vibration at 1 580 cm^{-1} to 1 330 cm^{-1} and ether group (-C-O-C-) stretch vibration at 1 259 cm^{-1} to 1 000 cm^{-1} were also visible. The PCA polymeric materials have similar spectra but the characteristic bands for the N-H absorption band, i.e. the stretching vibration shifts from 3 322 cm^{-1} for HMDI to 3 330 cm^{-1} for HMDIACCD. This suggests that part of the H bond attached to the NH group as donor between the polyurethane PU chains are replaced with the H bond on the OH donor from the fillers and polyurethane chains in the PCAD polymeric materials. A similar observation was reported by other researchers [18, 19].

However, with the introduction of more filler into the PU matrix, it was observed that the peak at 1 096 cm^{-1} for HMDI shifts to 1 073 cm^{-1} for HMDIACCD (Figure 9.1). Similar observations were noticed at peak 774 cm^{-1} for HMDI which shifted to 772 cm^{-1} for HMDIACCD and was completely absent in HMDICD. This peak shift is attributed to out-of-plane vibration of the CO-NH group. The stretching vibration observed for HMDIAC at 950 cm^{-1} is due to the C-O bond stretching vibration. The C-O bond stretching vibration observed at 802 cm^{-1} in HMDIAC was due to anhydroglucose ring stretching vibration [18, 25]. The hydroxyl (-OH) groups and the -O- groups from the filler, especially beta-cyclodextrin (β-CD) and activated carbon (AC), form H bonds with C=O groups and N-H groups from the polymeric PCAD material. This formation, i.e. hydrogen bond formation between the PU macromolecules and the fillers, results in the increase of physical cross-links in the PCA polymeric composite materials [20, 25, 27].

9.7.1.2 Surface morphology of PCAD polymeric materials

The surface morphology of PCAD polymeric material was observed by scanning electron microscope (SEM) (TESCAN VEGA 3 SBU, Czech). The representative SEM images (Figure 9.2) reveal the microstructure transformation on the surface of the polymeric material. All the PCAD polymeric material shows different surface morphology. The results show that the filler contributes significantly to the final texture of the polyurethane composite material PCA. The addition of the filler, indicated in Figure. 9.2A (HMDI) to Figure 9.2E (HMDIRT), shows that the soft segment part of the urethane chain NCO plays a more predominant role than the hard segment, especially in Figure 9.2B-9.2D. The HMDIACCD (Figure 9.2D) containing β-CD and AC is shown to be more porous than the remaining PCAD polymeric material. This might be due to the effect of β-CD which has inclusion properties and can incorporate AC as a guest into its moiety [14]. The result shown in Figure

9.2E (HMDIRT) indicates that raw tassel RT is acting as binder to reinforce the hard segment part of the PU chain.

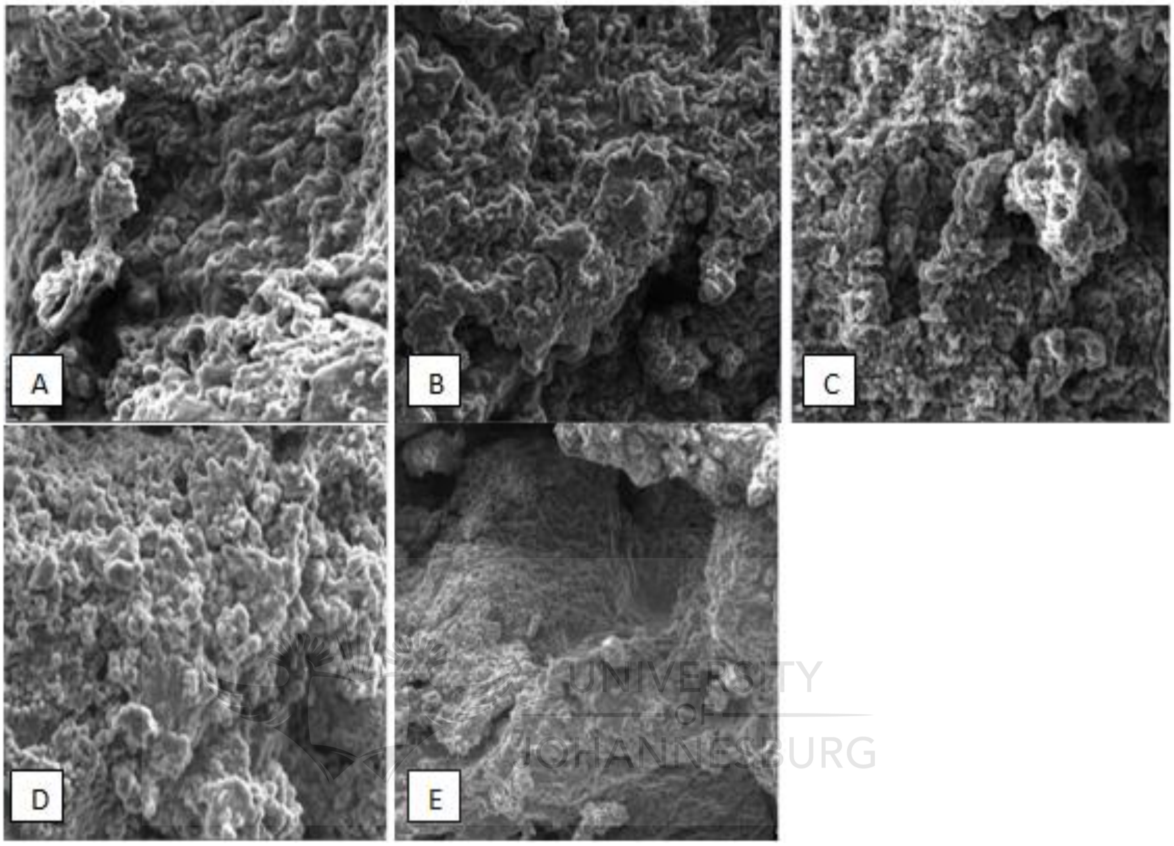

Figure 9.2: Scanning electron microscope (SEM) images of PCA polymeric material at × 20 nm (A) HMDI; (B) HMDIAC; (C) HMDICD; (D) HMDIACCD; and (E) HMDIRT

9.7.1.3 Effect of solution pH

The solution pH would change the property of PCAD polymeric material in aqueous medium and invariably influence the adsorption of the targeted analytes. In this study, the effect of solution pH on the extraction of the targeted analytes was carried out at a pH of between pH 3.0 and pH 10.0. Figure 9.3 revealed that the sorption percentage on the PCAD fluctuates minimally in the range between pH 3.0 and pH 6.0, while between pH 6.0 and pH 8.0 the sorption percentage rises sharply before reaching the maximum at pH 8.0, and then starts decreasing from pH 9.0 onwards. This suggests that PCAD is an excellent adsorbent for PCB removal from aqueous solution. However, with an increase in pH value greater than pH 8.0, the adsorption percentage of PCB decreases. The result observed is similar to those reported by other researchers [6]. This observation is due to the oxygen-containing group such as the -OH group present in the PCAD polymeric material. This is inconsistent with the observation reported for the surface functional group using FT-IR. Thus, the oxygen-containing group on the PCAD shields the PCB molecules which are closer to the adsorbent from getting adsorbed by allowing more water molecules into the matrix at higher pH value [6-8]. The hydrophilicity of the polymer enhances the dispersibility of the sorbent in water samples which invariably helps the extraction procedure [6].

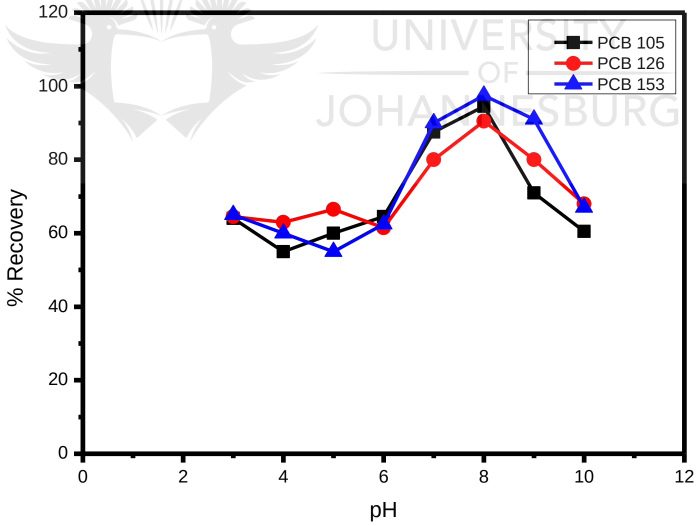

Figure 9.3: Effect of solution pH values on the recoveries of PCB mixtures in aqueous medium

9.7.1.4 Effect of elution solvent

The elution solvent plays vital role at every stage of the SPE extraction procedure. The application of different elution solvents for recovery efficiencies is important because the organic solvents possess physical and chemical properties that differ. In this study, five types of solvents (hexane, dichloromethane, hexane: dichloromethane (H: DCM 50:50 v/v), hexane: dichloromethane (H: DCM 60:40 v/v), and hexane: dichloromethane (H: DCM 80:20 v/v)) were evaluated for their use as eluents of the retained analytes. The solid phase was eluted with 10 mL of each solvent and the recoveries of PCBs were compared among all the solvents (Figure 9.4). The results given in Figure 9.4 indicate that different solvents possess diverse elution efficiency. The graph showed that the order of the overall elution performance was H: DCM 50:50 > H: DCM 60:40 > dichloromethane > H: DCM 80:20 > hexane. The average recoveries of most PCBs analytes in hexane were about 72%, while the performance of dichloromethane showed average recoveries of 60%. The performance of dichloromethane is lower than that of n-hexane. The mixture of the two solvents, namely n-hexane a non-polar solvent and dichloromethane a polar solvent, results in higher recovery efficiencies. It has been reported that a mixture of these two solvents is often used to elute PCB from silica gel column mainly due to their polar index ratio. The results given in Figure 9.4 show very good recovery efficiencies for all the hexane and dichloromethane mixtures that have over 70% recoveries, except in H: DCM 80:20 where the recovery efficiency was over 60%. However, the performance of H: DCM 50:50 is better than all the other solvents. Thus, H: DCM 50:50 was used as the solvent for elution of PCAD packed cartridge in the remaining experimental procedure.

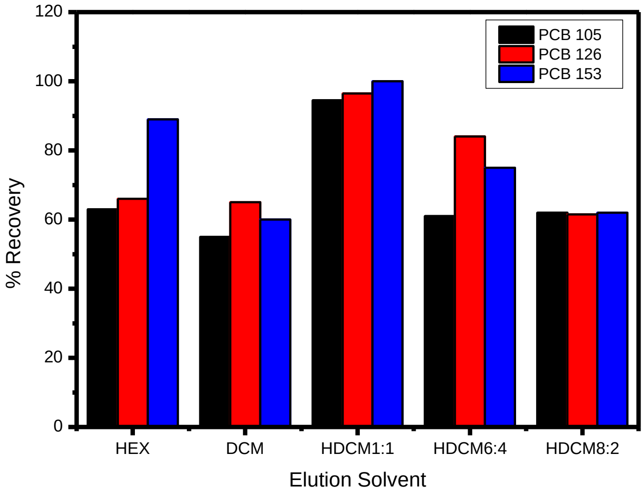

Figure 9.4: Effect of solvent types on the recoveries of PCB mixtures in aqueous medium

9.7.1.5 Effect of elution volume

The studies of eluent volume desorption which ranged from 5 mL to 25 mL were used to elute analytes from the PCAD solid-phase packed cartridge after the sample extraction and washing stage. Figure 9.5 shows that the highest recovery efficiency volume for the analytes was the one eluted at 10 mL and the average percentage recovery was over 99%. The result further revealed that elution at volumes greater than 10 mL leads to a sharp decrease in average recovery efficiency for all the analytes. This might be due to the affinity of the PCB for the polymeric material at lower eluent volume where the dilution distribution coefficient increases at lower volume [22, 28-30]. Thus, 10 mL became the volume of choice for elution in subsequent experimental test runs.

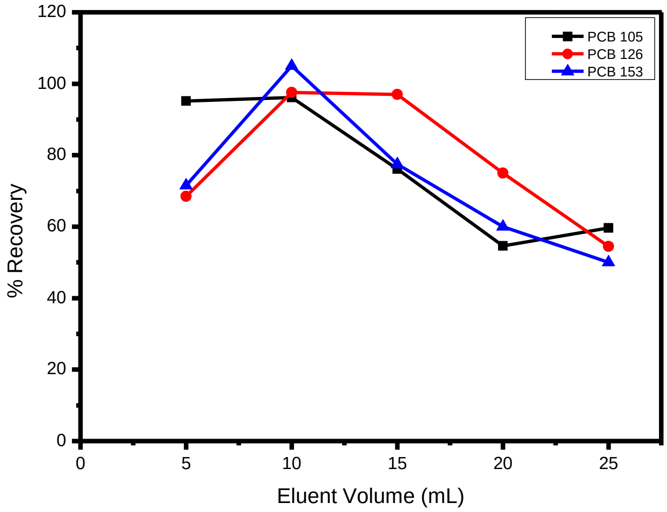

Figure 9.5: Effect of elution volume on the recoveries of PCB mixtures in aqueous medium

9.7.1.6 Effect of sample volume

The sample volume or breakthrough volume is another vital parameter which affects extraction efficiency when using the SPE method. This study employed different sample volumes ranging from 100 mL to 500 mL of the standard solution of the analytes to concentrate using the SPE method. The results showed that the recoveries of all the analytes decreased with an increase in volume (Figure 9.6). This result is interesting, considering the fact that there was no selective adsorption for any of the analytes in the sample volume which is the determinant factor in preconcentration of analytes. Thus, 100 mL was employed for further experimental test runs in order to save time because sample extraction is time-consuming when using larger volumes. Thus, the sample volume of 100 mL was selected for the subsequent experiments.

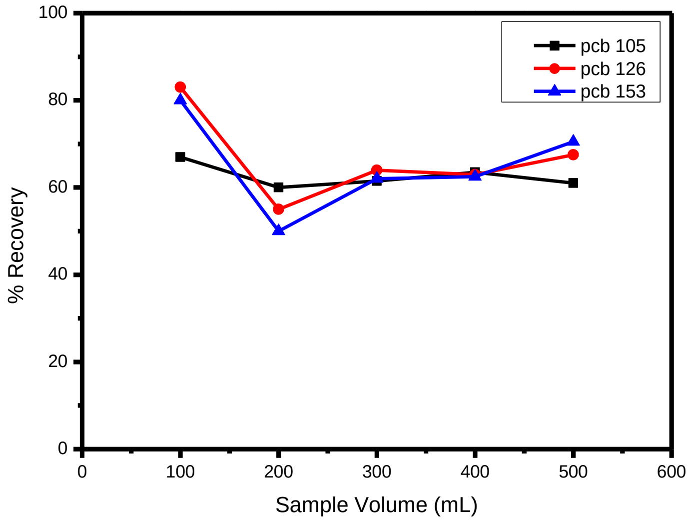

Figure 9.6: Effect of sample volume on the recoveries of PCB mixtures in aqueous medium

9.7.1.7 Effect of flow rate

In the SPE process method, the sample flow rate is another important parameter that affects both the time of passing through SPE cartridge and retention of the targeted analytes on the SPE cartridge. In this study, the flow rate was investigated in the range of 1 mL/min to 5 mL/min (Figure 9.7). The experimental results indicated that the optimum flow rate was 2 mL/min for the maximum recovery of all the analytes. The remaining results given in Figure 9.7 show no significant influence on the recoveries of PCBs at flow rates ranging from 3 mL/min to 5 mL/min. Therefore, 2 mL/min was selected for subsequent test runs.

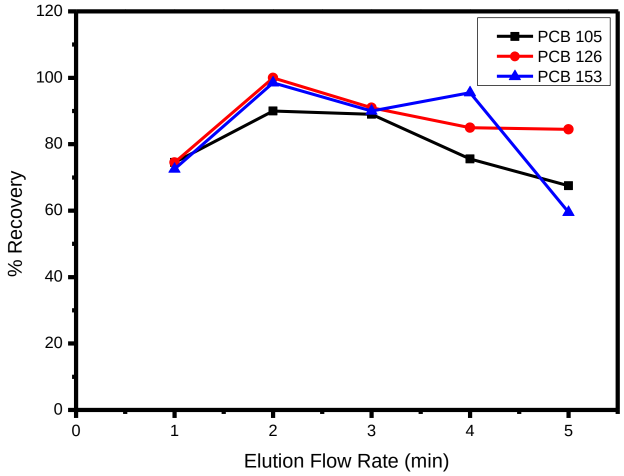

Figure 9.7: Effect of flow rate on the recoveries of PCB mixtures in aqueous medium

9.7.1.8 Comparison of PCA polymeric material with other extraction methods of PCBs

The comparison of PCAD polymeric material with other methods of extraction was carried out to show the extraction efficiency and determination of PCB analytes in water samples. The results of the study comparing the various extraction methods (Figure 9.8) showed that PCAD polymeric materials were applied as a stationary phase to preconcentrate and purify PCBs in aqueous solution. The average recoveries of PCB analytes for all PCAD polymeric material including AC and C18 (59% for HMDI, 82% for HMDIAC, 85% for HMDICD, 92% for HMDIACCD, 65% for HMDIRT, 70% for AC, 76% for C18 cartridge) revealed that the PU composite material with the filler β-CD and AC, i.e. HMDIACCD (Figure 9.8) enhanced the extraction efficiency of PCBs more than the other extraction techniques.

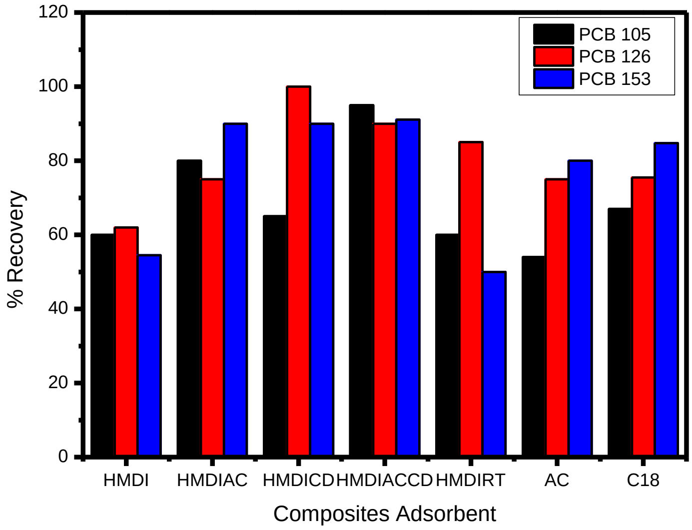

Figure 9.8: Effect of sample volume on the recoveries of PCB mixtures in aqueous medium

9.8 APPLICATION

9.9 METHOD VALIDATION

A series of standard solutions (10 ng/mL, 20 ng/mL, 40 ng/mL, 60 ng/mL, 100 ng/mL, 200 ng/mL and 500 ng/mL) were prepared to obtain a linear range for each of the PCB analytes. Table 9.2 shows the linearity range of standard solutions at concentrations of between 10 ng/mL and 500 ng/mL. The correlation coefficient (r^2) of the PCB analytes ranges between 0.993 and 0.998, while the limit of detection (LOD) which is a signal-to-noise ratio (3:1) or response of standard deviation to the slope of analytical curve $\left(3.3 \times \frac{s}{b}\right)$ ranges from 0.00483 ng/mL to 0.0132 ng/mL. The limit of quantification (LOQ) based upon the signal-to-noise ratio (10:1) or standard deviation of the blank on the residual regression line $\left(10 \times \frac{s}{b}\right)$ ranges from 0.015 ng/mL to 0.040 ng/mL of the analytes. The relative standard deviations RSD (n = 3) of the PCBs ranged from 1.5% to 4.4%.

Table 9.2: The limit of detection (LOD), limit of quantification (LOQ) and reproducibility method

Analytes	Calibration equations	Linear correlation coefficients (r^2)	LOD (ng/mL)	LOQ (ng/mL)	RSD (%)
PCB 105	$Y = 2.5482e^{+ 006x} - 330197$	0.993	0.01320	0.040	4.43
PCB 126	$Y = 1.6396e^{+006x}- 1.0134e^{+006}$	0.995	0.00483	0.015	3.14
PCB 153	$Y = 1.7601e^{+006x} - 120787$	0.998	0.00601	0.018	1.50

In order to validate the feasibility of this method for its use in this study to analyse the three PCB compounds, the performance of the method was evaluated with two environmental water samples from a local dam. Blanks of the two environmental water samples used were run to verify whether the target analytes were present or not. It was discovered that there were no peaks at the related location for all the three compounds in the sample solution. In order to show the merit of this method the environmental water sample was spiked with the three compounds (Figure 9.9), and even though the PCAD was reused more than 5 times, a good spiked recovery was achieved for the entire water sample.

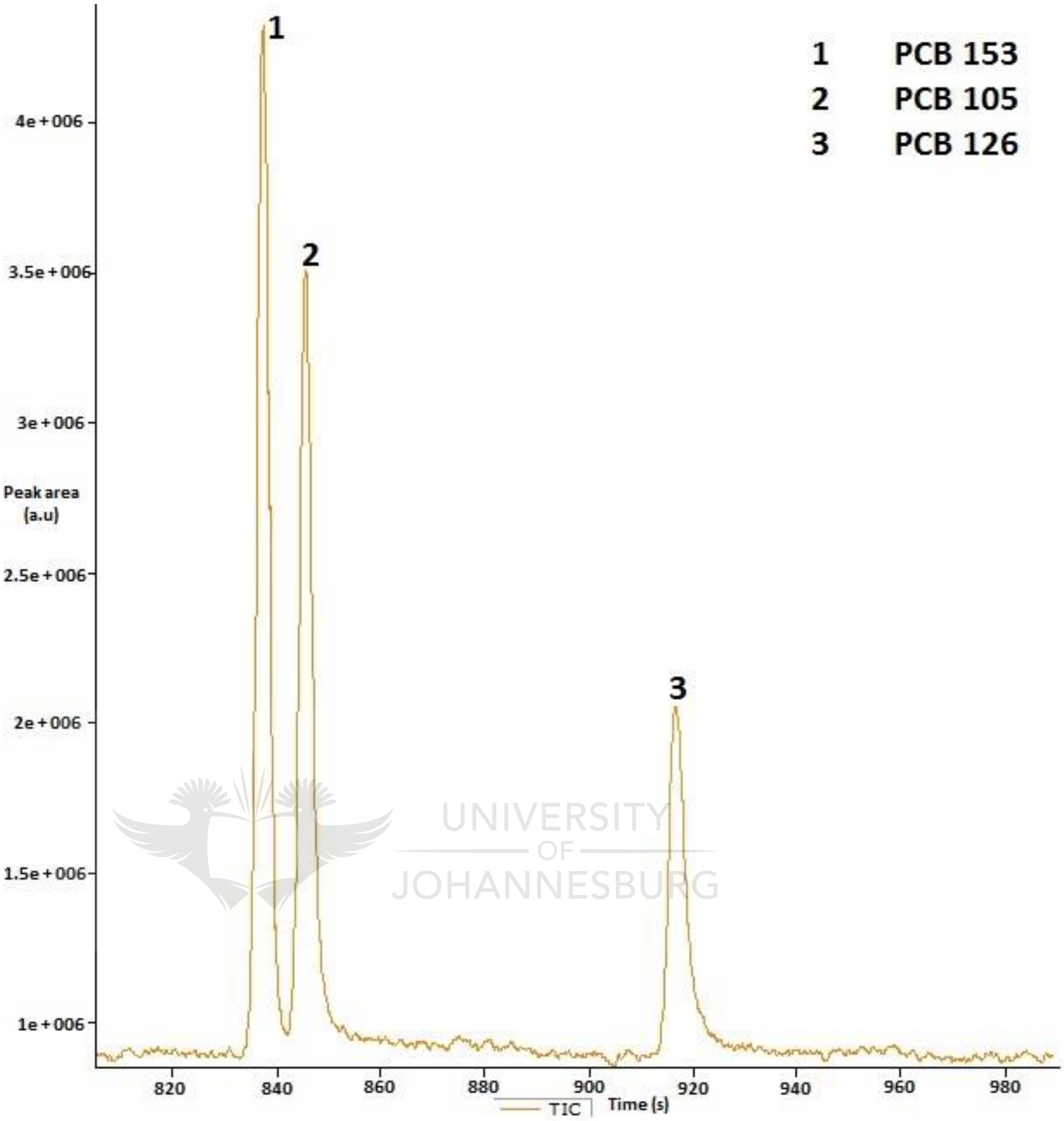

Figure 9.9: GC×GC TOFMS chromatogram of wastewater samples containing the PCB compounds

CONCLUSION

This study describes a cheap and simple method of analysis of polychlorinated biphenyl (PCB 105, PCB 126 and PCB 153) in a wastewater sample. The method was based on SPE using PCAD polymeric material and GC×GC TOFMS. PCAD, polymeric material produced from polyol prepolymer, is a cheap and an excellent material that can be employed in SPE columns for the enrichment of PCB 105, PCB 126 and PCB 153. This method allows concurrent determination of multiple PCB compounds without complicated protocols. The PCAD cartridge packed with polymeric material can be reused as many times as possible.

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CHAPTER TEN

GENERAL CONCLUSIONS AND RECOMMENDATIONS

10.1 CONCLUSIONS

This thesis reports the preparation of AC from waste residue which is a carbon precursor that can serve as an alternative to the expensive commercially available AC. The AC was successfully produced using the chemical vapour deposition technique in a reactor at a temperature ranging between 400°C and 500°C under inert atmosphere through carbonisation, and also through activation stage using both the physical and chemical methods to activate the charred material from RT using steam, CO_2 and phosphoric acid as activating agents. The AC produced was later incorporated as fillers for the production of a polymeric composite material.

The AC produced was applied in phytoremediation of both inorganic and organic species from environmental samples especially wastewater, in which over 90% and 80% removal were achieved respectively.

The composite material was produced basically by reaction of polyol, castor oil and diisocyanate to produce polyurethane composite. Various fillers such as AC, CD and RT were incorporated into the matrix of the polymer after thorough agitation by stirring.

Chemical interaction was obtained between the prepolymer from polyol and the fillers which were crosslinked via NCO bonding from the isocyanate. The hydrogen bonding between the hydroxyl groups of the fillers observed in PCAD improved the adsorption capacity of metal ions onto the polymers as over 70% recovery was obtained when applied as sorbent for metal-ion recovery. Furthermore, PCAD material was also shown to have 85% recovery of

POP contaminants, especially PCB, when applied at various concentrations in aqueous solution. The hydrophobic property of AC and the inclusion complex in the CD moieties play a major role in their adsorption capacity and retention of pollutants in their matrix.

The large SSA and the high pore volume obtained in the produced AC contributed to their effectiveness as an adsorbent.

Scanning electron microscopy (SEM) images showed a large pore size for AC which confirmed their ability for inorganic ion removal. The SEM monographs on PCAD also revealed proper blending between the polymer and the fillers and a very distinctive pore size was evident, especially for the polymer produced using HMDI as cross-linker. This factor plays a major role in their application as HMDI performed slightly better than MDI cross-linkers.

In general, both adsorbents (AC and PCAD) performed well and can be used as an alternative low-cost adsorbent for water decontamination.

10.2 RECOMMENDATIONS

The composite adsorbents have demonstrated their potential in water decontamination; however, there is still a lot of room for further research, which includes:

- Toxicity study of the polymeric material to evaluate their suitability for point-of-use application in small-scale water filters.
- Degradability study on the polymeric material to determine the extent of change on exposure to various climatic conditions.

- Techniques such as nuclear magnetic resonance (NMR), especially the solid-state NMR, could be used to further understand the degree of polymerisation and blending that takes place during the preparatory steps and to determine the exact chemical interactions between the materials.