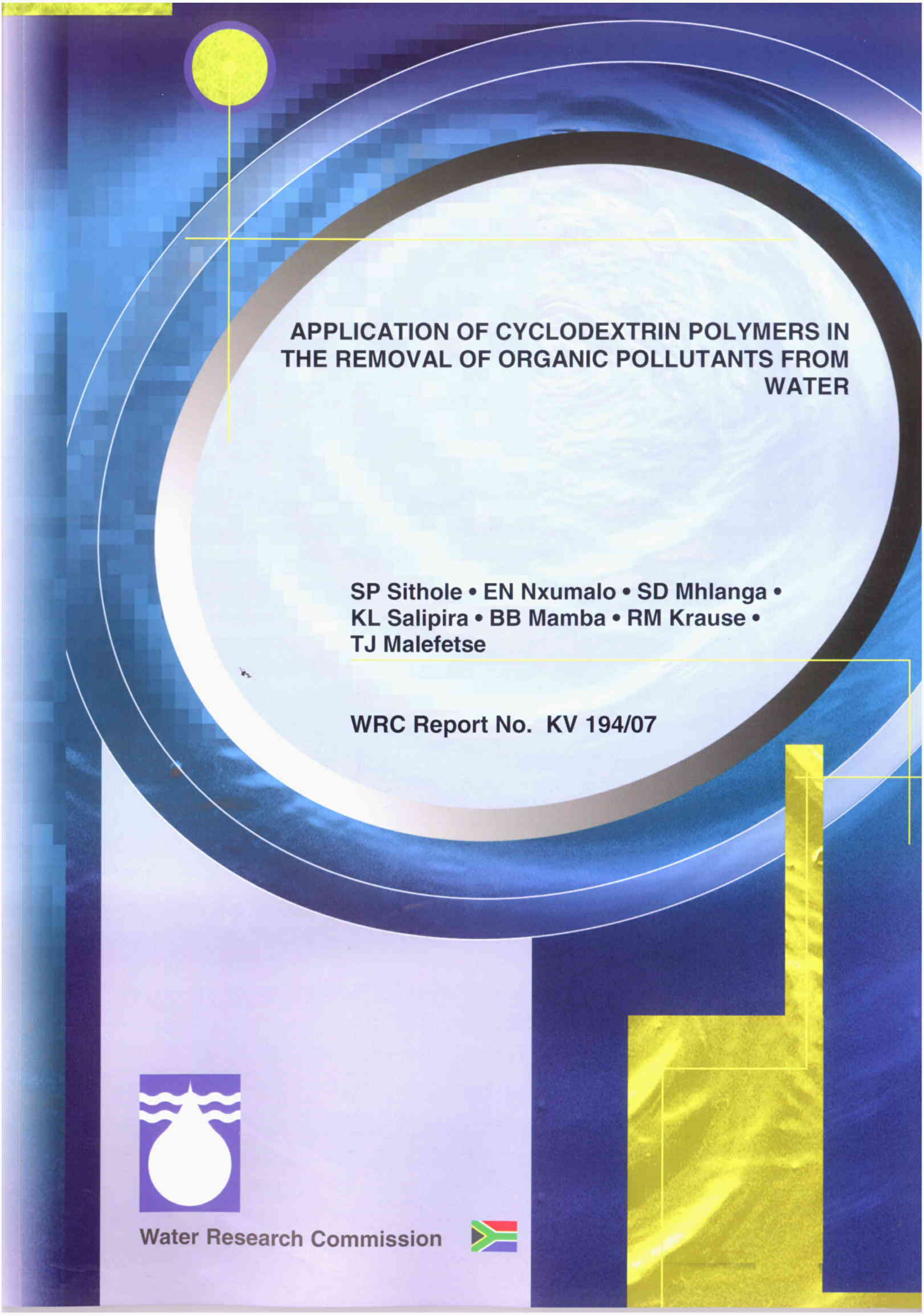

APPLICATION OF CYCLODEXTRIN POLYMERS IN THE REMOVAL OF ORGANIC POLLUTANTS FROM WATER

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WRC Report No. KV 194/07

Water Research Commission

APPLICATION OF CYCLODEXTRIN POLYMERS IN THE REMOVAL OF ORGANIC POLLUTANTS FROM WATER

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

The removal of organic pollutants from water in both industrial and municipal water is a great challenge to water providers worldwide. Some of these pollutants are very toxic and pose serious health risks to humans and animals. Additionally, the presence of organic pollutants in the water often leads to the corrosion of the turbines that are used for power generation at power stations. This obviously makes the power generation process less efficient and thus has cost implications, especially for the end user. Besides the corrosion of turbines, the removal of contaminants from water contaminated with organic pollutants also has a bearing on the total cost of generating clean water. To this end, municipalities and industries sourcing water from Rand Water's treatment plants and Eskom's power stations are plagued by high water costs.

Geosmin and 2-MIB are detectable by the human nose at concentration levels as low as 10 ng/L. These compounds are common water pollutants and are renowned to cause bad taste and odour in drinking water. Although geosmin and 2-MIB do not pose any serious health risks to humans, they impact on the aesthetic and consumer acceptability of drinking water. Currently available technologies such as activated carbon are unable to remove these pollutants to low levels (i.e. ppb levels). In our laboratories, we have found cyclodextrin polymers to be effective in the removal of a range of organic pollutants from water to ppb levels. However, these investigations were confined to water samples deliberately spiked with specific pollutants and have not been proven with "real" water samples. We sought to integrate data accumulated in the laboratory by testing and applying these polymers on a larger scale and on real systems.

Cyclodextrin-based polyurethanes were employed in the removal of 2-MIB, geosmin and other organic pollutants in environmental water sampled from Lethabo Power Station (Eskom) and Zuikerbosch Water Treatment Plant (Rand Water). The water samples were extracted using Solid Phase Microextraction (SPME) and thereafter identified and quantified using gas chromatography/mass spectroscopy (GC/MS). The new cyclodextrin polymer technology was compared with treatment methods currently applied at the power station and treatment plant. To determine the environmental friendliness of this technology, biodegradation studies were also carried out. These entail performing soil burial tests prior to the characterization of the polymers using thermogravimetric analysis (TGA), Fourier transform infra-red (FTIR), scanning electron microscopy (SEM) and Braunner Emmet Tellet (BET).

The extraction and analysis of geosmin, 2-MIB and other pollutants using SPME and analysed using GC/MS, respectively, were successful. Also, the removal of geosmin and 2-MIB from the two types of samples (i.e. the Rand Water and Eskom samples) to ppb levels was achieved using the cyclodextrin polymers. These polymers showed negligible degradation upon exposure to the different types of soil over a period of 119 days.

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- Water Research Commission (WRC)
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- Rand Water
- Industrial Urethanes (Pty) Ltd

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LIST OF ABBREVIATIONS

AC	Activated Carbon
BET	Braunner Emmet Teller
CD(s)	Cyclodextrin(s)
α-CD	*Alpha* Cyclodextrin
β-CD	*Beta* Cyclodextrin
γ-CD	*Gamma* Cyclodextrin
CO_2	Carbondioxide
DSC	Differential Scanning Calorimetry
EI	Electron Ionization
EtOAc	Ethyl acetate
FT-IR	Infra-red
GAC	Granular Activated Carbon
GC/MS	Gas Chromatography / Mass Spectrometry
HMDI	Hexamethylene diisocyanate
HPLC	High Pressure Liquid Chromatography
HTC	High Temperature Combustion
IC	Inorganic Carbon
K	Equilibrium Constant
KHP	Potassium Hydrogen Phthalate
LLE	Liquid-liquid Extraction
m/z	Mass to charge ratio
2-MIB	2-Methylisoborneol
µg/L	Micrograms per litre
mg	Milligram(s)
mg/L	Milligrams per litre
mL	Millilitre(s)
MPa	Mega Pascals
ng/L	nanograms per litre
NOM	Natural Organic Matter
NPOC	Non Purgeable Organic Carbon
PAC	Powdered Activated Carbon
PCP	Pentachlorophenol
POC	Purgeable Organic Carbon
ppb	Parts per billion
SA	Surface Area
TOC	Total Organic Carbon
XRD	X-ray diffractometry

CHAPTER ONE
INTRODUCTION

1.1 PROBLEM STATEMENT

The presence of organic pollutants in industrial water has been found to cause problems, especially for power generation institutions such as Eskom. The pollutants cause corrosion of the turbines that are used for power generation and this impact on the cost of electricity production. Likewise, organic compounds such as 2-methylisorbeneol (2-MIB) and geosmin often lead to malodorous and bad-tasting drinking water thus making water unsuitable for human consumption. The removal of the organic compounds has become a serious challenge for municipalities and industries in South Africa.

Technologies that are currently used by both industries and municipalities fail to remove the organic contaminants to desired levels. Treatment methods such as the use of activated carbon, reverse osmosis, advanced oxidation processes and membrane processes have been investigated by Eskom and were found to be ineffective and costly.[1] Activated carbon, which seems to be the technology of choice in the removal of organic species from water, has some limitations. Specifically, it fails to remove the pollutants to low desired levels (i.e. ng/L levels).

Water treatment techniques are generally becoming more ineffective as more pollutants get discovered. As a result, this has led to a search for new and more effective technologies that are capable of removing new and existing organic pollutants to desired levels. The use of water insoluble cyclodextrin polymers, the so-called “nanosponges”, in the removal of organic pollutants from aqueous media is a case in point.

In this study, the cyclodextrin polymers have been quantitatively evaluated for their ability to remove a range of organic pollutants from water. Standard unfunctionalised polymers were found to be effective in the absorption of organic to the desired ng/L levels.[2] Similarly, derivatives of these polymers (i.e. monofuctionalised cyclodextrin polymers) were also found to be effective in the removal of toxic phenolic compounds from water.[3] While it was possible to remove trichloroethylene to non-detectable levels, *p*-nitrophenol was removed from a 10 mg/L spiked water sample with a removal efficiency of 99%.[4]

Up to now, these polymers have however not been used in the removal of organic pollutants from real water samples. A substantial amount of data has only been collected at the laboratory scale and the implementation of the technology outside a laboratory setting was therefore deemed necessary.

1.2 JUSTIFICATION OF THE STUDY

The biggest challenge faced by the water treatment industry is the removal of trace quantities of toxic organic pollutants from water and the disposal of the used adsorbent. The removal of the organic contaminants from water is also a huge challenge for local government officials and scientists. To ensure good health and safety, many communities around the world are in need of cost effective technologies that are capable of removing toxic contaminants from their water supplies. As a result, there is a drive to search new technologies that can economically ensure high-quality municipal drinking water. Many governments, the South African government included, have imposed stringent environmental regulations on industries. These regulations compel them to remove contaminants before discharging the water into water bodies and the environment. There are currently no technologies available to remove organic from water to acceptable levels. However, research that involves the use of polymers of cone-shaped cyclodextrins interconnected by linkers in the removal of organic pollutants from water has been successfully demonstrated in our laboratories. These polymers have added advantage in that they can be recycled many times by flushing out the trapped organic pollutant and reused. This eliminates the need for disposal and also lowers the cost of the technology.

Enough information on the cyclodextrin polymers has been accumulated through laboratory studies and this technology has been found to be very competitive. While previous laboratory studies have generated valuable data, these investigations were limited to water samples spiked deliberately with specific pollutants. In a nutshell, results of our investigations have not yet been proven with real water samples. The aim of this study is, therefore, to integrate data accumulated in the lab by testing and applying these polymers on a larger scale and on real systems.

1.3 OBJECTIVES OF THE STUDY

This research project was undertaken with the following specific objectives:

- Use cyclodextrin-based polyurethane polymers in the removal of 2-MIB, geosmin and other organic pollutants in environmental water sampled from Lethabo Power Station (Eskom) and Zuikerbosch water treatment plant (Rand Water). Gas chromatography mass-spectrometry will be used to identify the presence of the pollutants and quantify them.

- Compare the cyclodextrin polymer technology with the treatment methods that are being used at the Lethabo Power Station and Zuikerbosch water treatment plants.

- Use soil burial tests to investigate the biodegradation of the polymers over a period of time. Characterization of the polymer after the prescribed periods of biodegradation will be assessed using thermogravimetric analysis (TGA), Fourier transform infra-red (FTIR), scanning electron microscopy (SEM) and Braunner Emmet Tellet (BET).

1.4 REFERENCES

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CHAPTER TWO
LITERATURE REVIEW

2.1 TASTE AND ODOUR CAUSING COMPOUNDS IN MUNICIPAL WATER

One of the challenges facing Rand Water is the removal of geosmin and 2-MIB from municipal water. Although these compounds pose no real health risk, they impact on the aesthetic quality and consumer acceptability of drinking water.[1] Geosmin and 2-MIB are detectable by the human nose at concentrations as low as 10 ng/L in water.[2] The presence of these compounds in municipal water has led to many consumer complaints. In this section, the occurrence of geosmin and 2-MIB is discussed and the current water treatment method used to remove these pollutants from water is reviewed. An overview of the water treatment processes used at the Zuikerbosch water treatment plant will also be discussed.

2.1.1 Geosmin and 2-MIB

Geosmin (**Figure 2.1**) and 2-MIB (**Figure 2.2**) cause earthy odours in drinking water and are produced by cyanobacteria (blue green algae) and actinomycetes (bacteria).

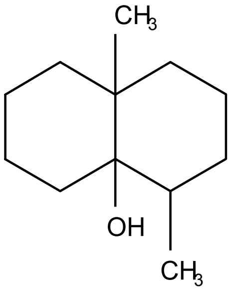


Figure 2.1: Structure of geosmin

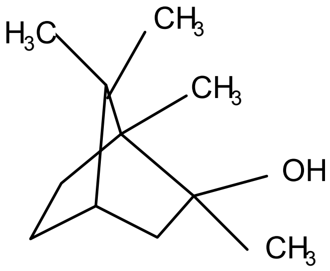


Figure 2.2: Structure of 2-MIB

Actinomycetes are mould-like, filamentous bacteria widely distributed in the environment; these are commonly found in soil and are introduced in the water system when soil is washed off during spring rains runoff. Tastes and odours that are associated with antinomycetes are woody, haylike, marshy, potato bin and bitter.[3] Actinomycetes can be a problem in water distribution systems since under certain conditions they can produce typical earthy, mouldy and musty tastes in pipes inside buildings.[4] Many scientists involved in the production of palatable water believe that algae are the main cause of taste and odour in raw water.[4] Algae contribute heavily to the organoleptic odours in water and the odours are described as fishy, grassy, must, septic and earthy. On the other hand, cyanobacteria (blue green algae) such as *Anabaena*, *Oscillator* and *Phormidium* species grow extensively in the summer season in reservoirs, rivers, canals, dams and within water treatment plants.[5]

The presence of these organic contaminants (i.e. geosmin and 2-MIB) is affected by several environmental factors such as light intensity, temperature, water depth and nutrients that are present in the water system. Light is an essential factor since algal blooms require light for photosynthesis in order to survive and multiply. In previous studies it was found that geosmin and 2-MIB was highest in cultures grown under continuous light.[6] Temperature also plays a vital role in the production of geosmin and 2-MIB. Lake water with temperatures of approximately 10^0C to 30^0C enhances the production of these compounds. For example, actinomycetes growth normally begins at 7-8^0C and the growth rate becomes rapid at a temperature range 33-34^0C.[4] Water depth is another important factor; surface algal blooms are exposed to harm (such as light and dry conditions) at the water surface and as a result die off far more quickly than deeper blooms.[6] The surface algal blooms decompose and this is accompanied by the release of the odorants on the surface of the water. Therefore, the surface water generally tends to have a higher concentration of geosmin and 2-MIB. The presence of nutrients such as nitrogen, phosphorus and iron are essential in the production of the organic contaminants. These nutrients are introduced in the water system due to industrial effluents and agricultural runoffs.

2.1.2 Technologies currently used for the removal of geosmin and 2-MIB from water

Various treatment methods are available for the removal of taste- and odour-causing compounds from water. However, these methods fail to remove geosmin and 2-MIB from water to the acceptable ng/L levels. Treatment methods such as activated carbon, ozonation, biological degradation and conventional methods (coagulation, flocculation and disinfection) used are used extensively by water providers. Currently, Rand Water employs activated carbon in conjunction with the convectional water treatment methods.

2.1.2.1 Activated carbon

Powdered activated carbon (PAC) is often used in most treatment plants for the mitigation of problem odours; it has proved to be inexpensive and can only be applied when required. By far, PAC has been rated as the most effective technology in the removal of geosmin and 2-MIB. Despite its effectiveness, water providers such as Rand Water are still plagued by taste and odour associated problems. The effectiveness of PAC depends on the type of activated carbon used and on the competitive effect of natural organic matter (NOM).[7] In water treatment plants PAC is added at the head of the treatment plant where the competition of NOM and other chemicals such as alum and chlorine is the highest.[6] NOM commonly exists in water at elevated levels (mg/L levels) than geosmin and 2-MIB (ng/L levels). Therefore, the NOM competes with the odorous compounds for adsorption sites on the PAC in water.[6,7] This renders the PAC ineffective in the removal of geosmin and 2-MIB.

2.1.2.2 Ozonation

Ozone the triatomic form of oxygen is a powerful oxidant and has been used in water treatment for the removal of geosmin and 2-MIB.[8] Despite ozone being a powerful oxidant, there are problems associated with this technology. Firstly, a high ozone dosage is needed to remove these compounds. NOM reacts a lot more quickly with ozone than with geosmin and 2-MIB and this often leads to fast ozone depletion. Overdosing is not an alternative as it is energy consuming and costly.[9] Secondly, the application of ozone leads to the formation of by-products such as bromates, which have been confirmed to be harmful by the World Health Organization (WHO).[9] Bromates are potential carcinogens and are currently limited to concentrations of 25 μg/L in potable water.[10]

2.1.2.3 Biological degradation

Geosmin and 2-MIB are susceptible to biological degradation by microorganisms; this is because they are similar to biodegradable alicyclic alcohols and ketones. In fact, research shows that biodegradation of geosmin leads to the formation of products such as 1,4a-dimethyl-2,3,4,4a,5,6,7,8-octahydronaphthalene and enone.[6] Conversely, the naphthalene and the enone have previously been used as precursors for the synthesis of geosmin.[6] Despite the susceptibility of geosmin and 2-MIB towards biological degradation, microbial control is difficult as these compounds exist only in low concentrations at the water surface. Moreover, geosmin and 2-MIB are often seasonal compounds, which means that the microbes must effectively remove the compounds when present, continue to survive when the problem ceases and repeat the cycle.[6]

2.1.3 Zuikerbosch water treatment plant

Rand Water abstracts its water from the Vaal dam to Zuikerbosch water treatment plant. In order to ensure that water meets the required drinking water standards, other water treatment processes are used to both remove suspended material and disinfect the water prior to pumping to municipalities. The purification processes used are coagulation, flocculation, sedimentation, stabilization, filtration, disinfection and chloramination and are discussed individually below.

2.1.3.1 Coagulation and flocculation

The coagulation process involves the addition of slacked lime and sodium silicate to destabilize the suspended particles. The suspended particles are clumped together to from larger particles known as floc. These flocs are settled out by gravity. Activated sodium silicate and ferric chloride is used to aid the flocculation process.[11]

2.1.3.2 Sedimentation

This is a physical separation of suspended material from water by the action of gravity.[3] The flocs that are formed during coagulation process are allowed to settle in specially designed tanks. These tanks are also engineered to remove the sludge that accumulates at the bottom of the tanks. [11]

2.1.3.3 Stabilisation

The addition of lime during the coagulation process raises the pH of the water to high levels. This high pH makes the water corrosive and this leads to the scaling of the pipes in the distribution system. To prevent scaling, the water is passed through carbonation bays where it is stabilized by bubbling CO_2 through the water. This reduces the pH of the water and water that is chemically stable that will not cause excessive scaling is produced.[11]

2.1.3.4 Filtration

In this process solids are removed from liquid by passing through a porous medium. Filtration is used to remove solids after chemical coagulation.[4] After the carbonation process the water is filtered through sand filters and the particles from the flocculation process are removed.[11]

2.1.3.5 Disinfection

This process entails the destruction of pathogenic organisms such as bacteria and viruses that might be present in water. About 1.5-4.0 mg/L of chlorine dosage is added to the water and this ensures that there is minimal re-growth of the microorganisms during the 6-8 hours that the water travels to the booster stations.[11]

2.1.3.6 Chloramination

This is the second disinfection stage where chlorine and ammonia are dosed at the pumping stations at a ratio of 4:1 forming monochloramine. A secondary disinfection by chloramination is needed since chlorine doesn't remain active for longer than 6 to 8 hours. Therefore, disinfection is repeated with a less powerful agent that remains active for long periods so that water is protected right up to the end consumer.[11]

2.2 LETHABO POWER STATION

Eskom, the electricity generating company in South Africa, supplies 95% of the country's electricity requirements. Its capacity of 41298 mw is fed by ten large fossil fire power plants, one nuclear power plant, hydroelectric and pump storage schemes.[12] Lethabo Power Station is one of the largest coal-fired power stations with a capacity of 6 × 600 mw units.

The station sources its water for power generation from the Vaal dam. This water is contaminated with organic and inorganic pollutants. The presence of such pollutants in the raw water is a major concern for power stations worldwide.[13] Organic compounds can enter the power plant through a number of pathways from chemical cleaning, lubricating oil, micro-organisms present and ion exchange leachates. The most likely source of contamination is from raw water.[14] It is known that on entering the boilers, these organic impurities are decomposed to halogenated acids and acetic acids. The high temperatures (540^0C) and high pressure (18 MPa) environments are responsible for the decomposition processes.[12] These newly formed acids cause a decrease in the pH of the boiler water which in turn leads to the corrosion of the turbines used for power generation. In a survey conducted in Russia it was observed that the decrease in pH at low pressure turbine stages could be attributed to the presence of organic compounds in the boiler make-up water.[14] It was further concluded that there was a strong correlation between the presence of impurities and the corrosion-erosion of the low pressure turbines. Other studies revealed that these organic compounds break down to smaller fraction organic acids such as fomates, oxalates, propionates and butyrates under pressure and temperature.

2.2.1 Water treatment at the Lethabo Power Station

To alleviate the problem of organic pollutants Eskom has employed a water treatment regime that is aimed at producing water with reduced organic contaminants. The treatment process that involves prechlorination of the raw water, followed by coagulation, clarification, sand filtration and deminerilisation (using ion exchange) has been adopted by Lethabo power station.[12]

2.2.1.1 Prechlorination

The raw water from the Vaal dam is dosed with chlorine. This pre-chlorination step is used to prevent the growth of pathogens and algal build up in the treatment system.[12] The chlorination process also oxidizes the natural organic matter and makes it more readily coagulated.[15] As an oxidant, chlorine is also used for manganese, iron and sulfide removal. Insoluble hydroxides from iron, manganese and sulfide oxidation are formed and these are subsequently removed by filtration.[15]

2.2.1.2 Coagulation and flocculation

After the chlorination process the water passes through to the flashmix chamber. In the flashmixer coagulants agents such as polyaluminium chloride and minimal polyelectrolyte are added. In the coagulation process smaller particles in the water are combined into larger bodies by destabilization.[16] These destabilized particles form larger masses that can be separated from the liquid (flocculation). Traditionally, Eskom has used aluminum sulphate (alum) as the primary coagulant for potable and demineralized water. While alum and polyaluminium chloride removes 90% and 60% of total organic carbon (TOC) from feed water respectively, the latter is preferred since it avoids the excess sulphate burden. This coagulant also minimizes the sludge volume in the clarifiers, reduces aluminum residuals by 50% in water and is more cost effective.[17]

2.2.1.3 Clarification

Water from the flashmixer enters the clarifiers. This is where floc formed at the previous stage sediments. The clarifiers contain lamella plates which lie at an angle of 60^0 in order to retain the floc at the base of the clarifier. Sludge that accumulates at the bottom of the clarifiers is removed by opening of valves every 30 minutes.[12]

2.2.1.4 Sand filtration

From the clarifiers the pipe separates into two streams one leading to the potable sand filter and the other to the demineralisation sand filter. At this treatment stage the water from the clarifiers are filtered through sand by means of gravity to remove settleable solid. Lime or sodium carbonate is added to adjust the pH before the water enters the potable chlorine tank where it dosed with chlorine for final disinfection.[12]

2.2.1.5 Demineralisation

This treatment stage consists of a strong acid cation exchange unit, degasser, weak base anion exchange unit, strong base anion exchange unit and a mixed bed ion exchange. An ion exchange resin is used for the removal of inorganic ions. The anion exchanger removes ions such as sulphate, chloride and silica. The cation exchanger removes sodium, magnesium and calcium. The mixed bed which consists both cation and anion exchanger removes the final traces of the inorganic compounds.[12] The degasser is placed between the cation exchange and anion exchange unit it is used to remove CO_2 that might have accumulated in the treatment pathway.

After the deminerilisation plant the water enters the boilers. At the boilers steam is generated and it is used to turn the turbines which are used for power generation.

The water treatment regime employed by Eskom and Rand water cannot completely remove organic pollutants from the water and this has had an impact on the water quality in South Africa. Therefore other treatment technologies have to be applied.

2.3 CYLODEXTRIN POLYMER TECHNOLOGY

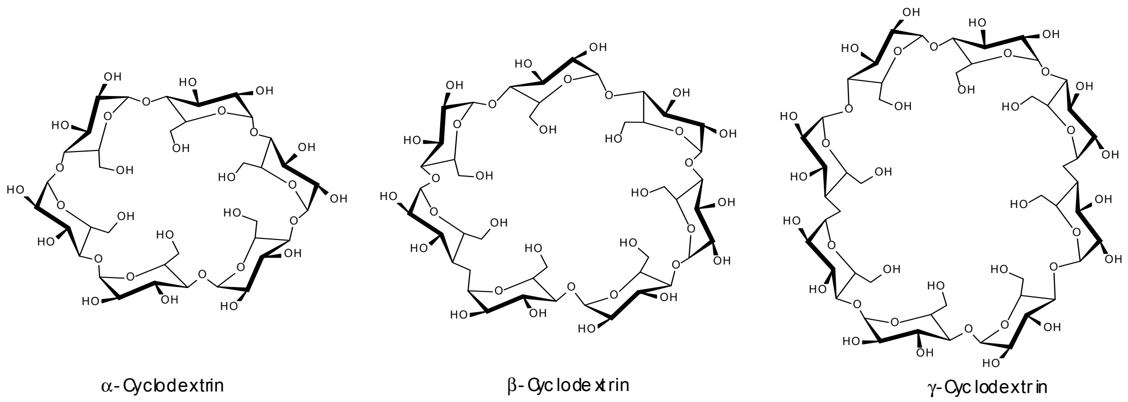
Treatment technologies such as the use of activated carbon, advanced oxidation and membrane processes have been investigated by Eskom and Rand Water in order to minimize organic pollutants in their treatment plants. However, these treatment methods were found to be ineffective and costly.[18] Thus a need to devise other water treatment technologies. In this chapter a new technology that is being used at our laboratories for the removal of organic pollutants will be reviewed. It has already been tested at the laboratory for the removal of organic pollutants and has been found to efficiently remove organic contaminants from water.

2.3.1 Source and nomenclature

Cyclodextrins (CDs) were first discovered in 1891 by Villiers.[19, 20, 21, 22] CDs, which are sometimes called Schardinger dextrins, cycloamyloses, or cycloglucans, are polysaccharides of low molecular weight belonging to the general class called oligosaccharides. They are produced by treating starch with amylase Bacillus macerans.[19, 22, 23]

2.3.2 Structure and physical properties of cyclodextrins

The three common types of cyclodextrins are α-CD, β-CD, γ-CDs, which are referred to as first generation or parent CDs. These CDs possess six, seven, and eight glucose units respectively, linked by α-(1, 4)-linkages **(Figure 2.3 and 2.4)**.



α-Cyclodextrin β-Cyclodextrin γ-Cyclodextrin

Figure 2.3: Structures of α-, β-, γ- CDs showing 6, 7 and 8 glucopyranose units respectively.

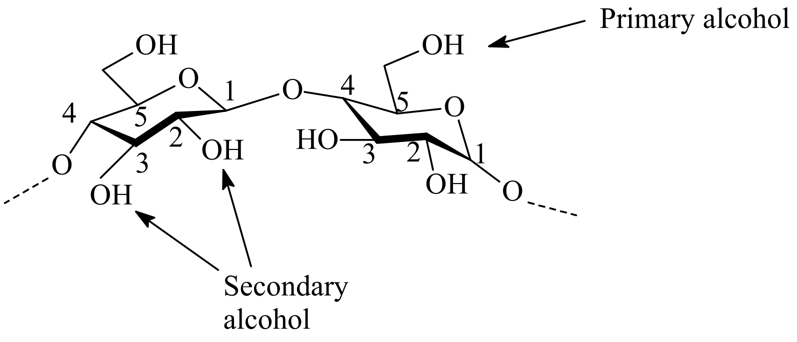


Figure 2.4: Illustration of α-(1, 4)-linkages and the primary and secondary alcohol groups.

Other higher molecular weight CDs have been isolated but, because they are currently too expensive and have as result not been used extensively in industry.[19,22] The β-CD is the most accessible, lowest in cost and generally most useful and has been used extensively in this study.

A characteristic feature of CDs is that they possess a toroidal shape that form well defined cylindrical cavities of about 8Å deep and 5-10Å in diameter.[19, 20, 23] The cone is formed by the carbon skeleton of the glucose units and the glycosidic oxygen atoms that are in between them. The primary hydroxyl (OH) group of the glucose is located at the narrow end of the cone (primary face) and the secondary OH groups are at the wider secondary face (See **Figure 2.5**). The main properties and dimensions of α-,β- and γ-CDs are summarized in **Table 2.1** below.[23]

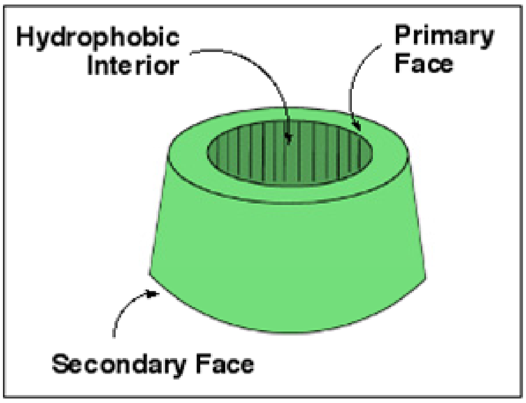


Figure 2.5: Illustration of the conical shaped structure of a cyclodextrin.

Table 2.1: Properties of cyclodextrins

Property	α-cyclodextrin	β-cyclodextrin	γ-cyclodextrin
Number of glucose units	6	7	8
MW (g/mol)	972	1135	1297
Water solubility (g/100mL)	14.5 at 25°C	1.85 at 25°C	23.2 at 25°C
Internal Diameter (Å)	4.9	6.2	7.9
External diameter (Å)	14.6	15.4	17.5
Cone height (Å)	7.9	7.9	7.9
Cavity volume (Å^3)	174	262	427

The primary and secondary hydroxyl groups on the outside of the CDs make them water soluble. CDs are also insoluble in most common organic solvents. The cavity of the CD ring consists of a ring of C-H groups, a ring of glycosidic oxygen atoms followed by another ring of C-H groups. This renders the cavity of the CD rings less polar. Another important feature is that, although CDs have a hydrophilic surface, they contain hydrophobic cavities that enable the encapsulation of the hydrophobic guest molecules into these cavities. Since parent CDs are soluble in water and some organic solvents (e.g. DMF and DMSO), they cannot be used directly in the absorption of organic pollutants from water. As a result, CD polymers that are insoluble in water but possess enhanced affinity for organic contaminants in water have been synthesized.[21,24,25] The design of these CD polymers is based primarily on the reactivity of the hydroxyl group.[26] Treatment of the hydroxyl groups of the parent CDs with a bifunctional group led to the generation of highly cross-linked nanoporous polymers.[24] These polymers can be prepared as granular solids, powders or films by a simple variation of ratios of the reacting species and other conditions.

2.3.3 Formation of cyclodextrins inclusion complexes

Inclusion complexation refers to a molecular phenomenon where one molecule of guest (organic contaminant) and one molecule of the host (CD) come into contact with one another to associate and from a complex (**Figures 2.6** and **2.7**).[27-36] Generally, the parent CDs can undergo molecular inclusion with a variety of low molecular weight compounds ranging from aliphatic non polar molecule to polar acids and amines. These non- covalent interactions are highly solvent dependent and typically have formation constants of the order 10^3 or higher.[28] Formation constants formed by CD-based polymers during polymer inclusion are several orders of magnitude greater than solution phase inclusion.[25]

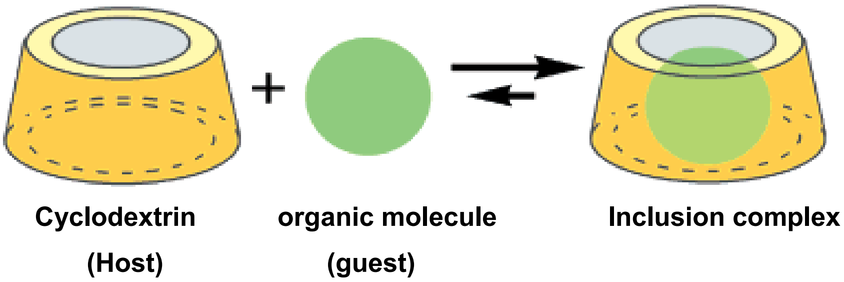


Figure 2.6: Formation of an inclusion complex with an organic guest molecule.

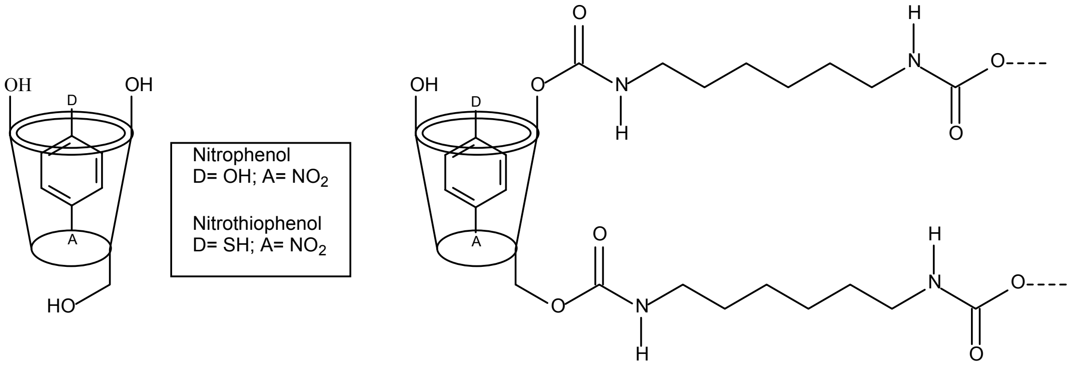


Figure 2.7: Depiction of an inclusion complex of a parent CD and a polymerized CD with an organic guest molecule

The relatively apolar cavity of the polar exterior enable CDs to form inclusion compounds with hydrophobic quest molecules in aqueous media. The formation of inclusion complexes involves hydrophobic interactions: no covalent bonds are broken or formed.[23,29] The main driving force behind formation of inclusion complex is the displacement of enthalpy-rich water molecules from the CD cavity by more hydrophobic guest molecule in the solution to acquire an apolar-apolar association an a decrease of the CD ring strain thus resulting in a more stable lower energy state.[27] It should, however, be noted that the possibility to form hydrophobic interactions represents only one of the requirements. Another important requirement is that the guest molecule must be able to fit into the cavity of the CD (geometric compatibility).[21, 30, 31] In general, many factors play a role during the inclusion complex formation process. These include geometric compatibility, polarity of the guest molecule, the medium and molecular weight. There are four energetically favorable interactions that help the equilibrium to form the inclusion complex, namely: [22]

The displacement of polar water molecules from the apolar CD cavity

- The increased number of hydrogen bonds formed as the displaced water returns to the larger pool.
- A reduction of the repulsive interactions between the hydrophobic guest and the aqueous environment.
- An increase in the hydrophobic interaction as the guest enters the apolar cyclodextrins cavity.

The type of complex can be of 1:1 ratio where one CD molecule includes one organic molecule.[27,32,33] The general equation is as follows:

$$\mathrm{S} + \mathrm{CD} \rightleftharpoons \mathrm{S{\cdot}CD}$$

Where S = organic pollutant (guest)
CD = cyclodextrin polymer (host)
S·CD = inclusion complex

It is also possible to form complexes where the guest molecules are significantly larger that the CD cavity. This is done in such a way that only certain groups or chains penetrate into CD cavity. A 2:1 complex of CD and guest molecule may be formed when the guest is too large or long to find complete accommodation in one cavity and having its other ends susceptible to complex formation.[27, 34] However, no universal method exists for the formation of inclusion complexes.

2.3.4 Characterization of CD inclusion complexes

It is evident from the literature that most complexes that have been studied are derived from β- and γ- CDs. As a result, a vast number of methods such as NMR spectrum, UV circular dichroism, fluorescence, HPLC and mass spectrometry have been used for the characterization of these complexes. However, due to the insoluble nature of the polymers synthesized thermoanalytical methods such as thermogravimetric analysis (TGA) and were chosen to fulfill this requirement.[35] From a TGA spectrum, the ratio of the host and guest can be ascertained by measuring changes in weight (mass) of a sample as a function of temperature and/or time. DSC, on the other hand, is useful in ascertaining the thermal stability of the polymers and the complexes.[35-38] Other techniques such as X-ray diffractometry (XRD) and scanning electron microscopy (SEM) can also be used for further characterization of CD inclusion complexes.[39] Different polymers exhibit different thermal transitions that are unique to the polymer. For instance, the DSC of a pure β-CD-HMDI polymer would differ from that of an inclusion compound formed by the same polymer.

2.4 BIODEGRADATION OF POLYMERS

Owing to the global rise in environmental awareness and waste management concerns, it is important to study the biodegradability of the CD polyurethane polymers.[40] Although these polymers can be recycled many times and reused, there remains a need to determine their eventual fate in the environment. While we have used the polymers in removing organic contaminants in water it is also crucial that the same polymers once they have been used should be disposed off in an environmentally friendly manner.

2.4.1 Mechanism of biodegradation

Biodegradation can be defined as a process by which bacteria, fungi, yeasts consume a substance as a food source so that its original form disappears.[41, 42] In order to achieve maximum degradation, environmental conditions such as ambient temperature, the presence of nutrient material and humidity are essential.[41] The process of biodegradation of a given type of polymer is not yet fully understood. It is assumed that microorganisms attack the biodegradable parts of the surface of the polymer.[42] This leads to a decrease in the cohesiveness of the polymer while the surface area to volume ratio is increased. The polymer is eventually exposed to the permeation of more microorganisms from water and soil leading to further degradation. Inevitably, changes are then brought about in the mechanical, thermal and morphological properties of the polymer.

2.4.2 Mode of biodegradation

Polymers can degrade in a variety of ways through reaction with sunlight (photo-oxidation), bacteria and fungi (microorganisms) and chemicals (acids).

2.4.2.1 Microorganisms

Biological agents such bacteria, fungi and their enzymes digest small fragments of the polymer to give end products that become part of the natural cycle.[41, 43] Bacteria can be single cell rods, cocci or spirilla and can be aerobic and anerobic.[41] Their degradative action is chiefly as a result of enzyme production which results in the breakdown of non-living material to obtain food. Bacteria present in soil are important in the degradation of polymers. Fungi (true fungi) are of particular importance in the degradation of polymers. True fungi break down non-living material to extract nutrients which are present in the polymer composition.[41] Microorganisms need food to survive; the presence of nutrients has an effect on the rate of biodegradation of the sample material.[43] Moisture is another factor that affects microbial activity. Too much moisture creates an anaerobic environment whilst if it’s too dry the microorganisms will dehydrate and die.[43] Biological environments such as soil, sewage and compost have a large number of microorganisms and are mainly used in biodegradation studies.

2.4.2.2 Photo-oxidation

Most polymers are prone to photo-degradation which involves the abstraction of hydrogen atoms from the polymer backbone molecules when exposed to ultra violet radiation (UV) (290-400 nm) assisted by visible (400-700 nm) and near infra-red radiation.[44,45] The near infra-red radiation accelerates the rate of biodegradation by raising the temperature. This type of degradation is also assisted by the presence of oxygen so that photo-oxidation is able to occur.[45] During sunlight exposure free radicals are formed and these react with oxygen to form peroxy radicals which initiate chain reactions. For example, polyolefins undergo oxidation to form free radicals on the polymer chain followed by reaction of alkyl radicals with oxygen leading to various products such as hydroperoxide, alcohols, acids, ketones and esters.[44] Polymer biodegradation using sunlight varies both seasonally and geographically. In Florida radiation is very strong due to high temperature, direct sunlight and relatively absence of pollution. Therefore a lot of sites in Florida are used to test polymer degradation by exposure to sunlight. Typically the polymers are put in suitable racks inclined at 45^0. [44, 45]

2.4.2.3 Chemicals

Chemicals such as acids are normally used for polymer biodegradation. Since some polymers are have the capacity to withstand outdoor weathering such as heat, light and UV therefore chemicals have been used instead. The polymer can be exposed to aggressive acidic solution for varying periods (1-12 weeks) or as a pre-digestion procedure and later exposed to microorganisms.[46] In a study conducted by Mitra et al. (2006) it was found that when a rubber was exposed to 20% Cr/H_2SO_4 it caused decrosslinking due to hydrolysis hence decreasing the crosslink density.[46] This process was evident that there was degradation of the rubber.

2.4.3 Testing methods for polymer degradation

The American Standard testing Method (ASTM) and the organization for Economic Cooperation and Development (OECD) have proposed several test methods for biodegradation studies.[47]

2.4.3.1 Soil burial test

Soil burial biodegradation test is commonly used because of its similarity to actual conditions of waste disposal.[40] In this test method the polymer is buried in soil beds. Complex biological environments such as marine areas, sewage and composts can be used to prepare the soil beds. [41] The polymer is exposed to the microorganisms present in these different environments. The soil beds containing the samples are buried for about 80 days and removed for the assessment of any changes on the surface morphology, thermal properties and weight loss of the polymer. Under controlled conditions the soil beds are incubated at a constant temperature and the moisture content is placed at 40-50%. In uncontrolled conditions the soil beds are exposed rain, sunlight and a variety of unknown microorganisms.

2.4.3.2 Environmental chamber method

The polymer is hung in the chamber and sprayed with a mixture of fungi and incubated for 28 to 56 days at a constant temperature.[41] It is exposed to humidity that is > 90%. A visual assessment is made on the amount of fungal growth on the polymer. If there is no growth it means the polymer doesn't provide a nutritive media for the fungi, if there is growth it means that the polymer is not resistant to fungal attack and thus contains nutritive substances. This method is used to test the effect of high humidity conditions on electronic components that are polymer based.[41]

2.4.3.3 Closed bottle test

The polymer is placed in closed bottles which have a mineral solution added to it. The microorganisms are added in the bottles and are incubated in the dark at approximately 20^0C. The dissolved oxygen is assed and compared with the theoretical chemical oxygen demand of the polymer.[41]

2.4.3.4 Petri dish screen

In this method the polymer is placed on petri dishes which have agar and sprayed with known fungi or bacteria. The Petri dishes are sealed and incubated at a constant temperature for 21-28 days. The test material is examined using visual assessment for the amount of growth of the micro-organisms. The more the growth on the surface of the agar, the more likely that the test material supports microbial growth. Hence the test material fails in service.[41]

2.4.4 Factors affecting polymer biodegradation

The rate of polymer biodegradation is influenced by several factors such as molar mass, chemical structure, hydrophilic/hydrophobic balance, chain mobility and stereochemistry.[48]

2.4.4.1 Polymer structure

In general polymers that contain hydrolysable linkages along the polymer chain for example ester, urea and urethane linkages are susceptible to biodegradation by microorganisms and hydrolytic enzymes. Since most of enzymatic reactions occur in an aqueous media the hydrophilic and hydrophobic character of the polymer has an effect on the biodegradation of the polymer. A polymer with both hydrophobic and hydrophilic entities is more susceptible to biodegradation than a polymer that has either hydrophobic or hydrophilic character.[41] Also the flexibility of the polymer structure affects the degradability of the polymer. The polymer chain should be flexible enough so that the enzyme fits on to the active site of the polymer. For example aliphatic polyesters are readily degraded due to their flexible structures. The rigid aromatic poly (ethylene terephthalate) is generally considered bio-inert and therefore is not readily degraded.[41, 49]

2.4.4.2 Polymer morphology

Polymers with short repeating units generally cause crystallization. Crystallization makes the hydrolysable groups in the polymer inaccessible to enzymes hence biodegradation becomes a slow process. Whilst polymers with long repeating units would be less likely to crystallize therefore enzymes will be able to hydrolyze the polymer resulting in biodegradation. In a study, a series of poly (amide-urethanes) were found to be more susceptible to biodegradation.

2.4.4.3 Molecular weight

Polymers will not biodegrade if their molecular weight is very high. For example many plastics such as polyethylene do not support microbial growth since their molecular weight is very high. Low molecular weight hydrocarbons can be degraded by microbes. They are taken into the microbial cell, acted upon by an enzyme and converted into cellular metabolites. However if the polymer has a high molecular they wont be taken up by the microbial cell, since these will be too large to enter the cell. Photodegradation or chemical degradation can be used a predigestion for high molecular weight polymers to the point where the polymer can then be degraded by the microbes.

2.4.4.4 Radiation and chemical treatments

Although photolysis with UV light can be used in biodegradation of polymers it can also affect it. During exposure to light radicals and or ions are formed which lead to cleavage and crosslinking. Generally this changes the polymers susceptibility to degradation. Therefore it is not advisable to have an open disposal for plastics even under constant light.[41]

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CHAPTER THREE

REMOVAL OF ORGANIC POLLUTANTS FROM WATER AT LETHABO POWER STATION USING WATER INSOLUBLE CYCLODEXTRIN POLYMERS

3.1 INTRODUCTION

Environmental water samples from Lethabo Power Station were analysed for the presence of organic pollutants. Solid phase microextraction (SPME) procedure was used for the extraction and the Gas chromatography/mass spectrometry (GC/MS) was used in the identification and quantification of the pollutants present in the water. The results on the efficiency of the cyclodextrin polymers in the removal of the organic pollutants will be discussed in this chapter. The flow diagram below shows the procedure of analysis of the water sample. This procedure was employed for the analysis of all water samples analysed in the whole research project.

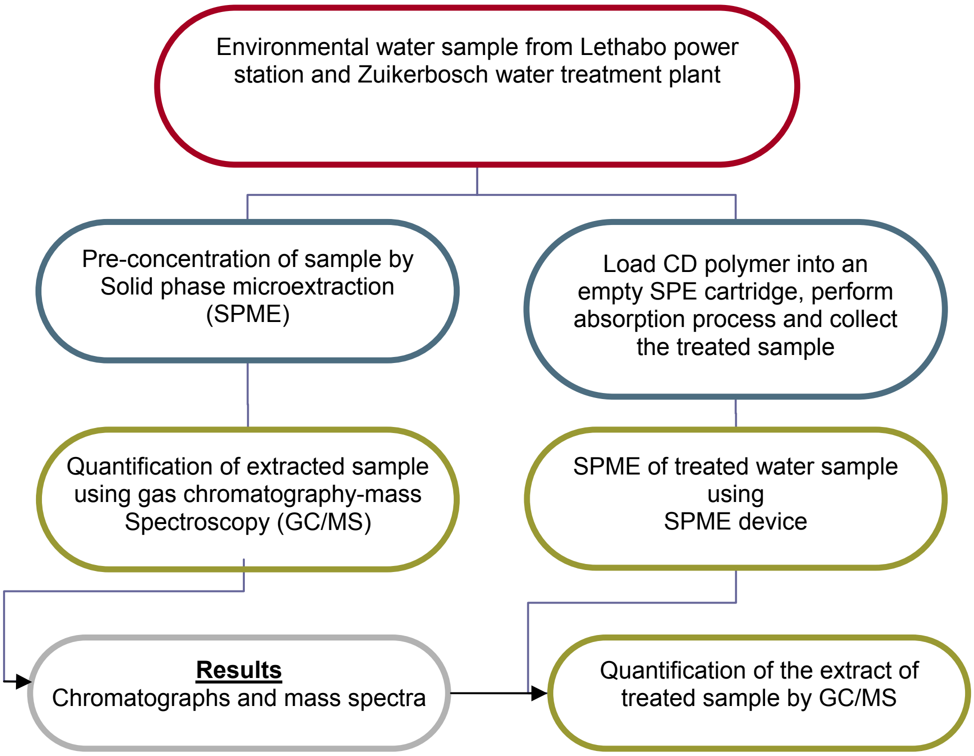

Figure 3.1: A flow diagram of the treatment and quantification of water samples.[1]

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Sampling site

Lethabo Power Station is located between Vereeniging and Sasolburg in the Free State Province. This area is highly industrialised, notably a conspicuous chemical and petroleum company, Sasol, is found in the large vicinity. Water samples (20 L) were collected from each of the five different sampling sites (raw water outlet, clarifier outlet, potable water inlet, weak base and strong base outlet) as shown in **Figure 3.2**.

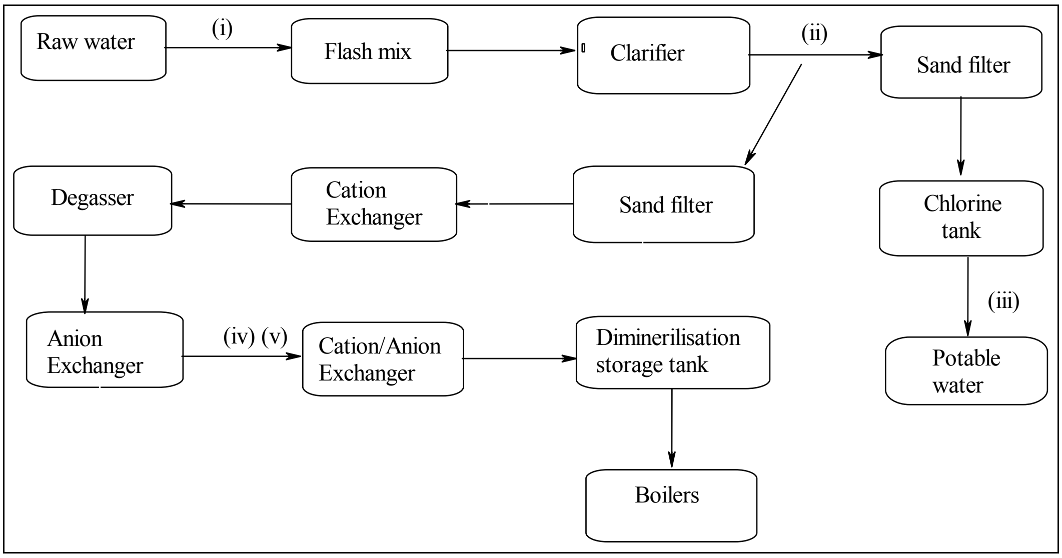

Figure 3.2: The Lethabo Power Station water treatment pathway showing the sampling points (i) raw water outlet, (ii) clarifier outlet, (iii) potable water inlet (iv) weak base outlet and (v) strong base outlet.

3.2.2 Synthetic preparation of cyclodextrin polymers

β-cyclodextrin (CD) polymers were synthesized by reacting β-CD with hexamethylene diisocyanate (HMDI) and tolylene 2,4 diisocyanate (TDI) linkers in a 1:8 molar ratio in N,N dimethylformamide (DMF). β-CD (4.00g) was dissolved in (40 ml) DMF and (4.01 ml) TDI was added dropwise. The solution was heated in an oil bath at ~ 70^0C for 24 hours under inert conditions. Precipitation of the solution with acetone produced a white polymer. Acetone was used to wash off excess DMF during vacuum pump. The same procedure was followed for the synthesis of the analogue β-CD HMDI polymer. The synthetic pathway is illustrated in **Figure 3.3**.

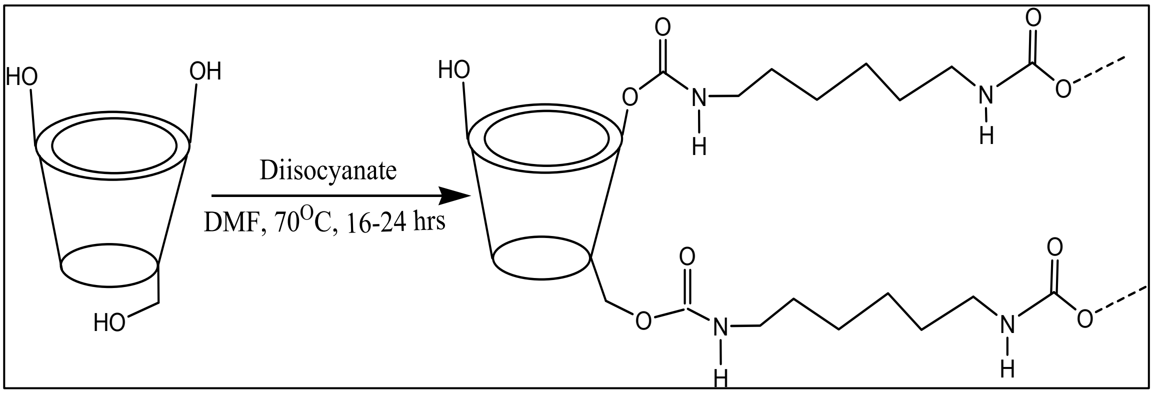

Figure 3.3: Synthetic pathway for the preparation of cyclodextrin polymers.

3.2.3 Treatment of water samples with cyclodextrin polymers

β-CD/TDI and β-CD/HMDI polymers (500 mg each) were loaded into an empty cartridge and 500 ml of the contaminated water samples were passed through. Filtration was enhanced by the use of a vacuum pump or water aspirator as illustrated in **Figure 3.4**. Water samples before and after treatment with cyclodextrin polymers were extracted using solid phase microextraction (SPME) and analyzed using Gas Chromatography/Mass Spectrometry (GC/MS) as per the procedure described in the following sections.

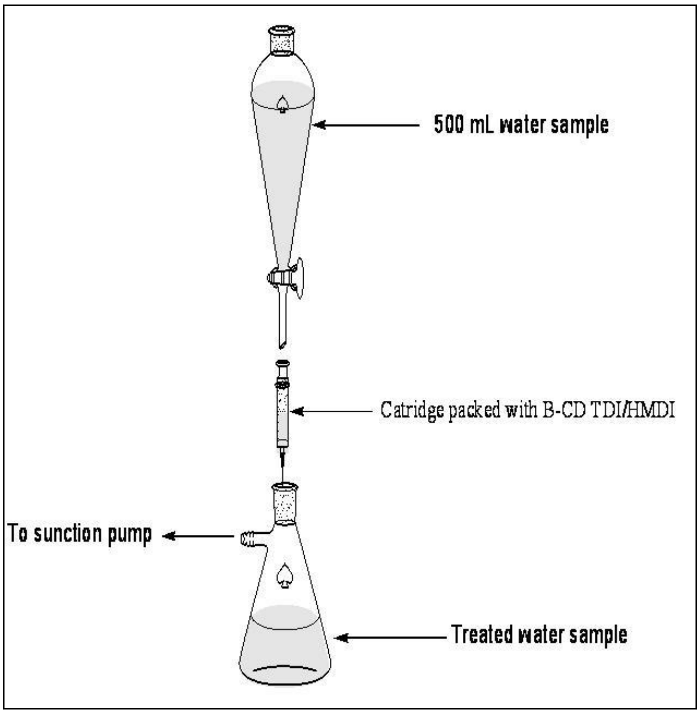

Figure 3.4: Experimental setup for the treatment of samples with cyclodextrin polymers.[2]

3.2.4 Solid phase microextraction technique

A solid phase microextraction (SPME) device was used for the extraction of the analytes from the water samples. This method was pioneered by Pawliszyn and colleague.[3] A fused silica fibre is coated with a suitable polymer (**Figure 3.5**), the type of polymer coating is chosen in order to match the characteristics of the analytes of interest.[3, 4] In this procedure, a fibre coated with polydimethylsiloxane/ divynylbenzene (PDMS/DVB) with film thickness of 65µm was used. PDMS/DVB is a non-polar polymer that is designed for the absorption of non-polar organic compounds.[5] In the SPME device, the fibre is attached to the tip of the syringe plunger and it is retracted as means to protect the delicate fibre. The needle is used to pierce through the septum of a sample vial and the fibre is extended into the sample as demonstrated in **Figure 3.5**. The fibre can be directly immersed in the sample or can be placed above the sample (headspace) during analysis. Full immersion of the fibre into the sample was used in the analysis of the water samples.

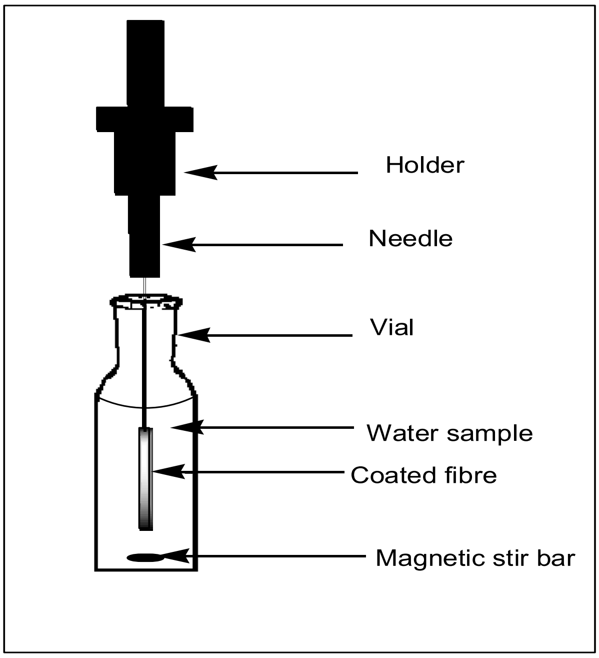

Figure 3.5: Solid phase microextraction device with fibre immersed in the sample.[3]

To ensure that the fibre was clean before performing an analysis it was first conditioned. The conditioning was performed by exposing the fibre to the similar injector analysis temperature of 220^{O}C for 30 minutes. This was followed by a blank analysis which was done by desorbing the fibre for a further 5 minutes at similar analysis temperature. Water samples (before and after treatment with cyclodextrin polymers) were extracted by immersing the fibre in 10 ml aliquots for 30 minutes at $60^{O}C$. It was necessary to constantly stir the sample at the required temperature in order to enhance the extraction efficiency. After the extraction of organic compounds the SPME fibre was retracted from the sample and placed in the Gas Chromatograph injector port. The analytes are thermally desorbed for 3 minutes and transferred into the column for separation and detection. The GC/MS instrument conditions used for the analysis are indicated in **Table 3.1**.

Table 3.1: GC/MS conditions for the analysis of organic pollutants extracted by SPME for treated and untreated water samples

Parameter	**Condition**
Column type	VF,5ms,30mx0.25mm,0.25μm
Injector	Splitless, 3 min sample exposure
Injector temperature	$220^{0}C$
Oven temperature	$50^{0}C$ (hold for 1 min) to $270^{0}C$ @ $10^{0}C\ min^{-1}$ hold for 10 min
Ionisation	Electron impact
Carrier gas	Helium
Flow rate	1 $mlmin^{-1}$
Detector	Mass spectrometer (ion trap)
Mode	Full Scan (*m/z* = 40 - 650)

3.2.5 Other extraction techniques

Initially solid phase extraction (SPE) and liquid-liquid extraction (LLE) techniques were used for the extraction of organic compounds. These techniques proved to be inefficient in the extraction of analytes present in the water at low concentrations, since GC/MS chromatograms demonstrated very few signals of the compounds extracted. Hence SPME was adapted and used for the analysis and this proved to be more successful than SPE and LLE.

3.2.5.1 Solid phase extraction

This extraction technique isolates a compound from a liquid sample by differences in its relative solubility between a liquid phase and a stationary phase.[6] The water sample is passed through a cartridge that is packed with a solid sorbent. C18 sorbent are commonly used and are efficient in trapping a variety of organic pollutants. The trapped pollutant is eluted from the sorbent by using a suitable solvent such as dichloromethane (CH_3Cl_2). The procedure for solid phase extraction is outlined in **Table 3.2.**

Table 3.2: SPE extraction procedure[1]

Loading procedure	**Flow rates**
Step 1: Process one sample using the following procedure	Condition flow: 10 mL/min
Step 2: Wash syringe with 2 mL MeOH	Load Flow: 10 mL/min
Step 3: Rinse column with 5 mL EtOAc into solvent waste	Rinse flow : 10 mL/min
Step 4: Rinse column with 5 mL of CH_2Cl_2 into solvent waste	Elute flow: 5 mL/min
Step 5: Condition column with 10 mL of MeOH into solvent waste	Condition air push: 10 mL/min
Step 6: Condition column with 10 mL of deionised water into aqueous waste	
Step 7: Load 500 mL of sample into the column	
Step 8: Dry column with gas for 15 minutes	
Elution procedure	
Step 1: Soak and collect 3 mL fraction using EtOAc	
Step 2: Collect 2 mL fraction into sample tube using EtOAc	
Step 3: Soak and collect 3 mL fraction using CH_2Cl_2	
Step 4: Collect 2 mL fraction into sample tube using CH_2Cl_2	
Step 5: END	

A set up similar to **Figure 3.4** was used in SPE extraction, instead of the cartridge packed with β-CD/HMID or β-CD/TDI a C-18 SPE cartridge was used.

3.2.5.2 Liquid-liquid extraction

The simplest LLE method is by stirring or shaking the sample with an appropriate organic solvent. This results in phase separation of the organic from inorganic layer. The organic pollutants are transferred to the organic layer which is further preconcentrated by evaporation with nitrogen.

Aliquots of 250 mL water samples were extracted using 30 ml of dichloromethane (CH_2Cl_2). The solution was shaken to ensure homogeneity and left to settle. The organic layer settled at the bottom and was further preconcetrated by using nitrogen. The extract was analysed using GC/MS.

The advantages of SPE over LLE are that there are no emulsions, passage of a sample is through a column and this avoids repeated extraction from LLE.[7] SPE has been used most frequently due to its advantages such as being a simple, rapid, inexpensive and detects concentrations at ppb levels. However, its application in this research was not successful. Hence SPME was selected as the method for extraction of organic pollutants from the water samples.

3.2.6 Analysis of water samples using Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analysis was carried out using a Varian CP-3800 capillary Gas Chromatograph coupled with a Varian Saturn 2000 Mass Spectrometer. This technique was used because of its ability to separate and uniquely identify organic compounds from a complex mixture. The samples are analysed by simple injection into the injector port. From the injector port the sample is swept by an inert stream of gas normally helium into the column. There is interaction of the gas stream and the coating of the column leading to the separation of the components in the mixture.[8] The mass spectrometer also takes in the injected sample, electrically charges it and accelerates the sample through a magnetic field. This results in the disintegration of the molecules into charged fragments which are detecting by the mass spectrometer.[9] A spectral plot displays the mass of each fragment, which can be used for qualitative determination of the unknown compound.

3.2.7 Total organic carbon (TOC) analysis of the water samples

In water carbon exists as inorganic and organic carbon. The inorganic carbon (IC) can exist as carbon dioxide (CO_2), bicarbonate ion (HCO_3^{2-}) or carbonate ion (CO_3^{2-}). Organic carbon can be divided into dissolved organic carbon (DOC), non-purgeable organic carbon (NPOC), purgeable organic carbon (POC) and volatile organic carbon. The sum of all these is referred to as TOC.10[1]. There are various TOC analysers that can be used for the measurement of TOC these only differ by the oxidation used and the technique that is employed. Two widely used oxidation techniques are UV persulfate and high temperature combustion (HTC).[10, 11] The former uses two persulfate oxidation techniques namely heated persulfate and UV persulfate oxidation. HTC is equipped with a reactor filled with platinum catalyst operating at a temperature of 680- 950^{O}C.

Both techniques measure NPOC by introducing that inorganic acid (IC) into an inorganic carbon removal chamber. Acidification of the sample leads to the formation of carbonic acid. POC is lost during the sparging of the sample. The NPOC measured is equivalent to TOC. Another method for TOC analyses requires separate measurement of total carbon (TC) and IC. This is known as TOC difference (TOC= TC-IC). The later method of TOC measurement is preferred.[11]

A Tekmar Dohrmann Apollo 9000, TOC combustion analyzer was used for the analysis of water samples collected from the five different sampling sites. This was done so as to investigate if there was a reduction of TOC after consistent water treatment using Eskom's technology. Aliquots of the water sample (20 ml) were poured into sample vials that have pierceable teflon septum caps. The vials were then placed on the TOC analyser autosampler rack for analysis. Three replicates were run for each sample. Standard potassium phthalate (KHP) samples of 10, 20, 30, 40 and 50 mgl^{-1} were also prepared and a calibration curve was plotted.

3.3 RESULTS AND DISCUSSION

3.3.1 Evaluation of the SPME technique

The SPME technique is simple to use, economical and quite fast. Additionally it requires no organic solvents; no dilution of the sample and it can be easily automated.[12] This technique is now widely used in numerous applications including the determination of volatile organic compounds in aqueous medium.

Three different fibres namely PDMS (100-µm), PDMS/DVB (65-µm) and CAR (carboxen)/PDMS (75-µm) were evaluated in order to determine which fibre extracts most of the organic species in the water. PDMS/DVB proved to be the most efficient since it extracted most of the organic compounds present in the water samples and was adopted for the study. These results are in line with an experiment conducted by Guilliot et al. (2005) where PDMS/DVB fibre proved to the most efficient for the extraction of test compounds of varying structure and polarity.[12] The fibre gave good extraction yields and most of the compounds were detected at very low concentrations.

3.3.2 Quantitative analysis of the water samples using SPME and GC/MS

The presence of organic compounds in raw water pretreated with cyclodextrin polymers was confirmed by the appearance of signals in the GC/MS chromatogram illustrated in **Figure 3.6**. The chromatograms showed reduced intensities after the coagulation and flocculation process (**Figure 3.7**). About 50% removal was obtained when taking into account the reduction in ion counts from raw water to the clarifier outlet. However, the persistence of these signals from water sampled at the clarifier outlet **(Figure 3.2)** even after treatment with polyaluminium chloride and the polyelectrolyte is evidence that the coagulation and the flocculation processes do not completely remove these pollutants from the water. GC/MS chromatograms of the other three sampling sites (potable water inlet, strong base and weak base outlets) showed a similar trend. This indicates a persistent presence of organic impurities in both potable and demineralised water. Additionally this serves to demonstrate the ineffectiveness of the ion exchanger in the removal of organic impurities. Without the proper treatment protocol, these impurities easily find their way into the turbines where they cause corrosion after decomposition to organic acids.

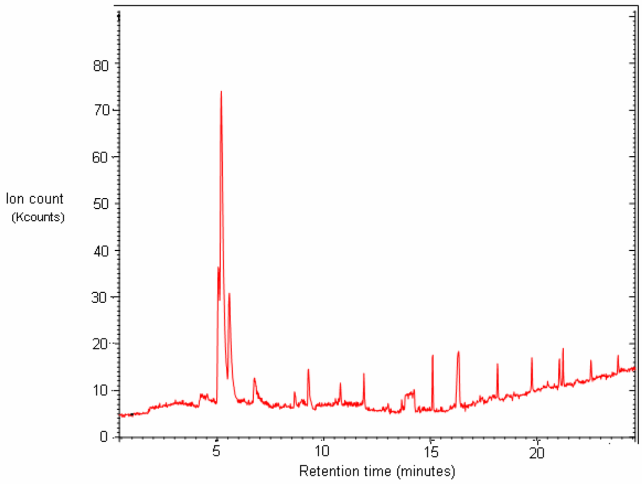

Figure 3.6: GC/MS chromatogram of raw water before treatment with cyclodextrin polymers and polyaluminium chloride with minimal polyelectrolyte.

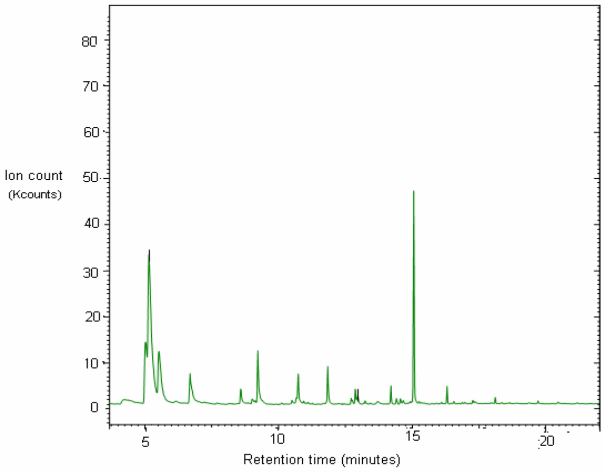

Figure 3.7: GC/MS chromatogram of clarifier after treatment with polyaluminium chloride and minimal polyelectrolyte

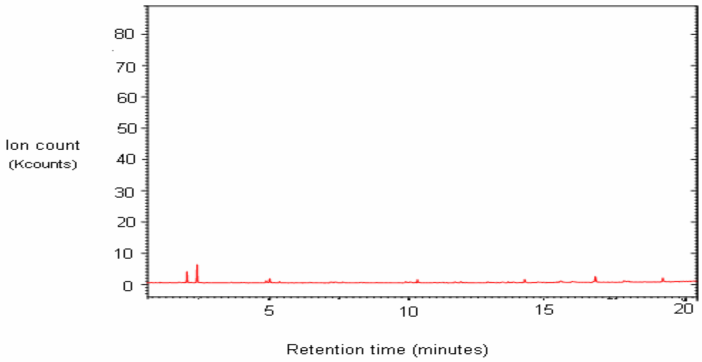

Figure 3.8: GC/MS chromatogram of raw water outlet after passing through β-CD/TDI polymer

It can be noted that after passing the raw water through β-CD/TDI polymer, an almost complete removal of the pollutants was observed as shown in **Figure 3.8**. A similar trend was noted when the raw water was passed through β-CD/HMDI polymer. A removal efficiency of 90% was estimated based on the ion counts before **(Figure 3.6)** and after treatment **(Figure 3.8)** with the cyclodextrin polymers.

This study suggests that water treatment with the polymers at the initial stages of the treatment plant (before the clarifier outlet) and before the ion exchange resin **(Figure 3.2)** should therefore remove most of the organic pollutants much earlier in the water treatment pathway. According to Gericke et al. (2000) the greatest impact of organics is mainly in the demineralisation plant and this affects the quality of the water at the boiler which is used for power generation.[13] Some organics can be removed by the ion exchange resin but fouling of the resin eventually occurs and this has a great impact on the overall performance of the treatment plant.[14] Therefore, the removal of the organics by the use of cyclodextrin polymers before they find their way into the demineralisation plant pathway and the boilers is crucial. This could potentially increase the performance of the plant and would help bring down the high costs of electricity production experienced by Eskom.

Other GC/MS chromatograms are illustrated in the appendix section.

3.3.3 Qualitative analysis of the water samples using SPME and GC/MS

Three organic pollutants were inferred using the MS online library (NIST library). The compounds are 4-chlorophenyl-phenlyether, 5-hydroxyindole and ethoxyquin. While 5-hydroxyindole and ethoxyquin were detected in all sampling sites the presence of 4-chlorophenyl-phenylether was only observed in the last two sampling sites (weak base and strong base outlet). 4-Chlorophenyl-phenylether is generally used as a dielectric fluid and can be released in the environment through its use in capacitors. It is labeled as a hazardous substance by the environmental protection agency. Ethoxyquin is utilised as a fungicide, preservative in animal feed and as an antidegradation agent. 5-Hydroxyindole is found in dye making industries, agrochemicals and perfumes. The presence of hydroxyindole and ethoxyquin in potable water poses a threat to human health since this water is mainly used for human consumption. All these compounds are probably from the industrial effluents which are eventually released into the river systems.

3.3.4 TOC analysis

The TOC levels of water treated using Eskom's technology were reduced at the different treatment sites where sampling was carried out. A reduction in TOC concentration was noted from the raw water (3.50 mg/L) down to 0.52mg/L at the strong base outlet sampling site. This reduction indicates that the coagulants and flocculants used were effective in removing the amount of total organic carbon in the water. The decreasing trend in TOC is illustrated in **Figure 3.9** below.

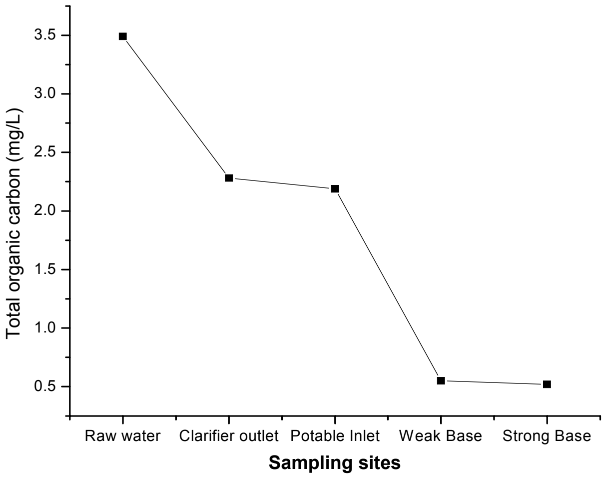

Figure 3.9: TOC levels at the different sampling sites

3.4 CONCLUSION

It was observed from the GC/MS results that the treatment processes employed by the Lethabo Power Station do not completely remove organic pollutants from raw water. These processes were only effective in the reduction of TOC. The GC/MS results also show the ability of the cyclodextrin polymers in the removal of organic pollutants that were not effectively removed by the coagulants and flocculants used at the treatment plant. A high removal of 90% was observed with the cyclodextrin polyurethanes; only 50% removal was observed for the flocculants and coagulants that are presently employed.

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CHAPTER FOUR

REMOVAL OF GEOSMIN AND 2-MIB FROM ZUIKERBOSCH WATER TREATMENT PLANT (Rand Water) USING β-CYCLODEXTRIN POLYMERS

4.1 INTRODUCTION

Environmental water samples from Zuikerbosch water treatment plant were analysed for the presence of geosmin and 2-MIB. SPME was used for the extraction of the pollutants from the sample and the GC/MS used for qualitative and quantitative analysis. The flow diagram (**Chapter three: Figure 3.1**) was employed for the analysis of the samples. Results obtained showing the efficiency of the polymers in the removal of these compounds will be discussed in this chapter. The same analysis procedures used in Chapter three (SPME procedure and treatment of water samples) were used.

4.2 EXPERIMENTAL

4.2.1 Sampling site

Zuikerbosch treatment plant is situated in Vereeniging, South of Johannesburg. Vereeniging receives water *via* a closed pipe system from the Vaal dam (a major reservoir in South Africa) whereas Zuikerbosch receives its water partly *via* an open canal system from the Vaal dam and partly *via* a pipe-line. The water undergoes a series of purification processes which involves seven stages namely coagulation, flocculation, sedimentation, stabilization, filtration, disinfection and chloramination.

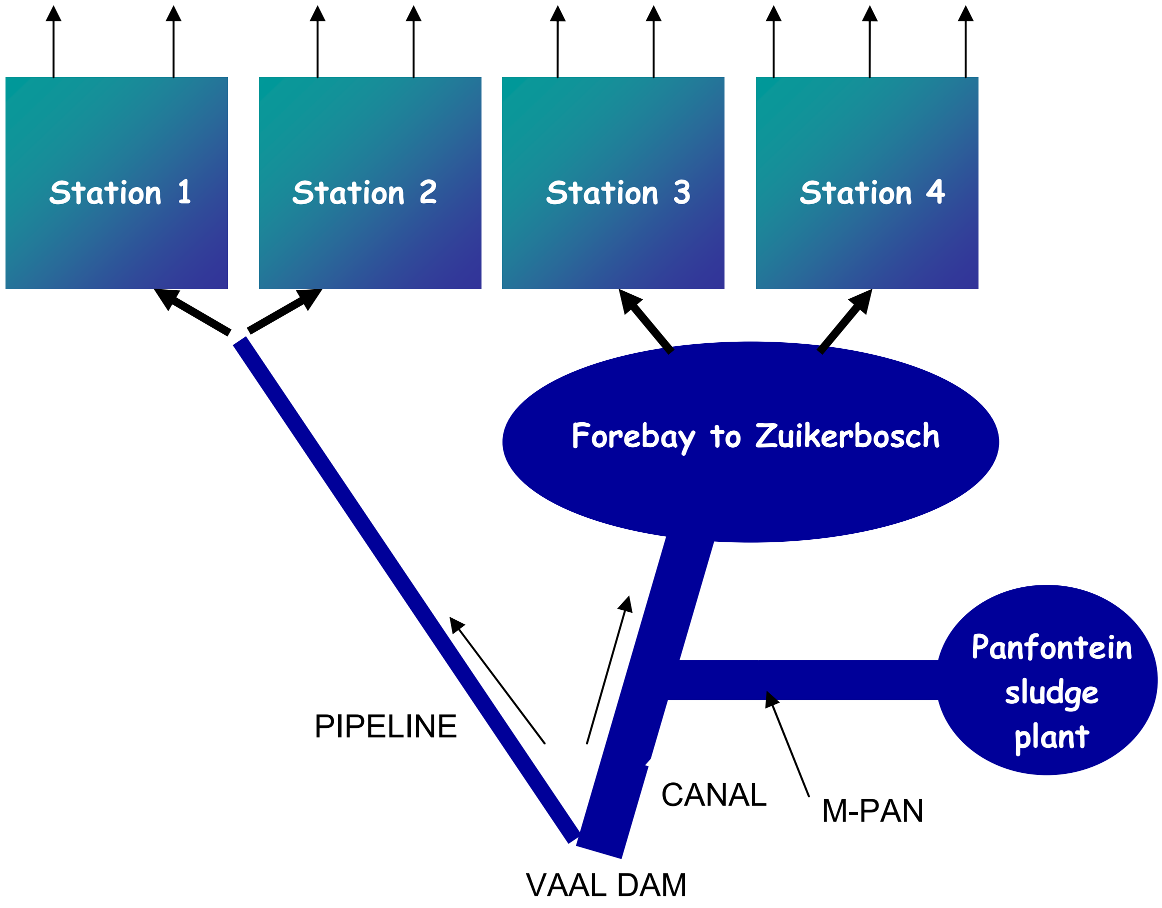

Figure 4.1: Zuikerbosch purification plant showing M-PAN sampling site.[1]

Water samples (1 L) were collected from two points at the M-Pan site illustrated in **Figure 4.1**. The M-Pan site is situated along a canal that draws water from the Panfontein sludge plant. The levels of geosmin and 2-MIB at this sampling site have previously been found to be elevated, especially during the rainy seasons. Therefore consistent monitoring of these compounds at these sites was necessary. When high levels of geosmin and 2-MIB are detected at M-Pan, the Panfontein canal is closed so that these compounds are not introduced into the main canal which eventually leads to the stations. The water at the Panfontein sludge plant is treated with activated carbon and polyectrolytes in order to reduce the levels of geosmin and 2-MIB in the water.

4.2.2 Extraction technique

Solid phase microextraction (SPME) device (**Figure 3.5**) was used for the extraction of geosmin and 2-MIB present from the water samples. The device has a polymer coated fibre that is fused within a syringe. The type of polymer coating is chosen in order to match the characteristics of the analytes of interest.[2] In this procedure, a fibre coated with polymethylsiloxane/divynylbenzene (PDMS/DVB) with film thickness of 65 µm was used.[3]

To ensure that the fibre was clean before performing an analysis it was first conditioned. The conditioning was performed by exposing the fiber to injector analysis temperature of 250°C for 30 minutes. This was of followed by a blank analysis which was done by desorbing the fiber for a further 5 minutes at similar analysis temperature. Water samples (before and after treatment with cyclodextrin polymers) were extracted by immersing the fibre in 10 ml aliquots for 30 minutes at 60°C. It was necessary to constantly stir the sample at the required temperature in order to enhance the extraction efficiency.

4.2.3 Analysis of water samples using Gas Chromatography/Mass Spectrometry (GC-MS)

After the extraction of the organic compounds the SPME fiber was retracted from the sample and placed directly in the GC injector port to desorb for 3 minutes. The GC-MS instrument conditions that were used are indicated in **Table 4.1**. GC-MS analysis was carried out using a Varian CP-3800 capillary Gas Chromatograph coupled with a Saturn 2000 Mass Spectrometer. This technique was used because of its ability to separate and uniquely identify organic compounds from a complex mixture.

Table 4.1: **GC-MS method for the analysis of geosmin and 2-MIB extracted by SPME**

Parameter	Condition
Column type	VF,5ms,30mx0.25mm,0.25µm
Injector	Splitless, 3 min sample exposure
Injector temperature	250°C
Oven temperature	50°C (hold for 10 min) to 180°C @ 10°C/min 275°C @ 40°C/min
Ionisation	Electron impact
Carrier gas	Helium
Flow rate	1 ml/min
Detector	Mass spectrometer (ion trap)
Mode	Full Scan (*m/z* = 40 - 650)

4.2.4 Preparation of geosmin and 2-MIB standards

Geosmin and 2-MIB standard samples were purchased from suppliers and standards were prepared at 50, 100 and 200 ngL^{-1} as these concentrations are typically observed in surface water. SPME was used to extract the geosmin and 2-MIB from the standards and the GC-MS was employed for the analyses of these compounds. A calibration curve was plotted in order to determine the concentration of the geosmin and 2-MIB present in the water samples before and after treatment with the polymers.

4.2.5 Treatment of water samples

Water samples were treated with β-CD/TDI and β-CD/HMDI polymers (Li and Ma, 1999). The adsorbents (500 mg) were loaded into empty SPE (solid phase extraction) cartridges and 500 mL of the contaminated water sample was passed through the polymers. A filtration rate of about 10 ml/min was used. Filtration was enhanced by the use of a vacuum pump or water aspirator. An experimental set up shown in **Figure 3.4** was used for the treatment of the contaminated water samples. Treated water sample were extracted using SPME before injection into the GC injector port.

4.3 RESULTS AND DISCUSSION

4.3.1 Evaluation of the SPME technique

Three different fibres namely PDMS (100-μm), PDMS/DVB (65-μm) and CAR (carboxen)/PDMS (75-μm) were evaluated in order to determine which fibre extracted most of the geosmin and 2-MIB in the water. PDMS/DVB proved to be the most efficient as a result was adopted for the study. These results are in line with an experiment conducted by Nakamura and Daishima (2005) where the PDMS/DVB fibre was used in the extraction of geosmin and 2-MIB.[2] The fibre gave good extraction yields and the compounds were detected at very low concentrations (ng/L levels).

4.3.2 Qualitative analysis of the water samples using GC-MS

The GC-MS chromatogram of 100 ngL^{-1} geosmin and 2-MIB standards (**Figure 4.2**) illustrates 2-MIB and geosmin peaks at retention times of 10.3 and 13.7 minutes, respectively. This chromatogram was used as the reference chromatogram in the determination of geosmin and 2-MIB in the water samples. The analytes were also detected by comparing their spectra with those in standard NIST reference libraries.

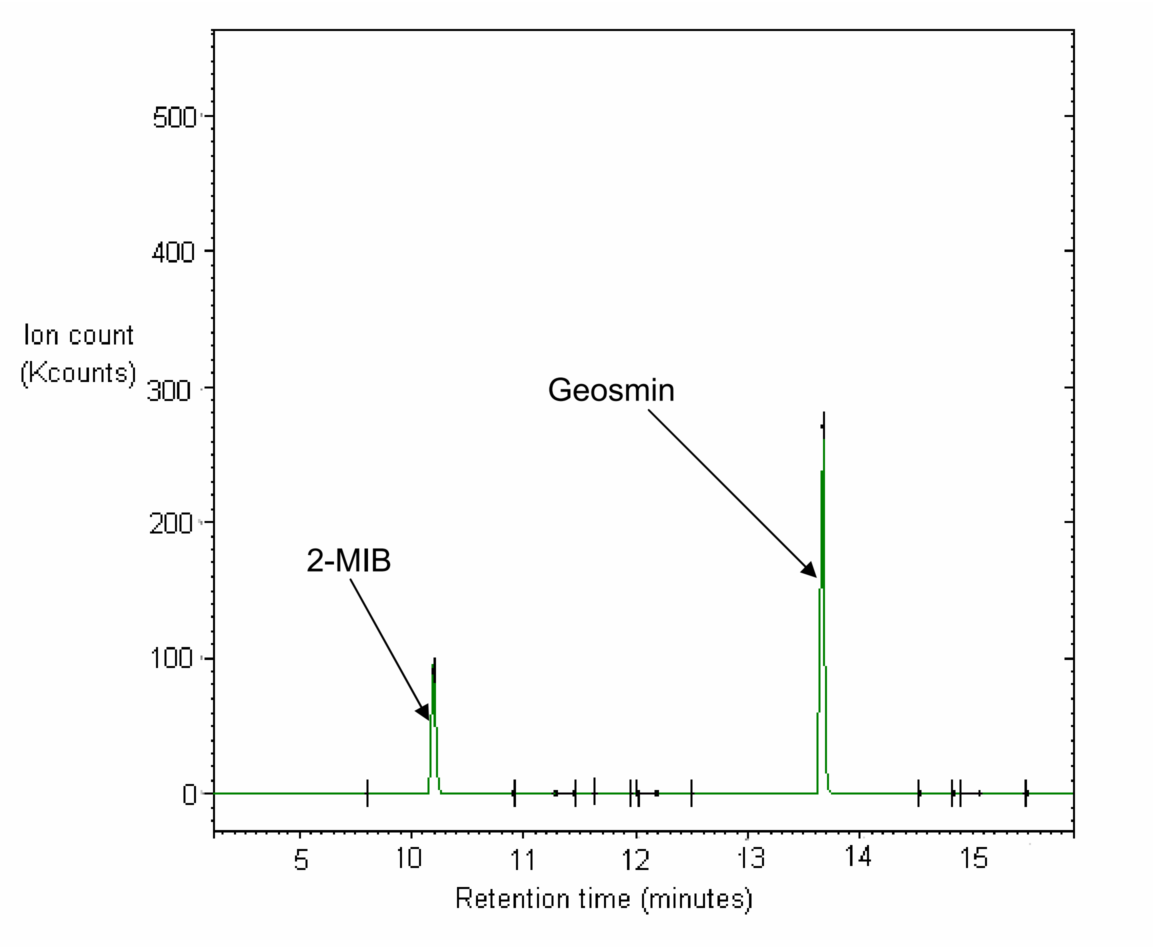

Figure 4.2: GC-MS of 100 ng/L geosmin and 2-MIB in standard solution.

The mass spectrum of the 100 ng/L geosmin and 2-MIB standard and the water sample from the M-Pan was also compared in order to confirm the identity of geosmin and 2-MIB in the water sample. The comparison of mass spectra showing 2-MIB in standard and water sample is illustrated in **Figure 4.3** and **4.4** respectively. The mass spectra of both standard and water sample showed quantitative ions of geosmin and 2-MIB at m/z of 112 and 95, respectively.

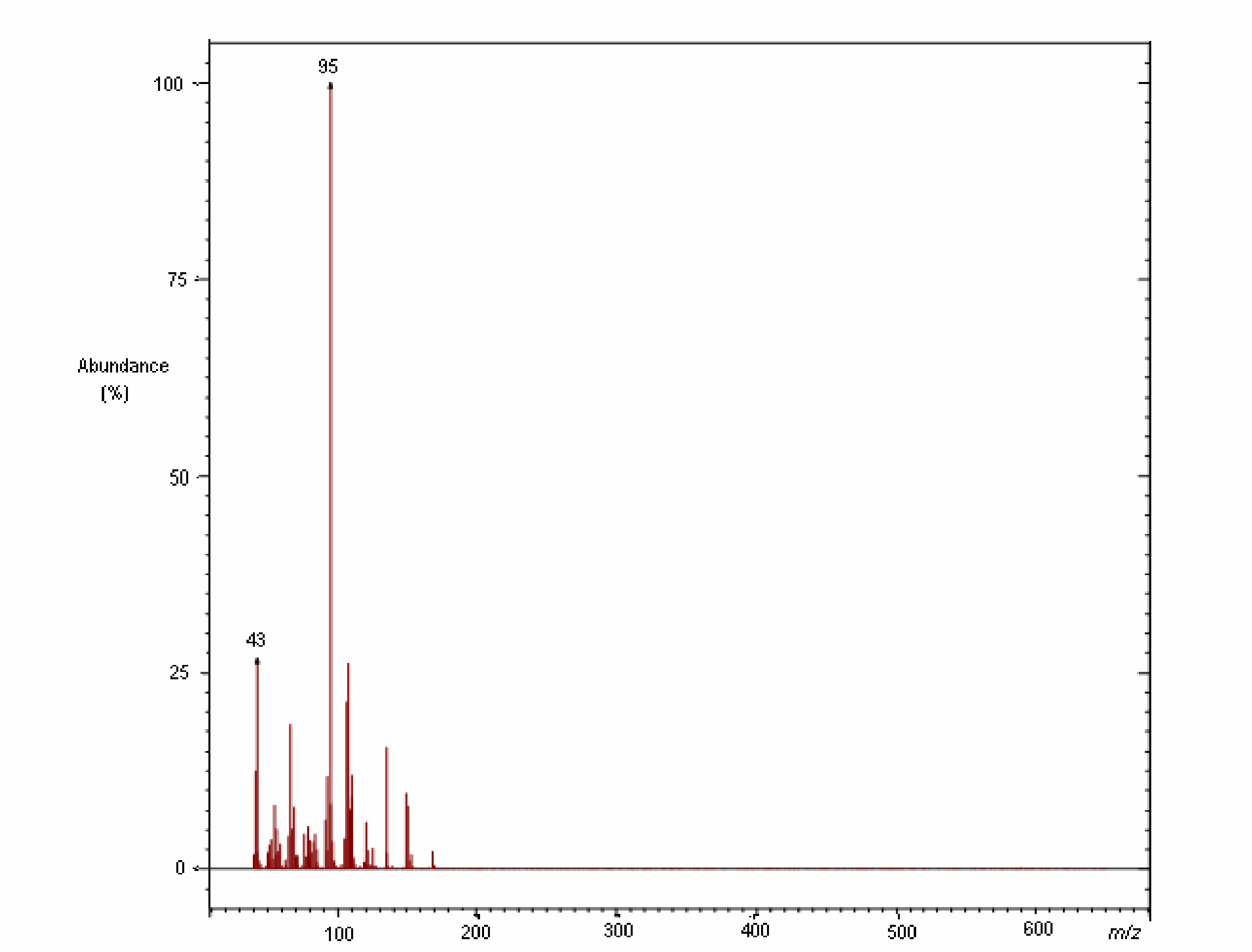

Figure 4.3: Mass spectra of 2-MIB from 100 ng/L geosmin and 2-MIB standard showing m/z of 95.

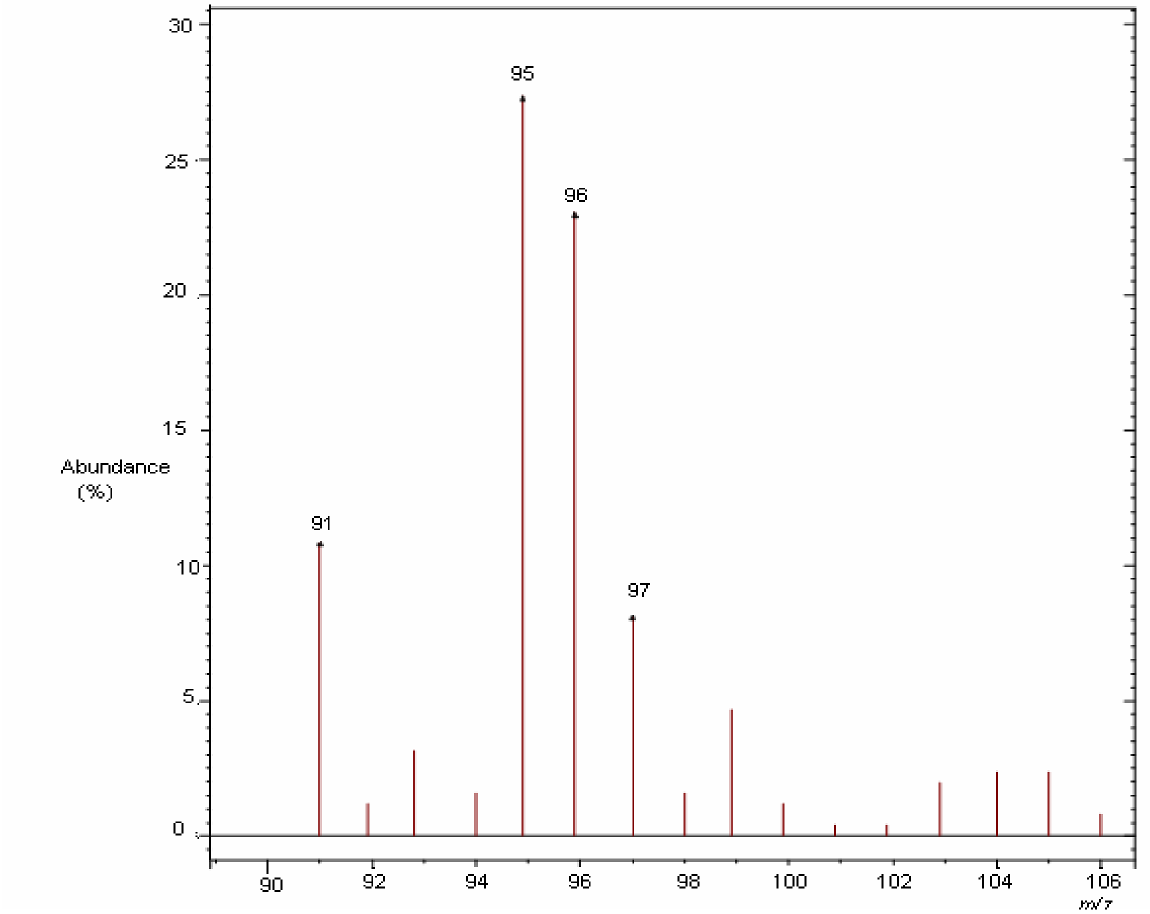

Figure 4.4: Mass spectra of 2-MIB from M-Pan water sample showing m/z of 95.

The presence of geosmin and 2-MIB in the M-Pan water samples was expected since the samples were collected after heavy rains had fallen which were followed by high temperatures. These rains bring about agricultural runoffs and industrial effluents which introduce nutrients (nitrogen and phosphorus) in the Vaal Dam. These nutrients coupled with an increase in water temperatures (180C-270C) promote algal growth and these conditions are suitable for the production of the geosmin and 2-MIB in water.[4]

4.3.3 Removal of geosmin and 2-MIB using β-CD/TDI and β-CD/HMDI polymers

Water samples from the M-Pan pretreated with cyclodextrin polymers were analyzed for the presence of geosmin and 2-MIB. Furthermore, these water samples were passed through β-CD/TDI and β-CD/HMDI polymers and the filtrate was analyzed in order to ascertain the efficiency of the polymers in the removal of these organic compounds. The GC-MS chromatogram of the water sample before passing through polymers is shown in **Figure 4.5A**. The 2-MIB and geosmin peaks are clearly identifiable at the retention times approximately 10.3 and 13.7 minutes, respectively. These retention times compare favorably with those of the standard samples.

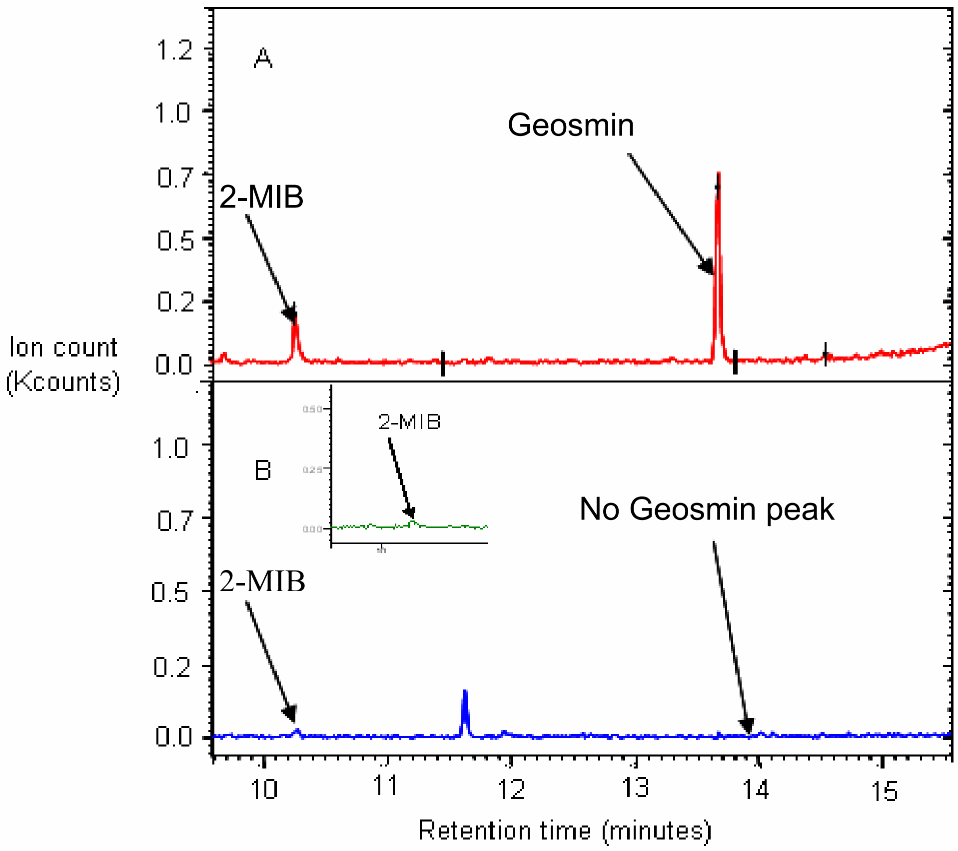

Figure 4.5: GC-MS chromatogram before (A) and after (B) treatment with β-CD TDI (insert= treatment with β-CD HMDI).

Figure 4.5B depicts chromatograms after passing the water sample through the β-CD/TDI polymer. It can be observed in this figure that the geosmin and 2-MIB were almost completely absorbed by the polymers. Similar results were also obtained when β-CD/HMDI polymers were used (see insert in **Figure 4.5B**). The appearance of an unknown peak in **Figure 4.5B**, which was not present before might be from the SPME fibre or the water sample.

Table 4.2 shows the initial concentration of geosmin obtained from the calibration curve in water samples and the percentage removed by the polymers.

Table 4.2: Percent absorption removal of geosmin by β-CD/HMDI

Sample point	Initial concentration (ngL^{-1})	Final Concentration (ngL^{-1})	% geosmin absorbed
M-PAN (382267)	59.90	6.96	88
M-Pan (380541)	104.16	5.61	95

The initial concentrations of 2-MIB (175 ngL^{-1}) at the M-pan site were also obtained from a calibration curve and confirmed using purge and trap chromatography analysis. However the percentage removal efficiency of 2-MIB was not impressive compared to that of geosmin, when taking into account the difference in ion count before (**Figure 4.5A**) and after (**Figure 4.5B**) passing the water through the polymers. This is probably attributed to the difference in structures of the two compounds. Geosmin has a structure which may render it more amenable to the absorption sites of the β-CD/TDI polymer resulting in high removal efficiency. The chair-like structure of 2-MIB might hinder its absorption on the sites of β-CD/HMDI. It is noted that previous work by Linde et al. (2000) involving the use of granular and powdered activated carbon in the removal of geosmin, showed a lower removal efficiency of these compounds compared to the polymers.[5] In another study by Cook et al. (2000) it was shown that while 2-MIB was sensitive to background organics present (NOM) in the water, a similar case for geosmin was not observed.[6] Geosmin adsorbed well than 2-MIB on activated carbon. The effect of background organics such as humic acid on the absorption of geosmin and 2-MIB by β-CD/TDI and β-CD/HMDI polymers is now a subject of our own investigation.

Noteworthy was that after passing the water sample through the polymers, the geosmin and 2-MIB odour in the treated water sample could not be detected whereas one could pick up the smell in the untreated water sample. This is an indication that the odorous compounds were indeed absorbed by the polymers. A previous study conducted by Mhlanga (2006) confirms that organic contaminants are absorbed by the polymers. In this study the polymers containing the contaminants were washed with 3 ml of diethylether and 2 ml of ethyl acetate.[7] The elute was analysed using GC-MS in order to determine the concentration of the eluted organic contaminants. It was also noted was that the concentration of the eluted contaminant compared very well with the concentration of the contaminant before absorption by the polymers. Thus confirming that the organic compounds were indeed absorbed by the polymers

4.4 CONCLUSION

Geosmin and 2-MIB were successfully extracted and analysed using SPME and GC-MS from the standards and the contaminated water samples. After treatment of the water samples with β-CD/TDI and β-CD/HMDI, a high percentage removal of geosmin and 2-MIB was observed. The difference in absorption of geosmin and 2-MIB by the polymers was also observed and could be attributed to the difference in the structure of the compounds, the type of polymers used and the effect of background organics (humic acids) present in the water sample. Humic acid tends to bind onto the adsorbent thus making it difficult for geosmin and 2-MIB to be adsorbed.

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CHAPTER FIVE
BIODEGRADATION STUDIES OF β-CYCLODEXTRIN POLYMERS USING SOIL BURIAL EXPERIMENTS

5.1 INTRODUCTION

Results on the bio-degradability of recycled β-CD/HMDI and β-CD/TDI polymers when exposed to different soil types by using soil burial test method over a period of time will be discussed in this section. Characterization techniques such as thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Braunner, Emmet and Teller (BET) and Fourier transform infra-red (FTIR) are discussed in detail. These techniques were used in the analysis of the morphology, surface area and the thermal stability of the polymer after exposure to the soil.

5.2 EXPERIMENTAL

5.2.1 Preparation of recycled polymers

Recycled polymers were used in the study in order to monitor the fate of the polymers after disposal. This is especially important since industries would probably recycle the absorbents several times before disposing them as landfills.

The cyclodextrin polymers were synthesized according to the method discussed in **Chapter three: section 3.2.2**. Polymers (0.5 g) were loaded onto empty SPE cartridges and para-nitrophenol (PNP) (30 ml) was flushed through. Ethanol (70%, 30 ml) was used to wash off the absorbed PNP from the polymer. The polymer was then dried under vacuum in preparation for the soil burial tests.

5.2.2 Soil burial tests

Three different soil types namely supermix (mixture of topsoil, kraal manure and compost), compost and topsoil were obtained. Soil was charged into plastic basins (30 x 23 cm) that had holes bored at the bottom in order to allow aeration in the soil. The recycled polymers (1 g) were loaded into glass containers and dug approximately 4 inches below the surface of the soil. These containers were porous both top and bottom, which allowed the circulation of air, moisture and microorganisms to be in contact with the polymers. The basins were then placed on the balcony exposed to rain and sunlight. Exposed samples were periodically taken out of the soil after 10, 20, 40, 60 and 119 days for % weight loss determination, surface morphology and thermal analysis. The last sampling interval (59 days) was delayed in order to allow further degradation of the polymer. It was not necessary to wash the polymers after they had been dugged out because the glass containers used were tightly closed. The polymers each time after being recalled from the soil were dried under vacuum for about 5 days to ensure that they were completely dry before analysis.

5.2.3 Weight loss (%)

The polymers were weighed before they were loaded onto the glass containers and after they were recalled from the soil. The weight before and after biodegradation was expressed as a percentage by using equation 1.

Weight loss (%) = (WO - Wf / WO) X 100 ……………………………………………..…..(1)

where, WO is the initial weight before biodegradation, Wf is the final weight after biodegradation at each designated day.

5.2.4 Fourier Transform Infra-Red (FTIR)

Infra-red (IR) refers broadly to the part of the electromagnetic spectrum between the visible and microwave regions. Infra-red radiation of frequencies is absorbed and converted by an organic molecule into energy of molecular vibration.[1] Molecules which have covalent bonds that have a dipole moment absorb infra-red energy and these are termed as infra-red active. Since different bonds have different frequencies, these will absorb IR at different wavelengths. Various functional groups will absorb at different wavelengths hence giving information about that particular molecule.[2]

FTIR was the technique used in these analysis it is cheap, fat and sensitive. Analysis of the polymers buried in supermix, compost and topsoil were obtained by using a Midac FTIR Spectrometer. Potassium bromate (KBr) pellets were prepared by mixing 1 part of the sample with 99 parts of KBr.

5.2.5 Scanning Electron Microscopy (SEM)

Surface analysis involve of the irradiation of the polymer surface with electrons. These electrons acts as energy source which penetrates and cause an emission from the surface which can be analyzed. In SEM a fine electron beams scanned across the polymer surface in synchronization with the beam in a cathode ray tube. This interaction produces an image with great depth field and an almost three dimensional appearance.[3] The combination of high magnification, larger depth of focus, greater resolution and ease of sample observation makes SEM the perfect technique for surface morphology analysis

Samples were mounted on glass slides and gold coated using an Emscope SC 500 sputter coater in order to prevent an electrical charge. The samples were then examined under a Joel JSM - 560 Scanning Electron Microscopy. The surface morphologies of the polymers were analysed after 10, 20, 40, 60 and 119 days of bio-degradation.

5.2.6 Braunner Emmet Teller (BET)

The technique was used to determine change in surface area of the polymers over the periodic intervals of the experiment. A micromeritis Flowprep 060 sample Degass system was used to degass samples for 5 hours prior to analysis. This was done in order to remove impurities from the samples. Samples (0.2 g) were analysed in micromeritis Tristar Surface area and Porosity analyser.

5.2.7 Thermogravimetric analysis (TGA)

The weight of the polymer is measured continuously on a thermobalance whilst it is exposed to heat under air or inert conditions.[2] Weight loss arises from the evaporation of moisture at high temperatures and this results from the polymer decomposition.[2]

A Perkin Elmer Pyris 1 TGA was used to investigate the stability of the polymers when heated up. The thermogravimetric analyses were carried out in air up to a temperature of 800^0C at a heating rate of 10^0C/min on a 20 mg sample.

5.3 RESULTS AND DISCUSSION

The three different soil types were used in order to compare the effects that these soils and the microorganisms found in them have on the biodegradation of the used polymers. An experiment conducted by Kim et al. (2006) showed that the number of microbial counts in compost soil were numerous than those in the natural soil because of nourishment provided by the compost.[4] Soil burial tests were conducted from the month of October (Spring) through to January (Summer) for a period of 119 days. Heavy rains and extremely high temperatures were intermittently experienced during this period.

5.3.1 Weight loss analysis

Figures 5.1 and **5.2** show the percentage weight loss of β-CD/TDI and β-CD/HMDI after burial in supermix, compost and topsoil. The biodegradation of the polymers did not exceed 30% in 119 days irrespective of which soil type they were buried under. Supermix soil had the maximum % weight loss of 30% at 119 days for both types of polymers. However, a drop in the % weight loss can be also observed in Figure 5.1 (e.g. after 20 days in supermix), which could be attributed to low microbial activity. Microbial activity is mainly affected by environmental conditions such temperature and moisture. According to Davis (2000) moisture is vital for the survival of microorganisms, but too much moisture creates anaerobic conditions; if the soil is too dry the microbes dehydrate.[5] During the period when the experiments were conducted, fluctuations in weather conditions (from lots of rainfall to extremely high temperatures) prevailed.

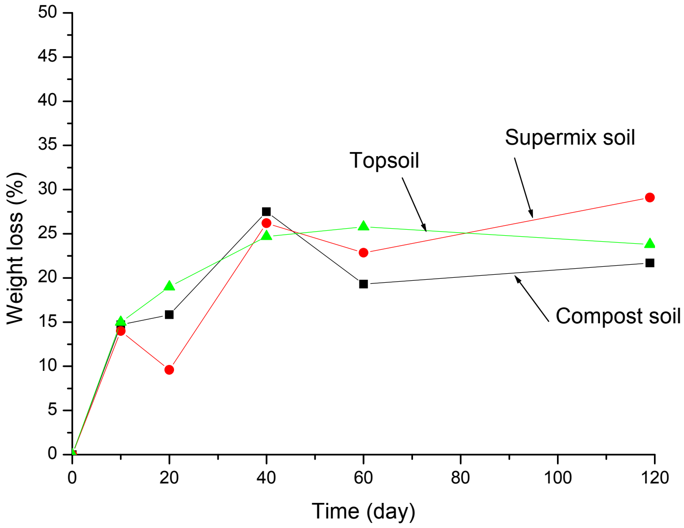


Figure 5.1: Weight loss of β-CD/TDI in the 3 different soil types

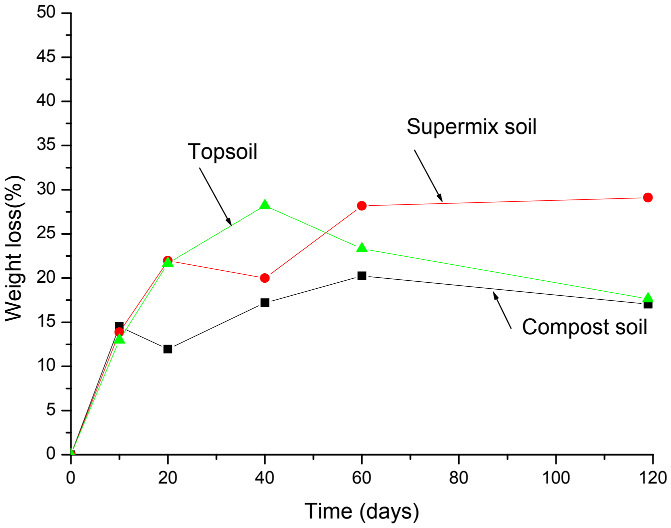


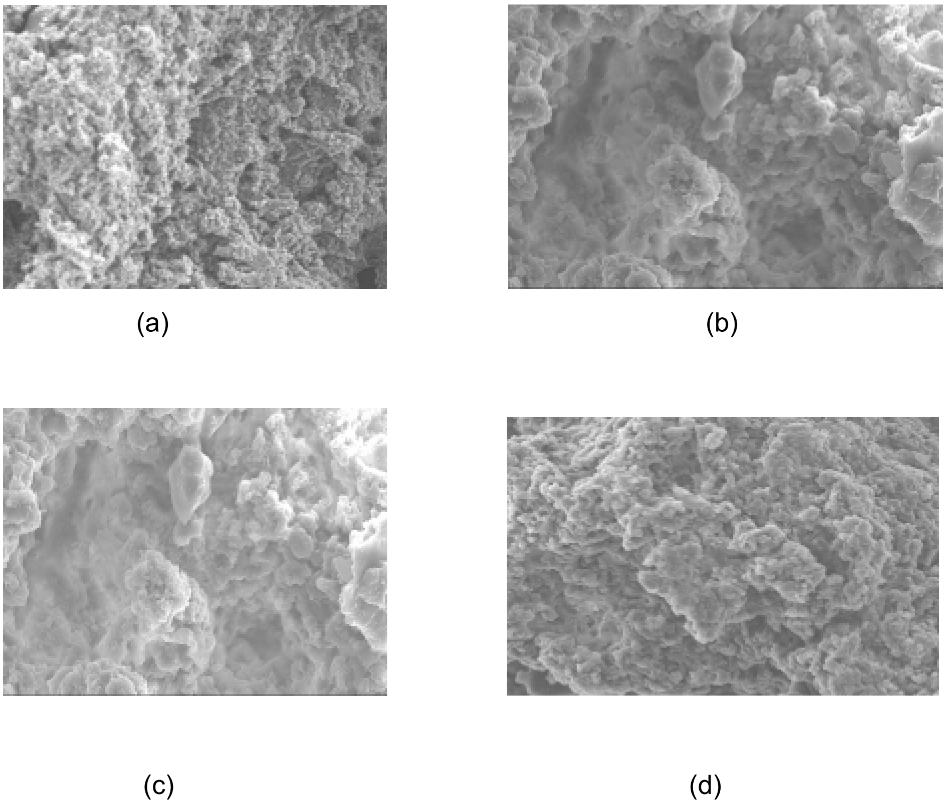
Figure 5.2: Weight loss of β-CD/HMDI in different soil types.

It is worth noting from the graphs that there were fluctuations in the weight losses which could be linked to the prevalence or otherwise of microorganisms when climatic conditions were favourable or less favourable for their activity. From the trends of percentage weight loss graphs, it can be deduced that the microorganisms played a role in the reduction of weight. SEM pictures of the polymers in the next section will further confirm this. From an environmental standpoint, the average biodegradation of between 15% and 30% in ach of the soil types would be considered not sufficient to justify the polymers' disposal under the soil. On the contrary, the low extent of weight loss results seems to suggest that these polymers were resistant to biodegradation.

5.3.2 Scanning Electron Microscopy (SEM) analysis

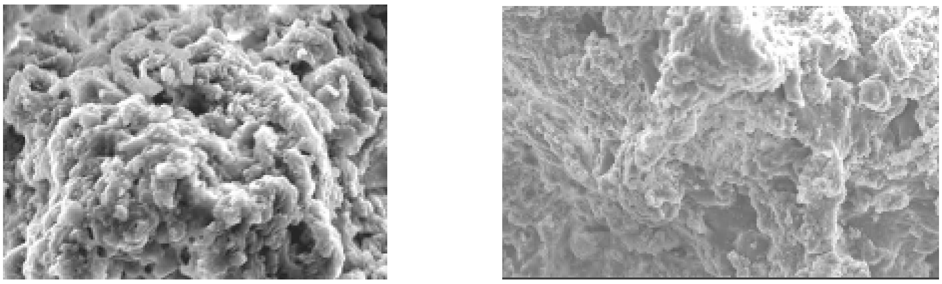
Figures 5.3(a) and 5.6(a) depict SEM analysis of recycled β-CD/HMDI and β-CD/TDI polymers respectively before biodegradation. From the micrographs it can be seen that at commencement of the experiment the polymers present a generally uniform surface. However, after the prescribed burial periods there were changes observed on the surface of the polymers. All the polymers showed morphological modifications throughout the soil burial tests in the three different soil types. This points to the substantial effect of the microorganisms on the polymers resulting in biodegradation.

The polymers buried in the supermix soil had surfaces that were significantly altered in the form of cracks as a result of biodegradation while polymers in compost soil and topsoil also showed noticeable surface modifications. When considering the weight loss of the β-CD/TDI polymer after 40 days (**Figure 5.2**) and the corresponding SEM micrograph (**Figure 5.6d, 5.7c, 5.8c**), one can observe that there is a correlation between weight loss and SEM analysis. In essence, generally a good correlation exists between the percentage weight loss and the morphology of the polymers within the soil types that were used in this study.



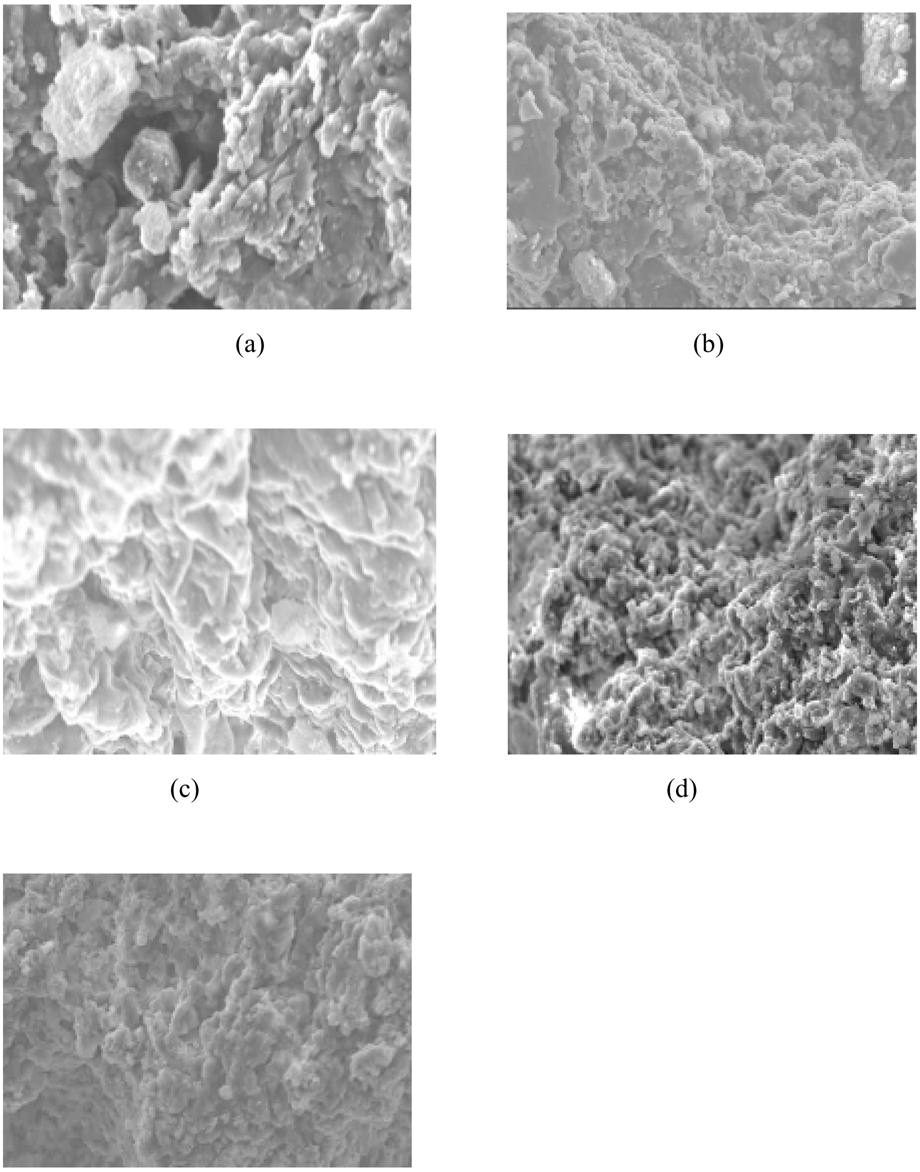
(a) (b)

(c) (d)



(e) (f)

Figure 5.3: SEM micrographs from β-CD/HMDI buried in compost soil (a) Recycled polymer before biodegradation (b) after 10 days (c) after 20 days (d) 40 days (e) 60 days (f) 119 days

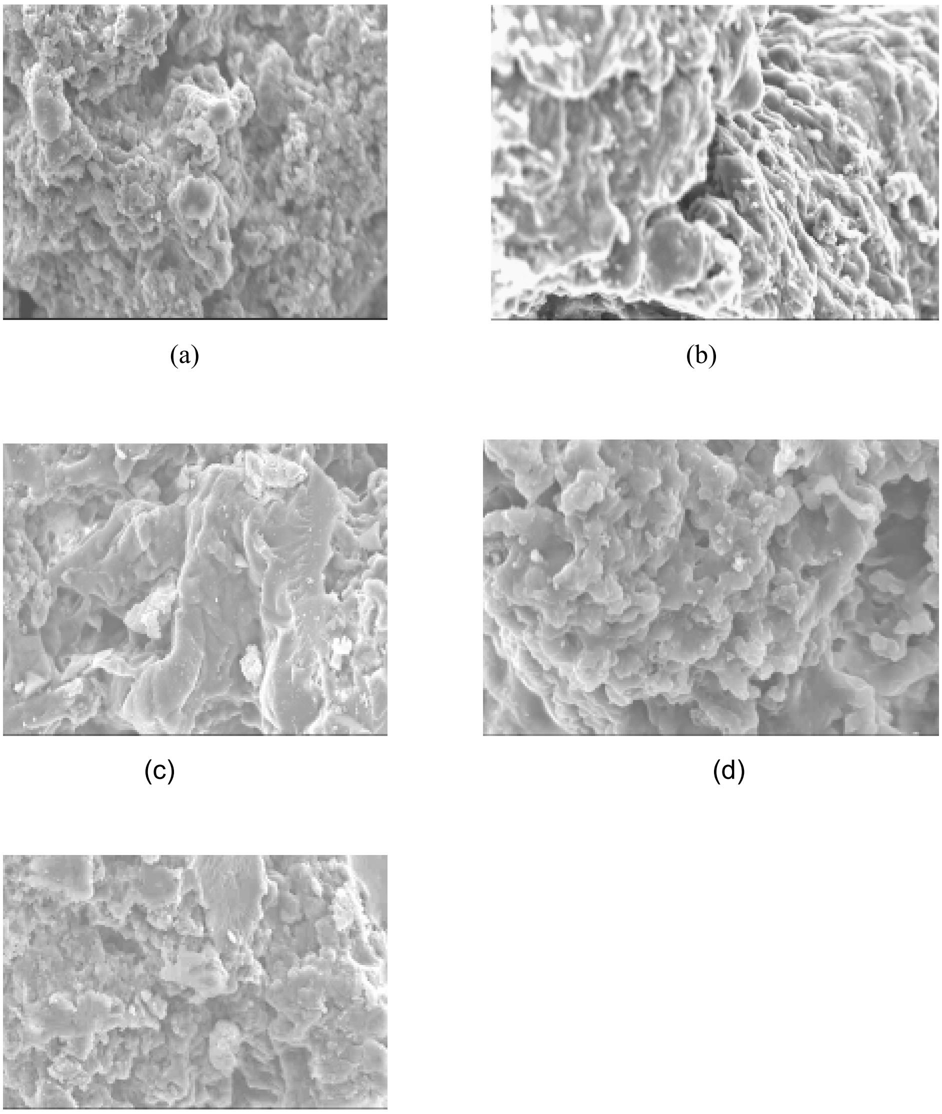


(a) (b)

(c) (d)

(e)

Figure 5.4: SEM micrographs from β-CD/HMDI buried in topsoil (a) after 10 days (b) after 20 days (c) 40 days (d) 60 days (e) 119 days

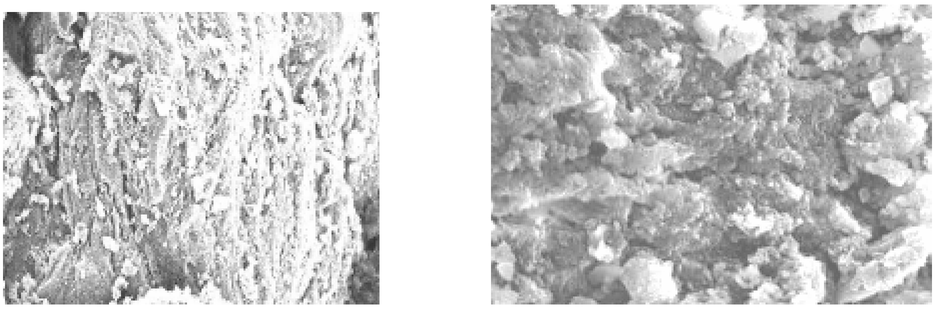


(a) (b)

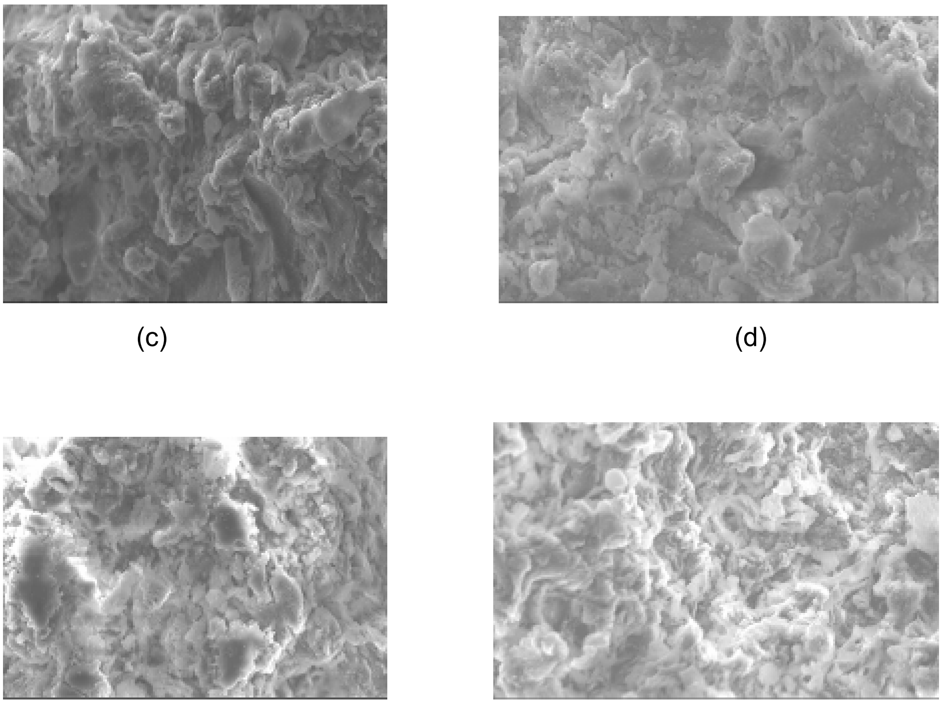
(c) (d)

(e)

Figure 5.5: SEM micrographs from β-CD/HMDI buried in supermix soil (a) after 10 days (b) after 20 days (c) 40 days (d) 60 days (e) 119 days



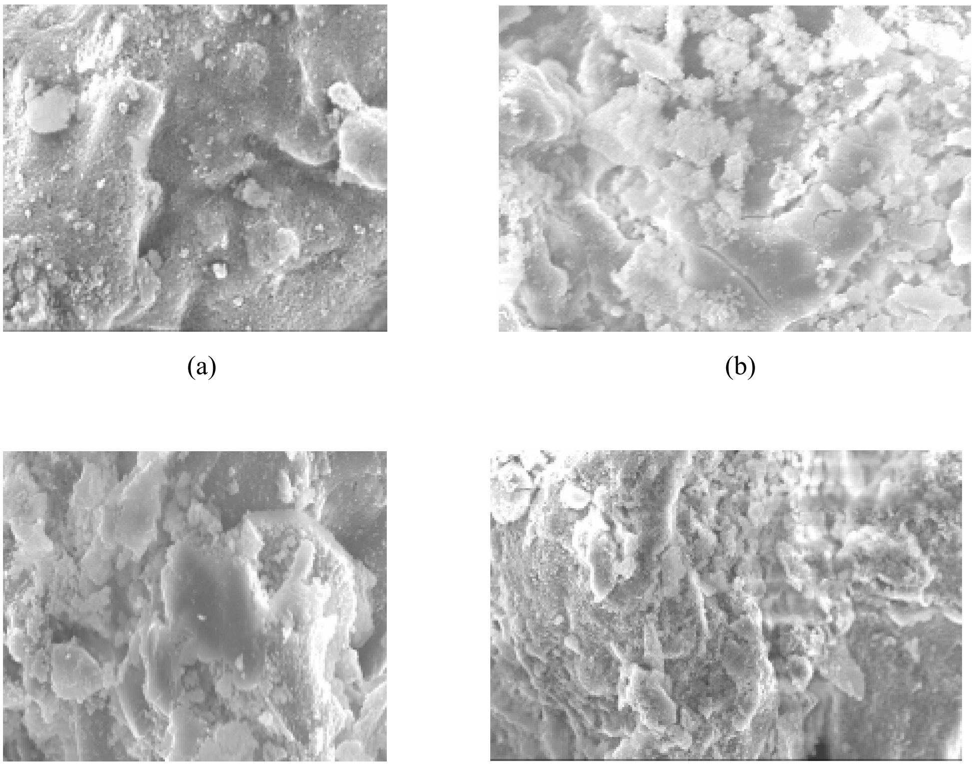
(a) (b)



(c) (d)

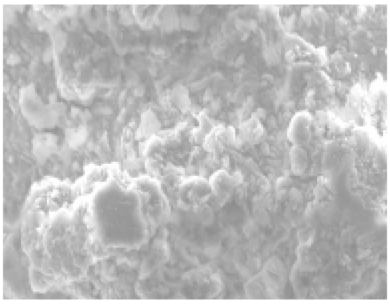
(e) (f)

Figure 5.6: SEM micrographs from β-CD/TDI buried in compost soil (a) Recycled polymer before biodegradation (b) after 10 days (c) after 20 days (d) 40 days (e) 60 days (f) 119 days



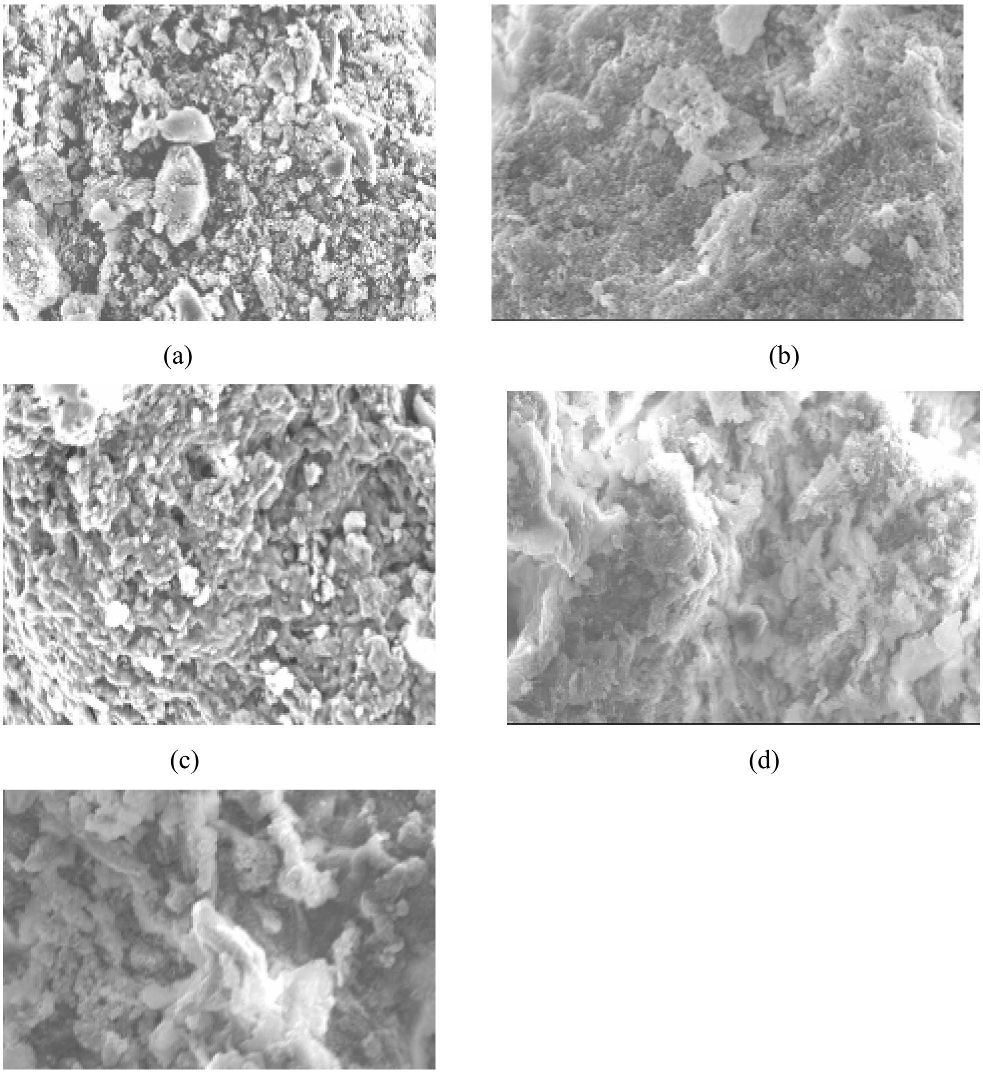
(a) (b)

(c) (d)



(e)

Figure 5.7: SEM micrographs from β-CD/TDI buried in supermix soil (a) after 10 days (b) after 20 days (c) 40 days (d) 60 days (e) 119 days



(a) (b)

(c) (d)

(e)

Figure 5.8: SEM micrographs from β-CD/TDI buried in Topsoil (a) after 10 days (b) after 20 days (c) 40 days (d) 60 days (e) 119 days

5.3.3 Thermogravimetric (TGA) analysis

Thermogravimetric analyses of the recycled polymers were carried out in order to determine how the biodegradation process affects the thermal stability of the polymers. It is noted in **Figure 5.9** that prior to biodegradation of β-CD/TDI in topsoil, the polymer undergoes water loss of about 10% of polymer weight. Secondly the polymer undergoes a significant weight loss between 200 - 300 ^{o}C of about 60%, which is the glass transition temperature of the polymer.

When considering the SEM and weight loss results, in contrast, the TGA graphs of the polymers buried under topsoil show no striking differences up to the 119 day period. The changes may be subtle but not immediately observable. Further, the TGA graphs of the other soil types there were no significant differences. It can be inferred that while there may have been biodegradation as observed from SEM analyses and weight loss results, biodegradation may have most likely been occurring at the peripheral or on the surface of the polymers. The “core structure” of the polymers remained by and large intact. This assertion is further supported by FTIR spectral evidence in **Figures 5.13** to **5.18** where the original functionalities in the polymers can still be found. Had there been severe alteration in the “core structure” of the polymer, other functional groups due to fragmentation may have emerged in the IR spectra.

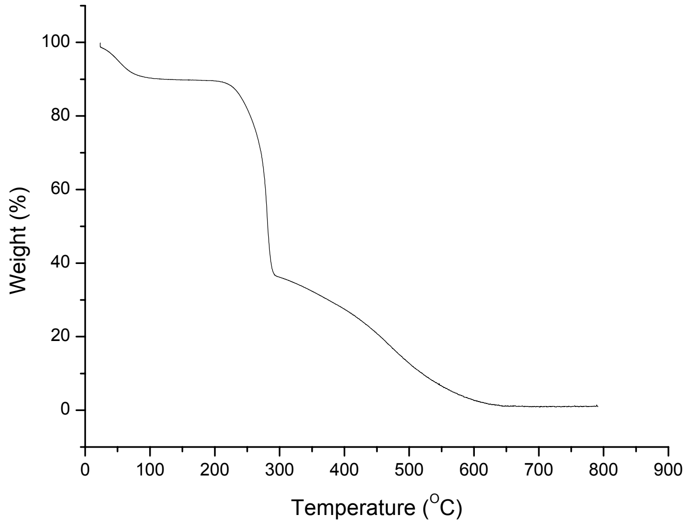


Figure 5.9: TGA curve of β-CD/TDI polymer before biodegradation in topsoil

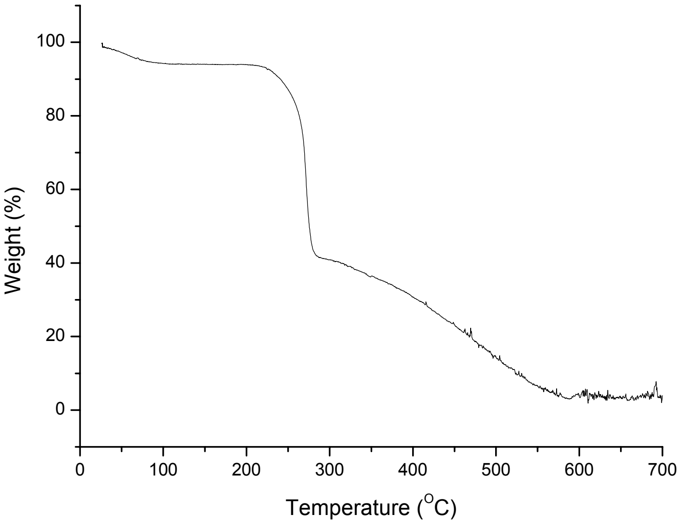


Figure 5.10: TGA curve of β-CD/TDI polymer after 20 days in topsoil

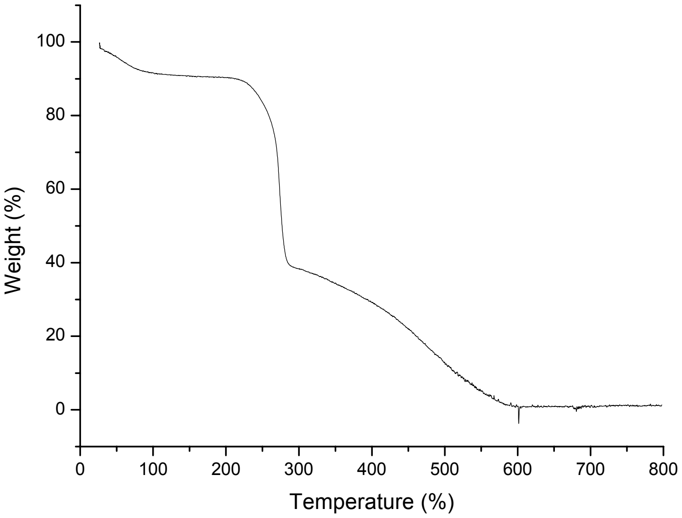


Figure 5.11: TGA curve of β-CD/TDI after 60 days in topsoil

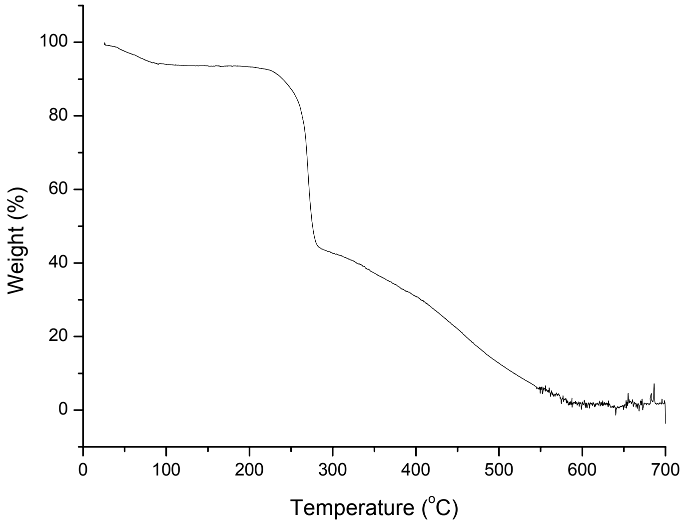
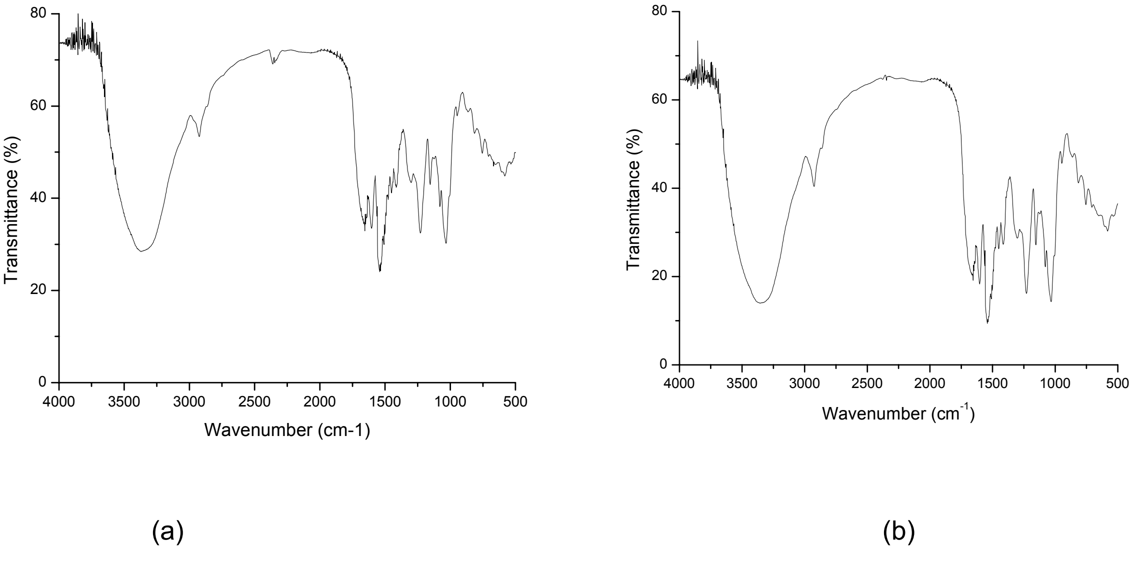


Figure 5.12: TGA curve of β-CD/TDI after 119 days in topsoil

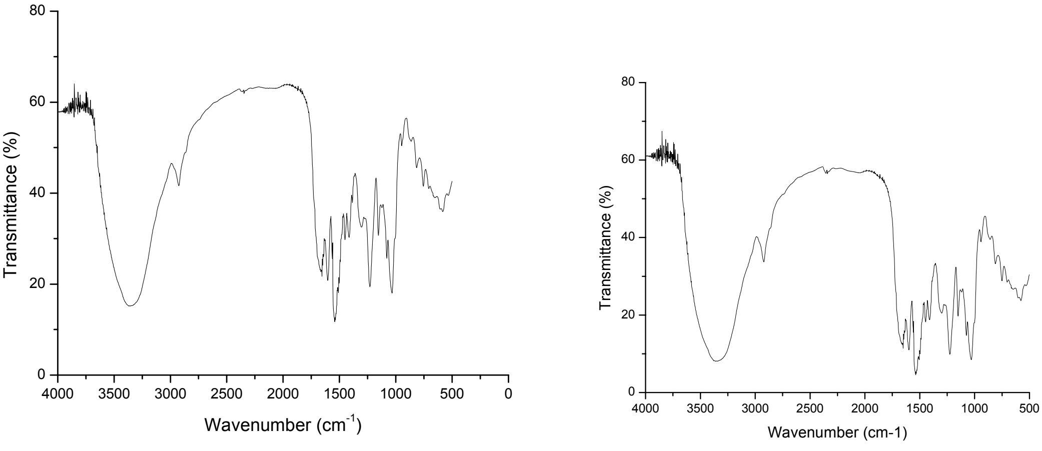
5.3.4 FT-IR analysis

As illustrated in **Figures 5.13 -5.18**, the skeletal structures of the variously linked CD polymers seem unaffected upon exposure to compost, supermix and topsoil over a period of 119 days.



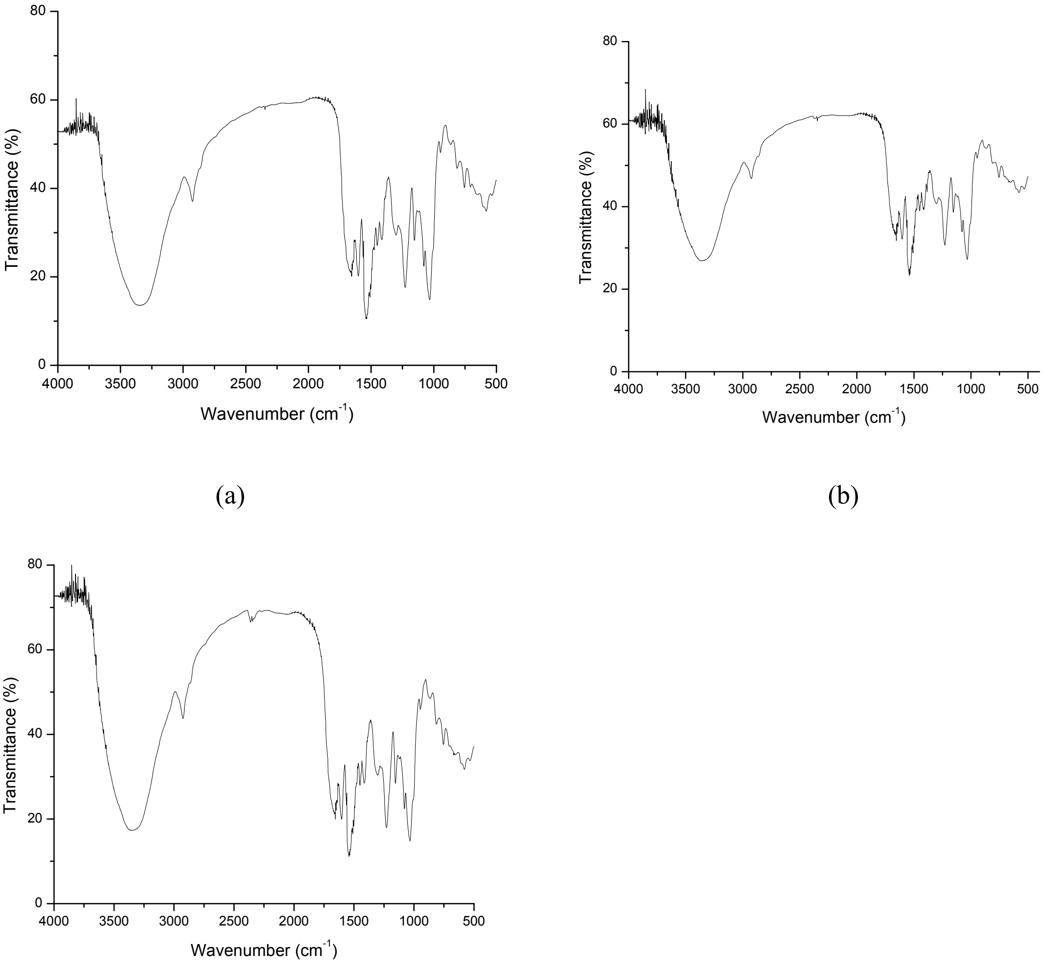
(a)

(b)



(c) (d)

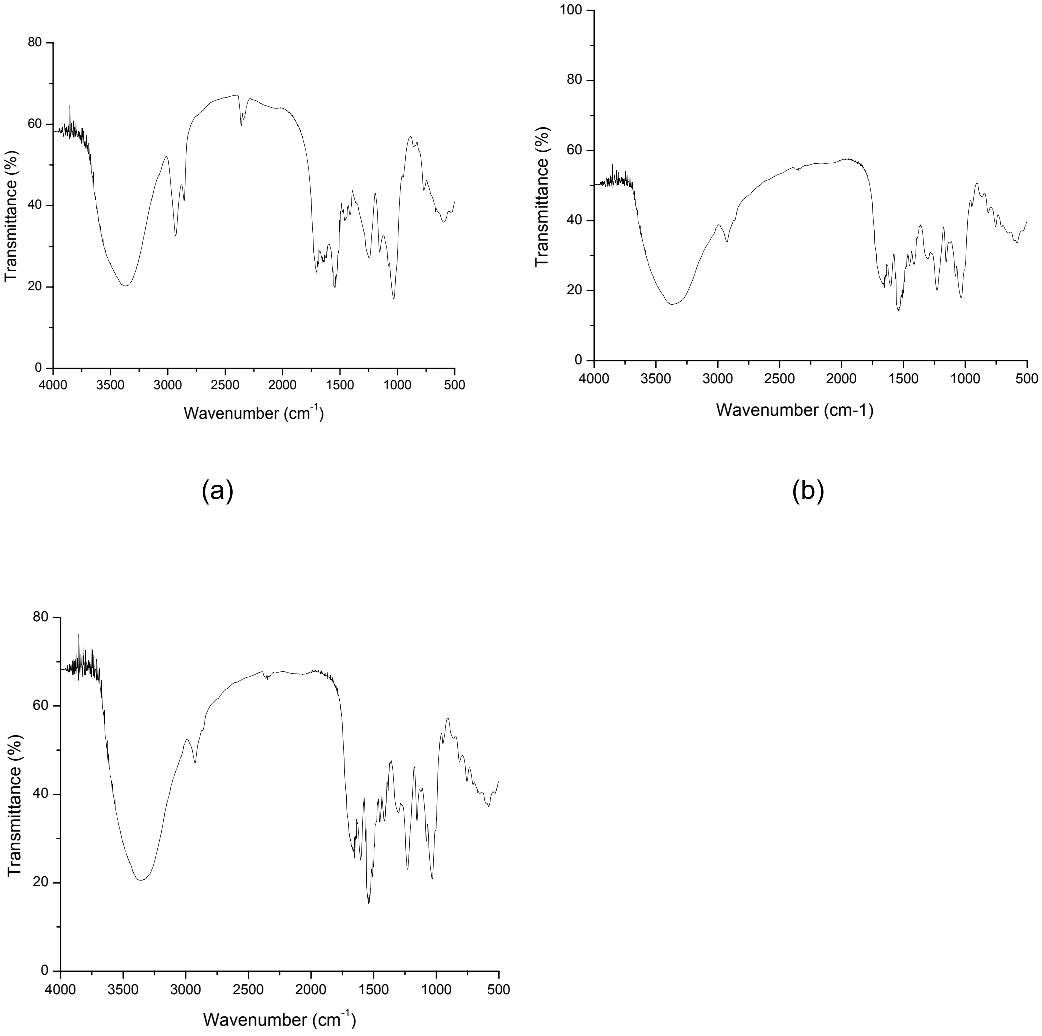
Figure 5.13: FTIR β-CD/TDI buried in compost soil (a) before biodegradation (b) after 10 days (c) 60 days (d) 119 days



(a) (b)

(c)

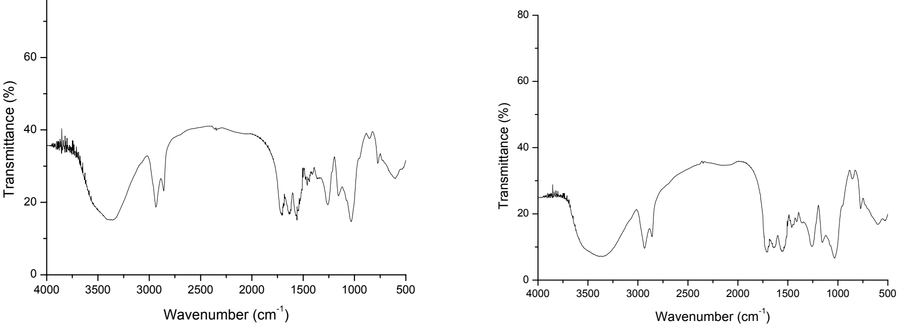
Figure 5.14: FTIR β-CD/TDI buried in supermix soil (a) after 10 days (b) 60 days (c) 119 days



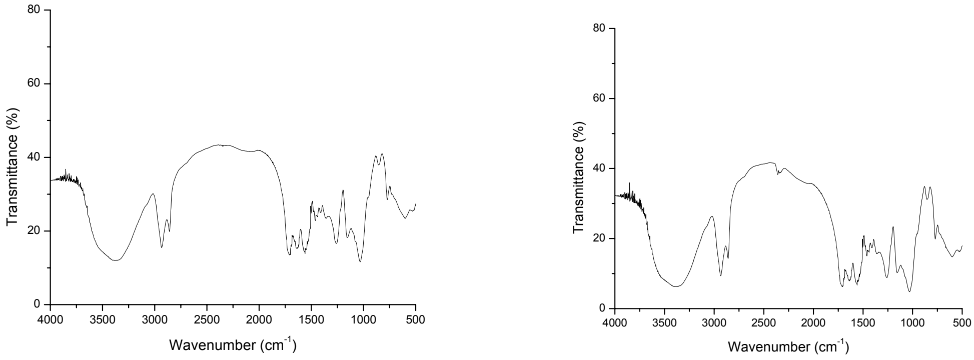
(a) (b)

(c)

Figure 5.15: FTIR β-CD/TDI buried in topsoil (a) after 10 days (b) 60 days (c) 119 days

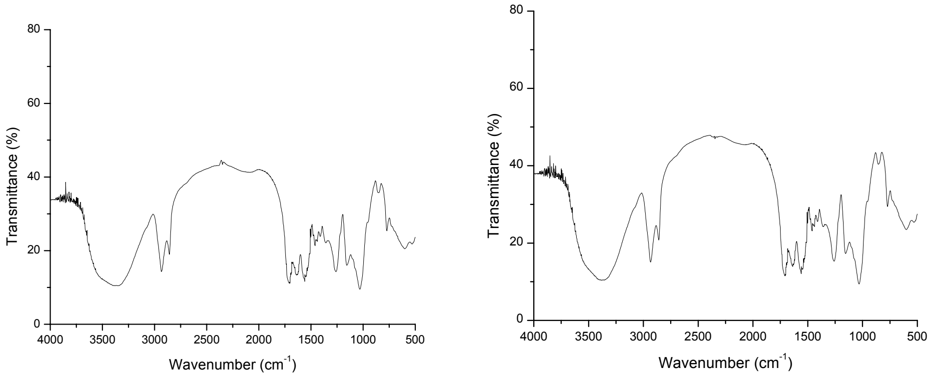


(a) (b)

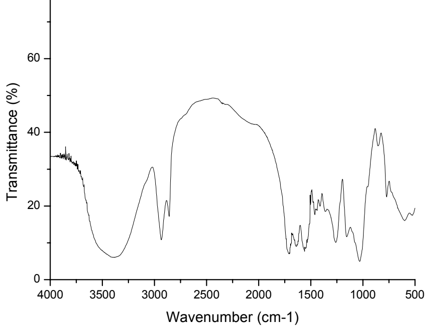


(c) (d)

Figure 5.16: FTIR β-CD/HMDI buried in supermix soil (a) before biodegradation (b) after 10 days (c) 60 days (d) 119 days

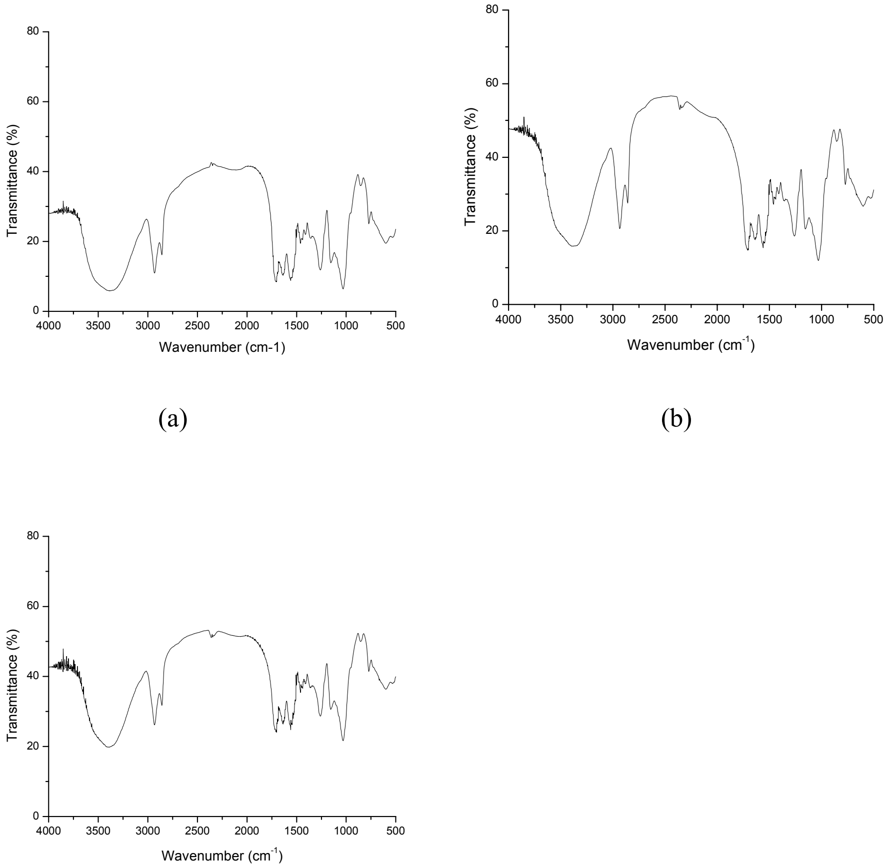


(a) (b)



(c)

Figure 5.17: FTIR β-CD/HMDI buried in compost soil (a) after 10 days (b) 60 days (c) 119 days



(a) (b)

(c)

Figure 5.18: FTIR β-CD/HMDI buried in topsoil (a) after 10 days (b) 60 days (c) 119 days

5.3.5 BET analysis

An increase in the surface area is noted after 20 days of biodegradation in supermix and compost soil but there is a sudden decrease after 40 and 119 days. It is expected that the surface area of the polymer should increase, since during biodegradation microorganisms attack the surface of the polymer. This in turn should reduce the cohesiveness of the polymer thus increasing its surface area.

The BET analyses (**Table 5.1**) of the polymers reveal that the surface areas of these polymers are generally small and this could be one reason why the microorganisms fail to break into the core structure of the polymers material. An important factor in the promotion of biodegradation is a large surface area. Thus if the polymers had been pre-treated before being buried in the soil there could have been an increase in surface area. This can be done by “chewing” the polyurethane polymer with a strong acid such a sulphuric acid, which should initiate a hydrolysis reaction. This hydrolysis should hopefully lead to an in increase in surface area prior to further microbial activity by microorganisms in the soil. Results demonstrated in **Table 5.2** showed that there was a drastic decrease in the surface area of β-CD/HMDI as compared to an almost negligible decrease with β-CD/TDI. This might be attributed to the structure of the polymers. β-CD/HMDI is derived from aliphatic diisocyanates whilst β-CD/TDI is from aromatic diisocyanates. It was observed in studies that polyurethanes derived from aliphatic diisocyantes are degraded faster than those derived from aromatic diisocyanates.[6]

Table 5.1: Surface area (SA) of β-CD/TDI before and after biodegradation

Soil type	SA(m^2/g) 0 days	SA(m^2/g) 20 days	SA(m^2/g) 40 days	SA(m^2/g) 119 days
Topsoil	20.02	20.28	17.63	15.91
Supermix	20.02	28.18	18.35	11.76
Compost	20.02	28.57	40.00	25.00

Table 5.2: Surface area (SA) of β-CD/HMDI before and after biodegradation

Soil type	SA(m^2/g) 0 days	SA(m^2/g) 20 days	SA(m^2/g) 40 days	SA(m^2/g) 119 days
Topsoil	19.7	0.75	0.95	0.78
Supermix	19.7	1.90	1.90	1.49
Compost	19.7	1.47	1.70	1.43

5.4 CONCLUSION

β-CD/TDI and β-CD/HMDI were biodegraded in compost, supermix and topsoil. The % weight loss, changes in the surface morphology and an increase in the surface area of the polymer, confirm that there was microbial attack. FTIR and TGA analysis, however, suggested that the “core” chemical structure of the polymer had remained intact even after exposure to compost, supermix and topsoil over the 119 day period. Pretreatment of the polymers with a strong acid needs to be investigated, which could lead to an increase in surface area. DRIFTS characterization will be carried out in order to ascertain any changes on the functional groups at the surface (on the peripheral) where biodegradation is supposed to have occurred in the soil burial studies that were carried out.

5.5 REFERENCES

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2 Silverstein R.M., Webster F.X., Kiemle D.J (2005) *Spectrometric identification of organic compounds*, John Wiley and Sons, inc, United States of America.

3 Stevens M.P. (1999) *Polymer Chemistry: an introduction*, Oxford University press, New York, Oxford

4 Kim HS, Kim HJ, Lee JW and Choi IG *Polymer Degradation and Stability* **91** (2006) 1117.

5 Davis G *Material Characterization* **51**(2003) 147.

6 Chandra R., Rustgi R. *Prog Polym. Sci* **23** (1998) 1273.

CHAPTER SIX

INTEGRATING CYCLODEXTRIN POLYURETHANE AND MEMBRANE TECHNOLOGY INTO WATER TREATMENT PROCESSES

6.1 THE PROCESS CHALLENGES

This project has demonstrated that crosslinked cyclodextrin polyurethanes have an excellent potential as a technology to remove a wide range of recalcitrant organic compounds from water. As such, the technology would have a wide range of applications in both potable water treatment and waste water treatment. The next stage would be to integrate this technology with other water treatment unit processes to develop effective water treatment systems. The challenges here would be as follows:

(i) To produce the cyclodextrin polyurethanes polymers in suitable forms that may be used in water treatment processes.

(ii) To identify innovative water treatment processes that could exploit the benefits of these water-insoluble cyclodextrin (CD) based polymers.

6.2 OPTIONS FOR "COMMERCIAL" FORMS OF THE TECHNOLOGY

To date CD polymers have been produced mainly in the form of a powder. This has been adequate for laboratory experimentation. However, for real process applications, the polymers may possibly have to be produced in different forms. Possible options are:

(i) as a resin (beads), similar to IX resin. This form could be used in a variety of contacting devices, including columns and as a layer in sand filters. The technical challenges here would be to ensure good contact between the water and the polymeric material, without having an excessive pressure drop. Hence, the size distribution and porosity of the beads would have to be very carefully engineered.

(ii) as a powder, to be used as a precoat on membranes/filters. The important criteria here would be the size distribution and density of the powder, since this will determine removal efficiency as well as the ease of recovery of the spent precoat.

(iii) directly cross-linked to membranes/filters. This would result in a single step process for the removal of suspended material and organics, in situations where the concentration of suspended material is fairly low.

6.3 PROCESSES OPTIONS

Whilst the CD-polyurethanes remove organics, most raw waters and waste waters contain various other contaminants, particularly suspended material. Hence, the polymers would have to be combined with other unit operations that could remove these other contaminants.

Whilst there are numerous processes that the technology can be combined with, or retrofitted to, the following have been identified since they are also South African developments, and are also focused on potable water treatment and waste water reclamation in developing economies.

6.3.1 Gravity-fed microfilter for rural water supply

The Durban University of Technology is currently executing a WRC project to develop a simple gravity-fed microfilter for safe water production in extreme rural areas, or for emergency relief during floods and other natural disasters. The CD-polymers could be produced as a resin and combined with the microfilter as in the figure below :

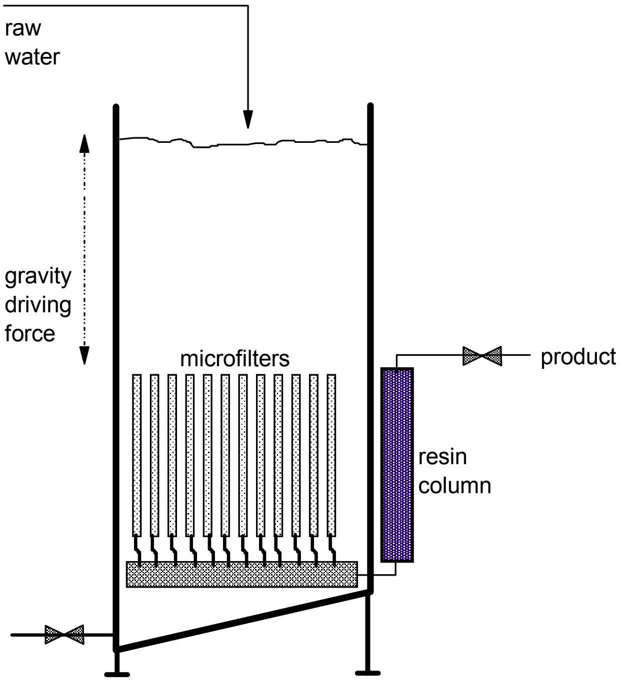

Figure 6.1: Resin combined with microfilter

The microfilter would remove all suspended material, including bacteria. The “clear” water would then pass through the resin column, also driven by gravity, where trace organics would be removed.

A major challenge with rural water system is servicing and maintenance. In the above system, both the microfilters and the resin column would have to be cleaned periodically. This can be sustainably achieved as follows:

(i) The microfilters and columns are designed with sufficient capacity to run for a long period (preferably one month) before cleaning is required.

(ii) Both the microfilters and columns are designed so that they can be easily removed.

(iii) Once a month a roving person, who is responsible for all the treatment systems in a region, removes the fouled microfilters and columns and replaces them with clean ones.

6.3.2 Capillary Ultrafilter for potable water production

Capillary microfilters and ultrafilters are rapidly becoming the preferred process for potable water production internationally, particularly since they guarantee the removal of pathogens. The South African Capillary Ultrafiltration (SACUF) system was developed under a WRC grant specifically to address the problem of potable water production in rural towns, farms, clinics, schools etc. However, capillary ultrafilters generally remove contaminants greater than about 50 nm in size, and hence cannot remove small organics.

Similar to the application above, resin columns could be fitted to the product side of the capillary ultrafilters to produce a one-step process for the removal of suspended solids, bacteria and organics. The outlet stream from the capillary ultrafilters is available at a pressure which would be sufficient to drive the water through the resin columns.

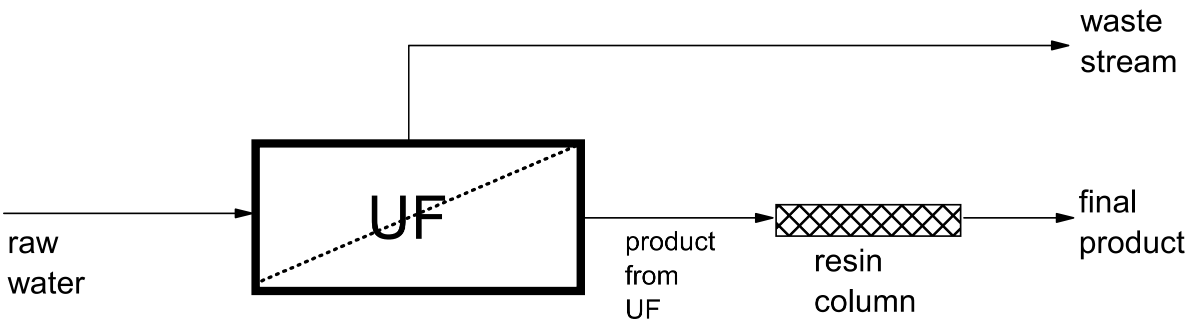

Figure 6.2: Ultrafiltration system

6.3.3 Active precoat microfilter

The APMF combines a PAC precoat with a woven fibre microfilter. Hence, the process can remove both suspended solids and some organics in a single step, making it a very powerful technology for the pretreatment of industrial waste waters. Previously, we have shown that cyclodextrin polyurethanes were more efficient at removing organics than PAC or GAC (WRC Report 1393/1/06). Further, the recovery and regeneration of spent PAC is quite difficult, whereas the regeneration of spent CD-polymers is fairly straightforward (WRC Report 1393/1/06). Hence, there could be significant advantages in using the polymers as a precoat on the woven fibre microfiltration system. Possible applications for this technology would include:

(i) pretreatment of industrial effluents

(ii) production of potable water from raw waters that have a high organic content, especially the "brown" waters of the Cape.

6.3.4 Floating Media Separator

The floating media separator (FMS) is an upflow filter that uses floating beads to effect the separation of suspended material from raw waters. It has various advantages over conventional sand filters, including ease of operation and cleaning and a higher water recovery. The current FMS devices use a bed of low density polyethylene beads of approximately 1 mm in diameter. Contaminants from raw waters are removed both by depth filtration, as well as by weak chemical bonding with the beads.

If the CD-polymers are produced in the form of low density beads, they could be used as the separating medium in FMS systems. This would result in a process that removes both suspended material and organics, while enjoying all the operational advantages of FMS.

6.4 CONCLUSION

The proposed integration of membrane water treatment processes and the cyclodextrin based polymer technology will most probably be effective in future water treatment applications. It is envisaged that piloting a synergetic application of these technologies in rural water treatment would surely remove not only the residual dirt in the water but also organic species which continue to pose a risk to human health. It is therefore recommended that a pilot project that combines the DUT (Durban University of Technology) water treatment protocol and the nanotechnology-water treatment process be commissioned as proposed in this write-up.

CHAPTER SEVEN
CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

All the objectives of the study were successfully achieved and conclusions that can be drawn from the study are listed below:

- Geosmin, 2-MIB and other organic pollutants were successfully extracted from water using SPME and GC/MS. SPME proved to be the most efficient extraction method than SPE and LLE which were techniques that were initially used in the study.

- SPME fibres were also evaluated and PDMS/DVB was found to be extremely effective in the preconcentration of the pollutants from the water.

- The use of β-cyclodextrin polymers in the removal of organic pollutants from Lethabo Power Station was a success. The removal was deduced from the difference in ion counts before and after passing the contaminated water through the polymers. However, Eskom technology did not completely remove the pollutants from water but was effective in TOC removal.

- The organic compounds that were identified using the NIST online library are not the organic acids that have been implicated in the corrosion of the turbines at Lethabo Power Station. These pollutants probably originated from industrial effluent and their presence in potable water is a threat to human health since potable water is used for human consumption.

- The removal of geosmin and 2-MIB from water at ng/L was effective. The removal efficiency was approximately 90%. The concentration of geosmin after passing through the polymers was observed to be below the human threshold concentration (10 ng/L).

- Biodegradation studies of the polymers on exposure to different soil types were carried out. Characterization techniques such as TGA, FTIR, SEM and BET were successfully used. TGA and FTIR showed that the polymers remained intact or stable even after the prescribed burial periods. Whilst BET and weight loss gave indication that there was degradation although it proved to be negligible to be picked up by TGA and FTIR analysis.

- The proposed integration of membrane water treatment processes and the cyclodextrin based polymer technology will most probably be effective in future water treatment applications.

7.2 RECOMMENDATIONS

The following recommendations were drawn from the studies:

- Pilot studies should be performed to investigate the efficiency of the polymers at a larger scale. These studies have revealed that indeed the polymers are effective in the removal of organic pollutants from real water samples. The proposed filter units incorporated with cyclodextrin polymers could be used in these pilot studies.

- Investigate the effect of humic acids in the removal of geosmin and 2-MIB from water using β-cyclodextrin polymers.

- A study that will specifically look into the identification of organic acids present at Lethabo Power Station and using techniques such as ^1H and ^{13}C Nuclear Magnetic Resonance (NMR).

- Pre-digestion of the polymers using acids such as sulphuric acid before burying the polymers in the soil. This is in progress at our laboratory.

- Run soil burial tests under controlled conditions such as humidity, temperature known microorganisms

- Study the effect that the polymers have on microorganisms. Polymer degradation might introduce toxins which in turn kill microorganisms in the soil hence the biodegradation process ceases.

APPENDIX A
GC/MS CHROMATOGRAMS FROM LETHABO POWER STATION WATER SAMPLES ANALYSIS

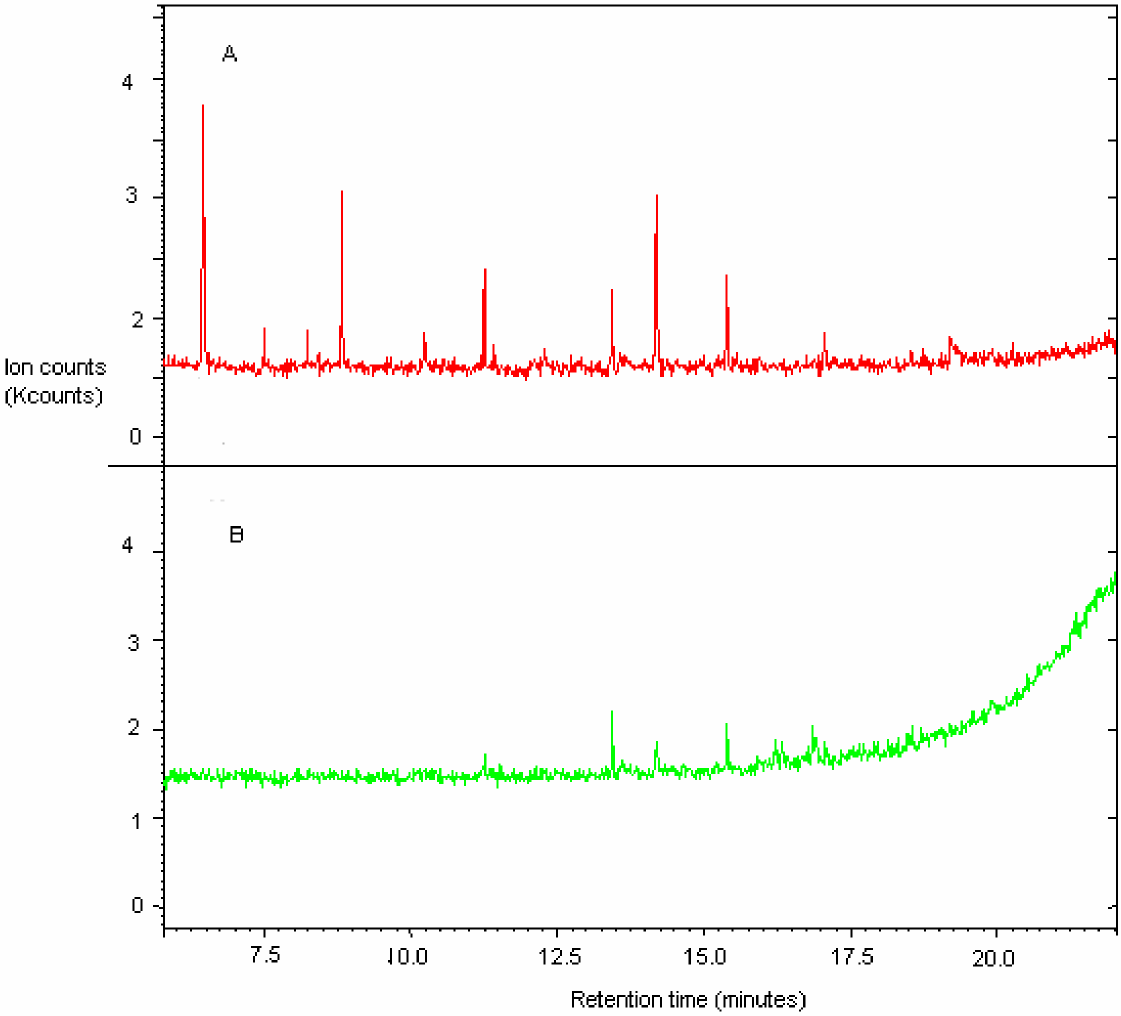

Figure A1: GC/MS chromatogram showing strong base outlet before (A) and after passing through β-CD/HMDI

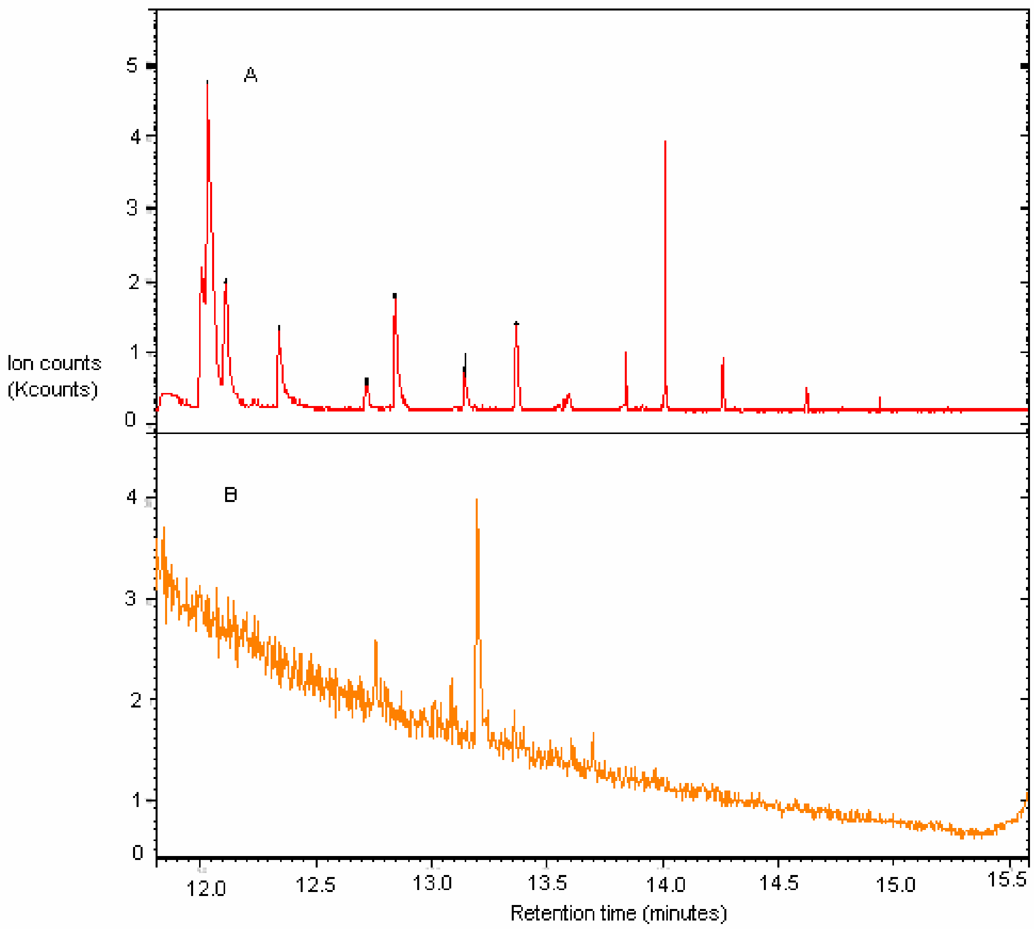

Figure A2: GC/MS chromatogram showing potable water outlet before (A) and after passing through β-CD/HMDI

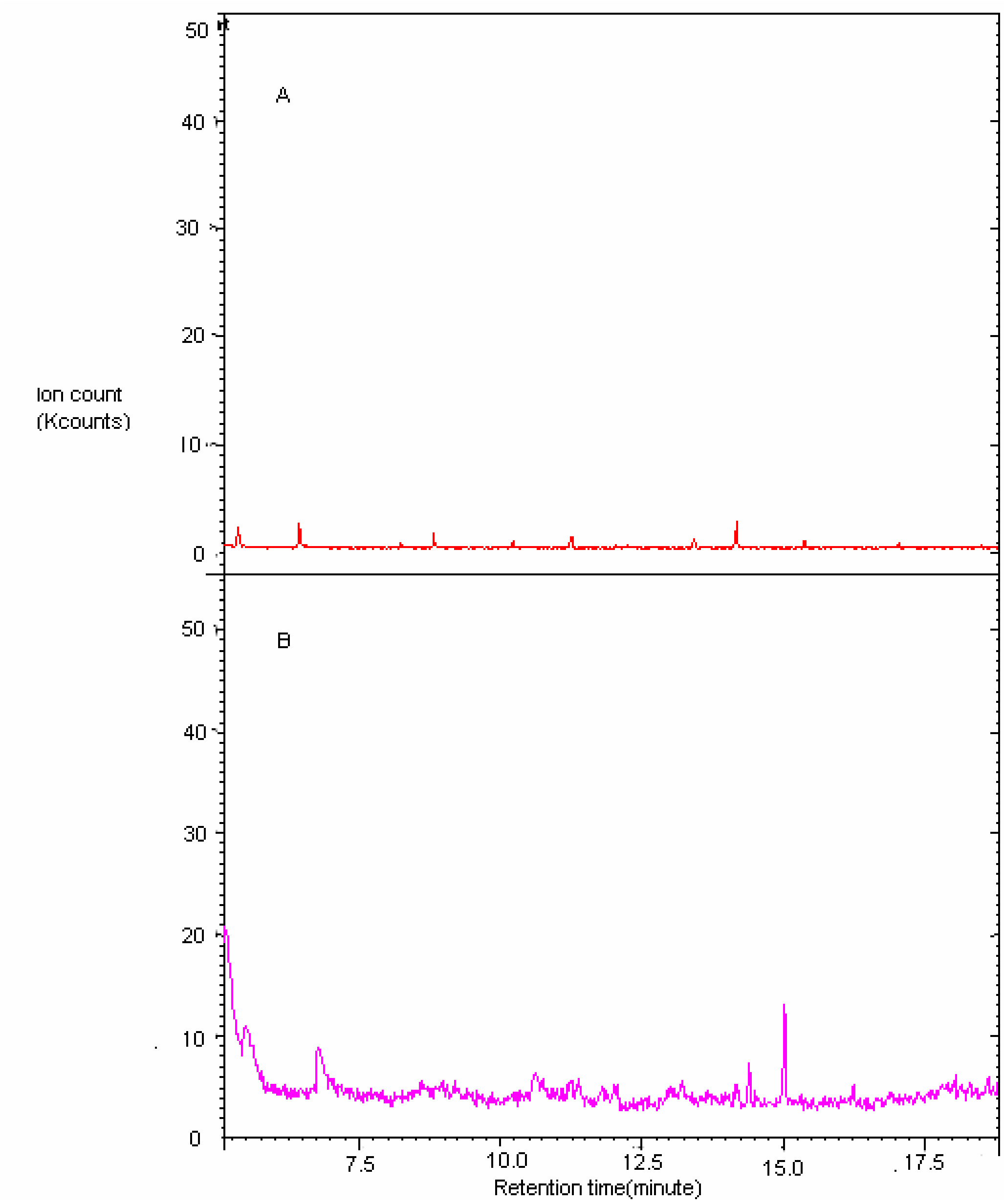

Figure A3: GC/MS chromatogram showing weak base outlet before (A) and after passing through β-CD/TDI

APPENDIX B

GC/MS CHROMATOGRAMS FROM ZUIKERBOSCH WATER SAMPLE ANALYSIS

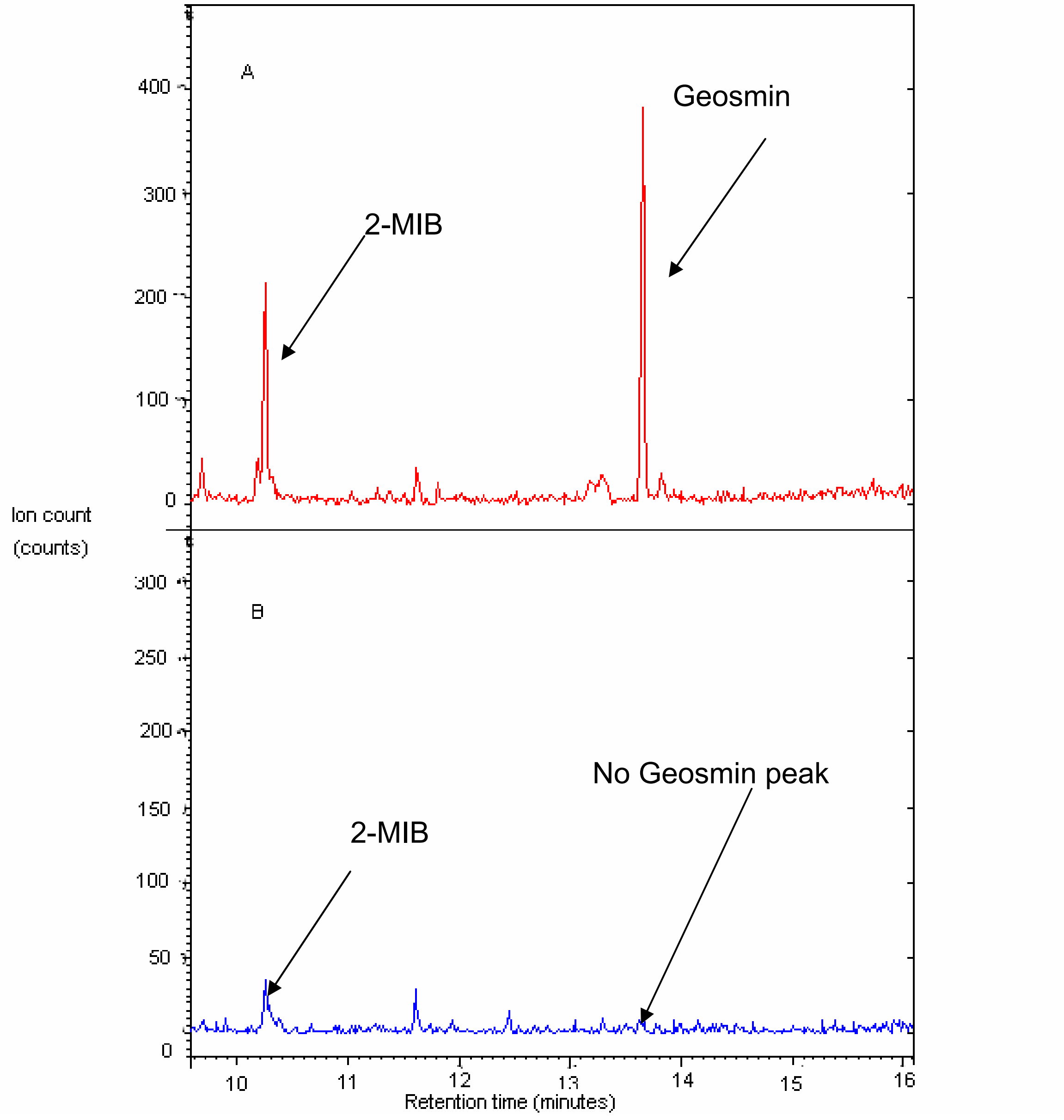

Figure B2: GC/MS chromatogram showing geosmin and 2-MIB in MA6 water sample before (A) and after (B) passing through β-CD/TDI polymer

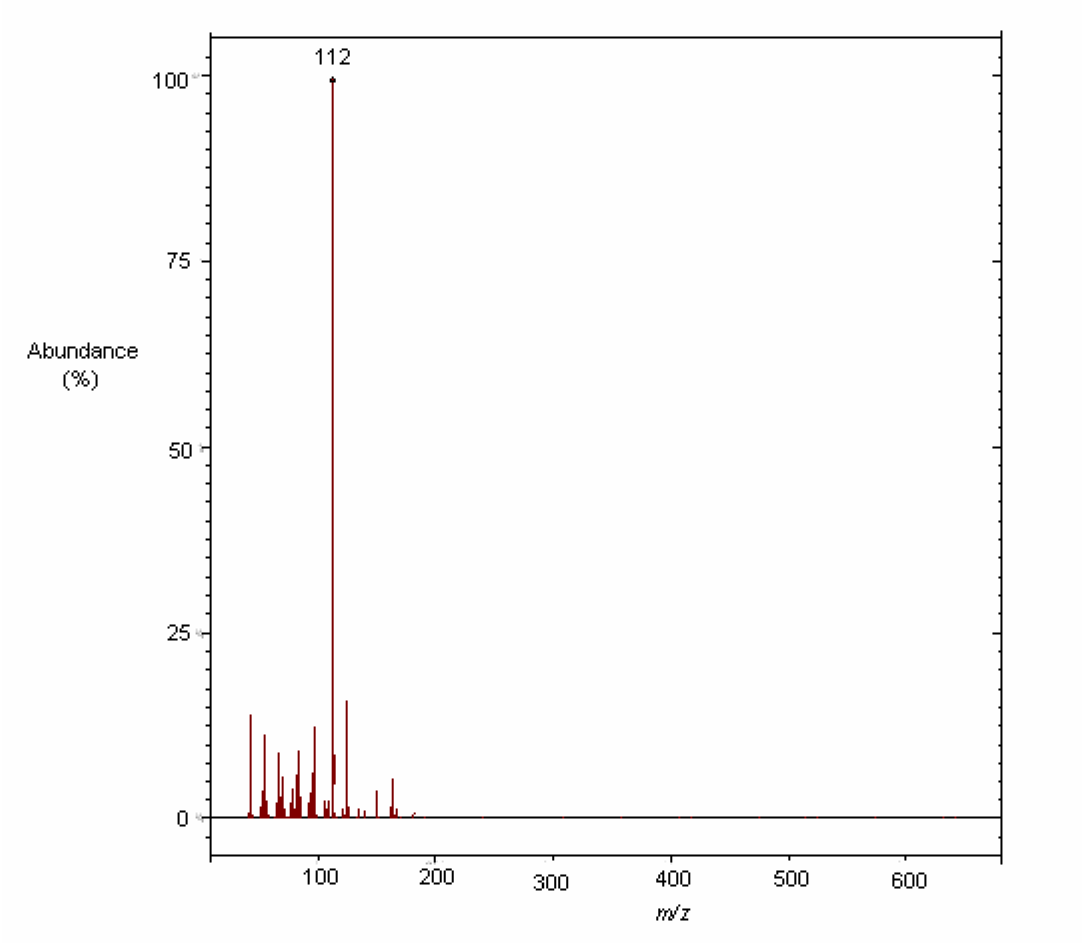

Figure B3: Mass spectra of geosmin in 100 ng/L standard showing *m/z* of 112

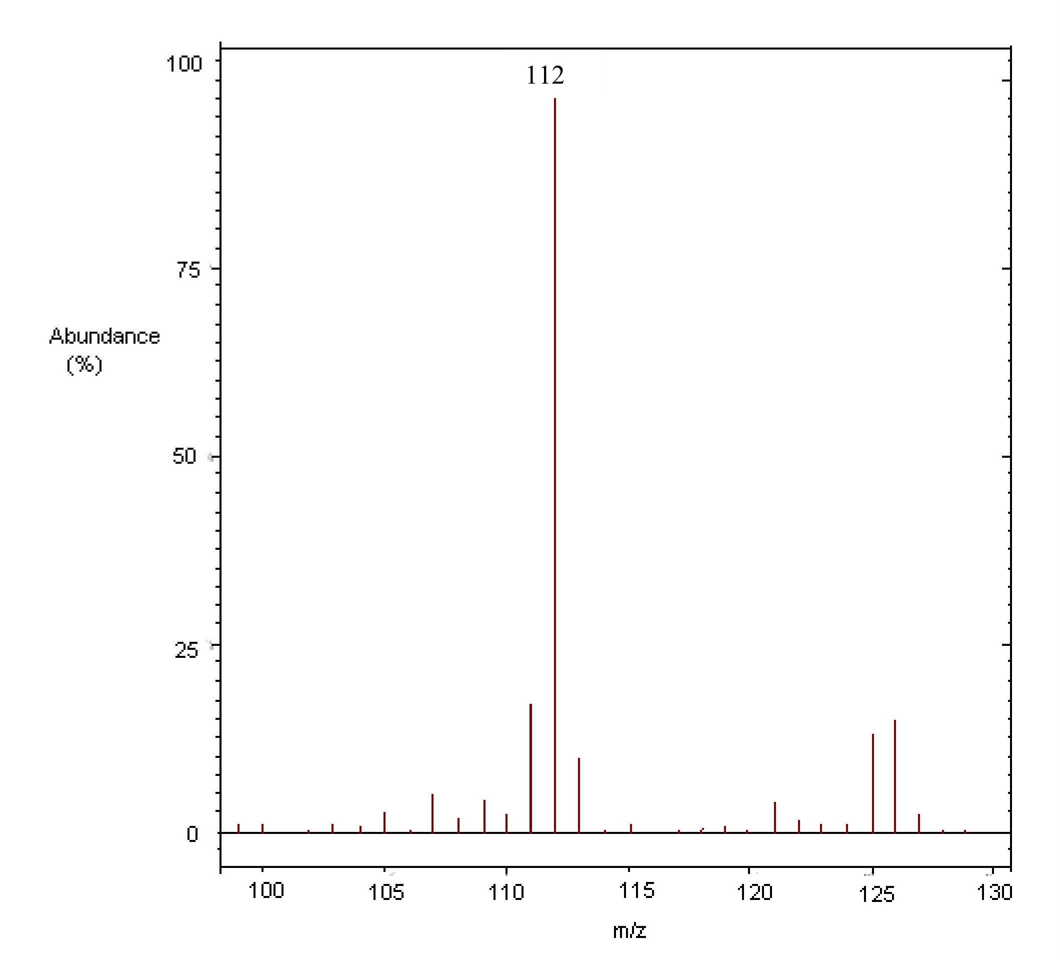

Figure B4: Mass spectra of geosmin in 0f sample showing *m/z* of 112
