CHAPTER 1

1.0 INTRODUCTION

This chapter gives the background of the synthesis of biodegradable superabsorbent polymers and the possibility of using avocado seed powder and its starch as one of the constituents. The chapter also covers the problem statement, aim, objectives, justification of the research and literature review.

1.1 BACKGROUND

Superabsorbent polymers (SAPs) are materials that have hydrophilic networks that absorb water or aqueous solutions up to several hundred times their own weight (10-1000 g/g) and turn into a natural gel within seconds (Zohuriaan-Mehr *et al.*, 2008). Superabsorbent polymers consist of ionic functional groups along the polymer chains to enable the diffusion of aqueous solutions into the network (Raju *et al.*, 2003). SAPs are widely used in fields such as hygienic products, agriculture, drug delivery systems, separation processes, water blocking tapes, coal dewatering and many other processes (Raju, Raju & Mohan, 2003).



Fig 1.0: Applications of SAP (*Zohuriaan-Mehr et al., 2012*)

The first commercial SAP was made by alkaline hydrolysis of starch-graft-polyacrylonitrile (SPAN) and its hydrolysis form (HSPAN) was developed in the 1970s at the Northern Regional Research Laboratory of the US Department of Agriculture (Buchholz and Graham, 1998). However, the product lacked sufficient gel strength. In 1978 Japan began the commercial production of the SAP for use in the feminine sanitary pads. In 1980 Germany and France also employed the use of SAP materials in baby diapers and further developments and the use of the SAP has grown since. (Zohuriaan-Mehr *et al.*, 2008).

Today SAPs are synthesized by gel polymerization, solution polymerization or suspension polymerization, with each process having its own advantages, but all yielding consistent quality of products. The majority of commercially available superabsorbent hydrogels are cross-linked sodium polyacrylates with extremely high molecular weights and limited biodegradablilty. (Yoshimura *et al.*, 2005).

Polyacrylates are made by polymerizing acrylic acid with a cross-linker. The acrylic acid is made from propene which is a byproduct of ethylene and gasoline production thereby making it a non-renewable material that is dependent on the petroleum industry. (Nnadi and Brave, 2011). The use of polyacrylates in superabsorbent hydrogels may result in environmental pollution because most of their applications are in disposable goods (Yoshimura *et al.*, 2005). Buchholz *et al.*, (1998) stated that there is need for the development of biodegradable superabsorbent hydrogels as substitutes for conventional synthetic polymers. Biodegradable polymers are defined as polymers that are degraded and catabolized to produce carbon dioxide and water, by naturally occurring microorganisms such as algae, bacteria or fungi. (Shi *et al.*, 2011).

Several studies have been undertaken to synthesize biodegradable superabsorbent polymers which include cross-linked poly (amino acid) such as poly(γ -glutamic acid) and poly(aspartic acid) and cross-linked sodium salt of carboxymethyl cellulose (CMC) (Yoshimura *et al.*, 2005). Yoshimura and co-workers (2005) also added that crosslinking of CMC has been investigated with several methods such as crosslinking agents and ionizing irradiation. They further stated that as environmental concerns continue to increase, various naturally occurring polymers such as cellulosic materials which are abundant on the earth can be used for various applications. In 2008, Mohammad and Kabiri also alluded to the use of polysaccharides such as chitin, cellulose, starch, natural gums and wheat in the synthesis of SAPs in a bid to reduce environmental pollution. Nnadi and Brave (2011), synthesized polymer complexes of cross-linked carboxymethyl cellulosic derivative containing sodium carboxylate is CMC that is incorporated through an ether linkage (Yoshimura *et al.*, 2005). Modelli and co-workers (2004), stated that the rate of biodegradation of CMC polymer complexes increases when starch is incorporated into the complexes.

Cross-linked CMC and starch superabsorbents can imbibe large amounts of water, saline solutions or physiological fluids as high as 10-1000 times their own weight because of the large amount of hydrophilic groups in their three dimensional structure which also gives them the ability not to dissolve in the media (Ramazani *et al.*, 2006).

In saline solutions of up to 0.9%, the absorbency of the SAP drops to approximately 50 times its weight due to the presence of valence cations in the solution which impedes the polymer's ability to bond with the water molecules. The absorbency and swelling capacity of the SAP are determined by the type and degree of cross-linkers used to synthesize the hydrogel. Low-density cross-linked SAPs usually have a higher absorption capacity and have a softer and stickier gel formation. In contrast high density cross-linking in polymers results in lower absorption capacity and swell but yield hydrogels which are firmer and that can retain their particle shape even under some pressure. (Zohuriaan-Mehr *et al.*, 2008). The absorbed water in SAPs is difficult to remove, even under some pressure due to the network of polymer chains that are cross-linked (Li *et al.*, 2004; Nnadi and Brave, 2011). These characteristics make it possible for SAPs to be used for a variety of applications which include agriculture, cosmetics, sanitary products, sealing composites and drug delivery systems in medicine (Li *et al.*, 2006).

This study focused on the synthesis of SAP material which incorporates avocado seed starch and CMC through crosslinking with aluminum ions from aluminum sulfate octadecahydrate to form non-permanent bonds when the complex imbibes water. A comparison of complexes made from CMC and avocado seed starch and that of CMC and analytical grade starch was also investigated. Complexes of CMC and starch will create an environmentally friendly SAP that is based on biopolymers which could be an alternative to petroleum based polymers that can find application as water retaining aids in irrigation (Nnadi and Brave, 2011). The synthesized SAP was characterized by looking at the structure through the use of Fourier transform infra-red spectrometry (FTIR), determination of the water absorbency capacity, physical observation of the integrity of the SAP particles in the swollen state, solubility fraction and ability to rehydrate (Braihi *et al.*, 2014; Nnadi and Brave, 2011).

1.2 PROBLEM STATEMENT

Biodegradable superabsorbent polymers (SAPs) have been developed as alternatives to the petrochemical based polymers which poise a problem of persisting in the environment after disposal. Over the past few years there has been a demand for biopolymers that are synthesized from feedstock such as starch or cellulose which have the advantages of sustainability, non-toxicity and biodegradation as compared to petroleum based polymers (Weerawarna, 2009). Biodegradable SAPs have been made from polysaccharides such as chitin, cellulose, starch, natural gums and wheat (Mohammad and Kabiri, 2008) but the use avocado seeds as a source of starch or polysaccharide material has not been studied in this regard. According to Elizalde-Gonzalez *et al* (2006) 10 -13% of the avocado fruit weight corresponds to the kernel seed and this is usually garbage after consumption.

1.3 AIM

To synthesise a superabsorbent polymer from avocado seed starch by copolymerization with CMC using aluminium ions as crosslinkers. The SAP can be used for various applications which include agriculture, medicine, hygiene products, separation methods and others.

1.4 SPECIFIC OBJECTIVES

- a) To extract starch from avocado seeds.
- b) To test the extracted starch for starch concentration and compare it with pure analytical grade starch.
- c) To determine the structural composition of the avocado seed powder and the avocado starch by FTIR.
- d) To carry out direct cross-linking of avocado seed starch with CMC using aluminium sulphate octadecahydrate and compare the SAP product with that made from pure starch.
- e) To characterize the various blends of avocado SAP formulations synthesized.
- f) To perform tests for the practical features of the SAP such as water absorption capacity, solubility in water, ionic swelling rate and effects of the amount crosslinker in the avocado SAP.
- g) Recommend the use of avocado seeds in the synthesis of superabsorbent polymers.

1.5 RESEARCH QUESTIONS

- a) Which materials are used in the synthesis of biodegradable polymers?
- b) How is starch extracted from avocado seeds?
- c) Is the starch extracted from avocado seeds comparable to pure starch from corn?
- d) Can a superabsorbent polymer be made from avocado seed starch?
- e) Are the properties of the synthesized polymer comparable to those of SAPs made from starch extracted from vegetables or cereals that have been synthesized by other researchers such as potatoes, corn and cassava?
- f) What combination of avocado seed starch and CMC gives the best SAP formulation?

g) Does the avocado seed starch maintain mineral composition when it is incorporated in the SAP?

1.6 RESEARCH PROPOSITION

Avocado seed starch makes a biodegradable superabsorbent polymer with properties that are comparable to those of SAPs that are synthesized from agricultural plant starches and carboxymethyl cellulose.

1.7 DELIMITATION OF STUDY

The superabsorbent polymer synthesis was carried out by using the *Hass* variety of avocados from a garden in Harare.

1.8 LIMITATIONS

- a) Instruments such as the scanning electron microscope (SEM) and differential scanning calorimetry (DSC) for structural determinations were not available at the time of the study.
- b) Applications of the SAP such as soil conditioning could not be conducted due to the limited time to complete the research.
- c) Mixing vessels for the synthesis of the SAP where improved by using a kitchen blender.

1.9 JUSTIFICATION OF THE RESEARCH

The main motivation of incorporating cellulose-based material in SAPs stems from the fact that the most widely used SAP products are not readily biodegradable. They are primarily synthesized from non-renewable resources which include petroleum derived acrylamide and acrylic acid monomers that usually use crosslinking agents that are from non-renewable resources as stated in background of the study (Zohuriaan-Mehr et al., 2008). Biodegradable products have little or no impact on the environment. Hence the use of avocado to make other products which are biodegradable will eliminate and/or reduce the challenge of having piles of useless biomass. The avocado seed constitutes about 8-25% of the avocado fruit. The seed and skin of the fruit are discharged as waste. Oil producers normally end up with millions of tonnes of the seed. As the ZIM-ASSET endeavors to venture into avocado oil production, challenges of seed disposal may arise. The use of the avocado seed in SAP synthesis specifically in combination with CMC crosslinked with aluminium ions results in the formation of a biodegradable polymer by virtue of the constinuests which are all natural polysaccharides (Braihi et al., 2014). Research carried out by Modelli and others (2004), indicated that the rate of biodegradation of CMC polymer complexes increases when starch is incorporated into the complexes. Utilisation of avocado seeds will create value from material that would otherwise have been discharged as compost or waste.

1.10 LITERATURE REVIEW

1.10.1 DEFINITIONS

Superabsorbent polymer

Superabsorbent polymers are three dimensional networks of hydrophilic polymers held together by crosslinking of covalent bonds or ionic and/or secondary forces that can be either hydrophobic interactions or hydrogen bonds with the ability to imbibe a large amount of water while maintaining the physical dimension structure (Kabiri et al., 2003). Esposito and others (1996), defined superabsorbent polymers are a class of polymers that can absorb enormous amounts of water, usually more than the traditional absorbent materials. Mechtcherine and Reinhardt (2012) stated that superabsorbent polymers can absorb up to 1500 g of water per gram of SAP. SAPs containing absorbed liquids are called hydrogels (Nystrand, 2010). According to Kabiri and others (2011), hydrogels that can imbibe and hold more than 10 g/g are called superabsorbents. Hydrophilic polymers have the ability to absorb water without dissolving provided that the chemical or physical crosslinks exist among the macromolecular chains (Sannino et al., 2009). This concurs with Raju and others (2003), who stated that superabsorbents have a network of polymer chains which have ionic functional groups that enable the diffusion of water in the network while preventing dissolution. Most SAPs are usually white-light yellow sugar-like hygroscopic materials (Zohuriaan-Mehr et al., 2008) used in a variety of applications. The SAP particle shape which maybe granular, fibrous or a film needs to be maintained after the absorption and swelling with water so that the swollen gel strength is high enough to prevent a loosening, mushy or slimy state (Zohuriaan-Mehr et al., 2008).

Superabsorbency

This is the ability of a material to absorb and retain large quantities of aqueous solutions more than a hundred times of its original weight (Buchholz and Graham, 1998). This is due to electrostatic repulsion between the charges on and the difference in the osmotic pressure between the interior and exterior of the SAP polymer chains (Ohmine and Tanaka, 1982).

Hydrogel

A hydrophilic polymer structure capable of absorbing a lot of water or saline solution of up to 10 g per gram of dry based material (Kabiri *et al.*, 2011)

1.10.2 HISTORY OF SUPERABSORBENT POLYMERS

The first water absorbent polymer was made in 1938 from thermal polymerization of acrylic acid (AA) and divinylbenzene in an aqueous medium (Buchholz and Graham, 1998). The first commercial SAP was made by alkaline hydrolysis of starch-graft-polyacrylonitrile (SPAN) and its hydrolysed form (HSPAN) was developed in the 1970s at the Northern Regional Research Laboratory of the United States Department of Agriculture (Buchholz and Graham, 1998). However, expenses and the lack of sufficient gel strength of the product resulted in its failure on the market. In 1978 Japan began the commercial production of the SAP for use in the feminine sanitary pads. In 1980 Germany and France also employed the use of SAP materials in baby diapers and further developments and uses of the SAP have since grown, for example in 1983 low-fluff diapers containing 4 to 5 grams SAP were made in Japan and thinner SAP diapers were introduced in the United States, Europe and other Asian countries because the polymer replaced the bulkier cellulose fluff that could not retain

liquid under pressure. The world production of SAP resins soared to more than one million tonnes in 1990. (Zohuriaan-Mehr *et al.*, 2008).

Over the years there has been growing environmental awareness over limited fossil fuel reserves which has stimulated the search for novel polymeric materials and production processes from sustainable, renewable feed stocks that minimize the detrimental environmental effects associated with their usage (Tschan *et al.*, 2012). This has resulted in a growing demand for biopolymers that are made from feedstocks such as starch or cellulose which have the advantage of biodegradability as compared to petroleum based polymers (Nnadi and Brave, 2011).

1.10.3 SYNTHESIS OF BIODEGRADABLE SUPERABSORBENT POLYMERS

Polyacrylate is the principle material used in the SAP industry (Nnadi and Brave, 2011). Superabsorbent polyacrylates are synthesized by polymerizing acrylic acid with a crosslinker (Heinze and Pfieffer, 1999). Polyacrylate however, has the disadvantage of being a nonrenewable material and thus the demand for biopolymers has increased over the past decade (Nnadi and Brave, 2011).

Biodegradable polymers have been synthesized by other researchers such as Suo and others (2007) and Weerawama (2009) by crosslinking CMC and starch with aluminum sulphate octadecahydrate. Carboxymethyl cellulose holds the lead position among the cellulose derived materials used in SAPs (Bin *et al.*, 2000). Carboxymethyl cellulose is a naturally occuring polysaccharide base which is made by reacting chloroacetic acid with sodium cellulose in slurry with isopropanol and water (Nnadi and Brave, 2013). According to Buchholz and Graham (1998), the synthesis of CMC based superabsorbents started during the 1970s and early 1980s. In a review Hubbe and others (2013), stated that there are several

ways in which CMC can be crosslinked which include; gamma irradiation (Bin *et al.*, 2000; Wach *et al.*, 2001; Liu *et al.*, 2002), or polyvalent carboxylic acids such as ctiric acid (Demitri *et al.*, 2008) or crosslinking CMC and a water-soluble polymer (El Salmawi, 2007).

The main drawback of using CMC was the cost of purification for most applications regardless of the relatively low cost of the reactants and thus CMC based SAPs were discontinued in favour of the petroleum based SAPs (Nnadi and Brave, 2013). Kono and Fijita (2012), proposed that the high cost of SAPs based on CMC constitute a key barrier to their use, but Liang and others (2009) believed that the high cost of acrylic-based SAPs and lack of biodegradability justified the development of high performing cellulose based SAPs. Studies conducted by Modelli and others (2004), showed that the rate of biodegradation of CMC polymers increased when complexes of CMC with starch were crosslinked with aluminium ions forming non-permanent bonds when the complex absorbs water to further justify the use of cellulose based materials.

SAPs that use cellulose based components such as CMC need to be crosslinked using crosslinking agents like divinylsulfone (DVS), epichlorohydrin, glutaraldehyde, ethyleneglycol dimethyl ether and diallytartardiamide which are the same as those used in non cellulose based SAPs (Hubbe *et al.*,2013). The highest swelling performance is observed at the lowest levels of crosslinking (Bin *et al.*, 2000). In the absence of crosslinking the SAP products would dissolve in water (Hubbe *et al.*, 2013). High crosslinking is desirable for mechanical resilience and resistance to dissolution of SAP products (Zohuriaan-Mehr *et al.*, 2010).

Nnadi and Brave (2011), prepared SAPs following a procedure described in literature (Suo *et al.*,2007; Weerawarna, 2009). In the experiments sodium carboxymethyl cellulose was mixed with water and gelatinized starch of cassava, corn, potato and yam separately. Varying

amounts of aluminium sulphate were added to the CMC starch mixtures to investigate the optimum crosslinkage. These mixtures were spread in Teflon baking pans and dried at 70°C until a film was formed. The film was shredded with a blender and ground into a powder with a pestle and mortar.

In another investigation a SAP was prepared by mixing CMC with hydroxyethyl cellulose (HEC) and aluminium ions (Al ³⁺) (Liu *et al.*, 2015). This involved dissolving and stirring 3%CMC and 1% HEC in water at a speed 300 rpm (pH=7.8) in a water bath at 25°C for 40 minutes. To this mixture 10 mL of aluminium sulphate solution at a pH of 3.4 was added drop by drop while stirring for about 20 minutes. The resulting hydrogel was poured into two petri dishes and one was free-dried and the other force air dried to a constant weight to make the superabsorbent sponge (Lui *et al.*, 2015).

1.10.4 CHEMISTRY OF CMC, AVOCADO STARCH AND ALUMINIUM SULPHATE

Superabsorbents can be synthesized with different functional groups such as carboxylic acid, amine, hydroxyl, amide and sulphonic acid groups which determine the hydrophilicity of the polymeric material (Zheng, Hua, & Wang, 2010).



Fig 1.1: Hydrophilic functional groups for the polymer backbone (Omidian, 1997)

These groups (figure 1.1) that are attached to the polymeric networks can be designed for specific applications such as agriculture, hygiene products, drug release and so on (Wang, Zhang & Wang, 2009). Carbohydrate polymers, such as alginate, starch, cellulose and chitosan are good structures for SAPs because of their biocompatibility, biodegradability and bioactivity (Lui *et al.*, 2009).

1.10.5 Starch

Starch is a hydrocolloid biopolymer that is found in abundance and is considered one of the cheapest biodegradable polymers (Vroman and Tghzert, 2009). Starch is mainly extracted from agricultural plants such as potatoes, corn, wheat and rice in the form of granules which are hydrophilic (Vroman and Tghzert, 2009). In literature (Vroman and Tghzert, 2009), it was stated that the stability of starch under stress is not high such that the glucoside links start to break at 150° Cand above 250° C the granules collapse but at lower temperatures reorganization of hydrogen bonds takes place during cooling. Chemically starches are polysaccharides, composed of a monosaccharide units linked together with α -D-(1,4) and α -D-(1,6) linkages (Ayoub and Rizvi, 2009). Starch consists of two structural components, namely, amylose which is a linear polymer constituting 30% of the starch and amylopectin which develops when the enzymatic condensation between glucose units occurs at carbon 1 and 6 (Whistler *et al.*, 1984).



Fig 1.2: Molecular structure of starch (Lu et al., 2009)

All starches are made up of the amylose and amylopectin in varying ratios which depend on the starch source. Starches have biological and chemical properties that make them suitable for industrial applications, such as non-toxicity, polyfunctionality and high chemical reactivity Starch can be crosslinked by crosslinking agents to enable the formation of intermolecular bridges between polysaccharide macromolecules. The crosslinking can be performed with bi-functional or multifunctional reagents that are capable of forming ester or ether linkages with hydroxyl groups in starch. (Ayoub and Rizvi, 2009). Starch granules have hydrophilic properties and strong inter-molecular bonds through hydrogen bonding formed by the hydroxyl groups on the surface of the granule (Lu *et al.*, 2009). In starch modification can be accomplished through oxidation, hydrolysis, esterification, etherification, dextrinization and grafting (Hubbe *et al.*, 2013). In its applications starch is either mixed or kept intact and is used in resins as a filler or melt for blending compounds (Vroman and Tghzert, 2009). The important functional groups in starch are the hydroxyl groups (-OH) which have a nucleophilic character and are susceptible to substitution reactions and ether bonds (C-O-C) (Vroman and Tghzert, 2009). Figure 1.3 shows a FTIR spectrum of native starch. It shows –O-H groups in the region 3600- 3000 cm⁻¹, -CH aliphatic stretching around 2931 cm⁻¹, water in the amorphous region of starch at 1642 cm⁻¹, C-O stretching at 1155cm⁻¹, glycosidic linkage -C-O-C at 930 cm⁻¹, -CH₂OH primary alcohol at 1079 cm⁻¹, C-O-H bending at 930 cm⁻¹ and -CH2 bending at 1420 cm⁻¹.



Fig 1.3: FTIR spectrum of native starch (Hebeish et al., 2010)

1.10.6 Avocado seed starch

The avocado (*Persea americana*, Miller) from the *Lauraceae* family, is an evergreen tree which grows to 10 metres or more that is native to Central/North America (Mexico) and has spread to subtropical and tropical areas (Vinha *et al.*, 2013). The fruits are known as 'avocado', 'alligator pear' or 'butter pear'. The chemical composition of the avocado seeds comprises of approximately 50% moisture, 1.24-1.34% ash, 2.38-2.45% protein, 2.21-3.50% total sugar, 27.54-29.80% starch, 3.65-4.41% crude fibre and 7.76-9.25% of other constituents (Vinha *et al.*, 2013). Arukwe *et al.*, (2012), stated that the avocado seed contains

approximately 0.30 sodium, 14.15 calcium, 26.16 magnesium, 31.33 phosphorus, 100.83 potassium, 0.09 zinc and 0.31 iron all in mg/100g. Studies have shown that isolated starch granules are oval-shaped with smooth surfaces that are free from pores, cracks and fissures, and are 5 to 35 μ m in size (Lacerda *et al.*, 2014).

Kahn (1987) stated that avocado seeds are a potential source of starch, constituting about 30% of the seed and having characteristics that are similar to those of corn starch. According to studies done by Hendra *et al.*, (2015) avocado starch consists of 32.5% amylose, 35.3 % amylopectin, 1% moisture, 1% ash, 1.86% fat and 10.44% protein. They also indicated that results from FTIR analysis showed that the avocado seed starch had O-H bound to hydrogen, C-H alkanes, C=O and C-O ethers showing that amylose, amylopectin and reducing sugars $(C_6H_{10}O_5)n$ are present.

The avocado is widely consumed as food and for medicinal purposes. It is said to consist of over 20 essential nutrients and various potentially cancer preventing phytochemicals. The compound classes can be divided into alkanols (aliphatic acetogeninis), terpenoid glycosides, furan ring-containing derivatives, flavonoids and coumarin. Avocado is also reported for its medicinal uses for wound healing and stimulating hair growth, as an aphrodisiac, treatment of dysentery and diarrhea. (Ding *et al.*, 2007).

1.10.7 Carboxymethyl cellulose

Carboxymethly cellulose is an anionic polyelectrolyte which has good water solubility resulting from the –CH₂COOH groups in its skeleton (Barbucci *et al.*, 2000). It also has unique characteristics such as transparency, high viscosity, hydrophilicity, non-toxicity, biodegradability, film forming ability and biocompatibility (Liu *et al.*, 2015). Hydrogels that are synthesized by crosslinking CMC have high absorptivity and possess dynamic

viscoelasticities and excellent physical properties (Lui *et al.*, 2015). Carboxymethyl cellulose in the form of NaCMC is considered a smart cellulose derivative that is sensitive to pH and ionic strength variations (Sannino *et al.*, 2009). On its own, carboxymethyl cellulose has a tendency of forming intramolecular rather than intermolecular crosslinks in a solution and thus another polysaccharide such as hydroxyethyl cellulose (HEC) can be introduced to avoid this (Seki *et al.*, 2014). Complexes of CMC are usually prepared through chemical crosslinking reactions resulting in the formation of crosslinked networks that are robust and with good water absorption and mechanical strength (Lui *et al.*, 2015).



Fig 1.4: Chemical structure of CMC (Hebeish et al., 2010)

Where R = H or CH_2COONa and n is the degree of polymerization.

The acidic groups in the CMC give it a polyelectrolytic character. It is therefore an anionic linear polymer in which the original H atom of cellulose hydroxyl group is replaced by carboxymethyl substituent (-CH₂-COO-). At pH 4, CMC behaves as a polyanion and is generally found in the sodium salt form which assumes solubility for CMC products (Hebeish *et al.*, 2010). Figure 1.5 shows a typical FTIR spectrum of CMC. The asymmetric stretching

vibration and symmetrical stretching of the carboxyl group (-COO⁻) in CMC shows absorption peaks at 1635 cm⁻¹ and 1424 cm⁻¹ respectively.



Fig 1.5: FTIR spectrum of CMC (Hebeish et al., 2010)

The presence of NaCMC in a cellulose based hydrogel provides the polymer with electrostatic charges anchored to the network, which have the double effect on the swelling capacity. The electrostatic repulsion that is between charges of the same sign forces the polymer chains to be elongated and the counterions that are found in the hydrogel induce macroscopic electrical neutrality so that water absorption and swelling is increased within the network due to the Donnan type effect (Sannino *et al.*, 2009). The polyelectrolyte nature of NaCMC make it ideal for the synthesis of SAPs with a smart behavior (Esposito *et al.*, 1996).

1.10.8 Aluminium sulphate octadeccahydrate

Aluminium sulphate octadecahydrate (Al₂(SO₄)₃·18H₂O) is cationic and forms Al³⁺ and Al(OH)²⁺ species in aqueous solution when the pH is less than 5, thus providing multivalent positive charges and a lot of sites for crosslinking with anionic groups (Lui *et al.*, 2015). Aluminium sulphate has been used as a crosslinking agent in the preparation of biomaterials because its low toxicity and good performance (Lui *et al.*, 2015).

1.10.9 CROSSLINKING IN SAPs

The cross-linking of polymer chains in SAPs forms three dimensional networks which prevent them from swelling to infinity and dissolving in water (Po, 1994). The cross-links can be formed by covalent, electrostatic, hydrophobic bonds or dipole-dipole interactions (Omidian *et al.*, 2004). Braihi *et al.*, (2014), stated that small quantities of cross-linkers play a significant role in adjusting the properties of SAPs such as, the swelling and mechanical properties. High levels of crosslinking are needed to achieve mechanical resilience and resistance to dissolution although it may restrict swelling (Hubbe *et al.*, 2013). Studies by Barbucci *et al.*, (2000) as cited in literature (Hubbe *et al.*, 2013) showed a monotonic decrease in swelling with increase in crosslinking up to a 50% level but a higher swelling at 100% crosslinking. This was attributed to the disruption of hydrogen bonding by the crosslinking agent. The efficiency of cross-linking depends on: steric hindrance, reduced mobility at the site of pendant double bonds, the tendency of the cross-linker to undergo intermolecular addition reactions and the solubility of the cross-linker in the monomer mixture (Zohuriaan-Mehr, 2006). Braihi *et al.*, (2014), indicated that covalent crosslinks are formed when the monomers such as acrylic acid are copolymerized with di-, tri-, or tetra

monomers such as N,N-methylene *bis*(acrylamide) while ionic bonds are formed between an oppositely charged polyvalent ion and a charged polymer chain.

Hydrogen bonds which form physical crosslinks occur between segments of one chain with the segments of another chain. Hubbe *et al.*, (2013), stated that hydrogels that have carboxylic groups usually show increasing absorbency with increasing pH, especially the pH range of approximately 3 to 7. This effect is said to result from the dissociation of the groups to carboxylate form (Barbucci *et al.*, 2000). These effects of pH are consistent with the fact that absorbency increases with increasing charge density (Hubbe *et al.*, 2013). According to Braihi *et al.*, (2014), there are two main types of cross-linking in most SAPs: Bulk or core crosslinking and surface crosslinking

Bulk crosslinking involves crosslinkers which are organic in nature and have two or more polymerisable double bonds. These organic molecules are incorporated into the backbone of the polymer chains as they elongate during the polymerisation reaction. The functionality of the cross-linker depends on its reactivity ratio. Buchholz and Peppas (1994), defined reactivity ratios as a measure of the affinity for each of the reaction components to react with each other. When the cross-linker has a high reactivity ratio most of it is consumed in the early stages of the polymerization and any polymer chains made at the latter stages will probably not cross-link and end up as extractable chains. Cross-linkers with a low reactivity have an opposite effect. The choice of cross-linker therefore determines the structure of the final polymer network. (Braihi *et al.*, 2014).

Surface crosslinking improves absorption against pressure and the swelling rate of a SAP through crosslinking the surface of the particles. This type of cross-linking is normally carried out on dried, milled and sized SAP as the final stage of the process. The surface cross-linked particles retain their shape even after swelling, creating a gel bed with air pockets

because the particles are less densely packed. The permeability of the surface cross-linked particles permit efficient use of the gel bed. (Braihi *et al.*, 2014).

According to Esposito et al., (1996), the degree of crosslinking in a SAP and the presence of ionic groups in the backbone of hydrogels can be detected by electron scanning microscopy. Their studies suggest that the synthesis of hydrogels with the desirable water absorption properties could be obtained by optimizing certain process parameters such as the amount of aluminium sulphate used for crosslinking. In studies conducted by Nnadi and Brave (2013) the results indicated that the optimal water retention was obtained when 2.3% Al₂(SO₄)₃.18H₂O was used in the crosslinking. The researchers observed that when less than 2.3% Al₂(SO₄)₃.18H₂O was used the SAP would be under-crosslinked and thus the complex would not have a network with appropriate sized void spaces for optimal water retention. On the other hand, over cross-linking showed that the polymer complex would have too many connections resulting in the void spaces being too small for optimal water absorption. This is in agreement with Braihi et al., (2014), who stated that under cross-linking results in high swelling capacity, low strength against pressure and a tacky feel due to the high extractable fraction and on the other hand over cross-linking results in low extractable fraction, low tackiness and low swelling capacity. Figure 1.6 shows the optimization of water retention of potato starch and CMC crosslinked with Al₂(SO₄)₃.18H₂O at various levels.



Figure 1.6: Optimisation of water retention of potato starch hydrogel at various levels of crosslinking (*Nnadi and Brave*, 2013).

In an investigation to determine whether the Al^{3+} ions or the SO_4^{2-} ions in the crosslinker, aluminium sulphate [$Al_2(SO_4)_3.18H_2O$], enters into the crosslinking reaction Braihi *et al.*, (2014) concluded that it was the Al^{3+} ions. This conclusion was drawn after conducting tests that involved immersing the CMC/starch blend in hot water at 70°C for 30 minutes, filtering the sample and testing for sulphate ions by adding barium sulphate to part of the filtrate and adding sodium hydroxide to the other part to test for Al^{3+} ions. The SO_4^{2-} ions were identified in the filtrate by the formation of a dense white precipitate of barium sulphate indicating that they did not participate in the crosslinking reaction, but the test for Al^{3+} ions was negative which showed that the ions were in the crosslinked network.

1.10.10 CLASSIFICATION OF SAPS

SAPs may be categorized into four groups according to the presence or absence of electrical charge located in the crosslinked chains (Zohuriaan-Mehr *et al.*, 2006):

- 1. Non-ionic,
- 2. Ionic (anionic and cationic),
- 3. Amphoteric electrolyte (ampholytic) composed of both acidic and basic groups
- 4. Zwitterionic (polybetaines) containing both anionic and cationic groups in each monomeric unit.

SAPs are also classified according to the monomeric units used in their chemical structure (Buchholz and Peppas, 1994):

- 1. Crosslinked polyacrylates and polyacrylamides
- 2. Hydrolysed cellulose-polyacrylonitrile (PAN) or starch-PAN graft copolymers.
- 3. Cross-linked copolymers of maleic anhydride.

However, conventionaly SAPs were classified as either synthetic (petrochemical-based) or natural (polysaccharides or polypeptide based). The natural based SAPs are usually prepared by addition of some synthetic parts onto the natural substrates such as in the case of graft copolymerization of vinyl monomers on polysaccharides. The main starting materials for SAPs include monomers such as acrylic acid (AA) and its potassium or sodium salts, acrylamide (AM), methacrylic acid (MAA), methacrylamide (MAM), acrylonitrile (AN), hydroxyethymethacrylate (HEMA) N-vinlyl pyrrolidone (NVP), vinyl sulphonic acid (VSA), vinyl acetate and many others. (Zohuriaan-Mehr *et al.*, 2008).

In the modified natural-based SAPs trunk biopolymers such as cellulose, starch, chitosan, gelatin and their derivatives such as carboxymethylcellulose (CMC) are used as the modifying substrate. N,N'-methylene bisacrylamide (MBA) is usually used as the water soluble cross-linking agent. Potassium persulphate (KPS) and ammonium persulphate (APS) are water soluble thermal initiators used frequently in both solution and inverse-suspension

methods of polymerisation. Redox pair initiators such as $Fe^{2+}-H_2O_2$ (Fenton reagent) and APS-sodium sulphate are also used in the solution method (Zohuriaan-Mehr *et al.*, 2008).

In literature (Ahmed,2013) it is stated that SAPs can be classified according to polymeric composition and this is exemplified by:

- a) Homopolymeric hydrogels: These are SAPs with polymer networks that are made up from a single species of monomer which forms the basic structural unit that makes up the polymer network (Takashi *et al.*, 2007)
- b) Copolymeric hydrogels: These are composed of two or more different monomer species with at least one hydrophilic component, arranged in a random, alternating or block configuration within the polymer network (Yang *et al.*, 2002).
- c) Multipolymer interpenetrating polymeric hydrogel (IPN): This polymer is composed of two independent crosslinked synthetic and/or natural polymers in a network. In the semi-IPN, one of the components is a crosslinked polymer and the other is non-crosslinked. (Maolin *et al.*, 2000).

Several other classifications have been made by Ahmed (2013) that include classification based on physical appearance, type of crosslinking, network electrical charge and on configuration.

1.10.11CHARACTERISATION OF SUPERABSORBENT POLYMERS

According to Zohuriaan-Mehr et al., (2004), the functional features of SAPs are:

- High water absorption capacity in water and saline
- Rate of absorption (preferred particle size and porosity)

- Highest absorbency under load (AUL)
- The lowest soluble content and residual monomer. The SAP should have good gel strength and should not become slimy and flow easily after swelling.
- Lowest price
- The highest durability and stability in the swelling environment and at storage
- The highest biodegradability without formation of toxic species following degradation
- pH neutrality after swelling in water
- colourlesness and odourlessness and absolute non-toxicity
- photostability
- Re-wetting capability (if required).

They further add that it is impossible for a SAP to fulfill all the above required features and therefore production reaction variables need to be optimized such that a balance between the properties is achieved, for example an agricultural SAP must have a high AUL and a low sensitivity to salinity while a hygienic SAP has a high absorption rate, low re-wetting and low residual monomer.

Zohuriaan-Mehr *et al.*, (2008), indicated that the variables affecting the final properties of a SAP are:

- Cross-linker type and concentration
- Monomer (s) type and concentration
- Type, size, and amount of inorganic particles in the SAP
- Initiator type and concentration
- Polymerization method
- Polymerization temperature
- Amount and type of surfactant used

- Drying method, drying temperature and drying time
- Stirrer/reactor geometry and rate of stirring
- Post-treatments such as surface crosslinking

They also mention that each variable has its own individual effects on the SAP properties and that in process optimization one should consider the variables that have special effects on the desired SAP product.

1.10.12 Water absorption capacity

The effectiveness and water retention properties of SAPs can be determined by testing their water retention capacity and the degree of crosslinking. Nnadi and Brave (2013) determined the water retention capacity of SAPs produced by crosslinking CMC and various starches with aluminium sulphate by immersing 0.1 g of the material in 100 mL of distilled water and then filtering the slurry formed through a coarse glass filter under a slight vacuum for 10 minutes. The amount of water retained by the SAP was calculated using the formula:

Water retention =
$$(Gs-Gi)/Gi$$
 (1)

where Gs was the weight of the swollen hydrogel and Gi was the initial weight of the SAP sample. Zohuriaan-Mehr *et al.*, (2008), described water absorption capacity as free absorbency capacity because the sample is freely swollen without the exertion of a load on it. The researchers also stated three methods that can be used to determine the water retention, namely the tea bag, centrifuge and sieve methods. Braihi *et al.*, (2014), determined the water absorption capacity (WAC) of SAP material by using the tea bag method.

a) Tea bag method

The tea-bag method is a conventional and fast method that can be used for limited amounts of sample, 0.1 to 0.3 g (Zohuriaan-Mehr *et al.*, 2004). In this method the sample is placed in a tea bag made of acrylic or polyester gauze with fine meshes. The tea bag is immersed in an excess amount of water or saline solution for one hour to reach equilibrium swelling and then taken out and hung so that all the excess solution runs off. The tea bag is weighed and the swelling capacity is calculated by equation (2). Zohuriaan-Mehr *et al.*,(2008), stated that the precision of the method is approximately $\pm 3.5\%$.

$$WAC = (W1 - W0)/W0$$
 (2)

Where W0 is the dry weight and W1 is the wet weight.

b) Sieve method

The SAP material is immersed into an excess amount of water or solution and dispersed by a magnetic stirrer to reach equilibrium swelling for a period of half an hour to three hours depending on the sample particle size. The swollen sample is then filtered through a weighed 100-mesh (150 μ m) wire sieve and then dewatered by using a piece of soft open-cell polyurethane foam by repeated rubbing under the gauze bottom and squeezing the foam until the gel no longer slips from the sieve when it is held in a vertical position. The swelling can be calculated as shown in equation (3).(Zohuriaan-Mehr *et al.*, 2003 and Omidian *et al.*, 1994).

$$S_t = [(A_t + B) - (B + W1)]/W1$$
 (3)

Where S_t =swelling at time t (g/g), A_t = weight of water-absorbed polymer at time t (g), W1 = weight of dry SAP and B =weight of sieve (g).

The researchers also indicated that this method which is also referred to as the filtering and rubbing method requires a large sample size of about 1 to 2 grams. The method however, has a standard deviation of around $\pm 2.1\%$ (Omidian *et al.*, 1999).

c) Centrifuge method

According to Buchholz and Peppas (1994) the centrifuge method is more accurate than the tea-bag method. In this method 0.2 grams of the SAP is placed into a non-woven bag with dimensions of 60 x 60 mm and immersed into 100 mL of water or solution at room temperature for half an hour. The bag is removed from the water or solution and the excess solution is eliminated by a centrifugal separator. The same process is conducted with an empty bag. The swelling capacity is calculated as shown in equation (4) (Zohuriaan-Mehr *et al.*, 2008).

$$S_{e} = (W_{2} - W_{0} - W_{1})/W_{1}$$
(4)

Where W1= weight of dry SAP, Se =swelling capacity, W2= weight of empty bag after centrifuge method (blank sample) and W0 = weight of empty bag.

1.10.13 Effects of salinity

Hubbe *et al.*, (2013), states that there is a strong contrast between the absorption of pure water by cellulose based absorbents as compared to corresponding amounts of saline solution which is often evaluated with 0.9% NaCl. They also added that in most cases saline solutions show an absorbency value which is less than half of the absorption capacity of pure water.

1.10.14 Absorbency under load (AUL)

Absorbency under load is described in the European standard EDANA ERT 442 as a test to measure a superabsorbent's ability to absorb 0.9% saline solution against a pressure of 50 g/cm². In this standard the SAP is placed in a plastic cylinder, that has a screen fabric at the bottom and a weight with the required pressure is put on top as shown in Figure 1.7. This cylinder arrangement is then submerged into a liquid source so that the SAP is soaked for an hour and the absorption capacity is measured in g/g. According to Zohuriaan-Mehr *et al.*, (2008), the AUL is a measure of the swollen gel strength of SAP materials.



Figure 1.7: Typical AUL testing apparatus (Zohuriaan-Mehr et al., 2008)

1.10.15 Wicking capacity and rate

The determination of wicking capacity (WC) was described by Zohuriaan-Mehr *et al.*, (2008), as follows: about 0.050 ± 0.0005 g (W₁) of SAP is placed in a tared, 9.0 cm fluted circle Whatman 54 filter paper. The cone is tapped lightly so that the SAP settles at the tip of the cone. The tip of the cone is then immersed into 9 cm petri dish containing 25 mL of water for 60 seconds. Water wicks up the whole paper in the 60 seconds. Excess water is drained by contacting the tip with a circle of dry filter paper on a square of absorbent towel. The weight

of the swollen SAP and wet paper is determined (A) and the absorbency of the sample is calculated in g/g using equation 5.

$$WC = (A - B - W_1)/W_1 \tag{5}$$

Where (B) is the wet filter paper without the SAP

1.10.16 Swelling rate

This technique is employed by technical laboratories and involves the following procedure: 50 g of water or saline solution is placed in a 100 ml beaker and the temperature is adjusted to 30°C and then stirred at 600 rpm with a magnetic stirrer (Stirrer bar length is 4 cm). A SAP sample with mesh size between 50-60 and weight of 0.50-2.0 g (W_o) is added while still stirring and a stopwatch is started. The time that elapses from the point of SAP addition to the time the vortex disappears (tvd, sec) is measured. The swelling rate is calculated from equation (6). (Zohuriaan-Mehr et al., 2008).

Swelling rate=
$$(50/W_o)/t_{vd}$$
 (6)

1.10.17 Soluble fraction

....

The soluble fraction (sol) is defined as the sum of all water soluble species including the non-crosslinked oligomers and starting material that has not reacted such as residual monomers. The sol content is determined by weighing a certain amount of SAP and immersing it in excess distilled water and stirring with a magnetic stirrer to reach equilibrium swelling. The swollen SAP is then filtered and dried in an oven. The sample weight loss is the soluble fraction. The gel content may be assumed as the actual yield of cross-linking polymerization and is given by equation (7). (Zohuriaan-Mehr et al., 2008).

Sol(%) + Gel(%) = 100

1.10.18 Ionic sensitivity

A dimensionless swelling factor, f, is used to make a comparison of sensitivity of SAP materials towards different aqueous fluids and is calculated by equation (8) (Zohuriaan-Mehr *et al.*, 2003).

f=1- (absorption in a given fluid/absorption in distilled water) (8)

a large f value indicates a higher absorbency-loss of the sample in salt solutions. SAPs with lower f are generally more desirable. Negative values of f show that the absorbency is not reduced but increased in salt solutions (Kabiri *et al.*, 2005).

1.10.19 Other properties of super-absorbing materials

Hygroscopic materials are generally categorized into two classes based on the mechanism by which they absorb water, namely chemical or physical absorptions. Chemical absorbers entrap water by reacting with water and converting their entire nature. Physical absorbers imbibe water through the following mechanisms:

- i. reversible changes of their crystal structure.
- ii. entrapment of water through capillary forces in their macro-porous structure
- iii. a combination of (i) and hydration of functional groups
- iv. a combination of (ii) and (iii) dissolution and thermodynamically favoured expansion of the macromolecular chains limited by cross-linkages.

SAPs fall into the fourth category being organic materials with huge water retention capability. They can imbibe deionized water in proportions as high as 1,000-100,000% (10-1000 g/g) as compared to absorption capacity of hydrogels that is not more than 100% (1g/g). The SAP particle shape is preserved even after water absorption and swelling thus the swollen gel strength should be high enough to prevent a loosening and slimy state. This the the main distinguishing feature of SAPs from hydrogels and other absorbing materials. (Zohuriaan-Mehr *et al.*, 2008).

1.10.20 Proposed crosslinking model

In studies of crosslinking CMC and starch with aluminium sulphate octadecahydrate, Braihi *et al.*, (2014) proposed the crosslinking model for CMC and Al ion as shown in figure 1.8, and the crosslinking model of CMC, starch and Al ion blend as shown in figure 1.9. The researchers postulated that since the Al ion is trivalent, three CMC molecules could connect to the Al as shown in figure 1.8 (based on one monomer unit having 1443 g/mol).



Figure 1.8: Proposed crosslinking model for Al ion and CMC (Braihi et al., 2014)



Figure 1.9: Proposed crosslinking model for Al ion /CMC/starch blend (Braihi et al., 2014)

The FTIR spectrum in figure 1.10 shows that there are no hydroxyl primary alcoholic groups on the starch molecule at 1078 cm⁻¹. This showed that the link between starch and CMC molecules occurs at this site which can be attributed to the lowest space hindrance at the site thereby resulting in the repeating units containing three additional starch molecules as shown in figure 1.9. (Braihi *et al.*, 2014).



Figure 1.10: FTIR spectrum for CMC, starch and CMC/starch blend (Braihi et al., 2014)

1.10.21 APPLICATIONS OF SAPS

Superabsorbent polymers are widely used in hygiene products such as disposable diapers and female napkins and in agriculture as granules for retaining soil moisture in arid areas (Zohuriaan-Mehr *et al.*, 2008). According to (Buchholz *et al.*, 1990) personal hygiene products account for over 95% of the market for manufactured SAPs. Zohuriaan-Mehr *et al.*, (2008), stated that most research is focused on hygienic grades of SAP because of the high consumption of products such as diapers, such that the AUL has increased to about 30 g/g and free absorbency has decreased to about 50 g (saline)/g (polymer) over the past two decades.

Superabsorbent polymers also find application in the agricultural field, where they are used as soil additives to increase the water retention of soils, which can replace peat, the traditional moisture retention aid for soil (Barbucci *et al.*, 2000). Buchholz and Graham (1998), stated that applications of the SAP should be approximately 0.1 to 0.5% by weight, because above
this range the soil may become too spongy when it is fully saturated or the effect may be negligible at lower concentrations than the prescribed amount. Other applications of SAPs include fields of civil engineering, for example mud conditioners, lubricants, sealing material and a small fraction of SAPs are used for artificial snow, artificial soil for hydroponics, polymer concrete compositions and many more.

CHAPTER 2

2.0 RESEARCH METHODOLOGY

2.1 INTRODUCTION

This chapter covers the research methodology that was used to carry out the research. In this chapter the researcher describes the research design and the research strategy used in the study. The research design includes, the sampling techniques, data collection and data analysis.

2.2 MATERIALS AND PROCEDURES

2.2.1 Materials

Carboxymethyl cellulose sodium salt, NaCMC, analytical grade starch (corn) from Associated Chemical Enterprises (ACE), aluminium sulphate Al₂(SO₄)₃18H₂O from SMM chemical (Pty) limited. The avocado seeds where obtained from a garden in Harare and were of the *Hass* variety.

2.2.2 Equipment

The equipment that was used to carry out the isolation of starch from avocado seeds, synthesize the SAPs, and characterize the SAPs includes:

Mortar and pestle, ThermoFisher Scientific Nicolet 6700 Fourier Transform Infra-red spectrophotometer (FTIR), GBC Quantima inductively coupled plasma optical emission spectrometer(ICP-OES), Shimadzu UV-160 spectrophotometer,1 liter beakers, magnetic

stirrer, Sun Beam electric blender (10 speed), P Selecta water bath, electric hot plate, Haseaus drying oven, porcelain plates, petri dishes, analytical balance, 100 mesh sieve, 300 ml beakers, cheese cloth, kitchen sieve, filter paper (540), poly urethane sponge and measuring cylinders.

2.2.3 Statistical evaluation of experimental results

The one-way and two-way Anova analysis was performed on all the experimental data using a statistical program called GraphPad Prism 6.0 at 95% confidence to determine the significant difference between the two types of SAPs made. The student t-test was also employed.

2.3 SYNTHESIS OF THE AVOCADO STARCH BASED SUPERABSORBENT POLYMER

The synthesis of the SAP involved the following steps:

- 1. Isolation of starch from avocado seeds.
- 2. Determination of starch content in the extracted avocado starch.
- 3. Superabsorbent polymer production.
- 4. Testing the synthesized SAP.

2.4 ISOLATION OF STARCH FROM AVOCADO SEEDS

Starch was isolated from avocado seeds. The method used in this research was adapted from Akbar *et al* (2013). The procedure is shown in figure 2.0.

Ripe avocados were cut into half and the seeds were removed and washed. The outer skins of the avocado seeds were peeled off. Seeds weighing 2 kg were grated with a kitchen grater.

The grated pieces of seed were soaked in 3 litres of distilled water for about 30 minutes and then small portions to fill about 50% of the blender jar were transferred to the blender. The mixture was blended into a smooth puree. More water was added to the puree so that it was free flowing and then filtered through a cheese cloth. The filtrate was allowed to settle for 60 minutes to allow precipitation of the starch. This was washed three times and allowed to air dry for about 48 hours. The starch isolated was loosened by gentle grinding with a pestle and mortar and further dried in an oven at 105°C.



Figure 2.0: Procedure for the extraction of starch

2.4.1 Determination of starch content in the extracted avocado seed starch

The amount of starch in the extract from the avocado seed was determined by using the phenol-sulphuric acid method by Nielson (2010). The procedure was as follows:

- a) Duplicate samples were weighed, 0.035 g (\pm 0.005 g) of each. Analytical grade starch was also weighed and this served as the reference material.
- b) Each avocado starch sample from (a) was extracted with 5 mL of absolute acetone and filtered and further washed four times with 80% hot ethanol.
- c) After washing the sample with hot 80% ethanol 5 mL of 1.1% hydrochloric acid was added to the sample and placed in a water bath at 100°C for 30 minutes.
- d) The sample was allowed to cool and was diluted to 20 mL with distilled water.
- e) In a clean dry test tube 2 mL of sample (d) was placed by pipetting and 0.5 mL of 5% phenol added and mixed by vortex.
- f) To the same test tube (e) 2.5 mL of concentrated sulphuric acid was added directly onto the surface of the sample, avoiding any sulphuric acid from getting in contact with the walls of the test tube. Vortex the sample to mix it thoroughly.
- g) The sample from (f) was allowed to stand for 10 minutes and the absorbance read on the UV-vis spectrophotometer at a wavelength of 490 nm.
- h) The standards were prepared by weighing 3.6 g of analytical standard glucose in 100 mL (36 mg/mL) of distilled water and aliquots measured as shown in table 2.0.

Standard	Blank	1	2	3	4	5
ml glucose stock solution	0	0.5	1.0	2.0	5.0	10.0
Concentration (mg/ml)	0	0.18	0.36	0.72	1.8	3.6

Table 2.0:	Glucose	standards
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The results were calculated using the equation:

Starch concentration $(mg/ml) = 0.9719 \text{ X} - 0.0666 \quad (X=absorbance in nm)$ (1)

2.4.2 Elemental analysis of the avocado seed powder and the starch

Dried avocado seed powder and avocado starch was tested for sodium, magnesium, potassium and calcium using an ICP-OES. Weights of one gram of each sample were weighed and digested with hydrochloric acid and nitric acid in the ration of 1:1. The samples were then filtered into 100 mL volumetric flasks and topped up to the mark with distilled water. Standards for the elements were prepared from 1000 ppm Merck analytical standards. The ICP-OES was calibrated and the samples tested against standard calibration curves.

2.4.3 Determination of the ratio of seed to fruit

The average weight of the seed was determined by weighing the whole ripe fruit and the weight of the seed separately. This enabled the verification of the percentage weight of the seed against the weight of the whole fruit.

2.5 SYNTHESIS OF THE AVOCADO SEED SUPERABSORBENT POLYMER (SAP)

The preparation of the SAP follows a procedure described by Suo *et al.*, (2007) and Weerawarna (2009). The researcher prepared two sets of SAP compositions with starch (analytical grade) and avocado seed starch in varying amounts and compared the products with similar quantities as shown in table 2.1. The synthesis of the SAPs was as follows:

- a) Carboxymethyl cellulose sodium salt (9.0 g) was mixed with 1.0 litre of distilled water in a blender until a homogenous gelatinous mixture was formed.
- b) Starch extracted from the avocado seeds weighing 1.1 g was gelatinized separately in 50 ml of distilled water at 80°C for 45 minutes.
- c) The gelatinized starch was added to the CMC solution and blended for five minutes at high speed. A mass of 0.24 g of aluminium sulphate was dissolved in distilled water and added into the blended mixture. The mixture was further blended for another five minutes.
- d) The mixture from step (c) was spread on porcelain plates and dried at 80°C until a thin film was formed and the mass of the plate and sample remained constant. The film was shredded with a blender and then ground into fine particles with a mortar and pestle.
- e) Steps (a) to (d) were repeated with varying proportions of avocado seed starch, analytical grade starch and CMC to determine the optimum amount of avocado starch required to make a SAP with maximum water retention. The different proportions of starch and avocado starch that were used are shown in table 2.1.
- f) An additional sample containing CMC (10.0 g) and aluminium sulphate octadecahydrate (0.24 g) was also made. The procedure (a) to (d) was followed with the exclusion of starch. The aim was to check the effect of adding starch into the polymeric complex.

Replicates samples of SAPs were made for each composition. The amount of aluminium sulphate octadecahydrate remained constant in all the experiments. This amount of approximately 2.3% aluminium sulphate was determined by Esposito *et al.*, (1996) and Nnadi and Brave (2013), as the quantity required for crosslinking in a SAP with optimal water retention.

Sample	Sample co	mposition			Test conditions		
number							
	CMC (g)	Starch (g)	Aluminum	Aluminum	CMC &	Gelatinisation of	Drying
			Sulphate (g)	Sulphate	Aluminum	starch(°C)	temp
				(%)	Sulphate blend		(°C)
					(°C)		
15	10.0	0.0	0.24	2.34	25	80 for 45min	80
28	9.0	1.0	0.24	2.34	25	80 for 45min	80
38	7.5	2.5	0.24	2.34	25	80 for 45min	80
4 S	5.0	5.0	0.24	2.34	25	80 for 45min	80
55	2.5	7.5	0.24	2.34	25	80 for 45min	80
6S	1.0	9.00	0.24	2.34	25	80 for 45min	80
	CMC (g)	Avocado	Aluminum	Aluminum	CMC &	Gelatinisation of	
		Starch (g)	Sulphate (g)	Sulphate	Aluminum	starch(°C)	
				(%)	Sulphate blend		
					(°C)		
1AS	10.0	0.0	0.24	2.34	25	80 for 45min	80
2AS	9.0	1.10	0.24	2.34	25	80 for 45min	80
3AS	7.5	2.73	0.24	2.34	25	80 for 45min	80
4AS	5.0	5.45	0.24	2.34	25	80 for 45min	80
5AS	2.5	8.18	0.24	2.34	25	80 for 45min	80
6AS	1.0	9.00	0.24	2.34	25	80 for 45min	80

Table 2.1: Material Compositions for SAP synthesis

Where ${\bf S}$ is analytical grade starch and ${\bf AS}$ is avocado starch.

2.6 INVESTIGATION OF OPTIMAL CROSSLINKING OF AVOCADO STARCH AND CMC WITH ALUMINIUM SULPHATE

The amount of aluminium sulphate octadecahydrate that gives optimal crosslinking with the highest water retention was investigated by using the method described by Suo *et al.* (2007) and Weerawarna (2009), steps (a) to (d) in 2.5. In step (c) the amount of aluminium sulphate octadecahydrate was varied so that each batch of samples had the following compositions as shown in table 2.2.

Sample	Sample co	mposition			Test conditions		
number							
	CMC (g)	AvocadoS	Aluminum	Aluminum	CMC &	Gelatinisation of	Drying
		tarch (g)	Sulphate (g)	Sulphate	Aluminum	starch(°C)	temp
				(%)	Sulphate		(°C)
					blend (°C)		
1	9.0	1.1	0.25	1.166	25	80 for 45min	80
2	9.0	1.1	0.50	2.304	25	80 for 45min	80
3	9.0	1.1	1.00	4.505	25	80 for 45min	80
4	9.0	1.1	1.50	6.608	25	80 for 45min	80
5	9.0	1.1	2.00	8.621	25	80 for 45min	80

Table 2.2: Investigation of optimal crosslinking for high water absorption capacity

2.7 CHARACTERISATION OF THE SUPERABSORBENT POLYMERS

2.7.1 Structural analysis

The synthesized SAPs were analysed on the Fourier Transform Infrared Spectrophotometer (FTIR- ThermoFischer) using the Attenuated Total Reflection accessory (ATR) to confirm the intermolecular interactions between the functional groups in the CMC, starch and aluminium sulphate before and after the synthesis of the SAPs. The samples were finely ground and then analysed on the FTIR. The infrared spectra were obtained by scanning at wavenumbers in the range 4000- 400 cm⁻¹.

Tests were conducted to investigate which ions participate in the cross linking reaction from the aluminium sulphate octadechydrate $[Al_2(SO_4)_3.18H_2O]$ crosslinker. When dissolved in water Al₂ (SO₄)₃.18H₂O dissociates into Al³⁺ and SO₄²⁻ ions. The following procedure was done:

- a) The CMC/avocado seed starch blend was immersed in hot water at 70°C for 30 minutes with occasional stirring. The mixture was filtered and the filtrate was divided into three parts, X, Y and Z.
- b) To filtrate X, 10 % barium chloride solution was added and the appearance of the solution was observed and recorded.
- c) To filtrate Y, concentrated sodium hydroxide solution was added, after shaking to mix the solution, ammonia solution was added and the resultant solution observed and recorded.

- d) To test that Na⁺ ions were released by the NaCMC in the ionic ligand formation with Al³⁺ ions, filtrate Z was tested for Na on the ICP-OES against the distilled water used in the formation of the filtrate.
- e) To further ascertain that aluminum is part of the SAP structure the crosslinked blend was ignited to 800°C for 2 hours in a muffle furnace. It was expected that all the hydrocarbons would be converted to carbon dioxide and water leaving behind aluminium oxide which was digested with a mixture of 50:50 hydrochloric acid and nitric acid. The digest was diluted with distilled water and analysed on the ICP-OES for aluminium.

The surface morphology could not be examined because there was no laboratory in Harare with a Scanning Electron Microscope (SEM).

2.7.2 Water absorption capacity (WAC)

The water absorption capacity of the SAP samples was measured by using the sieve method described by Zohuriaan-Mehr *et al.*, (2003). The following procedure was done:

- a) One gram of SAP was weighed and immersed in 100 ml of water and dispersed by a magnetic stirrer so that equilibrium swelling was reached. The samples were left overnight to ensure maximum water absorption.
- b) The swollen sample was then filtered through a 100 mesh sieve and excess water was removed by rubbing the bottom of the sieve with a polyurethane sponge and squeezing the sponge until the SAP was no longer slipping from the sieve when it is held in a vertical position.

c) The swollen SAP was carefully transferred to an oven dried and tared petri dish and weighed. The weight was recorded and the weight of the swollen SAP calculated from equation 1 as discussed in the chapter 1.

$$WAC = (W1 - W0)/W0$$
 (2)

Where W0 is the weight of dry SAP and W1 is the weight of swollen SAP.

2.7.3 Soluble fraction

The soluble fraction is the sum of all water soluble species including the non-crosslinked monomers. This was determined as follows:

- a) A 1.0 g of SAP was weighed and placed into a 300 mL beaker. Distilled water (100 mL) was added and the mixture was stirred with a magnetic stirrer to reach equilibrium.
- b) The swollen SAP was filtered through a 100 micrometer mesh sieve and sponged with a polyurethane sponge. The swollen SAP was then dried in an oven at 105^oC for 3 hrs. The beaker and dry sample were weighed.
- c) The dried gel (SAP) weight was determined and the soluble fraction is calculated from equation (3).

$$Sol(\%) + Gel(\%) = 100$$
 (3)

The gel content is considered the actual yield of cross-linking polymerization.

The other tests that were discussed in the literature review could not be carried out because some of the resources required to conduct the tests were not available.

2.7.4 Ability to rehydrate

Samples that were used in the soluble fraction experiment were used in this test as follows:

- a) Samples from experiment 2.7.3 were rehydrated with distilled water by pouring 100 mL of water into the beakers containing the swollen samples that were oven dried (2.7.3 b).
- b) The samples were observed after three hours.

The other tests that were discussed in the literature review could not be carried out because some of the resources required to conduct the tests were not available.

CHAPTER 3

3.0 RESULTS AND DISCUSSION

3.1 INTRODUCTION

In this chapter the researcher presents the research findings from the experimental work that was conducted to synthesize a superabsorbent polymer using avocado seed starch and carboxymethyl cellulose crosslinked with aluminium sulphate octadecahydrate. The results are presented in the form of graphs, tables and pictures to explain the analytical results obtained in the experiments that answer the research questions posed in chapter one. The findings are also discussed in this chapter.

3.2 EXTRACTION OF STARCH FROM THE AVOCADO SEED.

Figure 3.0 shows the schematic diagram of the extraction process of the starch from the seeds. Approximately 547 g of starch was obtained from 2270 g of fresh avocado seeds obtained from ripe avocado fruit. This translates to about 24.1% starch on wet basis. The starch however had a brown coloration. Experiments carried out by Andy (2013), showed that this was caused by oxidation reactions of the phenolic dopamine compound, 3,4-dihidroxy phenilalanin contained in the seeds.



3.2.1 RESULTS FOR THE ANALYSIS OF STARCH CONTENT OF AVOCADO SEED STARCH

The starch content in the extracted avocado seed starch was determined by the phenolsulphuric acid test method (Nielson, 2010). The starch concentrations were obtained calorimetrically. The results are shown in table 3.1 and the calibration for glucose standards are shown in figure 3.1.

Sample	Weight	Absorbance	Spectrophotometer	Amount	Starch
	(mg)	(nm)	Concentration	in 20ml	Concentration
			(mg/mL)	(mg)	(%)
Starch	37.96	1.767	1.8805	37.61	99.08
Avocado starch 1	36.81	1.613	1.7226	34.45	93.59
Avocado starch 2	30.06	1.260	1.3612	27.22	90.57

Table 3.1: Concentration of avocado starch



Figure 3.1: Calibration curve for glucose standards

The table 3.1 shows that the starch content in the extracted avocado starch was 92.08% (m/m). To further ascertain that the avocado seed starch and analytical grade starch were similar in structure and function, they were both analysed by FTIR and the spectra compared. Figure 3.2 shows the spectrum for starch and figure 3.3 shows the spectrum for avocado seed starch. Figure 3.4 shows that both starch samples had the same functional groups. The starch spectra showed C-C stretching at 760 cm⁻¹, C-O-C glycosidic stretching at 930 cm⁻¹, primary alcoholic stretching –CH₂OH at 1076 cm⁻¹, C-O stretching at 1143 cm⁻¹ and O-H stretching between 3000 and 3600 cm⁻¹. All these functional groups are characteristic of starch.





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Figure 3.3: FTIR spectrum for avocado seed starch



Figure 3.4: Starch and Avocado seed starch FTIR spectra

These spectra also compare to those of native starch obtained by Hebeish *et al.*, (2010), as shown in figure 1.3. The spectrum of avocado seed starch was a perfect match of the analytical grade starch. Therefore the two starches can be expected to behave in the same manner when incorporated into polymeric complexes since they have the same functional groups.

3.3 RESULTS OF MINERAL ANALYSIS OF AVOCADO STARCH AND DRIED AVOCADO POWDER

The starch was tested for minerals and the results are as indicated in table 3.2.

Sample	Method	Calcium	Magnesium	Potassium	Sodium
		(mg/L)	(mg/L)	(mg/L)	(mg/L)
Avocado powder	ICP-OES	4.936	11.80	124.2	1.568
Avocado starch	ICP-OES	2.227	1.959	22.70	1.065

The results in table 3.2 show that even after extraction the avocado seed starch retains some minerals. This could be an added advantage of using avocado starch in SAP synthesis as compared to utilizing synthetic materials in, for example agricultural applications were these minerals play an important role in soil fertility. However the significance of these minerals requires further investigation to determine their effects in the performance of SAPs for various applications.

3.4 SYNTHESIZED AVOCADO SEED STARCH SUPERABSORBENT POLYMER

The super absorbent polymer was synthesized by crosslinking avocado seed starch and CMC with aluminium sulphate octadecahydrate. A starch (analytical reagent grade) equivalent was also made so as to compare the properties with those of the avocado starch SAP. The diagram, figure 3.5 shows the SAPs that were synthesized.



3.5 RESULTS FOR TESTS OF THE SYNTHESIZED SUPERABSORBENT POLYMERS

A number of tests were performed to determine if the absorbent polymers synthesized from the starch extracted from avocado seeds were superabsorbent and had comparable properties to the SAPs made from analytical grade starch.

3.5.1 Fourier Transform Infrared Spectroscopy analysis results

Evidence of crosslinking between CMC and avocado seed starch/pure starch by aluminium ions was provided by FTIR analysis which showed the structural arrangement in the SAPs in comparison to the starting materials. Figure 3.6 shows an overlay of the spectra of CMC, analytical grade starch, avocado seed starch, aluminium sulphate octadecahydrate, CMC/starch and aluminium sulphate octadecahydrate, and CMC/avocado starch and aluminium sulphate octadecahydrate complexes.

The NaCMC showed absorption of carboxyl groups (-COO⁻) and the salt at wavenumbers of 1450- 1400 cm⁻¹, carboxymethyl ether > CH-O-CH₂ stretching at 1019.98cm⁻¹, asymmetry bridge stretching for –C-O-C at around 1111 cm⁻¹, C-H stretching of -CH₂ and -CH₃ at 2921.27 cm⁻¹, OH bending at 1322.28 cm⁻¹ and –OH stretching at 3250.31 cm⁻¹. The spectra in figure 3.6 show that starch and avocado starch are similar in structure since they are finger prints of each other. Both NaCMC and the starch have the following functional groups: primary alcohols -CH₂ OH stretching at 1077.01 cm⁻¹, C-O stretching at 1148.67 cm⁻¹, -CH₂ bending at 1414 cm⁻¹, OH stretching at 3600-3000 cm⁻¹ and water in the amorphous region at 1650-1600 cm⁻¹.



No peak table for the selected spectrum!

Figure 3.6: Superimposed spectra of CMC, starch, avocado starch, aluminium sulphate and synthesized SAPs

In Figure 3.6 it was observed that the primary alcoholic functional groups that were in the starches were no longer present in the synthesized SAP indicating that this was a reactive site between the starches with the NaCMC. The –COONa group found in the NaCMC was absent in the SAP showing that this was also a reactive site and the polymerization process was efficient. In figure 3.6 the spectra for the SAP composites and the starting materials also show that, at the sites of the reactive functional groups there is a smoothing and shifting of the peaks when they participate in crosslinking polymerization process.

Figure 3.7 shows the spectra obtained for the varying compositions of starch/CMC/Al ions (CMC 2 and 3) and for avocado starch/CMC/Al ions (CMC7-9) in the proportions shown in table 3.3. The FTIR spectra showed that there were intermolecular interactions between the starches and CMC in the blends because of the shifting of carboxyl (C=O) and hydroxyl (OH) groups.

Sample	Sample composition					
number						
	CMC (g)	Starch (g)	Avocado seed starch	Aluminum Sulphate (g)		
CMC1	10.0	0.0	-	0.24		
CMC2	9.0	1.0	-	0.24		
СМСЗ	7.5	-	2.5	0.24		
CMC7	9.0	-	1.0	0.24		
CMC8	7.5	-	2.5	0.24		
СМС9	5.0		5.0	0.24		

Table 3.3: Compositions of SAP analysed by FTIR



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No peak table for the selected spectrum!

Figure 3.7: A comparison of CMC SAP, starch/CMC composites and avocado starch/CMC

The spectra show that that are no structural variations in the SAPs produced by either avocado seed starch or starch. The spectra of CMC1 show that CMC can self-polymerize and a SAP that has an almost similar structure to the composites with the starch and avocado starch was produced. This is expected since the CMC has both the hydroxyl and carboxyl groups which are reactive sites for polymerisation.

Qualitative tests were also performed to investigate the ions that formed the polymer network. The filtrate formed after addition of water at 70° C and mixing of the SAP tested positive for the presence of sulphates. A white precipitate was formed after the addition of barium chloride, indicating the formation of barium sulphate. This showed that the SO₄²⁻ in the Al₂(SO₄)₃.18H₂O did not form part of the polymer network. The test for the presence of Al ³⁺ ions with sodium hydroxide and ammonia solution was negative, no precipitate was formed indicating that the Al ³⁺ ions were bonded in the polymer and thus were not found in the filtrate solution. Tests for sodium ions on the ICP-OES of the SAP filtrate indicated the presence of the ions. This showed that the intermolecular interactions of NaCMC and Al ³⁺ ions lead to the displacement of Na⁺ ions and formation of the aluminium and carboxyl ionic ligand as postulated by Braihi *et al.*, (2014). The analysis of the aluminium oxide formed after igniting the SAP at 800 degrees Celsius in the muffle furnace by ICP-OES provided further evidence that Al ³⁺ ions were part of the polymeric structure.

3.5.2 Water absorption capacity

The water absorption capacity (WAC) test enabled the researcher to determine the amount of water that could be imbibed by the absorbent polymer per gram weight. The pictures in Figure 3.8 below show the samples before (on the right) and after (on the left) imbibing

water. The proportion of CMC to starch was varied linearly in order to determine the most suitable composition that gave a good quality superabsorbent polymer. Varying the amount of CMC to starch also gave useful information about the reaction between the CMC, starch and aluminium ions. The graph in Figure 3.9 shows that as the amount of either pure starch or avocado seed starch is increased with the subsequent reduction in amount of CMC, the water absorption capacity also decreases linearly.



Swollen and dry avocado starch(5.5%), CMC and aluminium SAP



Swollen and dry avocado starch28%), CMC and aluminium SAP



Swollen SAPs with equivalent amounts of starch (starch on the left and avocado starch on the right)

Figur3.8: Water absorption of avocado starch and starch SAP



Figure 3.9: A comparison of pure starch SAPs against avocado seed starch SAPs

The graph in figure 3.9 shows that the WAC of the superabsorbent polymer that was made from CMC and aluminium sulphate without any starch was lower than that of the SAPs that were made by incorporating either pure starch or avocado seed starch. The maximum WAC of the composite SAPs was obtained when ratio of CMC: Starch/ avocado starch: aluminium sulphate was 87.89: 9.77:2.34 respectively. As the amount of starch increased the WAC also decreased from 46, 49 g/g to 6.23 g/g in the case of the SAP with pure starch and CMC and from 39.25 g/g to 5.2g/g for the avocado seed starch and CMC composition. It was also observed that the maximum WAC for the pure starch differed from that of the avocado seed starch by 7.24 g/g, but as the starch content was increased and that of CMC decreased the differences became as low as less than 2 g/g.

According to Hubbe *et al.*, (2013) the chemistry of cellulose contributes to absorbency because of the numerous hydrophilic –OH groups throughout the structure. This probably

explains the decline in the WAC as the amount of CMC is reduced. The reduction in the CMC concentration translates to a reduction of the hydroxyl groups which results in lower water absorption. The increase in the starch content also means an increase in the intermolecular interactions between the starch and CMC, leaving fewer hydrophilic groups to absorb water. This is due to the fact that the hydroxyl groups that are exposed on the surface of the absorbent material where hydrogen bonding is expected to take place with water are reduced with the increase in starch content. The increase in the starch content however, leads to a more compact polymer network and a less water soluble hydrogel complex as will be seen in the tests for soluble fraction.

Figure 3.10 shows the comparison of the two types of SAP with equivalent compositions. It shows that as the starch content and avocado seed starch was increased in either SAPs there was no significant difference in the WAC of the two SAPs.



Figure 3.10: A comparison of the WAC of pure starch SAPs vs avocado seed starch SAPs

Optimal crosslinking

An investigation of the effect of changing the aluminium sulphate octadecahydrate content while holding the avocado seed starch and the CMC content constant was also conducted. In figure 3.11 it was observed that at a concentration of 1.17% aluminium sulphate octadecahydrate the WAC was 25.21 g/g and when the concentration was increased to 2.34%, the WAC increased to 39 g/g. A further increase in the aluminium sulphate octadecahydrate content resulted in a decrease in the WAC. At 6.31% the WAC reduced to as low as 8.34g/g. The maximum crosslinking was therefore attained at 2.34% aluminium sulphate octadecahydrate. According to Braihi *et al.*, (2014) increasing the crosslinker effects an increase in the nodes of the polymer network and crosslinker density which is desirable to the retention and absorption of fluid.



Figure 3.11: The effect of aluminium sulphate concentration on WAC of SAPs

When the concentration of the crosslinker is low this leads to a low degree of crosslinking and an open network structure leading to low WAC, but when the concentration of the crosslinker is high the crosslinking density is high and the network pores are smaller making the absorption of fluid more restricted and hence a low WAC is obtained.

3.5.3 Soluble fraction

The soluble fraction test gave information about total water-soluble species that were in the synthesized SAPs. These species included the starting materials and non-crosslinked oligomers that did not form the polymer network of the superabsorbent polymer. Figure 3.12 shows a profile of the soluble fractions of the SAPs synthesized with compositions indicated in table 2.1 of chapter 2.



Figure 3.12: Soluble fraction of avocado and starch SAPs

The graph shows that the SAP consisting of CMC and aluminium sulphate only has the highest soluble fraction of close to 23% (m/m). When either pure starch or avocado starch is introduced by gradually increasing their quantity, it was observed that the solubility of the SAPs also decrease significantly to even less than 10%, but started to increase when the starch content was more than 24%. The differences in the solubility of the two main types of SAPs that were synthesized in this research show very low variance. The avocado starch SAPs were more soluble than the pure starch SAPs.

3.5.4 Ability to rehydrate

Experiments to demonstrate the SAPs ability to rehydrate after swelling and drying indicated that both the starch and avocado seed starch SAPs had the ability to rehydrate and retain their prior swollen structures. This was accomplished by visual examination of the rehydrated absorbent polymers. The SAPs can therefore be reused if necessary for certain applications.

3.5.5 Statistical analysis

The results obtained from the experiments were analysed by GraphPad Prism 6.0 using the one-way Anova with Bonferroni's multiple comparison test to determine the significance of the differences between the two SAP types (starch and avocado seed starch) at 95% confidence interval. The following output in table 3.4 shows the results.

Table 3.4: GraphPad Prism 6.0 statistical output

Bonferroni's multiple comparison test	Mean	Student t	Significant?	Summary
	difference		P<0.05?	
% starch SAP WAC vs Avocado SAP	19.78	1.567	no	ns
WAC				
% solubility starch SAP vs Solubility	-0.5055	0.040	no	ns
Avocado SAP				
% Aluminium sulphate	-18.25	1.446	no	ns
octadecahydrate vs WAC of avocado				
SAP				

The analysis show that there were no significant differences between the avocado SAP and the starch SAP for the parameters tested. Avocado starch can therefore be used as a substitute for starch and other starches form agricultural plants that have been successfully used to synthesize superabsorbent polymers.

Comparing overally the two samples



The comparison of the two SAPs shows that there are no significant differences between the two except for the outliers in the WAC of the SAPs.

3.6 DISCUSSION SUMMARY

Experiments that were conducted by Braihi *et al.* (2014), Brave and Nnadi (2013) and Espisito *et al.*, (1996) showed that the presence of ionic groups on the backbone of superabsorbent polymers, crosslinking density and macroscopic morphology could be manipulated to produce SAPs with the desired water absorption when certain process parameters are biased. The results of the experiments conducted in this research concur with these observations as evidenced by the FTIR analysis of the structures of the starting material and the final products, the water absorption capacities of the SAPs obtained when the compositions of starch was varied against sodium carboxymethyl cellulose while the
aluminium sulphate octadecahydrate content was held constant, and also determining the optimum crosslinking ratio.

3.6.1 Starting materials

The extraction of the avocado starch was a simple process and may be easily adapted at a commercial scale. The process was conducted with three major pieces of equipment which were the blender, kitchen sieve to hold the cheese cloth and a drying oven. The starch produced from the avocado seeds was comparable to the pure analytical grade starch which is mainly corn starch. The results showed that on average the purity of the starch was approximately 92% (m/m). Results from the FTIR spectra obtained for the avocado seed starch were a very close match to that of the pure analytical grade starch. These test results showed that the quality of avocado seed starch could parallel those of pure starch in the production of superabsorbent polymers.

3.6.2 Synthesis of the superabsorbent polymer

In the synthesis of the superabsorbent polymers the FTIR analysis indicated the absence of the functional groups that had been observed in the starting materials. The main reactive functional groups were the carboxyl groups, the hydroxyl groups and the aluminium ions. According to the crosslinking model by Braihi *et al.*, (2014), these are the reactive sites for the polymerization process. The FTIR spectra showed that the -O-H stretching which lies in the region of 3600-3000 cm⁻¹ resulting from the large amount of –OH groups in both the CMC and the starches becomes absent in the polymer blends. The primary alcoholic – CH₂OH and the C-O stretching which occurs between the 1350-1050 cm⁻¹ region are absent indicating that the link between CMC and starch occurs at this site. Braihi *et al.*, (2014), postulated that the reactivity of CMC with aluminium ions was such that one trivalent Al ion

connected three CMC ions which translates to 1443 g/mol for every repeating unit. The CMC also reacted with three starch molecules having a molecular weight of 1875 g/mol. They also indicated that there would be three Al ions per mer with a molecular weight of 83.45 g/mol. This would therefore mean that the ideal SAP blend would have CMC/starch/Al ions in the ratio of 42.42: 55: 2.45. The experiments conducted in the research however, show that this ratio does not produce a SAP with desired properties such as the water absorption capacity. The SAP with the best WAC and soluble fraction had a ratio of 88:9.7:2.3 of CMC, starch or avocado starch and Al ions respectively. Qualitative tests that involved the precipitation of ions such as Al ^{3+,} Na⁺ and SO₄³⁻ showed that the ions in the polymer network were Al ³⁺ ions which crosslink the polymer network.

3.6.3 Water absorption capacity of synthesized SAPs

The results from the WAC tests conducted on the synthesized SAPs showed that the highest WAC was obtained for the SAPs with the ratio of 88:9.7:2.3 for the CMC, starch and Al ions respectively, with the pure starch blend having a WAC of 46.45 g/g and the avocado seed starch with a WAC of 39.25 g/g. Self-crosslinking of CMC with aluminium sulphate resulted in a SAP that had much lower water absorbency than the blend. The points in the graphs which are equivalent to the ideal ratio of the SAP blend showed that the starch blend WAC reduced to approximately 13% and the avocado seed starch blend would be about 15% which translates to 3.5 and 2.5 times lower the 88:9.7:2.3. The differences in the water absorption of the different SAP blends emanates from the fact that the ideal SAP blend would have a very compact network with very few sites for hydrogen bonding to take place when water uptake takes place, thereby leading to very few water molecules bonding with the polymer.

However when the polymer network is less compact there is more room for bonding with water molecules thus leading to more water absorption.

3.6.4 Soluble fraction

The results showed that an increase in the starch proportion in the polymer blends resulted in increased solubility of the SAP. The self-crosslinked CMC and aluminium sulphate composite had the highest solubility of almost 23% which meant that the gel content was about 67% calculated from the equation, solubility fraction(%) + gel content (%) = 100%. The SAP with the highest WAC (88:9.7:2.3, CMC, starch and Al ions respectively) had the lowest solubility of 10% meaning that it had a gel content of 90%. According to Zohuriaa-Mehr *et al.*, (2008), the gel content could be considered as the actual crosslinking polymerization yield.

CHAPTER 4

4.0 CONCLUSION

4.1 INTRODUCTION

In this chapter the researcher makes inferences and conclusions from the research findings discussed in chapter 3. Recommendations and areas of further study are also discussed in this chapter

4.2 CONCLUSIONS

Superabsorbent polymers can be synthesized from avocado seed starch. The results that were obtained from the research show that the SAP produced from avocado seed starch has properties that are comparable to those produced from pure starch with a water absorption capacity of 39.25 g/g (3925%) for a composition of 88:9.7:2.3, CMC, avocado seed starch and Al ions respectively. This is consistent with the definition of a superabsorbent polymer in literature. The superabsorbent is made entirely from natural polymers which are decomposed by microorganisms to carbon dioxide and water thereby rendering them biodegradable.

The suitability of avocado seed starch in the synthesis of superabsorbent polymers

The starch that was extracted from avocado seeds of the *Hass* variety found in Harare in Zimbabwe had a high starch purity of approximately 92% m/m. Fourier Transform Infrared spectroscopy using the ATR mode showed similarities in the structures of the pure starch to the avocado seed starch rendering it suitable to perform similar functions and reactivity as pure starch. The spectra of the pure starch and that of the avocado starch were a very close match. The starch from avocado seeds also showed the presence of magnesium, sodium, potassium and calcium ranging from 1 to about 23 mg/l. This was an indication that residual

beneficial constituents in avocado seeds could be retained in the starch. These could possibly constitute the remaining 8% besides the starch and the few minerals that were quantitatively determined.

The ability of the SAP synthesized from avocado seed starch and CMC blend to imbibe water

The research findings showed that the superabsorbent polymers that were made by incorporating starch extracted from avocado seeds were capable of imbibing water up to 39.25 g/g when the avocado starch was 10% of the SAP composition, 29 g/g at 24% avocado starch and 17 g/g at 49% avocado starch composition. This means that the avocado seed starch SAP maintains superabsorbent properties even when it is up to 50% of the total SAP composition.

The effect of crosslinker concentration in the avocado starch superabsorbent polymer

The optimum crosslinking was attained when 2.34% aluminium sulphate octadecahydrate was incorporated into the avocado seed starch SAP and the analytical grade starch SAP. Concentrations lower or higher than 2.34% result in reduced water absorption capacity.

4.3 TEST OF THE RESEARCH PROPOSITION

The research proposition holds since the research proves that "avocado seed starch makes a biodegradable super absorbent polymer with properties that are comparable to those that are synthesized from cereal starches and carboxymethyl cellulose.

4.4 RECOMMENDATIONS

Avocado seeds are found in abundance in Zimbabwe and are usually thrown away as waste which amounts to thousands of tonnes over short periods of time. This problem of large piles of avocado seeds is also faced by avocado oil producers worldwide. The utilization of avocado seeds to produce starch which is subsequently incorporated into superabsorbent polymers is an innovative way to reducing this otherwise useless biomass. The added advantage of using avocado seeds is that they are renewable and biodegradable materials which, therefore do not cause problems of environmental pollution. Synthesis of an avocado seed starch and carboxymethyl cellulose superabsorbent polymer blends has implications of lowering costs of production in comparison to the conventional petroleum based SAPs. Another factor supporting the use of avocado seed starch in combination with carboxymethyl cellulose is fact that they have no serious implications on health and safety.

The research has shown that the starch from avocado seeds also retains some of its minerals even after extraction. This mineral retention would be useful for agricultural purposes where the superabsorbent polymer could be used as a soil conditioner. Further investigations need to be carried out to determine if the synthesized polymer has the added functions that are useful in avocado seeds such as the phytochemicals, alkanols, flavonoids, phosphorus, zinc, iron to name a few. These properties could be useful or detrimental in the final product and its applications.

Avocado seeds are a potential source of starch which can be used for other applications besides the synthesis of superabsorbent polymers. Most starch sources such as cereals and tubers compete with food consumption uses which normally take first preference as compared to avocado seeds that are generally not used as a food source.

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